

05 Chemical Energetics: Thermochemistry & Thermodynamics

GUIDING QUESTIONS

- What are the energy changes 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?
- How can we measure or find out the energy change in a chemical or physical process?

LEARNING OUTCOMES

Students should be able to:

- 7(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)
- 7(b)** construct and interpret an energy profile diagram, in terms of the enthalpy change of the reaction and of the activation energy (Refer to Topic 6 Reaction Kinetics)
- 7(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) (Refer to Topic 2 Chemical Bonding)
 - (iii) lattice energy (ΔH negative, i.e. gaseous ions to solid lattice)
- 7(d)** calculate enthalpy changes from appropriate experimental results, including the use of the relationship: $\text{heat change} = mc\Delta T$
- 7(e)** explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy (Refer to Topic 2 Chemical Bonding)
- 7(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 change of combustion
 - (ii) the formation of a simple ionic solid and of its aqueous solution
 - (iii) average bond energies
- 7(g)** explain and use the term *entropy*
- 7(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]
- 7(i)** predict whether the entropy change for a given process or reaction is positive or negative
- 7(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]

- 7(k) state whether a reaction or process will be spontaneous by using the sign of $\Delta G^\ominus$
- 7(l) understand the limitations in the use of $\Delta G^\ominus$ to predict the spontaneity of a reaction
- 7(m) predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes

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

LOOKING BACK

In the topic of Chemical Bonding, we saw how atoms are chemically bonded to each other. Energy changes take place when atoms combine to form different compounds. By measuring these energy changes, we can learn about the strength of the bonding that hold atoms together. For example, we saw that lattice energy is a measure of the strength of ionic bonding. Also, the concept of energy changes is fundamental to our understanding of the chemical reactions or physical processes that we observe in our everyday life. For example, the energy changes that took place during the dissolution of a solute help to explain its solubility. In this topic, we will look at other energy changes to understand why other chemical reactions or physical processes take place. We will also look at another factor, known as entropy change, which affects the spontaneity of a chemical reaction or physical process.

1 INTRODUCTION

All matter contains energy and energy changes take place when a matter undergoes either a physical or chemical change. Thermodynamics is the study of energy and its transformation. In this chapter, we will focus on thermochemistry, the study of heat change in chemical and physical processes. We will also be looking at why certain physical and chemical changes take place spontaneously.

1.1 Enthalpy and enthalpy changes

The total chemical energy of a substance is called its **enthalpy** (or **heat content**). Chemical energy consists of kinetic energy and potential energy. The potential energy, due to electrostatic attraction between the particles, is usually the main component of the total chemical energy.

During a chemical reaction, bonds are broken and new bonds are formed. The breaking of bonds requires energy while the formation of bonds releases energy. The energy change that occurs is called the **enthalpy change of reaction**. The symbol is ΔH_r and the units are J mol^{-1} or kJ mol^{-1} .

As most chemical reactions take place at constant pressure, the heat involved in the process (the flow of thermal energy) can be expressed as ΔH . Hence, when a reaction vessel feels warm, thermal energy is given off by the reaction and transferred to our hands. At the microscopic level, thermal energy can be represented by the movement of particles. The greater the average kinetic energies of the particles, the greater the amount of thermal energy of the system.

1.2 Endothermic and Exothermic processes

Enthalpy changes may be exothermic or endothermic as illustrated below.

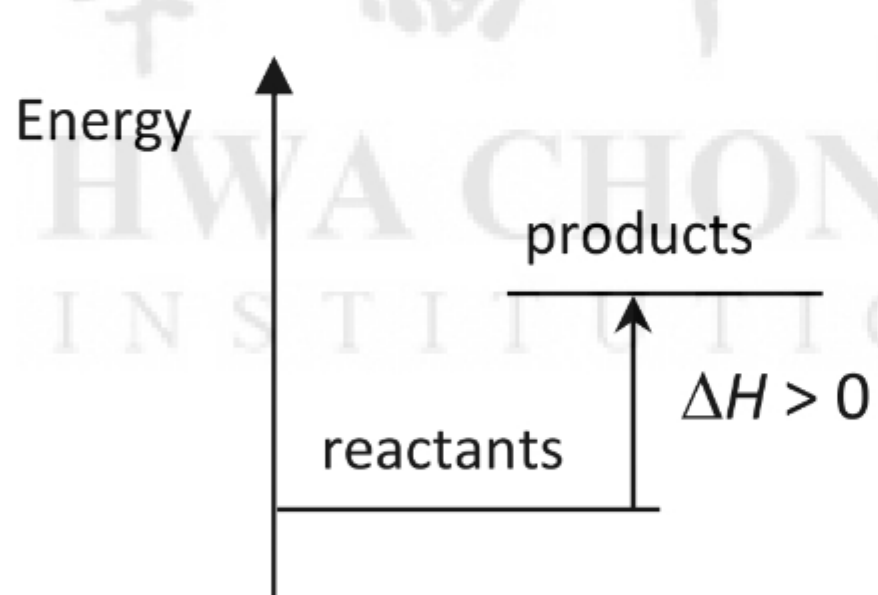
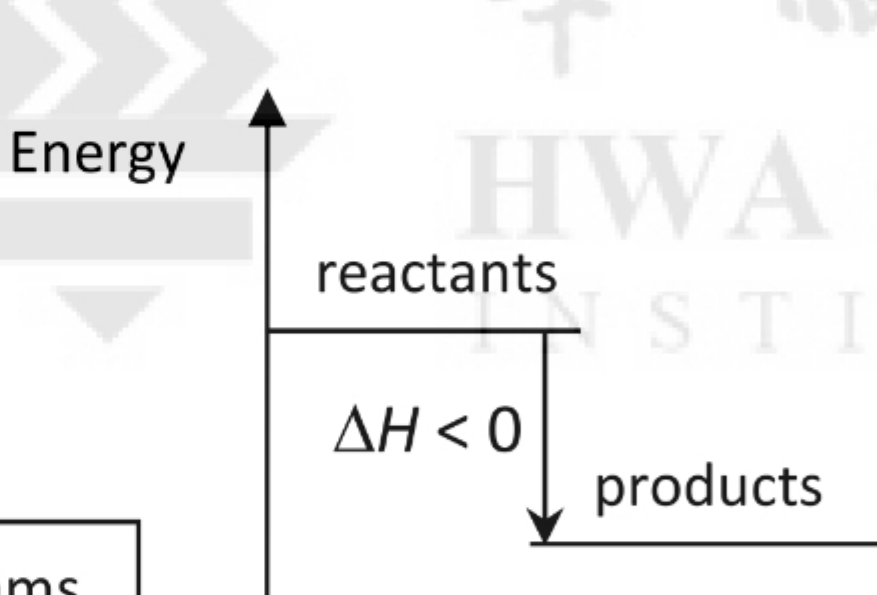
ΔH is positive, $\Delta H > 0$	ΔH is negative, $\Delta H < 0$
	
The products have <i>higher</i> energy content than the reactants.	The products have <i>lower</i> energy content than the reactants.
The reaction absorbs heat from the surroundings. The temperature of the surroundings decreases .	The reaction releases heat to the surroundings. The temperature of the surroundings increases .
The reaction is said to be endothermic .	The reaction is said to be exothermic .

Table 1. Endothermic and Exothermic reactions

If the energy level of the products is lower than that of the reactants, we say the products are **energetically more stable** than the reactants.

The **activation energy** of a reaction (E_a) is the **minimum energy** which the reacting particles must possess in order to overcome the energy barrier before becoming products.

The enthalpy change and activation energy of a reaction can be represented in a reaction pathway diagram or energy profile diagram as shown in Table 2 below. A reaction pathway diagram is different from the energy level diagrams in Table 1.

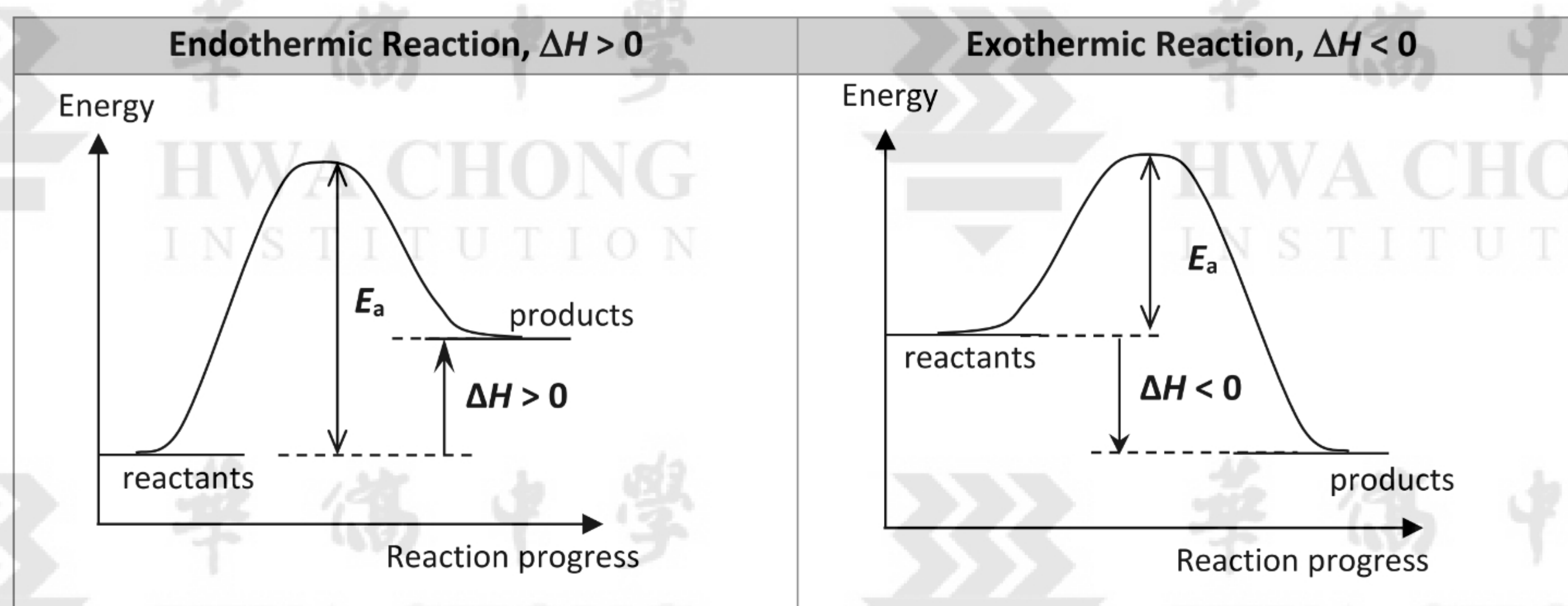
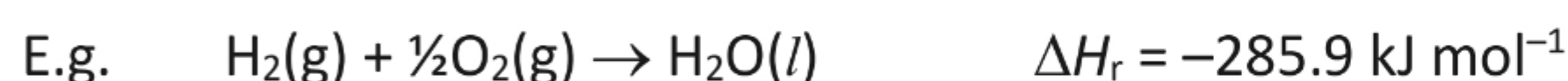


Table 2. Reaction pathway diagrams for 1-step endothermic and exothermic reactions

1.3 Thermochemical equation

A thermochemical equation is a balanced equation that includes the enthalpy change of the reaction.



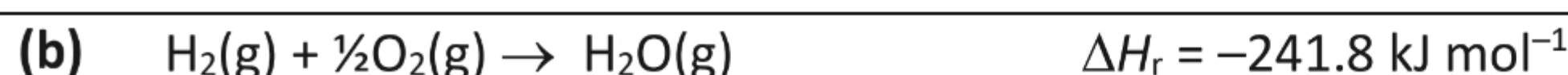
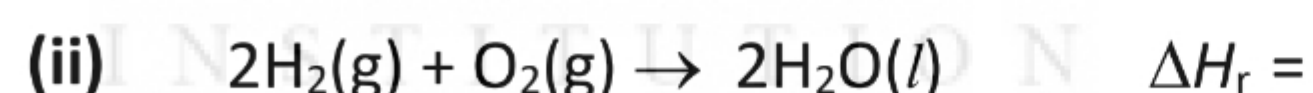
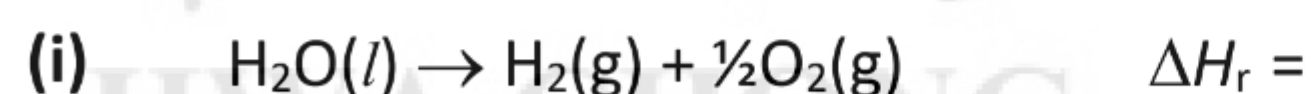
The equation indicates that 285.9 kJ of heat is released when 1 mole of H_2 gas reacts with 0.5 mole of O_2 gas to give 1 mole of liquid H_2O .

The term ' mol^{-1} ' in the ΔH_r units does not refer to 1 mole of H_2 or 1 mole of H_2O . Instead, it refers to the whole reaction as written, in this case, when 1 mole of H_2 gas reacts with 0.5 mole of O_2 gas.

It is important to include **state symbols** to all formulae given in a thermochemical equation since a change in state is accompanied by an appreciable change in energy.

Lecture Exercise 1.1

(a) Determine the enthalpy change of reaction for the following reactions:



Explain why the enthalpy change of the above reaction is less exothermic than $-285.9 \text{ kJ mol}^{-1}$.

1.4 Standard conditions and standard states

Besides the physical state of the substances, the enthalpy change of a reaction is also affected by the physical conditions of temperature and pressure. For valid comparison, a set of **standard conditions** have to be specified under which enthalpy changes are measured.

Standard Conditions for Thermochemical Measurements	
Temperature	298 K (25 °C)
Pressure	1 bar* (1 bar = 10^5 Pa)
Concentration of any solution	1.0 mol dm ⁻³

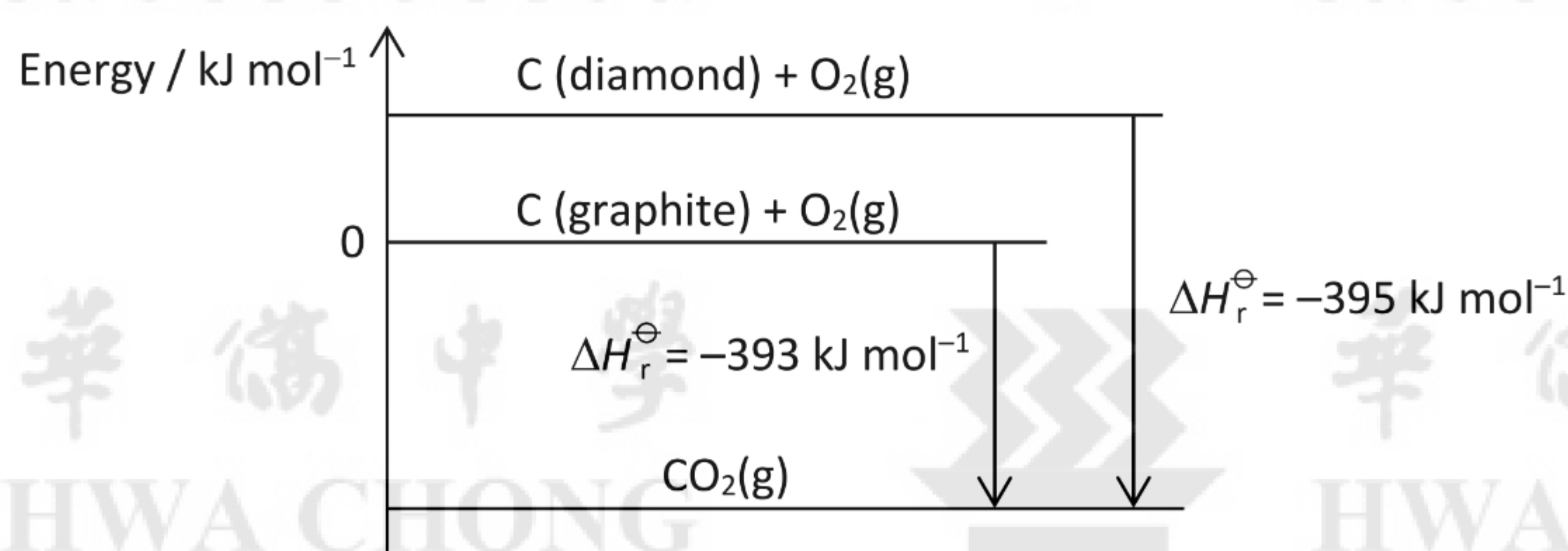
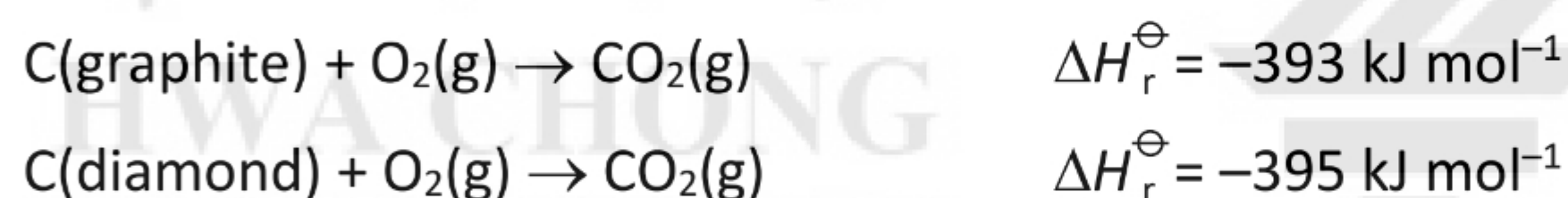
Table 3. Standard conditions for thermochemical measurements

*Note: According to IUPAC, the standard state pressure is 1 bar. In some books, 1 atm may be used as reference in thermodynamic data. 1 atm (1.013 bar) is a more practical and convenient unit of measure for pressure. The difference in thermodynamic values at 1 atm and 1 bar may not be very significant.

- A substance in its normal (most stable) physical state at 298 K and 1 bar is said to be in its **standard state**. E.g. I₂(s), Br₂(l), C(s) (Refer to note below).
- The actual enthalpy of an element cannot be measured. Hence, elements in their standard states under standard conditions are assigned **zero enthalpy ($H = 0$)**.
- When the enthalpy change is measured under standard conditions, it is referred to as the **standard enthalpy change** and is represented by the symbol $\Delta H^\ominus$.

Note:

C(s) refers to the graphite allotrope since graphite has a lower energy level and is thus energetically more stable than diamond.

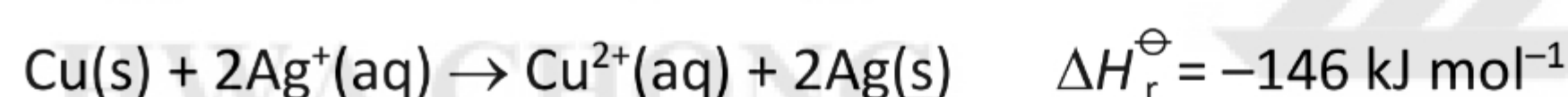
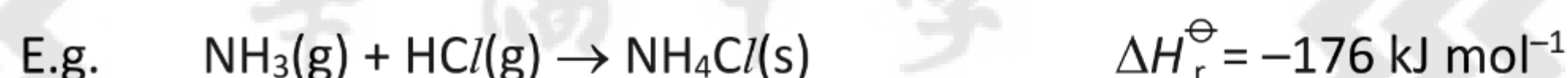


Why is graphite more stable than diamond? (Hint: Consider their structure and bonding)

2 COMMON ENTHALPY CHANGES

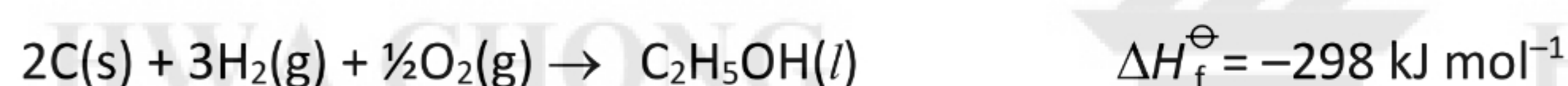
2.1 Standard enthalpy change of reaction

The enthalpy change when **molar** quantities of reactants as specified by the chemical equation react to form products at **1 bar and 298 K (standard conditions)**.



