

1. Hess's Law

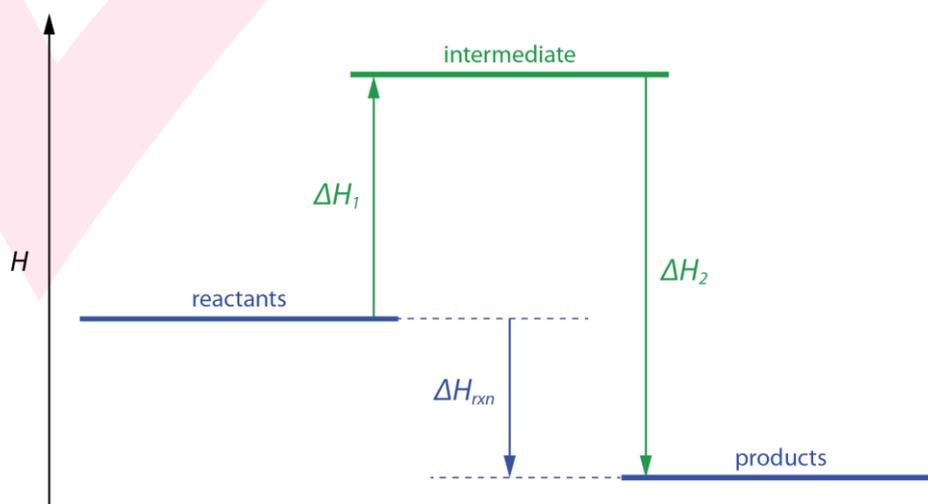
Students:

- investigate Hess's Law in quantifying the enthalpy change for a stepped reaction using standard enthalpy change data and bond energy data, for example:
 - carbon reacting with oxygen to form carbon dioxide via carbon monoxide
- apply Hess's Law to simple energy cycles and solve problems to quantify enthalpy changes within reactions, including but not limited to:
 - heat of combustion
 - enthalpy changes involved in photosynthesis
 - enthalpy changes involved in respiration

□ Hess's Law of Heat Summation

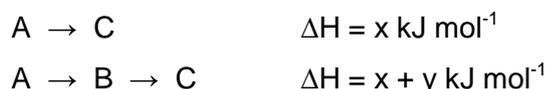
- The change in enthalpy accompanying many reactions can be experimentally measured using calorimetry.
- However, some reactions are difficult to conduct, so their enthalpy changes **cannot be directly measured** in calorimetric experiments.
- We can instead calculate their enthalpy changes using **Hess's Law**:

The total enthalpy change in a chemical reaction is constant, whether the reaction is performed in one step or several steps.



- ΔH is **pathway-independent**. It only depends on the relative enthalpies of the reactants and products.
- H is therefore called a **state function**, as opposed to a path function.

- Hess's Law is a form of the **law of conservation of energy** (first law of thermodynamics).
 - Suppose that Hess's Law was not true, and the energy required to convert A to C directly was less than the energy required to convert A to C through an intermediate B:



- Going backwards, converting C to A through B would produce $x + y$ energy:

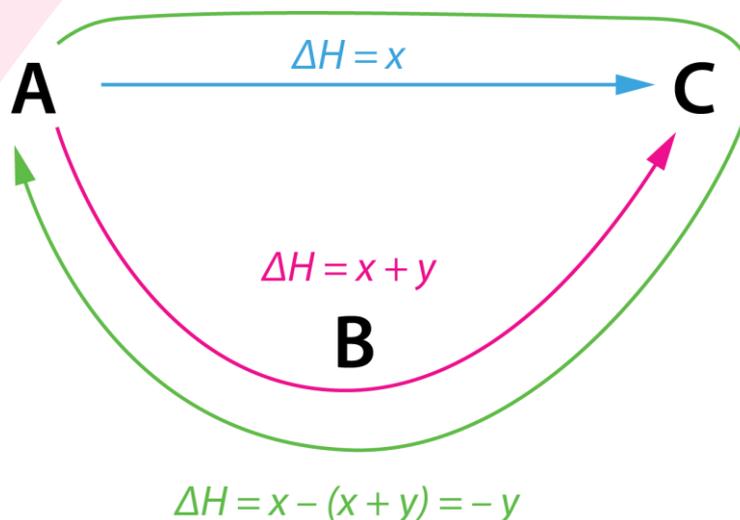


- If we converted A to C, then back to A through B, we would have turned A into A plus energy:



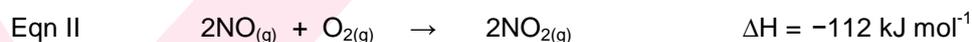
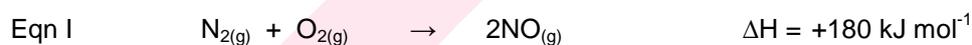
$$\text{Total } \Delta H = -y \text{ kJ mol}^{-1}$$

- Hence we would have created energy out of nothing, therefore Hess's Law must be true if the law of conservation of energy is true.



