

Thermochemical Systems and Calorimetry

When we study energy changes, the item in question is called a **system**. Since energy always flows from high to low, every system has its **surroundings**.

System + Surroundings = Universe

Energy exchange between a system and its surroundings can be represented as **heat lost or gained**.

Since the system and the surrounding are in thermal contact, they undergo a process represented by the following equation:

$$q_{\text{system}} = - q_{\text{surroundings}}$$

This is explained using the **First Law of Thermodynamics- any change in the energy of a system is accompanied by an equal and opposite change in the energy of the surroundings**.

To calculate heat energy gained or lost we have two equations we can use (so far!)

The formulae for q are:

$q = mc\Delta T$ Use when a mass is referred to or a specific heat capacity is given

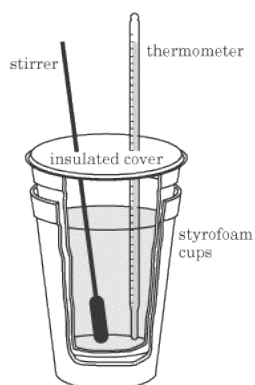
$q = C\Delta T$ Use when heat capacity is given or asked for

Sometimes we cannot directly measure the change in energy of a system. When this is the case we have to use the First Law of Thermodynamics and look at the surroundings. This is a branch of thermochemistry called **CALORIMETRY**.

Calorimetry is the study of the change in kinetic energy between a system and its surroundings. A calorimeter is the device used to measure the change. There are two types of calorimeters:

1. Coffee cup calorimeter (aka constant pressure calorimeter)

It is used to measure heat changes associated with heating, cooling, phase changes, solution formation, and chemical reactions that occur in aqueous solution, like acid-base neutralization.

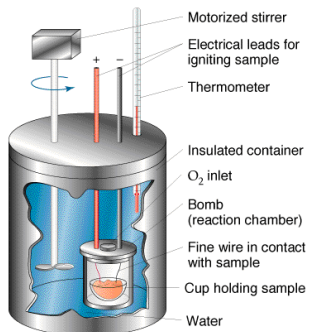


Important assumptions about coffee cup calorimeters

- system is isolated, no heat gets in or out
- the calorimeter itself doesn't absorb or release any heat
- the reaction or process is complete
- constant properties of the water (density, specific heat capacity)

2. Bomb Calorimeter (aka constant volume calorimeter)

It is used for combustion reactions. The heat measurements are more precise and the total heat capacity of a bomb calorimeter includes the heat capacities of all the separate parts.



Important assumptions about bomb calorimeters

- No energy is lost outside
- The calorimeter absorbs all the energy of combustion

Examples:

A simple calorimeter contains 150.0 g of water. A 5.20 g piece of aluminum alloy at 525°C is dropped into the calorimeter causing the temperature of the calorimeter water to increase from 19.30°C to 22.68°C. Calculate the specific heat capacity of the alloy. (Note that the alloy sample will lose heat to the calorimeter water until a thermal equilibrium occurs. Therefore the final temperature of the alloy sample is equal to the final temperature of the calorimeter water)

Write out your "givens":

$$m_{\text{Al}} = 5.20\text{g}$$

$$m_{\text{H}_2\text{O}} = 150.0\text{ g}$$

$$c_{\text{H}_2\text{O}} = 4.184\text{ J/g } ^\circ\text{C}$$

$$T_i \text{ Al} = 525\text{ } ^\circ\text{C}$$

$$T_f \text{ Al} = 22.68\text{ } ^\circ\text{C}$$

$$T_i \text{ H}_2\text{O} = 19.30\text{ } ^\circ\text{C}$$

$$T_f \text{ H}_2\text{O} = 22.68\text{ } ^\circ\text{C}$$

$$C_{\text{Al}} = ?$$

$$q_{\text{sys}} = -q_{\text{cal}}$$

$$(mc\Delta T)_{\text{Al}} = -(mc\Delta T)_{\text{H}_2\text{O}}$$

$$c_{\text{Al}} = \frac{-(mc\Delta T)_{\text{H}_2\text{O}}}{(m\Delta T)_{\text{Al}}}$$

$$= \frac{- (150.0\text{g} \times 4.184\text{ J/g } ^\circ\text{C} \times [22.68-19.30]\text{ } ^\circ\text{C})}{5.20\text{ g} \times [22.68-525]\text{ } ^\circ\text{C}}$$

$$= 0.812\text{ J/g } ^\circ\text{C}$$

The temperature in a simple calorimeter with a heat capacity of 1.05 kJ/°C changes from 25.0°C to 23.94°C when a very cold 12.8 g piece of copper was added to it. Calculate the initial temperature of the piece of copper. The specific heat capacity of copper is 0.385 J/g°C

Given:

$$C_{\text{cal}} = 1.05 \text{ kJ/}^\circ\text{C}^*$$

$$q_{\text{sys}} = -q_{\text{cal}}$$

$$T_i \text{ cal} = 25.0 \text{ }^\circ\text{C}$$

$$(mc\Delta T)_{\text{Cu}} = - (C\Delta T)_{\text{cal}}$$

$$T_f \text{ cal} = 23.94 \text{ }^\circ\text{C}$$

$$\Delta T = - \frac{(C\Delta T)_{\text{cal}}}{(mc)_{\text{Cu}}}$$

$$T_f \text{ Cu} = 23.94 \text{ }^\circ\text{C}$$

$$(mc)_{\text{Cu}}$$

$$m_{\text{Cu}} = 12.8 \text{ g}$$

$$= - \frac{(1.05 \times 10^3 \text{ J/}^\circ\text{C} \times [23.94 - 25.0])}{(12.8 \text{ g} \times 0.385 \text{ J/g}^\circ\text{C})}$$

$$C_{\text{Cu}} = 0.385 \text{ J/g}^\circ\text{C}^*$$

$$(12.8 \text{ g} \times 0.385 \text{ J/g}^\circ\text{C})$$

NOTE: C is in kJ/°C, but

$$= 225.9 \text{ }^\circ\text{C}$$

C is in J/g°C, so you convert

$$\text{If } \Delta T = T_f - T_i$$

$$C_{\text{cal}} = 1.05 \times 10^3 \text{ J/}^\circ\text{C}$$

$$\text{then } T_i = T_f - \Delta T$$

$$T_i = 23.94 \text{ }^\circ\text{C} - 225.9 \text{ }^\circ\text{C}$$

$$= -202.0 \text{ }^\circ\text{C}$$

Now you try these:

1. A very cold piece of silver with a mass of 78.41 g is added to a simple calorimeter that contains 150.0 g of water. The temperature of the calorimeter water changes from 19.73°C to 16.11°C. (The specific heat capacity of silver is 0.24 J/g°C.) How cold was the piece of silver?
2. A new ceramic material underwent for use as an insulator. Part of the analysis involved determining its specific heat capacity. A 20.00 g sample was heated to 200.00°C and added to a simple calorimeter with a heat capacity of 1.46 kJ/°C. The temperature in the calorimeter changed from 24.87°C to 27.15°C. Calculate the specific heat of the ceramic material.

