E10 ENTHALPY-OF-REACTION
Dissolution, acid/base reactions

THE TASK
To measure reaction enthalpies accurately and provide experimental confirmation of Hess' Law.

THE SKILLS
By the end of the experiment you should be able to:
- use calorimeters to obtain accurate reaction enthalpies,
- perform calculations to obtain molar dissolution and neutralisation enthalpies.

OTHER OUTCOMES
- You will develop generic scientific skills including the confirmation of a scientific law from careful experimental measurements and calculations.

INTRODUCTION

(1) *Forms of energy*

Associated with matter there are a number of forms of stored *energy*, including translational, rotational, and vibrational energy of the constituent particles. Matter also has a measurable *temperature*. Temperature is a measure of how hot or cold matter is - it is independent of the amount of matter present and hence is called an *intensive* property. When a pure, stable substance is heated, its temperature increases, leading to an increase in its stored energy. Its ability to store energy is its *heat-capacity*, with each substance having its own characteristic heat capacity.

Enthalpy is a property of matter related to its total energy and all matter has associated with it a quantity, H, of enthalpy. Enthalpy is dependent on the amount of matter present and hence is called an *extensive* property. Enthalpy is also a *function-of-state*: its value changes when the environmental conditions (temperature and pressure) change. To compare one substance with another we need to choose standard conditions; pressure of 100 kPa and usually (but not always) temperature of 298 K. Enthalpy values at 100 kPa pressure are indicated by the use of the superscripted symbol, $H^{\ominus}$.

(2) *Systems composed of a single substance*

A system may be composed of a single substance. The *state* of the system may be defined by its temperature and pressure. A particular combination of temperature and pressure may be designated as State 1, and the enthalpy of the system in State 1 may be designated as H_1. If a change occurs in the temperature or pressure or both, a new state of the system is set up. This may be designated as State 2 with the enthalpy of the system being designated as H_2. The change from State 1 to State 2 is thus accompanied by a change in enthalpy from H_1 to H_2. This enthalpy-change is defined as ΔH, where $\Delta H \equiv H_2 - H_1$. For any particular case ΔH may be positive, zero, or negative.

Absolute values of H are not measurable, but when a substance goes from one set of conditions to another, the enthalpy-change, ΔH, is (at least in principle) measurable. If the change from State 1 to State 2 (accompanied by an enthalpy-change ΔH) is carried out in a series of small steps, measurements show that the sum of these small enthalpy-changes is always equal to ΔH. For example, if a single temperature-increase of 30 K is replaced by the following series of steps - raise temperature 15 K, raise temperature 10 K, raise temperature 5 K, the enthalpy-changes accompanying these steps are each smaller than ΔH. Similarly, if a single temperature-increase of 30 K is replaced by the following steps - raise temperature 10 K, raise temperature 40 K, lower temperature 20 K - the enthalpy-change of the 30 K rise will be the same as the sum of the enthalpy-changes for the three steps.

A substance in a certain state defined by its temperature T_1 and its pressure p_1 has enthalpy H_1, and in a second state, defined by T_2 and p_2 has enthalpy H_2.

For the change from State 1 to State 2: $\Delta H = H_2 - H_1$

For the change from State 2 to State 1: $\Delta H = H_1 - H_2$

For the cycle State 1 → State 2 → State 1: $\Delta H = (H_2 - H_1) + (H_1 - H_2) = 0$

(3) *Systems composed of more than one substance*

A system may be composed of more than one substance. A change from State 1 to State 2 may simply be a change in conditions, as in (2), but it may also encompass a change in the kinds of substances present. For example, State 1 of a system may consist of 1.0 mole of ammonium chloride and 1.0 kilogram of water at room temperature and room pressure, the two substances being kept separate. State 2 (T and p as in State 1) may consist of the same materials freely mixed, now in the form of a water-solution of ammonium chloride. This change could be represented by the equation

$$NH_4Cl(s) \;\rightarrow\; NH_4^{+}(aq) \;+\; Cl^{-}(aq)$$

In going from State 1 to State 2, the system experiences, as in (2), an enthalpy-change ΔH. If $\Delta H > 0$ the system has gained enthalpy, and since energy is conserved, the enthalpy-increase must be accompanied by absorption of an equal quantity of heat energy from the surroundings of the system (so that T will remain constant). Because the surroundings are unlimited in extent, they can provide an unlimited supply of heat energy without suffering any observable fall in temperature. If $\Delta H < 0$, on the other hand, heat energy flows to the surroundings.