2.2 Standard enthalpy change of formation

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



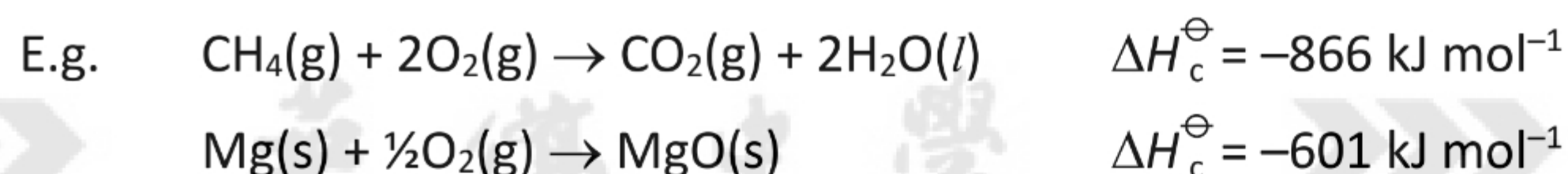
- From the definition, the enthalpy change of formation of **elements** in their standard state (at 298K and 1 bar) is **0 kJ mol⁻¹**.
- $\Delta H_{\text{f}}^{\ominus}$ is a measure of the energetic stability of a substance relative to its constituent elements.
 - If $\Delta H_{\text{f}}^{\ominus}$ is positive $\Rightarrow$ compound is less stable than its constituent elements
 - $\Rightarrow$ greater likelihood for compound to decompose into its constituent elements
 - If $\Delta H_{\text{f}}^{\ominus}$ is negative $\Rightarrow$ compound is more stable than its constituent elements
 - $\Rightarrow$ less likelihood for compound to decompose into its constituent elements
- Enthalpy changes of formation are often theoretical. Some reactions may not take place in practice. E.g. $\text{C}_2\text{H}_5\text{OH}$ cannot be formed by just mixing C, H_2 and O_2 . In such cases, $\Delta H_{\text{f}}^{\ominus}$ can be calculated indirectly using Hess' Law (Refer to Section 3).

Lecture Exercise 2.1

Write an equation to represent the standard enthalpy change of formation of $\text{CaSO}_4(\text{s})$.

2.3 Standard enthalpy change of combustion

The **heat evolved** when **1 mole** of a substance is **completely burnt in excess oxygen** at 298 K and 1 bar.



- The enthalpy change of combustion is **always exothermic** i.e. heat is always evolved in combustion.
- Scientists use combustion data to compare the energy values of fuels and food. The more exothermic the $\Delta H_c^\ominus$ (i.e. the more negative), the higher the energy value of the fuel.

Lecture Exercise 2.2

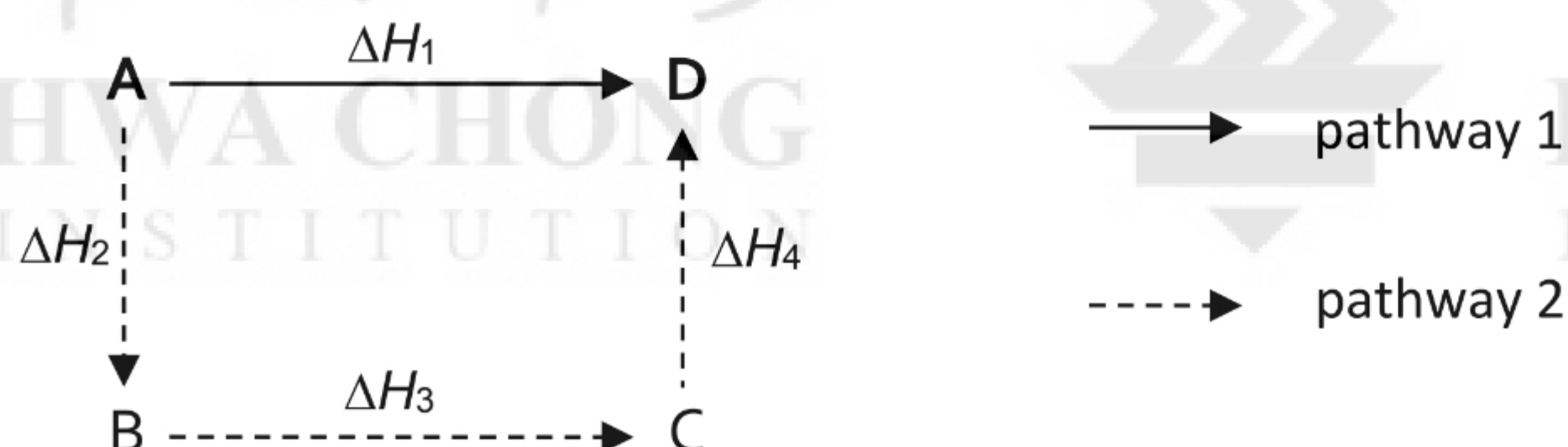
What is the enthalpy change represented by this equation: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$?

3 HESS' LAW AND ITS APPLICATIONS

Very few enthalpy changes of reaction can be determined directly by experiment. For reactions that are difficult to carry out directly, we can use Hess' Law to calculate the enthalpy changes of these reactions from other data such as enthalpy changes of combustion which can be measured accurately using a bomb calorimeter (Refer to Section 5).

3.1 Hess' law of constant heat summation

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



By Hess' Law, enthalpy change for pathway 1 = enthalpy change for pathway 2
 $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$

General steps to calculate ΔH of a reaction using Hess' Law:

1. Write the equation representing the enthalpy change that you are required to calculate.
2. Construct a fully labelled energy cycle incorporating the enthalpy changes provided, including state symbols.
3. Apply Hess' Law to calculate the required enthalpy change.

3.2 Application: Calculations using standard enthalpy change of combustion**Worked Example 3.1**

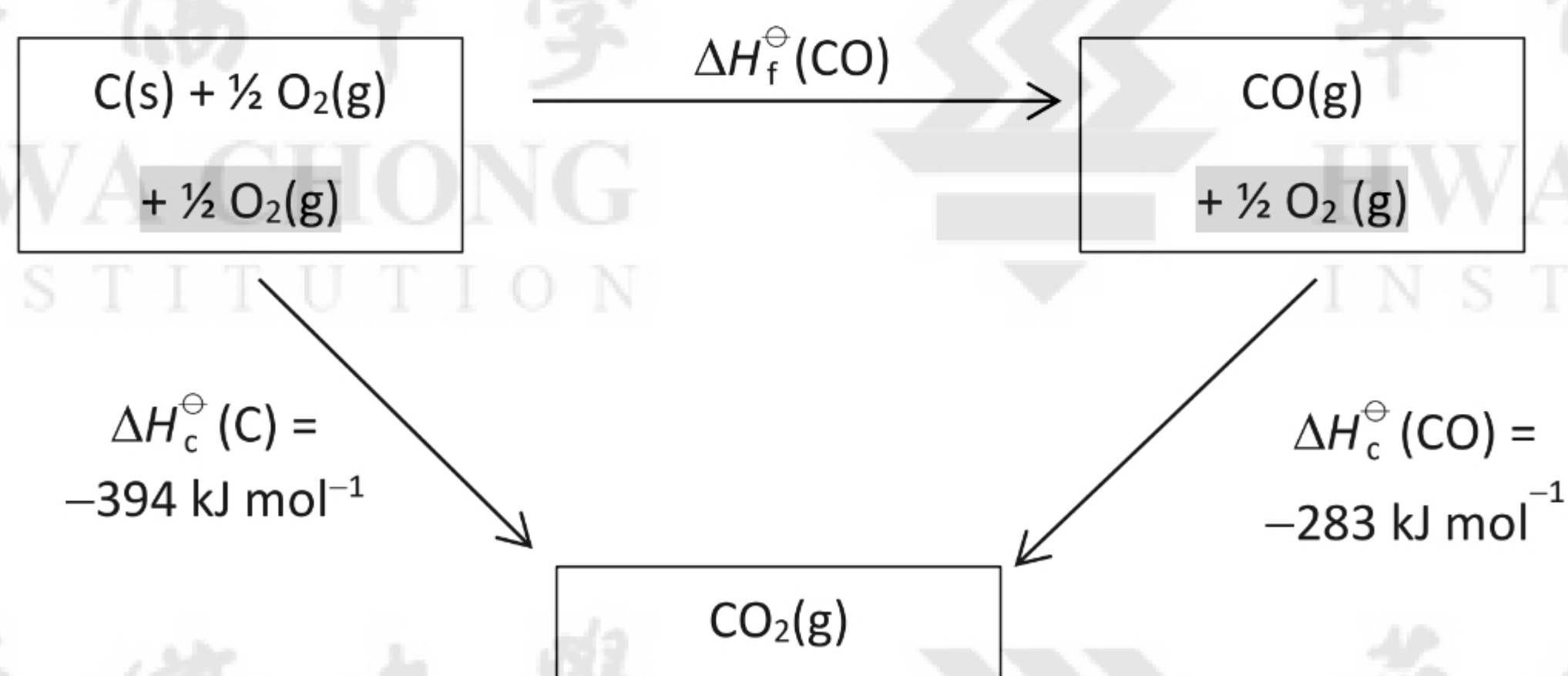
Given the following enthalpy changes of combustion, calculate the standard enthalpy change of formation of carbon monoxide.

$$\Delta H_c^\ominus (\text{carbon}) = -394 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\ominus (\text{carbon monoxide}) = -283 \text{ kJ mol}^{-1}$$

Method 1a: Constructing an Energy Cycle

- ① Start with the equation that represents $\Delta H_f^\ominus (\text{CO})$.
- ② Since $\Delta H_c^\ominus (\text{C})$ and $\Delta H_c^\ominus (\text{CO})$ are given, we can draw a cycle where C(s) on the left-hand side of the equation undergoes complete combustion to form $\text{CO}_2(\text{g})$. To do this we need to add $\frac{1}{2}$ mol of $\text{O}_2(\text{g})$. Hence $\frac{1}{2}$ mol of O_2 must also be added on the right-hand side of the equation. This $\frac{1}{2}$ mol of $\text{O}_2(\text{g})$ reacts with $\text{CO}(\text{g})$ to form $\text{CO}_2(\text{g})$.



By Hess' law,

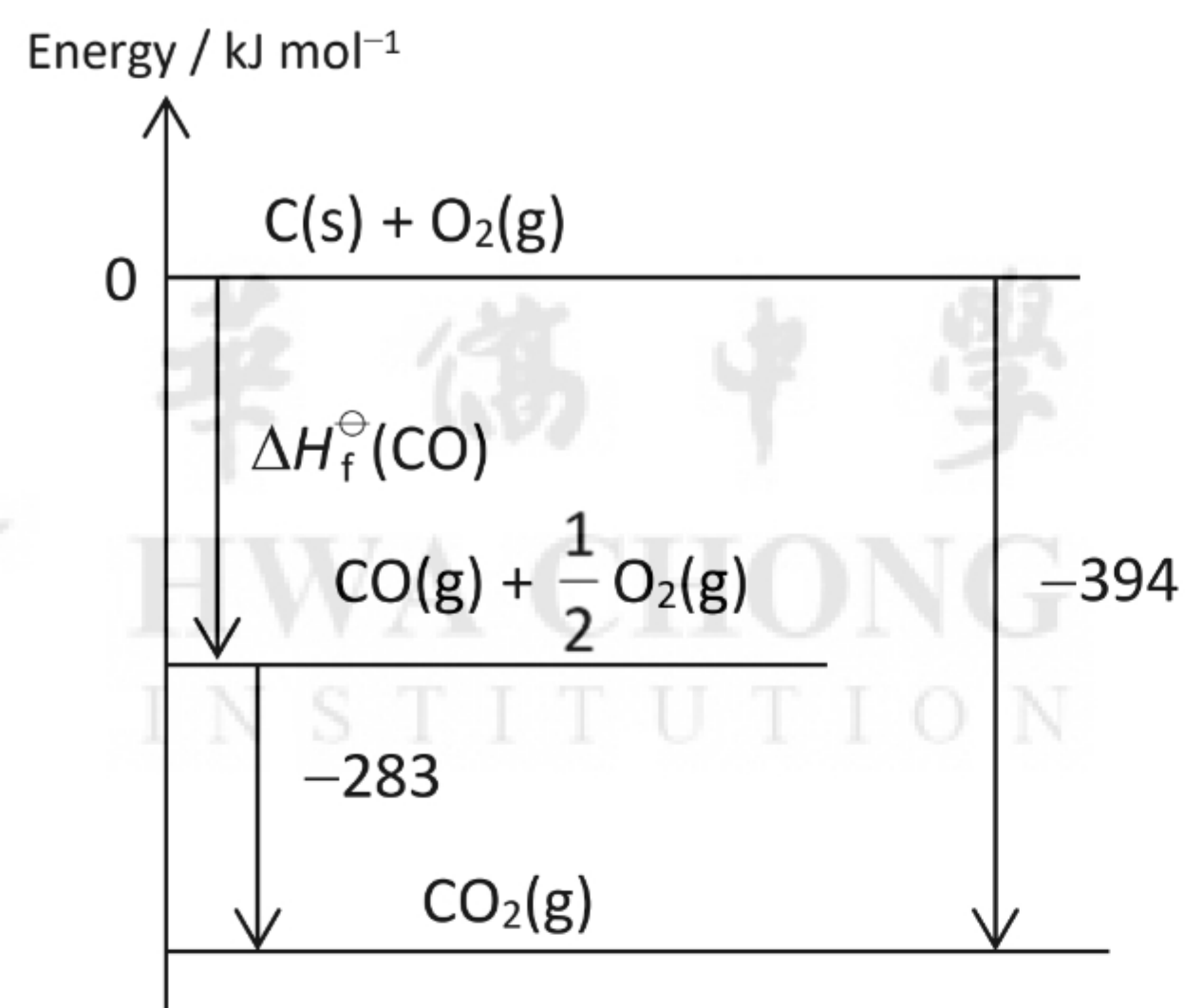
$$\begin{aligned} \Delta H_f^\ominus (\text{CO}) &= -394 - (-283) \\ &= -111 \text{ kJ mol}^{-1} \end{aligned}$$

Quick Check

- ☐ Equations are balanced
- ☐ State symbols are correct
- ☐ Sign of ΔH is consistent with direction of arrow

Method 1b: Constructing an Energy Level Diagram

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



By Hess' law,

$$\Delta H_f^\ominus(\text{CO}) + (-283) = -394$$

$$\Delta H_f^\ominus(\text{CO}) = -111 \text{ kJ mol}^{-1}$$

Quick check

- ☐ Equations are balanced and state symbols are correct
- ☐ Axis is labelled
- ☐ Zero energy level is labelled if applicable
- ☐ Sign of ΔH is consistent with direction of arrow

Method 2: Equation Method

$$\Delta H = \Delta H_c^\ominus(\text{C}) = -394 \text{ kJ mol}^{-1}$$



$$\Delta H = -\Delta H_c^\ominus(\text{CO}) = +283 \text{ kJ mol}^{-1}$$



$$\therefore \Delta H_f^\ominus(\text{CO}) = -394 + 283 = -111 \text{ kJ mol}^{-1}$$

Lecture Exercise 3.1

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

Substance	$\Delta H_c^\ominus / \text{kJ mol}^{-1}$
Graphite	-394
Hydrogen	-286
Propane	-2220

General 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-practice 3.1

Calculate the standard enthalpy change of formation of ethanol using the combustion data provided. **[−279 kJ mol^{−1}]**

Substance	$\Delta H_c^\ominus / \text{kJ mol}^{-1}$
Graphite	−394
Hydrogen	−286
Ethanol	−1367

3.3 Application: Calculations using standard enthalpy change of formation**Lecture Exercise 3.2**

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



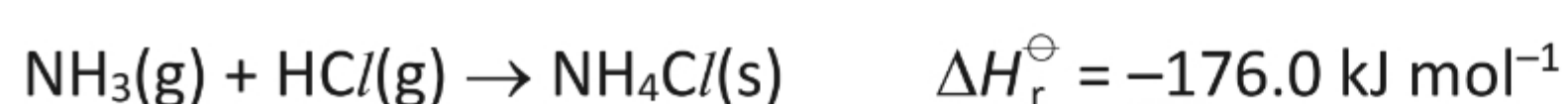
Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
CaCO ₃ (s)	−1207
CaO(s)	−635
CO ₂ (g)	−394

General 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 products and reactants in the given reaction.

Self-practice 3.2

Calculate the standard enthalpy of formation of solid ammonium chloride, NH₄Cl(s), using the given data.



$\Delta H_f^\ominus [\text{NH}_3(\text{g})] = -46.1 \text{ kJ mol}^{-1}$; $\Delta H_f^\ominus [\text{HCl}(\text{g})] = -92.3 \text{ kJ mol}^{-1}$ **[−314 kJ mol^{−1}]**

4 STANDARD ENTHALPY CHANGE OF NEUTRALISATION

The **heat evolved** when **1 mole of water** is formed in the neutralisation reaction between an acid and a base, at 298 K and 1 bar.

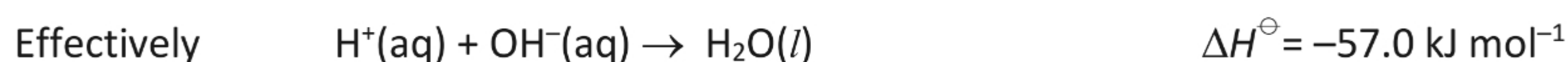
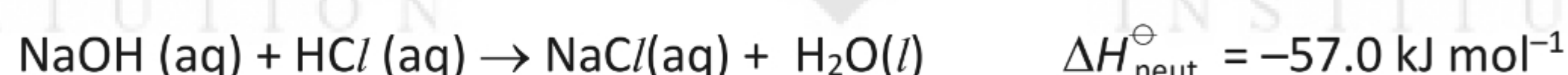
- Neutralisation is an **exothermic** reaction since it involves the attraction of H^+ and OH^- ions to form an O–H bond.



- The enthalpy change of neutralisation of a **strong acid** with a **strong base** is almost the **same** for all strong acids and bases ($-57.0 \text{ kJ mol}^{-1}$).

Reason:

Strong acids and strong bases **ionise completely** in dilute aqueous solution. Reaction between them is effectively the reaction between aqueous H^+ ions and OH^- ions.

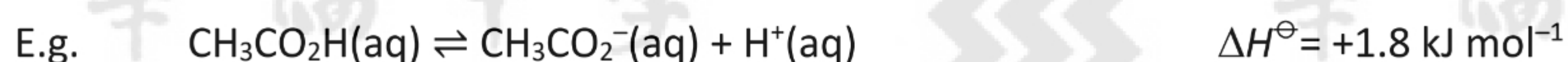


K^+ , NO_3^- , Na^+ and Cl^- ions are essentially spectator ions in the above neutralisation reactions.

- The enthalpy change of neutralisation involving a **weak acid** or **weak base** is slightly **less exothermic** than $-57.0 \text{ kJ mol}^{-1}$.

Reason:

Weak acids (or weak bases) **do not ionise completely** in dilute aqueous solution. During neutralisation, energy is absorbed to ionise the un-ionised weak acid (or weak base). Thus, **less energy is released** and the resulting $\Delta H^\ominus_{\text{neut}}$ is **less exothermic**.



