

Calorimetry: Heat of Neutralisation

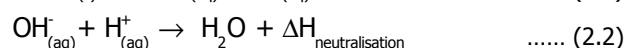
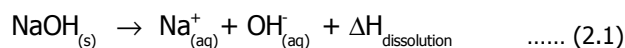
In this experiment, the heat of neutralisation of an acid – base reaction is measured using a simple self calibrating “coffee cup” calorimeter and an e-corder unit. A suitable reaction for this determination is solid NaOH being neutralised in excess HCl solution.

1. Aim

To experimentally determine the enthalpy change of an acid-base reaction, otherwise known as the heat of neutralisation.

2. Background

When solid NaOH is added to an aqueous HCl solution, the following two processes occur, each releasing energy in the form of heat.



From the first law of thermodynamics the total enthalpy change (ΔH_{total}) is the sum of the enthalpy change of dissolution ($\Delta H_{\text{dissolution}}$) and the enthalpy change of neutralisation ($\Delta H_{\text{neutralisation}}$).

Hence

$$\Delta H_{\text{neutralisation}} = \Delta H_{\text{total}} - \Delta H_{\text{dissolution}} \quad \dots (2.3)$$

The most common device for measuring the enthalpy change of a reaction, is the adiabatic bomb calorimeter. These are constant-volume reaction vessels designed to prevent heat exchange with their surroundings. As a calorimeter is adiabatic, the change in temperature (ΔT) of the calorimeter is proportional to the heat (q_v) that the reaction releases or absorbs. Therefore, by measuring ΔT we can determine q_v and hence the change in internal energy (ΔU). In reactions that only involve solids and liquids, the volume changes are miniscule and the values for ΔU and the enthalpy change ΔH are almost identical.

In this experiment a simple “coffee cup” calorimeter which is shown in **Figure 2.1** is used.

The calorimeter is made by placing two styrofoam coffee cups inside one another, and covering with another inverted cup. A resistance heater passes through the lid of the inverted cup in a manner that when in use, the heater pad is completely immersed in solution. The heater pad also does not touch the sides of the vessel, so all heat is exchanged with the solution.

Even heating is achieved by mixing the solution with a magnetic stirrer and to monitor temperature, a T-type thermocouple probe is inserted through the lid.

As some heat is absorbed by the components of the calorimeter, the best way to convert ΔT to q_v is by calibrating the calorimeter using a process of known energy output and determining the calorimeter constant (C) with the relationship

$$q_v = C \times \Delta T \quad \dots (2.4)$$

In this experiment, C is determined electrically by applying a potential (V) across the heater with resistance (R) for a known period of time (t)

$$q_e = \frac{V^2 t}{R} \quad \dots (2.5)$$

Prior to the laboratory class, the instructor will measure the resistance of each of the heaters with an accurate multimeter and mark the value on the outside of the calorimeter.

