4: Measuring enthalpy changes

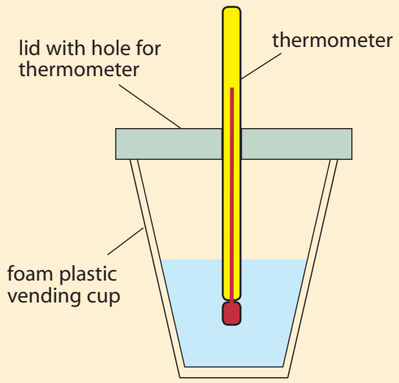
Measuring enthalpy changes: some simple examples

Industrial processes often involve gases and high temperature and/or pressure. They can't normally be performed in school/college. However, the principles of calculating ΔH are the same as for the simple examples below.

Example A

Method: using $q = mc\Delta t$

1 Measure out suitable amounts of reagents to give required mole ratio, as shown in the equation.
2 Measure their starting temperature, T_1 (if they differ, take the mean).
3 Mix the reactants well in a plastic vessel.
4 Record the highest or lowest temperature reached, T_2.



Example results
(for a neutralisation reaction: making sulfate of potash fertiliser)

$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$

	KOH	H_2SO_4
amounts of reactants	25 cm^3 2.0 mol dm^{-3} = 0.025 x 2.0 mol = 0.05 mol	25 cm^3 1.0 mol dm^{-3} = 0.025 x 1.0 mol = 0.025 mol
initial temperatures	19.0 °C	19.4 °C
highest temperature reached	32.8 °C	

Calculation

- Total volume = 50 cm^3
  so mass, *m*, of water heated by the reaction = 50 g
- Assume specific heat capacity, $c = 4.2$ J g^{-1} $°C^{-1}$ (same as water, since dilute solutions)
- T_1 (mean) = 19.2 °C
  T_2 = 32.8 °C
  temperature change, $\Delta t = 32.8 - 19.2 = 13.6$ °C
- Heat, *q*, evolved by 0.05 mol KOH + 0.025 mol H_2SO_4 = $mc\Delta t$
  $q = 50 \times 4.2 \times 13.6$ J = 2856 J = 2.86 kJ
  note units: g x J g^{-1} $°C^{-1}$ x °C = J
- Heat evolved by 1 mol KOH + 0.5 mol H_2SO_4 = $\frac{q}{0.05}$ kJ = 57 kJ
- Heat evolved by amounts shown in the equation (2 mol KOH + 1 mol H_2SO_4) = 114 kJ
- Since heat is evolved, ΔH is negative. So, $\Delta H = -114$ kJ mol^{-1}

Questions

4.3
Explain why such ΔH experiments should be done in plastic bottles or foam plastic cups rather than glass beakers.

4.4
(a) What difference would it make to the determination in *Example A* if the thermometer had 1°C divisions instead of 0.1°C?

(b) Confirm your answer by recalculating ΔH, using $T_1 = 19$ °C (for both) and $T_2 = 32$ °C.

4.5
What temperature change, Δt, would you expect to get if the determination was repeated using:

(a) 1.0 mol dm^{-3} potassium hydroxide instead of 2.0 mol dm^{-3}?

(b) 2.0 mol dm^{-3} sulfuric acid instead of 1.0 mol dm^{-3}?

(c) 50 cm^3 of 1.0 mol dm^{-3} sulfuric acid instead of 25 cm^3?

Explain your reasoning in each answer.

4.6
(a) What temperature change, Δt, would you expect to get if the original determination was repeated on a molar scale? That is, using 2 mol KOH and 1 mol H_2SO_4 (as in the equation), by mixing together 1 dm^3 of each solution in a large vessel.

