5.1 Measuring energy changes

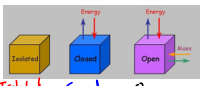
Energy is a measurement of the ability to do work. ✓

Heat is a mode of energy transfer that results from a temperature difference and causes an increase in disorder in how particles behave.

Work is a more ordered mode of energy transfer.

System and surroundings :

In thermodynamics we consider 3 types of system:



Isolated Closed Open

Enthalpy is the total amount of heat energy in a system. It is stored in chemical bonds and IMFs as potential energy. When substances react (at constant pressure), the difference between the enthalpy of products and reactants results in a heat change.

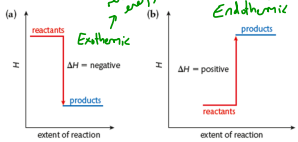
What is the symbol for enthalpy? → H ΔH

If the products in a reaction have a lower total enthalpy than the reactants, heat is released to the surroundings as seen in diagram (a).

The opposite is true for diagram (b).

releases energy → Exothermic

Endothermic → absorbs heat energy



We use the terms exothermic and endothermic to describe these processes.

Standard conditions and standard states for enthalpy changes:

$Cu_{(s)}$ $H_2O_{(l)}$ $Hg_{(l)}$ $O_{2(g)}$ $CO_{2(g)}$

The standard conditions for ~~enthalpy changes are:~~
- **a pressure of 100 kPa**
- **concentrations of 1 mol dm^{-3} for all solutions**
- **all the substances in their standard states.**

The standard state of a substance is the pure form of the substance under standard conditions of 298 K (25 °C) and 1.00 × 10^5 Pa. (100 kPa)

Selected standard conditions → 1atm + 25°C (298 K)

We use the term standard enthalpy change to describe reactions that have taken place under standard conditions and with all substances in standard states:

The combustion of methane can be described by the thermochemical equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -890 \text{ kJ mol}^{-1}$$

Which has a higher temperature and which more heat ?

The iceberg will have more heat energy as it has many more bonds + IMFs storing energy. (A much greater enthalpy)

Temperature is an measure of the average measurement of the kinetic energy of particles. Therefore at 0 K particles cease to move.

We can use temperature change information to calculate heat (enthalpy) changes.

In general, the increase in temperature when an object is heated depends on:
- the mass of the object
- the heat added
- the nature of the substance.

For water 4.18 J g^{-1} K^{-1}

heat change (q) = mass (m) × specific heat capacity (c) × temperature change (ΔT)

(- enthalpy)

- **The specific heat capacity (c) is defined as the heat needed to increase the temperature of unit mass of material by 1 K.**

$$\text{specific heat capacity } (c) = \frac{\text{heat change } (q)}{\text{mass } (m) \times \text{temperature change } (\Delta T)}$$

- **The heat capacity (C) is defined as the heat needed to increase the temperature of an object by 1 K.**

$$\text{heat capacity (C)} = \frac{\text{heat change } (q)}{\text{temperature change } (\Delta T)}$$

Worked example

How much heat is released when 10.0 g of copper with a specific heat capacity of 0.385 J g^{-1} °C^{-1} is cooled from 85.0 °C to 25.0 °C?

Solution

heat change = $m \times c \times \Delta T$
= 10.0 g × 0.385 J g^{-1} °C^{-1} × −60.0 °C (the value is negative as the Cu has lost heat)
= −231 J

The − sign means we have an exothermic process

1 When a sample of NH_4SCN is mixed with solid $Ba(OH)_2.8H_2O$ in a glass beaker, the mixture changes to a liquid and the temperature drops sufficiently to freeze the beaker to the table. Which statement is true about the reaction?
- A The process is endothermic and ΔH is −
- B The process is endothermic and ΔH is +
- C The process is exothermic and ΔH is −
- D The process is exothermic and ΔH is +

2 Which one of the following statements is true of all exothermic reactions?
- A They produce gases.
- B They give out heat.
- C They occur quickly.
- D They involve combustion.

3 If 500 J of heat is added to 100.0 g samples of each of the substances below, which will have the largest temperature increase?

