Anderson Serangoon Junior College H2 Chemistry CHEMICAL ENERGETICS I (THERMOCHEMISTRY)

Contents/Outline

- 1 Introducing enthalpy change, exothermic and endothermic reactions
- 2 Defining common enthalpy changes: ΔH of reaction, formation, combustion, neutralisation, atomisation and bond energy
- 3 Determining enthalpy changes using experiments and $q = mc\Delta T$
- 4 Defining enthalpy changes involving ionic compounds: ΔH of ionisation, electron affinity, lattice energy, hydration and solution
- 5 Determining enthalpy changes by applying Hess' Law through energy cycle (including Born–Haber cycles), formulae and algebraic manipulation.

Learning Outcomes

Students should be able to:

- (a) explain that some chemical reactions are accompanied by energy changes, principally in the form of heat energy; the energy changes can be exothermic (ΔH negative) or endothermic (ΔH positive)
- (b) construct and interpret a reaction pathway diagram, in terms of the enthalpy change of the reaction and of the activation energy
- (c) explain and use the terms:
 - (i) *enthalpy change of reaction* and *standard conditions*, with particular reference to: formation; combustion; hydration; solution; neutralisation; atomisation
 - (ii) *bond energy* (ΔH positive, i.e. bond breaking)
 - (iii) *lattice energy* (ΔH negative, i.e. gaseous ions to solid lattice)
- (d) calculate enthalpy changes from appropriate experimental results, including the use of the relationship heat change = $mc\Delta T$
- (e) explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy
- (f) apply Hess' Law to construct simple energy cycles, e.g. Born-Haber cycle, and carry out calculations involving such cycles and relevant energy terms (including ionisation energy and electron affinity), with particular reference to:
 - (i) determining enthalpy changes that cannot be found by direct experiment, e.g. enthalpy change of formation from enthalpy changes of combustion
 - (ii) the formation of a simple ionic solid and of its aqueous solution
 - (iii) average bond energies

References

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- 2. Understanding Advanced Physical Inorganic Chemisry, Jeanne Tan and Chan Kim Seng, WS education
- 3. Chemistry, The Molecular Nature of Matter and Change (Fourth Edition), Silberberg, McGraw Hill
- 4. Chemistry & Chemical Reactivity (Sixth Edition), Kotz, Treichel and Weaver, Thomson
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1 INTRODUCTION

- -
- What is enthalpy change?

What is an exothermic reaction and an endothermic reaction?

Thermodynamics is the study of the interaction between matter and energy. It considers both the energy change and flow of energy from one substance to another. This is used to predict the behaviours of chemical systems – to determine whether or not a change is possible.

Chemical energy of a matter is made up of kinetic and potential energy.



How do particles in a matter possess kinetic energy (K.E.)?

K.E. is the energy of motion arising from rotations, vibrations and translational movements of particles. The temperature of a system is a measure of the average kinetic energy of that system.



How do particles in a matter possess potential energy (P.E.)?

P.E. is the energy that particles store within the electrostatic attractions or repulsions that they experience with one another.

According to the First Law of Thermodynamics, energy can neither be created nor destroyed; it can only be transferred. The ways to change K.E. and P.E. from one form to another are through heat or work.

Most chemical reactions or phase changes are accompanied by the absorption or release of heat. **Thermochemistry** is thus the study of heat energy changes that occur during these changes.

1.1 System and Surrounding

To study heat energy changes, we focus on a particular part of the universe, which we call the 'system'. Everything else that can exchange energy with the system is called the 'surrounding'.

For a chemical reaction, at the start the system is the reactants, and at the end the system is the products.

e.g. For a neutralisation reaction between aqueous NaOH and aqueous HC*l*:

system $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$ surroundingeverything else, including the solution, beaker, air, etc.



1.2 Heat transfer

Heat is the energy that flows into or out of a system due to a difference in temperature between the system and its surroundings. When a system and its surroundings are in thermal contact, energy flows from the region of higher temperature to the one of lower temperature, until they reach the same temperature (thermal equilibrium).

1.3 Enthalpy and Enthalpy Change

Enthalpy, H

- The energy content of a substance under constant pressure.
 - ✓ The energy content includes the kinetic energy of the particles in the substance and the potential energy stored in the arrangements of the particles in the substance.
 - Enthalpy of a substance reflects its stability. A substance with higher enthalpy has higher energy and is thus less stable.

For your info: Why is a substance with higher energy content less stable?

Energy content is in the form of K.E. and P.E. If the particles have high K.E., they are moving faster and thus there are minimal attractive forces to keep them bonded. Similarly, if the particles have high P.E., they are further apart from one another with weak attractive forces. As a result, the substance is unstable.

✓ Absolute enthalpy cannot be measured, but we can measure the change in enthalpy accompanying a process by measuring the flow of heat into or out of the system.

Enthalpy Change, ΔH :

 Enthalpy change of reaction (ΔH_{rxn}) is the energy change in a chemical reaction when the molar quantities of reactants <u>specified in the chemical equation</u> react to form products.

 $\Delta \boldsymbol{H}_{rxn} = \boldsymbol{\Sigma} \boldsymbol{H}_{pdts} - \boldsymbol{\Sigma} \boldsymbol{H}_{rxts}$

where ΔH_{rxn} = enthalpy change of reaction ΣH_{pdts} = sum of enthalpies of products ΣH_{rxts} = sum of enthalpies of reactants

Units of ΔH_{rxn} : kJ mol⁻¹

All ΔH have accompanying signs, + or –, that indicate the direction of heat flow into or out of the system respectively.

1.4 Endothermic and Exothermic Reactions

In a chemical reaction, bonds in reactants are broken and bonds in products are formed.

The breaking of bonds requires energy and is an endothermic process. The formation of bonds evolves energy and is an exothermic process.

The difference between quantities of heat needed to break the bonds of the reactants and that evolved during the formation of new bonds in the products give rise to the enthalpy change of a reaction.

(a) Exothermic Reactions ($\Delta H < 0$)



- Enthalpy of reactants is higher than enthalpy of products $\Rightarrow \Delta H$ is negative.
- Products are energetically more stable than the reactants.
- The reaction released heat to the surroundings when the products are formed.
 ⇒ temperature of the surroundings increases.

(b) Endothermic Reactions ($\Delta H > 0$)



- Enthalpy of products is higher than enthalpy of reactants $\Rightarrow \Delta H$ is positive.
- Reactants are energetically more stable than the products.
- The reaction absorbed heat from the surroundings when the products are formed.
 ⇒ temperature of the surroundings decreases.

1.5 Standard Conditions and Standard States

(a) Standard Conditions

To compare energy changes, conditions under which the reaction was performed must be specified. Hence standard conditions for enthalpy changes refer to the following

(a) Pressure: **1 bar** (10⁵ Pa)

(b) Temperature: 298 K

(c) Concentration: 1 mol dm⁻³ (if solutions are used)

An enthalpy change stated under **standard conditions** is hence called **standard enthalpy change**, denoted by the symbol, ΔH° . The ' $^{\circ}$ ' indicates that ΔH was measured and calculated under standard conditions.

Note: Reactions need not take place under standard conditions. In this case, when quoting the enthalpy changes, temperature and pressure will be stated.

(b) <u>Standard States</u>

Under standard conditions, substances are in their standard states. The standard state of a substance is its most stable form under standard conditions.

Elements in their standard states under standard conditions are assigned **zero enthalpy**. E.g. $H_2(g)$, $O_2(g)$, C(s), Na(s).

Note: If an element exists in more than one form under standard conditions, the most stable form of the element is usually used. For example, graphite (not diamond) is the standard state for carbon.

