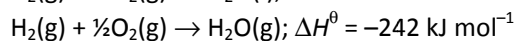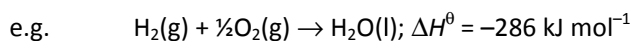# Chapter 5: Energetics/thermochemistry – fast facts

5.1 Measuring energy changes

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

- **Energetics** deals with heat changes in chemical reactions. Heat is a form of energy.
- Temperature is a measure of the average kinetic energy of the particles.
- Total energy is conserved in chemical reactions.
- Enthalpy is the amount of heat energy contained in a substance. It is stored in the chemical bonds as potential energy. When substances react, the difference in the enthalpy between the reactants and products (at constant pressure) results in a heat change which can be measured.
- The reaction mixture is called the **system** and anything around the system is called the **surroundings**.
- **Thermochemical equations** give the balanced equation with the enthalpy change.

    e.g. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H^{\theta} = -286$ kJ mol^{-1}
    $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$; $\Delta H^{\theta} = -242$ kJ mol^{-1}

    State symbols must be shown, as ΔH^{θ} depends on the state of the reactants or products.

- Chemical reactions that involve transfer of heat between the system and the surroundings are described as endothermic or exothermic.
- In **exothermic reactions** heat is released to the surroundings.
- In **endothermic reactions** heat is absorbed from the surroundings.
- The enthalpy change (ΔH) for chemical reactions is indicated in kJ mol-1.
- Exothermic reactions have negative ΔH values. The temperature of the reaction mixture rises as the chemicals give out heat.
- Endothermic reactions have positive ΔH values. The temperature of the reaction mixture falls as the chemicals absorb heat.
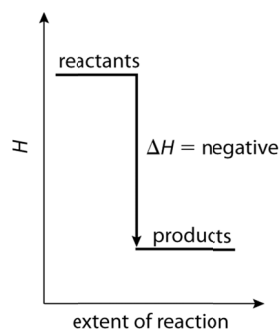
An exothermic reaction: the products are more **stable** than the reactants as they have a lower enthalpy.
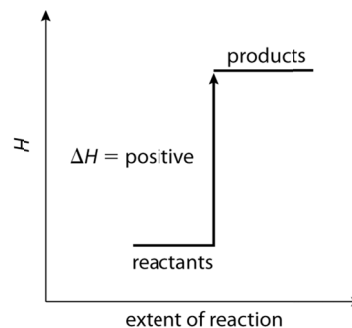
An endothermic reaction: the products are less stable than the reactants as they have a higher enthalpy.

- The **standard state** of an element or compound is its most stable state under the standard conditions (pressure 101.3 kPa, temperature 298 K).

- The **standard enthalpy change** (ΔH^{θ}) is the heat energy transferred under **standard conditions** (pressure 100 kPa, concentration 1 mol dm^{-3} and all substances in their standard states.)). Only ΔH^{θ} can be measured, not H for the initial or final state of a system.

- The **standard enthalpy change of combustion** $\left(\Delta H^{\theta}_{c}\right)$ is the enthalpy change for the complete combustion of one mole of a substance in its standard state in excess oxygen under standard conditions. All combustion reactions are exothermic.

- The **standard enthalpy change of formation** $\left(\Delta H^{\theta}_{f}\right)$ is the enthalpy change when one mole of a substance is formed from its elements in their standard states under standard conditions.

- **Calorimetry** is the technique of measuring heat changes in physical processes and chemical reactions.

- Heat changes can be calculated from the temperature changes:

  - heat change (q) = mass (m) $\times$ specific heat capacity (c) $\times$ temperature change (ΔT)

- The **specific heat capacity** is the amount of heat energy required to raise the temperature of unit mass (e.g. 1 kg or 1 g) of a substance, by 1 °C or 1 K.

- ΔH^{θ}_{c} for reactions in aqueous solutions can be calculated if it is assumed that all the heat goes into the water.

$$\Delta H^{\theta}_{C} = \frac{-m_{H_2O} \times c_{H_2O} \times \Delta T_{H_2O}}{n_{fuel}}$$

The experiment is performed with a calorimeter which is a good conductor. This allows heat from the flame to pass to the water.

$$\Delta H^{\theta}_{reaction} = \frac{-m_{H_2O} \times c_{H_2O} \times \Delta T_{H_2O}}{n_{limiting\ reagent}}$$

The experiment is performed with a calorimeter which is an insulator of heat, which reduces heat losses from the system.

