

# Heat changes, energy cycles and bond enthalpies

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

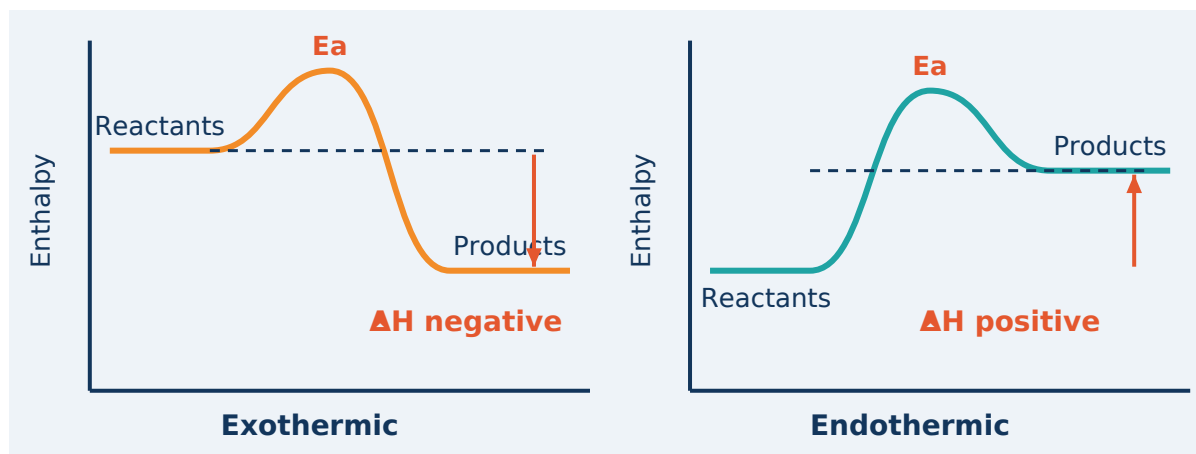
**Quick answer:** An enthalpy change  $\Delta H$  is the heat transferred at constant pressure; it is negative for exothermic reactions. Calorimetry gives it from  $q = mc\Delta T$  and  $\Delta H = -q/n$ . Hess's law says  $\Delta H$  is route independent, so it can be found from formation or combustion data or estimated from bond enthalpies.

**Level:** Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** IB R1.1-R1.2

## What is an enthalpy change?

### Definition

The enthalpy change  $\Delta H$  is the heat energy transferred between a reacting system and its surroundings at constant pressure. It is negative for an exothermic reaction (heat released) and positive for an endothermic reaction (heat absorbed). Standard values refer to 100 kPa and a stated temperature, usually 298 K.

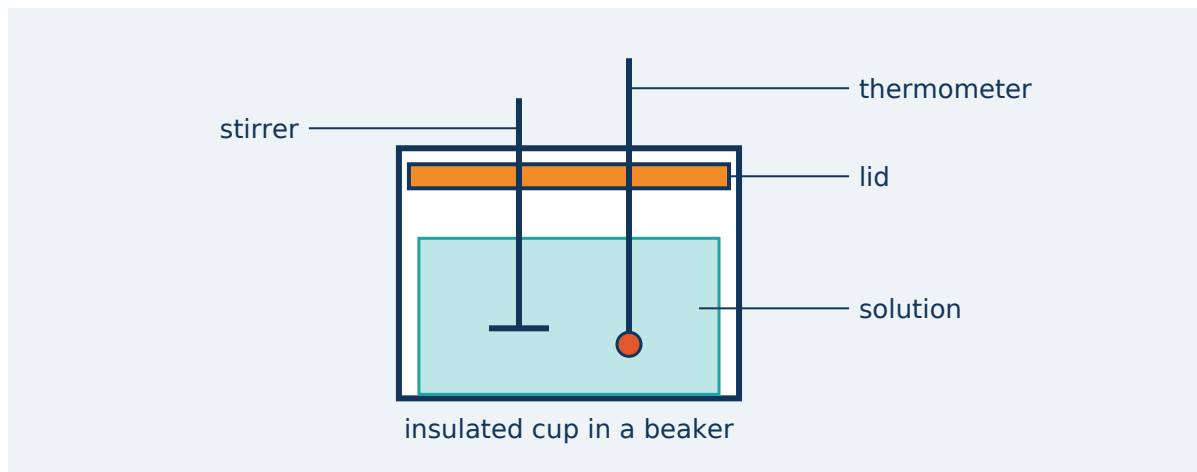


Enthalpy profiles: the sign of  $\Delta H$  is the product level minus the reactant level.

