

Calorimetry

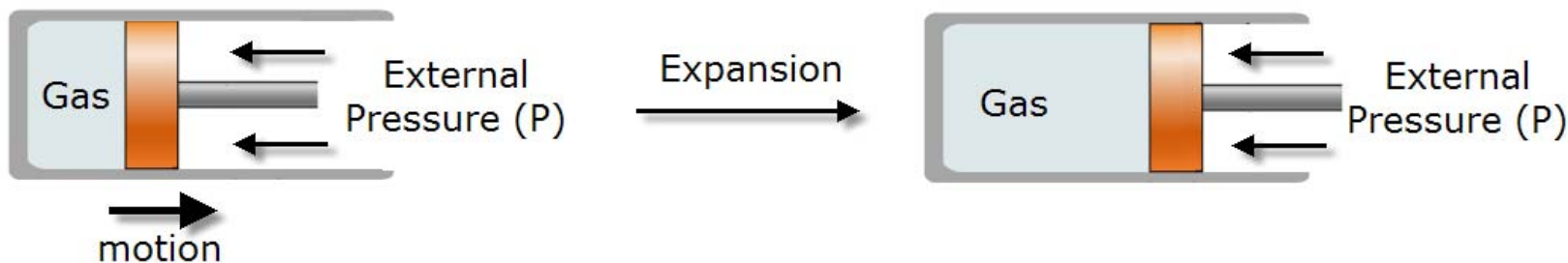
Comparing ΔE and ΔH

Since many reactions involve little PV work most of the energy change occurs as a transfer of heat. Therefore,

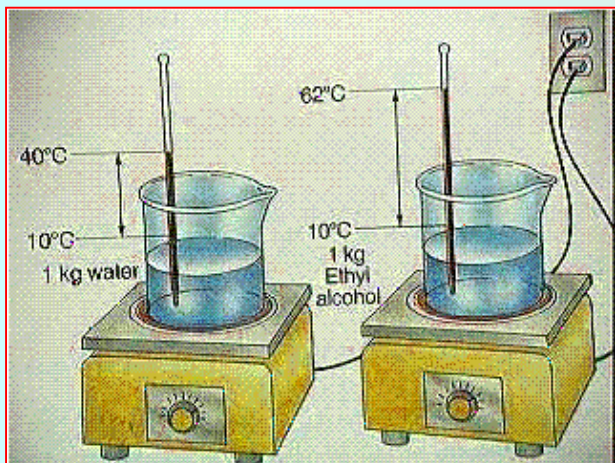
$$Q_p \approx Q_v$$

Here are three cases:

- Reactions that not involve gases
- Reactions in which the amount of gas does not change
- Reactions in which the amount of gas changes, but the amount of work done is negligible compared with the amount of heat



Calorimetry



<http://www.csulb.edu/~rtoossi/PhysicsBook/book/Chap17-Heat&Temperature/Multimedia/images/heat-capacity.gif>

Specific Heat Capacity

The **heat capacity** (C) indicates the relationship between the energy absorbed by a substance and its change in temperature.

$$C = \frac{q}{\Delta T}$$

The **specific heat capacity** (c) is the heat capacity of 1 g of a substance.

$$c = \frac{q}{m * \Delta T}$$

Calorimetry

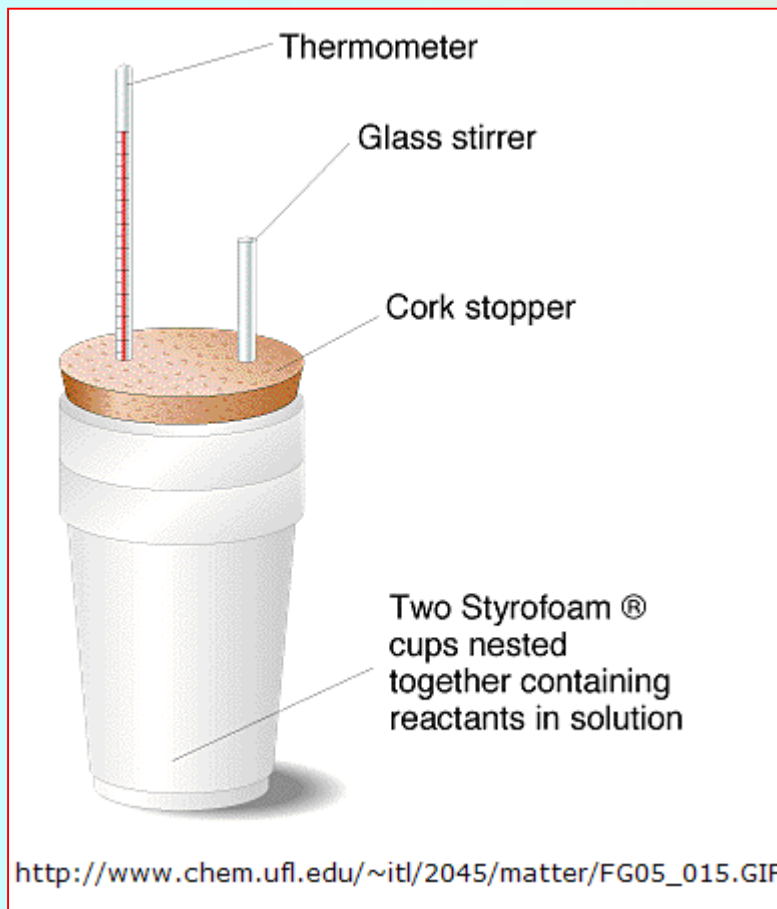
Constant-Pressure Calorimetry

For many reactions, such as those occurring in solution, it is easy to control pressure so that ΔH is measured directly.

