Cambridge (CIE) A Level Chemistry

Your notes

Hess's Law

Contents

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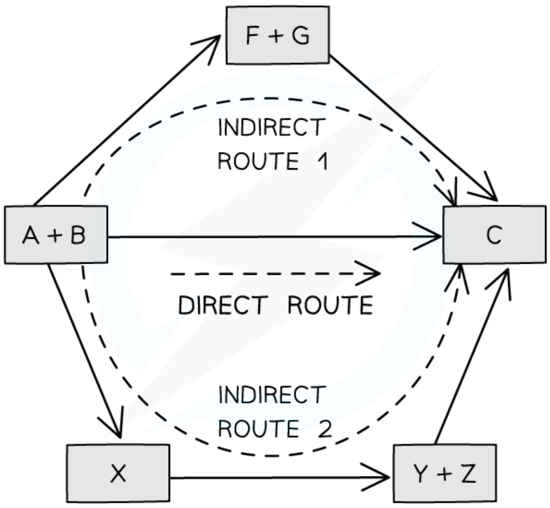
Hess Cycles

- **Hess's Law** states that:

"The total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same."

- This means that whether the reaction takes place in one or two steps, the total enthalpy change of the reaction will still be the same

Illustration of Hess's Law



According to Hess' Law, the enthalpy change of the direct route, going from reactants (A+B) to product (C), is equal to the enthalpy change of the indirect routes

- Hess' Law is used to calculate enthalpy changes which can't be found experimentally using **calorimetry**, e.g.:

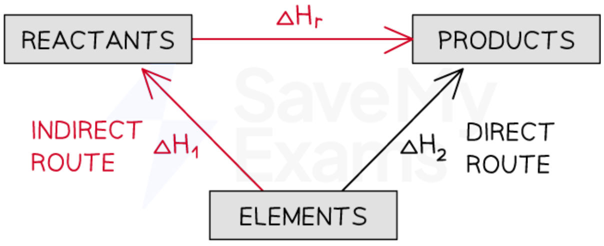
$$3C\ (s) + 4H_2\ (g) \rightarrow C_3H_8(g)$$

- ΔH_f (propane) can't be found experimentally as hydrogen and carbon don't react under standard conditions

Calculating ΔH_r from ΔH_f using Hess's Law energy cycles

- The products can be directly formed from the elements = ΔH_2 **OR** The products can be indirectly formed from the elements = $\Delta H_1 + \Delta H_r$

Applying Hess's Law



The enthalpy change from elements to products (direct route) is equal to the enthalpy change of elements forming reactants and then products (indirect route)

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- **Equation**

$$\Delta H_2 = \Delta H_1 + \Delta H_r$$

Therefore,

$$\Delta H_r = \Delta H_2 - \Delta H_1$$

Worked Example

Calculate ΔH_r for the following reaction:

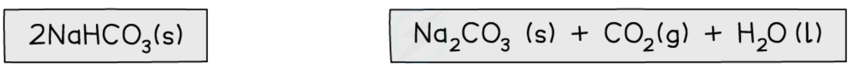
$$2NaHCO_3\,(s) \rightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(l)$$

The table shows the standard enthalpy of formations, $\Delta H^{\theta}{}_f$, relevant to this reaction.

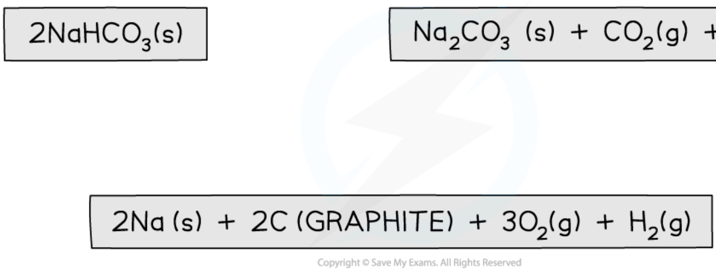
Molecule	$\Delta H^{\theta}{}_f$ kJ mol^{-1}
$NaHCO_3$ (s)	-950.8
Na_2CO_3 (s)	-1130.7
CO_2 (g)	-393.5
H_2O (l)	-285.8

