

Measurement of an enthalpy change

Measuring the Enthalpy Change for a Reaction Experimentally

Calorimetric method

For a reaction in solution we use the following equation

energy change = mass of solution x heat capacity x temperature change

$$Q \text{ (J)} = m \text{ (g)} \times c_p \text{ (J g}^{-1}\text{K}^{-1}) \times \Delta T \text{ (K)}$$

This equation will only give the energy for the actual quantities used. Normally this value is converted into the energy change per mole of one of the reactants. (The enthalpy change of reaction, ΔH)

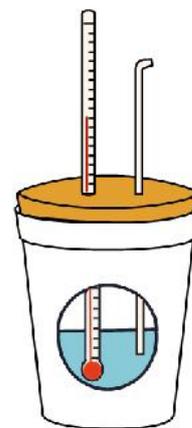
Calorimetric method

One type of experiment is one in which substances are mixed in an insulated container and the temperature rise measured.

This could be a solid dissolving or reacting in a solution or it could be two solutions reacting together

General method

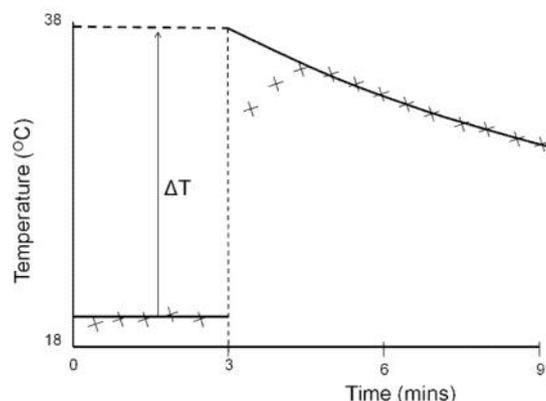
- washes the equipment (cup and pipettes etc) with the solutions to be used
- dry the cup after washing
- put polystyrene cup in a beaker **for insulation and support**
- measure out desired volumes of solutions with volumetric pipettes and transfer to insulated cup
- clamp thermometer into place making sure the thermometer bulb is immersed in solution
- measure the initial temperatures of the solution or both solutions if 2 are used. Do this every minute for 2-3 minutes
- at minute 3 transfer second reagent to cup. If a solid reagent is used then add the solution to the cup first and then add the solid weighed out on a balance.
- if using a solid reagent then use 'before and after' weighing method
- stirs mixture (**ensures that all of the solution is at the same temperature**)
- record temperature every minute after addition for several minutes



If the reaction is slow then the exact temperature rise can be difficult to obtain as cooling occurs simultaneously with the reaction.

To counteract this we take readings at regular time intervals and extrapolate the temperature curve/line back to the time the reactants were added together.

We also take the temperature of the reactants for a few minutes before they are added together to get a better average temperature. If the two reactants are solutions then the temperature of both solutions need to be measured before addition and an average temperature is used.



Errors in this method

- energy transfer from surroundings (usually loss)
- approximation in specific heat capacity of solution. The method assumes all solutions have the heat capacity of water.
- neglecting the specific heat capacity of the calorimeter- we ignore any energy absorbed by the apparatus.
- reaction or dissolving may be incomplete or slow.
- Density of solution is taken to be the same as water.

Read question carefully. It may be necessary to describe:

- Method
- Drawing of graph with extrapolation
- Description of the calculation

Calculating the enthalpy change of reaction, ΔH , from experimental data

General method

1. Using $q = m \times c_p \times \Delta T$ calculate energy change for quantities used
2. Work out the moles of the reactants used
3. Divide q by the number of moles of the reactant not in excess to give ΔH
4. Add a sign and unit (divide by a thousand to convert J mol^{-1} to kJ mol^{-1})

The heat capacity of water is $4.18 \text{ J g}^{-1}\text{K}^{-1}$. In any reaction where the reactants are dissolved in water we assume that the heat capacity is the same as pure water.

Also assume that the solutions have the density of water, which is 1 g cm^{-3} . Eg 25 cm^3 will weigh 25 g

Example 6. Calculate the enthalpy change of reaction for the reaction where 25.0 cm^3 of 0.20 mol dm^{-3} copper sulfate was reacted with 0.01 mol (excess of zinc). The temperature increased 7.0°C .