2 TYPES OF ENTHALPY CHANGES



What are some heat changes in a chemical or physical process?

2.1 Standard Enthalpy Change of Reaction, ΔH_r^{\ominus}

The amount of heat **absorbed or evolved** when **molar quantities of reactants as shown in the chemical equation** react together under standard conditions of **298 K and 1 bar**.

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

The equation states that 286 kJ of energy is evolved to the surrounding for every 1 mol of $H_2(g)$ and $\frac{1}{2}$ mol $O_2(g)$ consumed and 1 mol $H_2O(l)$ formed.

Factors affecting ΔH_{r}^{Θ}

(i) Amount of substance

The magnitude ΔH_r^{Θ} is directly proportional to the the number of moles of reactants and products represented by the coefficients in the **balanced equation**.

Multiplying a chemical equation by a factor \Rightarrow Multiply ΔH by the same factor

E.g.	$2H_2(g) + 1O_2(g) \longrightarrow 2H_2O(l)$	$\Delta H_{\rm r}^{\Theta} = 2(-286) = -572 \rm kJ mol^{-1}$
	$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l)$	$\Delta H_{\rm r}^{\Theta} = {\bf 4}(-286) = -1144 \text{ kJ mol}^{-1}$

(ii) Physical states of reactants and products

 ΔH_r^{Θ} depends on the physical states (s, *l*, g) of the reactants and products.

E.g.
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$$

 $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$
 $\Delta H_1^{\oplus} = -242 \text{ kJ mol}^{-1}$
 $\Delta H_2^{\oplus} = -286 \text{ kJ mol}^{-1}$
 $\Delta H_2^{\oplus} = -286 \text{ kJ mol}^{-1}$
 $H_2(g) + \frac{1}{2}O_2(g) \xrightarrow{\Delta H_1^{\oplus}} H_2O(g) \xrightarrow{-44.1} H_2O(l)$

The additional energy evolved in reaction (2) is due to the energy released when 1 mol of water vapour condenses to 1 mol of liquid water.

(iii) Direction of chemical equation

 ΔH_r^{Θ} is equal in magnitude, but opposite in sign, to ΔH_r^{Θ} for the reverse reaction.

Reversing a chemical equation \Rightarrow **reverse** the **sign** of ΔH

E.g.	$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$	$\Delta H_{\rm r}^{\Theta} = -572 \text{ kJ mol}^{-1}$
	$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$	$\Delta H_{\rm r}^{\ominus} = + 572 \rm kJ mol^{-1}$

IMPORTANT!!!

All thermochemical equations must be balanced chemical equations that include:

- the ΔH value
- the physical state of the reactants and products
- temperature and pressure, if necessary

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2.2 Standard Enthalpy Change of Formation, ΔH_{f}^{\ominus}

The amount of heat **absorbed or evolved** when **one mole** of a substance is formed from its **constituent elements**, all in their standard states at **298 K and 1 bar**.

E.g. Standard enthalpy change of formation of ethanol: $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l) \qquad \Delta H_f^{\ominus} = -298 \text{ kJ mol}^{-1}$

Standard enthalpy change of formation of water: $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H_f^{\ominus} = -286 \text{ kJ mol}^{-1}$

- Enthalpy changes of formation are often theoretical. Such reactions may not take place in practice.
 E.g. C₂H₅OH cannot be formed by just mixing C, H₂ and O₂.
- Such enthalpy changes of formation are usually calculated indirectly from other enthalpy changes of reaction.
- The enthalpy change of formation of elements in their standard states, at 298 K and 1 bar, is by definition <u>zero</u>.

E.g. ΔH_f^{\ominus} of $H_2(g) = 0$, ΔH_f^{\ominus} of He(g) = 0, ΔH_f^{\ominus} of Na(s) and ΔH_f^{\ominus} of Br₂(g) = 0

- $\Delta H_{\rm f}^{\ominus}$ is a measure of the energetic stability of the substance relative to their constituent elements.
 - ✓ Positive ∆H_t[⊖] implies that the substance is ______ stable relative to its constituent elements. Hence, more likely for decomposition of the substance to its constituent elements.
 - ✓ Negative ΔH_{f}^{\ominus} implies that the substance is ______ stable relative to its constituent elements. Hence, less likely for decomposition of the substance to its constituent elements.
- For any chemical reaction, e.g. $A + B \rightarrow C + D$ ΔH_r

the ΔH_r can be determined if the ΔH_f of A, B, C and D are known, using the following general equation:

 $\Delta H_{\rm r} = \underline{\Sigma \Delta H_{\rm f}} (\text{products}) - \underline{\Sigma \Delta H_{\rm f}} (\text{reactants})$

Refer to page 33 for the derivation and application of the equation.

Example 2.2.1

Compound	HF	HC <i>l</i>	HBr	HI
$\Delta H_{\rm f}$ / kJ mol ⁻¹	- 271.1	- 92.3	- 36.2	+ 26.5

Comment on the stability of the hydrogen halides from HF to HI.

Solution:



 $\Delta H_{\rm f}$ of the hydrogen halides become <u>less exothermic</u>

This implies that the hydrogen halides become less stable down the group (Group 17).

2.3 Standard Enthalpy Change of Combustion, ΔH_c^{\ominus}

The amount of heat **evolved** when **one mole** of a substance in its standard state is **completely burned** in excess oxygen under standard conditions of **298 K and 1 bar**.

E.g. Standard enthalpy change of combustion of methane: $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c^{\ominus} = -802 \text{ kJ mol}^{-1}$

Standard enthalpy change of combustion of methanol:

 $CH_{3}OH(l) + \frac{3}{2}O_{2}(g) \longrightarrow CO_{2}(g) + 2H_{2}O(l) \qquad \Delta H_{c}^{\ominus} = -726 \text{ kJ mol}^{-1}$

- ΔH_c is <u>always negative (exothermic)</u> as heat is always evolved in the combustion.
- ΔH_c[⊖] can be used to identify substances with large ΔH_c[⊖] as sources of fuel, and to determine calorific value of foodstuff e.g. fats and calculation of enthalpy change of reaction and formation.
 - Incidentally, C (s) + O₂ (g) \longrightarrow CO₂(g) ΔH_{f}^{e} of CO₂ = ΔH_{c}^{e} of C

 $\begin{array}{l} \mathsf{H}_2(\mathsf{g}) + \frac{1}{2} \mathsf{O}_2(\mathsf{g}) \longrightarrow \mathsf{H}_2 \mathsf{O}(l) \\ \Delta H_{\mathsf{f}}^{\mathsf{e}} \text{ of } \mathsf{H}_2 \mathsf{O} = \Delta H_{\mathsf{c}}^{\mathsf{e}} \text{ of } \mathsf{H}_2 \end{array}$

For any chemical reaction,
 e.g. A + B → C +D ΔH_r
 the ΔH_r can be determined if the ΔH_c of A, B, C and D are known, using the following general equation

 $\Delta H_{\rm r} = \underline{\Sigma \Delta H_{\rm c} \, (\text{reactants}) - \Sigma \Delta H_{\rm c} \, (\text{products})}$

Refer to page 31 for the derivation and application of the equation.

2.4 Standard Enthalpy Change of Neutralisation, $\Delta H_{neut}^{\ominus}$

The amount of heat **evolved** when **one mole of water** is formed from the neutralisation between an acid and a base, under standard conditions of **298 K and 1 bar**.

