CALORIMETRY

CALORIMETERS

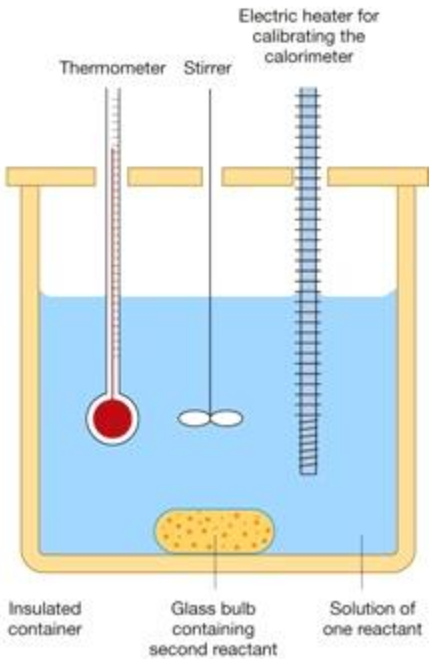
Calorimeters are instruments used to measure enthalpy changes during chemical reactions. Two types of calorimeters:

1. **Bomb Calorimeters:** Are used to measure enthalpy changes in reactions involving gaseous substances and food samples.

2. **Solution Calorimeters:** Are used to measure enthalpy changes in reactions involving reactants and products in solution.

EXAMPLES OF CALORIMETERS

A Solution Calorimeter:

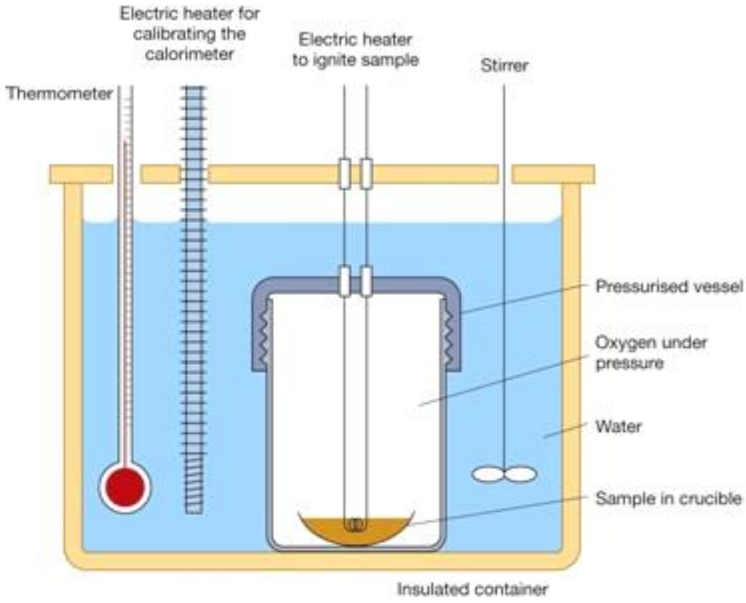


- A solution calorimeter consists of an insulated container with a thermometer, a stirrer and an electric heater for calibration (see later).

- The stirrer is important to maintain a uniform temperature in the solution and the thermometer registers any temperature changes during the reaction.

- Insulation is of particular importance, as any heat lost from the container would result in inaccurate enthalpy determinations.

A Bomb Calorimeter:



- The main difference in a bomb calorimeter compared with a solution calorimeter is the pressurised vessel where the gas reaction occurs and the electric heater to ignite the sample in pure oxygen.
- The temperature released by the reaction is transferred to the water.
- The rest is similar to a solution calorimeter.

SPECIFIC HEAT CAPACITIES AND CALIBRATION FACTORS

SPECIFIC HEAT CAPACITY

- The specific heat capacity of a substance is ***the amount of energy needed to raise the temperature of that substance by 1^{0}C.***

- Different substances have different specific heats depending on their chemical bond structure, and that helps explain why some substances heat up more rapidly than others.

- The higher the heat capacity, the longer it takes for the substance to heat up but, that substance will be able to store heat energy more efficiently.

- Water has the highest specific heat capacity, which is 4.184 J g^{-1} $^0C^{-1}$. This means that it takes 4.184 Joules of energy to raise the temperature of 1g of water by 1 degree Celsius.

EXAMPLE 1
Calculate the energy required to boil 150 mL of water if the initial water temperature is 15^{0}C.

