TEACHER COPY – WITH SUGGESTED SOLUTIONS

Anglo-Chinese School (Independent)

Year 5 (2022) IBDP Chemistry HL

TOPIC 5 Energetics & Thermochemistry

(IBDP syllabus Topic 5)

5.1 Measuring Energy Changes

- *Essential Idea: The enthalpy changes from chemical reactions can be calculated from their effect on the temperature of their surroundings.*

5.2 Hess' Law

– *Essential Idea: In chemical transformations energy can neither be created nor destroyed (the first law of thermodynamics).*

5.3 Bond Enthalpies

– *Essential Idea: Energy is absorbed when bonds are broken and is released when bonds are formed.*

(IBDP syllabus Topic 15)

15.1 Energy Cycles

– *Essential Idea: The concept of the energy change in a single step reaction being equivalent to the summation of smaller steps can be applied to changes involving ionic compounds.*

15.2 Entropy and Spontaneity

– *Essential Idea: A reaction is spontaneous if the overall transformation leads to an increase in total entropy (system plus surroundings). The direction of spontaneous change always increases the total entropy of the universe at the expense of energy available to do useful work. This is known as the second law of thermodynamics.*

5.1 Measuring energy changes

Essential idea: The enthalpy changes from chemical reactions can be calculated from their effect on the temperature of their surroundings.

Nature of Science:

- Fundamental principle—conservation of energy is a fundamental principle of science. (2.6)
- Making careful observations—measurable energy transfers between systems and surroundings. (3.1)

Understandings:

- Heat is a form of energy.
- Temperature is a measure of the average kinetic energy of the particles.
- Total energy is conserved in chemical reactions.
- Chemical reactions that involve transfer of heat between the system and the surroundings are described as endothermic or exothermic.
- The enthalpy change (ΔH) for chemical reactions is indicated in kJ mol^{-1}.
- ΔH values are usually expressed under standard conditions, given by ΔH^{θ}, including standard states.

Applications and skills:

- Calculation of the heat change when the temperature of a pure substance is changed using $q = mc\Delta T$.
- A calorimetry experiment for an enthalpy of reaction should be covered and the results evaluated.

Guidance:

- Enthalpy changes of combustion (ΔH^{θ}_{c}) and formation (ΔH^{θ}_{f}) should be covered.
- Consider reactions in aqueous solution and combustion reactions.
- Standard state refers to the normal, most pure stable state of a substance measured at 100 kPa. Temperature is not a part of the definition of standard state, but 298 K is commonly given as the temperature of interest.
- The specific heat capacity of water is provided in the data booklet in section 2.
- Students can assume the density and specific heat capacities of aqueous solutions are equal to those of water, but should be aware of this limitation.
- Heat losses to the environment and the heat capacity of the calorimeter in experiments should be considered, but the use of a bomb calorimeter is not required.

5.1 What is thermodynamics?

- **Energetics** (also known as thermochemistry) is the study of energy changes in chemical reactions. Total energy in a chemical reaction is conserved in a chemical reaction. Chemical potential energy is stored in the chemical bonds of reactants and products, while the temperature of the reacting mixture is a function of the kinetic energies of the atoms, ions and molecules present.

- **Heat**, q, is a form of thermal energy that is transferred from a warmer body to a cooler body, as a result of the temperature gradient. When heat is transferred to an object, the result is an increase in the average kinetic energy of its particles and therefore an increase in its temperature or a change in phase.

- At absolute zero, 0 K (−273.15 °C), all motion of the particles theoretically stops. The absolute temperature (in kelvin) is proportional to the average kinetic energy of the particles of matter. As the temperature increases, the kinetic energy of the particles increases

5.1.1 Enthalpy and thermochemistry

- **Enthalpy**, H, is a measure of the heat energy contained in a substance. It is stored in the chemical bonds and intermolecular forces as potential energy. The actual enthalpy of a substance is not quantifiable (cannot be directly measured). However, when substances react, the difference in enthalpy between the reactants and products (at constant pressure) results in a heat change which can be observed.

- Thermochemistry is the study of heat changes that occur during chemical reactions. At constant pressure, the change in enthalpy ΔH is defined as the heat transferred by a closed system during a chemical reaction. **The term "change in enthalpy" or "heat of reaction" is commonly used when describing the thermodynamics of a reaction. The unit of enthalpy change ΔH is kJ mol^{-1}**.

- All chemical reactions involve the breaking and forming of bonds. **Bond breaking requires energy to be absorbed and bond forming releases energy**. Thus, there is usually a net change in the total amount of energy of the reacting particles in most chemical reactions. This net change in the energy of the reacting particles is called the enthalpy change of reaction,

  $\mathbf{\Delta H = H_{products} - H_{reactants}}$ where $H_{reactants}$ = energy content of reactants
  $H_{products}$ = energy content of products

  The higher the enthalpy of a substance the less stable it is.

5.1.2 Enthalpy change of reaction, ΔH

- It is the enthalpy change when molar quantities of reactants as specified by the chemical equation reacts to form products.

  E.g. $N_2\ (g) + 3H_2\ (g) \rightarrow 2NH_3\ (g)$ $\Delta H = -100\ \text{kJ mol}^{-1}$

- According to the equation, 100 kJ of heat is evolved when 1 mole of N_2 (g) reacts with 3 moles of H_2 (g) to give 2 moles of NH_3 (g).

  E.g. $\frac{1}{2}N_2\ (g) + \frac{3}{2}H_2\ (g) \rightarrow NH_3\ (g)$ $\Delta H = -50\ \text{kJ mol}^{-1}$

5.1.3 Thermochemical equation

- A thermochemical equation shows the enthalpy change of a reaction besides the number of moles of reactants and products as well as their state symbols.

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

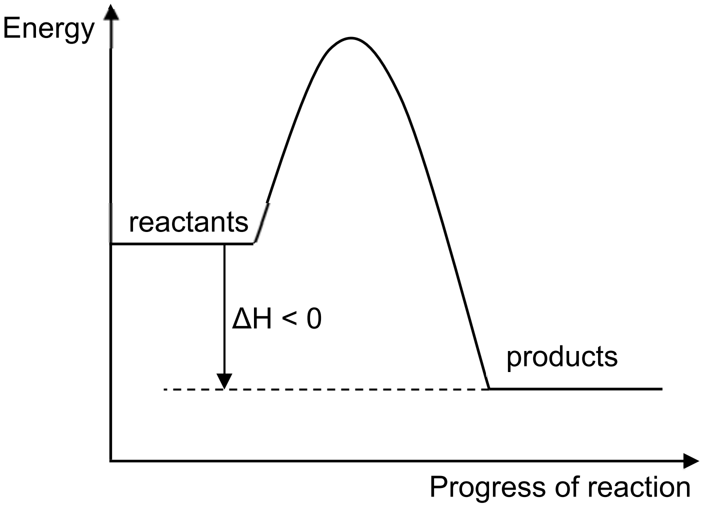
5.1.4 Exothermic reaction

- The **reaction mixture is called the system** and **anything around the system is called the surrounding or environment**.

- **Exothermic reaction** is a chemical reaction in which heat is transferred from the system to the surroundings that results in a net loss of energy where **ΔH is negative ($\Delta H < 0$)**.

- This net loss of energy is usually shown by **an increase in the temperature of the surrounding** as energy is released as heat to the surroundings. Exothermic reactions are common in chemistry. Neutralisation reactions between acids and alkalis liberate heat and result in an increase in temperature of the mixture. Combustion reactions where fuels, petrol or hydrogen gas are burnt in air or oxygen are exothermic reactions.

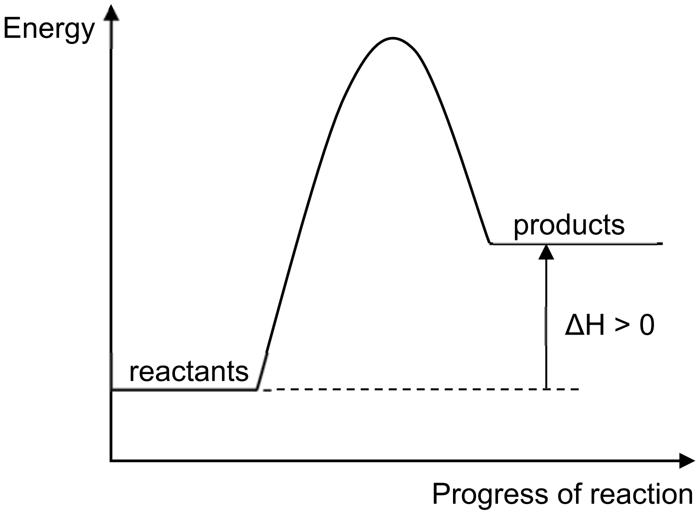
- For all exothermic reactions or changes, the **products are energetically more stable** than the reactants. A common way to represent the enthalpy change of an exothermic reaction is using the enthalpy diagram as shown:



5.1.5 Endothermic reactions

- **Endothermic reaction** is a chemical reaction that absorbs heat from their surroundings results in a net gain of energy where **ΔH is positive (ΔH > 0)**. This net gain of energy is usually shown by **a decrease in the temperature of the surrounding** as heat is taken in from the surrounding. An example is the dissolution of ammonium nitrate crystals in water. There is a decrease in temperature when ammonium nitrate crystals dissolve in water. The combination of nitrogen and oxygen is also endothermic.

- For all endothermic reactions or changes, the **products are energetically less stable** than the reactants. A common way to represent the enthalpy change of an endothermic reaction is using the enthalpy diagram as shown below.



- Note: The total energy is unchanged during a chemical reaction. Energy may be exchanged between the system and the surroundings but the total energy of the system and the surroundings remain constant. **This is known as the First Law of Thermodynamics**.

5.1.6 Feasibility of a reaction

- In general, **most chemical reactions are exothermic as they are more feasible (likely to occur) than endothermic reactions**. In the exothermic reactions, the products are energetically more stable than the reactants.

- However, **a feasible reaction does not imply that the reaction will happen instantaneously** when the reactants are mixed nor will react at a noticeably fast rate.

- For example, the combustion of hydrogen and oxygen is highly exothermic and highly feasible. However, a mixture of hydrogen and oxygen gas, left undisturbed, at room temperature and pressure will not react! Sometimes an energetically feasible reaction may not occur at all due other factors which you will learn in Topic 6 Chemical Kinetics.

5.1.7 Standard conditions

- The enthalpy change of a chemical reaction depends on many factors. The key factors are reactant(s) and product(s) of the reaction,
  - temperature,
  - pressure,
  - concentration of solutions and
  - state of the reactants and products.

- However, in the study of energetics, **a set of standard conditions is applied to all chemical reactions. The standard conditions are,**
  - **100 kPa**
  - **1 mol dm^{-3} for aqueous solutions**

- Thus, the standard enthalpy change of reaction, represented by ΔH^{θ}, refers to the enthalpy change when molar quantities of reactants as specified by the chemical equation react to form products under standard conditions of 100 kPa. Note that temperature is not defined under standard conditions. So, a temperature should be specified for a standard enthalpy change. **The temperature is assumed to be 298 K if there is no temperature stated.**

- Standard state refers to the normal, most pure stable state of a substance measured at 100 kPa. Temperature is not a part of the definition of standard state, but 298K is commonly given as the temperature of interest. Solid sodium chloride and not aqueous sodium chloride is taken to be the standard state. If allotropes exist, then the most stable allotrope is taken as the standard state. For example, the standard state of carbon is graphite and not diamond.

5.1.8 Definitions of standard enthalpy change of reactions

- Standard Enthalpy Change of Formation, ΔH^{θ}_{f}

> Enthalpy change when **one mole of a compound is formed from its elements** in their standard states under standard conditions of 298K and 100 kPa.

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

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

- By definition, the **ΔH^{θ}_{f} for all elements is zero**. There is no chemical change and so no enthalpy change when an element is formed from itself.
- $\Delta H^{\theta}_{reaction} = \Sigma\ \Delta H^{\theta}_{f}\ (products) - \Sigma\ \Delta H^{\theta}_{f}\ (reactants)$
- ΔH^{θ}_{f} can be positive or negative.
- In general, the more negative the ΔH^{θ}_{f} value for a compound, the more energetically stable is the compound.

- Standard Enthalpy Change of Combustion, ΔH^{θ}_{c}

> Enthalpy change when **one mole of substance in its standard state is completely burned** in excess oxygen under standard conditions.

E.g. $CH_4\ (g) + O_2\ (g) \rightarrow CO_2\ (g) + H_2O\ (l)$

$C_3H_6\ (g) + \frac{9}{2}O_2\ (g) \rightarrow 3CO_2\ (g) + 3H_2O\ (l)$

- ΔH^{θ}_{c} is **always negative** as heat is always evolved during combustion ($\Delta H^{\theta}_{c} < 0$).
- ΔH^{θ}_{c} values are also called **energy values** (calorific values) of fuel and food.
- Note: The **water in the equations describing ΔH^{θ}_{c} is in the liquid state**, not gaseous state, since water is a liquid at 298 K and 100 kPa. Energy will be needed to vapourise the water and the overall energy change if the combustion product is water vapour will be a combination of enthalpy change of combustion and enthalpy change of vapourisation.

- Standard Enthalpy Change of Neutralisation, ΔH^{θ}_{neu}

Enthalpy change when **one mole of water is formed** between the neutralisation of an acid and a base under standard conditions.

E.g. $H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$

$\frac{1}{2}H_2SO_4 (aq) + NaOH (aq) \rightarrow \frac{1}{2}Na_2SO_4 (aq) + H_2O (l)$

- ΔH^{θ}_{neu} is **always negative** as heat is always evolved during neutralisation ($\Delta H^{\theta}_{neu} < 0$).

- For neutralisation between a **strong alkali and strong acid**, the value of ΔH^{θ}_{neu} is approximately **-57.3 kJ mol^{-1}**.

- The nature of the acids and bases involved in the reaction will affect the values of ΔH^{θ}_{neu}.

  - Reason: **Weak acids and weak bases are only slightly ionised** in aqueous solution. **Part of the heat evolved from the neutralisation process is taken in to further dissociate the weak acid or weak base completely for further neutralisation reaction**, and thus the enthalpy change is less exothermic than the strong acid−strong base reaction where dissociation is spontaneous.

Reaction	**ΔH^{θ}_{neu} / kJ mol^{-1}**
$HCl (aq) + KOH (aq) \rightarrow KCl (aq) + H_2O (l)$	–57.3
$HCN (aq) + KOH (aq) \rightarrow KCN (aq) + H_2O (l)$	–12.0
$HCN (aq) + NH_3 (aq) \rightarrow NH_4CN (aq) + H_2O (l)$	–5.4

5.1.9 Measuring enthalpy change, ΔH

- **Calorimetry** is an experimental technique that can be used to measure heat changes in chemical reactions. By **measuring the change in temperature (ΔT), we can calculate the standard enthalpy change (ΔH) of that reaction using the relationship between the heat change and specific heat capacity (c).**

- **Specific heat capacity of a substance**, c, is the amount of heat required to raise the temperature of a unit mass of the substance by one Kelvin (or one degree Celsius).

