

# Topic 5: Energetics/ thermochemistry

## 5.1 Measuring energy changes

U1	Heat is a form of energy.
U2	Temperature is a measure of the average kinetic energy of the particles.
U3	Total energy is conserved in chemical reactions.
U4	Chemical reactions that involve transfer of heat between the system and the surroundings are described as endothermic or exothermic.
U5	The enthalpy change ( $\Delta H$ ) for chemical reactions is indicated in $\text{kJ mol}^{-1}$ .
U6	$\Delta H$ values are usually expressed under standard conditions, given by $\Delta H^\circ$ , including standard states.
A1	Calculation of the heat change when the temperature of a pure substance is changed using $q = mc\Delta T$ .
A2	A calorimetry experiment for an enthalpy of reaction should be covered and the results evaluated.

### IB definitions

**Exothermic reaction** – An exothermic reaction is one that releases heat to the surroundings as a result of forming products with stronger bonds than the reactants. Exothermic reactions have a **negative  $\Delta H$  value**.

**Endothermic reaction** – An endothermic reaction is one that absorbs heat from the surroundings as a result of forming products with weaker bonds than the reactants. Endothermic reactions have a **positive  $\Delta H$  value**.

**Standard enthalpy change of reaction** – Standard enthalpy change is the heat transferred during a reaction carried out under standard conditions: Unit: heat per mole ( $\text{kJ mol}^{-1}$ )

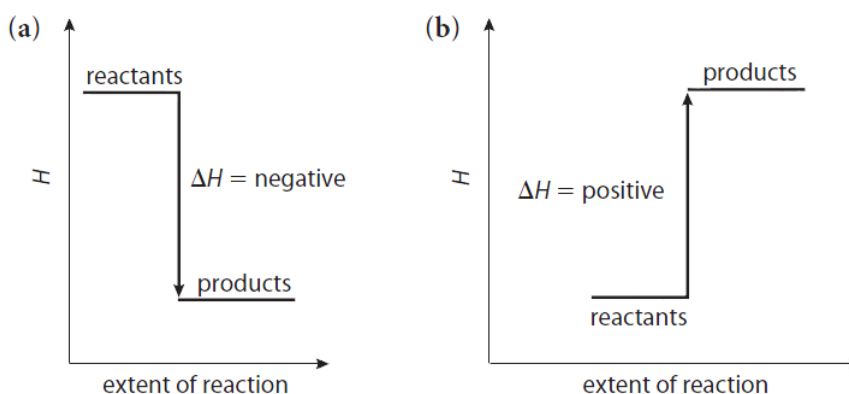
- pressure 100 kPa
- temperature 298 K
- all substances pure and in their standard state

Combustion, neutralisation and simple displacement are always **exothermic** reactions.

### Temperature changes and enthalpy changes

- a decrease in temperature of the system means that **energy is absorbed** in the reaction which means it is endothermic
- an increase in temperature of the system means that the **reaction gives out** energy which means it is exothermic

### Energy profile diagrams



### Bonding in reaction

- bond making release energy (more stable)
- bond breaking require energy (less stable)
- reaction energy release = bond making – bonding breaking = energy of products – energy of reactants

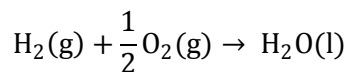
### Measurement of energy

$$Q = m \times c \times \Delta t$$

Specific heat capacity: amount of energy required to change the temperature of 1kg of substance by 1 degree

## Enthalpy of formation

Enthalpy change when **1 mole** of a molecule is formed from **its element** in their standard state

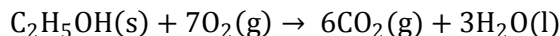


**\*\*Only 1 mole of product should be made\*\***

$\Delta H_f^\circ(\text{H}_2) = 0$ : For elements, its enthalpy of formation = 0

## Enthalpy of combustion

Enthalpy change is released when **1 mole** of a substance burns completely with oxygen under standard condition

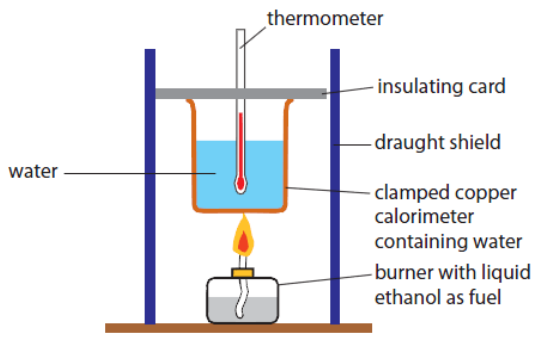
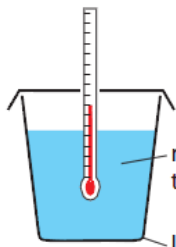


