DP IB Chemistry: HL

Your notes

5.2 Hess's Law

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5.2.1 Hess's Law

Your notes

Hess's Law

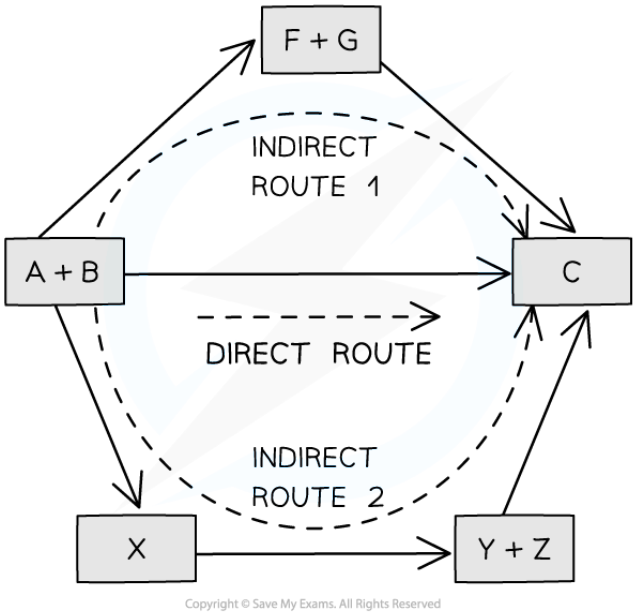
- In 1840, the Russian chemist Germain Hess formulated a law which went on to be known as **Hess's Law**
- This went on to form the basis of one of the laws of thermodynamics. The first law of thermodynamics relates to the **Law of Conservation of Energy**
- It is sometimes expressed in the following form:

> ***Energy cannot be created or destroyed, it can only change form***

- This means that in a closed system, the total amount of energy present is always constant
- Hess's law can be used to calculate the standard enthalpy change of a reaction from known standard enthalpy changes
- **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



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The diagram above illustrates 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

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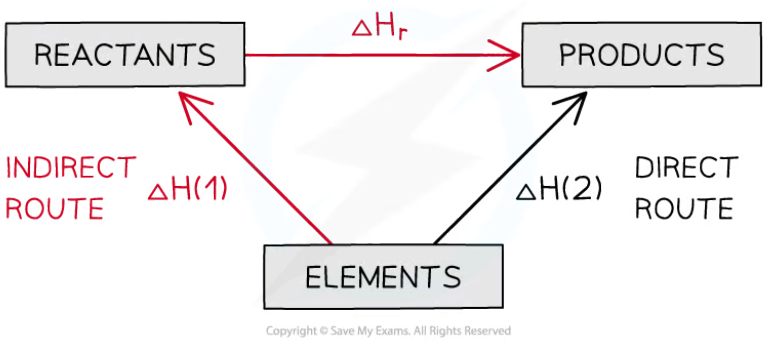
- Hess' Law is used to calculate enthalpy changes which can't be found experimentally using **calorimetry**, eg:

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

- [popover id="dGQl3oDiqUlQrR1A" label="ΔH_f"] , 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

- You can see the relationships on the following diagram:



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

- The products can be directly formed from the elements = ΔH_2

OR

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

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

Therefore for energy to be conserved,

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

Examiner Tip

You do not need to learn Hess's Law word for word as it is not a syllabus requirement, but you do need to understand the principle as it provides the foundation for all the problem solving in Chemical Energetics

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5.2.2 Using Hess's Law - Cycles

Your notes

Hess's Law using Cycles

- There are two common methods to solving Hess's Law problems, using cycles and using equations
- To be successful in using cycles you need to follow carefully a step-by-step plan using the information in the question to construct a cycle and add the given information
- The following example shows one way to lay out your solution:

Worked example

Calculate the enthalpy of reaction for

$$2N_2(g) + 6H_2(g) \rightarrow 4NH_3(g)$$

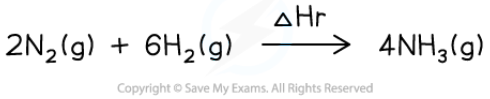
Given the data:

$$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(l), \quad \Delta H_1 = -1530 \text{ kJ mol}^{-1}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l), \quad \Delta H_2 = -288 \text{ kJ mol}^{-1}$$