- Heat change,

$$\boxed{Q = m\,c\,\Delta T}$$

- where, m = mass of substance (g),
  c = specific heat capacity of substance ($J\ g^{-1}\ K^{-1}$),
  ΔT = change in temperature of substance (K or ^{o}C).

- Enthalpy change of reaction is found by finding the heat change per mole of the limiting reagent, n_{lim}.

- If the reaction is **exothermic**, then

$$\boxed{\Delta H = -\frac{Q}{n_{lim}}}$$

- If the reaction is **endothermic**, then

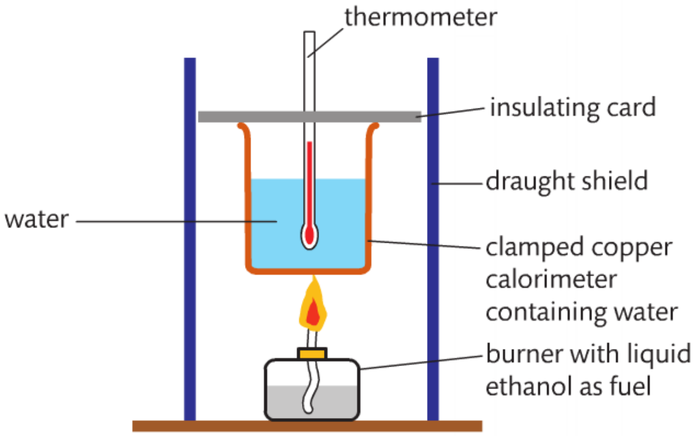
$$\boxed{\Delta H = +\frac{Q}{n_{lim}}}$$

- Water is commonly chosen as the "insulating liquid" as it has a high specific heat capacity ($4.18\ kJ\ kg^{-1}\ K^{-1}$ or $4.18\ J\ g^{-1}\ K^{-1}$). The "water−calorimeter" is commonly used to determine the ΔH_c, ΔH_{soln} and ΔH_{neut} in school laboratories. Note that if the calorimeter absorbs heat, then its mass and specific heat capacity must also be known.

Scan me to view a video on the a simple calorimetry set−up

Example 1

Ethanol, CH_3CH_2OH is burnt in a spirit burner and used to heat up the water for 5 minutes in an experiment shown below.



Scan me to view a video on how enthalpy change of combustion is determined experimentally

The temperature of the 500.000 g of water changes from 25.00 °C to 34.00 °C. The mass of the spirit burner changes from 10.000 g to 9.050 g after the reaction. Given that the specific heat capacity of water is 4.18 J g^{-1} K^{-1},

(a) Calculate the standard enthalpy change of combustion, ΔH^{θ}_{c}, of ethanol.

Temperature change, ΔT
$= (34.00 - 25.00)\ ^{o}C = 9.00\ ^{o}C$

Mass of ethanol that undergoes combustion
= Change in mass of ethanol
= (10.000 – 9.050) g
= 0.950 g

Amount of ethanol that reacted $= \frac{0.950}{46.08} = 0.0206$ mol

Amount of heat evolved
$= m\ c\ \Delta T$
= (500.000 x 4.18 x 9.00) J
= 18810 J
= 18800 J

Therefore, ΔH^{θ}_{c} (ethanol)
$= -\frac{Q}{n_{ethanol}}$
$= -\frac{18800}{0.0206}$ J mol^{-1}
= –912621 J mol^{-1} = **<u>–913 kJ mol^{-1}</u>**

(b) Comment on this value and the set−up of this experiment given the literature value of ΔH^{θ}_{c} (ethanol) = –1371 kJ mol^{-1}.

The calculated value of heat evolved is much lower than expected because:

- Complete combustion of ethanol may not have occurred
- Due to its volatility, some ethanol may have vaporised before combustion
- The heat transfer from the reaction to the calorimeter may not be efficient as heat is lost to the surrounding
- Only the specific heat capacity of water is considered. Heat is also used to warm up the beaker and thermometer

Example 2

250.0 cm^3 of 0.400 mol dm^{-3} aqueous sodium hydroxide of is mixed with 250.0 cm^3 of 0.400 mol dm^{-3} hydrochloric acid in a Styrofoam cup. Both solutions were at 20.00 °C before they were mixed. The final temperature of the solution after mixing is 22.60 °C.

(a) Calculate the standard enthalpy change of neutralisation, ΔH^{θ}_{neu}, for this reaction.

Amount of water produced
= 0.400 x 0.2500
= 0.100 mol

Total mass of mixture (in calorimeter)
= (250.0 + 250.0) x 1 g
= 500.0 g

Temperature change, ΔT
= 22.60 – 20.00 = 2.60 °C

Heat evolved from reaction
= m c ΔT
= 500.0 x 4.18 x 2.60
= 5434 J = 5430 J

Therefore, ΔH^{θ}_{neu}
$= -\frac{5430}{0.100}$ J mol^{-1}
= –54300 J mol^{-1}
= **–54.3 kJ mol^{-1}** (Literature value = –57.3 kJ mol^{-1})

(b) Would the value be the same if the HCl is replaced by ethanoic acid?

The value will be **less exothermic**.

(c) State the assumptions / approximations made for this set–up.

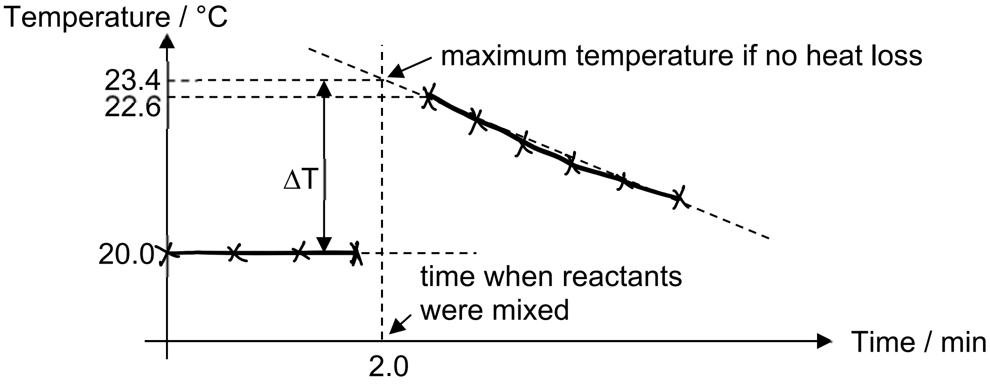
- There is minimal heat loss to the surroundings
- The Styrofoam cups do not absorb much heat
- The heat capacity of the mixture is the same as water
- The volume of water produced is negligible and does not contribute to volume of mixture

- The same experiment was now repeated using the same quantities of reactants but the temperature of the reaction mixture was recorded every half minute over a period of time. The reactants were mixed at time, t = 2.0 min. The following table gives the change in temperature of mixture.

  Recording of temperature:

Time / ± 0.1 min	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Temperature / ±0.1 °C	20.0	20.0	20.0	20.0	−	22.6	22.2	21.7	21.3	20.8	20.5

- A temperature−time graph can be plotted. The curve obtained is extrapolated to the time the reactants were first mixed. The temperature at this point would be the maximum that would have been observed if there was no heat loss at the point of mixing.



- This graphical method of obtaining the highest temperature reached is especially important for reaction that occurs at a slower rate. When the solution is being heated as the reaction proceeds, it is also losing heat to the surroundings. The extrapolated temperature will compensate for this heat loss to the surrounding and also the slow response time of the thermometer to register the highest temperature upon mixing of the reactants.

Scan me to view a video on the graphical method using calorimetry

Method to calculate enthalpy changes, ΔH

Step 1 :

Calculate quantity of heat absorbed / released **by solution**, **Q** using

$\mathbf{Q = m_{soln}\, c\, \Delta T}$, c = specific heat capacity

or $\mathbf{Q = C\, \Delta T}$, C = heat capacity

$\mathbf{m_{soln}}$ = **total volume of solution** (assume density of solution = 1 g cm^{-3})

Q or Q' is always a positive number

Step 2 :

Calculate quantity of heat absorbed / released **by reaction**, **Q'** using

Q' = Q (if assume no heat loss to surroundings ⇒ 100 % efficiency)

$\mathbf{Q = \frac{x}{100} Q'}$ (if **x** % efficiency)

Step 3 :

Calculate enthalpy change asked for in the question

$$\Delta H = \pm \frac{Q'}{n}$$

'+' for endothermic reactions (decrease in temperature / heat absorbed)
'–' for exothermic reactions (increase in temperature / heat released)

Exercise 1

1. Copper has a specific heat capacity of 400 J kg^{-1} K^{-1}. Find the temperature increase if a 50 g cylinder copper block absorbs 800 J of energy.

Heat evolved from reaction, $Q = m\,c\,\Delta T$

$$800 = \frac{50}{1000} \times 400 \times \Delta T$$

$$\Delta T = \frac{800}{\frac{50}{1000} \times 400} = \underline{\mathbf{40\ K}}$$

2. 1.40 g of zinc powder was added to 50.0 cm^3 of 0.100 mol dm^{-3} $AgNO_3$ in a polystyrene cup. Initially, the temperature was 21.10 °C and it rose to 25.40 °C. Calculate the enthalpy change of reaction between Zn and $AgNO_3$. Assume that the density of the solution is 1.00 g cm^{-3} and its specific heat capacity is 4.18 J g^{-1} K^{-1}.

$$Zn\ (s) + 2AgNO_3\ (aq) \rightarrow Zn(NO_3)_2\ (aq) + 2Ag\ (s)$$

Temperature change, ΔT
$= 25.40 - 21.10 = 4.30$ °C

Heat evolved from reaction
$= m\,c\,\Delta T$
$= 50.0 \times 4.18 \times 4.30$
$= 899$ J

Amount of zinc used in reaction
$= \frac{1.40}{65.38} = 0.0214$ mol

Amount of $AgNO_3$ used in reaction
$= 0.100 \times \frac{50.0}{1000} = 5.00 \times 10^{-3}$ mol

∴ $AgNO_3$ is the limiting reactant.

Therefore, ΔH^θ
$= -\frac{899}{\frac{0.00500}{2}}$
$= -359600$
$= \underline{\mathbf{-360\ kJ\ mol^{-1}}}$ (per mole of Zn reacted)

3. Some powdered magnesium was added to 75.00 cm^3 of 0.250 mol dm^{-3} silver nitrate solution in a polystyrene cup. Calculate the enthalpy change of the following reaction:

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

Weighing of solid:

Mass of weighing bottle and Mg / g	4.083
Mass of weighing bottle and residual Mg / g	3.111
Mass of Mg added / g	0.972

Temperature measurements:

Initial temperature of solution / °C	29.50
Highest temperature reached after mixing / °C	37.20

Temperature change, ΔT
$= 37.20 - 29.50 = 7.70$ °C

Heat evolved from reaction
$= m\ c\ \Delta T$
$= 75.00 \times 4.18 \times 7.70$
$= 2410$ J

Amount of Mg used in reaction
$= \frac{0.972}{24.31} = 0.0400$ mol

Amount of Ag^+ used in reaction
$= 0.250 \times \frac{75.00}{1000} = 0.0188$ mol

$\therefore$ Ag^+ is the limiting reactant.

Therefore, ΔH^{θ}
$= -\frac{2410}{\frac{0.0188}{2}}$
$= -256383$
$=$ **$\underline{-257\ kJ\ mol^{-1}}$** (per mole of Mg reacted)

5.2 Hess' law

Essential idea: In chemical transformations energy can neither be created nor destroyed (the first law of thermodynamics).

Nature of Science:

- Hypotheses—based on the conservation of energy and atomic theory, scientists can test the hypothesis that if the same products are formed from the same initial reactants then the energy change should be the same regardless of the number of steps. (2.4)

Understandings:

- The enthalpy change for a reaction that is carried out in a series of steps is equal to the sum of the enthalpy changes for the individual steps.

Applications and skills:

- Application of Hess's Law to calculate enthalpy changes.
- Calculation of Δ reactions using ΔH^{θ}_{f} data.
- Determination of the enthalpy change of a reaction that is the sum of multiple reactions with known enthalpy changes.

Guidance:

- Enthalpy of formation data can be found in the data booklet in section 12.
- An application of Hess's Law is $\Delta H^{\theta}_{reaction} = \Sigma\, \Delta H^{\theta}_{f}$ (products) – $\Sigma\, \Delta H^{\theta}_{f}$ (reactants)

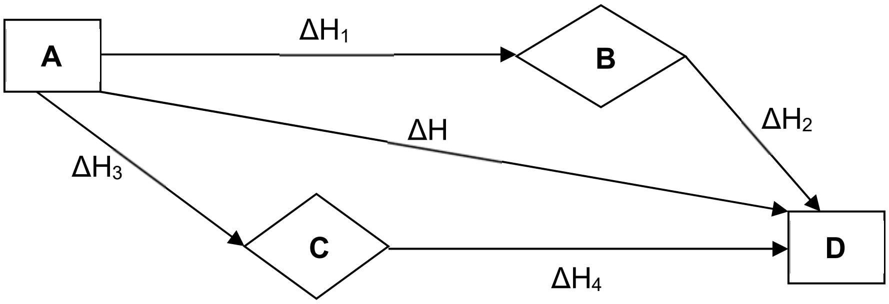
5.2.1 Hess' law

Testing hypothesis (Refer to pg 952 of chemistry course companion)

- Hess's Law is based on the Law of Conservation of Energy. **It states that the enthalpy change of a chemical reaction is the same whether the change is brought about in one stage or through many intermediate stages**. In other words, if the chemical reaction can occur by more than one route, the overall change in enthalpy is the same regardless which route is taken.

- Consider the following reaction pathway to produce D from A represented by the chemical reaction,

$$A\ (s) \rightarrow D\ (s) \qquad \Delta H$$



- The diagram shows that D can be formed from A either via route involving B or C.
- By Hess's Law, the enthalpy change of the reaction, ΔH, can be calculated by either of the two computations shown below:

  - $\Delta H = \Delta H_1 + \Delta H_2$ or
  - $\Delta H = \Delta H_3 + \Delta H_4$

- Hess's law is an important concept as it allows calculation of many standard enthalpies without actually carrying out the experiment. By manipulation of the relevant known thermodynamic data shown in the energy cycle of the reaction, the standard enthalpy change of the reaction can be determined.