Step 1: Calculate the energy change for the amount of reactants in the calorimeter.

$$Q = m \times c_p \times \Delta T$$

$$Q = 25 \times 4.18 \times 7$$

$$Q = 731.5 \text{ J}$$

Note the mass is the mass of the copper sulfate solution only. Do not include mass of zinc powder.

Step 2: calculate the number of moles of the reactant not in excess.

$$\begin{aligned} \text{moles of CuSO}_4 &= \text{conc} \times \text{vol} \\ &= 0.2 \times 25/1000 \\ &= 0.005 \text{ mol} \end{aligned}$$

If you are not told what is in excess, then you need to work out the moles of both reactants and work out using the balanced equation which one is in excess.

Step 3: calculate the enthalpy change per mole, ΔH (the enthalpy change of reaction)

$$\begin{aligned} \Delta H &= Q / \text{no of moles} \\ &= 731.5 / 0.005 \\ &= 146300 \text{ J mol}^{-1} \\ &= 146 \text{ kJ mol}^{-1} \text{ to 3 sf} \end{aligned}$$

Finally add in the sign to represent the energy change: if temp increases the reaction is exothermic and is given a minus sign e.g. -146 kJ mol^{-1}

Remember in these questions: **sign, unit**

Example 7. 25.0 cm^3 of 2.0 mol dm^{-3} HCl was neutralised by 25.0 cm^3 of 2.0 mol dm^{-3} NaOH. The temperature increased 13.5°C . Calculate the enthalpy change per mole of HCl.

Step 1: Calculate the energy change for the amount of reactants in the calorimeter.

$$Q = m \times c_p \times \Delta T$$

$$Q = 50 \times 4.18 \times 13.5$$

$$Q = 2821.5 \text{ J}$$

Note the mass equals the mass of acid + the mass of alkali, as they are both solutions.

Step 2: calculate the number of moles of the HCl.

$$\begin{aligned} \text{moles of HCl} &= \text{conc} \times \text{vol} \\ &= 2 \times 25/1000 \\ &= 0.05 \text{ mol} \end{aligned}$$

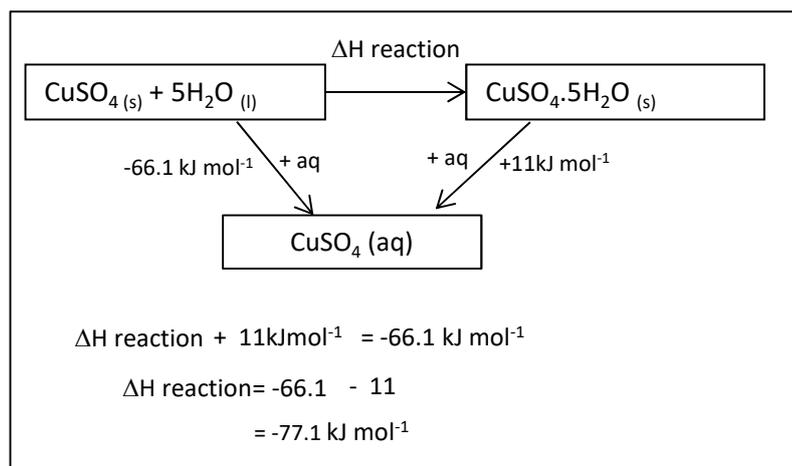
Step 3: calculate ΔH the enthalpy change per mole which might be called the enthalpy change of neutralisation

$$\begin{aligned} \Delta H &= Q / \text{no of moles} \\ &= 2821.5 / 0.05 \\ &= 56430 \text{ J mol}^{-1} \\ &= -56.4 \text{ kJ mol}^{-1} \text{ to 3 sf} \end{aligned}$$

Exothermic and so is given a minus sign

Remember in these questions: **sign, unit,**

Often Hess's law cycles are used to measure the enthalpy change for a reaction that cannot be measured directly by experiments. Instead alternative reactions are carried out that can be measured experimentally.



This Hess's law is used to work out the enthalpy change to form a hydrated salt from an anhydrous salt.

This cannot be done experimentally because it is impossible to add the exact amount of water without the solid dissolving and it is not easy to measure the temperature change of a solid.

