

Energy in chemical reactions

The total stored energy of a system is constant. Energy can only be converted from one form to another.

First law of thermodynamics (energy conservation) also this is physics

$$\Delta U = Q - W$$

ΔU : Change in internal energy

Q: Change in **heat** of the system (later referred to as enthalpy, this is what we are interested in)

W: Work done on the surrounding environment (usually due to change in pressure/volume)

Usually in chemistry, we perform our experiments at room temperature and pressure, hence there is no change in pressure or temperature in our reactions that we are studying $\rightarrow W = 0$. Giving us,

$$\Delta U \text{ Change in energy} = \Delta H (\text{Enthalpy change})$$

Will any of the above stuff be assessed, no*

The only thing to remember that enthalpy:

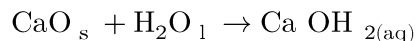
Enthalpy is the heat change in the system under constant pressure. (Assessed 2016 Q7a)

Exothermic and Endothermic reactions

Chemical bonds (no matter which bond) contains negative *potential energy*. In other words, molecules are more stable when they are bonded to other molecules.

- The process of bond forming releases energy (in terms of heat) to the surroundings.
 - It is **exothermic** ; $\Delta H < 0$
- The process of breaking bonds **consumes** energy, usually in the form of heat from the surroundings.
 - It is **endothermic** ; $\Delta H > 0$

Example:



This reaction is known to be exothermic! (think of what happens when you put quicklime into water, heat is released!)

In terms of bond forming and breaking, this is what happens during the reaction:

Bonds formed: ionic bonds between Ca^{2+} and OH^- + covalent bonds between O-H

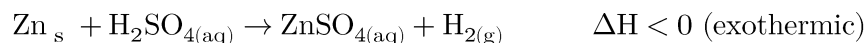
Bonds broken: Ionic bonds between Ca^{2+} and O^{2-} + covalent bonds between O-H (ionization of water)

The bonds formed releases **more energy** than the energy **consumed** during the bond breaking process, so the reaction releases energy, hence it is exothermic.

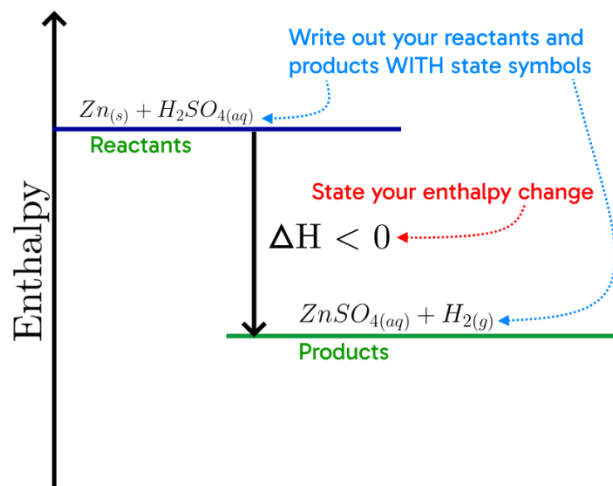
Enthalpy level diagrams

Sometimes you might be asked to draw an enthalpy level diagram to explain the changes in energy of a system during a specific reaction. The way to draw it is formulaic, to say the least.

Example: Consider this reaction between Zn and H_2SO_4



Note: It is VERY IMPORTANT to write state symbols when considering enthalpies (you will see soon in an example). This is why I always prefer to leave state symbols in your equations as a good habit.



Example questions:

1. a. Explain whether thermal decomposition of calcium carbonate is endothermic or exothermic in terms of energy bond formation or/and breakage.

Hint: The name *thermal decomposition* gives quite a large hint

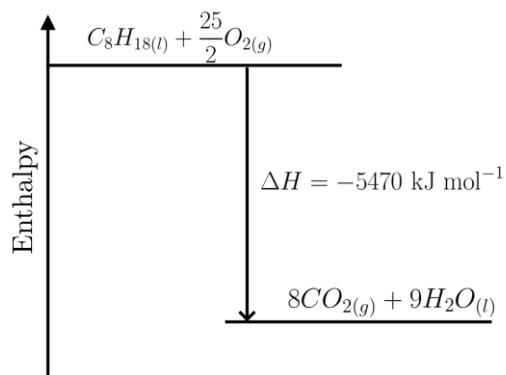


1. b. Draw the enthalpy level diagram for the reaction

2. a. Explain whether water freezing is endothermic or exothermic in terms of energy bond formation or/and breakage.

b. Draw the enthalpy level diagram for the reaction (pay attention to state symbols!)