Answer

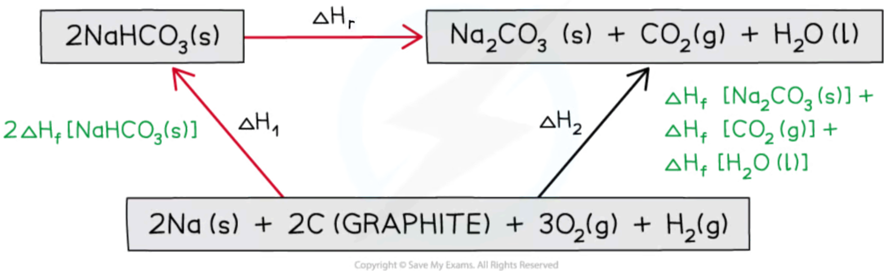
- **Step 1:** Write the balanced equation at the top



- **Step 2:** Draw the cycle with the elements at the bottom



- **Step 3:** Draw in all arrows, making sure they go in the correct directions. Write the standard enthalpy of formations

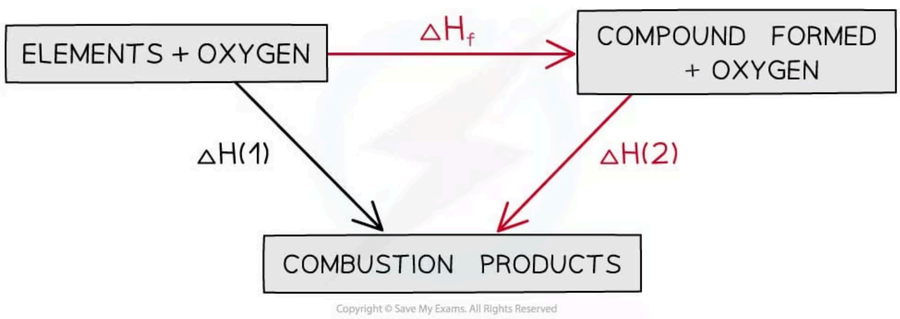


- **Step 4:** Apply Hess's Law:
  - $\Delta H_r = \Delta H_2 - \Delta H_1$
  - $\Delta H_r = (\Delta H_f[Na_2CO_3(s)] + \Delta H_f[CO_2(g)] + \Delta H_f[H_2O(l)]) - 2\Delta H_f[NaHCO_3(s)]$
  - $\Delta H_r = ((-1130.7) + (-393.5) + (-285.8)) - (2 \times -950.8)$
  - $\Delta H_r = +91.6$ kJ mol^{-1}

Calculating ΔH$_f$ from ΔH$_c$ using Hess's Law energy cycles

- The combustion products can be formed directly from elements to combustion products = **ΔH$_1$** **OR** The combustion products can be formed indirectly from elements to compounds to combustion products = **ΔH$_f$ + ΔH$_2$**

Hess's Law and combustion enthalpies



The enthalpy change going from elements to products (direct route) is equal to the enthalpy change of elements forming reactants and then products (indirect route)

Your notes

- **Equation**

$$\Delta H_1 = \Delta H_f + \Delta H_2$$

- Therefore,

$$\Delta H_f = \Delta H_1 - \Delta H_2$$

Your notes

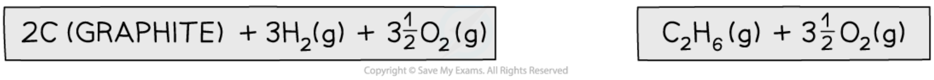
Worked Example

Calculate, using the standard enthalpy change of combustion values given, the enthalpy of formation of ethane.

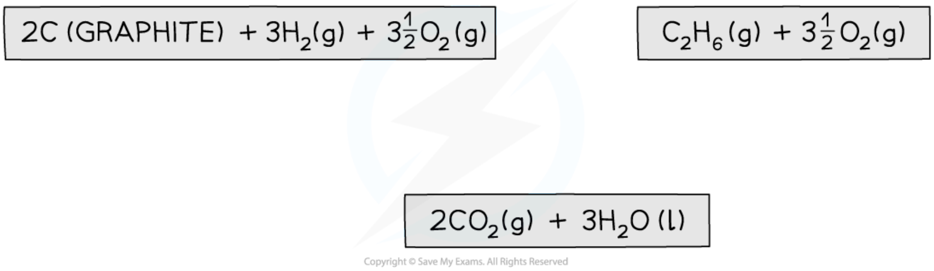
Reaction	**ΔH_c kJ mol^{-1}**
C (graphite) + O_2 (g) → CO_2 (g)	–393.5
H_2 (g) + ½O_2 (g) → H_2O (l)	–285.8
C_2H_6 (g) + 3½O_2 (g) → 2CO_2 (g) + 3H_2O (l)	–1559.7