	Substance	Specific heat capacity / J g^{-1} K^{-1}
A	gold	0.129
B	silver	0.237
C	copper	0.385
D	water	4.18

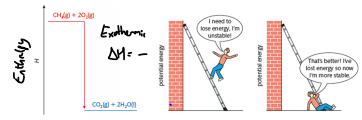
4 The temperature of a 5.0 g sample of copper increases from 27 °C to 29 °C. Calculate how much heat has been added to the system. (Specific heat capacity of Cu = 0.385 J g^{-1} K^{-1})
A 0.770 J B 1.50 J C 3.00 J D 3.85 J

5 Consider the specific heat capacity of the following metals.

Metal	Specific heat capacity / J g^{-1} K^{-1}
Al	0.897
Be	1.82
Cd	0.231
Cr	0.449

1 kg samples of the metals at room temperature are heated by the same electrical heater for 10 min. Identify the metal which has the highest final temperature.
A Al B Be C Cd D Cr

Enthalpy changes and the direction of change

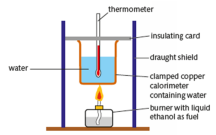


The enthalpy change in an exothermic reaction leads to products that are more stable (lower enthalpy) so in general we expect exothermic process to occur.

Endothermic processes are less common but do occur depending on other factors to do with the reaction.

Measuring enthalpy changes of combustion

For liquids such as ethanol, the enthalpy change of combustion can be determined using the simple apparatus shown in Figure 5.7.



Heat energy (J) = m · c · ΔT

m → mass; c → specific heat capacity; ΔT → change in temp

$4.18\ J\ g^{-1}\ K^{-1}$

Worked example

Calculate the enthalpy of combustion of ethanol from the following data. Assume all the heat from the reaction is absorbed by the water. Compare your value with the IB data booklet value and suggest reasons for any differences.

Mass of water in copper calorimeter / g	200.00
Temperature increase in water / °C	13.00
Mass of ethanol burned / g	0.45

1. Calculate heat given to water.
2. Calculate the no. of moles of ethanol.

ber of moles of ethanol = $\frac{m(C_2H_5OH)}{M(C_2H_5OH)}$ mol

f) = (12.01 × 2) + (6 × 1.01) + 16.00 = 46.08 g mol^{-1}

$\Delta H_{reaction} = -m(H_2O) \times c(H_2O) \times \Delta T(H_2O)$

$\Delta H_c = \Delta H_{reaction}$ (for one mole of ethanol)

$= \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{m(C_2H_5OH)/M(C_2H_5OH)}$ J mol^{-1}

$= \frac{-200\ g \times 4.18\ J\ g^{-1}\ °C^{-1} \times 13.00°C}{0.45 g / 46.08\ g\ mol^{-1}}$ J mol^{-1}

= −1112.883 J mol^{-1}

= −1112.883 kJ mol^{-1}

= −1100 kJ mol^{-1}

Heat energy = 200.00 × 4.18 × 13.00

= + 10900 J

ΔH = −10900 J

combustion = −10.900 kJ

No. of moles = $\frac{0.45}{46.08}$ = 0.0098 moles

Finally → to convert to kJ mol^{-1}:

$\frac{-10.900\ kJ}{0.0098\ mol}$ = −1100 kJ mol^{-1}

The IB data booklet value is −1367 kJ mol^{-1}. The difference between the values can be accounted for by any of the following factors:

- Not all the heat produced by the combustion reaction is transferred to the water. Some is needed to heat the copper calorimeter and some has passed to the surroundings.
- The combustion of the ethanol is unlikely to be complete owing to the limited oxygen available, as assumed by the literature value.
- The experiment was not performed under standard conditions.

9 A copper calorimeter was used to determine the enthalpy of combustion of butan-1-ol. The experimental value obtained was −2100 ± 200 kJ mol^{-1} and the data booklet value is −2676 kJ mol^{-1}. Which of the following accounts for the difference between the two values?

I random measurement errors
II incomplete combustion
III heat loss to the surroundings

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

10 1.10 g of glucose was completely burnt in a copper calorimeter. The temperature of the water increased from 25.85 °C to 36.50 °C.

(a) Calculate the enthalpy of combustion of glucose from the data below.

Mass of water / g	200.00
Specific heat capacity of water / g^{-1} K^{-1}	4.18
Mass of copper / g	120.00
Specific heat capacity of copper / g^{-1} K^{-1}	0.385

(b) Draw an enthalpy level diagram to represent this reaction.

11 The heat released from the combustion of 0.0500 g of white phosphorus increases the temperature of 150.00 g of water from 25.0 °C to 31.5 °C. Calculate a value for the enthalpy change of combustion of phosphorus. Discuss possible sources of error in the experiment.