Solution

Since the density of water is 1.0g mL^{-1}, the mass of 150 mL of water is 150g.

1. Calculate energy required to raise the temperature of 150g of water by 1^{0}C by using the specific heat capacity of water.

$$Energy = 150 \times 4.184 = 627.6J$$

2. Calculate total energy required to bring water to boiling temperature.

$$\Delta T = 100 - 15 = 85^0 C$$
$$Energy(Total) = 627.6 \times 85 = 53346J$$
$$= 53.346kJ$$

CALIBRATION FACTORS

- A calorimeter measures heat changes during reactions by changing the temperature of its contents.
- In order to determine the amount of energy transferred during a reaction, it is necessary to know the amount of energy required to change the temperature of the contents of the calorimeter by 1^0C.
- This is known as the **Calibration Factor** of the calorimeter, and in many ways it is similar to the specific heat capacity. In fact, in the past the calibration factor was also known as the specific heat of the calorimeter.
- Since different calorimeters don't have identical contents, each needs to be calibrated before use.

CALIBRATION OF A CALORIMETER

Electrical calibration is the most accurate and widely-used method today.

An electric heater is used and the voltage (potential difference) and current (amperes) are recorded so that the exact amount of electrical energy transferred can be calculated.

The formula used to calculate the electrical energy is as follows:

$$E = VIt$$

Where:

E = Energy in Joules

V = Potential difference in Volts

I = Current in Amperes

T = Time in seconds

The calibration factor is given by the energy divided by the rise in temperature during the calibration

OR

$$C.F. = \frac{E}{\Delta T}$$

Once the calibration factor is known, the change in energy after a reaction can be calculated by multiplying the change in temperature by the calibration factor of the calorimeter, according to the formula:

$$\Delta H = CF \times \Delta T$$

EXAMPLE 2

A certain calorimeter and its contents were calibrated by applying a current of 1.90 Amperes with a potential difference of 6.0 Volts for a period of 2 minutes (120 seconds). A temperature rise of 4.0^0C was recorded.

Calculate the calibration factor for the calorimeter and its contents.

Solution

1. Calculate energy:

$$E = VIt \therefore E = 6.0 \times 1.90 \times 120 = 1368J$$

2. Calculate calibration factor:

$$CF = \frac{E}{\Delta T} \therefore CF = \frac{1368}{4.0} = 342J\,^0C^{-1}$$

HEATS OF REACTION

'Heat of reaction' is the general term used to describe the enthalpy change or ΔH, for any given chemical reaction.

A definition for heat of reaction is:

- The quantity of heat evolved or absorbed by a system when the amounts of reactants shown in the equation completely react.

TYPES OF HEAT OF REACTION

According to the nature of the reaction, heats of reactions are given special names. Here are some examples:

1. Heat of formation:

When a compound forms from its constituent elements under specified conditions for example, formation of water from hydrogen and oxygen.

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \Delta H = -285 kJmol^{-1}$$

2. Heat of vaporisation:

When an element or compound changes from liquid to vapour for example, vaporisation of water.

$$H_2O(l) \rightarrow H_2O(g); \Delta H = +44 kJmol^{-1}$$

3. Heat of solution:

When a solid substance dissolves in a specific solvent for example, sodium chloride in water.

$$NaCl(s) + aq \rightarrow NaCl(aq); \Delta H = +3.88 kJmol^{-1}$$

4. *Heat of combustion:

When a substance undergoes complete combustion in oxygen for example, methane.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \Delta H = -890 kJmol^{-1}$$

***In the study of fuels and their energy outputs, heats of combustion are of particular importance.**

EXAMPLES OF CALCULATIONS INVOLVING HEAT OF REACTION MEASUREMENTS

EXAMPLE 3
Solid calcium oxide reacts with water according to the following reaction:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

The heat of reaction for the above was determined by adding 0.697g of calcium oxide to 200mL of water in a calorimeter. A temperature rise of 2.22^{0}C was recorded.

The calorimeter was electrically calibrated by applying a current of 2.80 Amps at 4.5 Volts for 1 minute. A temperature rise of 2.04^{0}C was recorded.

From the above information, calculate the heat of reaction according to the thermochemical equation above.

