

Chemistry

Teach Yourself Series

Topic 11: Thermochemistry

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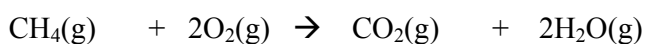
Chemical energy

On a cold winter's day, people can often be found sitting around a fire. This is a chemical process. The wood is combining with oxygen from the air and changing into a mixture of charcoal, carbon dioxide and water. Everyone feels hot because the combustion of wood releases energy. Every chemical reaction involves some change in energy.

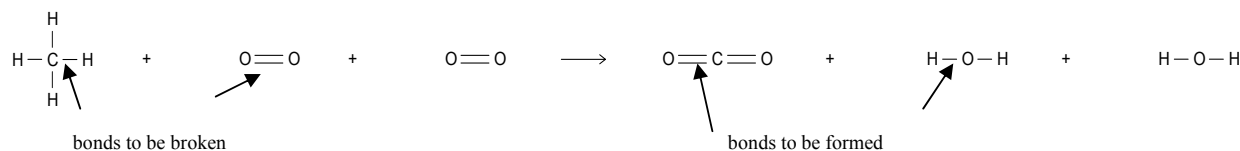
Enthalpy

As it appears in Unit 4

The equation for the combustion of methane is



If this equation is shown as structural diagrams it looks like this



In this way, it is evident that as this **reaction occurs, there are bonds broken and bonds formed.**

This is the same for all reactions: **bonds need to be broken so that new bonds can form.**

This also raises the following points:

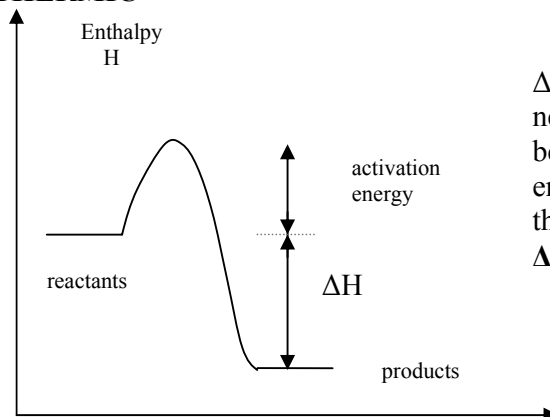
- Each substance has a **level of chemical potential energy** due to the fact that it contains moving, charged particles held in a particular arrangement.
- Most reactions have an **activation energy**. This is the **energy required to break the bonds** that are present to give the reaction a chance to occur.
- The products are unlikely to have the same amount of potential energy as the reactants. Therefore **all reactions will involve some energy change**

The chemical energy of a substance, its stored potential energy, is known as its **enthalpy**. Its symbol is ***H***. The enthalpy of products formed in a reaction will differ from that of the reactants. Therefore, each reaction has a change of enthalpy, a ΔH .

Reactions are either **exothermic or endothermic**.

Exothermic reaction:
Products have less potential energy than reactants => energy is released to the surroundings, warming the surroundings

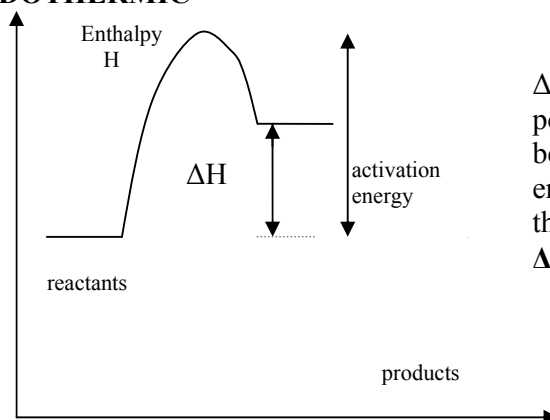
EXOTHERMIC



ΔH will have a negative value because the final enthalpy is less than the initial.
 $\Delta H = H_f - H_i = -ve$

Endothermic reaction:
Products have more potential energy than reactants => energy is absorbed from the surroundings, cooling the surroundings

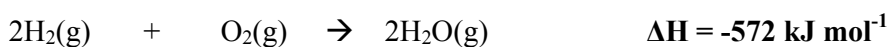
ENDOTHERMIC



ΔH will have a positive value because the final enthalpy is less than the initial.
 $\Delta H = H_f - H_i = +ve$

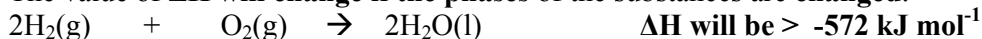
Notes: Magnitude of the activation energy is different for endothermic reactions and exothermic reactions.
The **sign of the activation energy is always positive.**

The reaction between hydrogen and oxygen is very exothermic



This means that 572000 Joule of energy is released if the amounts in the balanced equation are used.
2 mole of H_2 reacting with 1 mole of O_2 , releases 572000 Joule.
It does not mean that 1 mole of H_2 will release 572000 Joule.
Nor does it mean that negative energy is involved: the negative sign indicates a release of energy.