Example 1

The enthalpy changes for two displacement reactions are given below.

$Cu\ (s) + 2Ag^+\ (aq) \rightarrow Cu^{2+}\ (aq) + 2Ag\ (s) \quad \Delta H^\theta_1 = -148\ kJ\ mol^{-1}$ equation (1)
$Zn\ (s) + 2Ag^+\ (aq) \rightarrow Zn^{2+}\ (aq) + 2Ag\ (s) \quad \Delta H^\theta_2 = -363\ kJ\ mol^{-1}$ equation (2)

Calculate the standard enthalpy change for the reaction: $Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$

Method 1: Energy Cycle

$$\begin{tikzcd}
Zn\ (s) + Cu^{2+}\ (aq) + 2Ag^+\ (aq) \arrow[rr, "\Delta H^\theta"] \arrow[dr, "\Delta H^\theta_2"'] & & Zn^{2+}\ (aq) + Cu\ (s) + 2Ag^+(aq) \arrow[dl, "\Delta H^\theta_1"] \\
& Zn^{2+}\ (aq) + 2Ag\ (s) + Cu^{2+}\ (aq) &
\end{tikzcd}$$

By Hess's Law,

$\Delta H^\theta = \Delta H^\theta_2 - \Delta H^\theta_1 = (-363) - (-148) = \underline{\mathbf{-215\ kJ}}$

Method 2: Manipulating equations

$Cu^{2+}\ (aq) + 2Ag\ (s) \rightarrow Cu\ (s) + 2Ag^+\ (aq) \quad -\Delta H^\theta_1 = -(-148)\ kJ\ mol^{-1}$
$Zn\ (s) + 2Ag^+\ (aq) \rightarrow Zn^{2+}\ (aq) + 2Ag\ (s) \quad \Delta H^\theta_2 = -363\ kJ\ mol^{-1}$

Taking (2) – (1):

$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s) \quad \Delta H^\theta = \underline{\mathbf{-215\ kJ}}$

Example 2

The enthalpy change of combustion of carbon to carbon monoxide cannot be measured directly. Use the following information to determine the ΔH^{θ} for the reaction:

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

$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$ $\Delta H^{\theta} = -394\ kJ\ mol^{-1}$ equation (1)
$2CO\ (g) + O_2\ (g) \rightarrow 2CO_2\ (g)$ $\Delta H^{\theta} = -566\ kJ\ mol^{-1}$ equation (2)

Method 1: Energy Cycle

$$\begin{tikzcd}
2C\ (s) + 2O_2\ (g) \arrow[rr, "2 \times \Delta H^{\theta}_1"] \arrow[dr, swap, "\Delta H^{\theta}"] & & 2CO_2\ (g) \\
& 2CO\ (g) + O_2\ (g) \arrow[ur, swap, "\Delta H^{\theta}_2"] &
\end{tikzcd}$$

By Hess's Law,

$2 \times \Delta H^{\theta}_1 = \Delta H^{\theta} + \Delta H^{\theta}_2$
$\Delta H^{\theta} = 2\Delta H^{\theta}_1 - \Delta H^{\theta}_2 = 2(-394) - (-566) =$ **<u>-222 kJ</u>**

Method 2: Manipulating equations

$2C\ (s) + 2O_2\ (g) \rightarrow 2CO_2\ (g)$ $2 \times \Delta H^{\theta}_1 = 2(-394)\ kJ\ mol^{-1}$
$2CO_2 \rightarrow 2CO\ (g) + O_2\ (g)$ $-\Delta H^{\theta}_2 = -(-566)\ kJ\ mol^{-1}$

Taking 2 x (1) – (2):

$2C\ (s) + O_2\ (g) \rightarrow 2CO\ (g)$ **<u>-222 kJ</u>**

Example 3

The standard enthalpy change of combustion of carbon, hydrogen and ethyne are shown in the table below. Use the data to calculate the standard enthalpy change of formation of ethyne, C_2H_2.

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

$H_2\ (g) + \frac{1}{2}O_2\ (g) \rightarrow H_2O\ (\ell)$ $\Delta H^\theta = -286\ kJ\ mol^{-1}$ equation (2)

$C_2H_2\ (g) + \frac{5}{2}O_2\ (g) \rightarrow 2CO_2\ (g) + H_2O\ (\ell)$ $\Delta H^\theta = -1300\ kJ\ mol^{-1}$ equation (3)

Method 1: Energy Cycle

$$\begin{tikzcd}
2C\ (s) + H_2\ (g) \arrow[rr, "\Delta H^\theta_f"] \arrow[dr, swap, "\Delta H^\theta_c\ (H_2) + 2 \times \Delta H^\theta_c\ (C)"] \arrow[dr, "+\frac{5}{2}O_2"] & & C_2H_2\ (g) \arrow[dl, swap, "+\frac{5}{2}O_2"] \arrow[dl, "\Delta H^\theta_c\ (ethyne)"] \\
& 2CO_2\ (g) + H_2O\ (\ell) &
\end{tikzcd}$$

By Hess's Law,

$2 \times \Delta H^\theta_c\ (C) + \Delta H^\theta_c\ (H_2) = \Delta H^\theta_f + \Delta H^\theta_c\ (ethyne)$

ΔH_f^θ
$= 2\Delta H^\theta_c\ (C) + \Delta H^\theta_c\ (H_2) - \Delta H^\theta_c\ (ethyne)$
$= 2(-394) + (-286) - (-1300)$
$=$ **$\underline{+226\ kJ\ mol^{-1}}$**

Method 2: Manipulating equations

$2C\ (s) + 2O_2\ (g) \rightarrow 2CO_2\ (g)$ $2 \times \Delta H^\theta = 2(-394)\ kJ\ mol^{-1}$

$H_2\ (g) + \frac{1}{2}O_2\ (g) \rightarrow H_2O\ (\ell)$ $\Delta H^\theta = -286\ kJ\ mol^{-1}$

$2CO_2\ (g) + H_2O\ (\ell) \rightarrow C_2H_2\ (g) + \frac{5}{2}O_2\ (g)$ $-\Delta H^\theta = -(-1300)\ kJ\ mol^{-1}$

Taking 2 x (1) + (2) – (3):

$2C\ (s) + H_2\ (g) \rightarrow C_2H_2\ (g)$ **$\underline{+226\ kJ\ mol^{-1}}$**

Example 4

The standard enthalpy change of formation of aluminium oxide, Al_2O_3, and iron(III) oxide, Fe_2O_3, are –1669kJ mol^{-1} and –822 kJ mol^{-1} respectively. Using these values, calculate the standard enthalpy change, ΔH^θ, for the reaction shown below.

$$2Al(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s)$$

Method 1: Energy Cycle

$$\begin{tikzcd}
2Al(s) + Fe_2O_3\,(s) \arrow[rr, "\Delta H^\theta_r"] & & 2Fe\,(s) + Al_2O_3\,(s) \\
& 2Fe\,(s) + 2Al(s) + \frac{3}{2}O_2\,(g) \arrow[ul, "\Delta H^\theta_f\,(Fe_2O_3)"] \arrow[ur, "\Delta H^\theta_f\,(Al_2O_3)"'] &
\end{tikzcd}$$

By Hess's Law,

$\Delta H^\theta_f\,(Fe_2O_3) + \Delta H^\theta = \Delta H^\theta_f\,(Al_2O_3)$

$\Delta H^\theta = \Delta H^\theta_f\,(Al_2O_3) - \Delta H^\theta_f\,(Fe_2O_3) = (-1669) - (-822) = \underline{\mathbf{-847\ kJ}}$

Method 2: Manipulating equations

$Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + \frac{3}{2}O_2\,(g)$ $\qquad -\Delta H^\theta = -\,(-822)\ kJ\ mol^{-1}$

$2Al(s) + \frac{3}{2}O_2\,(g) \rightarrow Al_2O_3\,(s)$ $\qquad \Delta H^\theta = -1669\ kJ\ mol^{-1}$

Taking –(1) + (2):

$2Al(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s)$ $\qquad \underline{\mathbf{-847\ kJ}}$

This example shows a general rule between the standard enthalpy change of a reaction, ΔH^θ, and the standard enthalpy change of formation of the reactants, ΔH^θ_f (reactants) and of the products, ΔH^θ_f (products) of the reaction.

$$\boxed{\Delta H^\theta_{reaction} = \Sigma\,\Delta H^\theta_f\,(products) - \Sigma\,\Delta H^\theta_f\,(reactants)}$$

Exercise 2

1. The enthalpy changes for two reactions are given below.

$2Cr\ (s) + \frac{3}{2}O_2\ (g) \rightarrow Cr_2O_3\ (s)$ $\quad\Delta H^{\theta}_{1} = -1130\ \text{kJ mol}^{-1}$

$C\ (s) + \frac{1}{2}O_2\ (g) \rightarrow CO\ (g)$ $\quad\Delta H^{\theta}_{2} = -110\ \text{kJ mol}^{-1}$

What is the standard enthalpy change for the following reaction?

$Cr_2O_3\ (s) + 3C\ (s) \rightarrow 2Cr\ (s) + 3CO\ (g)$

$$\begin{tikzcd}
Cr_2O_3\ (s) + 3C\ (s) \arrow[rr, "\Delta H^{\theta}_{r}"] & & 2Cr\ (s) + 3CO\ (g) \\
& 2Cr\ (s) + \frac{3}{2}O_2\ (g) + 3C\ (s) \arrow[ul, "\Delta H^{\theta}_{1}"] \arrow[ur, "3 \times \Delta H^{\theta}_{2}"'] &
\end{tikzcd}$$

By Hess's Law,

$\Delta H^{\theta}_{1} + \Delta H^{\theta}_{r} = 3 \times \Delta H^{\theta}_{2}$

$\Delta H^{\theta}_{r} = 3 \times (-110) - (-1130) = \underline{\mathbf{+800\ kJ}}$

2. The enthalpy changes for two reactions are shown below:

$S\ (s) + O_2\ (g) \rightarrow SO_2\ (g)$ $\quad\Delta H^{\theta}_{1} = -300\ \text{kJ mol}^{-1}$

$2S\ (s) + 3O_2\ (g) \rightarrow 2SO_3\ (g)$ $\quad\Delta H^{\theta}_{2} = -800\ \text{kJ mol}^{-1}$

What is the enthalpy change for the following reaction?

$2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)$

$$\begin{tikzcd}
2SO_2\ (g) + O_2\ (g) \arrow[rr, "\Delta H^{\theta}_{r}"] & & 2SO_3\ (g) \\
& 2S\ (s) + 2O_2\ (g) + O_2\ (g) \arrow[ul, "2 \times \Delta H^{\theta}_{1}"] \arrow[ur, "\Delta H^{\theta}_{2}"'] &
\end{tikzcd}$$

By Hess's Law,

$2 \times \Delta H^{\theta}_{1} + \Delta H^{\theta}_{r} = \Delta H^{\theta}_{2}$

$\Delta H^{\theta}_{r} = (-800) - 2 \times (-300) = \underline{\mathbf{-200\ kJ}}$

3. Determine the ΔH^{θ}_{f} of ethanoic acid given the following data.

$CH_3COOH\ (l) + 2O_2\ (g) \rightarrow 2CO_2\ (g) + 2H_2O\ (l)$ $\Delta H^{\theta} = -876\ kJmol^{-1}$

$\Delta H^{\theta}_{f}\ (CO_2) = -394\ kJmol^{-1}$ and $\Delta H^{\theta}_{f}\ (H_2O) = -286\ kJmol^{-1}$

$\Delta H^{\theta}_{reaction} = \Sigma\ \Delta H^{\theta}_{f}\ (products) - \Sigma\ \Delta H^{\theta}_{f}\ (reactants)$

$-876 = 2(-394) + 2(-286) - [\Delta H^{\theta}_{f}\ (CH_3COOH)]$

$\Delta H^{\theta}_{f}\ (CH_3COOH) =$ **$\underline{-484\ kJ}$**

5.3 Bond enthalpies

Essential idea: Energy is absorbed when bonds are broken and is released when bonds are formed.

Nature of Science:

- Models and theories—measured energy changes can be explained based on the model of bonds broken and bonds formed. Since these explanations are based on a model, agreement with empirical data depends on the sophistication of the model and data obtained can be used to modify theories where appropriate (2.2)

Understandings:

- Bond−forming releases energy and bond−breaking requires energy.
- Average bond enthalpy is the energy needed to break one mol of a bond in a gaseous molecule averaged over similar compounds

Applications and skills:

- Calculation of the enthalpy changes from known bond enthalpy values and comparison of these to experimentally measured values.
- Sketching and evaluation of potential energy profiles in determining whether reactants or products are more stable and if the reaction is exothermic or endothermic.
- Discussion of the bond strength in ozone relative to oxygen in its importance to the atmosphere.

Guidance:

- Bond enthalpy values are given in the data booklet in section 11.
- Average bond enthalpies are only valid for gases and calculations involving bond enthalpies may be inaccurate because they do not take into account intermolecular forces

5.3.1 Bond enthalpies

- Bond Enthalpy / Energy, ΔH_{BE}

Energy needed to **break one mole of bonds in the gaseous molecules**, under standard conditions.

E.g. $SiCl_4\,(g) \rightarrow Si\,(g) + 4Cl(g)$ $\Delta H_{reaction} = 4 \times \Delta H_{BE}\,(Si–Cl)$

$H_2\,(g) \rightarrow 2H\,(g)$ $\Delta H_{reaction} = \Delta H_{BE}\,(H–H)$

- The magnitude of ΔH_{BE} of the molecule is an indication on the strength of the covalent bond.
- These values can be obtained from the Data Booklet Section 11, which is the average value derived from studying the same bond in a large number of different molecules.

5.3.2 Calculations using bond enthalpies, ΔH_{BE}

- The enthalpy change of reactions, ΔH, can also be calculated using bond energies as shown in the equation.

$$\boxed{\Delta H^{\theta}_{reaction} = \Sigma\ \Delta H_{BE}\text{ (bonds broken in reactants)} - \Sigma\ \Delta H_{BE}\text{ (bonds formed in products)}}$$

- This calculation is at best an approximation to the actual ΔH value of the reaction. There are various assumptions and restrictions that need to be considered when using ΔH_{BE} in the calculation of enthalpy changes. Possible assumptions:
    - Average bond enthalpies are only valid for gases and calculations involving bond enthalpies may be inaccurate because they do not take into account intermolecular forces
    - Average bond enthalpy is the average energy required to break a mole of the same type of bonds in the gaseous state in a variety of similar compounds. It is not the actual bond dissociation energy.

