Chem Factsheet

www.curriculum-press.co.uk Number 206

Enthalpy change of neutralisation, ΔH_n or ΔH_{neut}

Neutralisation is the name given to a reaction between an acid (a proton donor) and a base (a proton acceptor) to form a salt and water.

e.g.1 $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

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

e.g.3 $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$

e.g.4 $HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$

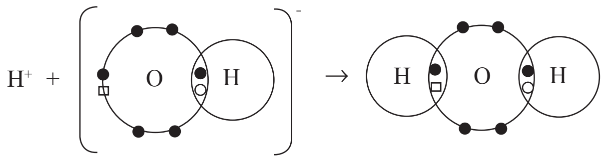
e.g.5 $HCl(aq) + NH_4OH(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$

e.g.6 $H_3PO_4(aq) + 3NaOH(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(l)$

There may be several bonding changes taking place (see later) during these reactions but the most important change is the combination of H^+ and OH^- ions to form covalent water.

i.e. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

This involves the *formation of a covalent bond* between the H^+ and O of the OH^- ion.



Consequently, since ***any** bond formation* is an exothermic process, then all neutralisation reactions are exothermic.

Definition

Like any enthalpy change (an energy change measured at constant pressure) it needs to be standardised in terms of definition and conditions of measurement to ensure that any person in any part of the world is referring to the same process.

The definition focuses on the common factor for all neutralisations – the formation of water! Apart from that, temperature, pressure and concentrations are fixed as in all other standard enthalpy changes.

Hence, the **standard** enthalpy change of neutralisation, ($\Delta H^\ominus_n$ or $\Delta H^\ominus_{neut.}$) is defined as follows:

> The standard enthalpy change of neutralisation is the enthalpy change when solutions of an acid and an alkali react together to produce 1 mole of water, measured at 298K and 100kPa pressure using 1.00moldm^{-3} solutions.

Hence, for the previous examples:

e.g.1 $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$; $\Delta H^\ominus_n$

e.g.2 $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + \mathbf{2}H_2O(l)$; $\underline{\mathbf{2}}\Delta H^\ominus_n$

e.g.3 $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow Ba(NO_3)_2(aq) + \mathbf{2}H_2O(l)$; $\underline{\mathbf{2}}\Delta H^\ominus_n$

e.g.4 $HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$; $\Delta H^\ominus_n$

e.g.5 $HCl(aq) + NH_4OH(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$; $\Delta H^\ominus_n$

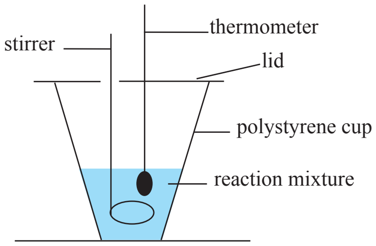
e.g.6 $H_3PO_4(aq) + 3NaOH(aq) \rightarrow Na_3PO_4(aq) + \mathbf{3}H_2O(l)$; $\underline{\mathbf{3}}\Delta H^\ominus_n$

Measuring an Enthalpy Change of Neutralisation

This is achieved by a technique called *calorimetry*.
Known quantities of acid and base (alkali) are mixed in a *calorimeter.* In a simple experiment, a polystyrene cup fitted with a lid is used – polystyrene is a very good thermal insulator and its use minimises heat loss during such experiments. Temperatures before and after mixing are also recorded. These data, along with a value for the specific heat capacity of water, allow the enthalpy change of neutralisation to be calculated.

Fully standardised, accurate enthalpy changes such as measured at the National Physical Laboratory (NPL) are measured using an electrically calibrated and compensated calorimeter such as that illustrated here.

Experiment



1. Pipette 50.0cm^3 of 1.00 moldm^{-3} acid into a polystyrene cup, stir it with a thermometer and record its steady initial temperature to 0.1°C – T_{acid}.
2. Pipette 50.0cm^3 of 1.05 moldm^{-3} alkali into a second polystyrene cup, stir it with a thermometer and record its steady initial temperature to 0.1°C – T_{alkali}.
3. Quickly pour the acid in to the alkali and fit a polystyrene lid. Stir the reacting mixture and record the *maximum* temperature achieved to 0.1°C – $T_{mixture}$.