In the NH_4Cl/H_2O case, mixing is accompanied by an increase in the enthalpy of the system, heat energy being absorbed from the surroundings.

Changes such as above, with T constant, are called *isothermal*. A thermostat is a device for providing a constant-temperature environment in which to study isothermal changes.

(4) *Isolated systems*

We saw in the NH_4Cl/H_2O example in (3) that when heat-exchange with the surroundings was allowed, there was a spontaneous process of dissolution, leading to a state of higher enthalpy. The increase in the enthalpy of the system was provided by the heat energy absorbed from the surroundings. If a system is isolated from its surroundings, whatever changes occur, there can be no exchange of heat energy with the surroundings. In (3), heat energy was absorbed from the surroundings. In an isolated system, any heat energy absorbed will come from the system itself and this will be observed as a fall in temperature.

An *endothermic* process in an isolated system causes a decrease in temperature. (Such a process in an isothermal system would cause an increase in enthalpy.) An *exothermic* process in an isolated system causes an increase in temperature. (Such a process in an isothermal system would cause a decrease in enthalpy.)

The temperature-change accompanying a thermally isolated process, combined with the heat-capacity of the system, gives an exact measure of the enthalpy-change which would accompany the process if it were allowed to take place at constant temperature.

Changes taking place in a thermally isolated system are called *adiabatic*. A calorimeter is a device for measuring temperature-changes in an isolated system.

(5) *Experiments performed in this exercise*

This exercise involves measurements of enthalpy-changes, namely heats-of-reaction for dissolution processes, acid/base reactions and combinations of these two.

Each experiment is carried out in a glass beaker (with a temperature probe and a stirring rod) surrounded by air. Thermal equilibration between system and surroundings is slow, so the system may be regarded as thermally isolated for short time-intervals. Thus a measure of the enthalpy-change accompanying a reaction can be obtained by reading the temperature of the contents of the beaker before and after the change in the system. These experiments approximate adiabatic conditions.

The likely principal sources of experimental error are:

(i) Heat energy lost/gained to/from the surroundings due to imperfect insulation of the system.

(ii) Limitations in reading the temperature.

(iii) Non-homogeneity of solutions due to incomplete mixing.

(6) *Total-heat-capacity of the calorimeter*

The calorimeter consists of a 250 mL glass beaker and a glass stirring-rod. The volume of solution used in each experiment is 200 mL. The observations consist of reading the solution temperature before and after some change in the system. These readings, in conjunction with the heat capacity of the system, are used to calculate the enthalpy-changes that have occurred.
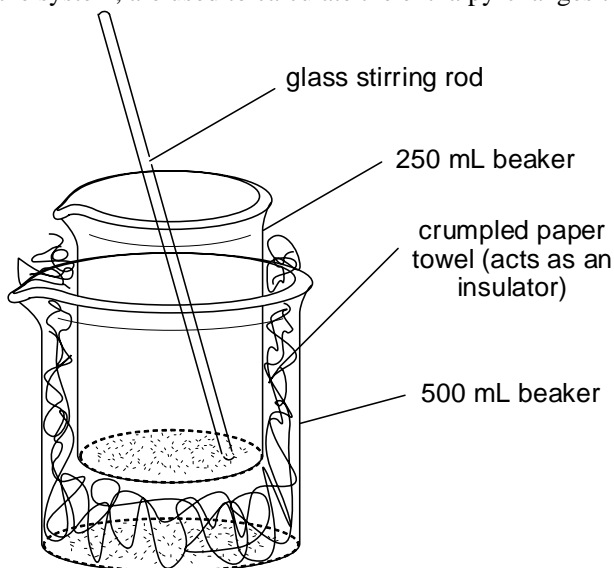
The system consists of two components, the calorimeter and the 200 mL of solution. The thermometer reads the temperature of the solution, but because some heat transfer occurs between the solution and the calorimeter, allowance must be made for the heat-capacity of the calorimeter. The heat gained/lost by the calorimeter is calculated as shown below, using the mass of the beaker and stirrer and the specific heat capacity of glass.

The temperature interval ΔT is the same for the calorimeter and the solution. The amount of heat gained/lost by the calorimeter per degree change in temperature is called the heat capacity of the calorimeter and is equal to the product of the mass of the calorimeter and its specific heat capacity.