      E.g. The C–H bond in ethane, ethene, ethyne are different though they are all assumed to have the same ΔH_{BE}(C–H) values of 412 kJ mol^{-1} in calculations.
      $\Rightarrow$ recall that the hybridisation of carbon is different in ethane, ethene and ethyne. Therefore their C–H sigma bonds formed will be different in strength due to different extents of orbital overlap.
    - The products and reactants involved are covalent compounds and this equation does not apply to reactions involving ionic compounds and metals.

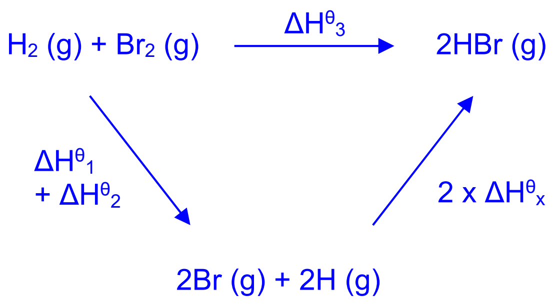
Example 1

The table below shows the standard enthalpy changes of some reactions. Use these values to calculate the standard enthalpy change, ΔH^{θ}_{x} for the reaction:

$$H\ (g) + Br\ (g) \rightarrow HBr\ (g)$$

Equation	Chemical Reaction	ΔH^{θ} / kJ mol^{-1}
1	$H_2\ (g) \rightarrow 2H\ (g)$	+436
2	$Br_2\ (g) \rightarrow 2Br\ (g)$	+193
3	$H_2\ (g) + Br_2\ (g) \rightarrow 2HBr\ (g)$	–104

Method 1: Energy Cycle



By Hess's Law,

$\Delta H^{\theta}_{1} + \Delta H^{\theta}_{2} + (2 \times \Delta H^{\theta}_{x}) = \Delta H^{\theta}_{3}$

ΔH^{θ}_{x}

$= \frac{1}{2}[\Delta H^{\theta}_{3} - \ \Delta H^{\theta}_{1} + \Delta H^{\theta}_{2}]$

$= \frac{1}{2}(-104 - 436 - 194)$

$= -366.5$ kJ mol^{-1}

= **$\underline{-367 \text{ kJ mol}^{-1}}$**

Method 2: Manipulating equations

$\mathrm{H\ (g)} \rightarrow \frac{1}{2}\mathrm{H_2\ (g)}$ $\quad -\frac{1}{2}\Delta H^{\theta}_{1} = -\frac{1}{2}(193)\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{Br\ (g)} \rightarrow \frac{1}{2}\mathrm{Br_2\ (g)}$ $\quad -\frac{1}{2}\Delta H^{\theta}_{2} = -\frac{1}{2}(436)\ \mathrm{kJ\ mol^{-1}}$

$\frac{1}{2}\mathrm{H_2\ (g)} + \frac{1}{2}\mathrm{Br_2\ (g)} \rightarrow \mathrm{HBr\ (g)}$ $\quad \frac{1}{2}\Delta H^{\theta}_{3} = \frac{1}{2}(-104)\ \mathrm{kJ\ mol^{-1}}$

Taking $-\frac{1}{2}(1) - \frac{1}{2}(2) + \frac{1}{2}(3)$:

$\mathrm{H\ (g) + Br\ (g)} \rightarrow \mathrm{HBr\ (g)}$ $\quad -366.5\ \mathrm{kJ}$

The bond dissociation of gaseous HBr can be represented by the equation,

$\mathrm{HBr\ (g)} \rightarrow \mathrm{H\ (g) + Br\ (g)}$

Bond dissociation energy of HBr = $-\Delta H^{\theta}_{x} = -(-367)\ \mathrm{kJ\ mol^{-1}}$= **$+367\ \mathrm{kJ\ mol^{-1}}$**

Example 2

Using the average bond enthalpy data from the Data Booklet and ΔH_{BE} (N–I) = 161 kJ $\mathrm{mol^{-1}}$, calculate the enthalpy change of reaction for the reaction:

$$\mathrm{N_2\ (g) + 3I_2\ (g) \rightarrow 2NI_3\ (g)}$$

$\Delta H^{\theta}_{reaction} = \Sigma\ \Delta H_{BE}$ (bonds broken in reactants) – $\Sigma\ \Delta H_{BE}$ (bonds formed in products)

$\Sigma\ \Delta H_{BE}$ (bonds broken in reactants)
= ΔH_{BE} (N≡N) + $3\Delta H_{BE}$ (I–I)
= 945 + 3(151)
= 1398 kJ $\mathrm{mol^{-1}}$

$\Sigma\ \Delta H_{BE}$ (bonds formed in products)
= $6\Delta H_{BE}$ (N–I)
= 6(161) kJ $\mathrm{mol^{-1}}$
= 966 kJ $\mathrm{mol^{-1}}$

$\Delta H^{\theta}_{reaction}$ = 1398 – 966 = **$+432\ \mathrm{kJ\ mol^{-1}}$**

Exercise 3

1. The bond energies for H_2 (g) and HF (g) are 435 kJ mol^{-1} and 565 kJ mol^{-1} respectively.

For the reaction $\frac{1}{2}H_2\ (g) + \frac{1}{2}F_2\ (g) \rightarrow HF\ (g)$, the enthalpy of reaction is –268 kJ mol^{-1} of HF produced. What is the bond energy of F_2 in kJ mol^{-1}?

$\Delta H^{\theta}_{reaction} = \Sigma\ \Delta H_{BE}$ (bonds broken in reactants) – $\Sigma\ \Delta H_{BE}$ (bonds formed in products)

$\Delta H^{\theta}_{reaction} = \frac{1}{2}BE\ (F–F) + \frac{1}{2}BE\ (H–H) – BE\ (H–F)$

$–268 = \frac{1}{2}BE\ (F–F) + \frac{1}{2}(435) – 565$

$\frac{1}{2}BE\ (F–F) = 79.5$

BE (F–F) = 79.5 x 2 = **+159 kJ mol^{-1}**

2. From a consideration of the following bond enthalpies:

C=C	615 kJ mol^{-1}
C–F	441 kJ mol^{-1}
C–C	348 kJ mol^{-1}
F–F	158 kJ mol^{-1}

What is the enthalpy change for the addition reaction between fluorine and ethene?

$$F_2\ (g) + CH_2{=}CH_2\ (g) \rightarrow CH_2FCH_2F\ (g)$$

$\Delta H^{\theta}_{reaction} = \Sigma\ \Delta H_{BE}$ (bonds broken in reactants) – $\Sigma\ \Delta H_{BE}$ (bonds formed in products)

$\Delta H^{\theta}_{reaction}$

= [4BE (C–H) + BE (C=C) + BE (F–F)] – [4BE (C–H) + 2BE (C–F) + BE (C–C)]

= [615 + 158] – [2(441) + 348]

= **–457 kJ mol^{-1}**

5.3.3 Ozone

- Ozone is a colourless and odourless gas made of oxygen.

  The molecules of ozone contain three oxygen atoms (O_3). It is a very reactive gas, and is toxic even at low concentrations. It occurs naturally in small amounts in the Earth's upper atmosphere, and in the air of the lower atmosphere after a lightning storm.

  Ozone is very effective at absorbing harmful long and short−wavelength UV radiation. This ozone layer absorbs solar radiation (electromagnetic radiation) of wavelengths less than 1140 nm. However, its importance lies in its ability to absorb harmful UV radiation of wavelengths between 240–310 nm. This "shielding" of harmful UV radiation is crucial as the flora and fauna on Earth will not be able to survive in the presence of high energy electromagnetic radiation. This absorption breaks down the ozone molecule to reform molecular oxygen and a single oxygen atom. Without the presence of ozone in the stratosphere, harmful UV radiation would damage cells in both plants and animals.

- How does the ozone layer shield UV radiation?

  - The shielding of UV radiation by the ozone layer is a cyclical process of ozone formation and destruction. This cyclical process can be summarised into 4 key steps:

    Step 1: $O_2\,(g) + h\nu \rightarrow 2O\bullet\,(g)$
    Step 2: $O_2\,(g) + O\bullet\,(g) + \mathbf{M} \rightarrow O_3\,(g) + M^*$(thermal energy)
    Step 3: $O_3\,(g) + h\nu \rightarrow O_2\,(g) + O\bullet\,(g)$
    Step 4: $O_3\,(g) + O\bullet\,(g) + \mathbf{M} \rightarrow 2O_2\,(g) + M^*$(thermal energy)

    *Note: **M** can represent N_2 or O_2 molecule

Scan me to view a video on ozone's function

- Step 1: $O_2\,(g) + h\nu \rightarrow 2O\bullet\,(g)$

  - This step involves the photo−dissociation of oxygen and it happens predominantly at the higher attitudes, ~120 km above sea level.

  - This process absorbs the high−energy, short wavelength UV radiation (≈240nm).

    $$\text{Energy of 1 O=O bond} = \frac{498000}{6.02\times10^{23}} = 8.27 \times 10^{-19}\ \text{J}$$

    Energy of photon, E, needed to break 1 O=O bond = 8.27×10^{-19} J

    $$E = h\nu = \frac{hc}{\lambda}$$

    $$\lambda = \frac{hc}{E} = \frac{6.63\times10^{-34}\times3.00\times10^{8}}{8.27\times10^{-19}} = 2.41 \times 10^{-7}\ \text{m} = 241\text{nm}$$

- Step 2: $O_2\,(g) + O\bullet\,(g) + \mathbf{M} \rightarrow O_3\,(g) + M^*$(thermal energy)

  - This step involves the formation of highly energised ozone.

  - The excess energy of the ozone is transferred through collision with nitrogen or oxygen molecules (denoted by **M** in the equation) as thermal energy. Thus the layer of gases at this level is warmer than the air below it.

  - This rise in temperature at the stratosphere is crucial in preventing vertical mixing of gases hence stabilising the ozone layer at this attitude.

- Step 3: $O_3\ (g) + h\nu \rightarrow O_2\ (g) + O\bullet\ (g)$

  - While oxygen at higher attitude absorbs radiation of wavelength less than 240nm, the ozone layer at ≈10−50 km above sea level is the main species "buffer" for absorbing solar radiation of wavelength less than 1140 nm, crucially those between 240 nm and 340 nm.

    Energy of 1 O−O bond in ozone = $\frac{362000}{6.02 \times 10^{23}} = 6.03 \times 10^{-19}$ J
    Energy of photon, E, needed to break 1 O−O bond = 6.03×10^{-19} J
    $E = h\nu = \frac{hc}{\lambda}$
    $\lambda = \frac{hc}{E} = \frac{6.63 \times 10^{-34} \times 3.00 \times 10^{8}}{6.03 \times 10^{-19}} = 3.30 \times 10^{-7}$ m = 330 nm

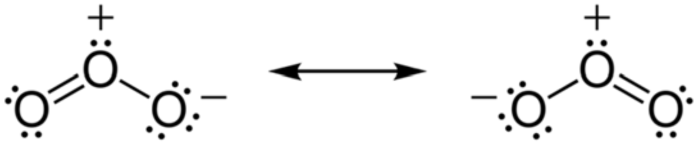
  - Thus Step 1 and Step 3 are the two essential steps that shield the Earth from harmful UV radiation.

- Step 4: $O_3\ (g) + O\bullet\ (g) + \mathbf{M} \rightarrow 2O_2\ (g) + M^*$(thermal energy)

  - Similar to Step 2, this is an exothermic process which helps to stabilise the ozone layer by keeping it at a higher temperature than the air below.

- For simplification, the shielding of UV by the ozone are often summarised into two steps:

  $O_3\ (g) + h\nu \rightarrow O_2\ (g) + O\bullet\ (g)$
  $O_2\ (g) + O\bullet\ (g) \rightarrow O_3\ (g)$ + thermal energy



Resonance forms of ozone, O_3

- Ozone is much more reactive than O_2. It is a very powerful oxidising agent, second among elements only to fluorine.

- Ozone is a V–shaped molecule with a bond angle of 116.8° and the two O–O bond lengths are equal i.e. 128 pm.

- The bond order for the O–O bond in ozone is calculated as follows:

  Each bond order in $O_3 = \frac{\text{total number of O-O bonding pairs}}{\text{number of O-O bond locations}} = \frac{3}{2} = 1.5$

- **Photodissociation**
  - The Sun emits radiation over a wide range of wavelengths. The shorter wavelength and higher energy radiations in the ultraviolet range of the spectrum are energetic enough to cause chemical changes.
  - The rupture of a chemical bond resulting from absorption of a photon by a molecule is called **photodissociation**. Photodissociation does not form ions. The bond cleavage leaves half the bonding electrons with each of the two atoms forming two neutral particles.
  - The equation below shows the photodissociation of an oxygen molecule.

$$O_2\ (g) \xrightarrow{h\nu} 2O\bullet\ (g)$$

  - Ozone also undergoes dissociation in the presence of UV radiation from the sun i.e.

$$\text{Fast:}\quad O_3\ (g) \xrightarrow{h\nu} O_2\ (g) + O\bullet\ (g)$$

$$\text{Slow:}\quad O_3\ (g) + O\bullet\ (g) \rightarrow 2O_2\ (g)$$

  - Both the bonds in oxygen and ozone can be broken by UV radiation.
  - The bond order in ozone is 1.5 but that in oxygen is 2. Hence the double bond in O=O is stronger and radiation of a shorter wavelength ($\lambda < 242$ nm) is required to break the bond in oxygen than in ozone molecules ($\lambda < 330$ nm).
  - Using $E = h\nu$ and given that the average bond enthalpy of an ozone and oxygen molecule are 362 kJ mol^{-1} and 498 kJ mol^{-1} respectively, the wavelength of the UV radiation required to break the O–O bond in ozone and the O=O double bond in oxygen can be calculated, as shown above.

- **Catalysis of ozone depletion when catalysed by CFCs**
  - CFCs are widely used in aerosols, refrigerants, solvents and plastics due to their low reactivity and low toxicity in the troposphere.
  - However, when they get into the stratosphere, the higher energy UV radiation breaks them down, releasing free chlorine atoms which are also reactive free radicals.
  - CFC, also known as Freon undergoes photochemical decomposition as follows:

    <u>**Initiation:**</u>

$$CCl_2F_2\ (g) \xrightarrow{h\nu} \bullet CClF_2\ (g) + Cl\bullet\ (g)$$

  - The weaker C–Cl bond breaks in preference to the C–F bond, and the chlorine radicals catalyse the decomposition of ozone.

Propagation:

$Cl\bullet\ (g) + O_3\ (g) \rightarrow O_2\ (g) + ClO\bullet\ (g)$
$ClO\bullet\ (g) + O_3\ (g) \rightarrow 2O_2\ (g) + Cl\bullet\ (g)$

Here, $Cl\bullet$ (g) has acted as the catalyst and the net reaction is:

$2O_3\ (g)\ (g) \rightarrow 3O_2\ (g)$

- The $Cl\bullet$ (g) and $ClO\bullet$ (g) radicals are removed.