3. Octane is used as petrol in cars. Refer to the following enthalpy level diagram for the combustion of octane.



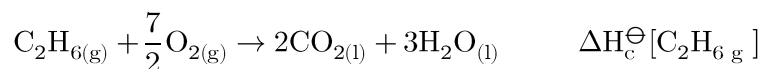
- a. State the energy released when 1 mole of octane undergoes complete combustion
- b. Calculate the energy released when 1 litre of pure octane petrol is completely burnt inside an internal combustion engine. Given: Density of octane = 0.7 kg dm^{-3}
- c. In reality, incomplete combustion may occur in engines due to insufficient supply of oxygen, will the actual amount of energy released be less than, more than or equal to that in (b)?

Standard enthalpy changes

Definitions: (please actually remember these)

1. Standard enthalpy change of combustion:

The enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions



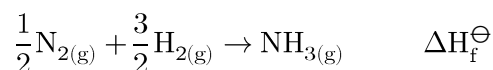
2. Standard enthalpy change of neutralization:

The enthalpy change when one mole of water is formed from the neutralization reaction between a base and an acid under standard conditions



3. Standard enthalpy change of formation

The enthalpy change when one mole of a substance is formed from its constituent elements under standard conditions



Standard conditions: (also remember these thanks)

- 25°C (298K)
- 1 atm pressure

Determining enthalpy changes by experimental methods

Usually this involves using an experiment to measure the heat change from a reaction, and then the experimental conditions and the heat released can be used to find ΔH^{\ominus}

Steps to solve these problems:

- Write down the chemical equation (thermochemical)
- Calculate the actual heat released measured

$$\Delta E = \sum_i^n m_i c_i \Delta T_i$$

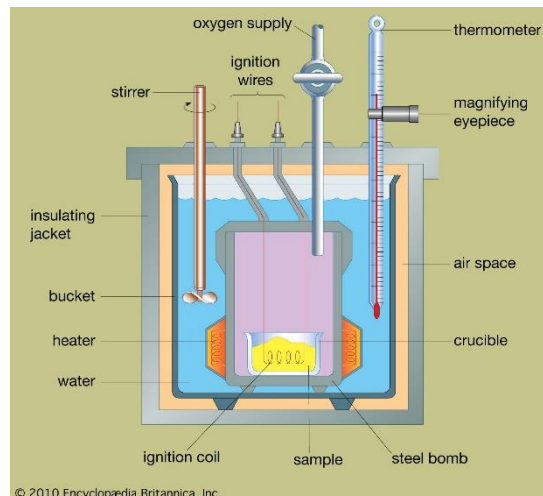
- That formula is grossly generalized for n-components being heated together, usually you only have to account for one.
- Calculate number of moles (n) of the reactant consumed
- Find the enthalpy change by the following formula

$$\Delta H = \frac{\Delta E}{n}$$

- Depending on your question, you might have to put the standard sign on the ΔH .

Example 1: Standard enthalpy change of combustion

A 0.39 g sample of quinone ($\text{C}_6\text{H}_4\text{O}_2$) is burnt in a bomb calorimeter that has a **heat capacity** of 1560 J K^{-1} . The temperature of the calorimeter after the reaction increases by 6.4°C . Calculate the enthalpy change of combustion of quinone.