(b) Check whether your logic was correct by calculating Δt as follows:
- $\Delta H = -114$ kJ mol^{-1}
  So 2 mol KOH and 1 mol H_2SO_4 give out 114 kJ = 114 000 J.
- $q = 114\,000$ J = $mc\Delta t$
- Work out Δt using:
  m = 2000 g, since volume of reactants = 2 dm^3
  $c = 4.2$ J g^{-1} $°C^{-1}$ as before

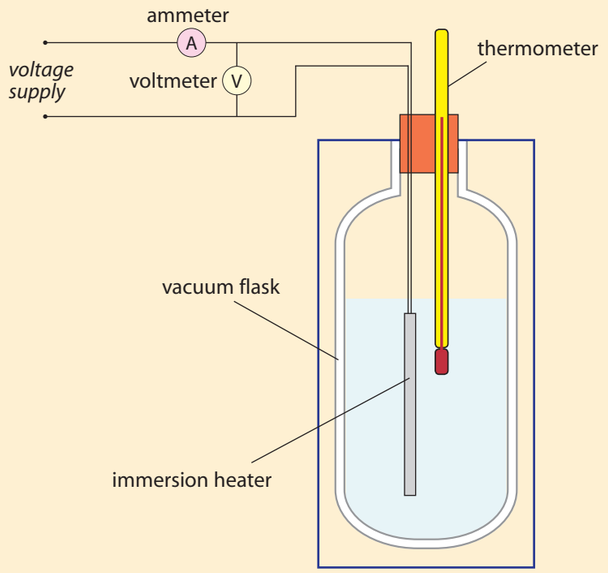
(c) Explain why the temperature rise is the same, even though much larger amounts of chemicals reacted.

Example B

Method: using electrical compensation

1 Measure out suitable amounts of reagents to give the required mole ratio, shown in the equation.
2 Measure their starting temperature, T_1. (If they differ, take the mean.)
3 Mix the reactants well in the vacuum flask.
4 Record the highest or lowest temperature reached, T_2, and thus temperature change Δt.
5 Switch on the heater and record the current, voltage and time required to:
- bring temperature back up to starting point, T_1
- or produce a further rise of Δt.

Alternatively, measure the electrical energy using a joulemeter.



Example results
(for neutralisation: making sodium citrate, an acidity regulator used in foodstuffs)

$C_3H_5O(COOH)_3(aq) + 3NaHCO_3(s) \rightarrow C_3H_5O(COONa)_3(aq) + 3CO_2(g) + 3H_2O(l)$
citric acid — sodium hydrogencarbonate — tri-sodium citrate

	Citric acid	$NaHCO_3$
amounts of reactants	100 cm^3 1.0 mol dm^{-3} = 0.10 mol	25.2 g = 25.2/84 mol = 0.30 mol
initial temperature	20.3 °C	
highest temperature reached:	32.8 °C	
electrical compensation	$V = 12$ V $I = 4.2$ A $t = 2$ min 20 s	

Note:
Molar mass, *M*, of sodium hydrogencarbonate = 84 g

Calculation

- Electrical compensation energy, $q = I\,t\,V = 4.2 \times 140 \times 12 = 7056$ J = 7.06 kJ
- Temperature dropped, so reaction is endothermic.
- Energy taken in by the reaction, causing temperature drop Δt
  = electrical energy needed to raise temperature by Δt back to T_1.
- So, heat absorbed by 0.1 mol citric acid + 0.3 mol $NaHCO_3$ = 7.06 kJ
- So, heat absorbed by amounts in the equation (1 mol acid + 3 mol $NaHCO_3$) = 70.6 kJ
- Since endothermic, $\Delta H = +70.6$ kJ mol^{-1}

Questions

4.7 Silver nitrate solution, used in making photographic film, is produced by reacting silver with concentrated nitric acid: $Ag(s) + 2HNO_3(aq) \rightarrow AgNO_3(aq) + NO_2(g) + H_2O(l)$

(a) 5.4 g of silver granules reacting with 25 cm^3 of 8 mol dm^{-3} nitric acid (density 1.2 g cm^{-3}) gave a temperature rise of 12.5 °C. Deduce which reactant was in excess, and thus how much of the silver actually reacted.

(b) Calculate ΔH for the reaction.

Dissolving

Simply dissolving a solid ionic compound in water produces an enthalpy change:
- sodium hydroxide – very exothermic
- ammonium nitrate – endothermic.

Bonds between ions break. New bonds form between ions and polarised water molecules. It's called solvation.