- It can be seen that one $Cl\bullet$ (g) is able to "destroy" many ozone molecules as the $Cl\bullet$ (g) radicals is re−generated and will continue to destroy the ozone molecules as shown in the two reactions of propagation stage.

Termination:

$Cl\bullet\ (g) + CH_4\ (g) \rightarrow HCl(g) + CH_3\bullet\ (g)$
$ClO\bullet\ (g) + NO_2\bullet\ (g) \rightarrow ClONO_2\ (g)$

- The termination step ends up with a $CH_3\bullet$ (g). This radical is "less harmful" as it is not involved in the two propagation steps.

Refer to page 343 of Chemistry Course Companion for the wavelength of light required to dissociate oxygen and ozone.
The mechanism of the catalysis of ozone depletion is also discussed in Topic 4 Chemical Bonding and Topic 6 Kinetics.

- **Catalysis of ozone depletion when catalysed by NO_x**
  - NO is produced in vehicle engines by direct combination of nitrogen and oxygen from the air at high temperatures.
  - NO is a free radical.
  - NO_2, which is formed from the oxidation of NO, is also a free radical.
  - The reactions of nitrogen oxides with ozone are:

$$NO\bullet\ (g) + O_3\ (g) \rightarrow NO_2\bullet\ (g) + O_2\ (g)$$
$$NO_2\bullet\ (g) + O\bullet\ (g) \rightarrow NO\bullet\ (g) + O_2\ (g)$$

Scan me to view a video on ozone depletion

15.1 Energy cycles

Essential idea: The concept of the energy change in a single step reaction being equivalent to the summation of smaller steps can be applied to changes involving ionic compounds

Nature of Science:

- Making quantitative measurements with replicates to ensure reliability—energy cycles allow for the calculation of values that cannot be determined directly. (3.2)

Understandings:

- Representative equations (e.g. $M^+ (g) \rightarrow M^+ (aq)$) can be used for enthalpy / energy of hydration, ionisation, atomisation, electron affinity, lattice, covalent bond and solution.
- Enthalpy of solution, hydration enthalpy and lattice enthalpy are related in an energy cycle.

Applications and skills:

- Calculation of the enthalpy changes from known bond enthalpy values and comparison of these to experimentally measured values.
- Construction of Born−Haber cycles for group 1 and 2 oxides and chlorides.
- Construction of energy cycles from hydration, lattice and solution enthalpy. For example dissolution of solid NaOH or NH_4Clin water.
- Calculation of enthalpy changes from Born−Haber or dissolution energy cycles.
- Relate size and charge of ions to lattice and hydration enthalpies.
- Perform lab experiments which could include single replacement reactions in aqueous solutions.

Guidance:

- Polarising effect of some ions producing covalent character in some largely ionic substances will not be assessed.
- The following enthalpy / energy terms should be covered: ionisation, atomisation, electron affinity, lattice, covalent bond, hydration and solution.
- Value for lattice enthalpies (section 18), enthalpies of aqueous solutions (section 19) and enthalpies of hydration (section 20) are given in the data booklet.

15.1.1 Definitions of other standard enthalpies

- Lattice energy, $\Delta H^{\theta}_{lattice}$

> It is the standard enthalpy change when **one mole of a solid ionic compound is separated into gaseous ions under standard conditions**.

E.g. $NaCl(s) \rightarrow Na^+ (g) + Cl^- (g)$ $\Delta H^{\theta}_{lattice} = +790 \text{ kJ mol}^{-1}$

- o The process is endothermic ($\Delta H^{\theta}_{lattice} > 0$). The greater the magnitude of $\Delta H^{\theta}_{lattice}$, the stronger the ionic bond.

- The magnitude of $\Delta H^{\theta}_{lattice}$ depends on the charges of the ions, their sizes and the arrangement of the ions in the solid. The magnitude of the lattice energy is given by the equation below,

$$|\text{Lattice Energy}| \propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$$

Where q_+ = charge of cation
q_- = charge of anion
r_+ = radius of cation
r_- = radius of anion

- The greater the charge of the ions, the stronger the electrostatic attraction between them.

- The smaller the ionic radius, the shorter the distance between the ions and hence the stronger the electrostatic attraction between them.

- Theoretical values are calculated based on the assumption that the solid is truly ionic while the experimental values are usually calculated by the Born−Haber cycle (see section 15.1.2). There is usually a difference between the two values which can be attributed to the partial covalent character in some ionic compounds.

Compound	$\Delta H^{\theta}_{lattice}$ / kJ mol^{-1} (Born–Haber)	$\Delta H^{\theta}_{lattice}$ / kJ mol^{-1} (Ionic model)
NaCl	+790	+769
AgCl	+918	+864

- Standard enthalpy change of atomisation of an element / compound, ΔH^{θ}_{at}

It is the standard enthalpy change when **one mole of gaseous atoms is formed from the element in its standard states.**

E.g. $\frac{1}{2}I_2\ (s) \rightarrow I\ (g)$
$Na\ (s) \rightarrow Na\ (g)$
$C_2H_5OH\ (l) \rightarrow 2C\ (g) + 6H\ (g) + O\ (g)$

- The process is endothermic ($\Delta H^{\theta}_{at} > 0$).

- Relationship between ΔH^{θ}_{at} and bond enthalpies ΔH_{BE}

For diatomic gaseous molecules X_2 (g),

$$\boxed{\Delta H_{BE}(X_2) = 2\,\Delta H^{\theta}_{at}(X_2)}$$

- Electron affinity, ΔH_{EA}

1st electron affinity is the standard enthalpy change when **one mole of gaseous electrons is added to one mole of gaseous atoms to form one mole of singly negatively charged gaseous ion.**

E.g. $O\ (g) + e \rightarrow O^{-}\ (g)$ 1st $\Delta H_{EA} = -141$ kJ mol^{-1}

- o The process is exothermic ($\Delta H^{\theta}_{EA} < 0$) for 1st electron affinity. This is because energy is released due to the attraction formed between the gaseous atom and the electron.

2nd electron affinity is the standard enthalpy change when **one mole of gaseous electrons is added to one mole of negatively charged gaseous ion to form one mole of doubly negatively charged gaseous ion.**

E.g. $O^{-}\ (g) + e \rightarrow O^{2-}\ (g)$ 2nd $\Delta H_{EA} = +798$ kJ mol^{-1}

- o The process is endothermic ($\Delta H^{\theta}_{EA} > 0$) for 2nd and all subsequent electron affinities. This is because energy is absorbed to overcome the repulsion between the singly negatively charged ion and the electron.

- 1st ionisation energy, ΔH_{IE}

It is the **minimum energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of singly positively charge gaseous ion.**

E.g. $Na\ (g) \rightarrow Na^{+}\ (g) + e$ 1st $\Delta H_{IE} = +496$ kJ mol^{-1}

- o The process is endothermic ($\Delta H^{\theta}_{IE} > 0$) for all ionisation energies. This is because energy is absorbed to overcome the effective nuclear charge between positively charged nucleus and the outgoing electron.

- o There is a general increase in successive ionisation energy. This is due to an increasing amount of energy required to remove successive electrons from an increasingly positive ion due to an increasing electrostatic force of attraction between the nucleus and valence electrons.

- Standard enthalpy change of hydration, ΔH^{θ}_{hyd}

It is the standard enthalpy change when **one mole of gaseous ions forms one mole of hydrated ions in water under standard conditions.**

E.g. $Na^{+}(g) \rightarrow Na^{+}(aq)$ $\Delta H^{\theta}_{hyd} = -406$ kJ mol^{-1}

- o The process is exothermic ($\Delta H^{\theta}_{hyd} < 0$). This is because energy is released due to the formation of ion−dipole interactions between ions and the polar water molecules.

- o Factors affecting this interaction are the size and charge of ions

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

- Standard enthalpy change of solution, ΔH^{θ}_{soln}

It is the standard enthalpy change when **one mole of a solute is dissolved in a solvent to infinite dilution under standard conditions.**

E.g. $NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$ $\Delta H^{\theta}_{soln} = +3.88$ kJ mol^{-1}

- o ΔH^{θ}_{soln} is exothermic ($\Delta H^{\theta}_{soln} < 0$) when the **heat released from hydration of ions is more than that used to break up the solid lattice structure and the H−bonds between water molecules**. Solutes whose ΔH^{θ}_{soln} is exothermic are **soluble in water**. However salts with slightly positive ΔH^{θ}_{soln} are also soluble in water as in the case of solid sodium chloride.

- o ΔH^{θ}_{soln} is endothermic ($\Delta H^{\theta}_{soln} > 0$) when **the heat released from hydration of ions is less than that used to break up the solid lattice structure and the H−bonds between water molecules**. Solutes whose ΔH^{θ}_{soln} is endothermic are usually **insoluble in water**.

- o In general, ΔH^{θ}_{soln} of ionic compounds can be calculated from the lattice energy and hydration energy by using Hess's Law.

$$\boxed{\Delta H^{\theta}_{soln} = \Delta H^{\theta}_{lattice} + \Delta H^{\theta}_{hyd}}$$

Example 1

Given the data in the table, determine the enthalpy change, ΔH, for dissolving potassium iodide, KI in water,

$$KI\ (s) \rightarrow K^+\ (aq) + I^-\ (aq)$$

Equation	Chemical Reaction	ΔH^θ / kJ mol^{-1}
1	$KI\ (s) \rightarrow K^+\ (g) + I^-\ (g)$	+629
2	$K^+\ (g) + I^-\ (g) \rightarrow K^+\ (aq) + I^-\ (aq)$	–615

Method 1: Energy Cycle

$$\begin{tikzcd}
KI\ (s) \arrow[rr, "\Delta H"] \arrow[dr, "\Delta H^\theta_1"'] & & K^+\ (aq) + I^-\ (aq) \\
& K^+\ (g) + I^-\ (g) \arrow[ur, "\Delta H^\theta_2"'] &
\end{tikzcd}$$

By Hess's Law,

ΔH
$= \Delta H^\theta_1 + \Delta H^\theta_2$
$= (+629) + (-615)$
= **<u>+14 kJ mol^{-1}</u>**

Method 2: Manipulating equations

$KI\ (s) \rightarrow K^+\ (g) + I^-\ (g)$ $\quad \Delta H^\theta_1 = +629$ kJ mol^{-1}
$K^+\ (g) + I^-\ (g) \rightarrow K^+\ (aq) + I^-\ (aq)$ $\quad \Delta H^\theta_2 = -615$ kJ mol^{-1}

Taking (1) + (2):

$KI\ (s) \rightarrow K^+\ (aq) + I^-\ (aq)$ $\quad$ **<u>+14 kJ mol^{-1}</u>**

Note:

- ΔH^θ_1 has the same value to the lattice energy of KI
- ΔH^θ_2 defined as the total enthalpy change of hydration of potassium and iodide ions.
- In general, the enthalpy change of solution of ionic compounds can be calculated by using the lattice energy and enthalpy change of hydration.

15.1.2 Born–Haber cycle

✍ Models for finding enthalpy changes (Refer to pg 239 of chemistry course companion)

- Lattice energy, $\Delta H^{\theta}_{lattice}$

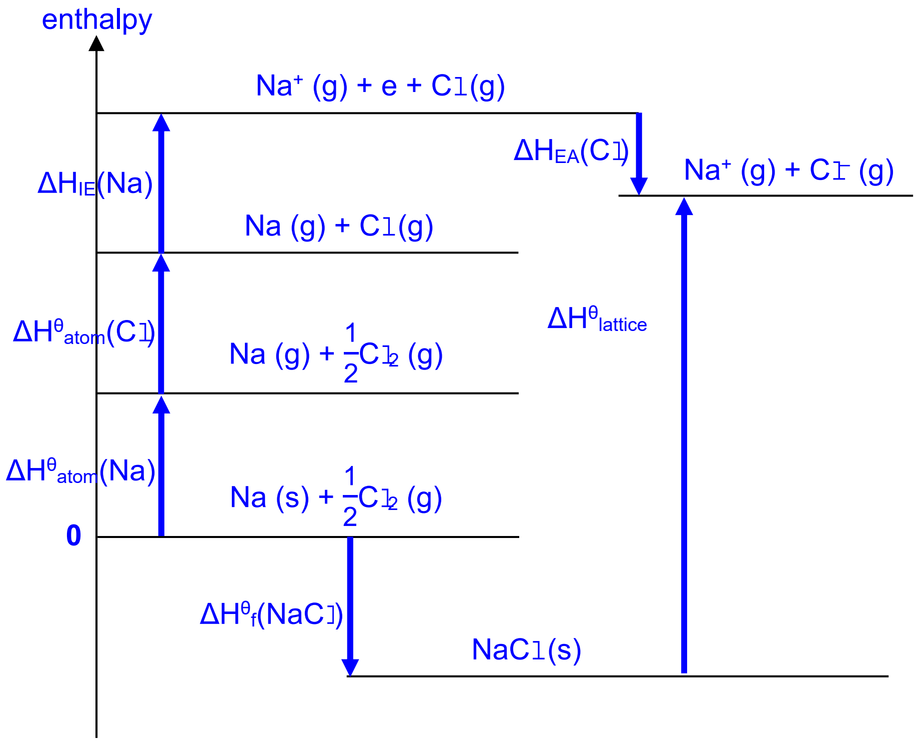
- An application of Hess's Law, the Born−Haber cycle, is a series of reactions that can be combined to determine the enthalpy of formation (ΔH^{θ}_{f}) or the lattice energy ($\Delta H^{\theta}_{lattice}$) of an ionic compound.

- It is crucial that a proper cycle, with all the relevant steps are labelled clearly. It involves 4 key steps:

Steps	**Remarks**
F	ΔH^{θ}_{f} , standard enthalpy change of formation of the ionic compound starting from the elements in their stable states under standard conditions
A	ΔH^{θ}_{atom} , standard enthalpy change of atomisation to form the gaseous atoms. This is to allow for the formation of ions in the subsequent step ΔH_{BE} , bond energy of non–metal molecules might be used if the ΔH^{θ}_{atom} is not given
I	For metals, ΔH_{IE} , ionisation energy. Number of ionisation energy will depend on the charge of the metal cation present in the ionic compound For non–metals, ΔH_{EA} , electron affinity. Number of electron affinity will depend on the charge of the non–metal anion present in the ionic compound Note that ionisation energy should always be done before electron affinity
L	$\Delta H^{\theta}_{lattice}$, lattice energy

- The Born−Haber cycle for sodium chloride is illustrated below.