Answer

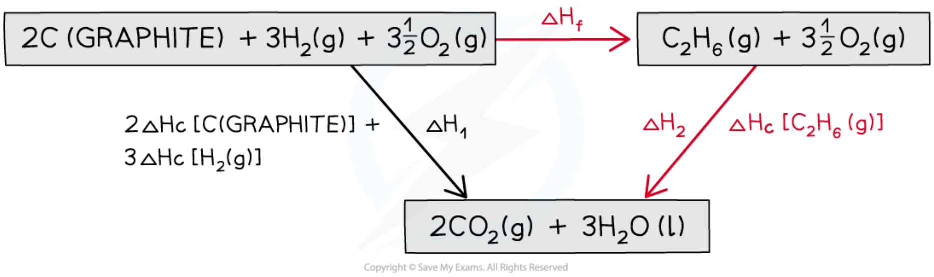
- **Step 1:** Write the equation for the enthalpy change of formation at the top and add oxygen on both sides



- **Step 2:** Draw the cycle with the combustion products at the bottom



- **Step 3:** Draw all arrows in the correct direction



- **Step 4:** Apply Hess's Law:
    - $\Delta H_f = \Delta H_1 - \Delta H_2$
    - $\Delta H_f = ((2 \times -393.5) + (3 \times -285.8)) - (-1559.7)$
    - $\Delta H_f = -84.7$ kJ mol^{-1}

Your notes

Calculating average bond energies using Hess's cycles

- Bond energies cannot be found directly so enthalpy cycles are used to find the **average bond energy**
- This can be done using enthalpy changes of **atomisation** and **combustion** or **formation**
- The **enthalpy change of atomisation** (ΔH^{θ}_{at}) is the enthalpy change when **one mole of gaseous** atoms is **formed** from its elements under standard conditions.
    - E.g. ΔH^{θ}_{at} [H_2] relates to the equation:

$$\frac{1}{2}H_2\,(g) \rightarrow H\,(g)$$

Worked Example

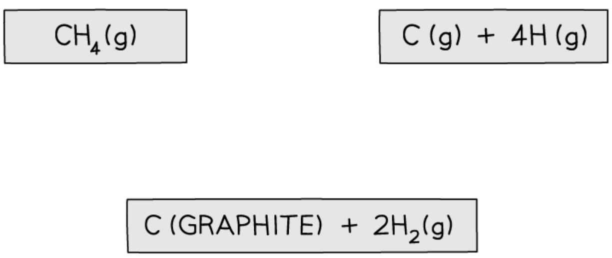
Calculate the average bond enthalpy of the C–H bond, using the relevant ΔH^{θ}_f and ΔH^{θ}_{at} values shown in the table.

	Energy kJ mol^{-1}
ΔH^{θ}_f [CH_4 (g)]	–74.8
ΔH^{θ}_{at} [½H_2 (g)]	+218
ΔH^{θ}_{at} [C (graphite)]	+717.7

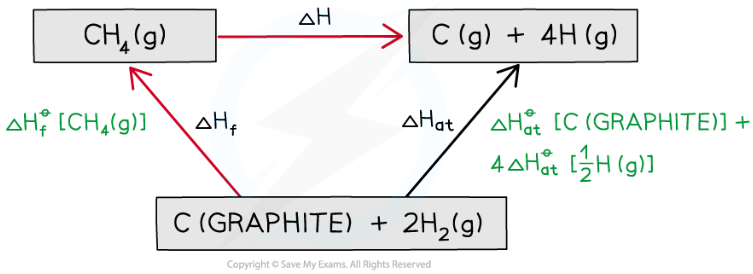
Answer

- **Step 1:** Write down the equation for the dissociation of methane at the top

- **Step 2:** Write down the elements at the bottom



- **Step 3:** Draw all arrows in the correct direction



- **Step 4:** Apply Hess's Law:
  - $\Delta H = \Delta H^\theta{}_{at} - \Delta H_f$
  - $\Delta H = ((+717.7) + (4 \times 218)) - (-74.8)$
  - $\Delta H_f = +1664.5$ kJ mol^{-1}
- **Step 5:** Calculate the bond energy for **one** C–H bond
  - There there are 4 C-H bonds in methane
  - Average bond enthalpy (C–H) = $\frac{+1664.5}{4}$
  - Average bond enthalpy (C–H) = +416 kJ mol^{-1} (to 3 significant figures)

Examiner Tips and Tricks

- Remember to take into account the number of moles of each reactant and product.
- For example, there are two moles of $NaHCO_3$ (s) so the ΔH_f value is multiplied by 2.

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