Calorimetry

Calorimetry is the study of heat measurements of chemical and physical systems using the *calorimeter,* a device consisting of closed container. The name calorimeter, however, is based on the *calorie*, a basic unit of energy.

Units of Energy

The **calorie** originally defined as the *amount of heat required to raise the temperature of one gram of water by one degree centigrade.* The calorie is the old unit but still it is in usage. Now there is a new SI unit. This unit is **joul**e (abbreviated as **J**) (named after the English scientist James Joule), which is defined as *the amount of energy or work required to accelerate 1 kilogram (kg) of object through 1 meter (m) per second(s).* Therefore,

$$1\ \text{J} = \text{kg m}^2\text{s}^{-2}$$

One joule is a rather small amount of energy and in most cases larger unit kilojoules (kJ) is used.

$$1\ \text{kJ} = 1000\ \text{J} = 1 \times 10^3\ \text{J}$$

The calorie and joule are related through the following relationship:

$$1\ \text{cal} = 4.184\ \text{J (exactly)}$$

The larger unit of calorie is the kilocalorie (kcal), which is 1000 calories that can also be related to kilojoules.

$$1\ \text{kcal} = 1000\ \text{cal} = 1 \times 10^3\ \text{cal}$$

$$1\ \text{kcal} = 4.184\ \text{kJ}$$

The Dietary (Nutritional) Unit

The energy content of food items are expressed in Calorie (note the capital C), which is actually 1 kilocalorie.

$$1\ \text{Cal} = 1000\ \text{cal} = 1\ \text{kcal} = 4.184\ \text{kJ}$$

The measurement of heat changes requires the understanding of two quantities, heat capacity and specific heat.

Heat Capacity and Specific Heat

The **heat capacity (C)** is defined as *the amount of heat necessary to raise the temperature of a given amount of substance by one degree Celsius.* The unit of heat capacity is cal/ ^{0}C or J/^{0}C. The **specific heat (s_H)**, on the other hand, is defined as the *amount of heat required to raise the temperature of one gram of the substance by one degree Celsius*. The unit of specific heat is cal/g x ^{0}C or J / g x^{0}C. The following table lists few specific heats of some common substances.

Substance	**Specific Heat (J/gx^{0}C)**
Aluminum	0.903
Carbon (graphite)	0.720
Carbon(diamond)	0.502
Copper	0.385
Ethanol	2.42
Glass(Pyrex)	0.75
Gold	0.128
Granite	0.79
Iron	0.449
Lead	0.128
Mercury	0.139
Sand	0.84
Silver	0.235
Water	4.184

Note the difference between the heat capacity and the specific heat; the heat capacity refers to the given amount of substance whereas the specific heat refers to one gram of substance. The heat capacity is the extensive property that means it depends on the volume of the object. The specific heat is an intensive property that means it does not depend on the volume of an object. The relationship between these two is,

$$C = \text{mass x specific heat} = m \text{ x } s_H$$

where m is the mass of the substance in grams. The amount of heat (q) is nothing but the heat capacity times the change in temperature, that is,

$$q = C \text{ x } \Delta t = m \text{ x } s_H \text{ x } \Delta t$$

where Δt is the change in temperature, which is

$$\Delta t = t_{final} - t_{initial}$$

The sign on q is depends upon whether the heat is absorbed or given off. It is positive (+) for absorption and negative for release.

Example

A cup of water (250 ml) is heated from room temperature (25 ^{0}C) to boiling point (100 ^{0}C) to make tea. What is the amount of heat absorbed by the water in kilocalories and kilojoules?

Answer

In order to calculate the heat, we need the mass of water. The volume of water is given but not the mass. Hence volume is converted into mass by using the density of water, which 1.0 g /ml. Therefore,

Mass of water = 250 ml x 1.0 g/ml = 250 g

Then the heat is evaluated using the following equation.

$$q = m \times s_H \times \Delta t = 250 \text{ g} \times 1.0 \text{ cal /g} \times {}^0\text{C} \times (100 - 25)\ {}^0\text{C}$$
$$= 1.875 \times 10^4 \text{ cal}$$
$$= 18.75 \text{ kcal}$$
$$= 78.45 \text{ kJ}$$

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Specific Heat of a Metal

In the laboratory, the specific heat of the metal is determined using the following procedure. A certain amount of metal is heated in boiling water for about 20-30 minutes to raise the temperature of the metal to the temperature of the boiling water. Then the hot metal is poured into the cold water and the final or the equilibrium temperature is measured.

The heat lost by the metal = - (mass x specific heat x change in temperature)$_{\text{metal}}$
= - $(m \times s_H \times \Delta t)_{\text{metal}}$

Similarly,

The heat gained by the water = (mass x specific heat x change in temperature) $_{water}$
= $(m \times s_H \times \Delta t)_{water}$

At the equilibrium,

Heat gained by the water = - Heat lost the metal

$(q \times s_H \times \Delta t)_{metal} = -(q \times s_H \times \Delta t)_{water}$

Solving this equation for the specific heat of metal assumes the following equation.

$$s_H = -\frac{(m\,x\,s_H\,x\Delta t)_{water}}{(m\,x\Delta t)_{metal}}$$

Knowing the mass of water, the specific heat of water, the temperature change of water, the mass of metal, and the temperature change of metal, the specific heat of metal is calculated using the above equation.

Once the specific heat of the metal is determined in this way, the approximate atomic mass of the metal can be calculated using the Dulong-Petit's law:

Atomic mass x Specific heat ($J / g \times {}^0C$) ≈ 25

or Atomic mass = 25 / Specific heat ($J / g \times {}^0C$)

Example

A 35.8 gram of metal is heated to 100^0 C and then poured into 40.0 ml (40 g) of water, which was originally at 25.0^0C. If the equilibrium temperature was 30.7 ^{0}C, what is the specific heat of the metal? What is its approximate atomic mass according to Dulong-Petit's laws?

Answer

The heat gained by the water = $(m \times s_H \times \Delta t)_{water}$
= 40 g x 4.184 J/gx ^{0}C x $(30.7 – 25)^0$C
= 953.952 J

The heat lost by the metal = -953.952 J

Therefore, the specific heat of the metal is,

s_H = - 953.952 J / (m x $\Delta t)_{metal}$ = - 953.952 J / (35.8 g x (30.7 – 100) ^{0}C
= 0.385 J/g x ^{0}C

According to Dulong-Peti's law,

Approximate atomic mass = 25 / 0.385 = 64.935

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