Solution

1. Calculate calibration factor:

$$E = VIt$$
$$\therefore E = 4.5 \times 2.80 \times 60 = 756J$$
$$CF = \frac{E}{\Delta T}$$
$$\therefore CF = \frac{756}{2.0} = 378J\,^0C$$

2. Calculate heat released by 0.697g of CaO:

$$Heat(released) = CF \times \Delta T$$
$$= 378 \times 2.22 = 839.2.6J$$

3. Calculate heat of reaction when 1 mol (56g) of CaO reacts with water:

0.697g releases 839.2 kJ
56g releases x kJ

By proportion: $\frac{56}{0.695} = \frac{x}{839.2} \Rightarrow x = \frac{56 \times 839.2}{0.695} = 67.6kJ$

$$\therefore \Delta H = -67.6kJmol^{-1}$$

EXAMPLE 4

A solution calorimeter containing water was calibrated by applying a current of 2.12 Amperes at 5.14 Volts for 2 minutes. An increase in temperature of 3.55^{0}C was observed.

After calibration, 7.24g of sodium chloride were added to the calorimeter and a temperature decrease of 1.35^{0}C was observed.

1. Calculate the calibration factor of the calorimeter.

2. Write an equation for the dissolution of sodium chloride.

3. Deduce whether the reaction is exothermic or endothermic.

4. Calculate the heat of solution of sodium chloride.

Solution

1. $E = VIt$

$\therefore E = 5.14 \times 2.12 \times 120 = 1307.6 J\,^0C$

$$CF = \frac{E}{\Delta T}$$

$$\therefore CF = \frac{1307.6}{3.55} = 368.3 J\,^0C$$

2. $NaCl(s) \rightarrow NaCl(aq)$

3. Since a decrease in temperature was observed the reaction is endothermic.

4. Calculate moles of NaCl in 7.24g:

$$n(NaCl) = \frac{7.24}{58.5} = 0.124 mol$$

Calculate energy released by 0.124 mol of NaCl:

$E = CF \times \Delta T$

$\therefore E = 368.3 \times 1.35 = 497.2 J$

0.124 mol absorb 497.2J
1 mol absorbs xJ

By proportion:

$$\frac{1}{0.124} = \frac{x}{497.2} \Rightarrow x = \frac{497.2 \times 1}{0.124} = 4009.6J = 4.1kJ$$

$$\therefore \Delta H = +4.1 kJmol^{-1}$$

MEASUREMENT OF ENERGY IN FOODS BY BOMB CALORIMETRY

Foods contain stored energy, which is released when the food undergoes oxidation in a process commonly known as cellular respiration.

An example is the oxidation of glucose shown below:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + H_2O(l); \Delta H = -2803 kJmol^{-1}$$

The amount of energy in a food sample can be determined by igniting a sample in oxygen inside a calibrated bomb calorimeter and by recording the temperature rise.

Energy in foods is normally expressed as **Kilojoules per gram of food (kJ g^{-1-}).**

Calorimetric determined energy values can be deceiving or misleading, however.

Here are some examples:

1. **Carbohydrates:**

   Most carbohydrates are highly digestible, but cellulose (dietary fibre) cannot be digested by humans and cannot be utilised as an energy source in the body.

   If a food sample containing cellulose is analysed in a calorimeter, it will give a higher energy value than would normally be available in the body because the cellulose will be oxidised during the analysis.

2. **Lipids:**

   Most of the lipid content in food is digested and oxidised, but only about 6% is lost in faeces.

3. **Proteins:**

   About 92% of protein is digestible, but the rest is lost when amino acids, urea and proteins are excreted in urine.

EXAMPLE OF ENERGY CONTENT DETERMINATION IN A FOOD SAMPLE

EXAMPLE 5
A bomb calorimeter with a calibration factor of 1360 J^0C^{-1} was used to burn a 1.0g sample of wholemeal bread in excess oxygen.

The temperature was noted to increase from 18.50^0C to 25.46^0C.

1. Calculate the energy content of the bread in kJ g^{-1}

2. Suggest a reason why the whole of that energy may not be available to a person eating the bread.

Solution

1. $$Energy(released) = CF \times \Delta T = 1360 \times (25.46 - 18.50)$$
$$= 1360 \times 6.96$$
$$= 9466 Jg^{-1} OR \ 9.47 kJg^{-1}$$

2. The sample consisted of wholemeal bread, which has a high cellulose (fibre) content. When ingested, the cellulose would be unavailable for energy since it cannot be digested (hydrolysed) by humans.