The value of ΔH will change if the phases of the substances are changed.

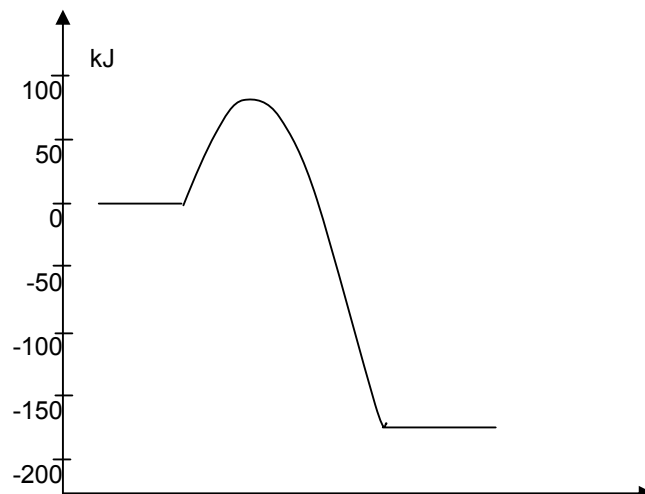


The ΔH of the reverse reaction



will be the opposite of the forward reaction.

Example: The reaction between carbon monoxide and oxygen gases is shown below



- Write an equation for the reaction.
- What is the magnitude and sign of the activation energy for the forward reaction?
- What is the value of ΔH for the reverse reaction?
- What is the magnitude and sign of the activation energy for the reverse reaction?

Solution

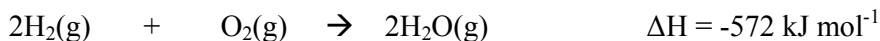
- $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$
- +78 kJ mol⁻¹
- +175 kJ mol⁻¹
- +253 kJ mol⁻¹

Energy calculations and Data book

As it appears in Unit 4

Example 1

Given the equation



Calculate the amount of energy released from the combustion of

- 10 g of hydrogen gas
- 0.48 g of hydrogen gas
- 5.6 g of oxygen gas

Solution

Perhaps deal with the 2 in the balanced equation first

2 mole of hydrogen gives 572 kJ so 1 mole gives 286 kJ.

a. $n = \frac{m}{M} = \frac{10}{2} = 5 \text{ mol}$

$$E = n \times \Delta H = 5 \times 286 = 1430 \text{ kJ}$$

b. $n = \frac{m}{M} = \frac{0.48}{2} = 0.24 \text{ mol}$

$$E = n \times \Delta H = 0.24 \times 286 = 68.6 \text{ kJ}$$

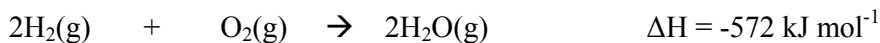
c. $n = \frac{m}{M} = \frac{5.6}{32} = 0.175 \text{ mol}$

$$E = n \times \Delta H = 0.175 \times 572 = 100.1 \text{ kJ}$$

(Note that 572 is used here as the question is about oxygen and the balanced equation has 1 mole of oxygen)

Example 2

The equation for the combustion of hydrogen gas is



The **Chemical Data Book** however gives a ΔH value of -286 kJ mol^{-1}

Notice the difference: $\Delta H = -572 \text{ kJ mol}^{-1}$ vs $\Delta H = -286 \text{ kJ mol}^{-1}$

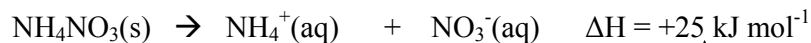
The first value is **double** the second. This is due to the 2H_2 in the equation.

The first value matches the balanced equation, the second refers to one mole of hydrogen without reference to the equation. Both values agree but students need to be careful when looking up the Data book.