**\*\*Only 1 mole of substance can be burnt\*\***

## 5.2 Hess's Law

- |    |   |
|----|---|
| U1 | The enthalpy change for a reaction that is carried out in a series of steps is equal to the sum of the enthalpy changes for the individual steps. |
| A1 | Application of Hess's Law to calculate enthalpy changes.  |
| A2 | Calculation of $\Delta H$ reactions using $\Delta H_f^\circ$ data   |
| A3 | Determination of the enthalpy change of a reaction that is the sum of multiple reactions with known enthalpy changes.                             |

## Enthalpy experiments

Measuring enthalpy of combustion	Measuring enthalpy of neutralisation
	

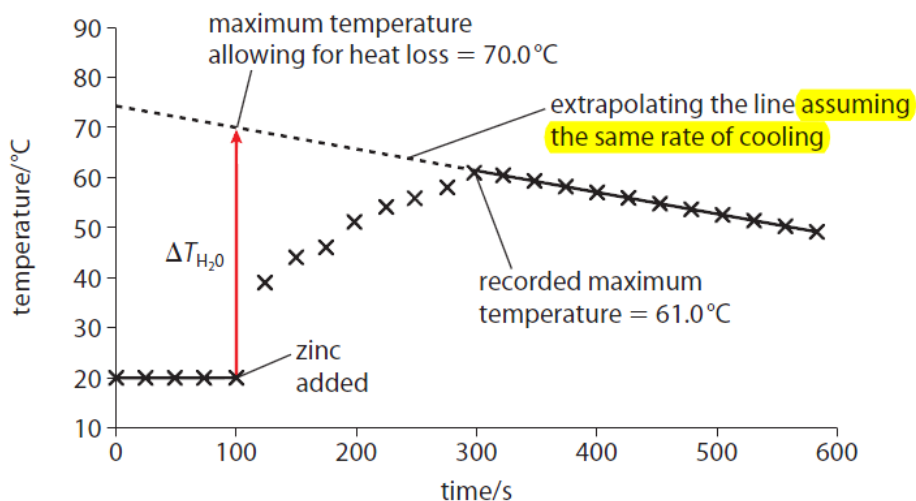
## Enthalpy calculations

$$\Delta H = \frac{Q}{n} = \frac{mc\Delta T}{n}$$

Where  $n$  is the number of moles reacted (in the combustion experiment this can be calculated from the change in mass of the fuel burner)

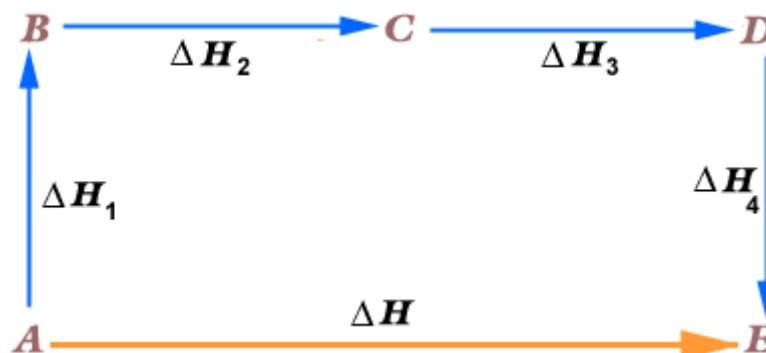
## Determining temperature change from graphs

You need to extrapolate **backwards** in order to compensate for the heat loss.



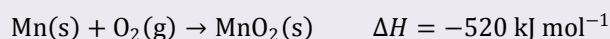
## Hess's Law

Total enthalpy change = the sum of all intermediated steps

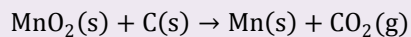


### Problem solving

Using the equations below:



What is the enthalpy change for the following reaction?



As you can see, if you reverse the second reaction (and change the sign of the enthalpy), it cancels to give the above reaction, therefore the enthalpy change is  $-390 + 520 = 130 \text{ kJ mol}^{-1}$ .