> The temperature will *always increase* because the acid and alkali release energy as they react (see above). This energy is transferred to the water present resulting in a rise in temperature.

4. Calculate the average temperature change (ΔT) using:
   $\Delta T = T_{mixture} - [(T_{acid} + T_{alkali})/2]$
5. Repeat the experiment until concordant (agree within 0.1°C) ΔT values are obtained.

Sample Results

Acid used = 50.0 cm^3 1.00 moldm^{-3} HCl(aq)
Alkali used = 50.0 cm^3 1.05 moldm^{-3} NaOH(aq)

Experiment	T_{acid}/°C	T_{alkali}/°C	$T_{mixture}$/°C	ΔT/°C	Concordant?
1	20.0	19.6	26.7	6.9	Yes
2	21.4	20.6	27.2	6.2	No
3	19.8	20.4	26.9	6.8	Yes

Calculation

The heat released (q) during the experiment is calculated using:

$q = m \times C \times \Delta T$

where m = the mass of the reaction mixture
C = the specific heat capacity of the reaction mixture
ΔT = the temperature change during the experiment.

1. It is assumed that the mass of the reaction mixture is the same as the mass of water in the mixture.
2. It is assumed that this mass of water in the mixture is numerically equal to the volume of the reaction mixture. This is based on assuming that the density of the mixture is the same as that of water at 25°C. i.e. 1.0 gcm^{-3}.
3. It is assumed that the specific heat capacity of the mixture is same as the specific heat capacity of water. i.e. 4.18 $Jg^{-1}°C^{-1}$.

Hence, m = 50.0 + 50.0 = 100g
C = 4.18 $Jg^{-1}°C^{-1}$
ΔT = 6.9 + 6.8 / 2 = 6.85°C.

→ q = 100 × 4.18 × 6.85 = 2863J = 2.863 kJ

Moles HCl used = CV/1000 = 1.00 × 50.0 / 1000 = 0.0500
and moles NaOH used = CV/1000 = 1.05 × 50.0 / 1000 = 0.0525

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

→ Moles water formed = moles HCl (NaOH slight excess) used
= 0.05

→ ΔH_{neut} = -2.863 / 0.05 = -57.3 $kJmol^{-1}$.

Remember to insert "-" to show that the reaction is exothermic.
q does not have a "+" or "-" sign!

Example 1

In a laboratory experiment to determine the molar enthalpy of neutralisation, 25.0 cm^3 of 1.00 mol dm^{-3} sulphuric acid and 50.0 cm^3 of 1.00 mol dm^{-3} sodium hydroxide, each at a temperature of 21.0 °C, were mixed together in a calorimeter.

The final temperature of the mixture was 30.1°C, and the following reaction occurred:

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

Calculate the molar enthalpy of neutralisation from the above data.

[Assume that all solutions have a density of 1.00 g cm^{-3} and a specific heat capacity of 4.18 $J°C^{-1}g^{-1}$].

Example 2

During a thermochemical experiment, 100cm^3 of 2.00 $moldm^{-3}$ CH_3COOH is reacted with 110 cm^3 2.00 mol dm^{-3} KOH. Given that the enthalpy change of neutralisation for this reaction is -54.0 $kJmol^{-1}$, calculate the average temperature rise during the experiment.