5 EXPERIMENTAL DETERMINATION OF ENTHALPY CHANGE OF REACTION

The First Law of Thermodynamics 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 **surrounding**.

The enthalpy change of a reaction at constant pressure appears as heat. The heat given out (or taken in) by a reaction is transferred to the surrounding. The surrounding is often some water or a solution containing the reactants and products.

For example, $\text{CuSO}_4(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu}(\text{s})$ $\Delta H = -219 \text{ kJ mol}^{-1}$

The system consists of the reactants and the products. The reaction between CuSO_4 and Zn takes place in an aqueous medium. Since the reaction is exothermic (sign of ΔH is negative), heat is released by the reaction and is transferred to the surrounding aqueous medium.

The heat that is absorbed by the aqueous medium or solution causes the temperature of the solution to rise. This amount of heat can be determined by measuring the temperature change.

$$q = mc\Delta T$$

q = heat change of solution (J)

m = mass of solution (g)

c = specific heat capacity of solution ($\text{J g}^{-1} \text{K}^{-1}$)

ΔT = change in temperature of the solution (K or $^{\circ}\text{C}$)

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 unit of specific heat capacity is $\text{J g}^{-1} \text{K}^{-1}$.

The **heat capacity**, C , is defined as the amount of heat required to raise the temperature of the substance by 1 K (or 1°C). The SI unit for heat capacity is J K^{-1} .

If heat capacity of the solution is given instead, then the heat that is absorbed (or released) by the solution can be calculated as follows:

$$q = C\Delta T$$

C = heat capacity of solution (J K^{-1})

Hence by measuring the temperature change of the solution, we can determine the heat transferred to the surrounding solution and hence the heat absorbed or released by the reaction.

The enthalpy change of reaction can be calculated as follows:

Endothermic reaction

$$\Delta H_r = + \frac{q}{n}$$

Sign of ΔH_r is positive. Heat is absorbed by the reaction. Temperature of the surrounding solution decreases.

Exothermic reaction

$$\Delta H_r = - \frac{q}{n}$$

Sign of ΔH_r is negative. Heat is released by the reaction. Temperature of the surrounding solution increases.

q = heat change (heat absorbed or released)

n = no. of moles of limiting reactant or product (depending on the definition of ΔH_r)

5.1 The calorimeter

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

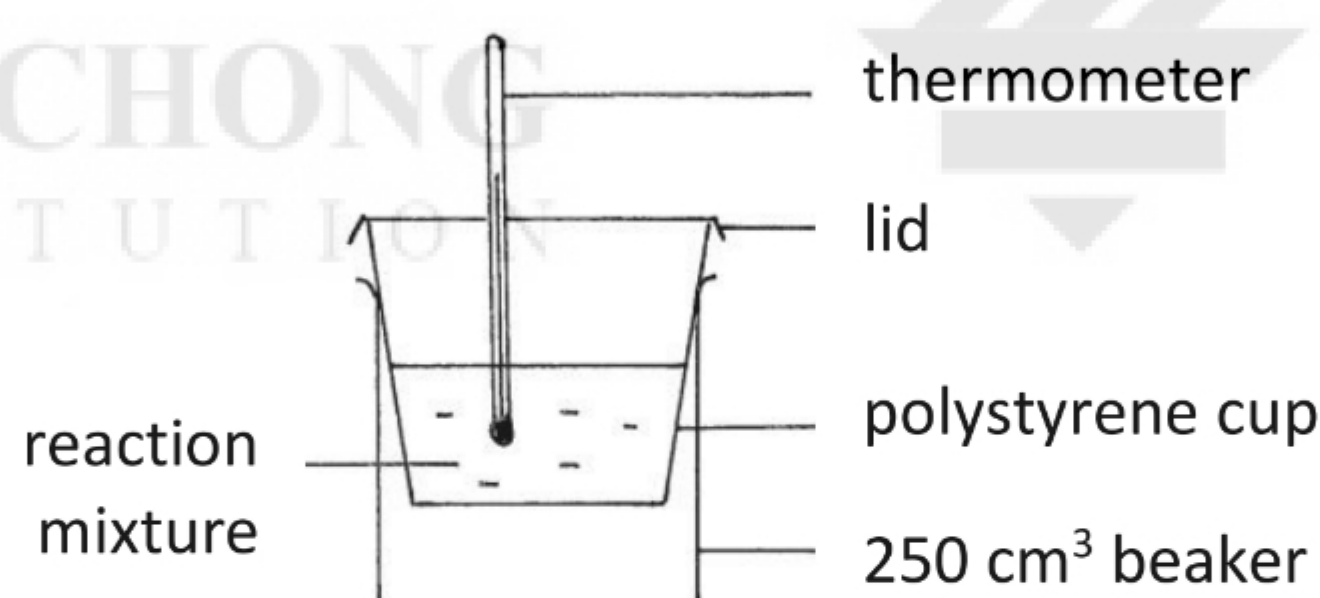


Figure 1. A simple calorimeter

Note:

- Polystyrene is an excellent insulator so heat loss from the sides is minimised. The lid also helps to minimise heat exchange with the surrounding air.
- The polystyrene cup is often supported in a 250 cm³ beaker or using a retort stand, to prevent toppling under the weight of the thermometer. The insulation can be improved by nesting two cups.
- The temperature changes are relatively small, so for accurate work the thermometer should have a precision of $\pm 0.1^\circ\text{C}$.

5.2 Assumptions in the calculations

To ensure accurate results, **all** the heat released (or absorbed) by the reaction must be used to raise (or lower) the temperature of the solution. In practice, we cannot totally eliminate heat exchanges with the surrounding air or apparatus so we make the following assumptions in our calculations.

- No heat loss to (or heat gain from) surrounding air
- Heat capacity of the calorimeter (e.g. polystyrene cup) is omitted

In addition, it is more convenient to measure the volume of the solution. Hence to calculate the mass of the solution, we assume that the density of the solution is the same as that of water (1.00 g cm^{-3}) since the solution is very dilute.

5.3 Reaction between two aqueous solutions



Generic Procedure for reactions involving mixing of two solutions

1. **Measure** (volume) cm^3 of (solution X) into a polystyrene cup using a measuring cylinder / pipette / burette. Record the **initial temperature** of solution X with a **thermometer**.
2. **Measure** (volume) cm^3 of (solution Y) in another measuring cylinder. Record the **initial temperature** of solution Y with the thermometer.
3. **Add** solution Y quickly to solution X in the polystyrene cup and stir the mixture gently.
4. Record the **highest / lowest temperature** reached with the thermometer.

Note:

- The initial temperature to use for calculations is the weighted average (by volume) of the initial temperatures of the two solutions.
- Solution Y is added quickly to minimise heat loss. Hence, it should not be measured with a burette or pipette.

Lecture Exercise 5.1

40.0 cm^3 of 2.0 mol dm^{-3} HCl(aq) were 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) / $^{\circ}\text{C}$	22.3
Initial temperature of NaOH (aq) / $^{\circ}\text{C}$	22.5
Highest temperature reached / $^{\circ}\text{C}$	34.6

Calculate the enthalpy change of neutralisation.

Self-practice 5.1

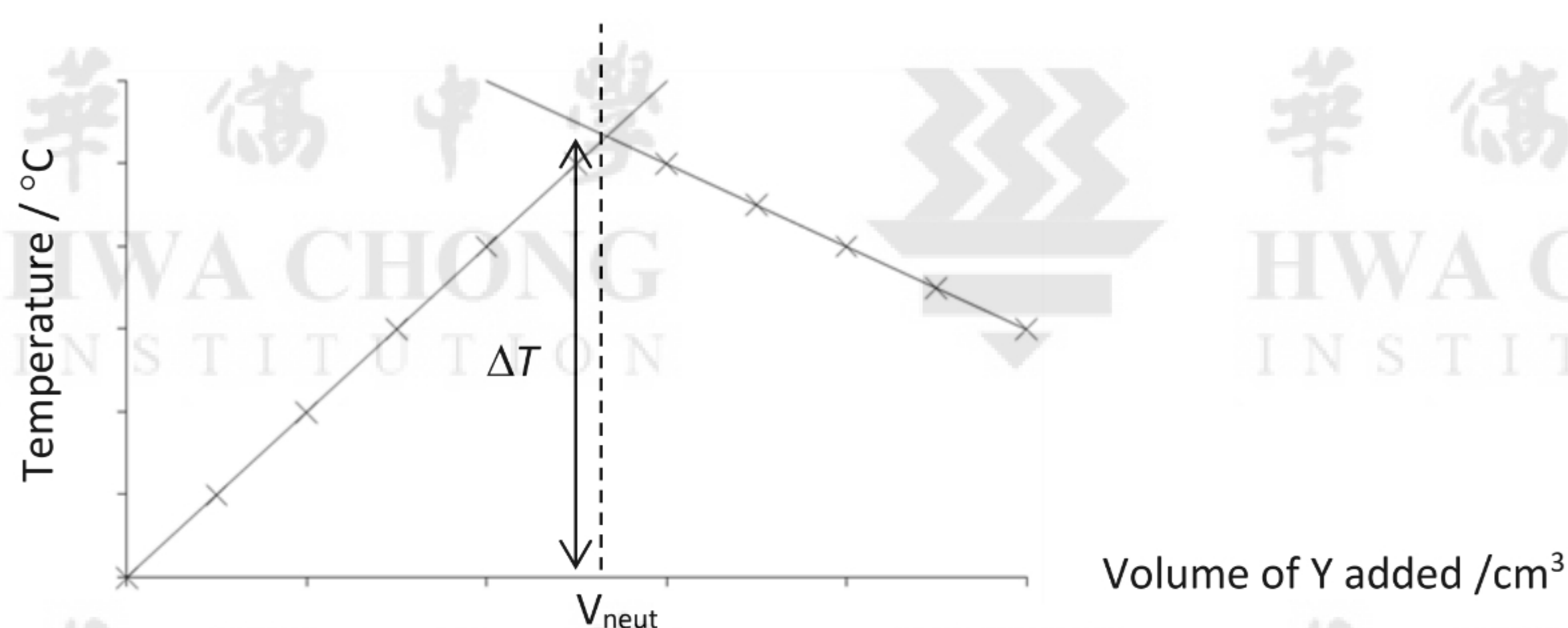
25.0 cm^3 of 2.0 mol dm^{-3} H_2SO_4 (aq) were added to 25.0 cm^3 of 2.0 mol dm^{-3} NaOH(aq) in a polystyrene cup. The initial temperatures of the solutions were 30.0 $^{\circ}\text{C}$ and 29.8 $^{\circ}\text{C}$ respectively. When the solutions were mixed, the highest temperature reached was 43.6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



Thermometric Titration

Suppose we need to determine a value for $\Delta H_{\text{neut}}^{\ominus}$ using aqueous sodium hydroxide and hydrochloric acid but the concentration of hydrochloric acid is unknown. In this case, we are unable to determine the limiting reactant and the amount of water formed. Hence the generic procedure for reactions involving mixing of two solutions given earlier cannot be used.

Instead, we can use thermometric titration in which a series of temperatures is recorded after each (small and fixed) addition of the solution from the burette until equivalence point is reached and passed. Extrapolation on the **temperature–volume graph** allows us to determine **both** the maximum temperature and the volume at which complete neutralisation is achieved. These results can then be used to determine the unknown concentration as well as a value for $\Delta H_{\text{neut}}^{\ominus}$.



Generic Procedure for Thermometric Titration

1. **Pipette** (volume) cm³ of (solution X) into a polystyrene cup.
2. **Record** the **temperature** of the solution with a **thermometer**.
3. From a burette, **add** (volume of each addition) cm³ of (solution Y) quickly to the polystyrene cup.
4. **Stir** the mixture with the thermometer and **record** its **temperature**.
5. Repeat steps 3 and 4 until (total volume) cm³ of (solution Y) has been added.

Note:

- No indicator is required.
- The total volume of solution added from the burette must be more than that required for complete reaction, such that there are sufficient data points to obtain a best-fit line for the downward slope of the graph.
- The actual experimental data may show gentle curves before and after the equivalence point. Before the equivalence point, each addition of solution Y releases the same amount of heat but it is spread over a larger volume of solution, thus resulting in a smaller temperature rise. After the equivalence point where the reaction is complete, further addition of solution Y that is of lower temperature cools the reaction mixture. As the temperature difference between solution Y and the reaction mixture decreases, the temperature drop becomes smaller.

5.4 Reaction between a solid and aqueous solution

**Generic Procedure for reactions involving adding a solid to a solution**

1. **Weigh** accurately (mass) g of (solid X) in a weighing bottle using an electronic balance.
2. **Measure** (volume) cm³ of (solution Y) into a polystyrene cup using a measuring cylinder / pipette / burette. Record the **initial temperature** of solution Y with a **thermometer**.
3. **Add** solid X quickly into the cup and stir the mixture gently.
4. Record the **highest / lowest temperature** reached with the thermometer.
5. **Re-weigh** the weighing bottle and the residual solid.

Note:

- The solid is added quickly to minimise heat loss.
- As the solid may not be transferred completely, the weighing bottle and the residual solid must be re-weighed to determine the exact mass of solid added.

Lecture Exercise 5.2

50.0 cm³ of 0.10 mol dm⁻³ silver nitrate solution were 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	4.31
mass of weighing bottle and residual Zn / g	3.51
mass of Zn added / g	0.80

Initial temperature of solution / °C	21.1
Highest temperature reached / °C	26.3
ΔT / °C	5.2

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

5.5 Temperature correction

In many experiments, the temperature may not immediately reach a maximum (or minimum), especially when the reaction is slow and 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.



Generic Procedure to obtain Maximum/ Minimum Temperature by Extrapolation

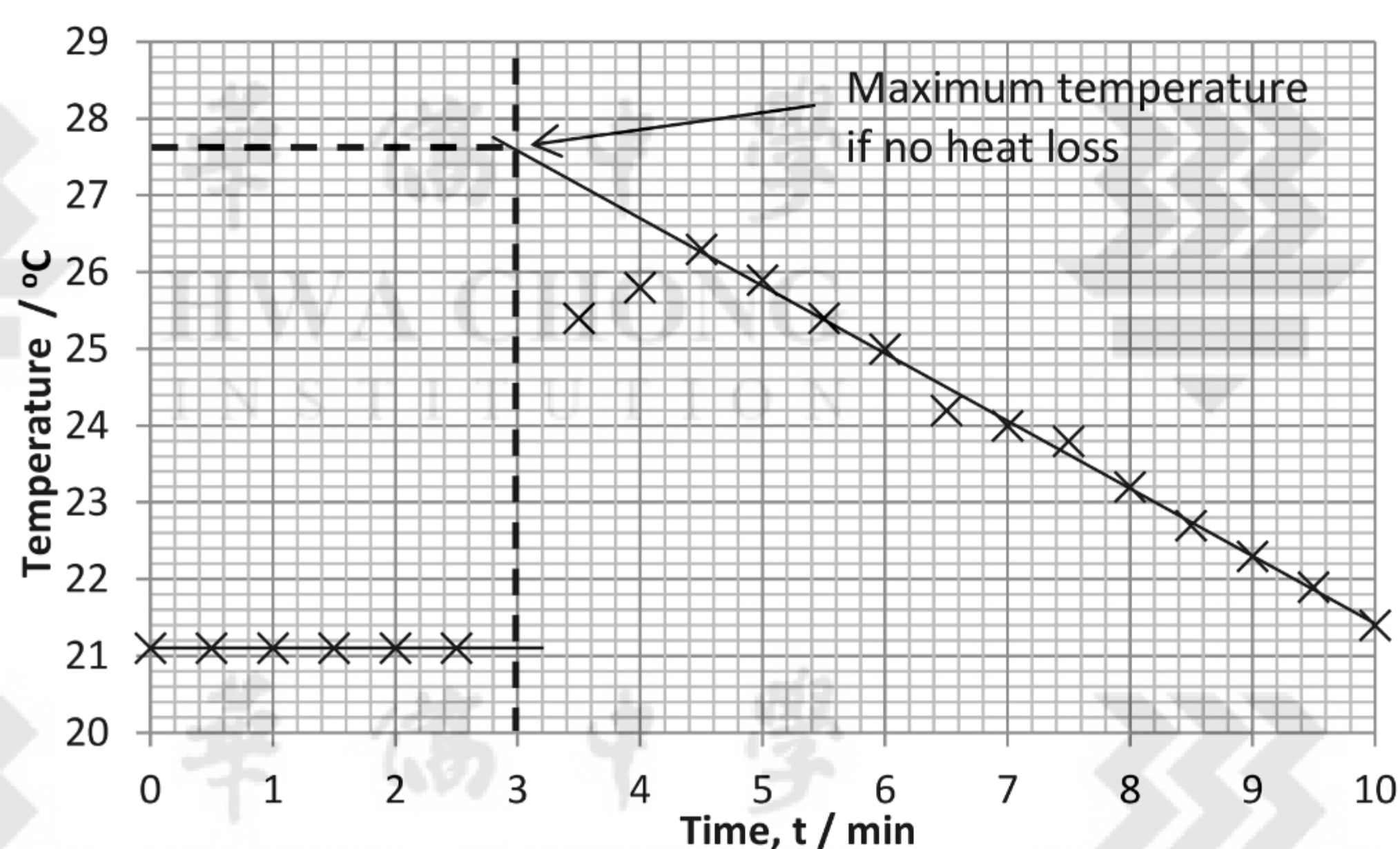
1. **Weigh** accurately (mass) g of (solid X) in a weighing bottle using an electronic balance.
/ **Measure** (volume) cm³ of (solution X) using a measuring cylinder.
2. **Measure** (volume) cm³ of (solution Y) into a polystyrene cup using a measuring cylinder / pipette / burette.
3. **Record** the **temperature** of solution Y every 30 seconds for 2.5 minutes using a **thermometer**.
4. At exactly 3.0 minutes, **add** solid X / solution X quickly into the cup and stir the mixture gently.
5. Continue to **record** the **temperature** every 30 seconds from 3.5 minutes to 10.0 minutes.
6. **Re-weigh** the weighing bottle and the residual solid (if a solid is used).

Lecture Exercise 5.3

The experiment in Lecture Exercise 5.2 was repeated using the above procedure (temperature was monitored for 10 minutes) and the following results were obtained.