Standard enthalpy change of atomisation of sodium, $\Delta H^{\theta}_{atom}(Na)$ = +108 kJ mol^{-1}
Standard enthalpy change of atomisation of chlorine, $\Delta H^{\theta}_{atom}(Cl)$ = +121 kJ mol^{-1}
Ionisation energy of sodium, $\Delta H_{IE}(Na)$ = +494 kJ mol^{-1}
Electron affinity of chlorine, $\Delta H_{EA}(Cl)$ = −364 kJ mol^{-1}
Lattice energy of sodium chloride, $\Delta H^{\theta}_{lattice}$ = +770 kJ mol^{-1}



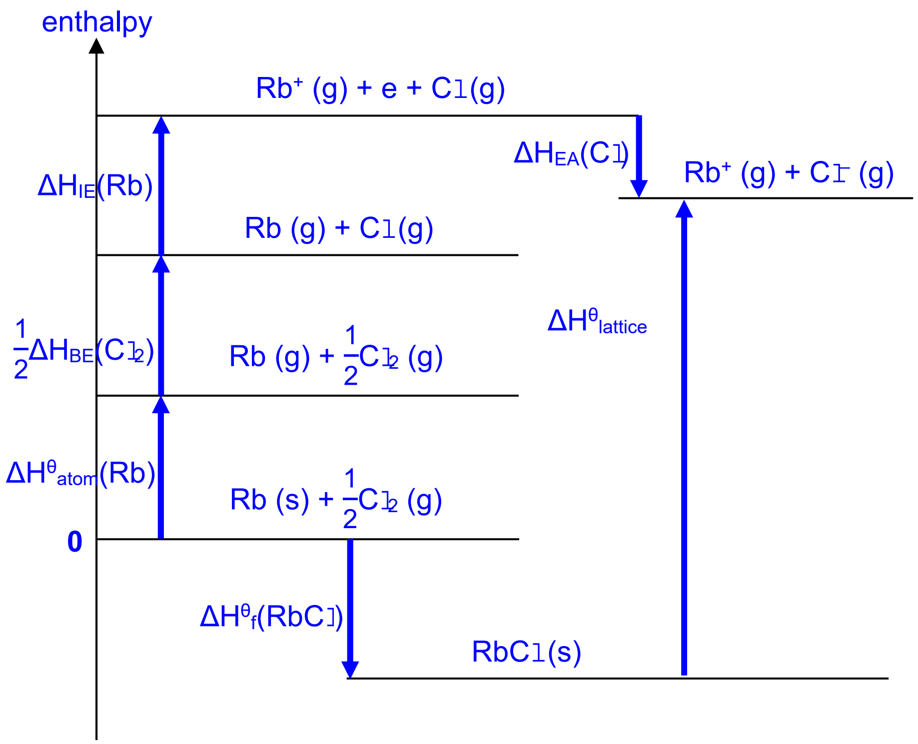
The energy level diagram reflects the change in energy level during the reaction pathways. The direction of the arrows indicates if the reaction is **exothermic (pointing down)** or **endothermic (pointing up)**.

By Hess' Law, (using either diagram)
$\Delta H^{\theta}_{f}(NaCl)$
$= \Delta H^{\theta}_{atom}(Na) + \Delta H^{\theta}_{atom}(Cl) + \Delta H_{IE}(Na) + \Delta H_{EA}(Cl) - \Delta H^{\theta}_{lattice}$
= [(+108) + (+121) + (+494) + (–364) – (+770)]
= **<u>–411 kJ mol^{-1}</u>**

Example 1

Using the data below, calculate the electron affinity of chlorine.

Standard enthalpy of formation of rubidium chloride:	−431 kJ mol^{-1}
Lattice energy of rubidium chloride:	+675 kJ mol^{-1}
First ionisation energy of rubidium:	+408 kJ mol^{-1}
Standard enthalpy of atomisation of rubidium:	+86 kJ mol^{-1}
Bond dissociation energy of chlorine gas:	+242 kJ mol^{-1}



By Hess' Law

$$\Delta H^\theta_f(RbCl) = \Delta H^\theta_{atom}(Rb) + \Delta H^\theta_{atom}(Cl) + \Delta H_{IE}(Rb) + \Delta H_{EA}(Cl) - \Delta H^\theta_{lattice}$$

$$\Delta H^\theta_f(RbCl) = \Delta H^\theta_{atom}(Rb) + \frac{1}{2}\Delta H_{BE}(Cl_2) + \Delta H_{IE}(Rb) + \Delta H_{EA}(Cl) - \Delta H^\theta_{lattice}$$

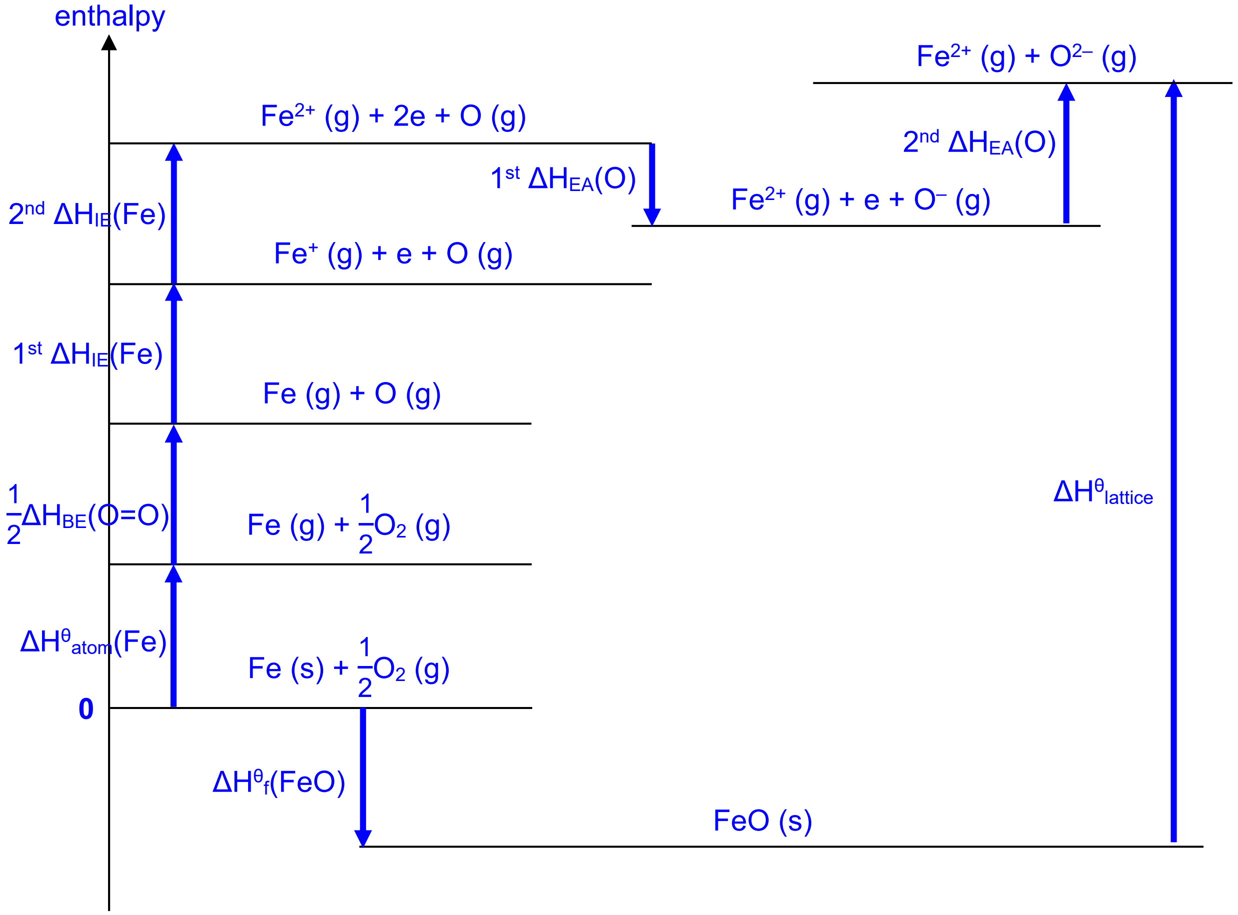
$$-431 = +86 + \frac{1}{2}(+242) + (+408) + \Delta H_{EA}(Cl) - (+675)$$

$\Delta H_{EA}(Cl) = \underline{\mathbf{-371\ kJ\ mol^{-1}}}$

Example 2

Using the data below, calculate the lattice energy of iron(II) oxide.

Standard enthalpy of formation of iron(II) oxide:	-266 kJ mol^{-1}
First ionisation energy of iron:	$+762$ kJ mol^{-1}
Second ionisation energy of iron:	$+1560$ kJ mol^{-1}
First electron affinity of oxygen:	-141 kJ mol^{-1}
Second electron affinity of oxygen:	$+753$ kJ mol^{-1}
Standard enthalpy of atomisation of iron:	$+415$ kJ mol^{-1}
Bond dissociation energy of oxygen gas:	$+498$ kJ mol^{-1}



By Hess' Law

$\Delta H^{\theta}_{f}(FeO)$

$= \Delta H^{\theta}_{atom}(Fe) + \frac{1}{2}\Delta H_{BE}(O{=}O) + 1^{st}\ \Delta H_{IE}(Fe) + 2^{nd}\ \Delta H_{IE}(Fe) + 1^{st}\ \Delta H_{EA}(O) + 2^{nd}\ \Delta H_{EA}(O) - \Delta H^{\theta}_{lattice}$

$-266 = +415 + \frac{1}{2}(+498) + (+762) + (+1560) + (-141) + (+753) - \Delta H^{\theta}_{lattice}$

$\Delta H^{\theta}_{lattice}$ = **+3864 kJ mol^{-1}**

Note: Comparison between Theoretical and Experimental Lattice Energy

- Calculations involving the Born–Haber cycle give the experimental value of lattice energy of an ionic compound.

- Lattice energy can be calculated theoretically based on the geometry of the crystal lattice. Here, it is assumed that a pure ionic compound is formed. Ions are regarded as point charges which exert non-directional electrostatic forces on their neighbours in the crystal lattice.

- The partial covalent character (due to polarisation of anion by cation) in the ionic bond has not been accounted for by the theoretical ionic compound model. This results in discrepancy between the experimental and theoretical lattice energies for ionic compounds with partial covalent character.

  E.g. Agreement is poor between $\Delta H^{\theta}_{lattice}$ (theoretical) and $\Delta H^{\theta}_{lattice}$ (experimental) for these ionic compounds with partial covalent character:

Ionic compound with partial covalent character	$\Delta H^{\theta}_{lattice}$ (theoretical) / kJ mol^{-1}	$\Delta H^{\theta}_{lattice}$ (experimental) / kJ mol^{-1}
CaI_2	+1826	+2068
BaI_2	+1772	+1869
AgCl	+864	+918
AgBr	+758	+890

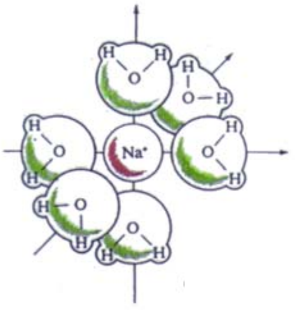
Reason:

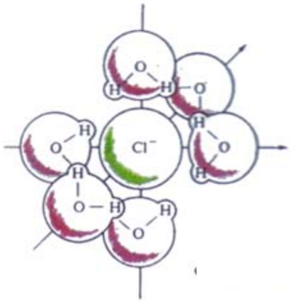
- Polarisation of anion by cation of high charge density results in the distortion of electron cloud of the anion
- Therefore, there is partial covalent character in the ionic bond.
- This is accounted for in the experimental values (using Born–Haber) but not in the theoretical values.

15.1.3 Solvation, dissolution and hydration

- Solvation is described as “any stabilising interaction of a solute and the solvent or a similar interaction of solvent with groups of an insoluble material. Such interactions generally involve electrostatic forces and London forces, as well as chemically more specific effects such as hydrogen bond formation.

- Water is a polar solvent with partial negative charges on the oxygen atom and partial positive charges on the hydrogen atoms. Water molecules orientate themselves so that their partial charges surround cations and anions, forming a solvation shell, also known as hydration shell when the solvent is water. When sodium chloride is mixed with liquid water, a new homogeneous phase is formed known as the solution. This is the process of dissolution.





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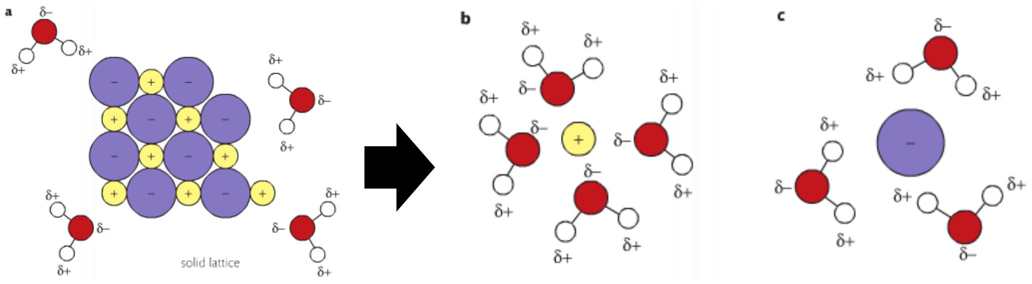
Process flow of dissolution of solid ionic lattice:



(a) Ionic lattice being broken up by polar water molecules. At the contact surface, partial charges in the water molecules are attracted to ions of opposite charge in the lattice, which may cause them to dislodge.

(b) The partial negatively charged oxygen atoms in the polar water molecules are attracted to the cations.

(c) The partial positively charged hydrogen atoms in the polar water molecules are attracted to the anions.

- The enthalpy change of hydration is a way of quantifying the amount of energy released during the process of solvation. The magnitude of the enthalpy of hydration is influenced by the charge and size of the ion.

Cation	**ΔH^{θ}_{hyd} / kJ mol^{-1}**	**Anion**	**ΔH^{θ}_{hyd} / kJ mol^{-1}**
Li^+	−538	F^-	−504
Na^+	−424	Cl^-	−359
Mg^{2+}	−1963	Br^-	−328
Al^{3+}	−4741	I^-	−287

Table of values on standard enthalpies of hydration
(more data is available in Section 20 of the Data Booklet)

- Down the Group 17 ions (F^-, Cl^-, Br^- and I^-), the enthalpy change of hydration becomes less exothermic as the ionic radius increases.

- Lithium has the most exothermic standard enthalpy change of hydration in Group 1 while fluoride also has the most exothermic value in Group 17.

- For cations and anions, an increase in charge on the ions combined with a decrease in size results in a significant large enthalpy of hydration.