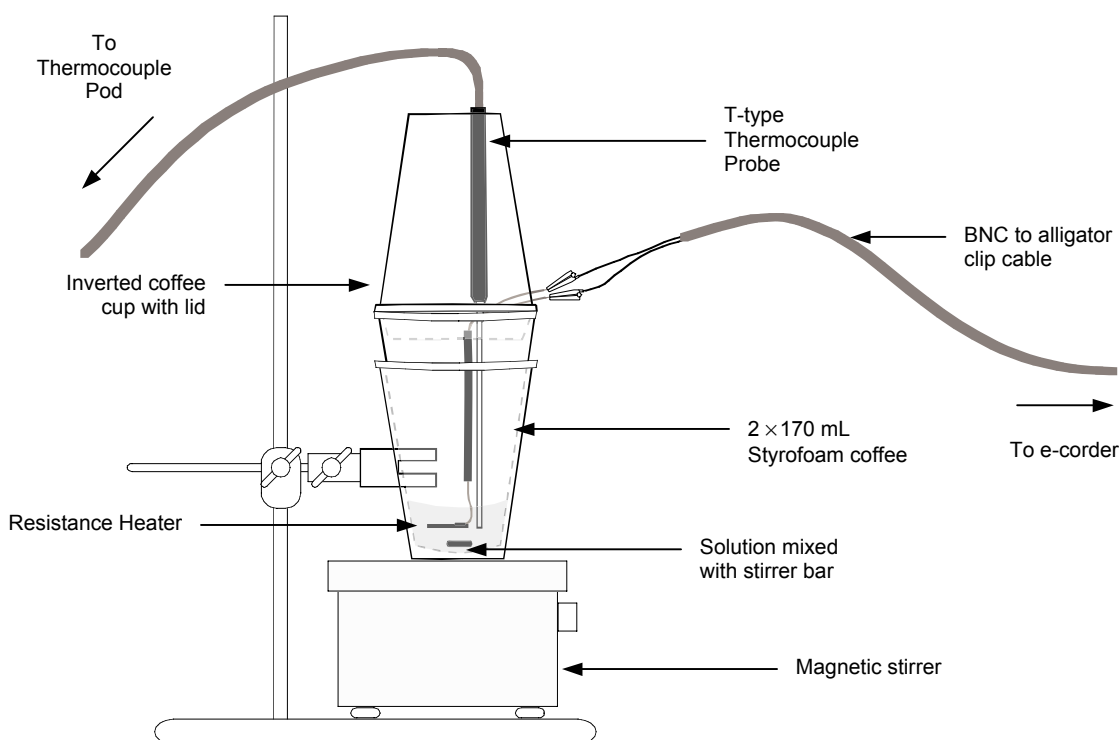


Figure 2.1 The coffee cup calorimeter

3. Hardware Required

Per Group:

- computer system with Chart and Thermocouple extension installed
- e-corder unit
- EP306 Thermocouple Pod

- coffee cup calorimeter*
- ET1400 T-type Thermocouple Probe
- resistance heater
- BNC T-piece
- BNC to BNC cable
- BNC cable terminating in two alligator clips
- magnetic stirrer with 10 mm stirrer bar
- retort stand with boss head and clamp
- tweezers
- watch glass
- 2 × 25 mL pipettes
- pipette bulb
- 2 × 250 mL beakers
- a box of lint free tissue

*See instructors notes for construction

Per Class:

- electronic balance (0.0001 g readability)
- dessicator jar
- multimeter
- printer

4. Reagents Required

- 200 mL distilled water
- 150 mL 0.1 M HCl
- NaOH pellets†

† Do not retrieve NaOH pellets from the dessicator until the group is ready to perform the dissolution and neutralisation reactions. Retrieve and weigh each pellet immediately prior to use.

5. Safety Notes & Instrument Care

- NaOH pellets are caustic. Avoid contact with skin!
- Wear gloves and protective eyewear throughout the experiment
- Avoid spilling liquids on the hardware by mixing reagents away from the units

- Rinse the tip of the thermocouple probe and the pad of the heater with distilled water after use

6. Procedure

6.1 Calorimeter Setup

- 6.1.1** Place one coffee cup inside the other and place the cups onto the magnetic stirrer. Secure the cups using the a retort stand and clamp and place the stirrer bar into the cups.
- 6.1.2** Pipette 25 mL of distilled water into the calorimeter. Set the magnetic stirrer to a moderate rate of stirring.
- 6.1.3** Invert the cup with the thermocouple probe and resistance heater emerging out of the lid, and place on top of the other cups. Make sure that the tip of the probe is at least 5 mm from the heater pad, and that both the pad and thermocouple tip will be immersed when 25 mL of solution is placed into the calorimeter.
- 6.1.4** Connect the plug of the T-type thermocouple into the rear of the Thermocouple Pod. The Thermocouple pod should be plugged into the DIN socket corresponding to channel 1 of the e-corder.
- 6.1.5** Plug a BNC T-piece to the + output of the e-corder. Using a BNC to BNC cable, connect one half of the T-piece to channel 2 of the e-corder. Attached the BNC connector of the cable terminating in two alligator clips to the other half of the T-piece. This splits the voltage output, enabling the voltage passed across the heater to be recorded simultaneously by Chart.

