Other types of enthalpy change

**Enthalpy of combustion** - often referred to as the ‘Heat of combustion’

The enthalpy change when 1 mol of a compound reacts completely with excess oxygen gas.

*Example:* The combustion of 1 mol of methane gas at 25 °C evolves 890.3 kJ.

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \quad \Delta H^{\circ}_{298\text{comb.}} = -890.3 \text{ kJ mol}^{-1} \]

\(\Delta H^{\circ}_{298\text{combust}}\) are easy to measure and often used to determine \(\Delta H^{\circ}_{f,298}\) values.

*Example* combustion of methane

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \]

\(\Delta H^{\circ}_{\text{comb}} = [2\Delta H^{\circ}_f(\text{H}_2\text{O}) + \Delta H^{\circ}_f(\text{CO}_2)] - [\Delta H^{\circ}_f(\text{CH}_4) + 2\Delta H^{\circ}_f(\text{O}_2)]\)

\[-890.3 = [2 \cdot (-285.8) + (-393.5)] - [\Delta H^{\circ}_f(\text{CH}_4) + 2 \cdot (0)]\]

\[-890.3 = -965.1 - \Delta H^{\circ}_f(\text{CH}_4)\]

\(\Delta H^{\circ}_f(\text{CH}_4) = 74.8 \text{ kJ mol}^{-1}\)
Enthalpies of phase change

Much more detail to come later. Consider S, L, G for now.

**solid to liquid:** melting or *fusion*.

Liquid molecules have greater motion than solid - energy has to be added to the solid - fusion is an endothermic process.

*The enthalpy of fusion, $\Delta H^{\text{fus}}$ is the energy required at 1 bar pressure to melt 1 mole of a pure component at its melting point, $T_m$."

An earlier name, still in common usage is that $\Delta H^{\text{fus}}$ is the *latent heat of fusion*. It essentially represents the energy needed to overcome the intermolecular forces in the solid,

Also, $\Delta H(\text{freezing}) = - \Delta H(\text{fusion})$

**liquid $\rightarrow$ vapour - vaporization.**
\( \Delta H^{\text{vap}} \) is the energy required at 1 bar pressure to vaporize 1 mole of a pure liquid at its boiling point, \( T_b \).

Vaporization is also endothermic. \( \Delta H^{\text{vap}} \) is considerably larger than \( \Delta H^{\text{fus}} \) since the molecules are completely separated in vaporization whereas a considerable degree of intermolecular interaction remains in liquids.

Solid \( \rightarrow \) vapour - sublimation.

Some compounds do not display a liquid phase an example is solid carbon dioxide which, at atmospheric pressure, sublimates at \(-78 \, ^\circ \text{C}\).

\[ \Delta H^{\text{(sublimation)}} = \Delta H^{\text{(fusion)}} + \Delta H^{\text{(vaporization)}} \]
Calculate the energy required to turn 100 g of ice at 0 °C into steam at 100 °C.

The process required can be conveniently split into three parts.

1. 100 g ice → 100 g water at 0 °C \[ \Delta H_1 = \Delta H_{\text{fus}} \text{ for } 100 \text{ g} \]
2. 100 g water, 0 °C → 100 g water, 100 °C \[ \Delta H_2 = c_p \Delta T \text{ for } 100 \text{ g} \]
3. 100 g water, 100 °C → 100 g steam, 100 °C \[ \Delta H_3 = \Delta H_{\text{vap}} \text{ for } 100 \text{ g} \]

100 g of water = \( \frac{100}{18} \) mol = 5.56 mol

\[ \Delta H_{\text{total}} = \Delta H_1 + \Delta H_2 + \Delta H_3 \]

\[ \Delta H_{\text{total}} = 5.56 \text{ mol} \left[ + 6.01 \times 10^3 + 75.1 (373 - 273) + 40.7 \times 10^3 \right] \]

\[ \Delta H_{\text{total}} = 301.46 \text{ kJ (100g)}^{-1} \]

Note that the factor of \( 10^3 \) occurs in \( \Delta H_1 \) and \( \Delta H_3 \) since they are measured in kJ mol\(^{-1}\) while \( c_p \) is in J K\(^{-1}\) mol\(^{-1}\).
A Solution Calorimeter

- Thermometer
- Insulating jacket
- Tilting mechanism to mix reactants
- Reactant 2
- Reactant 1
The complete combustion of 2.0026 g of sucrose (C\(_{12}\)H\(_{22}\)O\(_{11}\)) in a bomb calorimeter with a heat capacity of 11140 JK\(^{-1}\) at 25 °C resulted in a temperature increase of 2.966 °C. Calculate ∆H\(_{\text{combustion}}\) for sucrose.

The energy released on combustion is given by (11140 JK\(^{-1}\) \times 2.966 K) = 33.041 kJ

Since the bomb calorimeter is a constant volume device, this gives ∆U\(_{\text{combustion}}\). The experiment used 5.85 \times 10\(^{-3}\) moles.

Hence, ∆U\(_{\text{combustion}}\) = - 33.041 / 5.85 \times 10\(^{-3}\) = - 5647.5 kJ mol\(^{-1}\)

The chemical equation for the reaction is C\(_{12}\)H\(_{22}\)O\(_{11}\)\(_{(s)}\) + 12 O\(_2\)\(_{(g)}\) → 12 CO\(_2\)\(_{(g)}\) + 11 H\(_2\)O\(_{(l)}\)

so the number of moles of gas is the same before and after the reaction. Hence, ∆n\(_{\text{gas}}\) = 0 and ∆H\(_{\text{combustion}}\) = ∆U\(_{\text{combustion}}\)

∴ ∆H\(_{\text{combustion}}\) = - 5647.5 kJ mol\(^{-1}\)
Entropy in Chemistry

Can we predict:
- If a reaction or process can occur?
- How will it proceed?
- How fast will it go?

Thermodynamics tells us nothing about rates but tells everything about the rest.

So what determines whether things happen?

Systems generally try to minimise the energy but that isn’t the whole story.

Consider:
- isothermal expansion of an ideal gas \( \Delta U = 0 \)
- gas flows from high pressure to low
- heat flows from hot to cold
- gases, fluids diffuse into each other
- \( H_2 + O_2 \rightarrow H_2O \)

All these processes are SPONTANEOUS.
Another factor plays a part in determining whether reactions happen

The entropy, \( S \).

The easiest way to consider entropy is to consider the molecular state of the system.

Each physical situation (water later) results in a more random distribution of matter.

We describe the entropy as a measure of this randomness or \textit{disorder} of the system. A fundamental definition of entropy is given by \textit{the Boltzmann equation}.

\[
S = k_B \ln \omega
\]

where \( \omega \) is the number of ways of arranging the molecules of the system and \( k_B \) is the \textit{Boltzmann constant}.

The larger the number of arrangements, or the less organised the system, the larger the entropy.