The equation for the reaction is:

$$CH_3COOH(aq) + KOH(aq) \rightarrow CH_3COOK(aq) + H_2O(l)$$

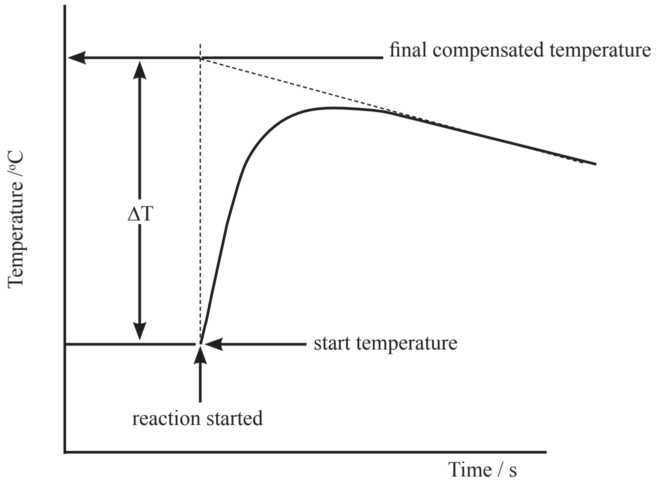
[Assume that all solutions have a density of 1.00 gcm^{-3} and a specific heat capacity of 4.18 $J°C^{-1}g^{-1}$].

In general, measured enthalpy changes using this sort of apparatus tend to be *lower* than standardised values because:
1. heat is lost to the surroundings
2. the reaction is incomplete
3. other reactions may occur

For neutralisation reactions, only heat loss is significant. This means the maximum temperature achieved by the reaction mixture will be *lower* than it should be.

Heat losses can be compensated for by plotting a cooling curve during the experiment. Since neutralisation reactions are very fast, this would need to be carried out using a thermocouple linked to data-logger and computer.

This would automatically produce a graph of the temperature of the reaction mixture against the time from the start of the experiment to well after the maximum observed temperature, measured say every 0.1s. Such a graph is shown below.



The cooling part of the curve is extrapolated back to the start of the reaction to give the "final compensated temperature" – this corresponds to the temperature that the mixture should have reached had the reaction been instantaneous with no heat loss. ΔT can be read from the graph and used in calculations as before.

Variations in ΔH_{neut} Values

This mostly depends on whether the acids and bases are strong or weak. In other words, whether they are fully or partially ionised in solution.

Reactions involving **strong** acids and alkalis invariably give ΔH_{neut} values between -57 and -58 $kJmol^{-1}$. They vary only slightly with different acid-alkali combinations.

Strong acids and strong alkalis are fully ionised in solution and the ions behave independently of each other. For example hydrochloric acid contains separate hydrogen ions and chloride ions in solution while sodium hydroxide solution consists of separate sodium ions and hydroxide ions in solution. When reacted, the hydrogen and hydroxide ions combine to form water and the remaining ions remain free in solution – they are "spectator ions", taking no part in the reaction.

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$

Hence, the equation for **any** strong acid being neutralised by a strong alkali is essentially: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

This means that reactions between any strong acid and any strong alkali will have the same enthalpy change of neutralisation, about -57 $kJmol^{-1}$.

Hence, for the previous examples:

e.g.1
$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l); \Delta H^\ominus_R = -57\ kJmol^{-1}$.

e.g.2
$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + \mathbf{2}H_2O(l); \Delta H^\ominus_R = -114\ kJmol^{-1}$.

e.g.3
$2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow Ba(NO_3)_2(aq) + \mathbf{2}H_2O(l); \Delta H^\ominus_R = -114\ kJmol^{-1}$.

e.g.4
$H_3PO_4(aq) + 3NaOH(aq) \rightarrow Na_3PO_4(aq) + \mathbf{3}H_2O(l); \Delta H^\ominus_R = -171\ kJmol^{-1}$.

Any slight variations are due to minor changes in the hydration of the different spectator ions during the mixing process.

Reactions involving **weak** acids and/or alkalis invariably give ΔH_{neut} values which are *less exothermic* than those for strong acid-strong alkali reactions. Furthermore they vary significantly for different acids and alkalis.

e.g.1
$HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)\ ; \Delta H_{neut} = -54\ kJmol^{-1}$.

e.g.2
$HCl(aq) + NH_4OH(aq) \rightarrow NH_4Cl(aq) + H_2O(l)\ ; \Delta H_{neut} = -52\ kJmol^{-1}$.

e.g.3
$HCN(aq) + NaOH(aq) \rightarrow NaCN(aq) + H_2O(l)\ ; \Delta H_{neut} = -12\ kJmol^{-1}$.