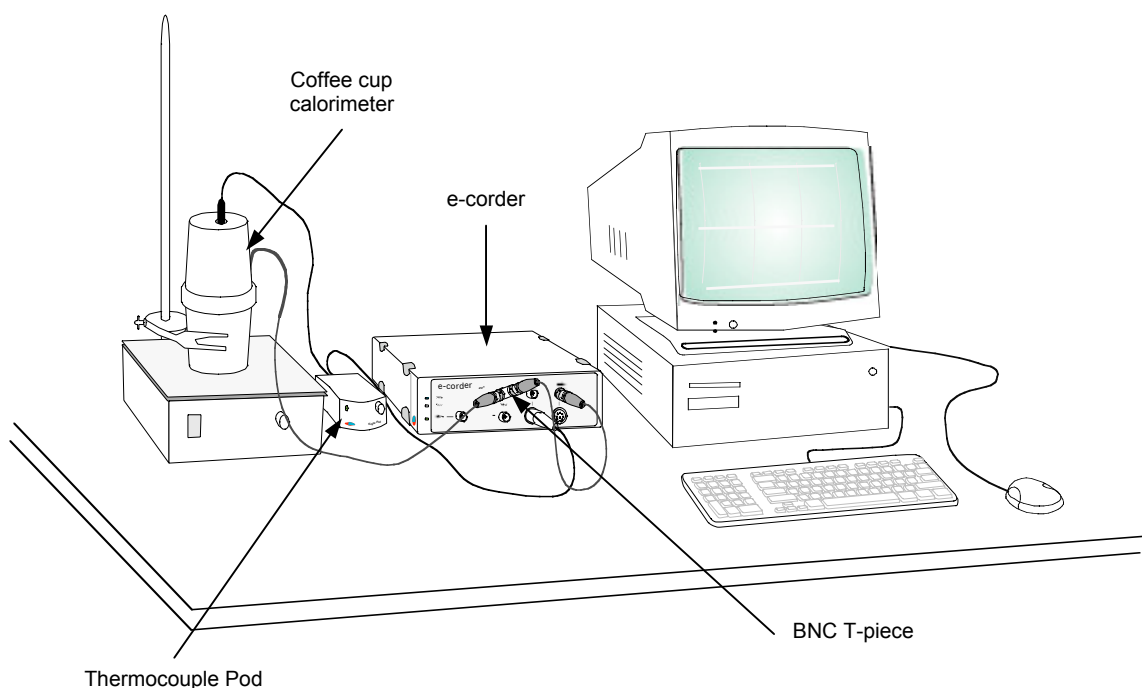


Figure 6.1 e-corder setup

6.2 General Chart Settings

6.2.1 Open Chart and load the settings file HofN.edset in the experiments gallery.

The settings for this file are as follows:

Number of Channels	2
Sampling	2 /s
Digital filter	1 Hz low pass
Initial temperature range	50 °C*
*T-type thermocouple set in the Thermocouple extension dialog box (automatic calibration of the T-type thermocouple)	

The file HofN.edset also includes a macro called Calorimeter Calibration, which defines the potential profile to be applied to the heater.

6.2.2 Check that **Thermocouple...** is selected in the Channel Functions pop-up menu for channel 1. In the Thermocouple extension dialog box, the T-type thermocouple radio button should be selected, the offset check box should NOT be selected at this stage and temperature should be recorded in °C to 3 decimal places.

6.2.3 Close the Thermocouple extension dialog box, click on **Start**, record the background temperature for a couple of seconds and make a note of this temperature.

6.2.4 In this experiment, the offset temperature mode of the Thermocouple Pod is used to measure temperature changes rather than absolute temperature. Using this mode, small temperature fluctuations can be measured with higher sensitivity by taking advantage of smaller temperature range settings. To switch to temperature offset mode, firstly choose **Thermocouple Pod...** under the Channel Functions pop-up menu. In the Thermocouple Pod dialog box, select the **Offset** radio box and an offset temperature range of $\Delta 25$ °C. Use the knob on the front of the thermocouple to adjust the signal to approximately 0. **Figure 6.2** shows a screenshot of this process.

