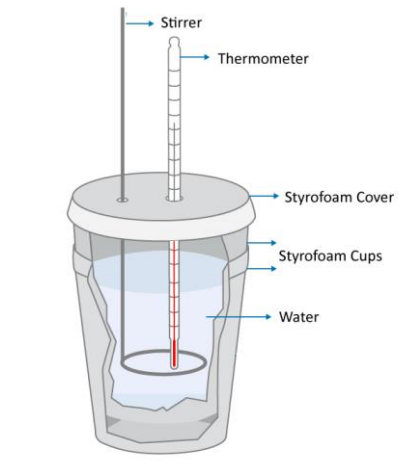
Lesson 1 Calorimetry

A **calorimeter** is a device used to measure heat of reaction. The reactants are enclosed in a vessel surrounded by a known amount of water. This amount of water is enclosed in a well, insulated vessel where heat loss is minimised. The reactants are allowed to react and at the end of the reaction the temperature change of the water is measured.
Calorimeters can be expensive or cheap and easy to construct such as the polystyrene cup calorimeter shown on the right.

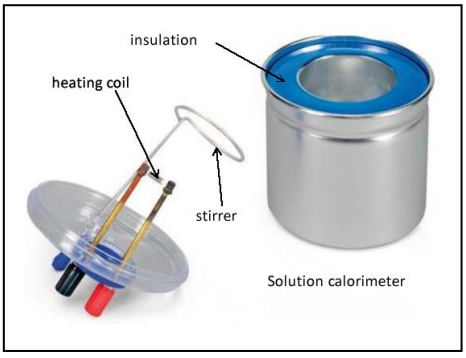


COFFEE CUP CALORIMETER EXAMPLE

Measuring the temperature change of the known body of water should be enough to calculate the amount of energy produced or absorbed by the reaction according to the formula E = 4.18 J/C^o/g X mass X ΔT, where ΔT is the change in temperature and mass is the mass of water. This, however, assumes that all the energy given out or absorbed by the reaction goes into or comes from the water. This is not the case as energy is used to heat the physical parts of the calorimeter and also escapes into the environment from poorly insulated containers, so not 100% of the energy involved can be measured.

In order to accurately determine the energy lost or absorbed by the reaction we must first calibrate the calorimeter. This is done by delivering a known amount of energy, most often done by passing a known electric current at a given voltage for a period of time measured in seconds. The change in temperature of water is then measured and the calibration factor (C_f) determined.
C_f = Energy / ΔT
The formula used to determine the electrical energy delivered is given by
E = VIt (Joules)

Example 1
A calorimeter is calibrated by passing a current of 1.20 A at 6.00 volts through the heating coil for 90.0 seconds. The temperature of the water rose by 12.2 ^{o}C.



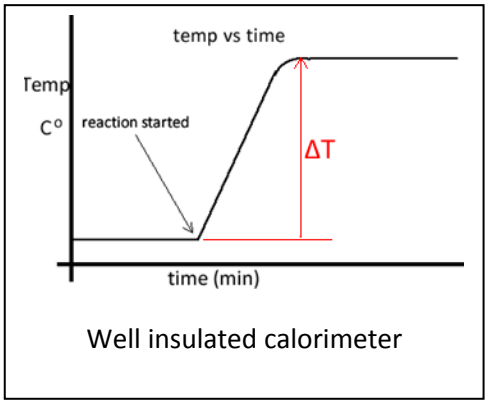
a) Calculate the C_f of the calorimeter.
Step 1 find the amount of energy delivered>
=> E = 6.00 X 1.20 X 90.0 = 648 J
Step 2 Calculate C_f = 648 / 12.2 = 53.1J/C^o

b) Magnesium metal was placed into a calorimeter containing 100 mL of 1.00 M HCl solution at 25.0^{o}C. Calculate the amount of energy released in kJ if the final temperature of the water reached 29.6^{o}C.
=> E = C_f X ΔT
=> E = 0.0531 kJ/C^o X (29.6 – 25.0) = 0.244 kJ

c) When calculating the C_f, in a) above, 100.0 mL of water was used. How would the C_f change if only 50.0 mL of water was used?
=> Since less water is used, with the same amount of energy, the temperature of the water would rise more with 50.0 mL of water than with 100.0 mL of water. Hence C_f would be lower with 50.0 mL of water than with 100.0 mL.

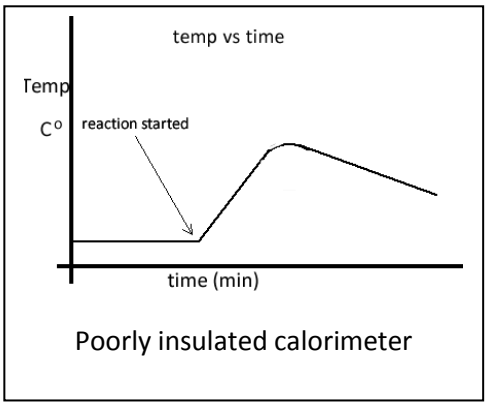
d) After the C_f has being calculated, what volume of solution should be used in the calorimeter every time it is used to measure energy?
=> Exactly the same volume as used in determining the calibration factor. Eg 100.0 mL

Working out the change in temperature (ΔT) is not difficult for a well insulated calorimeter. Simply subtract the starting temperature from the final temperature. A temperature vs time graph for a well insulated calorimeter is shown on the right.