Review questions

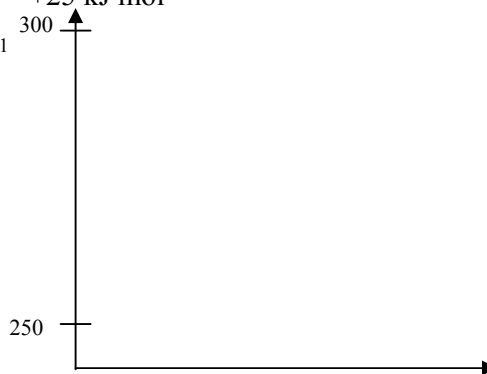
1. Draw the shape of an energy profile diagram for an exothermic reaction.
 - a. If a reactant is very unstable and dangerous to handle, how would this show on the diagram?
 - b. If the reactant is a very powerful fuel, how would this show on the diagram?

2. Ammonium nitrate, NH_4NO_3 dissolving in water is an endothermic reaction

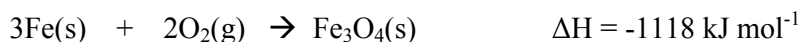


The activation energy for this reaction is $+33 \text{ kJ mol}^{-1}$

Use the axes provided to draw an energy profile diagram for this reaction. Give the reactants an enthalpy of 250 kJ.

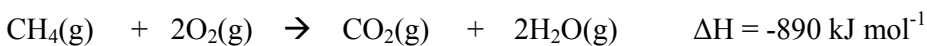


3. One of the possible reactions between iron and oxygen is



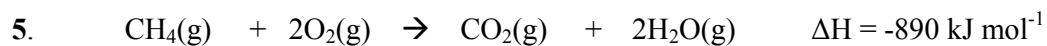
How much energy is released from the reaction of

- a. 1 mol of iron _____
 - b. 1 mole of oxygen gas _____
 - c. 3 mol of iron? _____
4. For the reaction between methane and oxygen



- a. Is this reaction endothermic or exothermic? _____
- b. Will the surroundings be hotter or cooler after this reaction has occurred?

- c. Which bonds need to be broken for this reaction to occur?



Calculate the amount of energy released when

- a. 25 mol of methane reacts

- b. 1 kg of methane reacts

- c. 1 kg of oxygen gas reacts

6. Use the Data Book to determine

- a. the energy released per mol of hexane

- b. the energy released per gram of hexane

Determining energy

As it appears in Unit 4

$$E = m \times c \times \Delta T$$

where E = energy, Joule: c = specific heat capacity, $\text{J } ^\circ\text{C}^{-1} \text{ g}^{-1}$:

m = mass, g: ΔT = change in temp in $^\circ\text{C}$ or K

The specific heat capacity of water is $4.18 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$

Example 1

Calculate the energy required to raise the temperature of a 12 g piece of copper by 58°C . The specific heat capacity of copper is $0.386 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$.

$$\begin{aligned} E &= m \times c \times \Delta T \\ &= 12 \times 0.386 \times 58 = 269 \text{ J} \end{aligned}$$

Example 2

Calculate the amount of energy required to raise the temperature of 500 mL of water from 12°C to 100°C .

(Since the density of water is 1 g mL^{-1} at 25°C , it is usual to assume the mass of water in g is equal to the volume of water in mL)

$$\begin{aligned} E &= m \times c \times \Delta T \\ &= 500 \times 4.18 \times 88 = 184000 \text{ J} = 184 \text{ kJ} \end{aligned}$$

Example 3

4500 Joule of energy is passed through a 650 mL beaker of water that is initially at 34.00°C . What will the final temperature of the water be?

$$\begin{aligned} E &= m \times c \times \Delta T \\ 4500 &= 650 \times 4.18 \times \Delta T \end{aligned}$$

$$\Rightarrow \Delta T = \frac{4500}{650 \times 4.18} = 1.66 \quad \Rightarrow \text{final temperature} = 34 + 1.66 = 35.66^\circ\text{C}$$

Calorimeters

As it appears in Unit 4

A **calorimeter must be used** to obtain **accurate ΔH** values for chemical reactions. Calorimeters **limit energy losses**, making measurement of temperature change more accurate.

Calorimetry can be performed using the value of 4.18 for water OR by using calibration.

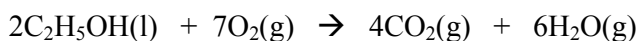
Calibration using 4.18

$$E = 4.18 \times m_w \times T$$

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

Example

A 20.00 g sample of ethanol is burnt under a 6.00 L beaker of water. The temperature of the water increases from 23.8 °C to 34.2 °C. Calculate ΔH for the combustion of ethanol



$$\begin{aligned} E &= m \times 4.18 \times \Delta T \\ &= 6000 \times 4.18 \times 10.4 = 254000 \text{ J} \end{aligned}$$

note the mass of water was used here, not the mass of ethanol

$$n = \frac{m}{M} = \frac{20}{46} = 0.435 \text{ mol}$$

$$\Delta H = \frac{E}{n} = \frac{254000}{0.435} = -584 \text{ kJ mol}^{-1}$$

Note: The final value for ΔH is $-1168 \text{ kJ mol}^{-1}$ as the balanced equation has a coefficient of 2 in it.