  To recap, factors affecting this interaction are the size and charge of ions

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

- Enthalpy changes in solution

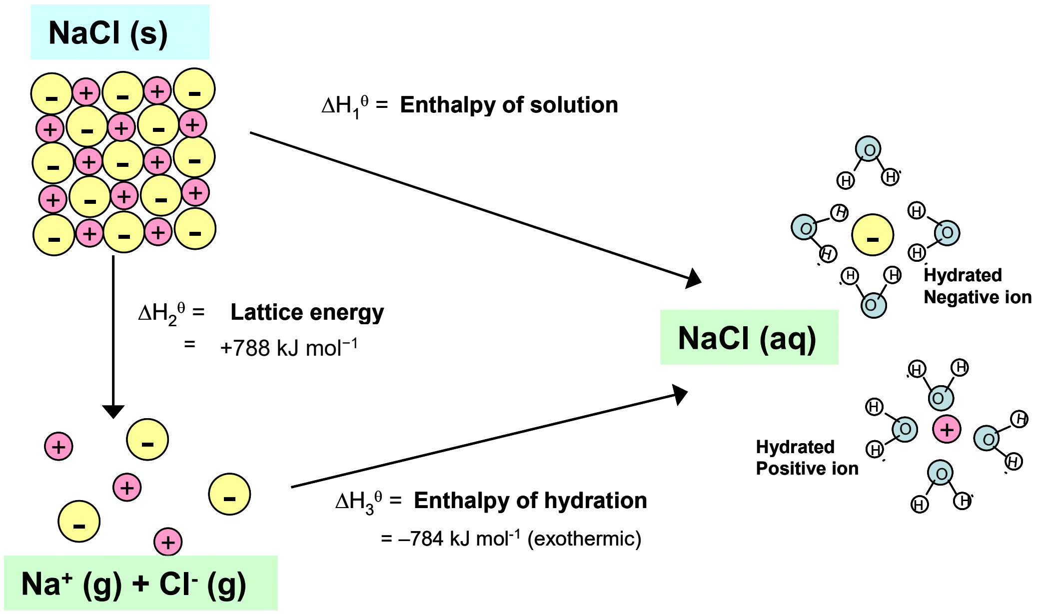
  Theoretically, dissolution can be divided into 2 processes:

  - Breaking up of the ionic lattice of the solid to form its constituent gaseous ions. Hence, this is an endothermic process.

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$$

  - Hydration of both gaseous cations and anions into aqueous ions. This is an exothermic process.

$$Na^+(g) + aq \rightarrow Na^+(aq)$$
$$Cl^-(g) + aq \rightarrow Cl^-(aq)$$



By Hess' law,

$\Delta H^{\theta}_1 = \Delta H^{\theta}_2 + \Delta H^{\theta}_3$
$\Delta H^{\theta}_{soln} = \Delta H^{\theta}_{lattice} + \Delta H^{\theta}_{hyd}$
$\Delta H^{\theta}_{soln} = (+788) + (-784) = +4 \text{ kJ mol}^{-1}$

- ΔH^{θ}_{soln} can be either be exothermic (negative) or endothermic (positive) depending on the values of ΔH^{θ}_{hyd} or $\Delta H^{\theta}_{lattice}$
  - If ΔH^{θ}_{soln} is:
  - **more exothermic**, the compound is **more likely to be soluble**.
    This is because hydration energy released is enough to compensate for the lattice energy required to break down the crystal.
  - **more endothermic**, the compound is **less likely to be soluble**.
    This is because hydration energy released is not enough to compensate for the lattice energy required to break down the crystal.

- For example:
  - ΔH^{θ}_{soln} of $NaCl$ is a small positive value (+4 kJ mol⁻¹), hence it is still soluble.
  - ΔH^{θ}_{soln} of $PbCl_2$ is a larger positive value, hence it is insoluble.

15.2 Entropy and spontaneity

Essential idea: A reaction is spontaneous if the overall transformation leads to an increase in total entropy (system plus surroundings). The direction of spontaneous change always increases the total entropy of the universe at the expense of energy available to do useful work. This is known as the second law of thermodynamics.

Nature of Science:

- Theories can be superseded – the idea of entropy has evolved through the years as a result of developments in statistics and probability. (2.2)

Understandings:

- Entropy (S) refers to the distribution of available energy among the particles. The more ways the energy can be distributed the higher the entropy.
- Gibbs free energy (G) relates the energy that can be obtained from a chemical reaction to the change in enthalpy (ΔH), change in entropy (ΔS), and absolute temperature (T).
- Entropy of gas>liquid>solid under same conditions.

Applications and skills:

- Prediction of whether a change will result in an increase or decrease in entropy by considering the states of reactants and products.
- Calculation of entropy changes (ΔS) from given standard entropy values (S^θ).
- Application of $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$ in predicting spontaneity and calculation of various conditions of enthalpy and temperature that will affect this.
- Relation of ΔG to position of equilibrium.

Guidance:

- Examine various reaction conditions that affect ΔG.
- ΔG is a convenient way to take into account both the direct entropy change resulting from the transformation of the chemicals, and the indirect entropy change of the surroundings as a result of the gain/loss of heat energy.
- Thermodynamic data is given in section 12 of the data booklet.

15.2.1 Entropy

- Many chemical reactions are usually exothermic. However, there are reactions that are endothermic and occur readily. Hence, there is another thermodynamic factor other than enthalpy that needs to be considered. This factor is known as entropy, S.

2nd Law of Thermodynamics states that in a **spontaneous change**, **entropy increases**. Entropy is a property that relates to the degree of disorder or randomness in a system. The more disordered a system, the larger its entropy. The unit for entropy is **J mol^{-1} K^{-1}**.

- In general, systems in nature tends towards greater disorder. Reactions that result in an increase in entropy (more randomness or disorderliness) of a system are more likely to happen.

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- Changes or reactions that lead to increase in entropy include
  - Mixing of particles (mixing two gases, dissolving sugar in water)
  - A change of state where the distance between the particles increases (melting, boiling and sublimation). In general, $S_{gas} >> S_{liquid} > S_{solid}$.
  - Increase in number of particles (base on stoichiometric/ mole ratio in the equation).
  - Increase in temperature during the reaction.

- Unlike enthalpy, absolute values for standard entropy, S, of any substance can be determined. The **unit for S, is J mol^{-1} K^{-1}**. This value is the change of entropy when 1 mole of a substance is heated from 0 K to 298 K.

- For any reaction the change in entropy, ΔS^{θ}, is defined as,

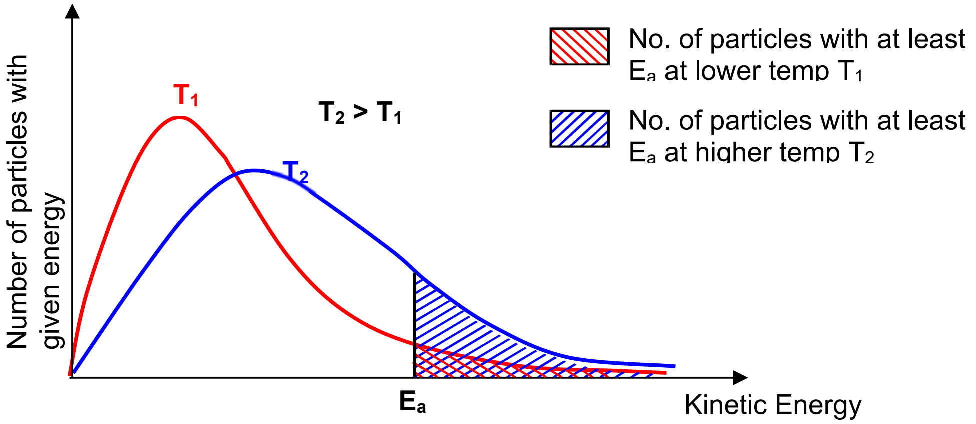
$$\boxed{\Delta S^{\theta} = \Sigma S^{\theta}\text{ (products)} - \Sigma S^{\theta}\text{ (reactants)}}$$

- Relating ΔS^{θ} to feasibility if reactions
  - Positive ΔS^{θ} (> 0):
    - the reaction is more feasible
    - final state is more disordered than the initial state
  - Negative ΔS^{θ} (< 0):
    - the reaction is not feasible
    - initial state is more disordered than the final state

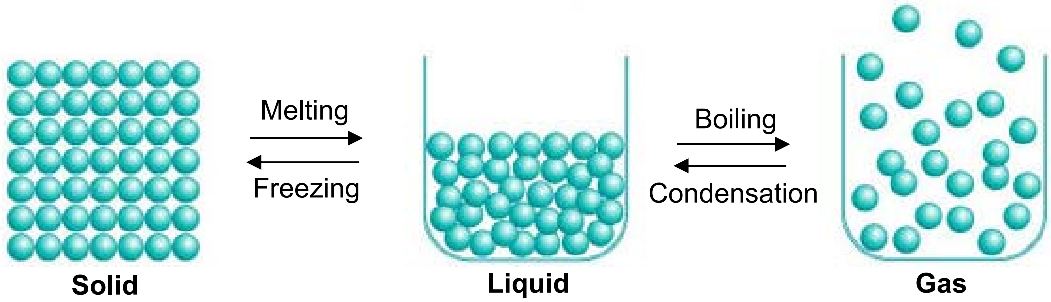
- Factors affecting entropy of a chemical system
  - Change in temperature
  - Change in phase (physical state)
  - Change in number of particles (especially gas molecules)
  - Mixing of particles

- Change in temperature
  - An increase in temperature would lead to an increase in entropy
  - This is because

    ⇒ particles move more randomly and vigorously
    ⇒ amount of energy in the system increases
    ⇒ broadening of the Boltzmann energy distribution
    ⇒ more ways of distributing energy in the system and greater disorder



- Change in phase (physical state)
  - **Entropy of solid < liquid < gas**



Lowest entropy because:	**Higher** entropy than solids because:	**Highest** entropy among the 3 states because:
• particles vibrate in their fixed positions. • less ways to arrange the particles and the distribute energy between the particles, • hence less disordered	• particles are free to move in the container. • more ways to arrange the particles and the distribute energy between these particles, • hence more disordered than solids	• particles are free to move about and are widely spaced. • even more ways to arrange the particles and distribute energy between the gaseous particles, • hence greatest disorder among the three states

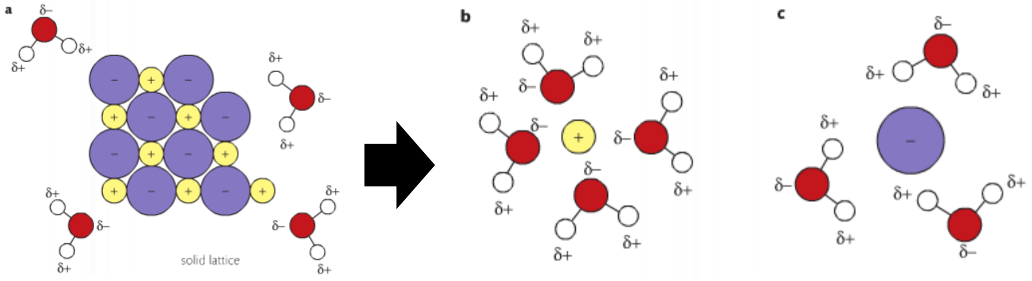
- Change in number of particles (especially gas molecules)
  - When there is an increase in the number of gaseous particles in reaction,
    ⇒ more ways of arranging the particles in the system
    ⇒ system becomes more disorderly
    ⇒ entropy increases
  - For example,

    $2N_2O\ (g) \rightarrow 2N_2\ (g) + O_2\ (g)$
    Change in the number of moles of gaseous particles
    $= n_{\text{gaseous products}} - n_{\text{gaseous reactants}}$
    $= +3 - 2$
    $= +1$ mol

- Mixing of particles

Before mixing After mixing

  - The two pure gases are mixed and allowed to move about randomly between the two vessels when the stop clock is opened
    ⇒ more ways of arranging the particles in the system as the particles are randomly mixed
    ⇒ system becomes more disordered
    ⇒ entropy increases



  - In solid NaCl, the ions are in a highly ordered, crystalline state.
    - When the solid dissolves, the ions are free to move about in the water. A more disordered system result.
    - However, water molecules are held around the ions as water of hydration. These water molecules become more ordered.
    - The disordering process is usually more dominant and thus the overall effect is an increase in disorder and entropy of the system for dissolving most salts in water.

Example 12

Predict whether the change in entropy of the system is positive or negative giving a reason in each case. Assume the temperature is 298K and pressure is 1 atm unless stated otherwise.

Process	Entropy, ΔS	Reason
H_2O (s) at 273 K → H_2O (l) at 273 K	Positive	• Melting process → change in phase from solid to liquid at constant temperature • Molecules in liquid state are free to move in the container • **More ways to arrange the molecules and the distribute energy** between these particles • **More disordered** than solids • Entropy **increases**
H_2O (l) at 298 K → H_2O (l) at 308 K	Positive	• Increase in temperature • Particles move more randomly and vigorously • Amount of energy in the system increases • **Broadening of the Boltzmann energy distribution** • **More ways of distributing energy** in the system and greater disorder • Entropy **increases**
Cl_2 (g) → $2Cl^{\bullet}$ (g)	Positive	• Increase in number of gaseous particles • **More ways of arranging the particles** in the system • **More disorder** in the system • Entropy **increases**
Na^+ (g) + Cl^- (g) → $NaCl$(s)	Negative	• Change in phase from gaseous to solid • Decrease in gaseous particles • Particles vibrate in their fixed positions. • **Less ways to arrange and distribute energy** between the particles • **Less disordered** as compared to gaseous state • Entropy **decreases**
Ag^+ (aq) + Cl^- (aq) → $AgCl$(s)	Negative	• Precipitation • Solid is formed from aqueous ions • Solid state formed is **less disordered** as compared to aqueous state • Entropy **decreases**
Ar at 2 atm → Ar at 1 atm constant temperature	Positive	• Decrease in pressure ⇒ increase in volume • **More ways of distributing the atoms** in the system • Entropy **increases**

Example 1

The standard entropies of nitrogen, hydrogen and ammonia are 192, 131 and 192 J K^{-1} mol^{-1} respectively. Calculate the entropy change for the reaction between nitrogen and hydrogen in Haber process. Comment on the feasibility of the reaction based on your answer.

Equation for the Haber process:

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

$\Delta S^\theta = \Sigma S^\theta$ (products) – ΣS^θ (reactants)

ΔS^θ
$= [2 \times 192] - [192 + (3 \times 131)]$
= **-201 J K^{-1} mol^{-1}**

Since $\Delta S^\theta < 0$ the reaction is likely not feasible.