Example: Specific heat-capacity of glass $= 0.84 \text{ J K}^{-1} \text{ g}^{-1}$

Mass of beaker + stirrer $= 92 \text{ g}$

Total heat capacity of calorimeter $= 92 \text{ g} \times 0.84 \text{ J K}^{-1} \text{ g}^{-1} = 77 \text{ J K}^{-1}$

ie For every 1 °C change in the temperature of the calorimeter, 77 joule is required.

NB   A 1 °C interval on the Celsius scale is equivalent to an interval of 1 kelvin on the absolute (thermodynamic) temperature scale.

(7) *Calculating* ΔH *from calorimetry experiments*

The specific heat capacity of dilute water solutions may be taken as $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ and the density of dilute water solutions as 1.00 g mL^{-1}.

In a typical experiment, the chemical change in the solution (200 mL) was accompanied by a +5.0 °C (= 5.0 K) change in temperature. The corresponding enthalpy change is calculated as follows:

Heat change undergone by the water $= \text{mass} \times \text{specific heat of water} \times \Delta T$

$= 200 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times 5.0 \text{ K}$

$= 4180 \text{ J}$

Heat change undergone by the calorimeter $= \text{heat capacity of calorimeter} \times \Delta T$

$= 77 \text{ J K}^{-1} \times 5.0 \text{ K} = 385 \text{ J}$

Total heat change undergone by the system $= 4180 \text{ J} + 385 \text{ J}$

$= 4565 \text{ J}$

$= 4.6 \text{ kJ}$

Hence if the chemical change had been carried out isothermally, the accompanying enthalpy change of the system would have been –4.6 kJ (to 2 significant figures). Note the importance of the sign in this answer. Exothermic reactions, recognised by the temperature of the water increasing, have negative enthalpy changes. Endothermic reactions, recognised by the temperature of the water decreasing, have positive enthalpy changes.

Note that a rough estimate of the heat capacity of the calorimeter was adequate because the specific heat capacity of glass is only one fifth that of water.

LAB-WORK

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- *You are provided with an accurate, expensive and **very fragile thermometer**. Handle it with great care. **Do not use it as a stirrer**.*

- *Take the density of the solutions used in all experiments as 1.00 g mL^{-1}.*

- *In this exercise, students work in pairs entering their results jointly, but carrying out all their calculations independently.*

Experiment 1: Heat capacity of the calorimeter

On a top-loading balance, weigh your clean dry 250 mL beaker and stirrer.

Mass of beaker + stirrer = $\boxed{\qquad\qquad\qquad\text{g}}$

Estimated total heat capacity of the calorimeter = $\boxed{\qquad \times 0.84\ \text{J K}^{-1}\ \text{g}^{-1} = \qquad \text{J K}^{-1}}$

Experiment 2 Enthalpy-of-dissolution: potassium nitrate in water

(2.1) Using a 100 mL measuring cylinder transfer tap water (200 mL) to a 250 mL conical flask.

(2.2) Clean and dry your calorimeter. Tare the beaker on a top loading balance, then use a nickel spoon to weigh into it from 9 to 11 g of KNO_3. Record the mass to 0.01 g.

KNO_3 weighed out $\boxed{\qquad\qquad\text{g}}$

Molar mass of KNO_3 $\boxed{\qquad\text{g mol}^{-1}}$

KNO_3 weighed out $\boxed{\qquad = \qquad\text{mol}}$

(2.3) In the table below, record the water temperature in the conical flask, then with rapid stirring quickly add its contents to the solid in the calorimeter. As soon as the water has been added, stir and then take an accurate temperature reading. Continue alternately stirring and reading the temperature. Readings should be taken until all of the solid has dissolved **and the temperature begins to turn back towards room temperature**. This will enable you to observe the maximum temperature change, which occurs when dissolution to give a homogeneous solution is complete.

Temperature of water before mixing $\boxed{\qquad °C}$

Readings (at intervals of 15 seconds or less)	1	2	3
Temperature after mixing (°C)			
Temperature difference (K)			

Maximum temperature difference $\boxed{\qquad K}$

(2.4) Calculations

Take the specific heat capacity of all solutions as 4.18 J K^{-1} g^{-1}.