| Enthalpy change          | Meaning (per mole)                                                       | Typical sign     |
|--------------------------|--------------------------------------------------------------------------|------------------|
| Formation, $\Delta H_f$  | One mole of a compound formed from its elements in their standard states | Usually negative |
| Combustion, $\Delta H_c$ | One mole of a substance burned completely in oxygen                      | Always negative  |
| Neutralisation           | One mole of water formed from an acid and an alkali                      | Negative         |

## How do you find $\Delta H$ from a temperature change?

In a calorimeter the heat absorbed by the water is  $q$ , and the reaction transferred the same amount in the opposite direction. Divide by the amount of the limiting reactant to get  $\Delta H$  per mole.



*A simple calorimeter: the lid and insulation reduce heat loss.*

### Formula

$$q = m \times c \times \Delta T \text{ and } \Delta H = -q / n$$

$q$  = heat absorbed by the solution (J),  $m$  = mass of solution (g),  $c = 4.18 \text{ J/(g K)}$ ,  $\Delta T$  = temperature change (K),  $n$  = moles of limiting reactant (mol),  $\Delta H$  in J/mol (divide by 1000 for kJ/mol).

### Worked example

Hannah in Boston mixes  $40.0 \text{ cm}^3$  of  $1.50 \text{ mol/dm}^3$  nitric acid with  $40.0 \text{ cm}^3$  of  $1.50 \text{ mol/dm}^3$  potassium hydroxide. The temperature rises by  $10.0 \text{ K}$ .

Mass =  $80.0 \text{ g}$ , so  $q = 80.0 \times 4.18 \times 10.0 = 3344 \text{ J}$ . Moles =  $0.0400 \times 1.50 = 0.0600 \text{ mol}$ .

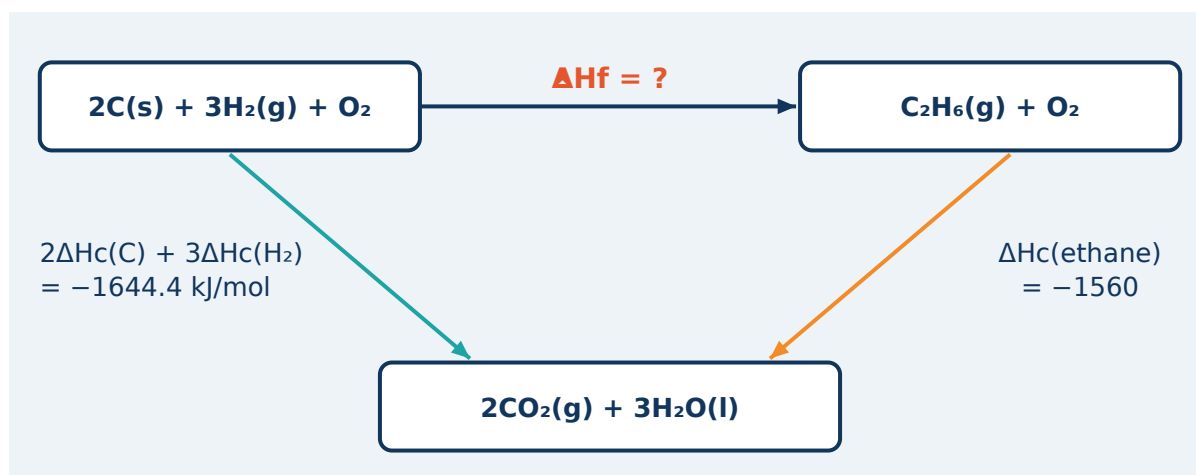
$\Delta H = -3344 / 0.0600 = -55\,733 \text{ J/mol} = \mathbf{-55.7 \text{ kJ/mol}}$ .

## What does Hess's law say?

### Key law

Hess's law: the total enthalpy change of a reaction is the same whichever route is taken, provided the initial and final conditions are the same. So  $\Delta H$  of a reaction equals the sum of  $\Delta H$  values of any route linking the same reactants and products.