## 5.3 Bond enthalpies

- |    |  |
|----|--|
| U1 | Bond-forming releases energy and bond-breaking requires energy.  |
| U2 | Average bond enthalpy is the energy needed to break one mol of a bond in a gaseous molecule averaged over similar compounds.   |
| A1 | Calculation of the enthalpy changes from known bond enthalpy values and comparison of these to experimentally measured values.                                       |
| A2 | Sketching and evaluation of potential energy profiles in determining whether reactants or products are more stable and if the reaction is exothermic or endothermic. |
| A3 | Discussion of the bond strength in ozone relative to oxygen in its importance to the atmosphere.   |

### IB definitions

**Bond enthalpy**—enthalpy change is required when 1 mole of bonds are broken to form atoms in their **gaseous state**. For example,  $\text{X}_2\text{(g)} \rightarrow 2\text{X(g)}$

It is an average value because it takes account of the different energies in a bond between the same atoms in different molecules.

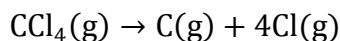
### Bond enthalpies and reaction enthalpies

- If the sum of the bond enthalpies in the reactants is greater than in the products then the reaction is **exothermic**.
- If it is less, the reaction is endothermic

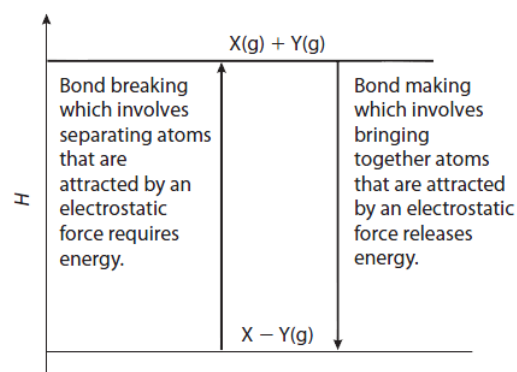
$$\Delta H^\circ_{\text{reaction}} = \Sigma \text{BE}(\text{reactants}) - \Sigma \text{BE}(\text{products})$$

$$\Delta H^\circ_{\text{reaction}} = \Sigma \Delta H^\circ_f(\text{products}) - \Sigma \Delta H^\circ_f(\text{reactants})$$

Bond-breaking is an endothermic process; bond-making is an exothermic process



\*\*All in gaseous state and only **1 mole of substance** is breaking down\*\*



# Topic 15: Energetics/thermochemistry (HL)

## 15.1 Energy cycles

- U1 Representative equations (eg.  $M^+(g) \rightarrow M^+(aq)$ ) can be used for enthalpy/energy of hydration, ionization, atomization, electron affinity, lattice, covalent bond and solution.
- U2 Enthalpy of solution, hydration enthalpy and lattice enthalpy are related in an energy cycle.
- A1 Construction of Born-Haber cycles for group 1 and 2 oxides and chlorides.
- A2 Construction of energy cycles from hydration, lattice and solution enthalpy. For example dissolution of solid NaOH or  $NH_4Cl$  in water.
- A3 Calculation of enthalpy changes from Born-Haber or dissolution energy cycles.
- A4 Relate size and charge of ions to lattice and hydration enthalpies.
- A5 Perform lab experiments which could include single replacement reactions in aqueous solutions.

### IB definitions

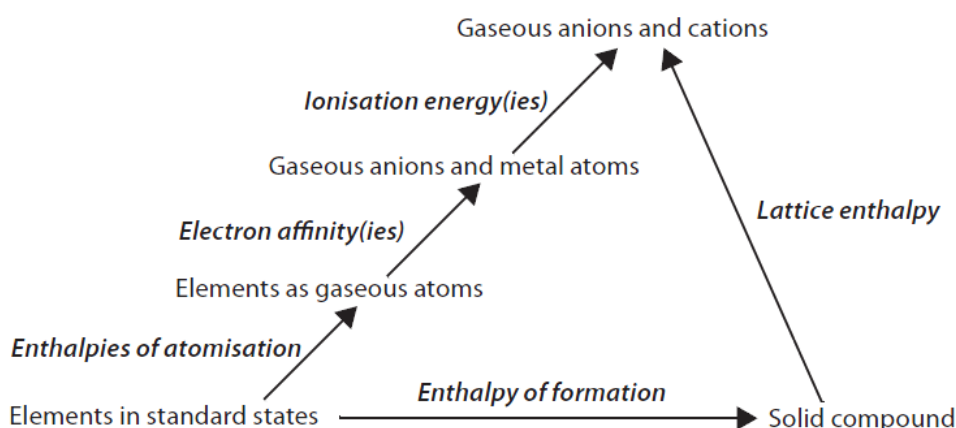
**Standard enthalpy of solution**—one mole of an ionic solid breaks into its aqueous ions in solution in standard state

