

Heat, enthalpy and Hess's law

AP Chemistry · Lesson

Quick answer: Thermochemistry measures heat changes in reactions. At constant pressure the heat is the enthalpy change ΔH : negative for exothermic, positive for endothermic. Calorimetry uses $q = mc\Delta T$, then divides by moles. Hess's law adds step enthalpies, and ΔH can also come from formation enthalpies or bond enthalpies.

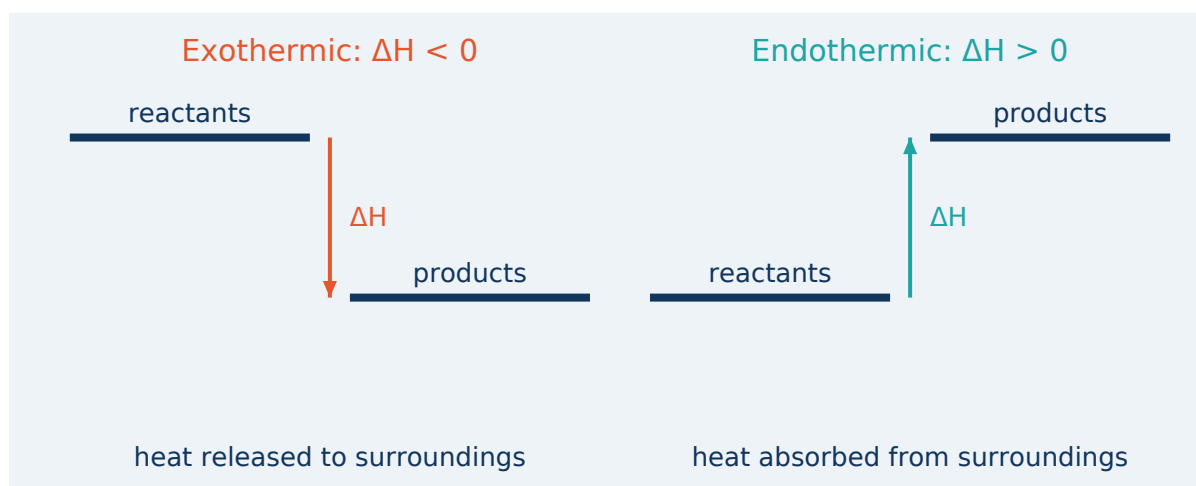
Level: AP Chemistry · **Curriculum:** AP Chem Unit 6

What is an enthalpy change?

At constant pressure, the heat exchanged with the surroundings in a reaction is the enthalpy change ΔH . An exothermic reaction releases heat ($\Delta H < 0$) and the surroundings warm up; an endothermic reaction absorbs heat ($\Delta H > 0$) and they cool down.

Definition

Enthalpy change $\Delta H = H(\text{products}) - H(\text{reactants})$, in kJ/mol of reaction as written. The **standard enthalpy of formation** ΔH_f° is the enthalpy change when 1 mol of a compound forms from its elements in their standard states; for an element in its standard state it is 0.



ΔH is the enthalpy of products minus the enthalpy of reactants; its sign shows the direction of heat flow.

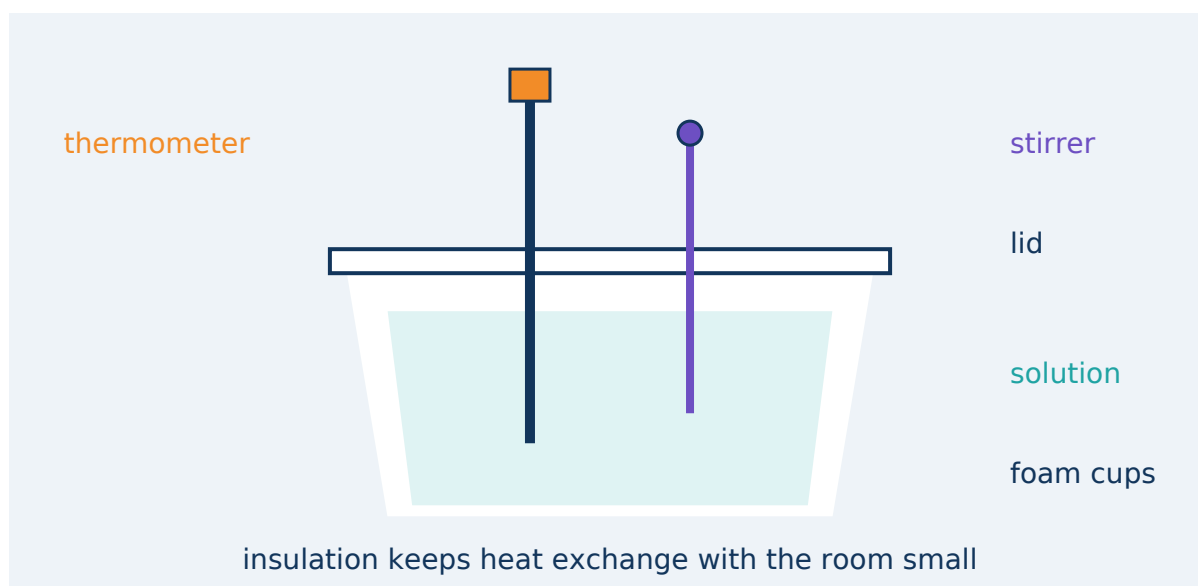
How does calorimetry measure heat?