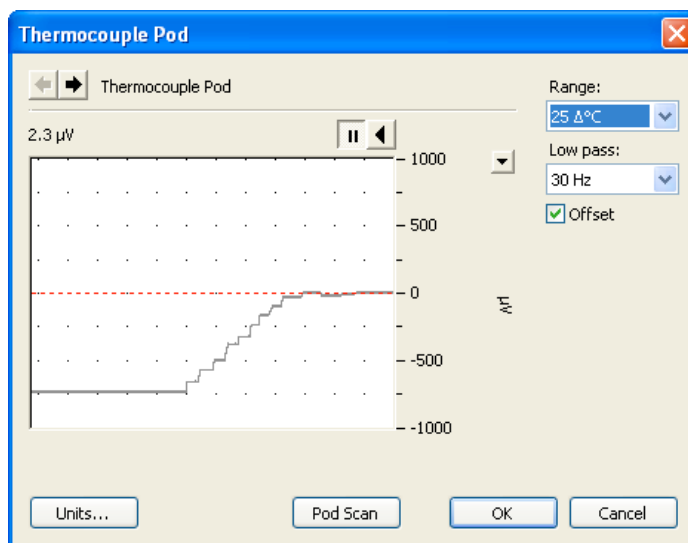


Figure 6.2 Adjusting the Thermocouple Pod output in Offset mode

- 6.2.5** In the Thermocouple Pod dialog box, select an offset temperature range of $\Delta 5\text{ }^{\circ}\text{C}$. Close the Thermocouple Pod dialog box and open the Thermocouple extension dialog box again. Select the **Offset** and the **New Blocks** checkbox's and enter the temperature recorded in **6.2.3** as the initial temperature (T_i).

6.3 Calorimeter Calibration

- 6.3.1** Under the Macro menu, select Calibration. Chart will begin recording at 0 V applied voltage, then after 30 seconds a 5 V voltage is passed across the resistor in the heater for a period of 4 minutes. After this period, the applied voltage is switched back to 0 V and chart continues recording for 30 seconds, then stops. The water temperature inside the calorimeter should gradually rise whilst the 5 V potential is being applied.

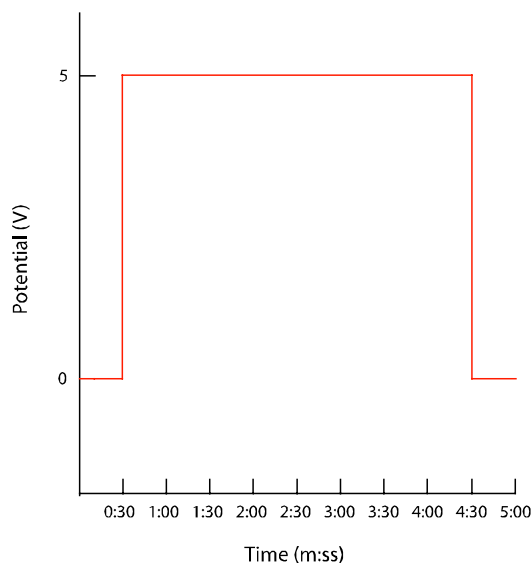


Figure 6.3 Profile of the voltage applied across the heater with time

- 6.3.2** Run the Calibration macro an additional 2 times. The data collected should look similar to **Figure 6.4**.