Example 2: Standard enthalpy change of neutralization

Determine the enthalpy change of neutralization of 25 cm^3 of 1.25 M hydrochloric acid and 25 cm^3 of 1.25 M sodium hydroxide solution using the following data:

Initial temperature of acid = 15.5°C

Initial temperature of alkali = 15.5°C

Final temperature of the reaction mixture = 21.6°C

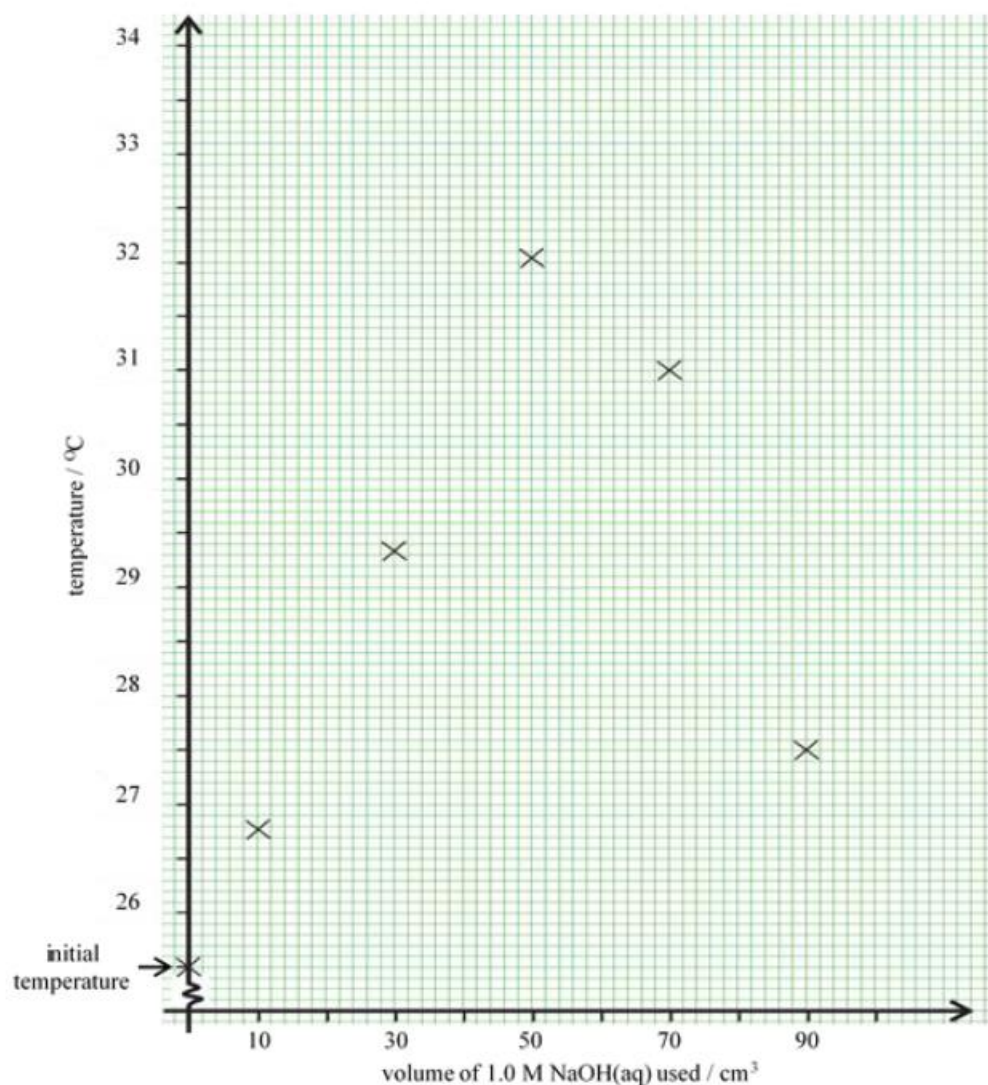
(Specific heat capacity of water = $4.2 \text{ J g}^{-1} \text{ K}^{-1}$, density of water = 1 g cm^{-3})

Identify every assumption you have made.

DSE Example 2019-Q8

Several trials of an experiment were performed for determining the enthalpy change of neutralization for a reaction. For each trial, a total volume of 100.0 cm³ of a solution was obtained from mixing specified volumes of a HCl(aq) and 1.0 M NaOH(aq) as shown below in an expanded polystyrene cup. The HCl(aq) and NaOH(aq) were kept at the same initial temperature before mixing.

Trial	1	2	3	4	5
Volume of HCl used	90	70	50	30	10
Volume of 1.0M NaOH used	10	30	50	70	90



- It is estimated from the graph that 58.0 cm³ of NaOH(aq) (and 42.0 cm³ of HCl(aq)) is required for obtaining the possible maximum temperature reached in this experiment. Show how this estimation can be done in the above graph.