E.g.	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$	$\Delta H_{\text{neut}}^{\ominus}$ = -57.3 kJ mol ⁻¹
	$HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$	$\Delta H_{\rm neut}^{\ominus}$ = -57.3 kJ mol ⁻¹
	$\frac{1}{2}H_2SO_4(aq) + NaOH(aq) \longrightarrow \frac{1}{2}Na_2SO_4(aq) + H_2O(l)$	$\Delta H_{\rm neut}^{\ominus}$ = -57.3 kJ mol ⁻¹
	$H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$	$\Delta H_{\rm r}^{\ominus} = 2(-57.3)$ = -114.6 kJ mol ⁻¹

 Neutralisation is always exothermic since it involves the attraction of H⁺ and OH[−] ions to form H₂O.

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

For neutralisation reactions between strong acids and strong bases, ∆H_{neut}[○] is almost the same at -57.3 kJ mol⁻¹.

Reason: Strong acids and bases are _____ ionised in aqueous solution.

• For neutralisation involving weak acids/bases, $\Delta H_{neut}^{\ominus}$ will be slightly less exothermic.

Reason: Weak acid/base only dissociates partially in solution. Some of the energy evolved from the neutralisation process is used to dissociate the weak acid/ base completely. Hence the net heat change is smaller and the ΔH_{neut}° less exothermic.

E.g. For the neutralisation reaction between NaOH(aq) and CH₃COOH(aq)

NaOH(aq) → Na⁺(aq) + OH⁻(aq)	$\Delta H^{\rm e} = 0$
$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$	$\Delta H^{e} = + 1.8 \text{ kJ mol}^{-1}$
$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	$\Delta H^{\rm e} = -57.3 \text{ kJ mol}^{-1}$

NaOH(aq) + CH₃COOH(aq) \rightarrow CH₃COO⁻Na⁺(aq) + H₂O(*l*) $\Delta H_{\text{neut}}^{\Theta} = -57.3 + 1.8$

= - 55.5 kJ mol⁻¹

2.5 Standard Enthalpy Change of Atomisation, ΔH_{at}^{\ominus}

(a) ΔH_{at}^{\ominus} of an Element

The amount of heat **absorbed** when **one mole** of free **gaseous atoms** is formed from its element under standard conditions of **298 K and 1 bar**.

E.g. Standard enthalpy change of atomisation of sodium: Na(s) \longrightarrow Na(g) $\Delta H_{at}^{\ominus}(Na) = +108.4 \text{ kJ mol}^{-1}$

> Standard enthalpy change of atomisation of chlorine: $\frac{1}{2}Cl_2(g) \longrightarrow Cl(g) \qquad \Delta H_{at}^{\ominus}(Cl_2) = +122 \text{ kJ mol}^{-1}$

- Enthalpy changes of atomisation are **always positive (endothermic)**, because energy must be absorbed to pull the atoms far apart and break all the bonds between them.
- Enthalpy changes of atomisation of the noble gases = 0 kJ mol⁻¹

Reason: Elements are already in the form of free gaseous atoms under standard conditions.

• Enthalpy change of atomisation is **NOT** always the same as the enthalpy change of vaporisation.

Atomisation (I atoms formed)	:	½ I₂(s) → I(g)	$\Delta H^{\ominus} = +107 \text{ kJ mol}^{-1}$
Vaporisation (I2 molecules remained)	:	$I_2(l) \longrightarrow I_2(g)$	$\Delta H^{\ominus} = +42 \text{ kJ mol}^{-1}$

- ✓ In the atomisation of I₂, I₂ molecules are no longer present as I–I covalent bonds are broken to form I atoms.
- ✓ However in vaporisation of I₂, I₂ molecules are still present. Only the instantaneous dipole-induced dipole attraction is weakened which results in the I₂ molecules being further apart from each other.

(b) ΔH_{at}^{\ominus} of a Compound

The amount of heat **absorbed** when **one mole of compound** in its standard state is broken into **gaseous atoms** of its **constituent elements** under standard conditions of **298 K and 1 bar.**

E.g. Standard enthalpy change of atomisation of ethanoic acid: $CH_3CO_2H(l) \longrightarrow 2C(g) + 4H(g) + 2O(g) \qquad \Delta H_{at}^{\ominus}(CH_3CO_2H)$

Standard enthalpy change of atomisation of ammonium nitrate: NH₄NO₃(s) \longrightarrow 2N(g) + 4H(g) + 3O(g) ΔH_{at}^{\ominus} (NH₄NO₃)

2.6 Bond Energy

Bond energy of a covalent bond is the **average** amount of heat **absorbed** to break **one mole** of the **covalent bond** in **gaseous state.**

E.g. Bond energy of Cl-Cl bond: $Cl_2(g) \longrightarrow 2Cl(g)$ Bend energy of H-F bond: $HF(g) \longrightarrow H(g) + F(g)$ Be $(H-F) = +570 \text{ kJ mol}^{-1}$

- In the Data Booklet, most bond energy values are provided but not accompanied by signs.
- Bond energies are **always positive (endothermic)** because energy is required to break covalent bonds. Conversely, the same amount of energy is given off (exothermic) when one mole of the covalent bonds is formed in the reverse process.
- Bond energy only applies for **covalent** molecules and is an indication of bond strength. The stronger the covalent bond, the larger the bond energy.

Refer to Chemical Bonding lecture notes for the factors affecting the strength of covalent bond.

• For polyatomic molecules with identical bonds, the bond dissociation energy of individual bonds varies.

bond dissociation energy

$CH_4(g) \longrightarrow CH_3(g) + H(g)$	$CH_3 - H = +438.6 \text{ kJ mol}^{-1}$
$CH_3(g) \longrightarrow CH_2(g) + H(g)$	$CH_2 - H = +458.7 \text{ kJ mol}^{-1}$
$CH_2(g) \longrightarrow CH(g) + H(g)$	$CH - H = +425.7 \text{ kJ mol}^{-1}$
$CH(g) \longrightarrow C(g) + H(g)$	$C - H = +340.6 \text{ kJ mol}^{-1}$

- All the bond dissociation energies have different values since the electronic environment of the bond within the different species (CH₄, CH₃, CH₂, CH) is different.
- The average bond energy BE(C–H) in CH₄ is calculated from the energy required to break all the bonds homolytically.

 $\mathsf{BE}(\mathsf{C}-\mathsf{H}) = \frac{+438.6 + 458.7 + 425.7 + 340.6}{4} = +416 \text{ kJ mol}^{-1}$

- This value (+416) is different from the value in the Data Booklet (+410) since the value in the Data Booklet is determined by considering the C-H bond dissociation energies in various molecules.
- Important!!! The bond energy of a particular type of covalent bond as given in the *Data Booklet* is the average bond dissociation energies of that particular bond for all types of molecules.