Volume of solution = $\boxed{\qquad mL}$

Using density of solution =1.00 g mL^{-1}, mass of solution = $\boxed{\qquad g}$

Heat capacity of calorimeter (from Experiment 1) = $\boxed{\qquad J K^{-1}}$

Total heat change = $\boxed{\qquad + \qquad = \qquad J}$

$\boxed{\qquad mol}$ of KNO$_3$ dissolves in 200 mL of water and $\boxed{absorbs/liberates \qquad J}$

1.00 mol of KNO$_3$ dissolves in water and $\boxed{absorbs/liberates}$

$\boxed{= \qquad J = \qquad kJ}$

For the reaction $\quad$ KNO$_3$(s) $\rightarrow$ K$^+$(aq) + NO$_3^-$(aq)

the molar heat-of-dissolution ΔH (sign and magnitude) = $\boxed{\qquad kJ mol^{-1}}$

Demonstrator's Initials	

Experiment 3 Enthalpy-of-dissolution: sodium hydroxide in water

*   *Solid sodium hydroxide is highly reactive, and in contact with moist skin can cause severe burns.*

*   *Because sodium hydroxide tends to absorb water vapour and carbon dioxide gas from the atmosphere it is usually supplied in pellets, which must be kept covered as much as possible. When handling sodium hydroxide work quickly but do not rush: a 10 minute exposure of a sample causes an increase in mass of only about 1 per cent.*

(3.1) Repeat (2.1).

(3.2) You are supplied with a specimen tube containing pellets of NaOH. Repeat the procedure of (2.2), weighing into the beaker 2.0 g of NaOH (to the nearest pellet).

NaOH weighed out | g

Molar mass of NaOH | g mol^{-1}

NaOH weighed out | = | mol

(3.3) Repeat the procedure of (2.3), being particularly careful to hold the thermometer well above the pellets remaining on the bottom each time a temperature reading is taken.

Temperature of water before mixing | °C

Readings (at intervals of 15 seconds or less)	1	2	3	
Temperature after mixing (°C)				
Temperature difference (K)				

Maximum temperature difference | K

(3.4) Calculations

Mass of solution = [   ] g

Total heat change = [+   =   ] J

[mol] of NaOH dissolves in 200 mL of water and [absorbs/liberates   ] J

1.00 mol of NaOH dissolves in water and [absorbs/liberates]

[=   J =   kJ]

For the reaction $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$

the molar heat-of-reaction ΔH = [kJ mol^{-1}]

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Experiment 4 Enthalpy-of-reaction: solid sodium hydroxide with hydrochloric acid

(4.1) Transfer 0.25 M HCl (200 mL) to a 250 mL conical flask.

(4.2) You are supplied with a specimen tube containing pellets of NaOH. Repeat the procedure of (2.2), weighing into the beaker 2.0 g of NaOH (to the nearest pellet).

NaOH weighed out [   ] g

NaOH weighed out [=   mol]

(4.3) Repeat the procedure of (2.3), using the HCl solution in the conical flask instead of water.

Temperature of 0.25 M HCl before mixing | °C

Readings (at intervals of 15 seconds or less)	1	2	3
Temperature after mixing (°C)			
Temperature difference (K)			

Maximum temperature difference | K

(4.4) Calculations

Mass of solution = | g

Total heat change = | + = J

| mol of NaOH dissolves in 200 mL of 0.25 M HCl and absorbs/liberates

| J

1.00 mol of NaOH dissolves in 0.25 M HCl and absorbs/liberates

= J = kJ

For the reaction $NaOH(s) + H^+(aq) \rightarrow Na^+(aq) + H_2O$

the molar heat-of-reaction ΔH = | kJ mol^{-1}

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Experiment 5 Enthalpy-of-reaction: sodium hydroxide solution with hydrochloric acid

(5.1) Transfer 0.50 M HCl (100 mL) to a 250 mL conical flask. Take 0.50 M NaOH (100 mL) in your calorimeter.

(5.2) Record the temperature of both reactant solutions (rinsing the thermometer thoroughly between solutions). Then with rapid stirring quickly add the contents of the flask to the calorimeter. Since mixing is immediate, the maximum temperature difference can be recorded almost immediately after mixing.