□ Using Hess's Law for Energy Cycles

- If we know the enthalpy changes of the **intermediate steps** for a reaction, we can use Hess's Law to determine the enthalpy of reaction.
- In other words, if a chemical equation can be written as the **sum of other chemical equations**, its enthalpy change equals the **sum of the enthalpy changes** of the other chemical equations.
- For example, we can work out ΔH for the overall equation for the synthesis of NO_2 from its elements using Hess's Law.
 - The two intermediate steps are shown below.
 - Add the two equations together, cancelling out any terms that appear on both sides.
 - Then add the enthalpy changes together to determine the value of the enthalpy change for the summed equation.



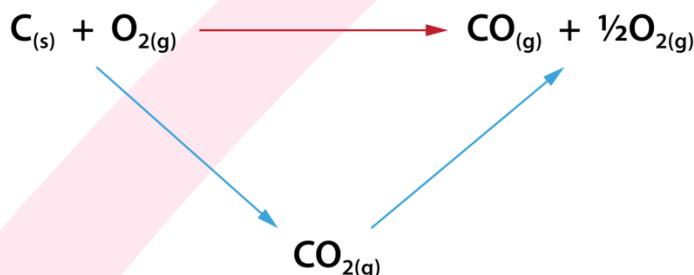
- Sometimes you will need to make additional transformations.
- For example, it is difficult to combust carbon to carbon monoxide (it will usually combust further to form some carbon dioxide), so its enthalpy of reaction cannot be determined experimentally:



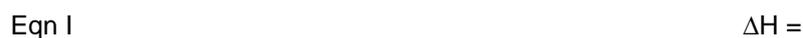
- However, it is easy to combust carbon to carbon dioxide, and carbon monoxide to carbon dioxide:



- Using Hess's Law, we can work out ΔH for Eqn I if we calculate the enthalpy changes required to convert carbon to carbon dioxide, then back to carbon monoxide:



- We take the reverse of Eqn III and combine it with Eqn II.
 - Complete the missing values below.

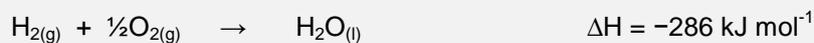
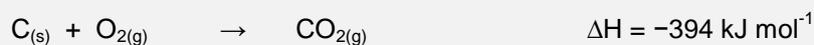


Note to students

- ΔH for the **reverse** reaction is the **negative** of the ΔH for the forward reaction.
- When you **multiply** an equation by a coefficient, you must also **multiply the ΔH** .

EXAMPLE

The standard enthalpies of combustion for carbon, hydrogen and methane are shown below:



Calculate the standard enthalpy for the synthesis of methane from its elements ($\text{C}_{(s)}$ and $\text{H}_{2(g)}$).¹

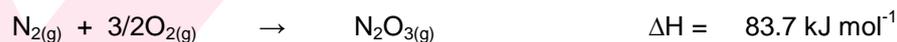


Step 1. Analyse what must happen to each of the given equations to get the target equation.

Step 2. Perform the necessary transformations to both the equations and the ΔH values.

Step 3. Add the ΔH values to determine the final answer.

- Given the following data:



- Calculate the enthalpy change for the decomposition of dinitrogen trioxide:²



□ Standard Enthalpy Change Data

- When discussing enthalpy changes, we usually refer to the values obtained under standard conditions, with all substances in their standard states.
- This is known as the **standard enthalpy change**, ΔH^\ominus . The Plimsoll symbol \ominus is used to indicate that **standard conditions** are used:
 - Pressure of **100 kPa**
 - Concentration of **1 mol L⁻¹** for aqueous solutions
 - A temperature of **298.15 K (25 °C)** is usually used
 - Substances are in their **standard states** (their most stable form under standard conditions)
- There are a few common reactions where standard enthalpy data is readily available. You will need to be familiar with these definitions:
- **Standard enthalpy of formation ΔH_f^\ominus** refers to the enthalpy change when one mole of a substance is formed from its elements at standard state, under standard conditions. It is usually (but not always) negative.
 - The standard enthalpy of formation for silver bromide is $-99.5 \text{ kJ mol}^{-1}$. Write a balanced chemical equation for this reaction, with its ΔH value.³

 - The standard enthalpy of formation for carbon dioxide is $-393.5 \text{ kJ mol}^{-1}$. Write a balanced chemical equation for this reaction, with its ΔH value.⁴

- **Standard enthalpy of combustion ΔH_c^\ominus** refers to the enthalpy change when one mole of a substance undergoes complete combustion with oxygen, under standard conditions with everything in its standard state.
 - The standard enthalpy of combustion for methane gas is -882 kJ mol^{-1} . Write a balanced chemical equation for this reaction, with its ΔH value.⁵
