Worksheet 5.2

Chapter 5: Energetics – fast facts

5.1 Exothermic and endothermic reactions

- **Energetics** deals with heat changes 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. \[ \text{H}_2 (g) + \frac{1}{2}\text{O}_2 (g) \rightarrow \text{H}_2\text{O} (l); \Delta H^\theta = -286 \text{ kJ mol}^{-1} \]
  \[ \text{H}_2 (g) + \frac{1}{2}\text{O}_2 (g) \rightarrow \text{H}_2\text{O} (g); \Delta H^\theta = -242 \text{ kJ mol}^{-1} \]
  State symbols must be shown as \( \Delta H^\theta \) depends on the state of the reactants or products.
- In **exothermic reactions** heat is released to the surroundings.
- In **endothermic reactions** heat is absorbed from the surroundings.
- The **standard enthalpy change** \( (\Delta H^\theta) \) is the heat energy transferred under **standard conditions** (pressure 101.3 kPa, temperature 298 K). Only \( \Delta H^\theta \) can be measured, not \( H \) for the initial or final state of a system.
- The **standard enthalpy change of combustion** \( (\Delta H^\theta_c) \) 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 **enthalpy of neutralization** \( (\Delta H^\theta_{\text{neut}}) \) is the enthalpy change when one mol of \( \text{H}^+ (aq) \) reacts with one mol of \( \text{OH}^- (aq) \) ions. The reaction is exothermic as bond formation takes place: \( \text{H}^+ (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O} (l) \).
- Exothermic reactions have negative \( \Delta H \) values. The temperature of the reaction mixture rises as the chemicals give out heat.
- Endothermic reactions have positive \( \Delta H \) 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.

5.2 Calculation of enthalpy changes

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

- Heat changes can be calculated from the temperature changes:
  
  $\text{heat change (} q \text{)} = \text{mass (} m \text{)} \times \text{specific heat capacity (} c \text{)} \times \text{temperature change (} \Delta T \text{)}$.

- 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.

- $\Delta T_C^0$, and for reactions in aqueous solutions can be calculated if it is assumed that all the heat goes into the water.

  $$\Delta T_C^0 = -m_{\text{H}_2\text{O}} \times c_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}/n_{\text{fuel}}$$

  $$\Delta T_{\text{reaction}}^0 = -m_{\text{H}_2\text{O}} \times c_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}/n_{\text{limiting reagent}}$$

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

  If a calorimeter absorbs heat: $Q = (m_{\text{H}_2\text{O}} \times c_{\text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}) + (m_{\text{calor}} \times c_{\text{calor}} \times \Delta T_{\text{calor}})$.

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

\[ \Delta H_3 = \Delta H_1 + \Delta H_2 \]

5.4 Bond enthalpies
- **Average bond energy** is the energy required to break one mole of the same type of bonds 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.

\[ \Delta H_{\text{reaction}}^\theta = \sum E_{\text{bonds broken}} - \sum E_{\text{bonds formed}} \]

When \( \sum E_{\text{bonds broken}} > \sum E_{\text{bonds formed}} \), the reaction is endothermic.
When \( \sum E_{\text{bonds formed}} > \sum E_{\text{bonds broken}} \), the reaction is exothermic.

15.1 Standard enthalpy changes of reaction
- 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 of combustion** \( \Delta H_C^\theta \) is the enthalpy change for the complete combustion of one mole of a substance in its standard state in excess oxygen under standard conditions.
- The **standard enthalpy change of formation** \( \Delta H_f^\theta \) is the enthalpy change when one mole of a substance is formed from its elements in their standard states under standard conditions.
- 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 $\Delta H_f^\theta$ to find $\Delta H_{\text{reaction}}^\theta$

Using $\Delta H_c^\theta$ to find $\Delta H_{\text{reaction}}^\theta$

$\Delta H_{\text{reaction}}^\theta = \Sigma \Delta H_f^\theta (\text{products}) - \Sigma \Delta H_f^\theta (\text{reactants})$

$\Delta H_{\text{reaction}}^\theta = \Sigma \Delta H_c^\theta (\text{reactants}) - \Sigma \Delta H_c^\theta (\text{products})$

$\Delta H_{\text{reaction}}^\theta$ calculated from $\Delta H_f^\theta$ or $\Delta H_c^\theta$ are more accurate than $\Delta H_{\text{reaction}}^\theta$ values based on bond enthalpies, which refer only to the gaseous state and are average values.

15.2 Born–Haber cycles

- The first electron affinity is the enthalpy change when one mole of gaseous atoms attracts one mole of electrons: $X (g) + e^- (g) \rightarrow X^- (g) \Delta H_e^\theta$.

- 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: $\text{MX (s)} \rightarrow \text{M}^+ (g) + \text{X}^- (g) \Delta H_e^\theta$.
  - $\Delta H_{\text{lat}}^\theta$ depends on the attraction between the ions:
    - an increase in the ionic radius of the ions decreases $\Delta H_{\text{lat}}^\theta$.
    - an increase in ionic charge increases $\Delta H_{\text{lat}}^\theta$.
  - 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.
  - Differences between the theoretical and experimental lattice enthalpies give an indication of the covalent character of the compound; the greater the difference the more covalent the compound.
Born–Haber cycle for NaCl

\[ \Delta f^\theta_{\text{lat}} = 411 + 107 + \frac{1}{2}(+243) + 496 - 349 = +786.5 \text{ kJ mol}^{-1} \]

15.3 Entropy

- **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 \(S_{\text{universe}}\) increases.
- \(\Delta S^\theta_{\text{reaction}} = \Sigma S^0\) (products) – \(\Sigma S^0\) (reactants).

15.4 Spontaneity

- **Gibbs' free energy** \((G)\) is the criterion for predicting the spontaneity of a reaction or process: it is related to \(\Delta S^\theta_{\text{total}}\). It gives the energy available to do useful work and is related to the enthalpy and entropy changes of the system: \(\Delta G^\theta_{\text{system}} = \Delta H^\theta_{\text{system}} - T \Delta S^\theta_{\text{system}}\).
- \(\Delta G_{\text{sys}} < 0\) for a spontaneous process. \(\Delta G_{\text{sys}} = 0\) at equilibrium.

Calculating \(\Delta G^\theta_{\text{reaction}}\) (when \(T = 298\) K)

\[ \Delta G^\theta_{\text{reaction}} = \Sigma \Delta G^\theta_f\) (products) – \(\Sigma \Delta G^\theta_f\) (reactants) \]

Calculating \(\Delta G^\theta_{\text{reaction}}\) (for all \(T\))

\[ \Delta G^\theta_{\text{reaction}} = \Delta H^\theta_{\text{reaction}} - T \Delta S^\theta_{\text{reaction}} \]

\(T\) is 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.

- \(\Delta G_{\text{sys}}\) and thus the direction of change varies with temperature.

At low temp: \(\Delta G^\theta_{\text{system}} \approx \Delta H^\theta_{\text{system}}\): exothermic reactions are spontaneous.
At high temp: $\Delta G_{\text{system}}^\theta = -T\Delta S_{\text{system}}^\theta$; this allows some endothermic reactions to occur if $\Delta S_{\text{system}}^\theta > 0$. 