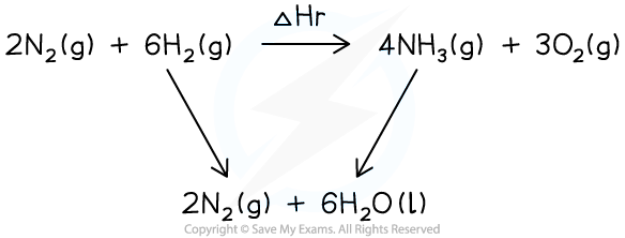
Answer:

- Begin by writing the target enthalpy change at the top of your diagram from left to right:



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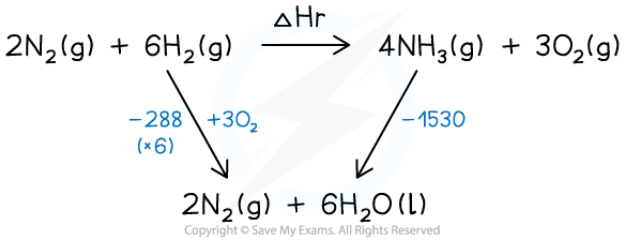
- Next, write the alternative route at the bottom of your cycle and connect the top and bottom with arrows pointing in the correct directions:



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- Add the enthalpy data and adjust, as necessary, for different molar amounts

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Your notes

- Write the Hess's Law calculation out:

$$\Delta H_r = +6\Delta H_2 - \Delta H_1 = +(-288 \times 6) - (-1530) = -198 \text{ kJ}$$

- Two important rules:
  - If you follow the direction of the arrow you **ADD** the quantity
  - If you go against the arrow you **SUBTRACT** the quantity

Worked example

What is the enthalpy change, in kJ, for the reaction below?

$4FeO(s) + O_2(g) \rightarrow 2Fe_2O_3(s)$

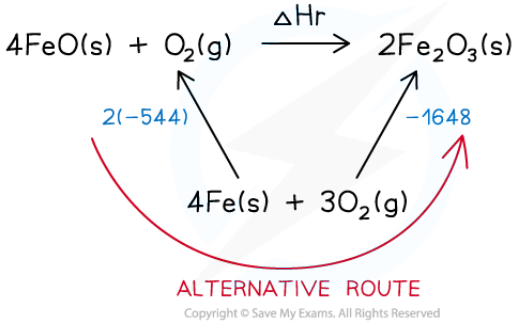
Given the data:

$2Fe(s) + O_2(g) \rightarrow 2FeO(s)$ $\Delta H = -544$ kJ

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ $\Delta H = -1648$ kJ

Answer:

- Draw the Hess cycle and add the known values



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- Write the Hess's Law calculation out:

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Follow the alternative route and the process the calculation

$$\Delta H_r = -(-544 \times 2) + (-1648) = -560 \text{ kJ}$$


Your notes

Examiner Tip

It is very important you get the arrows in the right direction and that you separate the mathematical operation from the sign of the enthalpy change. Many students get these problems wrong because they confuse the signs with the operations. To avoid this always put brackets around the values and add the mathematical operator in front

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5.2.3 Using Hess's Law - Equations

Your notes

Hess's Law using Equations

- We can use Hess's Law to solve unknown enthalpy changes by combining equations
- This requires a methodical step-by-step approach
- It is necessary to identify how the given equations relate to the target equation as the following example illustrates

Solving Hess's Law problems using equations step-by-step :

Worked example

Consider the following reactions.

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H = +180$ kJ

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ $\Delta H = +112$ kJ

What is the *ΔH value, in kJ, for the following reaction?*

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$

Answer:

1. Identify which given equation contains the product you want

This equation contains the desired product on the left side:

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ $\Delta H = +112$ kJ

2. Adjust the equation if necessary, to give the same product. If you reverse it, **reverse the ΔH value**

Reverse it and reverse the sign

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H = -112$ kJ

3. Adjust the equation if necessary, to give the same number of moles of product

The equation contains the same number of moles as in the question, so no need to adjust the moles

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Next steps

4. Identify which given equation contains your reactant

This equation contains the reactant

$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H = +180\ kJ$

5. Adjust the equation if necessary, to give the same reactant. If you reverse it, reverse the ΔH value

No need to reverse it as the reactant is already on the left side

6. Adjust the equation if necessary, to give the same number of moles of reactant

Final steps

7. Add the two equations together

$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H = +180\ kJ$

$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \quad \Delta H = -112\ kJ$

8. Cancel the common items

$N_2(g) + O_2(g) + \cancel{2NO(g)} + O_2(g) \rightarrow \cancel{2NO(g)} + 2NO_2(g)$

9. Add the two ΔH values together to get the one you want

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \quad \Delta H = +180 - 112 = +68\ kJ$

Your notes

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Your notes

Worked example

The enthalpy changes for two reactions are given.