A calorimeter isolates the reaction so that its heat goes into a known mass of water. We use $q = mc\Delta T$, then divide by the amount in moles to get ΔH . The heat gained by the solution is equal in size and opposite in sign to the heat released by the reaction.

Calorimetry

$q = mc\Delta T$, with q in J, m in g, c in J/(g °C) (4.18 for dilute solutions) and $\Delta T = T_{\text{final}} -$

T_{initial} in °C. Then $\Delta H = -q(\text{solution})/n$, with n in mol, giving J/mol.



A coffee-cup calorimeter at constant pressure: the heat released or absorbed by the reaction changes the temperature of the water.

Worked example 1

Wanjiru in Nairobi mixes 100.0 mL of 1.00 M HCl with 100.0 mL of 1.00 M NaOH, both at 22.0 °C. The mixture reaches 28.6 °C. Take the density as 1.00 g/mL and $c = 4.18 \text{ J/(g } ^\circ\text{C)}$.

Mass = 200.0 g; $\Delta T = 6.6 \text{ } ^\circ\text{C}$; $q = 200.0 \times 4.18 \times 6.6 = 5.52 \times 10^3 \text{ J}$.

Water formed: $n = 0.1000 \text{ L} \times 1.00 \text{ mol/L} = 0.100 \text{ mol}$.

$\Delta H = -5.52 \text{ kJ}/0.100 \text{ mol} = \mathbf{-55 \text{ kJ/mol}}$.

How does Hess's law work?

Hess's law

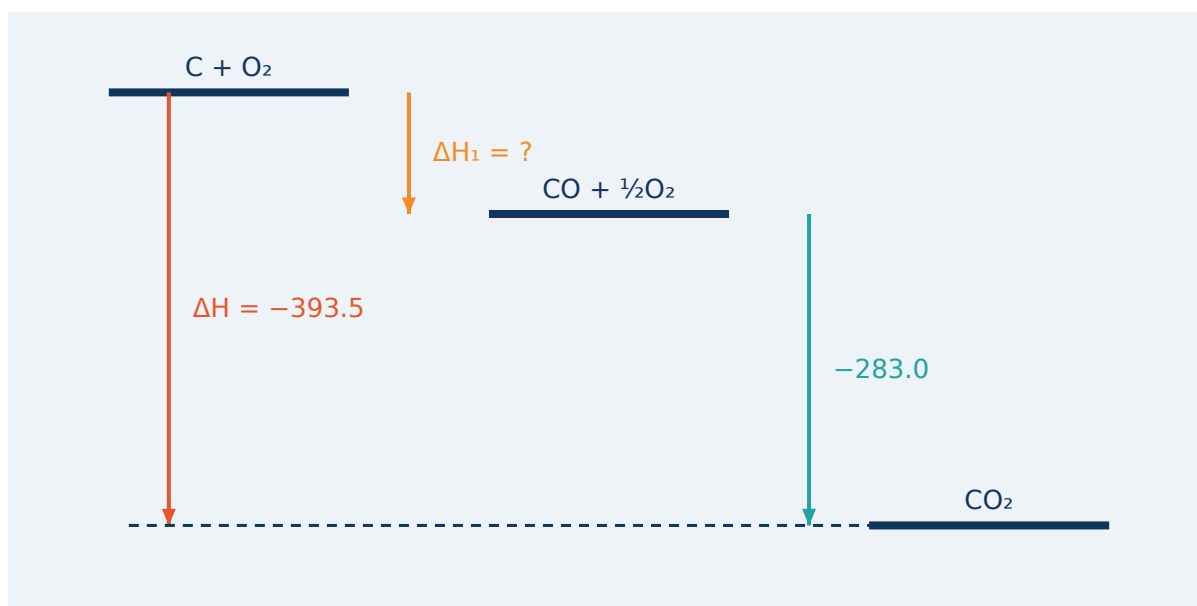
The enthalpy change of a reaction is the same whether it takes place in one step or several, because enthalpy is a state function. Reversing an equation changes the sign of ΔH ; multiplying an equation by n multiplies ΔH by n .