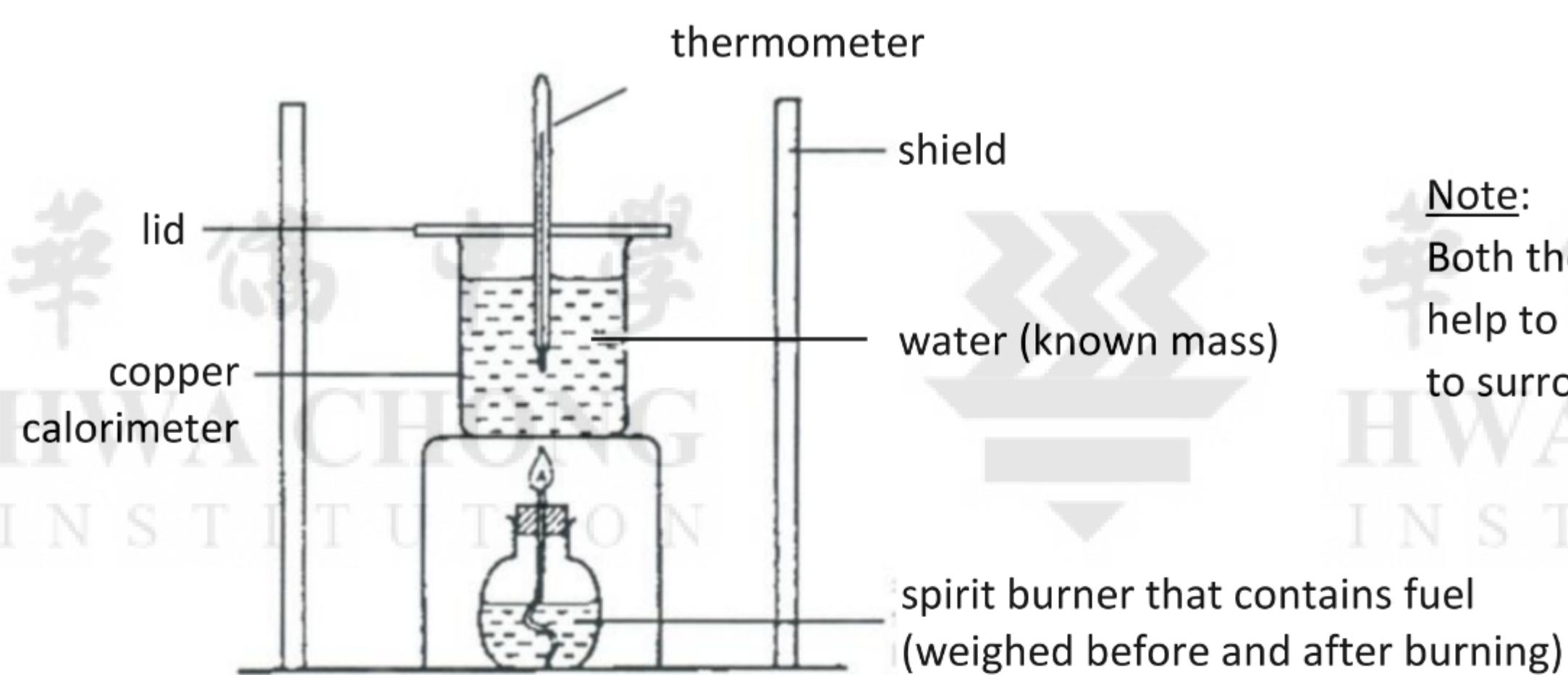
Time, t / min	0	0.5	1.0	1.5	2.0	2.5	3.5	4.0	4.5	5.0
Temperature / °C	21.1	21.1	21.1	21.1	21.1	21.1	25.4	25.8	26.3	25.9
Time, t / min	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
Temperature / °C	25.4	25.0	24.2	24.0	23.8	23.2	22.7	22.3	21.9	21.4

Use the data to calculate the enthalpy change for the reaction $\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$.



5.6 Experimental method to determine enthalpy change of combustion

The following experiment set-up can be used to determine the $\Delta H_c^\ominus$ for a fuel such as ethanol. The heat released during combustion is used to heat a known mass of water in a copper calorimeter.



Note:

Both the shield and lid help to reduce heat loss to surroundings.

Figure 2. Experimental set-up to determine enthalpy change of combustion of a fuel



Generic Procedure for Combustion Reactions

1. **Weigh** the spirit burner containing the fuel using an electronic balance.
2. Using a pipette / burette/ measuring cylinder, place 100 cm³ of water in a **copper calorimeter**. Record the **initial temperature** of the water with a **thermometer**.
3. Set up the apparatus as shown in the diagram.
4. **Ignite** the fuel and **heat** up the water. Stir gently with the thermometer.
5. When a temperature rise of about (temperature change) °C is reached, **extinguish** the flame and record the **maximum temperature** reached with the thermometer.
6. Allow the spirit burner to **cool** to room temperature. **Re-weigh** the spirit burner containing the remaining fuel.

Note:

1. Unlike the polystyrene cup, the heat absorbed by the copper calorimeter is usually included in the calculation of heat, q , because copper is a good conductor of heat. In some cases, the total heat capacity of the copper can and water may be given.
2. Although liquids are usually added by measuring their volumes, it is possible to measure the mass of water that was transferred to the copper calorimeter in Step 2 using an electronic balance.

Lecture Exercise 5.4

In an experiment to determine $\Delta H_c^\ominus$ for ethanol, the following results were obtained. Calculate $\Delta H_c^\ominus$ for ethanol. Compare the experimental value with the literature value of $-1368 \text{ kJ mol}^{-1}$ and account for any difference.

Mass of water in calorimeter / g	250.00
Mass of burner and ethanol before combustion / g	16.20
Mass of burner and ethanol after combustion / g	15.67
Temperature of water before combustion / °C	29.6
Temperature of water after combustion / °C	40.0

A bomb calorimeter is used to obtain highly accurate values of ΔH_c as heat losses are minimised.

Experimental Method using a Bomb Calorimeter

1. A **known mass** of the substance (whose ΔH_c is to be determined) is burnt in **excess oxygen** in a bomb calorimeter.
2. The heat released is transferred to a known mass of water in the calorimeter.
3. The rise in temperature of the water is then measured.
4. Allowance is made for the heat capacity of the bomb calorimeter and the heat evolved in burning the iron ignition wire used to ignite the substance. Thus ΔH_c can be measured accurately.

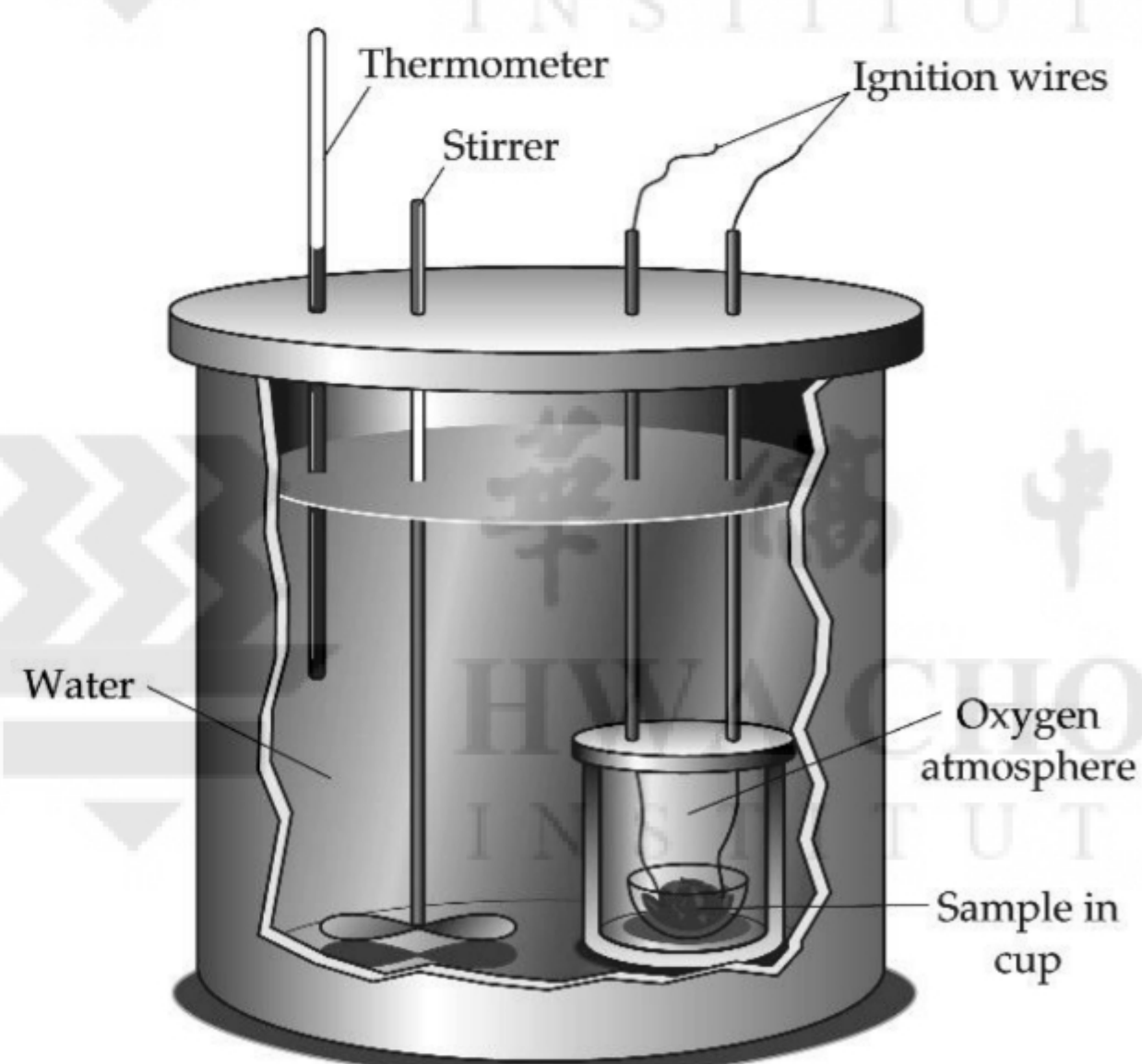


Figure 3. Bomb calorimeter

6 BOND DISSOCIATION ENERGY, BOND ENERGY AND STANDARD ENTHALPY CHANGE OF ATOMISATION

6.1 Bond dissociation energy, B.D.E.

Bond dissociation energy is the **energy required** to **break 1 mole** of a particular **covalent bond** in a specific molecule in the **gaseous state**.

- To break the covalent bond, energy is needed to pull the two atoms apart so bond dissociation energy is **always positive** (endothermic process).

When the same bond is formed, the same amount of energy is *released* (because the process is exothermic).

- Bond dissociation energy is a measure of the strength of covalent bonds. The **more endothermic** the bond dissociation energy, the **stronger** is the covalent bond. (Refer to Topic 2 Chemical Bonding for factors affecting the strength of a covalent bond.)
- In a molecule like methane, the **successive** bond dissociation energies of each of the four C–H bonds are different.

	B.D.E / kJ mol^{-1}
$\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g})$	+425
$\text{CH}_3(\text{g}) \rightarrow \text{CH}_2(\text{g}) + \text{H}(\text{g})$	+470
$\text{CH}_2(\text{g}) \rightarrow \text{CH}(\text{g}) + \text{H}(\text{g})$	+416
$\text{CH}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{H}(\text{g})$	+335

Table 4. Successive bond dissociation energies of C–H bonds in methane

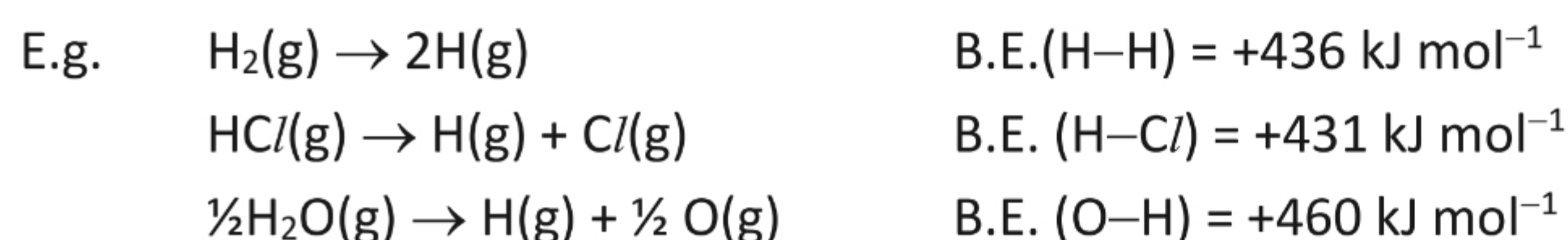
- Bond dissociation energy of the same type of bond in **different molecules** may differ.

E.g. B.D.E. of C–H bond in CH_4 is smaller than the B.D.E. of C–H bond in $\text{CH}_2=\text{CH}_2$

- Due to the above two reasons, it is more convenient to use an average value called **bond energy**.

6.2 Bond energy, B.E.

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

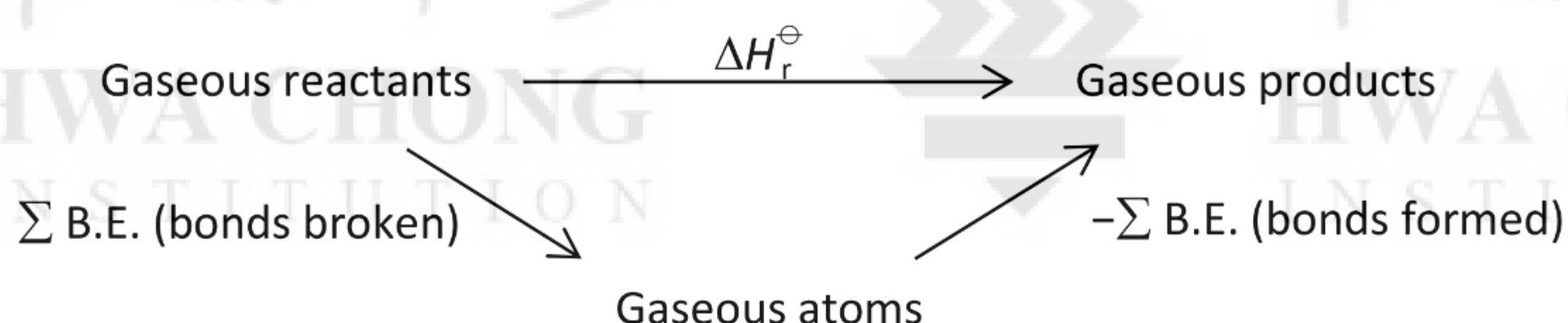


- The bond energy data in the *Data Booklet* are **average values** derived from a large range of molecules containing that particular covalent bond.

E.g. B.E. (C–Cl) = +340 kJ mol⁻¹ (from *Data Booklet*)
However, B.D.E (C–Cl) in CCl₄ = +327 kJ mol⁻¹

6.2.1 Calculations using bond energy

- During the reaction, energy is absorbed to break all the bonds in the reactants and released when bonds in the product are formed. The enthalpy change of a reaction involving **gaseous molecules** can be calculated using bond energy values.

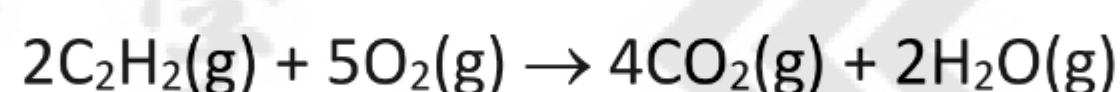


$$\Delta H_r^\ominus = \sum \text{B.E. (bonds broken)} - \sum \text{B.E. (bonds formed)}$$

- As the bond energy data in the *Data Booklet* are average values, 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.

Lecture Exercise 6.1

- (a) Oxyacetylene torches, which operate at temperatures as high as 3300 °C, are fuelled by the combustion of acetylene (i.e. ethyne), C₂H₂. The equation is given below:



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

- (b) Calculate another value for the ΔH_r of this reaction using the following enthalpy changes of formation.

$$\Delta H_f [\text{C}_2\text{H}_2(\text{g})] = +227 \text{ kJ mol}^{-1}; \Delta H_f [\text{CO}_2(\text{g})] = -394 \text{ kJ mol}^{-1}; \Delta H_f [\text{H}_2\text{O}(\text{g})] = -242 \text{ kJ mol}^{-1}$$

- (c) Suggest a reason for the difference in the values of ΔH_r , obtained in parts (a) and (b).

Self-practice 6.1

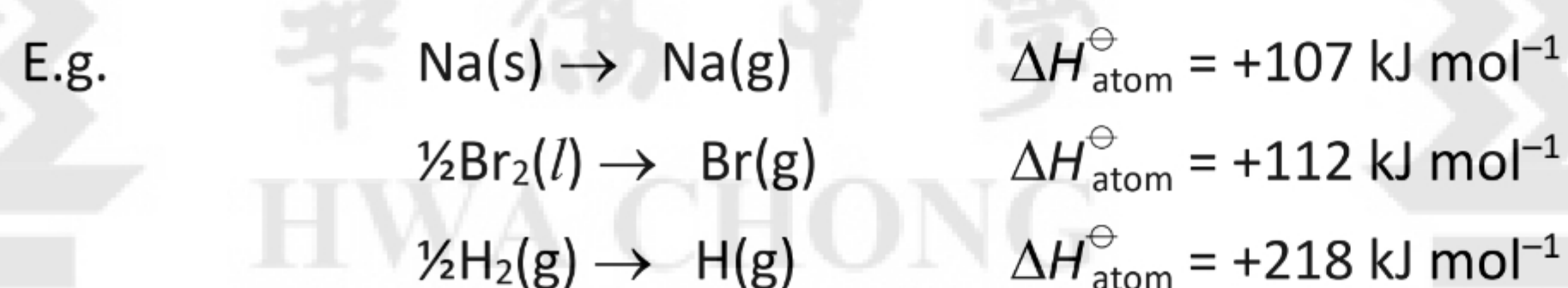
Sulfur hexafluoride can be made by reacting sulfur tetrafluoride with fluorine.



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]**

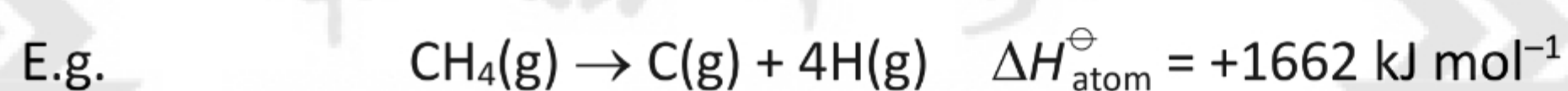
6.3 Standard enthalpy change of atomisation

$\Delta H_{\text{atom}}^\ominus$ for an element is the **energy required** when **1 mole of gaseous atoms** is formed from the **element** at 298 K and 1 bar.

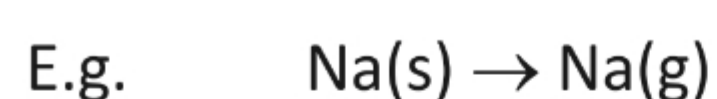


What are some elements with enthalpy change of atomisation = 0 kJ mol⁻¹?

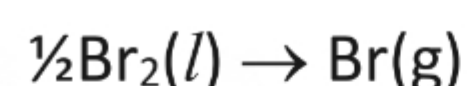
$\Delta H_{\text{atom}}^\ominus$ for a compound is the **energy required** to convert **1 mole of the compound** into **gaseous atoms** at 298 K and 1 bar.



- $\Delta H_{\text{atom}}^{\ominus}$ values are **always positive** since atomisation involves **breaking bonds**.
- Depending on the type of substance, atomisation is associated with different processes.



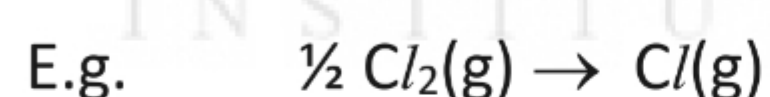
$$\Delta H_{\text{atom}}^{\ominus} = \Delta H_{\text{fus}}^{\ominus} + \Delta H_{\text{vap}}^{\ominus}$$



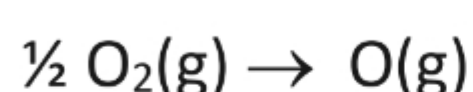
$$\Delta H_{\text{atom}}^{\ominus} = \frac{1}{2} \times (\Delta H_{\text{vap}}^{\ominus} + \text{B.E.}(\text{Br-Br}))$$

- For gaseous diatomic elements, enthalpy change of atomisation and bond energy are related:

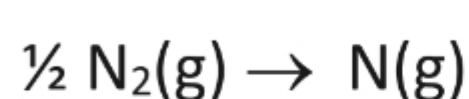
$$\Delta H_{\text{atom}}^{\ominus}(\text{X}_2) = \frac{1}{2} \times \text{B.E.}(\text{X-X})$$



$$\Delta H_{\text{atom}}^{\ominus} = \frac{1}{2} \times \text{B.E.}(\text{Cl-Cl}) = \frac{1}{2}(244) = +122 \text{ kJ mol}^{-1}$$



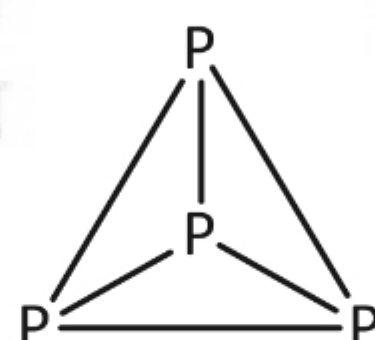
$$\Delta H_{\text{atom}}^{\ominus} = \frac{1}{2} \times \text{B.E.}(\text{O=O}) = \frac{1}{2}(496) = +248 \text{ kJ mol}^{-1}$$



$$\Delta H_{\text{atom}}^{\ominus} = \frac{1}{2} \times \text{B.E.}(\text{N}\equiv\text{N}) = \frac{1}{2}(944) = +472 \text{ kJ mol}^{-1}$$

Lecture Exercise 6.2

Phosphorus exists as P_4 molecule with the following structure.