- If a calorimeter absorbs heat: $Q = \left(m_{H_2O} \times c_{H_2O} \times \Delta T_{H_2O}\right) + \left(m_{calor} \times c_{calor} \times \Delta T_{calor}\right)$

- Heat loss and incomplete combustion can lead to **systematic** errors in experimental results.
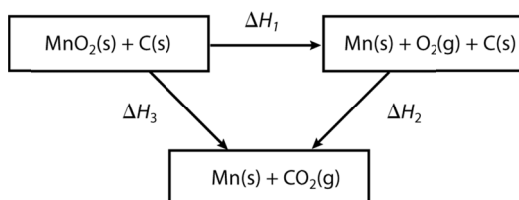
5.2 Hess's law

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

- Hess's law states that the total enthalpy change for a reaction is independent of the route taken. It is a special case of the law of conservation of energy.

e.g.
Hess's law:
$\Delta H_3 = \Delta H_1 + \Delta H_2$

- $\Delta H_{reaction}$ = $\sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants)

5.3 Bond enthalpies

> Energy is absorbed when bonds are broken and is released when bonds are formed.

- **Average bond energy** is the energy required to break one mole of the same type of bond in the gaseous state averaged over a variety of similar compounds.

- Bond breaking absorbs energy and is endothermic. Bond making releases energy and is exothermic.

  $\Delta H^{\theta}_{reaction} = \Sigma\, E_{bonds\ broken} - \Sigma\, E_{bonds\ formed}$

  when $\Sigma\, E_{bonds\ broken} > \Sigma\, E_{bonds\ formed}$: the reaction is endothermic
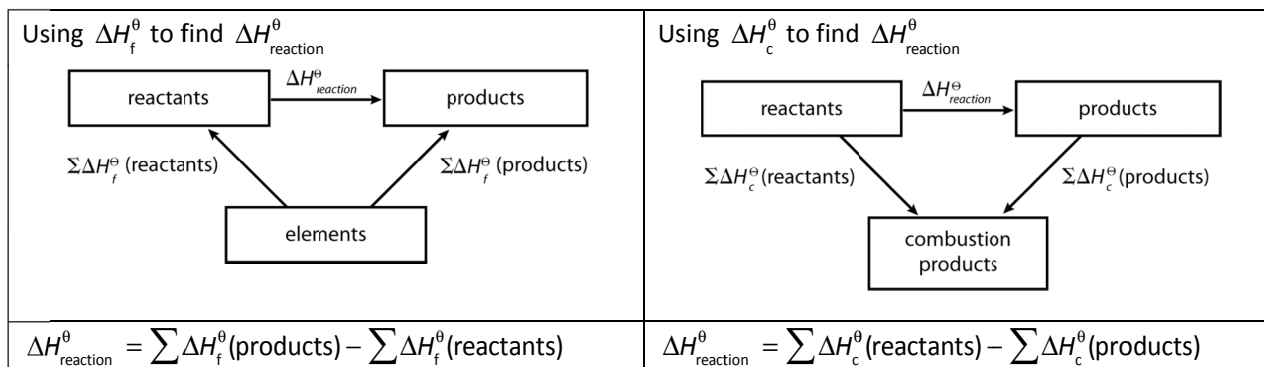
  when $\Sigma\, E_{bonds\ formed} > \Sigma\, E_{bonds\ broken}$: the reaction is exothermic

- The bonds in oxygen, O_2, are stronger than those in ozone, O_3 and are broken by UV light of different wavelengths.

- The ozone cycle describes how ozone is both formed and depleted by natural processes in the atmosphere.

15.1 Energy cycles

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

- The enthalpy of formation of any element in its stable state is zero, as there is no enthalpy change when an element is formed from itself.
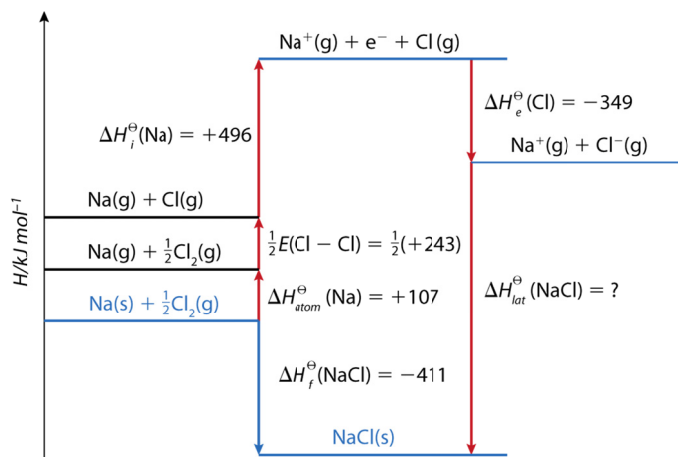