Worked example 2

Find ΔH for $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)}$ given: (1) $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$, $\Delta H = -393.5 \text{ kJ}$; (2) $\text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$, $\Delta H = -283.0 \text{ kJ}$.

Keep (1). Reverse (2): $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2$, $\Delta H = +283.0 \text{ kJ}$. Add: $\text{C} + \text{O}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2$, and cancel $\frac{1}{2}\text{O}_2$.

$\Delta H = -393.5 + 283.0 = \mathbf{-110.5 \text{ kJ}}$.



Two routes between the same levels give the same total ΔH : $-393.5 = \Delta H_1 + (-283.0)$.

How do you use enthalpies of formation and bond enthalpies?

With formation data: $\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{f}}(\text{products}) - \sum \Delta H^\circ_{\text{f}}(\text{reactants})$, each multiplied by its coefficient. With bond enthalpies: $\Delta H \approx \sum(\text{bonds broken}) - \sum(\text{bonds formed})$. Breaking bonds costs energy; forming bonds releases it. Bond-enthalpy answers are estimates because the values are averages for gases.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
C-H	413	O=O	498
C=O (in CO_2)	799	O-H	463
H-H	436	C-C	347

Worked example 3

Estimate ΔH for $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$.

Broken: $4 \text{ C-H} + 2 \text{ O=O} = 4(413) + 2(498) = 1652 + 996 = 2648 \text{ kJ}$.

Formed: $2 \text{ C=O} + 4 \text{ O-H} = 2(799) + 4(463) = 1598 + 1852 = 3450 \text{ kJ}$.

$\Delta H \approx 2648 - 3450 = -802 \text{ kJ}$.

Worked example 4

For $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$, use $\Delta H^\circ_{\text{f}}$ (kJ/mol): C_3H_8 -103.8 , CO_2 -393.5 , $\text{H}_2\text{O}(\text{l})$ -285.8 , O_2 0.

$\Delta H^\circ = [3(-393.5) + 4(-285.8)] - [-103.8 + 0] = (-1180.5 - 1143.2) + 103.8 = -2219.9 \text{ kJ}$.

Common mistake

Students often swap the order and use reactants minus products with formation data, or forget that bond enthalpies work the other way round: broken minus formed. Also, do not

drop the sign of ΔT or of q : the water gains heat, so the reaction has the opposite sign.

Lina's tip

Write the sign rule on the page margin: formation data are products – reactants, bond data are broken – formed. Then check the sign with your common sense: if the beaker got warmer, ΔH must be negative.

Which enthalpy words should you know?

Standard conditions mean 1 bar and a stated temperature, usually 298 K. Combustion enthalpy is for burning 1 mol in oxygen. Neutralisation enthalpy is for forming 1 mol of water from an acid and a base, about -57 kJ/mol for strong acids and strong bases.

Key points to remember

- $q = mc\Delta T$; $\Delta H(\text{reaction}) = -q(\text{solution})/n$.
- Hess's law: reverse an equation, change the sign; multiply, multiply ΔH .
- $\Delta H^\circ = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})$; ΔH°_f of an element is 0.
- Bond enthalpies: $\Delta H \approx \sum(\text{broken}) - \sum(\text{formed})$, an estimate for gases.
- Exothermic: $\Delta H < 0$, surroundings warm; endothermic: $\Delta H > 0$, surroundings cool.

Heat, enthalpy and Hess's law: frequently asked questions

What is the difference between heat and temperature?

Temperature measures the average kinetic energy of particles, while heat is energy transferred because of a temperature difference. A large bath at 40°C can carry more heat than a spark at 1000°C .

Why is ΔH negative for an exothermic reaction?

Because the system loses enthalpy: the products have less enthalpy than the reactants and the difference goes to the surroundings as heat.

Why does Hess's law work?

Enthalpy is a state function, so ΔH depends only on the initial and final states, not on the route taken between them.

Why are bond-enthalpy answers only estimates?

The tabulated values are averages over many different molecules and refer to gaseous species, so the result differs a little from values measured by calorimetry.

Why is the standard enthalpy of formation of $\text{O}_2(\text{g})$ zero?

It is an element in its standard state, so forming it from itself involves no change. Only compounds and non-standard forms have non-zero values.