Instead both salts are dissolved in excess water to form a solution of copper sulfate. The temperature changes can be measured for these reactions.

Detailed method for measuring enthalpy change of solution of anhydrous copper(II) sulfate

1. Weigh out between 3.90 g and 4.10 g of anhydrous copper(II) sulfate in a dry weighing bottle. The precise mass should be recorded.
2. Using a volumetric pipette, place 25 cm³ of deionised water into a polystyrene cup and record its temperature at the beginning (t=0), start the timer and then record the temperature again every minute, stirring the liquid continuously.
3. At the fourth minute, add the powdered anhydrous copper(II) sulfate rapidly to the water in the polystyrene cup and continue to stir, but do not record the temperature.
4. Reweigh the empty weighing bottle
5. At the fifth minute and for every minute up to 15 minutes, stir and record the temperature of the solution in the polystyrene cup.
6. Plot a graph of temperature (on the y-axis) against time. Draw two separate best fit lines; one, which joins the points before the addition, and one, which joins the points after the addition, extrapolating both lines to the fourth minute.
7. Use your graph to determine the temperature change at the fourth minute, which theoretically should have occurred immediately on addition of the solid.
8. Using $q = m \times c_p \times \Delta T$ calculate energy change
 $= 20 \times 4.18 \times \Delta T$
9. Calculate $\Delta H_{\text{solution}}$ by dividing q by number of moles of anhydrous copper(II) sulfate in mass added

The above method is then repeated using hydrated copper sulfate. The two $\Delta H_{\text{solution}}$ can then be used to calculate the ΔH for the enthalpy change of forming a hydrated salt as in the example above

Measuring Enthalpies of Combustion using Flame Calorimetry

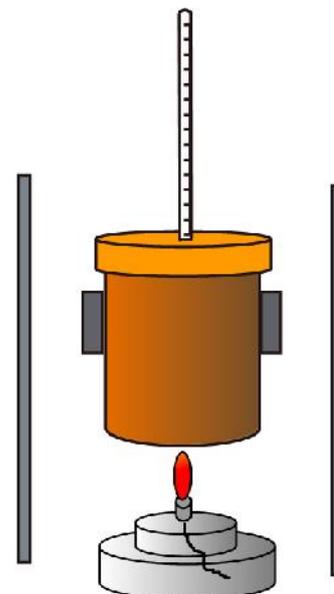
Enthalpies of combustion can be calculated by using calorimetry. Generally the fuel is burnt and the flame is used to heat up water in a metal cup.

Need to measure

- Mass of spirit burner before and after
- Temperature change of water
- Volume of water in cup

Errors in this method

- Energy losses from calorimeter
- Incomplete combustion of fuel
- Incomplete transfer of energy
- Evaporation of fuel after weighing
- Heat capacity of calorimeter not included
- Measurements not carried out under standard conditions as H_2O is gas, not liquid, in this experiment



Example 8. Calculate the enthalpy change of combustion for the reaction where 0.65g of propan-1-ol was completely combusted and used to heat up 150g of water from 20.1 to 45.5°C

Step 1: Calculate the energy change used to heat up the water.

$$Q = m \times c_p \times \Delta T$$

$$Q = 150 \times 4.18 \times 25.4$$

$$Q = 15925.8 \text{ J}$$

Note the mass in this equation is the mass of water in the calorimeter and not the alcohol

Step 2 : calculate the number of moles of alcohol combusted.

$$\begin{aligned} \text{moles of propan-1-ol} &= \text{mass} / M_r \\ &= 0.65 / 60 \\ &= 0.01083 \text{ mol} \end{aligned}$$

Step 3 : calculate the enthalpy change per mole which is called $\Delta_c H$ (the enthalpy change of combustion)

$$\begin{aligned} \Delta H &= Q / \text{no of moles} \\ &= 15925.8 / 0.01083 \\ &= 1470073 \text{ J mol}^{-1} \\ &= 1470 \text{ kJ mol}^{-1} \text{ to 3 sf} \end{aligned}$$

Finally add in the sign to represent the energy change: if temp increases the reaction is exothermic and is given a minus sign eg **-1470 kJ mol⁻¹**

Remember in these questions: **sign, unit**