**Standard enthalpy of hydration** —one mole of gaseous ions becomes aqueous ions in standard state

**Lattice enthalpy** —enthalpy change when one mole of an ionic compound breaks down into its ions in the gaseous state

**Enthalpy of atomisation** —enthalpy change when one mole of substance change state from solid to gas

### Born- Haber Cycle



Oxides	Chlorides

$$-\Delta H_f^\circ + \Delta H_{\text{ionisation}}^\circ + \text{Bond Enthalpy} + \text{Ionisation energy} + \text{Electron affinity} = \Delta H_{\text{lattice}}^\circ$$

Factors affect lattice enthalpy value:

- Charge of the ions (greater charge, stronger interaction, greater lattice enthalpy value)
- Distance (smaller size, stronger interaction, greater enthalpy value)

### Enthalpy of solution and hydration:

- Enthalpy of solution is always **positive** (except the group 1 element) – endothermic reaction
- Enthalpy of hydration is always **negative** – exothermic reaction
- Charges of ions and size of ions may affect the enthalpy of solution value due to the interaction between ions and water

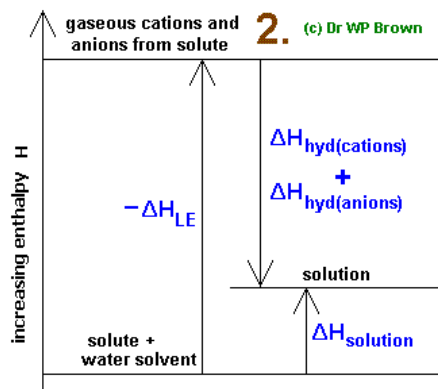
### Energy cycle:

Lattice enthalpy: solid to gaseous ions

Enthalpy of hydration: gaseous ions to aqueous ions

Enthalpy of solution: solid into aqueous ions

$$\Delta H_{\text{solution}}^{\circ} = \Delta H_{\text{lattice}}^{\circ} + \Delta H_{\text{hydration}}^{\circ}$$



## 15.2 Entropy and spontaneity

- U1 Entropy (S) refers to the distribution of available energy among the particles. The more ways the energy can be distributed the higher the entropy.
- U2 Gibbs free energy (G) relates the energy that can be obtained from a chemical reaction to the change in enthalpy ( $\Delta H$ ), change in entropy ( $\Delta S$ ), and absolute temperature (T).
- U3 Entropy of gas > liquid > solid under same conditions.
- A1 Prediction of whether a change will result in an increase or decrease in entropy by considering the states of the reactants and products.
- A2 Calculation of entropy changes ( $\Delta S$ ) from given standard entropy values ( $S^{\circ}$ ).
- A3 Application of  $G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$  in predicting spontaneity and calculation of various conditions of enthalpy and temperature that will affect this.
- A4 Relation of  $\Delta G$  to position of equilibrium.

**Entropy:** how energy is distributed in a system

- Entropy increases **from order to disorder**
- More ways to distribute energy, greater the entropy
- This tends to increase over time in a closed system. Gases mixing together increase the entropy.
- Unit of entropy:  $\text{JK}^{-1}\text{mol}^{-1}$

### Factors that increase the entropy of a system ( $\Delta S > 0$ )

- mixing different types of particles
- a change in state where the distance between the particles increases (solid < liquid < gas)
- the increased movement of particles
- increasing the number of particles
- the greatest increase is usually found where the number of particles in the gaseous state increases

$$\Delta S^{\ominus} = \Delta S^{\ominus}(\text{products}) - \Delta S^{\ominus}(\text{reactants})$$

**Gibbs' free energy:** energy available to do useful work

The sign of  $\Delta G$  must be **negative** for a process or reaction to be spontaneous.

**Spontaneous reaction:** reaction happens itself without outside energy.

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

The fact that we use standard conditions implies that the temperature is 298K.

## Calculating $\Delta G$

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

Depending on the values of  $\Delta H$  and  $\Delta S$ , a reaction might become spontaneous at a certain temperature.

$\Delta H^{\ominus}$	$\Delta S^{\ominus}$	$T$	$\Delta G$	Spontaneity
positive	positive	low	positive $\approx \Delta H^{\ominus}$	not spontaneous
positive	positive	high	negative $\approx -T\Delta S^{\ominus}$	spontaneous
positive	negative	low	positive $\approx \Delta H^{\ominus}$	not spontaneous
positive	negative	high	positive $\approx -T\Delta S^{\ominus}$	not spontaneous
negative	positive	low	negative $\approx \Delta H^{\ominus}$	spontaneous
negative	positive	high	negative $\approx -T\Delta S^{\ominus}$	spontaneous
negative	negative	low	negative $\approx \Delta H^{\ominus}$	spontaneous
negative	negative	high	positive $\approx -T\Delta S^{\ominus}$	not spontaneous