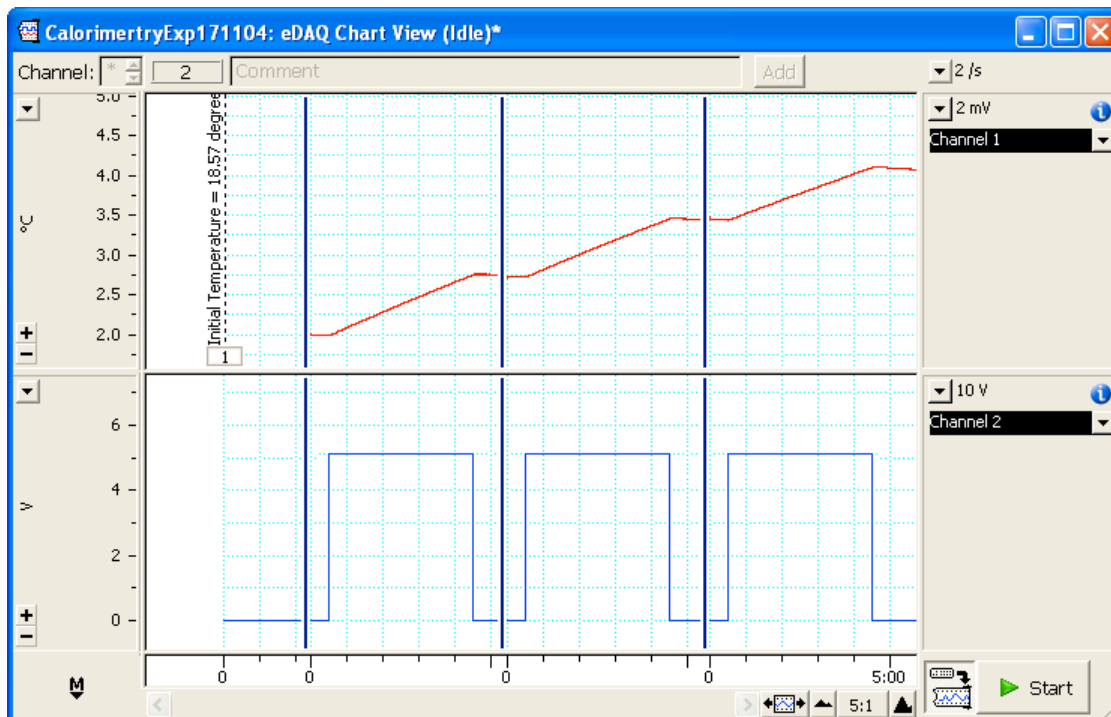


Figure 6.4 Typical data obtained after running the Calibration macro three times

- 6.3.3** In the first block of data collected, use the mouse to select a region of data prior to the potential being applied ($t < 30$) where the temperature has stabilised. Note the average temperature that is displayed in the Data Pad cell and call it T_1 .
- 6.3.4** In a similar manner, select a region of data after the potential was applied ($t > 4:30$), but before the temperature begins to drop again. Call the average temperature obtained T_2 .
- 6.3.5** Calculate ΔT for the first block, i.e. $\Delta T = T_2 - T_1$.
- 6.3.6** Calculate the heat released by the heater using **Equation 2.5**.
- 6.3.7** Calculate the Calorimeter Constant for the first block (C_1) using Equation 4.
- 6.3.8** Repeat Steps **6.3.3** to **6.3.7** for the remaining two blocks of data. Calculate an average Calorimeter Constant (C_{av}) for the three blocks of data.

6.4 Total Enthalpy Change

- 6.4.1** Carefully remove the lid of the calorimeter, empty the inner cup and rinse together with the stirrer bar with distilled water. Dry with lint free tissue.
- 6.4.2** Pipette 25 mL of 0.1 M HCl into the calorimeter and replace the lid (keeping the heater in place, even though it is not used in the rest of the experiment).

NB. Steps **6.4.3** to **6.4.5** should be performed without delay as solid NaOH pellets rapidly absorb moisture from the atmosphere.

- 6.4.3** Accurately weigh and record the mass of a single NaOH pellet on a watch glass, remembering to tare out the mass of watch glass.
- 6.4.4** Prior to dropping the NaOH pellet into the calorimeter, click on **Start** to begin recording the background temperature.
- 6.4.5** After approximately 10 seconds, briefly remove the lid of the calorimeter and drop the NaOH pellet into the HCl solution. Observe the change in temperature over the next 5 minutes or so, until the temperature reaches a maximum.
- 6.4.6** Record the initial temperature (T_1) and the final temperature (T_2) at which the system stabilises and before the temperature begins to drop again.
- 6.4.7** Calculate ΔT , and with the Calorimeter Constant (C_{av}) calculated in **6.3.8**, determine the amount of heat released (q). Convert this number the molar enthalpy change in units of kJ/mol.
- 6.4.8** Repeat steps **6.4.1** to **6.4.7** an additional two times. Calculate the average total molar enthalpy change.