$Br_2(l) + F_2(g) \rightarrow 2BrF(g) \quad \Delta H = x\ kJ$

$Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(g) \quad \Delta H = y\ kJ$

What is the enthalpy change for the following reaction?

$BrF(g) + F_2(g) \rightarrow BrF_3(g)$

A. x – y

B. y - x

C. ½ (–x + y)

D. ½ (x – y)

Answer:

The correct option is **C**.

- The second equation contains the desired product, but it needs to be halved to make 1 mole

  $Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(g) \quad \Delta H = y$ becomes

  $\mathbf{½Br_2(l) + 1½F_2(g) \rightarrow BrF_3(g) \quad ½\Delta H = ½y}$

- The first equation contains the reactant, but it needs to be reversed and halved:

  $Br_2(l) + F_2(g) \rightarrow 2BrF(g) \quad \Delta H = x$ becomes

  $\mathbf{BrF(g) \rightarrow ½Br_2(l) + ½F_2(g) \quad ½\Delta H = -½x}$

- Combine the two equations and cancel the common terms:

  $\cancel{½Br_2(l)} + 1½F_2(g) \rightarrow BrF_3(g) \quad ½\,\Delta H = y\ kJ$

  $BrF(g) \rightarrow \cancel{½Br_2(l)} + \cancel{½F_2(g)} \quad ½\ \Delta H = -x\ kJ$

  $\mathbf{BrF(g) + F_2(g) \rightarrow BrF_3(g) \quad \Delta H = ½y + -½x = ½(-x + y)}$

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Examiner Tip

If doesn't matter whether you use equations or cycles to solve Hess's Law problems, but you should be familiar with both methods and sometimes one is easier than another



Your notes

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5.2.4 Using ΔHf° to Find Enthalpy Changes

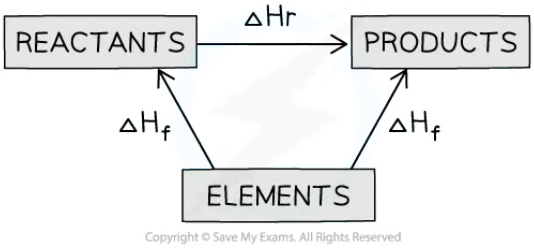
Your notes

Using ΔHf° to Find Enthalpy Changes

- Standard Enthalpy of Formation is defined as

> **"The enthalpy change when one mole of a compound is formed from its elements under standard conditions"**

- We can use enthalpy of formation of substances to find an unknown enthalpy change using a Hess cycle
- In this type of cycle the elements are always placed at the bottom of the diagram



Enthalpy changes using enthalpy of formation

- In this cycle the arrows will always be pointing upwards because the definition of the enthalpy of formation must go from elements to compounds
- This means the Hess's Law calculation of ΔH will always be in the same arrangement

$$\Delta H_r = \Sigma \Delta H_{f\ products} - \Sigma \Delta H_{f\ reactants}$$

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- Try the following worked example:

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Worked example

Given the data:

Substance	$B_2H_6(g)$	$B_2O_3(g)$	$H_2O(g)$
ΔH_f / kJ mol^{-1}	+31.4	−1270	−242

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Calculate the enthalpy of combustion of gaseous diborane given that it burns according to the following equation:

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$$

Answer

Step 1: Find the sum of the enthalpies of combustion of the products

$\Delta H_f = +(-1270) + (-242 \times 3) = -1996$ kJ

Step 2: Find the sum of the enthalpies of combustion of the reactants

$\Delta H_f = +(+31.4) + 0 = +31.4$ kJ

There is no enthalpy of formation for oxygen as ΔH_f of elements by definition is zero

Step 3: Calculate the enthalpy change

$\Delta H = \Delta H_{f\ products} - \Delta H_{f\ reactants} = -1996 - (+31.4) =$ **−2027.4 kJ**

Examiner Tip

In Paper 1, Enthalpy of Formation data will given in the question. For Paper 2, you may need to refer to Section 12 of the Data Booklet where you will find Thermodynamic Data for Selected Compounds

Your notes

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