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

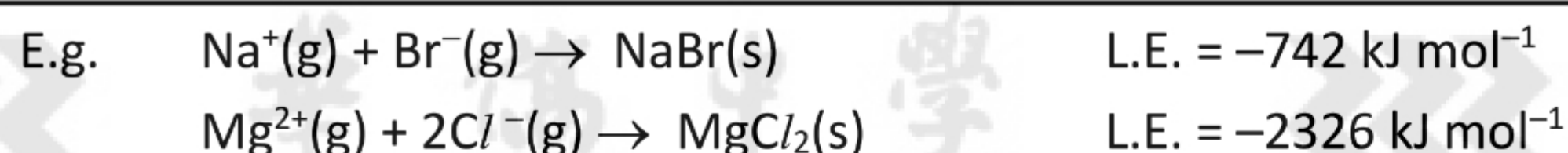
Standard enthalpy change of formation of $\text{P}_4(\text{g}) = +58.91 \text{ kJ mol}^{-1}$

Standard enthalpy change of atomisation of phosphorus = $+314.4 \text{ kJ mol}^{-1}$

7 LATTICE ENERGY AND BORN–HABER CYCLE

7.1 Lattice energy, L.E.

The **heat evolved** when **1 mole of solid ionic compound** is formed from its **constituent gaseous ions**.



- Lattice energy is **always negative** as heat is evolved in forming **electrostatic forces of attraction** between oppositely charged ions (i.e. ionic bonding).
- 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.

7.1.1 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.

$$\text{L.E.} \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

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	L.E. / kJ mol^{-1}
NaCl	+1	-1	0.095	0.181	-776
NaBr	+1	-1	0.095	0.195	-742
MgCl ₂	+2	-1	0.065	0.181	-2375

Table 5. Factors affecting lattice energy

- NaCl and NaBr have the same cation. Br^- ion has the same charge but larger ionic radius than Cl^- ion. Since $\text{L.E.} \propto \frac{q_+ \times q_-}{r_+ + r_-}$, L.E. of NaBr is less exothermic than that of NaCl.
- MgCl₂ and NaCl have the same anion. Mg^{2+} has a higher charge and smaller ionic radius than Na^+ . Since $\text{L.E.} \propto \frac{q_+ \times q_-}{r_+ + r_-}$, L.E. of MgCl₂ is more exothermic than that of NaCl.

7.2 Born–Haber cycle

Lattice energy cannot be determined directly (by reacting the constituent gases ions). It can be calculated using a Born-Haber cycle. A Born-Haber cycle is usually presented in the form of an energy level diagram where the ‘zero reference line’ refers to the elements in the standard states.

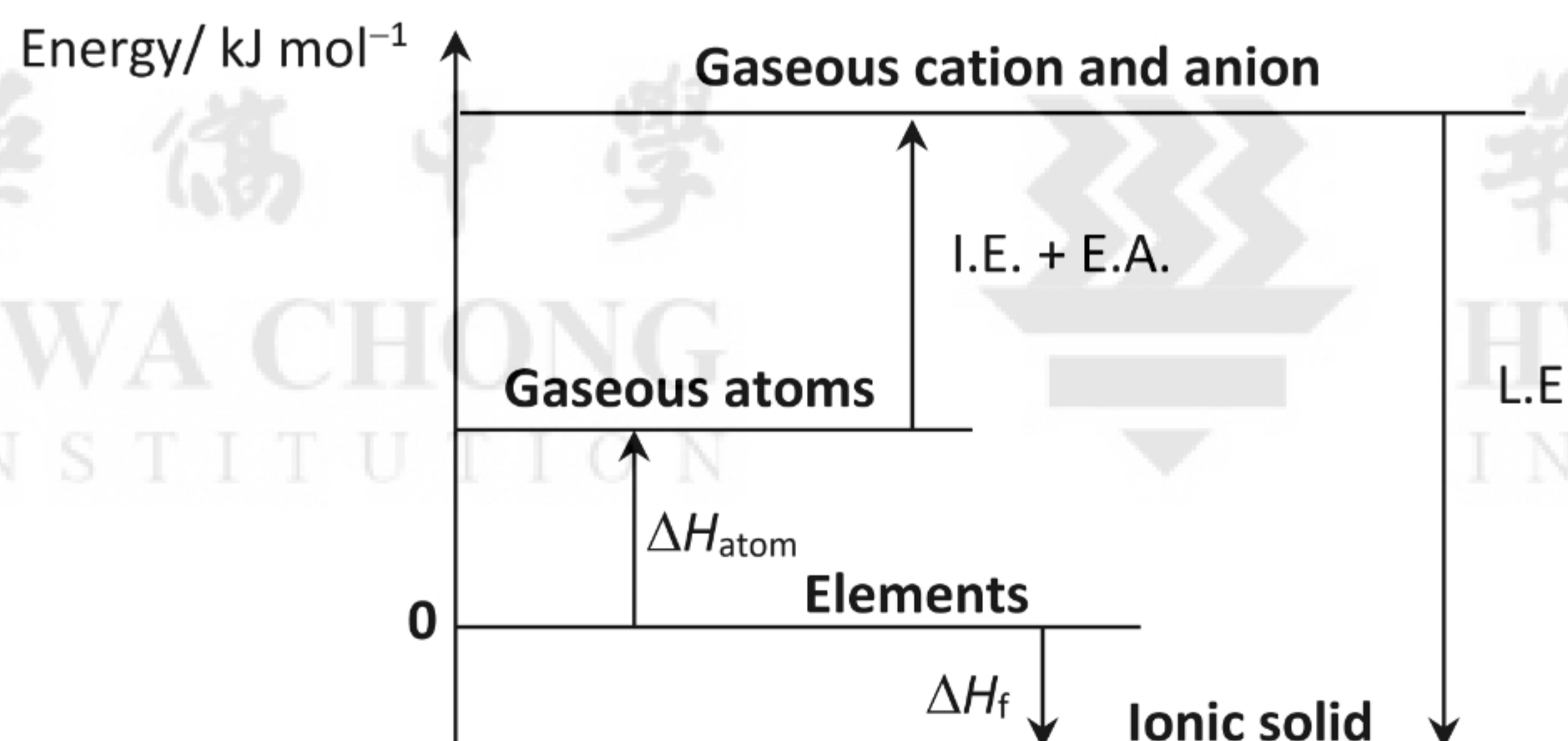


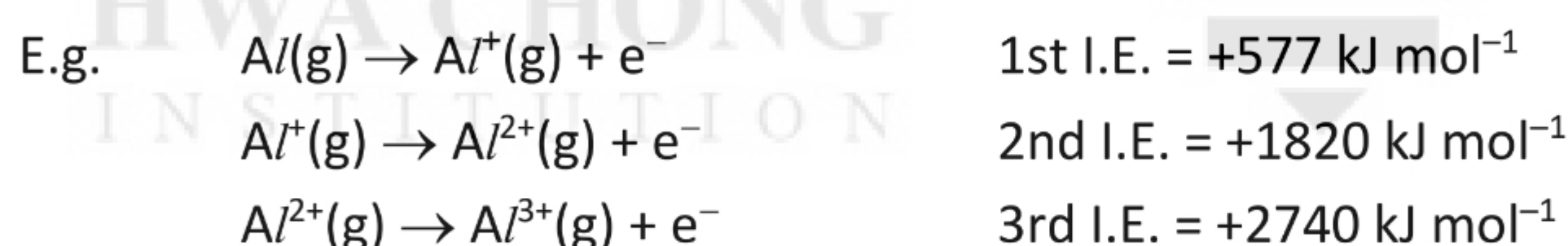
Figure 4. A general Born-Haber cycle

Note: I.E. and E.A. should be represented by separate arrows. Refer to Lecture Exercise 7.1.

7.2.1 Ionisation Energy, I.E.

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**.

- I.E. is **always positive** since energy is required to remove an electron (endothermic process).
- Further removal of electrons require more energy as the number of protons remain the same but the shielding effect is reduced since there are less electrons.



7.2.2 Electron Affinity, E.A.

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

- 1st E.A.** is usually **negative** as the effective nuclear charge of the atom leads to an attraction of the incoming electron. When the attraction is stronger, the energy given off is greater and hence E.A. is more negative.
- 2nd and subsequent E.A.** are always **positive** because energy is required to overcome the electrostatic repulsion between the incoming electron and the anion.



Lecture Exercise 7.1

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:

	$\Delta H/\text{kJ mol}^{-1}$
Enthalpy change of formation of $\text{Na}_2\text{O}(\text{s})$	–414
Enthalpy change of atomisation of sodium	+107
First electron affinity of oxygen	–141
Second electron affinity of oxygen	+844

Self–practice 7.1

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_{atom} of $\text{Ca} = +178 \text{ kJ mol}^{-1}$; ΔH_{f} of $\text{CaCl}_2 = -796 \text{ kJ mol}^{-1}$; First E.A. of $\text{Cl} = -349 \text{ kJ mol}^{-1}$;

[–2260 kJ mol^{–1}]

7.3 Experimental versus theoretical lattice energies

- **Experimental** lattice energy refers to the value found from experimental results **using the Born–Haber cycle**.
- Theoretical lattice energy refers to the value calculated based on a **model** which assumes that the **compound is completely ionic**.
- There is always a difference between the two values which suggests that no compound is completely ionic (Refer to Topic 2 Chemical Bonding for the continuum from a theoretical pure ionic model to purely covalent compounds.)
- A small difference shows that the ionic model is a good one for the compound.
- A large difference shows that there is **covalent character** in the ionic compound. This is most apparent when a cation with a high charge density distorts an anion with a large electron cloud.

Compound	Theoretical L.E. / kJ mol^{-1}	Experimental L.E. / kJ mol^{-1}
CsCl	– 657	– 659
MgCl ₂	– 2326	– 2375
AgF	– 953	– 967
AgI	– 808	– 889

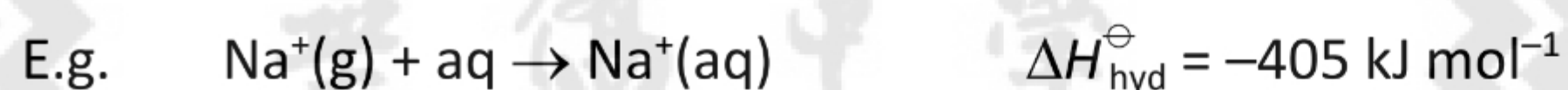
Table 6. Theoretical and Experimental lattice energies of the some compounds

- There is good agreement between the theoretical and experimental lattice energy for CsCl but the discrepancy is greater for MgCl₂. Mg²⁺ has higher charge and smaller ionic radius than Cs⁺. Mg²⁺ thus has higher charge density and greater polarising power than Cs⁺. Hence Mg²⁺ distorts the electron cloud of Cl[–] to a larger extent, resulting in greater covalent character in MgCl₂.
- 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.

8 STANDARD ENTHALPY CHANGES OF HYDRATION AND SOLUTION

8.1 Standard enthalpy change of hydration

The heat **evolved** when **1 mole of free gaseous ions** is dissolved in an infinite volume of water at 298 K and 1 bar.



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

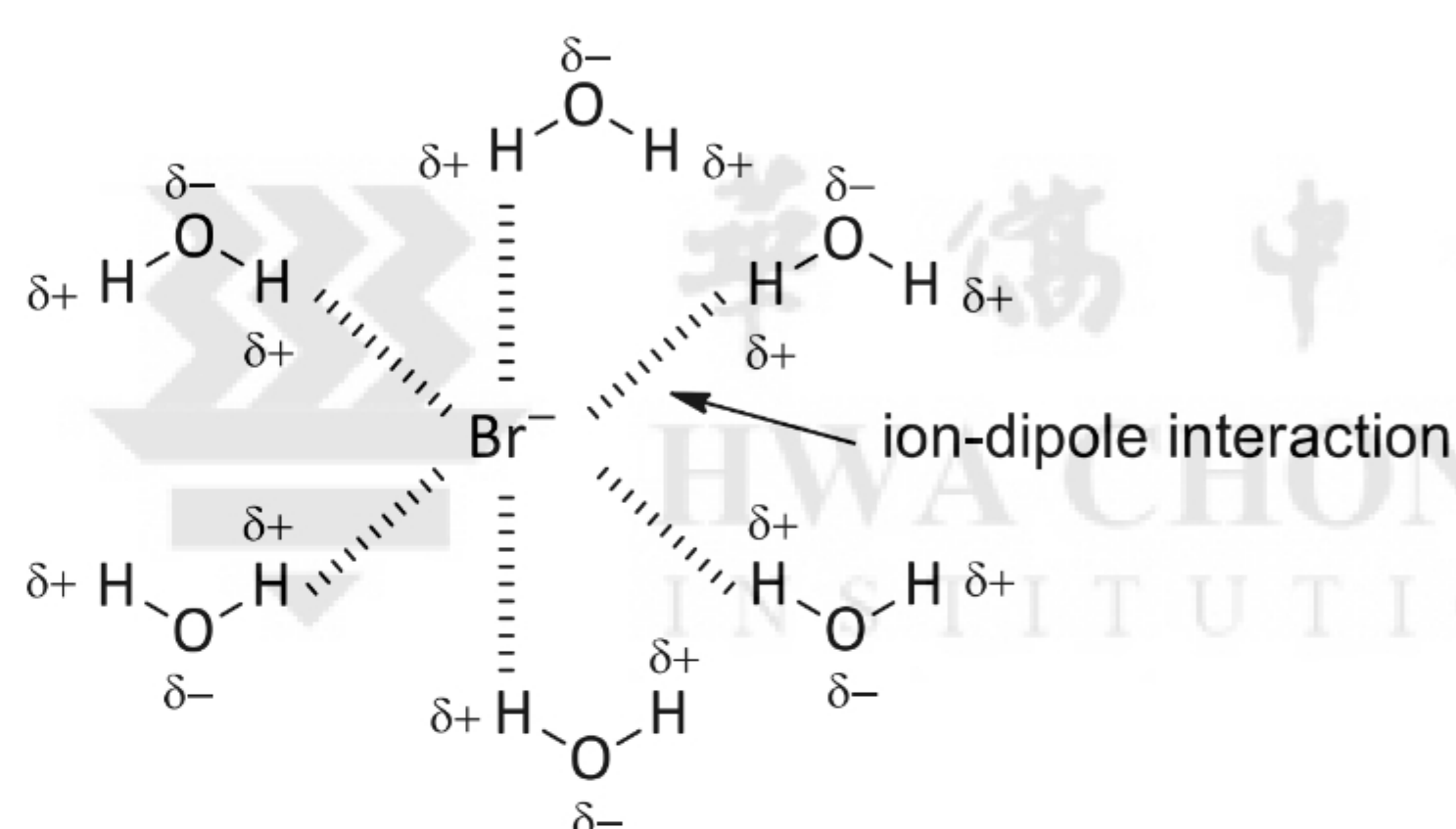
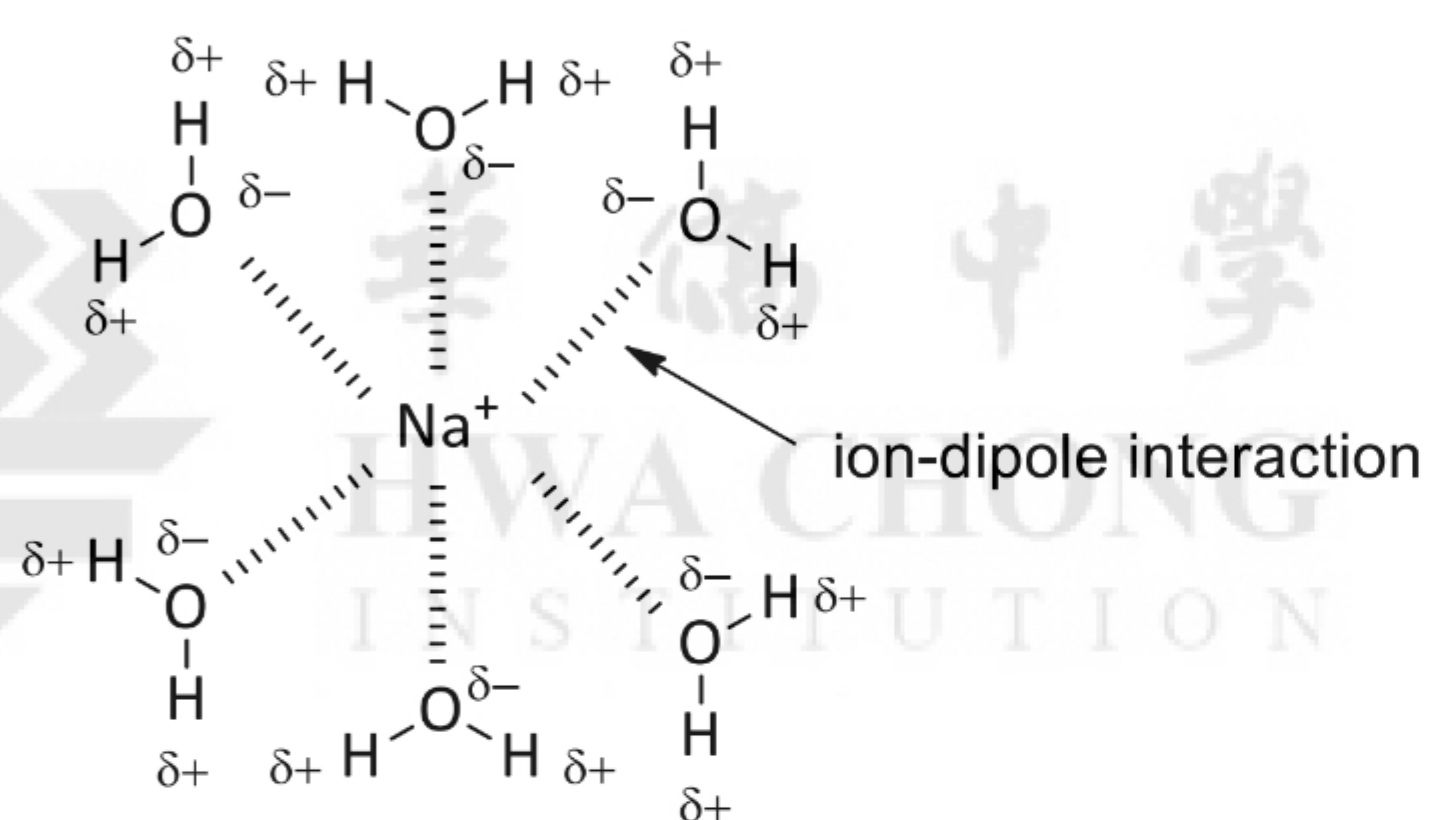
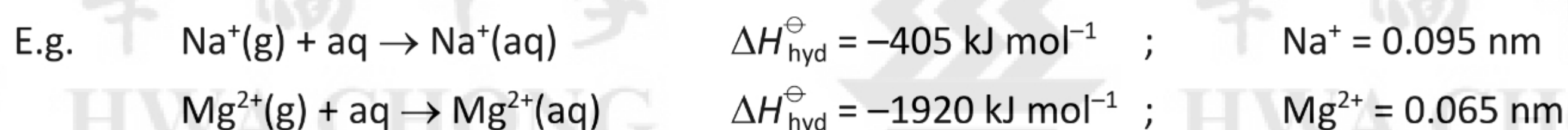


Figure 5. Hydrated Na^+ and Br^- ions

- The magnitude of $\Delta H_{\text{hyd}}^{\ominus}$ of an ion depends on its **charge density**. (Refer to Topic 2 Chemical Bonding for the definition of charge density.)