Temperature of NaOH solution | °C

Temperature of HCl solution | °C

Mean temperature of reacting solutions | °C

Temperature after mixing | °C

Temperature difference | K

(5.3) Calculations

Volume of NaOH solution = | mL

Volume of HCl solution = | mL

Total mass of solutions = | g

Total heat change = | + | = | J

| mol | of NaOH in solution reacts with | mol | of HCl in solution

and | absorbs/liberates | | J

1.00 mol of NaOH in solution reacts with | mol | of HCl in solution

and | absorbs/liberates | | = | J = | kJ

For the reaction $OH^-(aq) + H^+(aq) \rightarrow H_2O$

the molar heat-of-reaction ΔH = | kJ mol^{-1}

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Experiment 6 Enthalpy-of-reaction: sodium hydroxide solution with nitric acid

Repeat Experiment 5, replacing 0.50 M HCl with 0.50 M HNO_3.

Temperature of
NaOH solution | | °C   Temperature of
HNO_3 solution | | °C

Mean temperature of reacting solutions | | °C

Temperature after mixing | | °C

Temperature difference | | K

Total mass of solutions = | | g

Total heat change = | + = | J

| mol | of NaOH in solution reacts with | mol | of HNO_3 in solution

and | absorbs/liberates | | J

1.00 mol of NaOH in solution reacts with | mol | of HNO_3 in solution

and | absorbs/liberates | = J = kJ

For the reaction | |

the molar heat-of-reaction $\Delta H =$ | kJ mol^{-1}

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Experiment 7 Enthalpy-of-Reaction: potassium hydroxide solution with nitric acid

Repeat Experiment 5, replacing 0.50 M NaOH with 0.50 M KOH and 0.50 M HNO_3.

Temperature of
KOH solution
| °C |

Temperature of
HNO_3 solution
| °C |

Mean temperature of reacting solutions | °C |

Temperature after mixing | °C |

Temperature difference | K |

Total mass of solutions = | g |

Total heat change = | + | = J |

| mol | of KOH in solution reacts with | mol | of HNO_3 in solution

and | absorbs/liberates | J |

1.00 mol of KOH in solution reacts with | mol | of HNO_3 in solution

and | absorbs/liberates | = J = kJ |

For the reaction | |

the molar heat-of-reaction ΔH = | kJ mol^{-1} |

| **Demonstrator's Initials** | |

INTERPRETATION OF RESULTS

(1) Summarise the results of Experiments 2 and 3, which deal with ΔH for the reaction
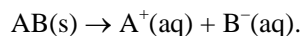
$$AB(s) \rightarrow A^+(aq) + B^-(aq).$$

TABLE E10-1 MOLAR ENTHALPY-OF-DISSOLUTION

AB	Reaction	ΔH (kJ mol^{-1})
KNO$_3$		
NaOH		

What do you notice about the signs of ΔH?

Rationalise this observation in terms of lattice enthalpy and hydration energy.

(2) Summarise the results of Experiments 3, 4, and 5.

TABLE E10-2 MOLAR ENTHALPY-OF-REACTION

Experiment	Reaction	ΔH (kJ mol^{-1})
3		$\Delta H_3 =$
5		$\Delta H_5 =$
3 + 5		$\Delta H_3 + \Delta H_5 =$
4		$\Delta H_4 =$

Discuss the results.

(3) Summarise the results of Experiments 5, 6, and 7.

TABLE E10-3 MOLAR ENTHALPY-OF-REACTION

Experiment	Reaction	ΔH (kJ mol^{-1})
5		$\Delta H_5 =$
6		$\Delta H_6 =$
7		$\Delta H_7 =$

Discuss the results.

(4) In each of these experiments the heat-of-reaction was found for 1.00 mole of a specified reactant but no account was taken of the volume of the solvent. If a different volume had been used, each heat-of-reaction would have been somewhat different: to obtain a standard heat-of-reaction it is necessary to specify not only the single mole of reactant, but also the final volume of solution, as well as the conditions (temperature, pressure). The standard conditions often chosen are 298 K / 100 kPa / 1.00 mole of reactant / infinite volume of solution.

With the standard volume infinite, the corresponding concentration is referred to as "infinite dilution", under which conditions the interactions among ions are negligible.

In these experiments you found the molar heat-of-dissolution for

KNO_3 to be [   ] kJ mol^{-1} and for NaOH to be [   ] kJ mol^{-1}

If in each case you had dissolved one mole of solute in a much larger volume of water, how would the new enthalpy values compare with your values?

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