For combustion data the working is  $\Delta H = \sum \Delta H_c(\text{reactants}) - \sum \Delta H_c(\text{products})$ . For formation data it is  $\Delta H = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$ .



Hess cycle:  $\Delta H_f = (-1644.4) - (-1560) = -84.4 \text{ kJ/mol}$ .

### Worked example

Calculate  $\Delta H_f$  of ethane from  $\Delta H_c$ : carbon  $-393.5$ , hydrogen  $-285.8$ , ethane  $-1560 \text{ kJ/mol}$ .

Route through the elements burning:  $2(-393.5) + 3(-285.8) = -787.0 - 857.4 = -1644.4 \text{ kJ}$ .  $\Delta H_f = -1644.4 - (-1560) = \mathbf{-84.4 \text{ kJ/mol}}$ .

## How do bond enthalpies estimate $\Delta H$ ?

### Definition

Mean bond enthalpy is the average energy needed to break one mole of a given bond in gaseous molecules. Breaking bonds absorbs energy and making bonds releases it, so  $\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$ .

| Bond | Mean enthalpy (kJ/mol) | Bond                    | Mean enthalpy (kJ/mol) |
|------|------------------------|-------------------------|------------------------|
| H-H  | 436                    | C=O (in $\text{CO}_2$ ) | 805                    |
| O=O  | 498                    | O-H                     | 464                    |
| C-H  | 413                    | C-C                     | 347                    |
| C=C  | 612                    | H-Cl                    | 432                    |

### Worked example

Estimate  $\Delta H$  for  $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(g)}$ .

Broken:  $2 \times 436 + 498 = 1370 \text{ kJ}$ . Formed:  $4 \times 464 = 1856 \text{ kJ}$ .  $\Delta H = 1370 - 1856 = \mathbf{-486 \text{ kJ}}$  (for the equation as written).

### Common mistake

Do not use the mass of the solid in  $q = m c \Delta T$ : the heated mass is the solution or water. Also do not forget the minus sign in  $\Delta H = -q / n$ : a temperature rise means an exothermic reaction and a negative  $\Delta H$ .

**Lina's tip**

Draw the Hess cycle before you calculate. Label each arrow with its  $\Delta H$ , then follow the two routes. Arrows against the arrow direction change sign.

Bond enthalpy results are approximate because the values are means taken from many compounds and refer to the gas phase, so they differ a little from calorimetric data.

**Key points to remember**

- $q = m c \Delta T$  with  $c = 4.18 \text{ J/(g K)}$ ;  $\Delta H = -q / n$  in  $\text{J/mol}$ .
- Hess's law:  $\Delta H$  depends only on the initial and final states, not on the route.
- $\Delta H = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$  and  $\Delta H = \sum \Delta H_c(\text{reactants}) - \sum \Delta H_c(\text{products})$ .
- Bond enthalpies:  $\Delta H = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$ , a gas-phase estimate.
- Exothermic reactions have  $\Delta H$  below zero; endothermic reactions have  $\Delta H$  above zero.

## Heat changes, energy cycles and bond enthalpies: frequently asked questions

### What is the difference between enthalpy of formation and combustion?

Formation is the enthalpy change when one mole of a compound forms from its elements in their standard states. Combustion is the change when one mole of a substance burns completely in oxygen.

### Why is $\Delta H$ negative for an exothermic reaction?

The products have less enthalpy than the reactants because heat is released to the surroundings.  $\Delta H$  is the enthalpy of products minus reactants, so it is below zero.

### How do you use Hess's law with an energy cycle?

Draw the cycle with the unknown enthalpy change on one arrow and known values on the others. Add the values along one route and compare it with the other route, changing the sign of any arrow followed backwards.

### Why are bond enthalpy results only approximate?

Mean bond enthalpies are averages over many different molecules and apply to gases. The real bond energy in a particular molecule differs a little, so the result differs from calorimetric values.

### Why is heat loss a problem in calorimetry?

Some heat escapes to the surroundings, so the measured temperature change is too small. The calculated  $\Delta H$  is then less exothermic than the true value. Lids, insulation and graph extrapolation reduce the error.