- During a reaction:
 - ✓ energy is absorbed to break bonds in the reactants (endothermic), and
 - ✓ energy is given out to form bonds in the products (exothermic).
- Thus, the enthalpy change of a reaction involving only **GASEOUS reactants and products** can be calculated from Bond Energy values given in the *Data Booklet* using the formula below:

$$\Delta H_{\rm r}^{\ominus} = \Sigma BE(\text{bonds broken}) - \Sigma BE(\text{bonds formed})$$

Example 2.6.1

By using appropriate bond energy data from the *Data Booklet*, calculate a value for the enthalpy change of the following reaction.

$$H-C=C-H + 2H_2 \longrightarrow CH_3-CH_3$$

Solution	•••				
Step 1: Draw the displayed formula of the reactants and products	Reactants: H–C≡C–H and 2 of H–H		Product:	H H - HCC- H H	—H
Step 2: Identify the type of bonds broken and formed		Bonds broken BE(C=C) = 840	Bonds BE(C–C	formed C) = 350]
Step 3: Find the bond energy associated with these bonds		BE(C–H) = 410 BE(H–H) = 436	BE(C–H) = 410		
Step 4: Find the enthalpy change of reaction	$\Delta H_r^{\ominus} = \Sigma \text{ BE(bonds broken)} - \Sigma \text{ BE(bonds formed)}$ = [840 + 2(410) + 2(436)] - [350 + 6(410)] = - 278 kJ mol ⁻¹				

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• Relationship between BE and enthalpy change of atomisation of diatomic gases:

$$Cl-Cl(g) \longrightarrow 2Cl(g) \qquad BE(Cl-Cl) = +244 \text{ kJ mol}^{-1}$$

$$\frac{1}{2} Cl_2(g) \longrightarrow Cl(g) \qquad \Delta H_{at}^{\ominus}(Cl_2) = +122 \text{ kJ mol}^{-1}$$
Hence, BE(Cl_2) = $\underline{2} \times \Delta H_{at}^{\ominus}(Cl_2)$

Therefore, for **diatomic gases**, X_2 , **BE(X₂) = 2** $\Delta H_{at}^{\ominus}(X_2)$



3 EXPERIMENTAL METHOD TO DETERMINE ENTHALPY CHANGE

How can we measure the heat change in a chemical or physical process?

3.1 Calorimeter

• The enthalpy change of a reaction can be determined by measuring the heat given out or taken in during the reaction. A calorimeter is an apparatus designed to measure such heat change.

A simple calorimeter can be constructed using poor thermal conductor such as a polystyrene cup.



- For an exothermic reaction, assuming that there is no loss of heat to the air (surrounding), the heat evolved from the system (the chemical reaction) increases the temperature of the solution (surrounding) in the cup. Hence, the heat change of a reaction can be determined by measuring the rise in the temperature of solution.
- Similarly, for an endothermic reaction, assuming that there is no gain of heat from the air (surrounding), the heat absorbed by the system (the chemical reaction) decreases the temperature of the solution (surrounding) in the cup. Hence, the heat change of a reaction can be determined by measuring the fall in the temperature of solution.

Using the equation below:

Heat evolved (or absorbed) from (or by) the system = heat gained (or loss) by the solution of the reaction mixture.

$$\mathbf{Q} = \mathbf{m}\mathbf{C}\Delta\mathbf{T} = \mathbf{C}\Delta\mathbf{T}$$

The enthalpy change of the reaction, ΔH_r , can be determined:

For an exothermic reaction:

For an endothermic reaction:

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

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

where:		units
Q	 P heat energy released from the system (the chemical reaction) to the solution (surrounding) (or heat energy absorbed by the system from the solution) that causes a change in temperature of the solution 	
m	mass of solution (= volume of solution if solution is dilute, since density of water = 1 g cm^{-3})	
с	<pre>specific heat capacity of solution (quantity of heat required to raise the temperature of 1 g of the solution by 1 K)</pre>	
с	heat capacity of solution (quantity of heat required to raise the temperature of a given mass of solution by 1 K)	J K⁻¹
ΔT	Change in temperature	
n	no of moles of limiting reagent / product based on definition of the enthalpy change	mol

Assumptions made in calculating the enthalpy change using the above equations:

- No other forms of heat loss to the air (or heat gain from the air) due to insulation (i.e. **100% efficient**)
- The cup does not absorb or lose heat (i.e. heat capacity of the cup is omitted).
- The density of the solution of the reaction mixture unless otherwise stated, approximates to that of water i.e. 1 g cm⁻³.
- The specific heat capacity of the solution of the reaction mixture unless otherwise stated, approximates to that of water i.e. $4.18 \text{ J g}^{-1} \text{ K}^{-1}$.

When 50 cm³ of 1 mol dm⁻³ of HC*l* were added to 100 cm³ of 1 mol dm⁻³ of NaOH in a plastic beaker, there was a temperature rise of 4.5 °C. Assuming it takes 4.18 J to raise the temperature of 1 g of solution by 1.0 °C, calculate the enthalpy change of neutralisation.

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

Solution

Steps	Working
(1) Determine Q	Q = mc∆T
	$= (50+100)(1.00) \times 4.18 \times 4.5$
	= 2821.5 J
(2) Determine no of moles reagents added	$n(HCl)$ added = $\frac{50}{1000} \times 1 = 0.05$ mol
	n(NaOH) added = $\frac{100}{1000} \times 1 = 0.1$ mol
	Since 0.05 mol HC/ reacts with 0.05 mol NaOH
	NaOH is in excess and HCl is the limiting
	reagent.
	5
(3) Determine the enthalpy change of	$n(H_2O)$ formed = $n(HCl)$ reacted = 0.05 mol
neutralisation	
 Recall definition (n = n(water)) 	Q
Determine if the reaction is avothermic or endothermic and	$\Delta \Pi_{neu} = -\frac{1}{n(H_2O)}$
indicate it with the correct sign	
	$\Delta H_{neu} = - \frac{1}{0.05}$
	= – 56400 J mol ⁻¹
	= − 56.4 kJ mol ⁻¹

How do we know that the reaction is exothermic (i.e. $\Delta H_{neut} < 0$)?

The increase in temperature of the solution (surrounding) indicates that the system (the neutralisation reaction) had released heat to the solution (surrounding).

3.2 Temperature Correction

- A graphical method involving temperature correction can be used to account for heat loss to the surrounding or heat gain from the surrounding or slow response of the thermometer or reaction.
- An experiment is performed by measuring the temperature of the solution of the reaction mixture at regular time interval. A graph of temperature against time is plotted and extrapolation is performed to determine the maximum (or minimum) temperature at the time of mixing.
- The process of extrapolation looks like the following for an exothermic reaction and an endothermic reaction respectively:



Example 3.2.1

In an experiment to determine the enthalpy change of reaction between magnesium and hydrochloric acid, the following procedure was followed.

- The temperature of 40 cm³ of 1 mol dm⁻³ hydrochloric acid was recorded for 2.5 minutes.
- 0.25 g of magnesium powder was added to the acid at 3 minutes.
- The temperature of the mixture was recorded at regular intervals from 3.5 minutes.



The following results were obtained.

- (i) From the graph obtained, determine the maximum temperature reached.
- (ii) Write an equation for the reaction between magnesium and hydrochloric acid.
- (iii) Calculate the enthalpy change of the reaction. [You may assume the specific heat capacity of the mixture to be 4.2 J $g^{-1} K^{-1}$.]

Solution

- (i)
- (ii)
- (iii)

)	Steps	Working
	(1) Determine Q	Q = mc∆T
		=
	(2) Determine no of moles of reagents	$n(HCl) = (40/1000) \times 1 = 0.04 \text{ mol}$
	added	$n(Mg) = \frac{0.25}{24.3} = 0.01029 \text{ mol}$
		Since 0.01029 mol Mg is required to react with 0.02058 mol HC <i>l</i> , HC <i>l</i> is in excess and Mg is the limiting reagent.
	(3) Determine the enthalpy change of	n =
	reaction	$\Delta H_r = -\frac{Q}{2}$
		n
		=

3.3 Experimental method to determine enthalpy change of combustion

The heat evolved from the combustion of a fuel can be used to heat up a known volume of water. Enthalpy change of combustion of the fuel can be determined by measuring the temperature rise of the water. Fuel used could be organic compound such as ethanol, propanol, octane, etc.

fuel(l) + O₂(g)
$$\longrightarrow$$
 CO₂(g) + H₂O(l) ΔH_c

The figure below shows a simple apparatus to measure the enthalpy change of combustion $(\Delta H_{\rm c})$ of a liquid fuel.