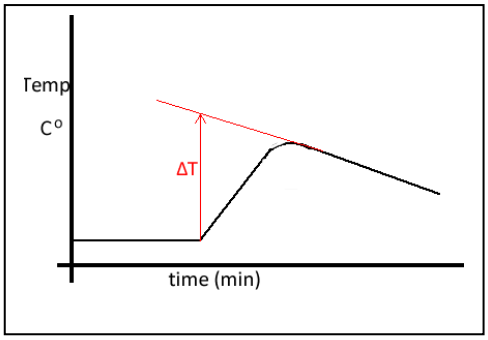
Well insulated calorimeter

Working out ΔT for a poorly insulated calorimeter, however, is more involved. A temperature vs time graph for a poorly insulated calorimeter is shown on the right. Finding the final temperature is not that easy.



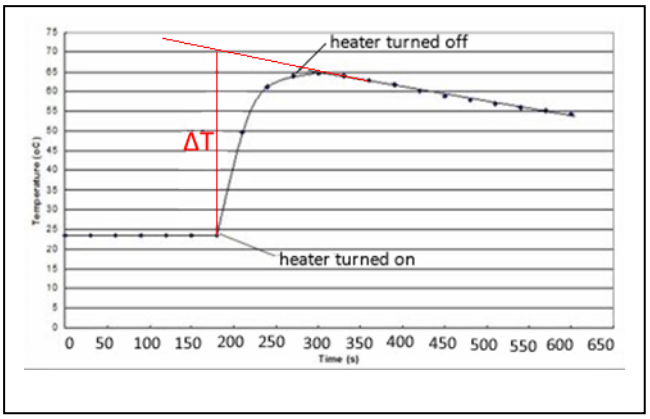
Poorly insulated calorimeter

To find the final temperature of the solution in the calorimeter we extrapolate backward the line of decreasing temperature, as shown on the right, in red. The point where the extrapolated line and the starting temperature intersect is the final temperature.



Two types of calorimeters exist, a bomb calorimeter and a solution calorimeter. A bomb calorimeter is one that burns compounds to calculate the heat of combustion while a solution calorimeter is one that measure the heat of reaction of solutions.

1)A solution calorimeter filled with 100 mL of water at 23.5 ^{o}C was calibrated using a current of 1.20 Amperes at 2.00 V for 100.0 seconds. The temperature was recorded over time and results plotted on the set of axes shown on the right.



a) Determine the calibration factor for this calorimeter.

Step 1 find the ΔT

=> ΔT = 70.0 -23.5 = 46.5 ^{o}C

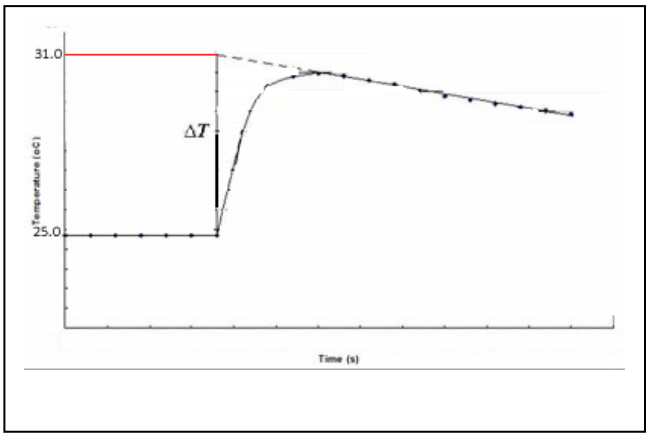
Step 2 Find the amount of energy delivered

=> E = 2.00 X 1.20 X 100.0 = 240 J

Step 3 calculate C_f

=> 240 / 46.5 = 5.16 J/^{o}C

b) 50.0 mL of 0.012 M HCl and 50.0 mL of 0.012 NaOH, both at 25.0 ^{o}C, were placed in the calorimeter mentioned in a) and mixed together. The temperature of the resulting solution was recorded and plotted on the set of axes shown on the right.



i. Calculate the energy given out by the reaction.

=> E = C_f X ΔT

=> E = 5.16 X 6.0 = 31 J

ii. Calculate the energy per mol of HCl reacting.

=> E/mol = 31 J / 0.0006 = 51 kJ mol^{-1}

c) Write a balanced thermochemical equation for the neutralisation reaction taking place.

$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$ ΔH = -51kJ mol^{-1}

d) Is this calorimeter well insulated? Explain.

No the calorimeter is not well insulated as evident by the gradient of the temperature change after the reaction has ceased.

e) How does the ΔH calculated for this reaction compare with the literature? Give a reason for this.

The literature value of the ΔH = -55.90 kJ mol $^{-1}$. This is more than the experimental value derived for this reaction. Heat loss to the environment can explain the discrepancy.

f) In another experiment the same calorimeter was used to dissolve excess magnesium metal powder in 100.0 mL of a 0.0100 *M HCl solution.* The ΔT was calculated at 4.20 ^{o}C. Write a balanced thermochemical equation for the reaction between HCl solution and magnesium metal.

Step 1 Find the mole of HCl involved in the reaction.

=> n_{HCl} = C X V = 0.100 X 100.0 = 0.00100 mol

Step 2 Find the energy released by 0.00100 mol of HCl

=> E = C_f X ΔT = 5.16 J/^{o}C X 4.20 = 21.7 J

Step 3 Find the energy per mol of HCl released.

=> 21.7 / 0.001 = 21.7 kJ

Step 4 Write a balanced chemical equation for the reaction.

$2HCl(aq) + Mg(s) \rightarrow MgCl_2(aq) + H_2(g)$

Step 5 Write the balanced thermochemical equation for the reaction.
$2HCl(aq) + Mg(s) \rightarrow MgCl_2(aq) + H_2(g) \quad \Delta H = -43.4$ kJ mol-

- *Note – we double the amount of energy released per mol of HCl because the reaction states that two mol of HCl reacts.*