Calorimetry using calibration

As it appears in Unit 4

Calorimeters still have inefficiencies. Calibration allows for these inefficiencies.

$$CF = \frac{VIt}{\Delta T} = \frac{\text{energy}}{\Delta T} \qquad E = CF \times \Delta T \qquad \Delta H = \frac{E}{n}$$

Example 1

A current of 5.0 amps and a voltage of 6.0 V is applied to a calorimeter for 4.0 minutes. The temperature increases from 18.7 °C to 22.6 °C.

0.4 g of sodium is then added to the calorimeter and the temperature rises further to 32.3 °C

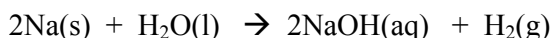
Calculate ΔH for the reaction of sodium in water

$$CF = \frac{VIt}{\Delta T} = \frac{6 \times 5 \times 4 \times 60}{3.9} = 1850 J ^\circ C$$

$$n = \frac{m}{M} = \frac{0.4}{23} = 0.017 mol$$

$$E = CF \times \Delta T = 1850 \times 9.7 = 18000 J$$

$$\Delta H = \frac{E}{n} = \frac{18000}{0.017} = -1060 kJ mol^{-1}$$

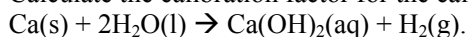


$$\Rightarrow \Delta H = -1060 \times 2 = -2120 kJ mol^{-1}$$

Example 2

9000 Joule of energy is passed through a calorimeter containing 100 g of water. The temperature of the water rises from 17.8 °C to 36.6 °C. A 0.200 mol of calcium is then added to the calorimeter and the temperature rises a further 18.0 °C.

Calculate the calibration factor for the calorimeter and then calculate ΔH for the reaction



Solution

$$CF = \frac{\text{energy}}{\Delta T} = \frac{9000}{18.8} = 480 J ^\circ C^{-1} \quad \text{it makes no difference that the voltage and current are not given}$$

$$E = CF \times \Delta T = 480 \times 18 = 8600 J$$

$$\Delta H = \frac{E}{n} = \frac{8600}{0.2} = -43000 J mol^{-1} = -43.0 kJ mol^{-1}$$

Review questions

Decide which method to employ on the questions below – if calibration data is supplied, it should be the preferred method.

7. The combustion of 0.086 g of ethene causes an 80.0 mL sample of water to increase in temperature by 3.2 °C. Calculate ΔH for the combustion of ethene.

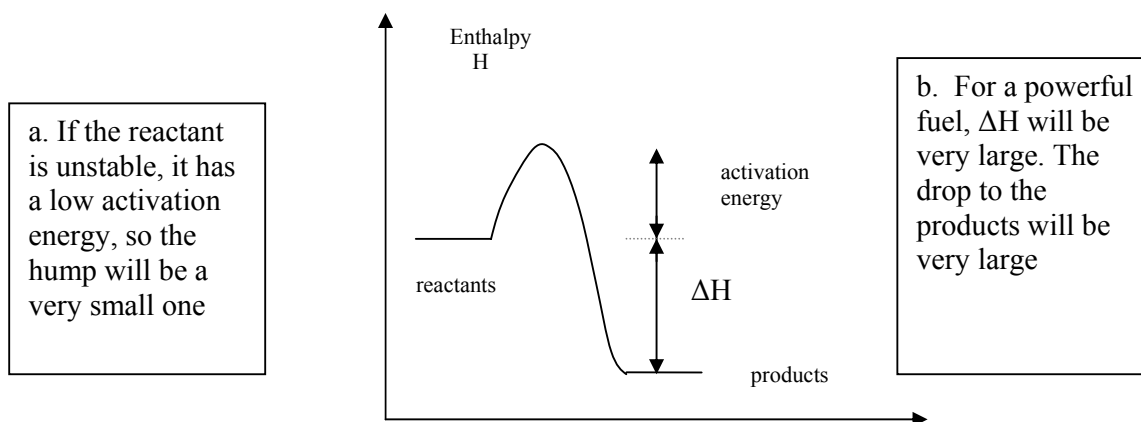
8. A voltage of 4.0 volts and a current of 4.2 amps is passed through a calorimeter for 5.0 minutes. The temperature increases from 12.7 °C to 17.1 °C. When 0.080 g of lithium is added to the calorimeter the temperature increases further to 20.5 °C. Calculate ΔH for the reaction of lithium and water.