6.5 Enthalpy Change of Dissolution and Neutralisation

- 6.5.1** To calculate $\Delta H_{\text{dissolution}}$, repeat **6.4.1** to **6.4.6** in Section **6.4**, substituting the 25 mL of 0.1 M HCl with 25 mL of distilled water.
- 6.5.2** With the Calorimeter Constant (C_{av}) calculated in **6.3.8**, determine the amount of heat released (q). Convert this number to the amount of heat released per mole of NaOH, which is equivalent to $\Delta H_{\text{dissolution}}$.
- 6.5.3** Repeat **6.5.1** and **6.5.2** a total of three times. Calculate the average molar enthalpy change of dissolution.
- 6.5.4** Calculate the molar enthalpy change of neutralisation ($\Delta H_{\text{neutralisation}}$) using **Equation 2.3**.

7. Results

Resistance of heater = _____ Ω

Initial temperature (T_i) = _____ $^{\circ}\text{C}$

7.1 Calorimeter Calibration

Block 1

$T_1 =$ _____ $^{\circ}\text{C}$

$T_2 =$ _____ $^{\circ}\text{C}$

$\Delta T =$ _____ K

Block 2

$T_1 =$ _____ $^{\circ}\text{C}$

$T_2 =$ _____ $^{\circ}\text{C}$

$\Delta T =$ _____ K

Block 3

$T_1 =$ _____ $^{\circ}\text{C}$

$T_2 =$ _____ $^{\circ}\text{C}$

$\Delta T =$ _____ K

Heat released by heater (q_e) =

Calorimeter constant =

$C_1 =$ _____ J/K

$C_2 =$ _____ J/K

$C_3 =$ _____ J/K

$C_{av} =$ _____ J/K

7.2 Total Enthalpy Change

Block 4

$m = \text{_____ g}$

$T_1 = \text{_____ } \Delta^\circ\text{C}$

$T_2 = \text{_____ } \Delta^\circ\text{C}$

$\Delta T = \text{_____ K}$

$q = \text{_____ J}$

Block 5

$m = \text{_____ g}$

$T_1 = \text{_____ } \Delta^\circ\text{C}$

$T_2 = \text{_____ } \Delta^\circ\text{C}$

$\Delta T = \text{_____ K}$

$q = \text{_____ J}$

Block 6

$m = \text{_____ g}$

$T_1 = \text{_____ } \Delta^\circ\text{C}$

$T_2 = \text{_____ } \Delta^\circ\text{C}$

$\Delta T = \text{_____ K}$

$q = \text{_____ J}$

$\Delta H_{\text{total}} = \text{_____ kJ/mol}$

$\Delta H_{\text{total}} = \text{_____ kJ/mol}$

$\Delta H_{\text{total}} = \text{_____ kJ/mol}$

$\Delta H_{\text{total}} \text{ (average)} = \text{_____ kJ/mol}$

7.3 Enthalpy change of dissolution and neutralisation

Block 7

$m = \text{_____ g}$

$T_1 = \text{_____ } \Delta^\circ\text{C}$

$T_2 = \text{_____ } \Delta^\circ\text{C}$

$\Delta T = \text{_____ K}$

$q = \text{_____ J}$

Block 8

$m = \text{_____ g}$

$T_1 = \text{_____ } \Delta^\circ\text{C}$

$T_2 = \text{_____ } \Delta^\circ\text{C}$

$\Delta T = \text{_____ K}$

$q = \text{_____ J}$

Block 9

$m = \text{_____ g}$

$T_1 = \text{_____ } \Delta^\circ\text{C}$

$T_2 = \text{_____ } \Delta^\circ\text{C}$

$\Delta T = \text{_____ K}$

$q = \text{_____ J}$

$\Delta H_{\text{dissolution}} = \text{_____ kJ/mol}$

$\Delta H_{\text{dissolution}} = \text{_____ kJ/mol}$

$\Delta H_{\text{dissolution}} = \text{_____ kJ/mol}$

$\Delta H_{\text{dissolution}} \text{ (average)} = \text{_____ kJ/mol}$

$\Delta H_{\text{neutralisation}} \text{ (average)} = \text{_____ kJ/mol}$

- 9.2** How does the value for the calculated heat of reaction compare with the value obtained experimentally? List possible sources of systematic error.