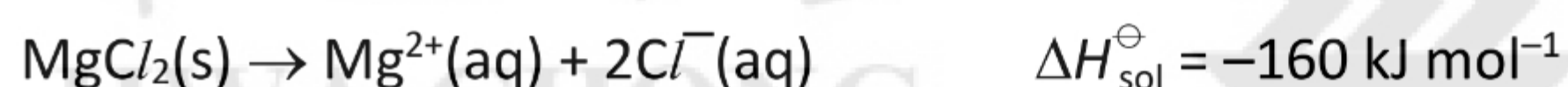
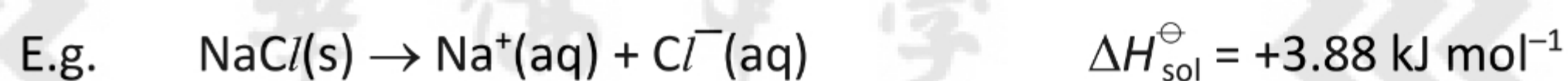
$$\Delta H_{\text{hyd}} \propto \frac{q}{r}$$

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



8.2 Standard enthalpy change of solution, $\Delta H_{\text{sol}}^{\ominus}$

The enthalpy change when **1 mole of solute** is completely dissolved in an infinite volume of solvent at 298 K and 1 bar.



- The solute is usually an ionic compound while the solvent is usually water.
- $\Delta H_{\text{sol}}^{\ominus}$ can be either positive or negative.

If $\Delta H_{\text{sol}}^{\ominus}$ is highly positive $\Rightarrow$ salt is likely insoluble

If $\Delta H_{\text{sol}}^{\ominus}$ is negative $\Rightarrow$ salt is likely soluble

Note: There are salts with positive $\Delta H_{\text{sol}}^{\ominus}$ and are soluble e.g. NaCl, KCl, NH_4NO_3 due to positive entropy change (Refer to Section 9).

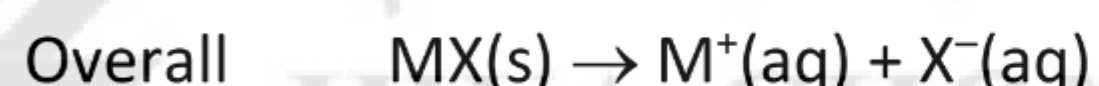
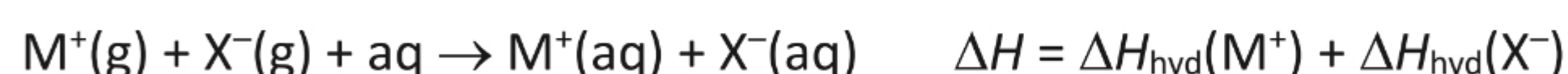
8.3 Relationship between lattice energy, enthalpy changes of hydration and enthalpy change of solution

- The dissolution of an ionic solid MX(s) can be divided into 2 processes:

- Breaking up the solid ionic lattice to form isolated gaseous ions.
Process is **endothermic** (overcoming ionic bonding) and the enthalpy change is ' $-\text{LE}$ '.



- Hydration of the gaseous ions.
Process is **exothermic** (forming ion–dipole interactions between ion and water).



$$\Delta H_{\text{sol}}^{\ominus} = -\text{L.E.} + \text{sum of } \Delta H_{\text{hyd}}^{\ominus}$$

If $|\text{L.E.}| > |\Delta H_{\text{hyd}}^{\ominus}| \Rightarrow \Delta H_{\text{sol}}^{\ominus} > 0$ (endothermic) – Refer to diagram below

If $|\text{L.E.}| < |\Delta H_{\text{hyd}}^{\ominus}| \Rightarrow \Delta H_{\text{sol}}^{\ominus} < 0$ (exothermic) – try drawing the energy level diagram

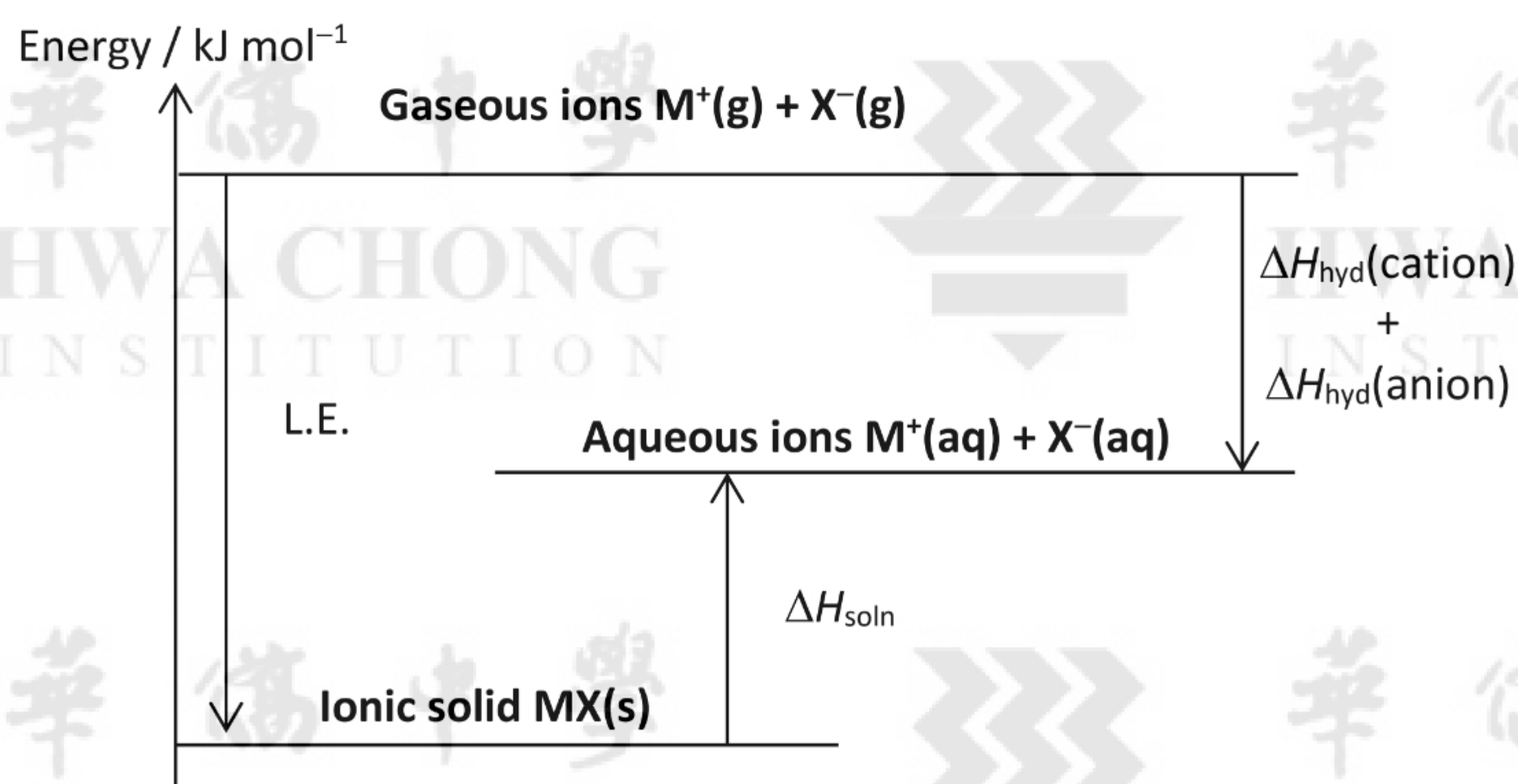


Figure 6. Energy level diagram to determine enthalpy change of solution of an ionic solid

Lecture Exercise 8.1

- (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 NaCl(s) =	+5 kJ mol ⁻¹
Enthalpy change of hydration of Na ⁺ (aq) =	–390 kJ mol ⁻¹
Lattice energy of NaCl(s) =	–776 kJ mol ⁻¹

- (b) The enthalpy change of hydration of iodide ion was found to be –296 kJ mol⁻¹. Comment on the difference between this value and the value found in (a).

9 ENTROPY AND GIBBS FREE ENERGY

9.1 Spontaneous processes

From our experience, there are processes that take place on its own. For example, if we ignite a mixture of hydrogen and oxygen, they combine rapidly to form water. An iron nail rusts slowly when left to stand. All of these chemical reactions can be described as *spontaneous*. There are also physical processes which are *spontaneous*. For example, when a drop of dye is placed in a beaker of water, diffusion takes place resulting in a uniformly coloured solution.

A **spontaneous process** is one that takes place naturally in the direction stated. In other words, 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, $\text{N}_2\text{O}_5(\text{s}) \rightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H = +109.5 \text{ kJ mol}^{-1}$

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

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

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.

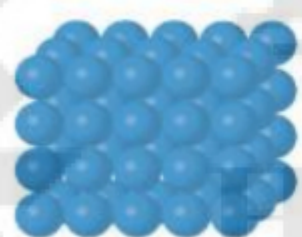
Similarly, dissolving a salt separates the ions in the crystalline solid. The ions in the aqueous state have greater freedom of motion (or are more disordered) and their energy of motion is more distributed.

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**.

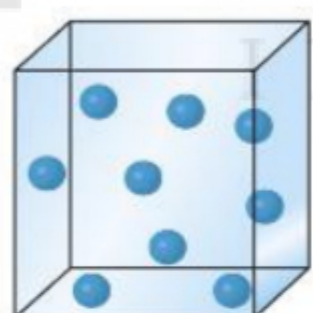
9.2 Entropy and entropy changes

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 through the motion of its particles. Units: $\text{J mol}^{-1} \text{K}^{-1}$.

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



In a solid, the particles are relatively fixed and possess the least kinetic energy. There are few ways that the energy of particles is distributed.



In a gas, the particles 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.

Figure 7. Arrangement of particles in solid and gaseous state

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

- If a reaction or process results in more ways to disperse or distribute the energy, entropy increases ($\Delta S > 0$).
- If a reaction or process results in less ways to disperse or distribute the energy, entropy decreases ($\Delta S < 0$).

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 surrounding) 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.

9.2.1 Predicting the sign of ΔS for some processes

(1) Change in temperature

As temperature increases, the **average kinetic energy** of the particles and the **range of energies** increase as shown in the Maxwell–Boltzmann distribution curves below. (Refer to Topic 3 The Gaseous State for explanation on the shape of the curves.) There are **more ways to disperse the energy** among the particles. Hence, **entropy increases** ($\Delta S > 0$).

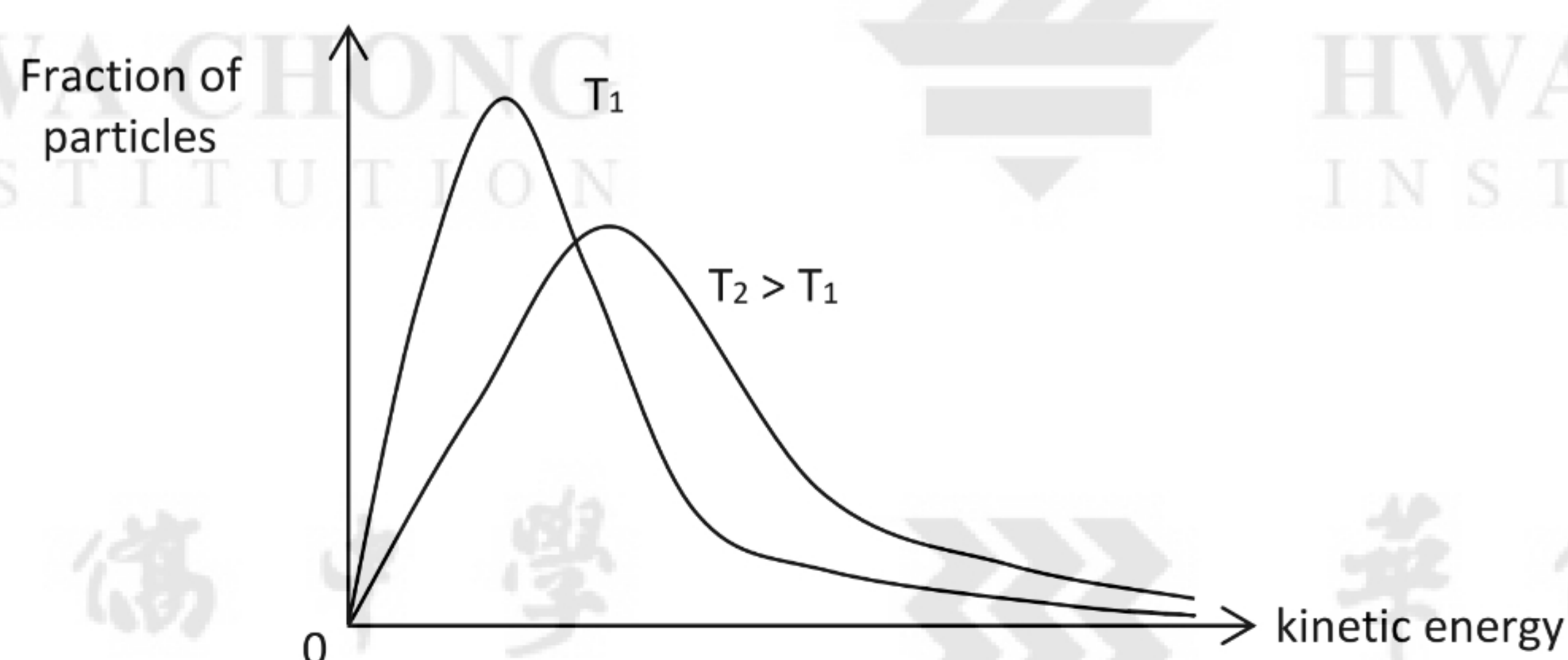


Figure 8. Maxwell–Boltzmann distribution curve

(2) Change in phase

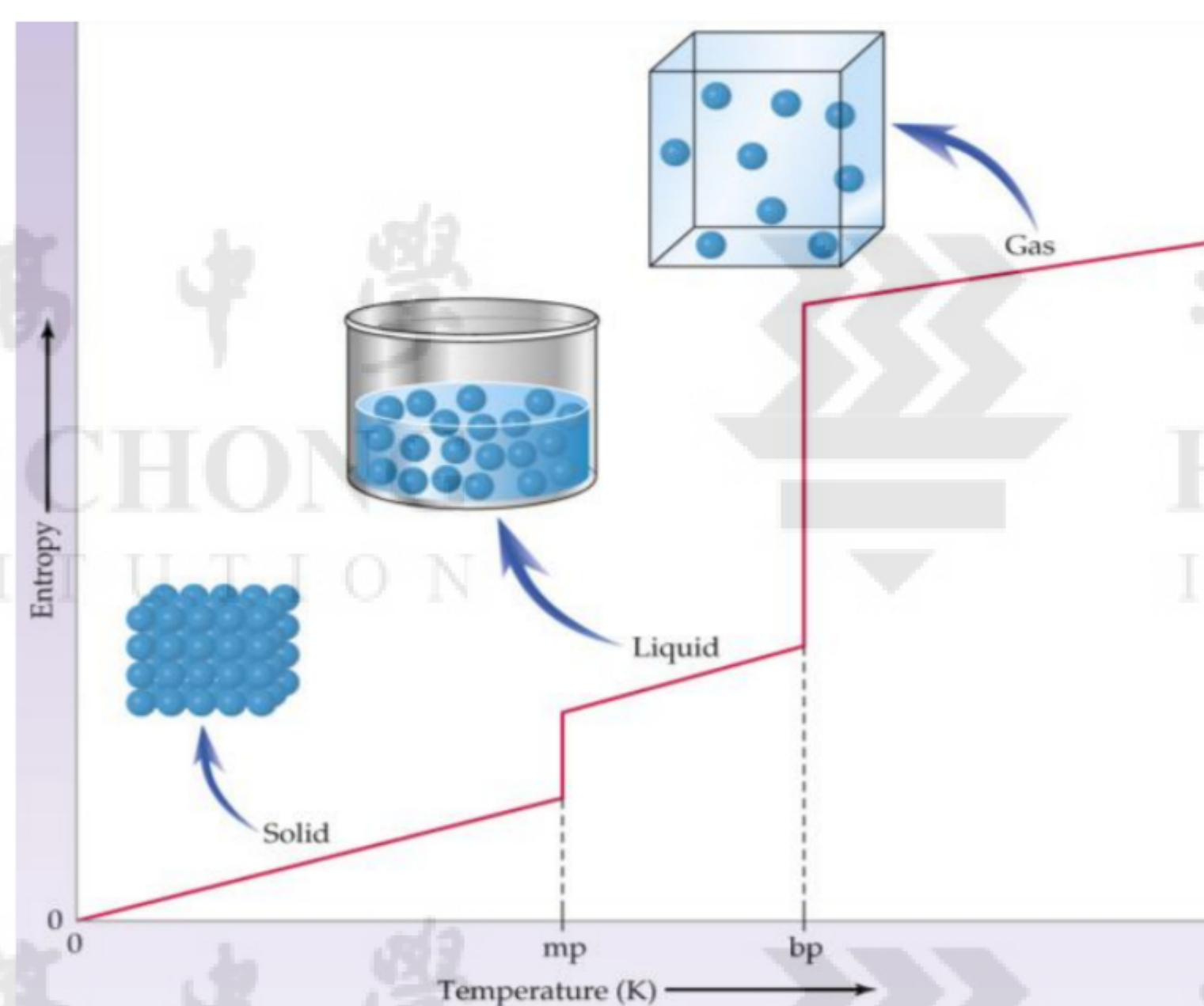


Figure 9. Change in entropy during phase change

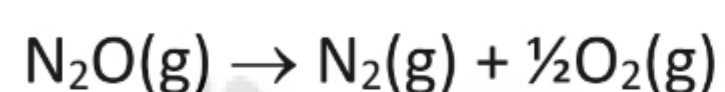
- The particles in the solid state vibrate about their fixed positions. The energy is thus the least dispersed and the solid has the lowest entropy.
- When temperature increases, entropy increases gradually as the kinetic energy of the particles increases.
- When the solid melts, the **particles move more freely in the liquid state and become more disordered**. Hence there is an abrupt increase in entropy ($\Delta S > 0$) as there are **more ways to distribute the particles and their energy in the liquid state**.

- Likewise, as the liquid is heated, its entropy increases as the particles gain kinetic energy. During vaporisation, the liquid converts to a gas where the **particles are able to move even more freely**. Hence there is a large increase in entropy ($\Delta S \gg 0$) as there are **more ways to distribute the particles and their energy in the gaseous state**.