9. a. An experiment is conducted in a calorimeter. The calorimeter is calibrated well after the experiment. Can accurate results be obtained if calibration is conducted after the actual experiment?

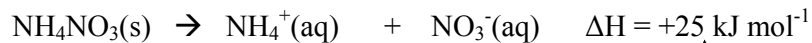
- b. During calibration the current is run for 5 minutes instead of 4 minutes. If the experimenter did not realise this, how will the mistake impact upon the final result for the calibration factor?

Solutions to Review Questions

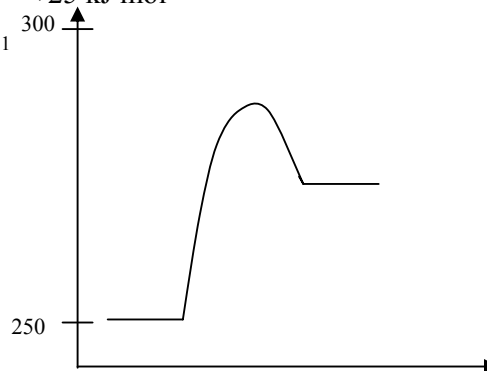
1. Draw the shape of an energy profile diagram for an exothermic reaction.



2. Ammonium nitrate, NH_4NO_3 dissolving in water is an endothermic reaction

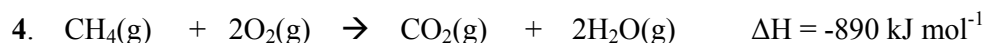


The activation energy for this reaction is $+33 \text{ kJ mol}^{-1}$
Use the axes provided to draw an energy profile diagram for this reaction. Give the reactants an enthalpy of 250 kJ.



3. $3\text{Fe}(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow \text{Fe}_3\text{O}_4(\text{s}) \quad \Delta H = -1118 \text{ kJ mol}^{-1}$

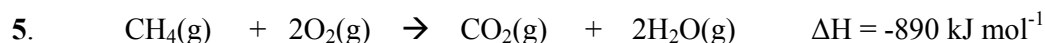
- | | |
|-------------------------|----------------|
| a. 1 mol of iron | <i>373 kJ</i> |
| b. 1 mole of oxygen gas | <i>559 kJ</i> |
| c. 3 mol of iron? | <i>1118 kJ</i> |



a. exothermic

b. The surroundings will be hotter: an exothermic reaction releases energy

c. The bonds in methane and the double bonds in oxygen need to be broken. Once they are broken, the new bonds can form.



a. $E = 25 \times 890 = 22250 \text{ J} = 22.3 \text{ kJ}$

b. $n = \frac{m}{M} = \frac{1000}{16} = 62.5 \text{ mol}$

$$E = n \times \Delta H = 62.5 \times 890 = 55600 \text{ J} = 55.6 \text{ kJ}$$

c. $n = \frac{m}{M} = \frac{1000}{16} = 62.5 \text{ mol}$

1 kg of oxygen gas reacts

6. a. the energy released per mol of hexane 4158 kJ

b. energy per gram = $4158/86$ as hexane is C_6H_{14}
 $= 48.3 \text{ kJ g}^{-1}$

7. $E = 4.18 \times 80 \times 3.2 = 1070 \text{ J}$

$$n = \frac{m}{M} = \frac{0.06}{28} = 0.00214 \text{ mol}$$

$$\Delta H = \frac{1070}{0.00214} = 500 \text{ kJ}$$

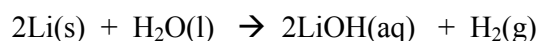
8.

$$CF = \frac{VIt}{\Delta T} = \frac{4 \times 4.2 \times 5 \times 60}{4.4} = 1150 \text{ J } ^\circ\text{C}$$

$$n = \frac{m}{M} = \frac{0.08}{6.9} = 0.0116 \text{ mol}$$

$$E = CF \times \Delta T = 1150 \times 3.4 = 3910 \text{ J}$$

$$\Delta H = \frac{E}{n} = \frac{3910}{0.0116} = -337 \text{ kJ mol}^{-1}$$



$$\Rightarrow \Delta H = -337 \times 2 = -674 \text{ kJ mol}^{-1}$$

9. a. Calibration can be conducted after the chemical experiment. This presumes the same volume is used and that the calorimeter is not damaged or changed by the experiment. The water in the calorimeter should be replaced before calibration.
- b. The temperature change will be higher than it should be. This will lead to the calibration factor being low. The ΔH values obtained will be low.