$$\Delta H = q_p$$

The heat produced by the reaction (q_{rxn}) is absorbed by the solution

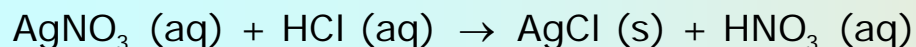
$$q_{\text{solution}} = -q_{\text{rxn}} = (\text{specific heat}) * (\text{mass}) * \Delta T$$



Calorimetry

Exercise #1

When 50 mL of 0.1 M AgNO₃ and 50 mL of 0.1 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.3 °C to 23.11 °C. The reaction produced is:



Calculate ΔH for this reaction, assuming that the combined solution has a mass of 100 g and a specific heat of 4.18 J/g °C

Solution

The heat absorbed by the solution is:

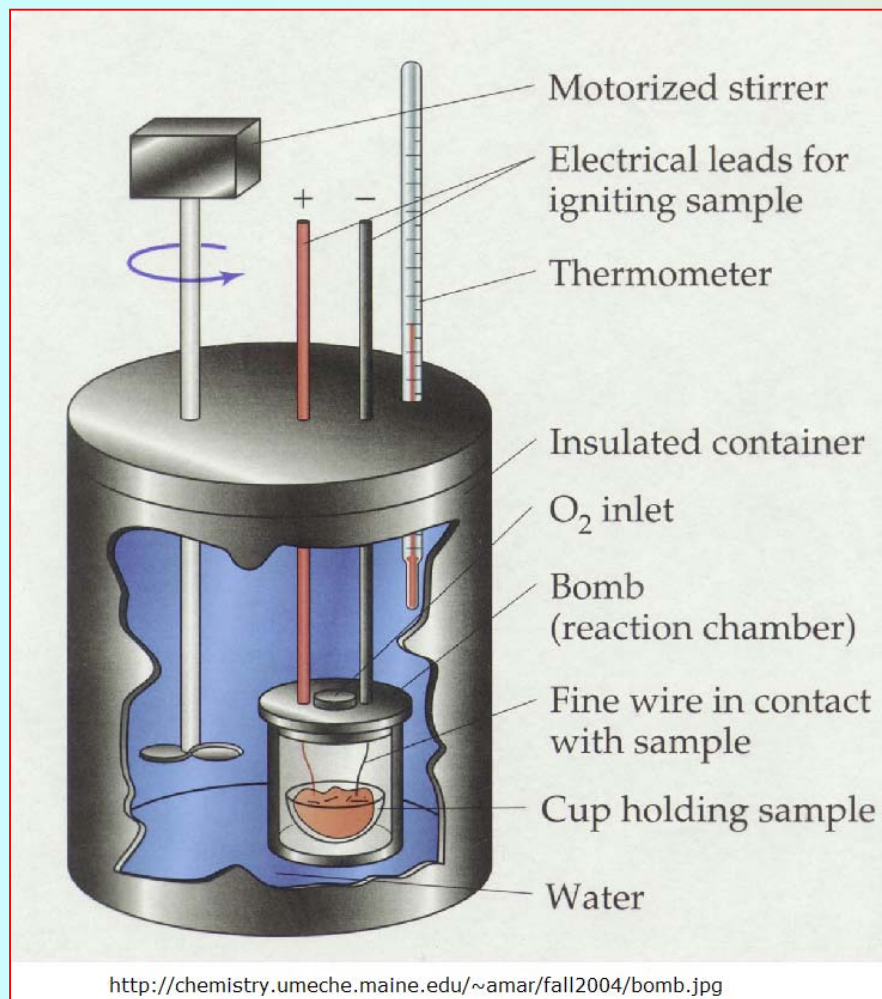
$$Q_p = 100 \text{ g} * 4.18 \frac{\text{J}}{\text{g } ^\circ\text{C}} * (23.11 \text{ } ^\circ\text{C} - 22.3 \text{ } ^\circ\text{C})$$

$$Q_p = 338.6 \text{ J}$$

The change of enthalpy per mol of each reactant is:

$$Q_p \text{ (per mol)} = 338.6 \frac{\text{J}}{0.005 \text{ mol}} = 67.7 \frac{\text{kJ}}{\text{mol}}$$

Calorimetry



Constant-Volume Calorimetry (bomb calorimeter)

The substance is placed within a sealed vessel called a bomb. The bomb is pressurized with oxygen.

The combustion reaction is initiated by passing an electrical current.

To calculate the heat of combustion it is necessary to know the heat capacity of the calorimeter.

$$C_{\text{cal}}$$

We can calculate the heat of reaction using this expression:

$$Q_v = C_{\text{cal}} * \Delta T$$

Exercise #2

A 0.5865-g sample of lactic acid is burned in a calorimeter whose heat capacity is 4.812 kJ/°C. The temperature increases from 23.10 °C to 24.95 °C.

Calculate the heat of combustion per gram.

Solution

The heat released by the sample is:

$$Q_v = 4.812 \frac{\text{kJ}}{^\circ\text{C}} * (24.95 \text{ }^\circ\text{C} - 23.10 \text{ }^\circ\text{C})$$

$$Q_v = 8.9 \text{ kJ}$$

The heat released per gram is:

$$Q_v \text{ (per gram)} = 8.9 \frac{\text{kJ}}{0.5865 \text{ g}} = 15.2 \frac{\text{kJ}}{\text{g}}$$