

CALORIMETRY

Measurement of Heat Flow & Enthalpy Change

Coffee Cup and Bomb Calorimetry

A calorimeter is a device used to measure the quantity of heat flow in a chemical reaction. Two of the most common types of calorimeters are the coffee cup calorimeter and the bomb calorimeter.

Coffee Cup Calorimeter

A coffee cup calorimeter is essentially a polystyrene (Styrofoam) cup with a lid. The cup is partially filled with a known volume of water and a thermometer is inserted through the lid of the cup so that its bulb is below the water surface. When a chemical reaction occurs in the coffee cup calorimeter, the heat of the reaction is absorbed by the water. The change in the water temperature is used to calculate the amount of heat that has been absorbed (used to make products, so water temperature decreases) or evolved (lost to the water, so its temperature increases) in the reaction.

Heat flow is calculated using the relation:

$$q = (\text{specific heat}) \times m \times \Delta t$$

where q is heat flow, m is mass in grams, and Δt is the change in temperature. The specific heat is the amount of heat required to raise the temperature of 1 gram of a substance 1 degree Celsius. The specific heat of water is $4.18 \text{ J}/(\text{g} \times ^\circ\text{C})$.

For example, consider a chemical reaction which occurs in 200 grams of water with an initial temperature of 25.0°C . The reaction is allowed to proceed in the coffee cup calorimeter. As a result of the reaction, the temperature of the water changes to 31.0°C . The heat flow is calculated:

$$q_{\text{water}} = 4.18 \text{ J}/(\text{g} \times ^\circ\text{C}) \times 200 \text{ g} \times (31.0^\circ\text{C} - 25.0^\circ\text{C})$$

$$q_{\text{water}} = +5.0 \times 10^3 \text{ J}$$

In other words, the products of the reaction evolved 5,000 J of heat, which was lost to the water. The enthalpy change, ΔH , for the reaction is equal in magnitude but opposite in sign to the heat flow for the water:

$$\Delta H_{\text{reaction}} = -(q_{\text{water}})$$

Recall that for an **exothermic** reaction, $\Delta H < 0$; q_{water} is positive. The water absorbs heat from the reaction and an increase in temperature is seen. For an **endothermic** reaction, $\Delta H > 0$; q_{water} is negative. The water supplies heat for the reaction and a decrease in temperature is seen.

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Bomb Calorimeter

A coffee cup calorimeter is great for measuring heat flow in a solution, but it can't be used for reactions which involve gases, since they would escape from the cup. The coffee cup calorimeter can't be used for high temperature reactions, either, since these would melt the cup. A bomb calorimeter is used to measure heat flows for gases and high temperature reactions.

A bomb calorimeter works in the same manner as a coffee cup calorimeter, with one big difference. In a coffee cup calorimeter, the reaction takes place in the water. In a bomb calorimeter, the reaction takes place in a sealed metal container, which is placed in the water in an insulated container. Heat flow from the reaction crosses the walls of the sealed container to the water. The temperature difference of the water is measured, just as it was for a coffee cup calorimeter. Analysis of the heat flow is a bit more complex than it was for the coffee cup calorimeter because the heat flow into the metal parts of the calorimeter must be taken into account:

$$q_{\text{reaction}} = -(q_{\text{water}} + q_{\text{bomb}})$$

$$\text{where } q_{\text{water}} = 4.18 \text{ J/(g} \times \text{ }^\circ\text{C)} \times m_{\text{water}} \times \Delta t$$

The bomb has a fixed mass and specific heat. The mass of the bomb multiplied by its specific heat is sometimes termed the calorimeter constant, denoted by the symbol C with units of joules per degree Celsius. The calorimeter constant is determined experimentally and will vary from one calorimeter to the next. The heat flow of the bomb is:

$$q_{\text{bomb}} = C \times \Delta t$$

Once the calorimeter constant is known, calculating heat flow is a simple matter. The pressure within a bomb calorimeter often changes during a reaction, so the heat flow may not be equal in magnitude to the enthalpy change.