In a weak acid such as methanoic acid, at ordinary concentrations, only about 1% of the molecules are ionised. This means that the enthalpy change of neutralisation will include other enthalpy change terms for the ionisation of the acid as well as the reaction between the hydrogen ions and hydroxide ions. Since such ionisations involve bond breaking, they will be endothermic giving an overall less exothermic enthalpy change.

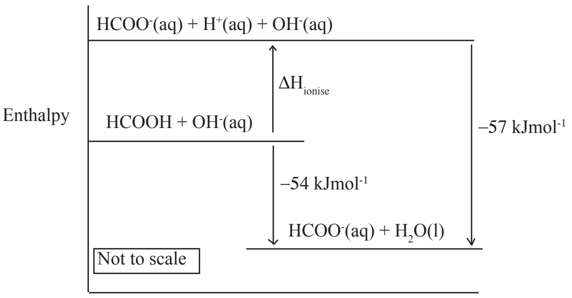
"Weak" **does not** mean the acid reacts less or more slowly giving a less exothermic reaction. It is important to realise that the weak acid **DOES** react completely. The acid is in equilibrium with its ions: $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

As the alkali is added, OH^- ions combine with and remove the H^+ ions thus, by Le Chatelier's Principle, pulling the equilibrium completely to the right. Energy is absorbed as the CH_3COOH molecules ionise during this shift.

Similarly, in a weak alkali such as ammonia solution, the ammonia is also present mostly as ammonia molecules.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq).$$

Again, there will be other endothermic enthalpy changes involved in forming these ions, apart from the simple formation of water from hydrogen ions and hydroxide ions.



The *difference* between a ΔH_{neut} for a weak acid / alkali and the standard -57 $kJmol^{-1}$ for a strong acid-alkali neutralisation can be used as a **net** *measure* of the energy required to complete the initial ionisation.

Using Hess's Law and the energy cycle shown, this can be seen to be +3kJmol-1 for methanoic acid. This is a fairly small value because the endothermic O-H bond ionisation must be mostly cancelled by the net exothermic hydration changes – the changes from hydrated HCOOH molecules to more hydrated H^+ and $HCOO^-$ ions.

Answers

Example 1

m = 25.0 + 50.0 = 75g
C = 4.18 $Jg^{-1}°C^{-1}$
$\Delta T = 30.1 - 21.0 = 9.1°C$.

$\rightarrow q = 75 \times 4.18 \times 9.1 = 2853J = 2.853\ kJ$

Moles H_2SO_4 used = CV/1000 = 1.00 × 25.0 / 1000 = 0.0250
and moles NaOH used = CV/1000 = 1.00 × 50.0 / 1000 = 0.0500

$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

→ Moles water formed = moles NaOH used = 0.05

$\rightarrow \Delta H_{neut} = -2.853 / 0.05 = -57.1\ kJmol^{-1}$.

Example 2

m = 100.0 + 100.0 = 200g
C = 4.18 $Jg^{-1}°C^{-1}$
$\Delta T = \times\ °C$.

Moles CH_3COOH used = CV/1000 = 2.00 × 100.0 / 1000 = 0.20
and moles KOH used = CV/1000 = 2.00 × 110.0 / 1000 = 0.22

$CH_3COOH(aq) + KOH(aq) \rightarrow CH_3COOK(aq) + H_2O(l)$

→ Moles water formed = moles CH_3COOH (KOH slight excess) used = 0.20

$\rightarrow q = \Delta H_{neut} \times$ Moles H_2O formed $= 54000 \times 0.20 = 10800J$.

$\rightarrow 10800 = 200 \times 4.18 \times \Delta T$

$\rightarrow \Delta T = 10800 / 200 \times 4.18 = 12.9°C$.

Acknowledgements: *This Factsheet was researched and written by Mike Hughes.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.*
ISSN 1351-5136