10 (a) ΔT = 36.50 − 25.85 = 10.65 °C (or K)

$q = mc\Delta T$

$q = m(H_2O) \times c(H_2O) \times \Delta T(H_2O) + m(Cu) \times c(Cu) \times \Delta T(Cu)$

= (200.00 g × 4.18 J g^{-1} K^{-1} × 10.65 K) + (120.00 g × 0.385 J g^{-1} K^{-1} × 10.65 K)

= 8900 J + 492 J

q = 9392 J

$n(C_6H_{12}O_6) = \frac{1.10\ g}{180.18\ g\ mol^{-1}}$

~~= 6.11 × 10^{-3} mol~~

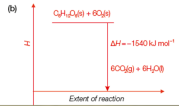
In calculating the enthalpy change of combustion, ΔH_c, we have to recognize that this is an exothermic reaction and that ΔH_c will therefore be a negative value.

$\Delta H_c = -\frac{9392\ J}{6.11 \times 10^{-3}\ mol}$

= −1.54 × 10^5 J mol^{-1}

= −1540 kJ mol^{-1}

(b)



11 $q = mc\Delta T$

q = 150.00 g × 4.18 J g^{-1} K^{-1} × (31.5 − 25.0) K

= 4075.5 J = 4100 J (to 2 s.f.)

$n(P) = \frac{0.0500\ g}{30.97\ g\ mol^{-1}}$

= 1.61 × 10^{-3} mol

$\Delta H_c = \frac{-4100\ J}{1.61 \times 10^{-3}\ mol}$

= −2525 × 10^3 J mol^{-1}

= −2500 kJ mol^{-1}

The precision of the answer is limited by the precision of measurement of the temperature difference. The value is lower than the literature value owing to heat losses and incomplete combustion.

Complete combustion

$CH_4 + .O_2 \rightarrow CO_2 + .H_2O$

Incomplete combustion

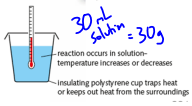
$CH_4 + O_2 \rightarrow CO_2 + H_2O + CO + C$

Not

Enthalpy changes of reaction in solution

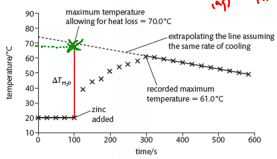
The enthalpy changes of reaction in solution can be calculated by carrying out the reaction in an insulated system, for example, a polystyrene cup (Figure 5.8). The heat released or absorbed by the reaction can be measured from the temperature change of the water.

30 cm³ solution = 30g



Take the reaction between a copper sulfate solution and excess zinc powder (to ensure the reaction goes to completion).

$CuSO_{4(aq)} + Zn_{(s)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$



The largest source of error is the loss of heat to the surroundings during the reaction (it is exothermic). To compensate for this we canextrapolate the graph back to the start of the reaction to find the maximum temperature acheived.

To proceed we can make the following assumptions:

1. no heat loss from the system
2. all the heat goes from the reaction to the water
3. the solution is dilute: $V(CuSO_4) = V(H_2O)$ →
4. water has a density of 1.00 g cm^{-3}.

For an exothermic reaction, $\Delta H_{reaction}$ is negative as heat has passed from the reaction into the water.

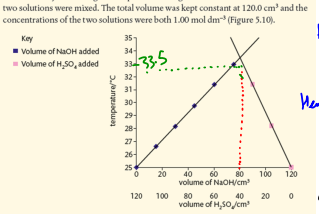
$$\Delta H(\text{water}) = m(H_2O) \times c(H_2O) \times \Delta T(H_2O)$$

The limiting reactant must be identified in order to determine the molar enthalpy change of reaction.

$$\Delta H_{reaction} = \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{\text{moles of limiting reactant}}$$

Worked example

The neutralization reaction between solutions of sodium hydroxide and sulfuric acid was studied by measuring the temperature changes when different volumes of the two solutions were mixed. The total volume was kept constant at 120.0 cm³ and the concentrations of the two solutions were both 1.00 mol dm^{-3} (Figure 5.10).



$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Heat = m · c · ΔT

120 cm³ = water

120 g water

c = 4.18 ΔT = 8.5

80 cm³ NaOH / 40 cm³ H_2SO_4

Conc = 1.00 mol dm^{-3}

$c \times V = 1.00 \times \frac{80}{1000}$

= 0.08 moles NaOH

0.08 → 4.2636

1 → x

x = 50 kJ mol^{-1}

(a) Determine the volumes of the solutions which produce the largest increase in temperature.

(b) Calculate the heat produced by the reaction when the maximum temperature was produced.