Using ΔH^{θ}_{f} to find $\Delta H^{\theta}_{reaction}$	Using ΔH^{θ}_{c} to find $\Delta H^{\theta}_{reaction}$
$\Delta H^{\theta}_{reaction} = \sum \Delta H^{\theta}_{f}(products) - \sum \Delta H^{\theta}_{f}(reactants)$	$\Delta H^{\theta}_{reaction} = \sum \Delta H^{\theta}_{c}(reactants) - \sum \Delta H^{\theta}_{c}(products)$

$\Delta H^{\theta}_{reaction}$ calculated from ΔH^{θ}_{f} or ΔH^{θ}_{c} is more accurate than $\Delta H^{\theta}_{reaction}$ values based on bond enthalpies, which refer only to the gaseous state and are average values.

- The first **electron affinity** is the enthalpy change when one mole of gaseous atoms attracts one mole of electrons: $X(g) + e^{-}(g) \rightarrow X^{-}(g)$ ΔH^{θ}_{e}

- The **lattice enthalpy** is the enthalpy change that occurs when one mole of a solid ionic compound is separated into gaseous ions under standard conditions. For example, for alkali metal halides: $MX(s) \rightarrow M^{+}(g) + X^{-}(g)$ ΔH^{θ}_{lat}

- ΔH^{θ}_{lat} depends on the attraction between the ions:
  - an increase in the **ionic radius** of the ions decreases ΔH^{θ}_{lat}
  - an increase in **ionic charge** increases ΔH^{θ}_{lat} .

- The **Born–Haber cycle** is a special case of Hess's law for the formation of ionic compounds. It allows the **experimental lattice enthalpy** to be calculated from other enthalpy changes.

- **Theoretical lattice enthalpies** can be calculated using a (purely) **ionic model** from the ionic charges and radii.
- The hydration enthalpy of an ion depends on the attraction between the ions and the polar water molecules.

Born–Haber cycle for NaCl

$H/kJ\,mol^{-1}$

Na$^+$(g) + e$^-$ + Cl(g)

$\Delta H_e^\ominus(Cl) = -349$

Na$^+$(g) + Cl$^-$(g)

$\Delta H_i^\ominus(Na) = +496$

Na(g) + Cl(g)

Na(g) + ½Cl$_2$(g)

Na(s) + ½Cl$_2$(g)

$\frac{1}{2}E(Cl-Cl) = \frac{1}{2}(+243)$

$\Delta H_{atom}^\ominus(Na) = +107$

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

$\Delta H_f^\ominus(NaCl) = -411$

NaCl(s)

$\Delta H_{lat}^\ominus$ = 411 + 107 + ½(+243) + 496 – 349 = **+786.5 kJ mol⁻¹**

15.2 Entropy and spontaneity

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

- **Entropy** (*S*) is a property which quantifies the degree of disorder or randomness in a system.
- Ordered states have low *S*, disordered states have high *S*: *S* (s) < *S* (l) < *S* (g)
- Generally matter and energy become more disordered, and $S_{universe}$ increases.
- $\Delta S_{reaction}^\ominus$ = Σ$S^\ominus$(products) – Σ$S^\ominus$(reactants)
- **Gibbs' free energy** (*G*) is the criterion for predicting the spontaneity of a reaction or process: it is related to $\Delta S_{total}^\ominus$. It gives the energy available to do useful work and is related to the enthalpy and entropy changes of the system: $\Delta G_{system}^\ominus = \Delta H_{system}^\ominus - T\Delta S_{system}^\ominus$
- ΔG_{sys} < 0 for a spontaneous process, ΔG_{sys} = 0 at equilibrium.

  Calculating $\Delta G_{reaction}^\ominus$ (when *T* = 298 K)   Calculating $\Delta G_{reaction}^\ominus$ (for all *T*)

  $\Delta G_{reaction}^\ominus = \sum \Delta G_{(products)}^\ominus - \sum \Delta G_{(reactants)}^\ominus$ $\Delta G_{reaction}^\ominus = \Delta H_{reaction}^\ominus - T\Delta S_{reaction}^\ominus$

  T must be in K. As the units of *S* are J mol⁻¹ K⁻¹ and *H* are kJ mol⁻¹ they need to be changed to be consistent.
- ΔG_{sys} and thus the direction of change varies with temperature.

  At low temperature:

  $\Delta G_{system}^\ominus \approx H_{system}^\ominus$: exothermic reactions are spontaneous.

  At high temperature:

  $\Delta G_{system}^\ominus = -T\Delta S_{system}^\ominus$: this allows some endothermic reactions to occur if $\Delta S_{system}^\ominus > 0$