As a fairly basic calorimeter is used in the experiment, there is likely to be a net flux of heat out of the calorimeter, resulting in enthalpy values with absolute values less than expected.

The electrical heating doesn't exactly model the heating due to energy released from the chemical reaction and hence systematic errors in the calculation of the calorimeter constant are likely. The rate of heating using the resistance heater is fairly constant, whilst the rate of heating from the neutralisation reaction diminishes with time as the NaOH is consumed.

Errors in measuring the resistance of the heater and the voltage applied would add systematic errors to the result.

Contaminants in the calorimeter may cause systematic errors.

All measuring devices have a degree of uncertainty and may have systematic offsets. In the case of the ET1400 T-type thermocouple probe, this uncertainty is less than ± 0.1 °C when used with the Thermocouple Pod. For temperature differences, this offset is likely to be cancelled out.

- 9.3** List possible random errors? What precaution was made to reduce the influence of random error?

Random errors include errors measuring temperature and solution volume between samples. To reduce random errors, repeat analyses were made.

- 9.4** Would the heat from molar equivalents of solid NaOH and KOH dropped in an excess of HCl be the same?

No. Whilst the heat released due to neutralisation reaction would be the same, the heat from the dissolution of KOH would be different.

10. Instructors Notes

10.1 Software and Files Required

For each groups computer, eDAQ Chart with the Thermocouple extension must be installed. The thermocouple extension automatically calibrates the output of the EP306 Thermocouple Pod to standard NIST thermoelectric voltages for T- and K-type thermocouple probes, and is accurate to the limits specified by the probes manufacturer. For the ET1400 T-type thermocouple probe, the accuracy is $\pm 0.1^{\circ}\text{C}$.

The Thermocouple extension can be downloaded from the eDAQ website:

http://www.edaq.com/chart_extns_list.html

NB. eDAQ Chart requires Windows XP.

The settings file 'HofN.edset' found in the EXP009 resources folder, needs to be placed in Chart's experiments gallery folder for each group. Refer to the Chart Software Manual on the eDAQ Installer CD for instructions. This file has a macro called "Calibration" that sets up the required voltage profile for calibration, plus the Chart settings for the experiment.

The Calibration macro was created by:

- First creating a macro called '0 V' was recorded by choosing **Stimulator...** under the **Setup** menu and setting the **Stimulator mode** to pulse, the **Baseline** voltage to 0 V and the **Amplitude** to 0 V.
- Similarly creating a second macro called '5 V' was recorded changing the **Baseline** voltage to 5 V in the Stimulator dialog box.
- The final Calibration macro was recorded by
 1. Calling the macro '0 V' under the **Macro** menu.
 2. Clicking on the **Start** button and selecting **Do other macro steps during (slow) sampling** in the **Macro Sampling** dialog box and also selecting to **Stop** sampling after a **Fixed Duration** of 5 minutes.
 3. Selecting **Macro Commands/Wait...** under the **Macro** menu, and entering 30 second in the dialog box.
 4. Calling the macro '5 V' under the **Macro** menu.
 5. Selecting **Macro Commands/Wait...** under the **Macro** menu, and entering 4 minutes in the dialog box.
 6. Once again calling the macro '0 V'.

This instructs the e-corder to output the voltage profile shown in **Figure 6.3**.

10.2 Constructing the Coffee Cup Calorimeter

10.2.1 Use 170 mL Styrofoam coffee cups with tapered lids.

10.2.2 The recommended resistance heater is the MINCO 5951 available from:

MINCO Products Inc. 7300 Commerce Lane/Minneapolis, Minnesota 55432-3177
U.S.A. (www.minco.com).

These heaters have a large surface area and a low thermal mass. Order the heaters with sealed terminals.

Specifications:

Area:	1 in ²
Resistance:	58 Ω
Voltage:	12 V
Watt Density:	2.5 W/in ²

10.2.3 Peel off the backing tape of the MINCO 5951 resistance heater, and remove the adhesive by wiping with a tissue soaked in acetone.