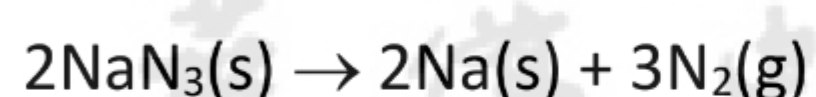
(3) Change in the number of particles (especially for gaseous systems)

- When a chemical reaction results in an **increase in the number of gas particles**, there is a large increase in entropy. This is because the particles in gas are the **most disordered** so the number of **ways that the particles and the energy can be distributed increase greatly**.

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

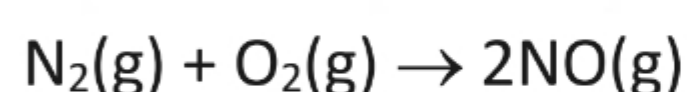


no. of **gas** particles increase by 0.5 mol, $\Delta S > 0$



no. of **gas** particles increase by 3 mol, $\Delta S > 0$

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



$\Delta S \approx 0$

(4) Mixing of particles

- 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 pressure of each gas is reduced by half but total pressure remains constant.

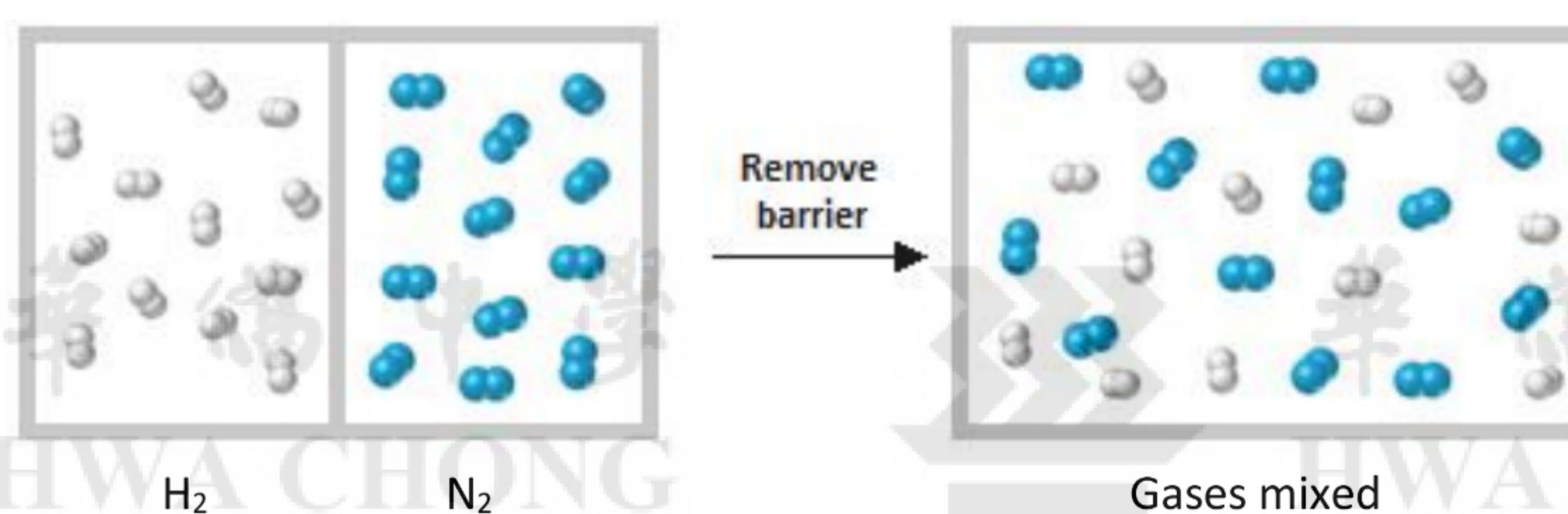


Figure 10. Mixing of 2 gases at constant pressure

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

Note:

When a gas expands, 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**.

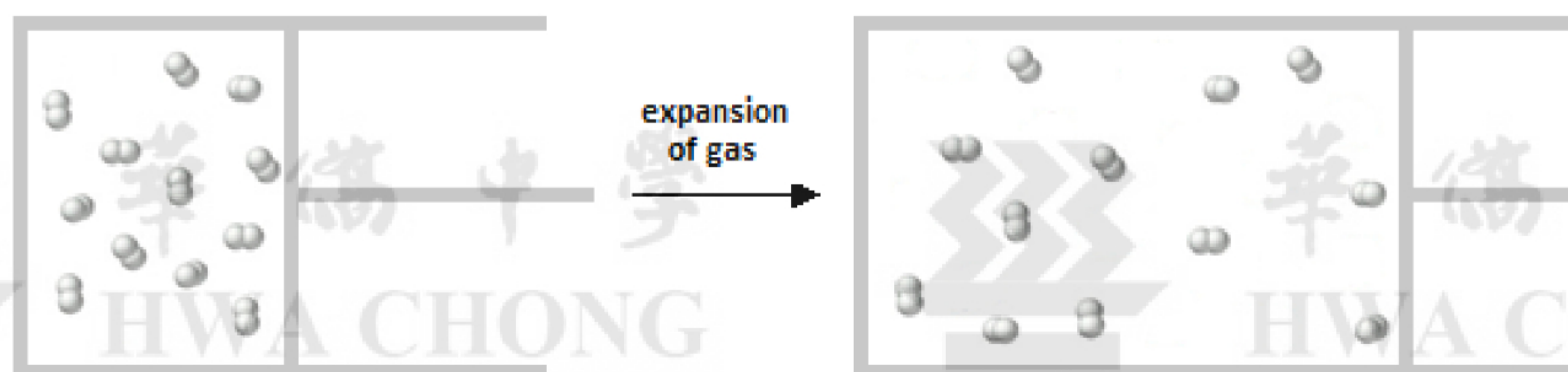


Figure 11. Expansion of gas

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

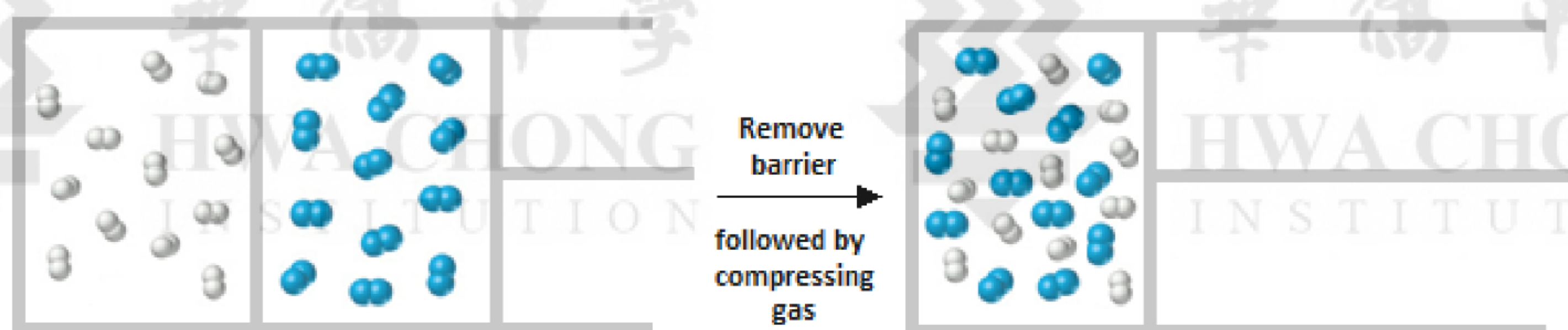


Figure 12. Mixing of 2 gases at constant volume

- 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 hence their energy.

(5) 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 restricted in motion as they arrange themselves around the ions.

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

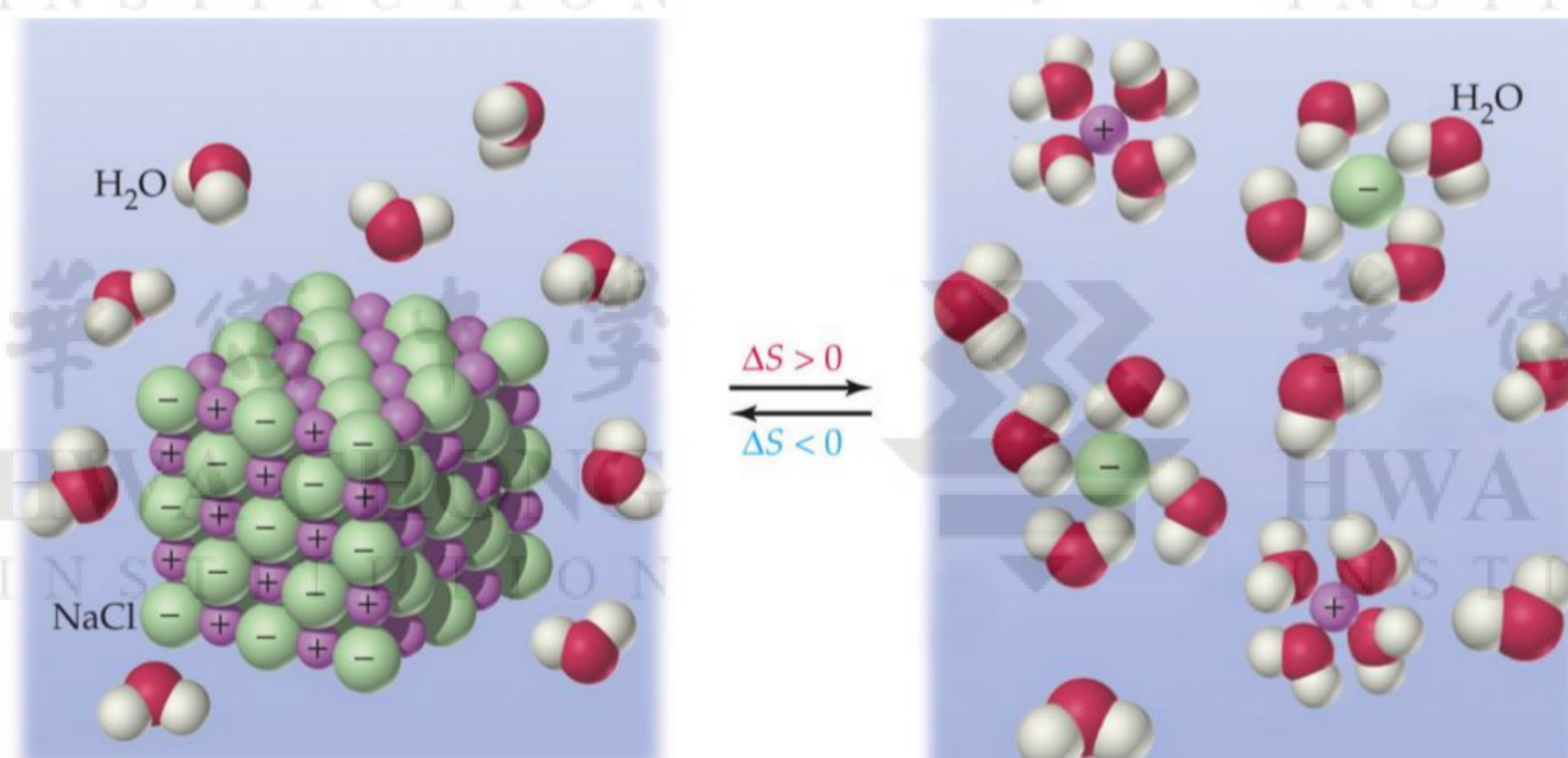
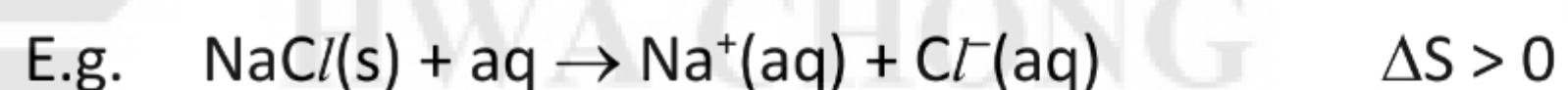


Figure 13. Entropy change during dissolution of an ionic solid

In Topic 2 Chemical Bonding, we saw that dissolution of a compound depends on the energy change. In addition to enthalpy change, the entropy change also plays a part when predicting the solubility of a compound.

Self-practice 9.1

Predict whether ΔS is positive or negative in each of the following processes.

Process	Sign of ΔS	Explanation
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$		
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$		
$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$		
1 mol of $\text{Cl}_2(\text{g})$ at 298K is heated to 373K		
$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$		
$\text{Ar at 2 atm} \rightarrow \text{Ar at 1 atm}$		

9.3 Gibbs Free Energy

To predict whether a process is spontaneous, we need to apply the Second Law of Thermodynamics which states that the entropy of the universe increases for a spontaneous change. We have to consider the entropy change that takes place both in the system and in the surrounding.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

In chemistry, to simplify discussion, the focus of analysis is on the **system**. Hence it is more convenient if ΔS_{system} and $\Delta S_{\text{surrounding}}$ are combined together in a single function known as the **change in Gibbs free energy**. The derivation is beyond the scope of the syllabus. The change in Gibbs free energy is named after Josiah Willard Gibbs and is given the symbol ΔG . ΔG can be expressed in terms of ΔH and ΔS of the system:

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

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

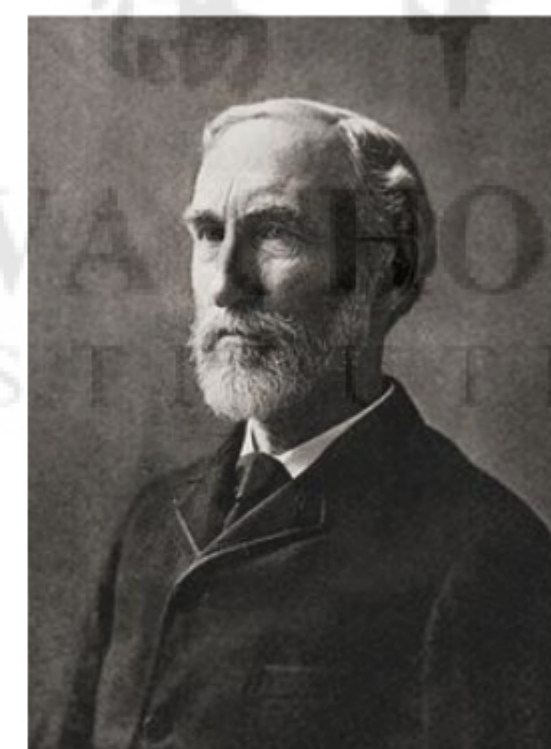


Figure 14. Josiah Willard Gibbs (1839 – 1903), the father of chemical thermodynamics

The **standard** Gibbs free energy change of reaction, $\Delta G^\ominus$, is the change in Gibbs free energy needed to convert reactants into products at 1 bar and at constant temperature (usually at 298 K).

When ΔG is negative (Gibbs free energy is lowered), $\Delta S_{\text{universe}}$ is positive and vice versa. Hence we can use the sign of ΔG to predict if a reaction is spontaneous.

$\Delta G < 0$	$\Delta G = 0$	$\Delta G > 0$
The reaction takes place spontaneously .	The system is at equilibrium . There is no net reaction in the forward or backward direction.	The reaction cannot take place spontaneously . It is spontaneous in the reverse direction.
The reaction is said to be <i>exergonic</i> .	E.g. $\Delta G = 0$ during melting and boiling at the melting point and boiling point respectively	The reaction is said to be <i>endergonic</i> .

Table 7. Sign of ΔG and spontaneity of reaction

9.3.1 Calculations using $\Delta G = \Delta H - T\Delta S$ **Lecture Exercise 9.1** Calculating ΔG from ΔH and ΔS

Chemical Reaction	$\Delta H^\ominus / \text{kJ mol}^{-1}$	$\Delta S^\ominus / \text{J mol}^{-1} \text{K}^{-1}$
$2\text{Fe(s)} + \frac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)}$	–825	–272

Calculate the standard free energy change for the rusting of iron.

Self-practice 9.2

Chemical Reaction	$\Delta H^\ominus / \text{kJ mol}^{-1}$	$\Delta S^\ominus / \text{J mol}^{-1} \text{K}^{-1}$
$2\text{NaHCO}_3\text{(s)} \rightarrow \text{Na}_2\text{CO}_3\text{(s)} + \text{H}_2\text{O(g)} + \text{CO}_2\text{(g)}$	+130	+335

Calculate the standard free energy change for the decomposition of **one mole** of sodium hydrogen carbonate.
[+15.1 kJ mol^{–1}]

Lecture Exercise 9.2 Calculating ΔS for phase change

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

Self-practice 9.3

Given the enthalpy change of vaporisation of water is 44.0 kJ mol^{-1} , calculate the entropy change which accompanies the boiling of water. **[+118 J mol⁻¹ K⁻¹]**

Comment on the difference in magnitude of $\Delta S_{\text{vaporisation}}$ with ΔS_{fusion} for water.

9.3.2 Calculations of ΔG_r from ΔG_f

Like enthalpy change (ΔH), Gibbs free energy change (ΔG) is a state function. This means that the value that it takes only depends on the state of the substance, and not how it was brought to that state. The 'state' is specified by variables such as temperature and pressure. Hence ΔG of a reaction can be calculated in a similar way as ΔH in Section 3. Likewise, ΔS is a state function and ΔS of a reaction can also be calculated a similar way.

Lecture exercise 9.3

Calculate $\Delta G^\ominus$ for the reaction $\text{C}_2\text{H}_6(\text{g}) + \frac{7}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$ using the data below.

$\Delta G_f^\ominus(\text{C}_2\text{H}_6(\text{g})) = -32.9 \text{ kJ mol}^{-1}$; $\Delta G_f^\ominus(\text{CO}_2(\text{g})) = -394.4 \text{ kJ mol}^{-1}$; $\Delta G_f^\ominus(\text{H}_2\text{O}(\text{l})) = -237.2 \text{ kJ mol}^{-1}$;

9.3.3 Temperature Dependence of ΔG

The term $[-T\Delta S]$ in the equation $\Delta G = \Delta H - T\Delta S$ indicates that ΔG is temperature-dependent. However, we can assume that **ΔH and ΔS remain roughly constant** regardless of temperature and use them to calculate ΔG 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	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J mol}^{-1} \text{K}^{-1}$	$T\Delta S/\text{kJ mol}^{-1}$	$\Delta G/\text{kJ mol}^{-1}$
$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$	298	-184.6	+20.0	+6.0	-190.6
$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$	500	-185.6	+17.5	+8.8	-194.4

If we were to assume that ΔH and ΔS do not change with temperature, we can use the values of ΔH and ΔS at 298 K to calculate a value for ΔG at 500 K as shown:

$$\begin{aligned}\Delta G_{500\text{K}} &\approx \Delta H_{298\text{K}} - 500 \times \Delta S_{298\text{K}} \\ &= -184.6 - 500 \times \frac{20.0}{1000} = -194.6 \text{ kJ mol}^{-1}\end{aligned}$$

This approximate value of ΔG ($-194.6 \text{ kJ mol}^{-1}$) is close to the actual value ($-194.4 \text{ kJ mol}^{-1}$) obtained by using values of ΔH and ΔS at 500 K.

The assumption that ΔH and ΔS 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 ΔH and ΔS change significantly. For example, consider the synthesis of hydrogen iodide at 298 K and 500 K.

	T/K	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J mol}^{-1}\text{K}^{-1}$	$T\Delta S/\text{kJ mol}^{-1}$	$\Delta G/\text{kJ mol}^{-1}$
$\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightarrow 2\text{HI}(\text{g})$	298	+53.0	+166	+49.5	+3.5
$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$	500	-11.0	+18	+9.0	-20.0

As a result of the phase change in I_2 (from solid to gaseous), ΔG 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 .

Lecture Exercise 9.4 Calculating the temperature 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 $\text{CO}(\text{g})$ and of $\text{CO}_2(\text{g})$ are as follows.