- b. Calculate the number of moles of NaOH(aq) reacted with HCl(aq) in (a). Hence, find the concentration of the HCl(aq).
- c. Given that the initial temperature of the mixture for each trial is 25.5°C, calculate the enthalpy change of neutralization of the reaction, in kJ mol⁻¹.
(Density of the mixture 1.00 g cm⁻³; specific heat capacity of the mixture 4.18 J g⁻¹K⁻¹; heat capacity of the expanded polystyrene cup : negligible)
- d. The one determined above is not the standard enthalpy change of neutralisation. What, then, is meant by the term ‘standard enthalpy change of neutralisation’ ?

Hess law

Unexpectedly complex.

Hess law states that:

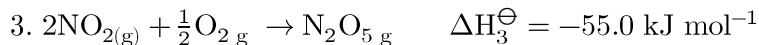
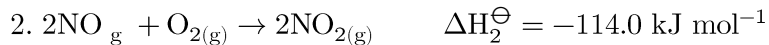
The total enthalpy change of a chemical reaction is **independent of the pathway** between the initial and final states. (Assessed in DSE 2017-Q7 I am not joking)

General ways to tackle a problem with Hess’s Law (analogous to vectors from M2):

- Write the thermochemical equation
- Construct an enthalpy change cycle with the reactions given
- Draw the arrows to determine the enthalpy change of your desired reaction from values already known/given
- Add the values together

Example: Formation of N₂O₅ Dinitrogen pentoxide

Consider the following reactions:

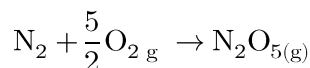


a. Why is the standard enthalpy change of N₂O_{5(g)} not directly measured experimentally?

Side products may be formed from the direct reaction between N_{2(g)} and O_{2(g)}.

b. Determine, by drawing an enthalpy change cycle, the standard enthalpy change of formation of N₂O_{5(g)}

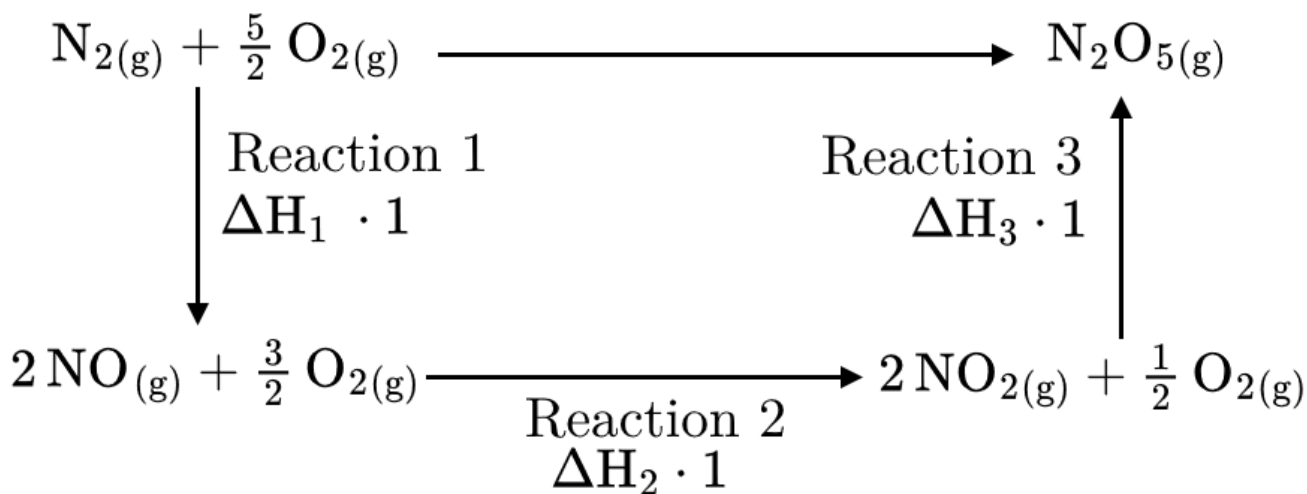
Step 1: write out the reaction whose enthalpy change you are interested in



Step 2: Find a way to reaction from left side to right side (or both sides to the same substances) by using the given reactions (you may add extra reagents **to both sides** if required)

Here we can use (1) to make NO and then use reaction (2) to turn NO into NO₂ and finally into N₂O₅ by reaction (3).