Since the setup is not insulated, not all the heat released from the combustion process is absorbed by the water in the can.

Example 3.3.1

An experiment was conducted to determine the enthalpy change of combustion of ethanol. When 1.00 g of ethanol was burned under a container of water, it was found that 100 g of water was heated from 15 °C to 85 °C. Assuming the process is 80% efficient; calculate the enthalpy change of combustion of ethanol.

Solution

Steps	Working
(1) Determine Q, the heat absorbed by water	Q =
(2) Determine the heat released by combustion	Heat released by combustion =
(3) Determine no of mole of fuel combusted	n(ethanol) burnt = $\frac{1.00}{46.0}$ = 0.02174 mol
(4) Determine the enthalpy change of combustion Recall definition (1 mol of fuel)	$\Delta H_{\rm c}$ =

total heat absorbed by water

Note: efficiency of the process = $\frac{100 \text{ all heat absoluted by water}}{100 \text{ total heat released from combustion}} \times 100\%$

4 ENTHALPY CHANGES INVOLVING IONIC COMPOUNDS



What are some heat changes in a chemical or physical process?

4.1 Ionisation Energy, IE

The first IE of an element is the energy **absorbed** to remove **one mole of electrons** from **one mole of the gaseous atoms** to form **one mole of singly charged gaseous cations**.

E.g. First ionisation energy of sodium: Na(g) \longrightarrow Na⁺(g) + e⁻

I.E. = + 494 kJ mol⁻¹

4.2 Electron Affinity, EA

(a) <u>First EA</u>

The amount of heat **absorbed or evolved** when **1 mole of electrons** is added to **one mole of gaseous atoms** to form **one mole of singly charged gaseous anions**.

E.g. First electron affinity of oxygen: $O(g) + e^{-} \longrightarrow O^{-}(g)$

1st EA = - 141 kJ mol⁻¹

- First EA is **mostly negative (exothermic**) as the energy released when the nucleus attracts an electron is larger than the energy taken in to overcome inter-electronic repulsion.
- The stronger the affinity for the electron, the greater the amount of energy is given off in the formation of the anion and hence the more negative (exothermic) the EA is.
- (b) <u>Second EA</u>

The amount of heat **absorbed** when **1 mole of electrons** is added to **one mole of gaseous singly charged gaseous anions** to form **one mole of doubly charged gaseous anions**.

E.g. Second electron affinity of oxygen: $O^{-}(g) + e^{-} \longrightarrow O^{2^{-}}(g)$

2nd EA = + 790 kJ mol⁻¹

- Second EA is **always positive (endothermic)** because energy is required to overcome the electrostatic repulsion of the second electron by the single negative charge on the anion.
- Note: 2nd EA is NOT O(g) + 2e⁻ → O²⁻(g) This equation shows the sum of the 1st and 2nd EA

4.3 Lattice Energy, LE

(a) Definition

The amount of heat **evolved** when **one mole** of the **solid ionic compound** is formed from its constituent **free gaseous ions** under standard conditions of **298 K and 1 bar**.

- E.g. Lattice energy of sodium chloride: $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$ LE (NaCl) = -771 kJ mol⁻¹ Lattice energy of magnesium chloride:
- Lattice energy is always negative (exothermic) as heat energy is evolved when forming strong electrostatic forces of attraction between oppositely charged ions.

LE $(MaCl_2) = -2489 \text{ kJ mol}^{-1}$

- Lattice energy is a **measure of ionic bond strength** and hence the stability of the ionic compound (relative to its constituent gaseous ions).
 - ✓ The more exothermic the LE, the stronger the ionic bond and the more stable the ionic compound.
- Lattice energy is useful in discussing the structure, bonding and properties of ionic compounds.
- Lattice energies cannot be measured directly but can be deduced from Born–Haber cycles. (*Refer to page 37*)
- (b) The Ionic Model Factors Affecting the Magnitude of Lattice Energy

 $Mg^{2+}(g) + 2Cl^{-}(g) \longrightarrow MgCl_{2}(s)$

- In the simple ionic model based on Coulomb's Law, the ions are assumed to be spherical with even charge distribution.
- The strength of attraction between oppositely charged ions increases with higher charge and decreases with larger inter-ionic distance.

Hence



 q_+ and q_- : charge of the cation and anion respectively r_+ and r_- : ionic radius of the cation and anion respectively



Based on the ionic model, the magnitude of lattice energy is dependent on two factors:

- Charge of ion
 - As charge of ion increases, $(q_+ x q_-)$ increases
 - electrostatic attraction between the ions becomes stronger (strength of ionic bond increases)
 - ✓ lattice energy becomes **more** exothermic
- Radius of ion

As size of ion increases, inter–ionic distance, $(r^+ + r^-)$, increases

- electrostatic attraction between the ions becomes weaker (strength of ionic bond decreases)
- ✓ lattice energy becomes **less** exothermic

Example 4.3.1

Lattice energies (kJ mol⁻¹) of some ionic solids are given below:

	Br⁻	Cl⁻	F⁻
Na⁺	-742	-771	-915
Mg ²⁺	-2414	-2489	-2883

- (i) Why does the lattice energy become more exothermic along the series NaBr, NaC*l* and NaF?
- (ii) Why is the lattice energy of MgBr₂ more exothermic than NaBr?

Solution

- (i) Along the series,
 - q_+ , q_- and r_+ are the same but **radius** of the anion **decreases** from Br^- to F^- .
 - Inter-ionic distance between the Na⁺ and halide anion decreases.
 - Electrostatic forces of attraction between the Na⁺ and halide anion becomes stronger.
 - Lattice energy becomes more exothermic.
- (ii) Mg²⁺ has a larger charge and a smaller cationic radius than Na⁺.
 - Inter-ionic distance between Mg²⁺ and Br⁻ is shorter.
 - Electrostatic forces of attraction between the Mg²⁺ and Br⁻ is stronger.
 - Lattice energy becomes more exothermic.

- (c) The Ionic Model Limitation
 - Theoretical lattice energy is based on the simple ionic model using Coulomb's Law.
 - ✓ This ionic model is satisfactory for predominantly ionic compounds as shown by the good agreement with the experimental lattice energy values derived using Born-Haber cycle.

ionic compound	LE(theoretical) / kJ mol ⁻¹	LE(experimental) / kJ mol ⁻¹
NaC <i>l</i>	- 766	- 771
NaBr	- 732	- 733
NaI	- 686	- 684
BaF₂	- 2309	- 2347

✓ Agreement is **poor** between ∆H_{latt}(theoretical) and ∆H_{latt}(experimental) for these ionic compounds with **partial covalent character**:

ionic compound	LE(theoretical) ∕ kJ mol ^{−1}	LE(experimental) / kJ mol ⁻¹
CaI ₂	-1826	-2068
BaI ₂	-1772	-1869
AgCl	-770	-905
AgBr	-758	-890

✓ AgCl: Experimental lattice energy is more exothermic than the theoretical lattice energy. This suggests that the bonding in AgCl is stronger than that predicted by the ionic model

Reason:

- There is some degree of covalent character in the ionic bond between Ag⁺ and Cl⁻.
- Ag⁺ polarises (or distorts) the electron cloud of Cl⁻ (due to high polarising power of Ag⁺ ion and high polarisability of the large Cl⁻ ion).
- This covalent character strengthens the ionic bond and this makes the experimental value more exothermic than the theoretical value.



Diagram showing the difference in polarising power of Na⁺ and Ag⁺

- Therefore, the discrepancy between ΔH_{latt} (theoretical) and ΔH_{latt} (experimental) is the largest when a cation has a high charge density and is able to distort an anion with a large electron cloud.
- Note: Covalent character does not always strengthen an ionic bond.