(c) Calculate the heat ~~4.2636 kJ~~ 6 kJ per mole of sodium hydroxide. 4.2636 kJ

(d) The literature value for the enthalpy of neutralization is = −57.5 kJ mol^{-1}.

Calculate the percentage error value and suggest a reason for the discrepancy between the experimental and literature values.

Solution

(a) From the graph: $V(NaOH) = 80.0$ cm³
$V(H_2SO_4) = 40.0$ cm³

(b) Assuming 120.0 cm³ of the solution contains 120.0 g of water and all the heat produced by the neutralization reaction passes into the water.

$$\Delta H_{reaction} = -m(H_2O) \times c(H_2O) \times \Delta T(H_2O)\ \text{J}$$
$$= -120.0\ \text{g} \times 4.18\ \text{J g}^{-1}\ \text{K}^{-1} \times (33.5 - 25.0)\ \text{K}$$
$$= -4264\ \text{J}$$

(c) $\Delta H_{reaction} = \frac{-4264}{n(NaOH)}\ \text{J mol}^{-1}$

$= \frac{-4264}{1.00 \times 80.0 / 1000}\ \text{J mol}^{-1}$

$= \frac{-4264}{80.0}\ \text{kJ mol}^{-1}$

$= -53.3\ \text{kJ mol}^{-1}$

(d) $\%\ \text{error} = \frac{-57.5 - -53.3}{-57.5} \times 100\% = 7\%$

The calculated value assumes:

- no heat loss from the system
- all heat is transferred to the water
- the solutions contain 120 g of water.

Exercises

12 Calculate the molar enthalpy change from the data in Figure 5.9. The copper sulfate has a concentration of 1.00 mol dm^{-3} and a volume of 1.00 dm³.

13 Calculate the enthalpy of neutralization based on the following data.

Initial temperature of solutions / °C	24.5
Concentration of KOH(aq) / mol dm^{-3}	0.950
Concentration of HNO_3(aq) / mol dm^{-3}	1.050
Volume of HCl(aq) / cm³	50.00
Volume of NaOH(aq) / cm³	50.00
Final temperature of mixture / °C	32.3

State the assumptions you have made in your calculation.

14 A student added 5.350 g of ammonium chloride to 100.00 cm³ of water. The initial temperature of the water was 25.55 °C but it decreased to 21.79 °C. Calculate the enthalpy change that would occur when 1 mol of the solute is added to 1.000 dm³ of water.

15 Explain the meaning of the term ΔH and describe how it is measured.

12 $q = mc\Delta T$
= 1000 g × 4.18 J g^{-1} K^{-1} × (70.0 – 20.0) K
= 209 kJ, for 1 mole of 1 mol dm^{-3} solution
ΔH = –209 kJ mol^{-1}

13 ΔT = 32.3 – 24.5 = 7.8 K
$q = m(H_2O) \times c(H_2O) \times \Delta T(H_2O)$
= 100.00 g × 4.18 J g^{-1} K^{-1} × 7.8 K
= 3300 J
$n(NaOH) = \frac{50.00}{1000} \times 0.950 = 0.0475$ mol
$\Delta H = \frac{-3300\ \text{J}}{0.0475\ \text{mol}} = 69 \times 10^3$ J mol^{-1}
= –69 kJ mol^{-1}
Assumptions: no heat loss, c(solution) = c(water), m(solution) = $m(H_2O)$, density(H_2O) = 1.00

14 If the mass of the solution is taken as 105.04 g (mass of water + mass of NH_4Cl dissolved), ΔH = +16.5 kJ mol^{-1}.
If the mass of the solution is instead assumed to be 100.00 g (mass of water only), ΔH = +15.7 kJ mol^{-1}.
$q = mc\Delta T$
= 100.00 g × 4.18 J g^{-1} K^{-1} × (21.79 – 25.55)
= –1570 J for 5.35 g
q = 293.6 J per g
$n(NH_4Cl)$ = 53.50 g mol^{-1}
ΔH = 293.6 J g^{-1} × 53.50 g mol^{-1}
= 15.7 kJ mol^{-1}

15 ΔH is change in enthalpy, the heat content of a system. Enthalpy cannot be measured directly but enthalpy changes can be calculated for chemical reactions and physical processes from measured temperature changes using the equation $q = mc\Delta T$, where q is the heat change, m is the mass of the substance(s) changing temperature, c is the specific heat capacity of the substance(s) changing temperature and ΔT is the measured temperature change occurring in the substance(s).