Step 3: Draw out the enthalpy change cycle and label the enthalpy change of each step.



4. Add up the enthalpy changes, pay attention to the signs and multiply correctly.

$$\Delta H_f^\ominus[\text{N}_2\text{O}_{5\text{g}}] = \Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus = +180 + -114 + (-55)$$

$$\Delta H_f^\ominus[\text{N}_2\text{O}_{5\text{g}}] = +11 \text{ kJ mol}^{-1} \text{ (Leave the + sign there to indicate an endothermic reaction)}$$

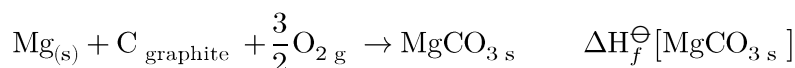
Example 2: standard enthalpy change of formation of $\text{MgCO}_3(\text{s})$

a. Explain why, instead of direct method, an indirect method is used to obtain the enthalpy changes of formation of $\text{MgCO}_3(\text{s})$.

b. Using the information given below calculate the standard enthalpy change of formation of $\text{MgCO}_3(\text{s})$

Standard enthalpy change for the reaction of $\text{MgCO}_3(\text{s})$ with $\text{H}_2\text{SO}_4(\text{aq})$	$= -50 \text{ kJ mol}^{-1}$	(1)
Standard enthalpy change for the reaction of $\text{Mg}(\text{s})$ with $\text{H}_2\text{SO}_4(\text{aq})$	$= -467 \text{ kJ mol}^{-1}$	(2)
Standard enthalpy change of formation of $\text{CO}_2(\text{g})$	$= -394 \text{ kJ mol}^{-1}$	(3)
Standard enthalpy change of formation of $\text{H}_2\text{O}(\text{l})$	$= -286 \text{ kJ mol}^{-1}$	(4)

Step 1: Write out the thermochemical equation of the reaction we are interested in

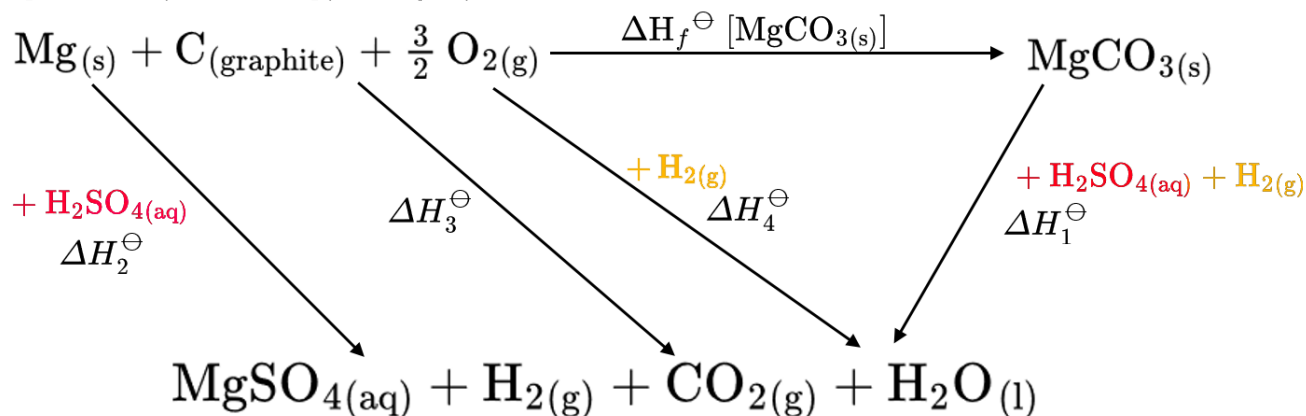


Step 2: Find a way to react the left side and right side reactants to form the same substances from the given reactions.

Left hand side: React Mg with acid to form MgSO_4 , and form CO_2 and H_2O .