4.4 Standard Enthalpy Change of Hydration, ΔH_{hyd}^{\ominus}

(a) Definition

The amount of heat **evolved** when **one mole** of free **gaseous ions** is **dissolved** in a **large amount of water** forming a solution at infinite dilution at **298 K and 1 bar**.

E.g. Standard enthalpy change of hydration of sodium ion: Na⁺(g) \longrightarrow Na⁺(aq) $\Delta H_{hyd}^{\ominus} = -406 \text{ kJ mol}^{-1}$

> Standard enthalpy change of hydration of chloride ion: $Cl^{-}(g) \longrightarrow Cl^{-}(aq) \qquad \Delta H_{hyd}^{\ominus} = -381 \text{ kJ mol}^{-1}$

- ΔH_{hyd}^{\ominus} is always negative (exothermic).
 - Reason: Heat is produced when **ion-dipole attractions** are formed between the ions and polar water molecules.



Diagram showing the positive and negative ends of the water dipoles orientated towards CF and Na⁺ ions respectively

- (b) Factors affecting the magnitude of ΔH_{hyd}^{\ominus}
 - ΔH_{hyd}^{\ominus} is a measure of the strength of ion–dipole attraction. The stronger the attraction, the more negative (exothermic) the ΔH_{hyd}^{\ominus} .
 - The magnitude of the hydration energy depends on the
 - (i) the charge of the ions

charge density of ion,
$$\frac{q}{r}$$

(ii) the radius of the ions

$$\left|\Delta H_{\mathsf{hyd}}^{\ominus}\right| \propto \left|\frac{\mathsf{q}}{\mathsf{r}}\right|$$

A higher charge and smaller ionic radius (i.e. higher charge density) will lead to

- stronger ion-dipole attractions between the ion and water molecules
- > more exothermic ΔH_{hyd}^{\ominus}

Example 4.4.1

lon	Na⁺	Mg ²⁺	A <i>l</i> ³⁺	Cl⁻	Br⁻	I-
ΔH_{hyd}^{\ominus} / kJ mol ⁻¹	- 406	- 1926	- 4680	- 378	- 348	- 308

Explain the trend of ΔH_{hyd}^{\ominus} among the cations and that of the anions.

Solution

• ΔH_{hyd}^{\ominus} for cations from Na⁺ to Al³⁺ become **more exothermic**.

Reason:

- ✓ An **increase** in **ionic charge** and a **decrease** in the **ionic radius** from Na⁺ to Al^{3+} , resulting in an increase in charge density of cations.
- ✓ Hence, forming stronger ion-dipole attractions between cations and water molecules.
- ΔH_{hyd}^{\ominus} for anions from Cl^{-} to I⁻ become less exothermic.

Reason:

- ✓ An **increase** in the **ionic radius** from Cl^{-} to I^{-} ,
- \checkmark resulting in a decrease in the charge density of anions.
- ✓ Hence, forming weaker ion-dipole attractions between anions and water molecules.

4.5 Standard Enthalpy Change of Solution, ΔH_{sol}^{\ominus}

The amount of heat absorbed or evolved when one mole of a solute is dissolved in an infinite volume of water under the standard conditions of 298 K and 1 bar.

E.g. Standard enthalpy change of solution of sodium chloride: NaCl(s) \longrightarrow Na⁺(aq) + Cl⁻(aq) $\Delta H_{sol}^{\ominus}(NaCl) = +5 \text{ kJ mol}^{-1}$

> Standard enthalpy change of solution of magnesium sulfate: MgSO₄(s) \longrightarrow Mg²⁺(aq) + SO₄²⁻(aq) ΔH_{sol}^{\ominus} (MgSO₄)= - 91.2 kJ mol⁻¹

• The dissolution of a solid ionic compound can be *imagined* to comprise two stages:



Stage 1: Separation of the ions in solid ionic lattice into gaseous ions

✓ an **endothermic** process, i.e. energy is absorbed to overcome the ionic bonds $\checkmark -\Delta H_{\text{latt}}$ (i.e. *reverse of lattice energy*).



Stage 2: Hydration of the gaseous ions by water molecules

An exothermic process, i.e. energy is evolved due to the ion-dipole attractions formed between ions and water.



• The enthalpy change of solution when an ionic solid dissolves in water is the sum of the enthalpy changes in stages 1 and 2

Enthalpy change of solution, ΔH_{sol}^{\ominus}	
= – lattice energy + ΔH_{hyd}^{\ominus} (cation & anion)	
$= \Delta H_{hyd}^{\ominus}$ (cation & anion) – lattice energy	

- In general, the more exothermic $\Delta H_{soln} \xrightarrow{\bullet} \Rightarrow$ the more soluble the ionic compound
 - ✓ Salt is *likely* to be **soluble** if $\Delta H_{soln}^{-\bullet} < 0$: $|\Delta H_{hyd}^{-\bullet}| > |LE|$

Hydration energy released is enough to **compensate** for the lattice energy required to break down the crystal lattice \Rightarrow ionic compound is likely to be **soluble** in water.

✓ Salt is *likely* to be **insoluble** if $\Delta H_{soln}^{-\bullet} > 0$: $|\Delta H_{hyd}^{-\bullet}| < |LE|$

Hydration energy released is **not** enough to **compensate** for the lattice energy required to break down the crystal lattice \Rightarrow ionic compound is likely to be **insoluble** in water.

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Example 4.5.1

Compound	LE/ kJ mol ⁻¹	Sum of ∆ <i>H</i> _{hyd} [⊖] of cation & anion / kJ mol ⁻¹	$\Delta H_{\rm sol}^{\ominus}$ / kJ mol ⁻¹	Solubility (mol dm ⁻³)
LiCl	-862	-883	-21	19
NaC <i>l</i>	-771	-770	+1	6
KC <i>l</i>		-695	+23	5
AgC <i>l</i>	-905	-830		1.3 x 10 ⁻⁵ (insoluble)

Calculate the LE(KC*l*) and $\Delta H_{sol}^{\ominus}(AgCl)$.

Solution:

 $\Delta H_{sol}^{\ominus} = -$ lattice energy + ΔH_{hyd}^{\ominus} (cation & anion)

For KCl,

For AgCl,

5 HESS' LAW

-

S LAW

How can we determine the heat change in a chemical or physical process?

5.1 Hess' Law of Constant Heat Summation

Most enthalpy change of reactions cannot be determined experimentally (e.g. enthalpy change of formation of $KIO_3(s)$, lattice energy of NaCl(s) and etc.).

Hess' law allows us to calculate enthalpy change of reactions from other data that can be measured experimentally. Hess' law is based on the principle of conservation of energy.

Hess' law states that the enthalpy change of a chemical reaction is dependent only on the **initial states** of the **reactants** and the **final states** of the **products** and is **independent** of the **reaction pathway** taken.



initial: A + Bfinal: X + Ypath 1: ΔH_1 path 2: ΔH_2 and ΔH_3 and ΔH_4

By Hess' law, $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$

Note that any point in the cycle can be used as the starting point.