Note: The decrease in entropy agrees with the “decrease” in randomness of the system as 4 moles of gaseous reactants are reduced to 2 moles of gaseous products after the reaction.

Exercise 4

1. Predict if the ΔS^θ for the following changes / reactions would be positive or negative or zero.

(a) $2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (l)$ **Negative**

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

(c) $2H_2O_2\ (l) \rightarrow 2H_2O\ (l) + O_2\ (g)$ **Positive**

(d) $NH_4NO_3\ (s) \rightarrow 4NO\ (g) + O_2\ (g) + 2H_2O\ (l)$ **Positive**

(e) $H_2\ (g) + Cl_2\ (g) \rightarrow 2HCl (g)$ **Zero**

15.2.2 Spontaneity

- Gibb's free energy, G, is used to predict if a reaction is spontaneous. Standard enthalpy change, ΔH^{θ}, and standard entropy change, ΔS^{θ}, of a reaction are related to ΔG by the Gibbs−Helmholtz equation.

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

where T = temperature in Kelvin, K
ΔG is the change in Gibb's free energy in kJ mol^{-1}
ΔH^{θ} is the standard enthalpy change in kJ mol^{-1}
ΔS^{θ} is the standard entropy change in kJ K^{-1} mol^{-1}

- Using Hess' law, the change in Gibb's free energy, ΔG_r, can also be expressed as

$$\boxed{\Delta G_r = \Sigma G^{\theta}_f \text{ (products)} - \Sigma G^{\theta}_f \text{ (reactants)}}$$

where ΔG^{θ}_f is the standard free energy change of formation

- Hence it follows that reactions or changes that result in:
  - Negative ΔG (< 0) : spontaneous **forward** reaction; non–spontaneous **reverse** reaction
  - Positive ΔG (> 0) : non–spontaneous **forward** reaction; spontaneous **reverse** reaction
  - $\Delta G = 0$: reaction is at equilibrium

- The table below shows how the spontaneity of a reaction or change is linked to the ΔG, ΔH^{θ} and ΔS^{θ}.

ΔH^{θ}	ΔS^{θ}	$T\Delta S^{\theta}$	ΔG	Spontaneity of reaction
+	–	–	**Positive** at all temperatures	Not spontaneous at all temperatures
+	+	+	**Positive** at **low** temperatures **Negative** at **high** temperatures	**Not spontaneous** at **low** temperatures **Spontaneous** at **high** temperatures
–	–	–	**Negative** at **low** temperatures **Positive** at **high** temperatures	**Spontaneous** at **low** temperatures **Not spontaneous** at **high** temperatures
–	+	+	**Negative** at **all** temperatures	Spontaneous at all temperatures

- An important point to note is that even if a reaction is spontaneous ($\Delta G < 0$), it does not imply that the reaction will happen the moment the reactants are mixed together.

- The **ΔG only reflects the energetic stability of the products with respect to the reactants**. It does not dictate or indicate the rate or kinetics of the reaction. For any reaction to occur, the reactants must possess a minimum amount of energy known as activation energy. Thus, a reaction with $\Delta G < 0$ and yet do not occur readily when the reactants are mixed can be described as under kinetic control.

- Consider a mixture of methane and oxygen, where methane may undergo combustion as shown,

  $$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l), \quad \Delta G = -580\ kJ\ mol^{-1}$$

  Though the reaction is spontaneous as $\Delta G < 0$, a mixture of methane and oxygen (excess) does not burst into flames when they are first mixed. The mixture would remain “inert” until a spark or a flame is introduced. There would be a strong reaction as the introduced spark or flame would provide the necessary activation energy to start the reaction. Subsequent reactions would then be triggered by the energy released from the initial reaction.

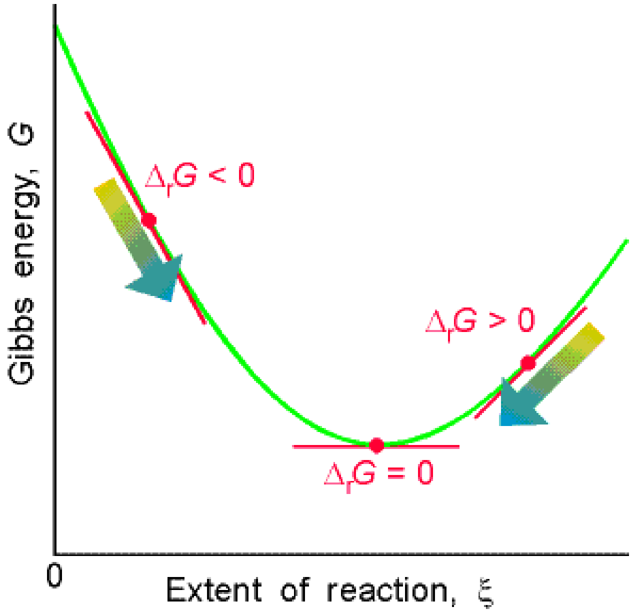
- Another example of a spontaneous reaction under kinetic control would be that between graphite and diamond. Both graphite and diamond are allotropes of carbon with graphite being the energetically more stable one as shown by the equation below.

  $$C\ (diamond) \rightarrow C\ (graphite), \qquad \Delta G = -2.90\ kJ\ mol^{-1}$$

  The reaction is exothermic. This means that diamond, being of a higher enthalpy content, is energetically unstable relative to graphite. In other words, by energetic considerations, the conversion of diamond to graphite should occur.

  The reaction, however, does not happen under normal conditions. Although the diamond is energetically unstable, it is kinetically stable due to high activation energy for this reaction.

- The spontaneity of a reaction at constant temperature and pressure is related to the Gibbs free energy as follows (see diagram below):
    - If $\Delta G_r < 0$ the forward reaction is spontaneous.
    - If $\Delta G_r > 0$, the reverse reaction is spontaneous.
    - If $\Delta G_r = 0$, the reaction is at equilibrium.



- So far we have considered reactions in which it is assumed that all the reactants are converted into products. Many reactions do not go to completion but instead reach equilibrium, as will be discussed in Topic 7. From the time when a reversible reaction commences to the point where it reaches equilibrium, the Gibbs free energy is changing as the ratio of the reactants to products alters. As the amount of products increases and the reaction moves towards completion (for non−reversible reactions) or equilibrium (for reversible reactions) the Gibbs free energy decreases, At the point of equilibrium the system has reached its minimum Gibbs free energy.

Example 1

Consider the two equations,

$2Fe\ (s) + O_2\ (g) \rightarrow 2FeO\ (s)$, $\Delta G_1 = -450\ kJ\ mol^{-1}$ at 500 K
$2CO\ (g) + O_2\ (g) \rightarrow 2CO_2\ (g)$, $\Delta G_2 = -480\ kJ\ mol^{-1}$ at 500 K

Calculate the standard free energy change for the reaction at 500 K. Hence, state if the reduction of iron(II) oxide by carbon monoxide, shown below, is feasible at 500 K.

$FeO\ (s) + CO\ (g) \rightarrow Fe\ (s) + CO_2\ (g)$

Method 1: Energy Cycle

$$\begin{tikzcd}
2FeO\ (s) + 2CO\ (g) \arrow[rr, "2\Delta G"] & & 2Fe\ (s) + 2CO_2 \\
& 2Fe\ (s) + 2CO\ (g) + O_2\ (g) \arrow[ul, "\Delta G_1"] \arrow[ur, "\Delta G_2"'] &
\end{tikzcd}$$

By Hess's Law,

$2\Delta G$
$= -\Delta G_1 + \Delta G_2$
$= -(-450) + (-480)$
$= -30\ kJ\ mol^{-1}$

$\Delta G =$ **$-15\ kJ\ mol^{-1}$**

Method 2: Manipulating equations

$2FeO\ (s) \rightarrow 2Fe\ (s) + O_2\ (g)$ $-\Delta G_1 = +450\ kJ\ mol^{-1}$
$2CO\ (g) + O_2\ (g) \rightarrow 2CO_2\ (g)$ $\Delta G_2 = -480\ kJ\ mol^{-1}$

Taking –(1) + (2):

$2FeO\ (s) + 2CO\ (g) \rightarrow 2Fe\ (s) + 2CO_2\ (g)$ $-30\ kJ\ mol^{-1}$
$FeO\ (s) + CO\ (g) \rightarrow Fe\ (s) + CO_2\ (g)$ **$-15\ kJ\ mol^{-1}$**

Since $\Delta G < 0$ at 500K for the reaction, iron(II) oxide can be reduced by carbon monoxide at 500 K.

Example 2

But–2–ene can exist in 2 geometric isomers, the cis– and the trans–but–2–ene. The thermodynamic data of the 2 isomers are shown below.

Isomer	cis–but–2–ene	trans–but–2–ene
ΔH^θ_f / kJ mol^{-1}	–5.7	–10.1
S^θ / J K^{-1} mol^{-1}	301	296

Calculate the Gibb's free energy, ΔG for the transition of the cis–but–2–ene to trans–but–2–ene and that of trans–but–2–ene to cis–but–2–ene. Hence identify the more stable isomer.

cis–but–2–ene → trans–but–2–ene, ΔG_{c-t}
trans–but–2–ene → cis–but–2–ene, ΔG_{t-c}

Using,
$\Delta H^\theta_{c-t} = \Sigma\Delta H^\theta_f \text{ (products)} - \Sigma\Delta H^\theta_f \text{ (reactants)}$
$\Delta H^\theta_{c-t} = [(-10.1) - (-5.7)] = -4.4 \text{ kJ mol}^{-1}$

Using,
$\Delta S^\theta_{c-t} = \Sigma S^\theta \text{ (products)} - \Sigma S^\theta \text{ (reactants)}$
$\Delta S^\theta_{c-t} = [296 - 301] = -5 \text{ J K}^{-1} \text{ mol}^{-1}$

Using,
$\Delta G = \Delta H^\theta - T\Delta S^\theta$

ΔG_{c-t}
$= \Delta H^\theta_{c-t} - T\,\Delta S^\theta_{c-t}$
$= (-4.4) - 298(-0.005) = -2.91 \text{ kJ mol}^{-1}$

ΔG^θ_{t-c}
$= -\Delta G^\theta_{c-t}$
$= -(-2.91 \text{ kJ mol}^{-1}) = +2.91 \text{ kJ mol}^{-1}$

Since ΔG^θ_{c-t} is negative, thus the trans–but–2–ene is more stable than the cis–form.

Example 3

Determine if the following reaction is feasible at 20 °C and 500 °C respectively.

Fe_2O_3 (s) + $3H_2$ (g) → 2Fe (s) + $3H_2O$ (g)

Substance	Fe_2O_3	H_2	Fe	H_2O
ΔH^θ_f / kJ mol^{-1}	−822	0	0	−242
S^θ / kJ K^{-1} mol^{-1}	0.090	0.131	0.027	0.189

Using,
$\Delta H^\theta = \Sigma\Delta H^\theta_f \text{ (products)} - \Sigma\Delta H^\theta_f \text{ (reactants)}$
$\Delta H^\theta = [0 + 3 \times (-242)] - [(-822) + 0] = +96 \text{ kJ mol}^{-1}$

Using,
$\Delta S^\theta = \Sigma S^\theta \text{ (products)} - \Sigma S^\theta \text{ (reactants)}$
$\Delta S^\theta = [(2 \times 0.027) + (3 \times 0.189)] - [(0.090) + (3 \times 0.131)] = +0.138 \text{ kJ K}^{-1} \text{ mol}^{-1}$

Using,
$\Delta G = \Delta H^\theta - T\Delta S^\theta$

At 20 °C (293 K)

$\Delta G = \Delta H^\theta - T\Delta S^\theta$
$= +96 - [293 \times (+0.138)] = +55.6 \text{ kJ mol}^{-1}$

At 500 °C (773 K)
$\Delta G = \Delta H^\theta - T\Delta S^\theta$
$= +96 - [773 \times (+0.138)] = -10.7 \text{ kJ mol}^{-1}$

The reduction of iron(II) oxide is not feasible at 20 °C as $\Delta G > 0$ while it is feasible at 500 °C as $\Delta G < 0$.

Exercise 5

1. Calculate ΔG for the following reaction:

$4HCl(g) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(g)$ $\Delta H^\theta = -114\ \text{kJ mol}^{-1}$
$\Delta S^\theta = -129\ \text{J K}^{-1}\ \text{mol}^{-1}$

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

$= -114 - [298 \times (-\frac{129}{1000})]$

$= \underline{\mathbf{-75.6\ kJ\ mol^{-1}}}$

2. The decomposition of limestone at room temperature is a non–spontaneous process.

(a) Determine the ΔG for the decomposition of limestone at standard temperature.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\Delta H^\theta = +178\ \text{kJ mol}^{-1}$
$\Delta S^\theta = +165\ \text{J K}^{-1}\ \text{mol}^{-1}$

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

$= +178 - [298 \times (\frac{+165}{1000})]$

$= \underline{\mathbf{+129\ kJ\ mol^{-1}}}$

(b) Explain how would you change the condition to make the decomposition of limestone a spontaneous reaction?

$\Delta G = \Delta H^\theta - T\Delta S^\theta < 0$ for reaction to be spontaneous

$+178 - [T \times (\frac{+165}{1000})] < 0$

$0.165\ T > 178$

$\underline{\mathbf{T > 1079\ K}}$

3. Reactions in which a substance decomposes by losing carbon dioxide are called decarboxylation reactions. The decarboxylation of ethanoic acid proceeds as follows:

$$CH_3CO_2H\ (l) \rightarrow CH_4\ (g) + CO_2\ (g)$$

By using the given data, determine the minimum temperature at which this process will be spontaneous under standard conditions. Assume that ΔH^θ and ΔS^θ do not vary with temperature.

$\Delta H^\theta_f\ (CH_4\ (g))$	–74.8 kJ mol^{-1}
$\Delta H^\theta_f\ (CH_3CO_2H\ (l))$	–487 kJ mol^{-1}
$\Delta H^\theta_f\ (CO_2\ (g))$	–393.5 kJ mol^{-1}
ΔS^θ of reaction	+186.3 J K^{-1} mol^{-1}

$\Delta H^\theta_{reaction} = \Sigma\ \Delta H^\theta_f$ (products) – $\Sigma\ \Delta H^\theta_f$ (reactants)

$\Delta H^\theta_{reaction} = -393.5 + (-74.8) - (-487) = +18.7$ kJ mol^{-1}

$\Delta G = \Delta H^\theta - T\Delta S^\theta < 0$ for reaction to be spontaneous

$18.7 - [T \times (\frac{+186.3}{1000})] < 0$

$0.1863\ T > 18.7$

$T > 100.4$ K