	$\text{CO}(\text{g})$	$\text{CO}_2(\text{g})$
$\Delta H_f^\ominus/\text{kJ mol}^{-1}$	-110.5	-393.5
$\Delta G_f^\ominus/\text{kJ mol}^{-1}$	-137.2	-394.4

- (a) Calculate the standard entropy change of formation, $\Delta S_f^\ominus$, in $\text{J mol}^{-1}\text{K}^{-1}$, of $\text{CO}(\text{g})$ and of $\text{CO}_2(\text{g})$.
[+89.6 $\text{J mol}^{-1}\text{K}^{-1}$; +3.02 $\text{J mol}^{-1}\text{K}^{-1}$]

- (b) Using the $\Delta H_f^\ominus$ values given and your answers in (a), show that the reaction:
 $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$ is not spontaneous at 298 K and calculate the minimum temperature at which reaction becomes spontaneous.

Self-practice 9.4

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

Chemical Reaction	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{J mol}^{-1}\text{K}^{-1}$
$2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g})$	+130	+335

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

9.3.4 Effect of Temperature on spontaneity of a reaction

For a reaction to be **spontaneous**, ΔG should be **negative**. The sign of ΔG depends on the signs and magnitudes of ΔH and ΔS , as well as temperature. We observe that most exothermic reactions are spontaneous as the enthalpy contribution to ΔG is much more than the entropy contribution. Hence a highly negative ΔH is likely to make ΔG negative. However, the temperature of a reaction influences the magnitude of the term $T\Delta S$ and hence the spontaneity of many reactions depends on the temperature. We can use the equation $\Delta G = \Delta H - T\Delta S$ to predict the sign of ΔG when temperature is varied (assuming ΔH and ΔS do not change with temperature).

There are four possibilities:

If ΔH is	and ΔS is	$\Delta G (= \Delta H - T\Delta S)$ is	Reaction is
negative	positive	always negative	<i>spontaneous at all temperatures</i>
positive	negative	always positive	<i>not spontaneous at all temperatures</i>
negative	negative	negative if $ \Delta H > T\Delta S $	<i>spontaneous at low temperatures (reaction is enthalpy driven)</i>
positive	positive	negative if $\Delta H < T\Delta S$	<i>spontaneous at high temperatures (reaction is entropy driven)</i>

Table 8. Effect of Temperature on spontaneity of a reaction

(1) ΔH negative and ΔS positive

These reactions are spontaneous 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	ΔH / kJ mol ⁻¹	ΔS / J mol ⁻¹ K ⁻¹
Organic combustion	$\text{C}_8\text{H}_{18}(\text{l}) + \frac{25}{2} \text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{g})$	-5109	+238
Decomposition of nitroglycerine	$2\text{C}_3\text{H}_5\text{N}_3\text{O}_9(\text{s}) \rightarrow 3\text{N}_2(\text{g}) + 6\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	-3617	+1840

Table 9. Examples of reactions that are spontaneous at all temperatures

The decomposition of propane-1,2,3-trinitrate or nitroglycerine ($\text{C}_3\text{H}_5\text{N}_3\text{O}_9$) results in an explosion as the reaction gives off a large quantity of gas at high temperature which expands rapidly.

(2) ΔH positive and ΔS negative

Reactions of this type are **not** spontaneous 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	ΔH / kJ mol ⁻¹	ΔS / J mol ⁻¹ K ⁻¹
Photosynthesis	$6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g})$	+2803	-225

Table 10. Examples of reactions that are not spontaneous for all temperatures

(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	ΔH / kJ mol ⁻¹	ΔS / J mol ⁻¹ K ⁻¹
Precipitation	$\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$	-65.5	-33.0
Condensation	$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-44.0	-118
Freezing	$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$	-6.0	-22.0

Table 11. Examples of reactions where ΔH and ΔS are both negative

Can you explain the signs of ΔH and ΔS for the above reactions?

(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	$\Delta H / \text{kJ mol}^{-1}$	$\Delta S / \text{J mol}^{-1} \text{K}^{-1}$
Melting	$\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$	+6.0	+22.0
Boiling	$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$	+44.0	+118
Decomposition of Group 2 carbonate	$\text{MgCO}_3\text{(s)} \rightarrow \text{MgO(s)} + \text{CO}_2\text{(g)}$	+100.3	+174
	$\text{BaCO}_3\text{(s)} \rightarrow \text{BaO(s)} + \text{CO}_2\text{(g)}$	+269.3	+172

Table 12. Examples of reactions where ΔH and ΔS are both positive

At 25°C , $\Delta G_{\text{vap}}^\ominus(\text{H}_2\text{O}) = 44.0 - 298(118 \times 10^{-3}) = +8.84 \text{ kJ mol}^{-1} > 0$. This means that boiling of water is not spontaneous at room temperature which is consistent with our observation. When temperature is raised to 100°C , $\Delta G = 0$ which means liquid water and steam are in equilibrium. At temperature above 100°C , $\Delta G < 0$ and hence the boiling of water is spontaneous.

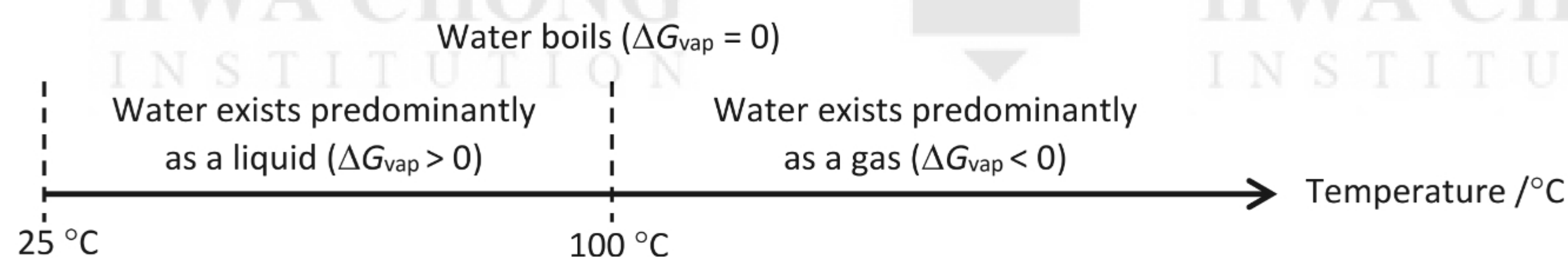


Figure 15. Effect of temperature on spontaneity of boiling of water

Likewise, we observe that the decomposition of metal carbonate is not 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 ΔH than BaCO_3 while ΔS is almost similar for both carbonates. Since decomposition becomes spontaneous when $\Delta G < 0$ (i.e. $T > \Delta H / \Delta S$), 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.*

Self-practice 9.5

For each of the following reactions, explain whether the reaction is spontaneous at all temperatures, at low temperature, at high temperature or not spontaneous at all temperatures. Predict how ΔG will change with increasing temperature.

Reaction	Explain whether the reaction is spontaneous at all temperatures, at low temperature, at high temperature or not spontaneous at all temperatures.	Predict how ΔG will change with increasing temperature.
<i>Example</i> $2\text{N}_2\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g})$ $\Delta H = +197.1 \text{ kJ mol}^{-1}$	<u>ΔS is positive</u> since there is an increase in number of moles of gas. Hence there are more ways to distribute the particles and their energies. $\Delta G = \Delta H - T\Delta S$ <u>ΔG is negative when $T\Delta S > \Delta H$, i.e. when temperature is high.</u> <u>$\therefore$ The reaction is spontaneous when temperature is high.</u>	When temperature increases, <u>$T\Delta S$ becomes more positive.</u> $\Delta G = \Delta H - T\Delta S$ Hence <u>ΔG becomes more negative.</u>
$2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ $\Delta H = -196 \text{ kJ mol}^{-1}$		
$3\text{O}_2(\text{g}) \rightarrow 2\text{O}_3(\text{g})$ $\Delta H = +286 \text{ kJ mol}^{-1}$		
$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ $\Delta H = -198 \text{ kJ mol}^{-1}$		

9.4 Limitation in the use of $\Delta G^\ominus$ to predict spontaneity of a reaction

9.4.1 Non-standard condition

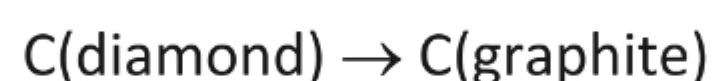
$\Delta G^\ominus$ can only be used to predict spontaneity of a reaction under standard conditions. Under non-standard conditions, ΔG must be calculated. Refer to example under Section 9.3.4 (4) on the boiling of water. At temperature above 100 °C, say at 150 °C, $\Delta G = 44.0 - 423 (118 \times 10^{-3}) = -5.91 \text{ kJ mol}^{-1} < 0$. Hence the boiling of water is spontaneous at 150 °C.

9.4.2 Kinetics consideration

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 (E_a) before reaction can occur.

Some reactions are **thermodynamically** (or energetically) **favourable** (ΔG is negative) but **kinetically not favourable** (occur very slowly). Such reactions are spontaneous but slow, for example rusting. Another example is the conversion of diamond into graphite.



With respect to graphite, diamond is thermodynamically less stable ($\Delta G < 0$). However, due to the high activation energy for the reaction, diamond does not turn into graphite overnight. We say that diamond is kinetically stable.

LOOKING AHEAD

We have seen in this topic that energy is the key consideration for any transformation to take place – energy (and/or matter) tends to be dispersed during a chemical or physical change. However, not all transformations take place at considerable rate (as mentioned in Section 9.4) and transformation from reactants to products may not occur to completion. In the next two topics, we will be looking at some characteristics of chemical and physical change, such as the rate of change (reaction kinetics) as well as the extent of change (chemical equilibrium). We will revisit the concept of Gibbs free energy change and learn how the value of $\Delta G^\ominus$ can allow us to predict the extent of change (chemical equilibrium).

Summary of enthalpy terms

Enthalpy change	Definition	Examples	Sign
Enthalpy change of formation			
Enthalpy change of combustion			
Enthalpy change of neutralisation			
Bond energy			
Enthalpy change of atomisation			
Lattice energy			
Ionisation energy			
Electron affinity			
Enthalpy change of hydration			
Enthalpy change of solution			

APPENDIX: The Global Energy Crisis

Article from Peter Cann & Peter Hughes, *Cambridge international AS & A level Chemistry*, Hodder Education, page 102-104

Energy sources**Fossil fuels**

Our main source of energy is the combustion of **fossil fuels**, namely coal, oil and natural gas. They give out large amounts of energy when burnt, but there are two main disadvantages to their use. The first is that supplies are finite and may run out in the foreseeable future. The second is that this combustion produces carbon dioxide, which contributes to the greenhouse effect, and also other pollutants.

Coal, oil and natural gas are respectively solid, liquid and gaseous fuels. The following considerations are made when choosing which to use.

- Ease of combustion - solid fuels are difficult to ignite and do not burn at a constant rate. For this reason, coal is often powdered before being injected into a furnace.
- Storage and ease of transport - for local use, natural gas does not need to be stored, as it is carried by pipeline from the source. Oil is easily stored and can also be distributed by pipeline. In both cases, expensive pipelines must be laid. Coal has the disadvantage that it needs to be carried by road or rail to where it will be used. To transport methane without a pipeline, it must be liquefied, which requires expensive refrigeration. This makes natural gas of limited use as a vehicle fuel, though propane and butane are more useful as they can be liquefied by pressure

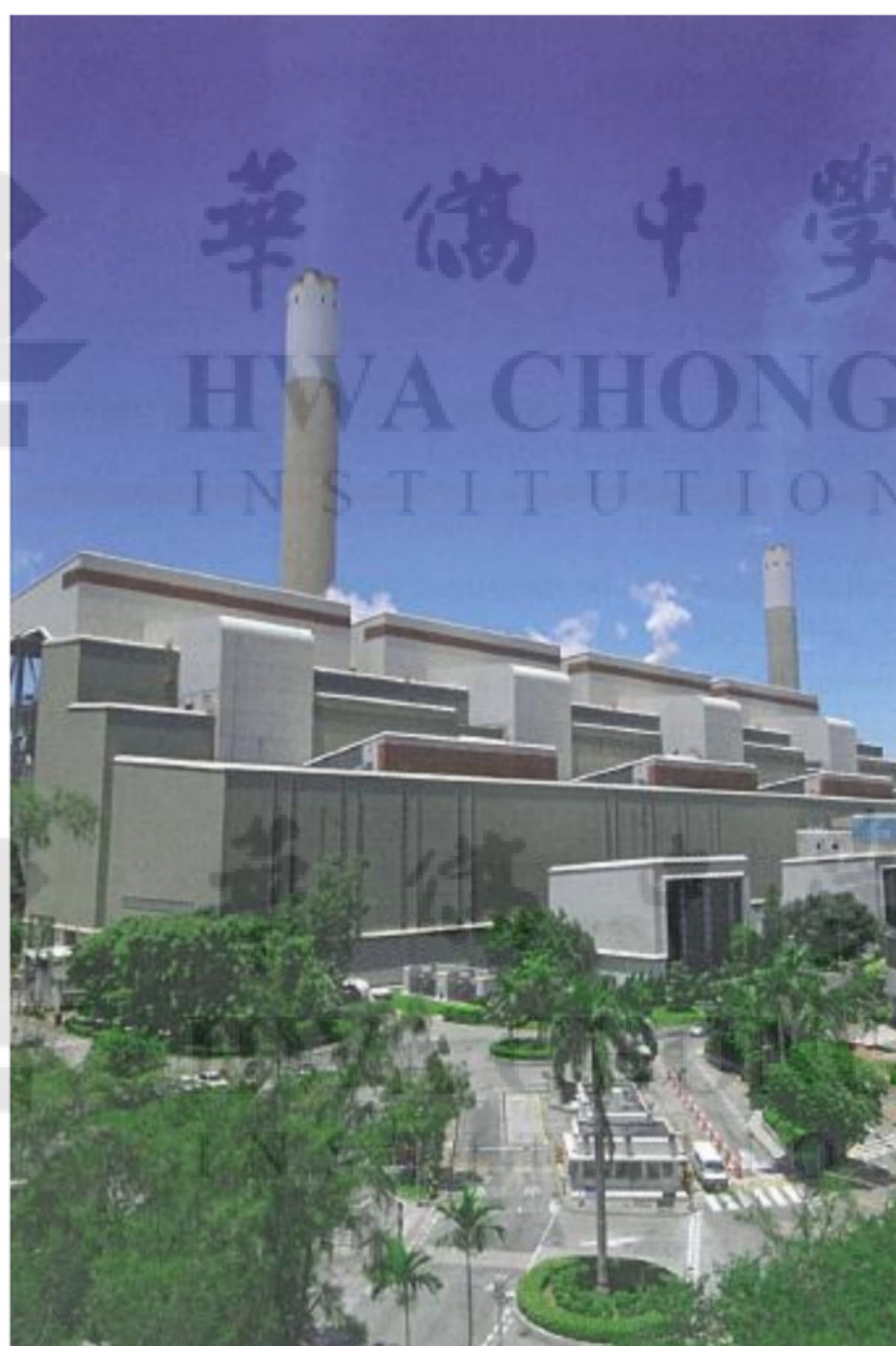


Figure 16. A coal-burning power station. Coal has the highest energy density of the fossil fuels, giving out 76 kJ of energy for each cm^3 of coal burnt.

alone (and are then called liquefied petroleum gas, LPG). LPG is an important fuel for cooking and heating in rural areas without piped natural gas. As increasing numbers of pipelines for natural gas are installed throughout the world, for example in India and China, the use of LPG in factories and homes is gradually being phased out. But it will still be the fuel of choice in most rural areas of the world. The use of coal for driving steam engines and trains was once important but is now of only historical interest throughout the world.

- Pollution - coal contains many impurities and, when burnt, gives off much sulfur dioxide. The same is true of oil, unless it is carefully refined before use. Crude oil is notorious for the environmental damage caused by spillage from tankers or from the oil extraction and flaring of the associated natural gas.

- Economic and political considerations - the relative prices of coal, oil and gas must take into account the costs of transport, storage and pollution-reducing measures, as well as political expediency, and are subject to wide local variations. Fuel taxes raise revenue for governments, and the resulting increased price of fossil fuels may encourage people to reduce their energy consumption.

Because there are serious problems associated with burning fossil fuels, much research has been carried out to find alternative energy sources. These are increasingly important, but it is unlikely that they will provide more than a quarter of our energy demands during the next few years. Many alternative energy sources are **renewable** - they can be replaced as fast as they are used.

Alternative energy sources

Alternative energy sources do not rely on the combustion of fuels. The following are some of those in current use.

- **Hydroelectric power** - there are many places in the world where rivers have been dammed and the resulting difference in water level used to provide energy to generate electricity, for example at Kariba on the Zambezi river between Zimbabwe and Zambia, at Itaipu on the Parana river between Brazil and Paraguay, and the Three Gorges dam on the Yangtze river in China. The last two examples alone generate over 6×10^{17} J of energy per year, the equivalent of burning 6×10^7 tonnes of coal in a coal-fired power station. This saves pumping millions of tonnes of carbon dioxide into the atmosphere. However, there can be resultant damage to the environment, which needs to be considered as it may be unacceptable.
- **Tidal and wave power** - these are little used, even though the large-scale tidal power generator at La Rance in northern France first produced electricity 50 years ago.



Figure 17. Wind farms provide pollution-free energy, but have visual effect on the landscape.

- **Wind power** - the use of wind turbines is increasing, although there is some objection to the construction of large windmills in isolated regions as they have a dramatic effect on the landscape. The wind speed is not always high enough to turn the blades in summer, but it usually is in winter, when the demand for electricity is highest. Another difficulty is that the places which are the most windy (and therefore the most suitable for the production of wind power) are often not the most populous, so the power has to be transported to where it is needed or power lines constructed to link to a national grid.

- **Geothermal power** - potentially this could be an easy way to provide energy for home heating, though it can only be carried out at sites with particular geological features. Water is pumped from deep under the ground and comes to the surface at a temperature near to boiling point. It is not usually possible to use this hot water to produce electricity, because superheated steam is needed in order to obtain a reasonable energy conversion. However, the Philippines, New Zealand and Costa Rica obtain a reasonable proportion of their energy from this source.
- **Solar panels** - the direct conversion of sunlight into electricity using solar cells used to be quite expensive, but the application of conducting polymers has reduced the cost of these, and in sunny places, for example in California, Spain and India, solar energy is now economically viable.
- **Nuclear power** - the use of nuclear reactors based on **fission reactions**, in which large nuclei split into two smaller nuclei and give out nuclear energy, has sharply declined as a result of accidents such as that at Chernobyl in 1986. There is much debate over the long-term implications of the disposal of nuclear waste, and most countries had cut back on their nuclear programmes until a few years ago, when concern for the rise in atmospheric carbon dioxide caused a rethink. There is the possibility that reactors using **fusion reactions**, in which lighter nuclei join to form a heavier one, may be developed in the next few decades. These provide the best hope for a long-term solution to the energy problem, because they are 'cleaner' and do not produce radioactive waste.

Renewable fuels

Most of the alternative energy sources listed above are renewable because they are powered by the Sun, and so are always available. Some fuels are made out of resources that can be replaced quickly. For example, tropical countries such as Brazil can grow fast-ripening crops such as corn or sugar cane which can be used to produce ethanol cheaply and this can be used mixed with petrol in motor vehicles.

Hydrogen is another renewable energy resource. It has the advantage of being pollution free, since its combustion produces water only, and can be used in fuel cells. Its great disadvantage is the difficulty of transporting it (being much lighter than natural gas, it is difficult to contain it), though there is hope that the use of metal hydrides (compounds of transition metals with hydrogen) may overcome this problem.

For special applications, for example in space rockets, special synthetic fuels are being developed.