By Hess' law, $\Delta H_3 = -\Delta H_2 + \Delta H_1 + (-\Delta H_4)$

Hess' law is applicable for determining enthalpy change of reactions that cannot be found by direct experiment through the use of the:

1. Energy cycle or Energy level diagram method

2. Formula method

 $\checkmark \qquad \Delta H_{\rm r} = \Sigma \ \Delta H_{\rm c} \, ({\rm reactants}) - \Sigma \ \Delta H_{\rm c} \, ({\rm products})$

- $\checkmark \qquad \Delta H_{\rm r} = \Sigma \ \Delta H_{\rm f} \, ({\rm products}) \Sigma \ \Delta H_{\rm f} \, ({\rm reactants})$
- \checkmark $\Delta H_{sol} = \Delta H_{hyd}$ (cations & anions) LE
- \checkmark $\Delta H_{\rm r} = \Sigma \text{ BE (bonds broken)} \Sigma \text{ BE (bonds formed)}$
- 3. Algebraic method

Use Hess' law to determine the standard enthalpy change of formation of CO if the standard enthalpy change of combustion of C and CO are -393 kJ mol⁻¹ and -283 kJ mol⁻¹ respectively.

Solution

Method 1: Energy Cycle

General steps in constructing an energy cycle

- 1. Write the balanced equation representing the enthalpy change of reaction that you are required to calculate. (Need to follow the definition and also include state symbols)
- 2. Write the balanced equations with state symbols that illustrate the other enthalpy changes that are given in the question.
- 3. Inspect the equations in step 2 for common species linked to the reactant or product in the equation in step 1.
- 4. Create an alternative pathway by linking the common species in the equations in step 1 and step 2.
- 5. Apply Hess' law to calculate the required enthalpy change of reaction.

To solve	$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$	$\Delta H_{ m f}^{\ominus}$
Given	$C(s) + O_2(g) \longrightarrow CO_2(g)$ $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$	ΔH_{c}^{\ominus} = -393 kJ mol ⁻¹ ΔH_{c}^{\ominus} = -283 kJ mol ⁻¹

Energy cycle diagram

$$C(s) + \frac{1}{2} O_2(g) \xrightarrow{\Delta H_f^{\ominus}} CO(g)$$

By Hess' law, $\Delta H_{\rm f}^{\ominus} = -393 - (-283)$ = − 110 kJ mol⁻¹ Method 2: Formula

Reaction: $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$ $\Delta H_r = \Delta H_r^{\ominus}[CO(g)]$

 $\Delta \textbf{H}_{r} = \Sigma \Delta \textbf{H}_{c} \text{ (reactants)} - \Sigma \Delta \textbf{H}_{c} \text{ (products)}$

$$\Delta H_{\rm f}^{\ominus} = \Delta H_{\rm c}^{\ominus}({\rm C}) + \Delta H_{\rm c}^{\ominus}({\rm O}_2) - \Delta H_{\rm c}^{\ominus}({\rm CO})$$

=
=



Method 3: Algebraic Method

General steps involved in algebraic method (similar to solving "simultaneous equations")

- 1) Write the balanced equation representing the enthalpy change of reaction* that you are required to calculate. (Need to follow the definition and also include state symbols)
- 2) Write the balanced equations with state symbols that illustrate the other enthalpy changes that are given in the question.
- 3) Inspect the equations in step 2 and write down the equations for these reactions such that
 - Reactants of reaction* appear on the left-hand side
 - Products of reaction* appear on the right-hand side
- 4) Add the equations to obtain reaction* by cancelling out the intermediates.

Enthalpy change of reaction* is equal to the **algebraic sum** of the given enthalpy changes of the reactions that have been added.

Given:	$C(s) + O_2(g) \longrightarrow CO_2(g) (1)$	ΔH_{c}^{Θ}	= –393 kJ mol ⁻¹
	CO (g) + ½ O ₂ (g) CO ₂ (g) (2)	ΔH_{c}^{Θ}	= –283 kJ mol ⁻¹
Aim:	C (s) + $\frac{1}{2}$ O ₂ (g) \rightarrow CO (g)	$\Delta H_{\rm f}$ $^{\rm e}$	= ?
(1):	$C(s) + O_2(g) \rightarrow CO_2(g)$	ΔH_{c}^{e}	= −393 kJ mol ⁻¹
Reverse (2):	$\text{CO}_2(\mathbf{g}) \rightarrow \text{CO}(\mathbf{g}) + \frac{1}{2} \text{O}_2(\mathbf{g})$	ΔH_{c}^{e}	= +283 kJ mol ⁻¹
	$C (s) + \frac{1}{2} O_2(g) \rightarrow CO (g)$	$\Delta H_{\rm f}^{\Theta}$	= (-393) + 283
			= – 110 kJ mol⁻¹

Use Hess' law to determine the standard enthalpy change of combustion of propane, $\Delta H_c^{\ominus}[C_3H_8(g)]$, given the following data:

 $\Delta H_{f}^{\ominus}([C_{3}H_{8}(g)] = -104 \text{ kJ mol}^{-1}, \Delta H_{f}^{\ominus}([CO_{2}(g)] = -394 \text{ kJ mol}^{-1}, \Delta H_{f}^{\ominus}([H_{2}O(l)] = -286 \text{ kJ mol}^{-1}$

Solution

Method 1: Energy Cycle

To solve
$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$
 $\Delta H_c^{\ominus}[C_3H_8(g)]$
Given $3C(s) + 4H_2(g) \longrightarrow C_3H_8(g)$ $\Delta H_f^{\ominus}[C_3H_8] = -104 \text{ kJ mol}^{-1}$
 $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_f^{\ominus}[CO_2] = -394 \text{ kJ mol}^{-1}$
 $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H_f^{\ominus}[H_2O] = -286 \text{ kJ mol}^{-1}$

 $\Delta H_c^{\ominus}[C_3H_8(g)]$ $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

By Hess' law,

$$\Delta H_{c}^{\ominus}[C_{3}H_{8}(g)] = -(-104) + 3(-394) + 4(-286)$$

= -2220 kJ mol⁻¹

Method 2: Formula

 $\Delta H_{\rm r} = \Sigma \Delta H_{\rm f}$ (products) – $\Sigma \Delta H_{\rm f}$ (reactants)

By Hess' law, $\Delta H_c^{\ominus}[C_3H_8(g)] = \{ \underline{3} \Delta H_f^{\ominus}[CO_2] + \underline{4} \Delta H_f^{\ominus}[H_2O] \} - \{ \Delta H_f^{\ominus}[C_3H_8] + \underline{5} \Delta H_f^{\ominus}[O_2] \} =$



The standard enthalpy change of formation of $SiCl_4(g)$ is -610 kJ mol^{-1} .

The standard enthalpy changes of atomisation of the elements silicon and chlorine are +338 kJ mol⁻¹ and +122 kJ mol⁻¹ respectively. By means of an <u>energy level</u> diagram, find the Si–Cl bond energy.

Approach in drawing an energy level diagram

- 1. Start from zero energy level
 - > Place elements in standard states under standard condition at the energy level.
- 2. Use \downarrow for exothermic reaction and \uparrow for endothermic reaction.
- 3. Each arrow should represent one type of enthalpy.
- 4. The length of the arrow should be proportional to the magnitude of the enthalpy change.