Right hand side: React MgCO_3 with acid to form MgSO_4 , CO_2 and H_2O

Step 3: Draw your enthalpy change cycle



Step 4: Add up all the enthalpy changes, **pay attention to signs and multiply carefully**

$$\Delta H_f^\ominus [\text{MgCO}_3(\text{s})] = -\Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus$$

$$\Delta H_f^\ominus [\text{MgCO}_3(\text{s})] = -(-50) + (-467) + (-394) + (-286)$$

$$\Delta H_f^\ominus [\text{MgCO}_3(\text{s})] = -1097 \text{ kJ mol}^{-1} \text{ (Leave the negative sign there to indicate an exothermic reaction)}$$

Hess Law with standard enthalpy changes of formation

Theorem 1: For any reaction,

$$n_1R_1 + n_2R_2 + n_3R_3 + \cdots \rightarrow n'_1P_1 + n'_2P_2 + n'_3P_3 + \cdots \quad \Delta H^\ominus$$
$$\Delta H^\ominus = \sum_j n'_j \Delta H_f^\ominus [P_j] - \sum_i n_i \Delta H_f^\ominus [R_i]$$
$$// \Delta H^\ominus = \sum \Delta H_f^\ominus [\text{Products}] - \sum \Delta H_f^\ominus [\text{Reactants}]$$

Definition: The standard enthalpy change for any element in its standard state is equal to zero.

$$\Delta H_f^\ominus [\text{N}_{2(g)}] = \Delta H_f^\ominus [\text{H}_{2(g)}] = \Delta H_f^\ominus [\text{O}_{2(g)}] = \Delta H_f^\ominus [\text{Na}_{(s)}] = \Delta H_f^\ominus [\text{Hg}_{(l)}] = 0 \text{ kJ mol}^{-1}$$

Example: Multiple choice question!

Given the following information,

$$\Delta H_f^\ominus [\text{CO}_{2(g)}] = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus [\text{H}_2\text{O}_{(l)}] = -285.8 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus [\text{C}_2\text{H}_5\text{OH}_{(l)}] = -277.7 \text{ kJ mol}^{-1}$$

Calculate the standard enthalpy change of combustion of ethanol

- a. -408.0 kJ mol⁻¹
- b. -957.0 kJ mol⁻¹
- c. -1224 kJ mol⁻¹
- d. -1367 kJ mol⁻¹

Example: Long question

Barium nitrate (Ba(NO₃)₂) is one of the components of 'sparklers'. The standard enthalpy change of formation of solid barium nitrate is -992 kJ mol⁻¹

- a. Write an equation for the process to which $\Delta H_f^\ominus [\text{BaNO}_{3(s)}]$ refers. Include the physical state of each species in the equation.
- b. When sparklers burn, aluminium reacts with barium nitrate to give barium oxide, aluminium oxide and nitrogen.
 - i. Write an equation for the above reaction. Include the physical state of each species in the equation.
 - ii. Calculate the standard enthalpy change of the reaction in part (b)(i) using the data given below.

Substance	ΔH_f^\ominus (kJ mol ⁻¹)
Ba(NO ₃) ₂ (s)	-992
BaO(s)	-554
Al ₂ O ₃ (s)	-1676

Hess Law and standard enthalpy change of combustion

Theorem 2: For any reaction,

$$n_1R_1 + n_2R_2 + n_3R_3 + \cdots \rightarrow n'_1P_1 + n'_2P_2 + n'_3P_3 + \cdots \quad \Delta H^\ominus$$
$$\Delta H^\ominus = \sum_j n_j \Delta H_c^\ominus [R_j] - \sum_i n'_i \Delta H_c^\ominus [P_i]$$
$$// \Delta H^\ominus = \sum \Delta H_f[\text{Reactants}] - \sum \Delta H_f[\text{Products}]$$

Example:

- a. Define the term ‘standard enthalpy change of formation’ of a substance. (1 mark)
- b. Consider methylbenzene (C_7H_8)
 - i. Write a chemical equation with state symbols which corresponds to the enthalpy change of formation of liquid methylbenzene (C_7H_8).
 - ii. The table below lists the standard enthalpy changes of combustion of three substances.

Substance	ΔH_c^\ominus (kJ mol ⁻¹)
C(graphite)	-394
H ₂ (g)	-286
C ₇ H ₈ (l)	-3909

Use the above enthalpy changes to construct an enthalpy change cycle and use them to calculate the standard enthalpy change of formation of liquid methylbenzene.