10.2.4 Bend the wires near the heater pad, so that the pad will be horizontal when the heater is placed into the coffee cup. And use some heat shrink to stiffen the wires, starting approximately 2 cm from the heater pad, and leaving the terminals free. See **Figure 10.1** below.

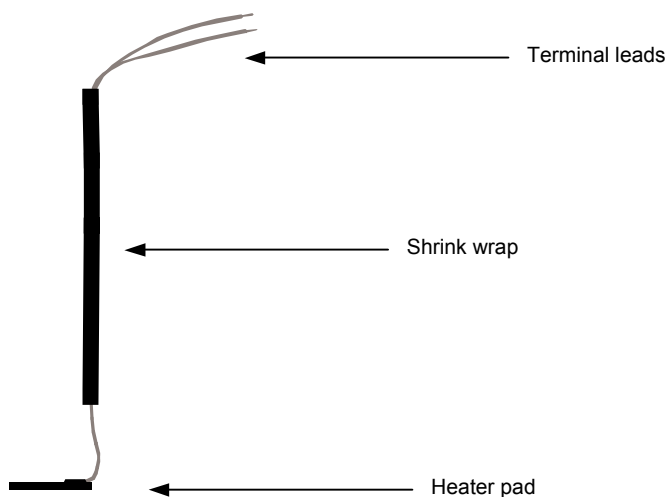


Figure 10.1 MINCO 5951 resistance heater with shrink wrap supporting wires

10.2.5 Pierce the lid and base of a coffee cup, slightly off center and insert the ET1400 T-type Thermocouple Probe as shown in **Figure 10.2**.

10.2.6 Push the terminal end of resistance heater through the hole in the lid of the coffee cup and make a small incision in the side of the coffee cup and pull the terminals of the resistance heater through.

- 10.2.7** Level the heater pad with the tip of the thermocouple probe, and with the heater pad in the same orientation as shown in **Figure 10.2**, secure the resistance heater with sticky tape halfway up the shaft of the probe.

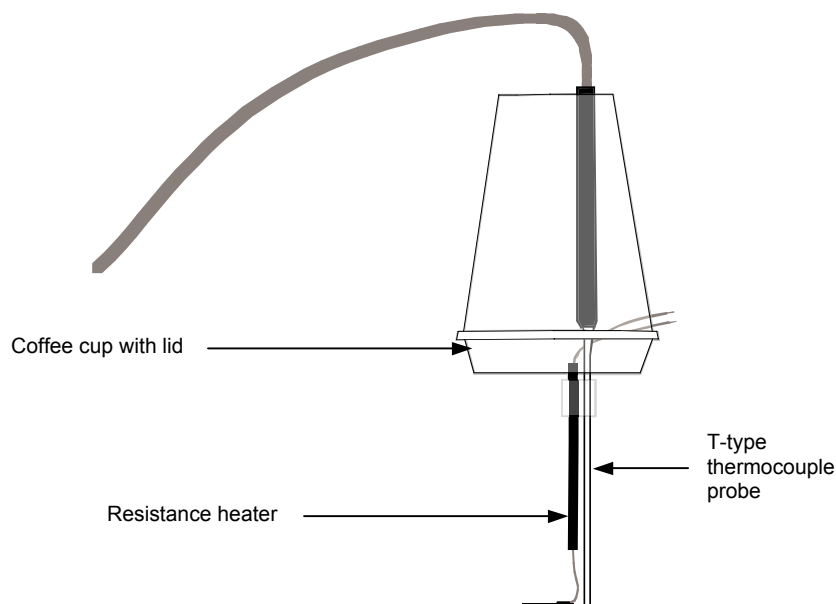


Figure 10.2 Coffee cup calorimeter lid

- 10.2.8** Measure and record the resistance of the heater with an accurate multimeter to three decimal places. Mark this resistance on the coffee cup, so that students can use this value in their calculations.

10.3 Reagents Required

- Distilled water (at least 250 mL per group)
- 0.1 M HCl prepared in distilled water (at least 200 mL per group)
- Dry NaOH pellets with an approximate mass of 100 mg per pellet. Store the NaOH pellets in a dessicator jar, especially if you are working in a humid environment.