Solution:

To solve	$SiCl_4(g) \longrightarrow Si(g) + 4Cl(g)$
Given	$Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(g)$
	Si(s) — Si(g)
	$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$

4BE(Si–Cl) ΔH_{f}^{\ominus} [SiCl₄] = - 610 kJ mol⁻¹ ΔH_{at}^{\ominus} [Si] = + 338 kJ mol⁻¹ ΔH_{at}^{\ominus} [Cl₂] = +122 kJ mol⁻¹

Energy level diagram





4BE(Si–C*l*) = (**+610**) **+ 338 + 488** BE(Si–C*l*) = **+359 kJ mol**⁻¹

Phosphorus can react with chlorine to form phosphorous pentachloride and phosphorus trichloride. Some thermochemical data related to these elements and compounds are shown below:

Data:

(a)

Enthalpy change of formation of gaseous PCl ₃	= –315 kJ mol ^{–1}
Enthalpy change of formation of gaseous PCl ₅	= -408 kJ mol ⁻¹
Enthalpy change of atomisation of phosphorus	= +314 kJ mol ⁻¹

 $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

- (a) By using the relevant data given above, construct a labeled energy level diagram to help to determine the average P-Cl bond energy in PCl_3 . [+332]
- (b) Calculate the enthalpy change for the reaction given below and hence obtain a second estimate of the mean bond energy of P-Cl. [+93; +169]

Solution:
(a) Energy / kJ mol⁻¹
P (g) + 3 Cl (g)

$$^{3}/_{2}(244)$$

P (g) + $^{3}/_{2}Cl_{2}(g)$
+314
P (s) + $^{3}/_{2}Cl_{2}(g)$
-315
PCl₃(g)

$$3BE(P-Cl) = (+315) + 314 + \frac{3}{2}(244)$$

 $BE(P-Cl) = + 332 \text{ kJ mol}^{-1}$

(b)
$$\Delta H_{rxn}^{\Phi} = \Delta H_{f}^{\Phi} (PCl_{3}) - \Delta H_{f}^{\Phi} (PCl_{5})$$

= -315 - (-408)
= +93 kJ mol⁻¹

Let the bond energy of P–Cl bond in PCl₅ be $x \text{ kJ mol}^{-1}$

$$\Delta H_{rxn}^{-\Theta} = \Sigma BE(bonds broken) - \Sigma BE(bonds formed) +93 = 5x - [3 BE(P-Cl) + BE(Cl-Cl)] +93 = 5x - [3 (332) + 244] x = +169 kJ mol-1$$

Given the following data,

ΔH_{hyd}^{\ominus} for sodium ion	= −390 kJ mol ⁻¹
ΔH_{hyd}^{\ominus} for chloride ion	= −381 kJ mol ⁻¹
L.E for sodium chloride	= -776 kJ mol ⁻¹

calculate the ΔH_{sol}^{\ominus} for NaCl.

Solution

Method 1: Energy cycle Energy cycle diagram

NaC*l*(s)
$$\Delta H_{sol}^{\ominus}$$

 $\Delta H_{sol}^{\ominus}(NaCl) =$

Method 2: Formula

$$\Delta H_{sol}^{\ominus}(NaCl) = -L.E (NaCl) + \Delta H_{hyd}^{\ominus}(Na^{+}) + \Delta H_{hyd}^{\ominus}(Cl^{-})$$

= - (-776) + (-390) + (-381)
= + 5 kJ mol^{-1}



5.2 Born-Haber Cycles

The lattice energies of some compounds *cannot* be found directly from experiment.

However, lattice energy can be calculated indirectly from other known enthalpy changes of reaction by means of an **energy cycle** that traces the enthalpy changes involved in converting **elements in their standard states** into a **solid ionic compound**. Such a cycle constructed to find the lattice energy is called a **Born-Haber cycle**.

How to draw a Born-Haber cycle?		
Elements in their standard states	<u>F</u> ormation	> Ionic solid
↓ <u>A</u> tomisation		\uparrow
Gaseous atoms Convert to gas ↓ (Ionisation ene	eous <u>l</u> ons ergy & Electron affinity)	<u>L</u> attice energy
Gaseous cations and anions	s	
By Hess' law, $\Delta H_{\rm f}^{\ominus} = \Delta H_{\rm at}^{\ominus} + 1.E$. + E.A. + L.E.	☺ How to remember? ☺ F = A.I.L

Construct a Born–Haber cycle and use it to determine the lattice energy of sodium chloride given the following information:

Enthalpy change of atomisation of Na	Na(s) —→ Na(g)	ΔH_{at}^{\ominus} = +109 kJ mol ⁻¹
Enthalpy change of atomisation of Cl	$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$	$\Delta H_{at}^{\ominus} = +121 \text{ kJ mol}^{-1}$
First ionisation energy of sodium	Na(g) —→ Na⁺(g) + e	1 st IE = +494 kJ mol ⁻¹
First electron affinity of chlorine	$Cl(g) + e \longrightarrow Cl^{-}(g)$	1 st EA = −364 kJ mol ⁻¹
Enthalpy change of formation of NaCl	$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$	$\Delta H_{\rm f}^{\ominus} = -411 \text{ kJ mol}^{-1}$
Lattice energy of NaCl	$Na^{+}(g) + Cl^{-}(g) \longrightarrow NaCl(s)$	

Solution:

Energy cycle diagram

Na(s) +
$$\frac{\Delta H_{f}^{\ominus} = -411 \text{ kJ mol}^{-1}}{\longrightarrow} \text{ NaCl(s)}$$

By Hess' law,

$$\Delta H_{f}^{\ominus} = \Delta H_{at}^{\ominus}(Na) + \Delta H_{at}^{\ominus}(Cl) + 1^{st} IE(Na) + EA(Cl) + LE$$

$$LE = \Delta H_{f}^{\ominus} - [\Delta H_{at}^{\ominus}(Na) + \Delta H_{at}^{\ominus}(Cl) + 1^{st} IE(Na) + EA(Cl)]$$

$$= (-411) - [109 + 121 + 494 + (-364)]$$

$$= -771 \text{ kJ mol}^{-1}$$

Energy level diagram



By Hess's law, -411 = +109 + 494 + 121 - 364 + LE

LE = **-771 kJ mol**⁻¹

OR

By inspection, |LE| = [411 + 109 +121 + 494] - 364

= + 771 kJ mol⁻¹

 $LE = -771 \text{ kJ mol}^{-1}$

Construct a Born–Haber cycle for the formation of calcium oxide. Using the given information and values from the *Data Booklet*, calculate the standard enthalpy change of formation of calcium oxide.

Ca(s) —→ Ca(g)	$\Delta H_{\rm at}^{\ominus}$ = +177 kJ mol ⁻¹
½O₂(g) → O(g)	$\Delta H_{\rm at}^{\ominus}$ = +248 kJ mol ⁻¹
$Ca(g) \longrightarrow Ca^{+}(g) + e$	1 st IE = +590 kJ mol ⁻¹
Ca⁺(g) → Ca²⁺(g) + e	2^{nd} IE = +1150 kJ mol ⁻¹
O(g) + e → O ⁻ (g)	1 st EA = -141 kJ mol ⁻¹
O⁻(g) + e O²⁻(g)	$2^{nd} EA = +790 \text{ kJ mol}^{-1}$
Ca ²⁺ (g) + O ^{2−} (g) → CaO(s)	LE = −3414 kJ mol ⁻¹

Solution:

Energy cycle diagram



By Hess' law,

 $\Delta H_{f}^{\ominus} = \Delta H_{at}^{\ominus}(Ca) + \Delta H_{at}^{\ominus}(O_{2}) + 1^{st} IE(Ca) + 2^{nd} IE(Ca) + 1^{st} EA(O) + 2^{nd} EA(O) + LE$ = 177 + 248 + 590 + 1150 + (-141) + 790 + (-3414) = -600 kJ mol⁻¹





By Hess' Law,

 $\Delta H_{f}^{\ominus} = \Delta H_{at}^{\ominus}(Ca) + \Delta H_{at}^{\ominus}(O_{2}) + 1^{st} IE(Ca) + 2^{nd} IE(Ca) + 1^{st} EA(O) + 2^{nd} EA(O) + LE$ = 177 + 248 + 590 + 1150 + (-141) + 790 + (-3414) = -600 kJ mol⁻¹

END