Calorimetry (under constant P and constant V Conditions)

By Shawn P. Shields, Ph.D.

This work is licensed by Shawn P. Shields-Maxwell under a [Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License](#).

Calorimetry

Calorimetry is a means to measure heat transfer during chemical or physical processes.

Since it is hard to directly measure “heat”, heat transfer is measured in terms of temperature changes.

Calorimetry

- In a calorimetric experiment, the heat lost or gained in the reaction is related to the temperature change of the calorimeter.

$$q_{\mathrm{calorimeter}} = -q_{\mathrm{rxn}}$$

As shown in the equation, the amount of heat released (or absorbed) by the reaction is exactly equal to the amount of heat absorbed (or released) by the calorimeter, except opposite in sign.

Heat Flow and Temperature

When heat flows into an object, it makes sense that its temperature increases.

How *much* the object increases in temperature is dependent on its *heat capacity.*

General Definition of Heat Capacity (C)

The heat capacity (C) is the quantity of heat required to raise the temperature of "something" 1 K or 1 °C.

$q = C\Delta T$ where $\Delta T = T_f - T_i$

Tf is the final temperature of the object, and Ti is its initial temperature.

Specific Heat Capacity (cs)

The specific heat capacity (cs, aka “specific heat”) is the quantity of heat required to raise the temperature of 1 gram of a substance 1 K or 1 °C.

$$q = mcs\,\Delta T \quad \Delta T = Tf - Ti$$

m is the mass of the substance (in g)

cs is the specific heat capacity of the substance (given in a table).

Molar Heat Capacity (cn)

The molar heat capacity (cn) is the quantity of heat required to raise the temperature of 1 mole of a substance 1 K or 1 °C.

$$q = ncn\,\Delta T \qquad \Delta T = Tf - Ti$$

n is the moles of the substance

cn is the molar heat capacity of the substance (found in a table).

Two Main Types of Calorimeters

Bomb Calorimeter- A calorimeter that maintains *constant volume* during the process (i.e., constant volume calorimetry).

Constant pressure calorimeter- (e.g., a “coffee cup calorimeter) The calorimeter maintains constant pressure, but volume changes may occur.

Bomb Calorimeters

Bomb Calorimeter- A calorimeter that maintains *constant volume* during the reaction.

Because the volume is constant, no PV work is done during the process.

Therefore ΔU_{rxn} is measured.

Bomb Calorimetry and ΔU

Recall: $\Delta U = q + w$ and $w = -P_{ext}\Delta V$

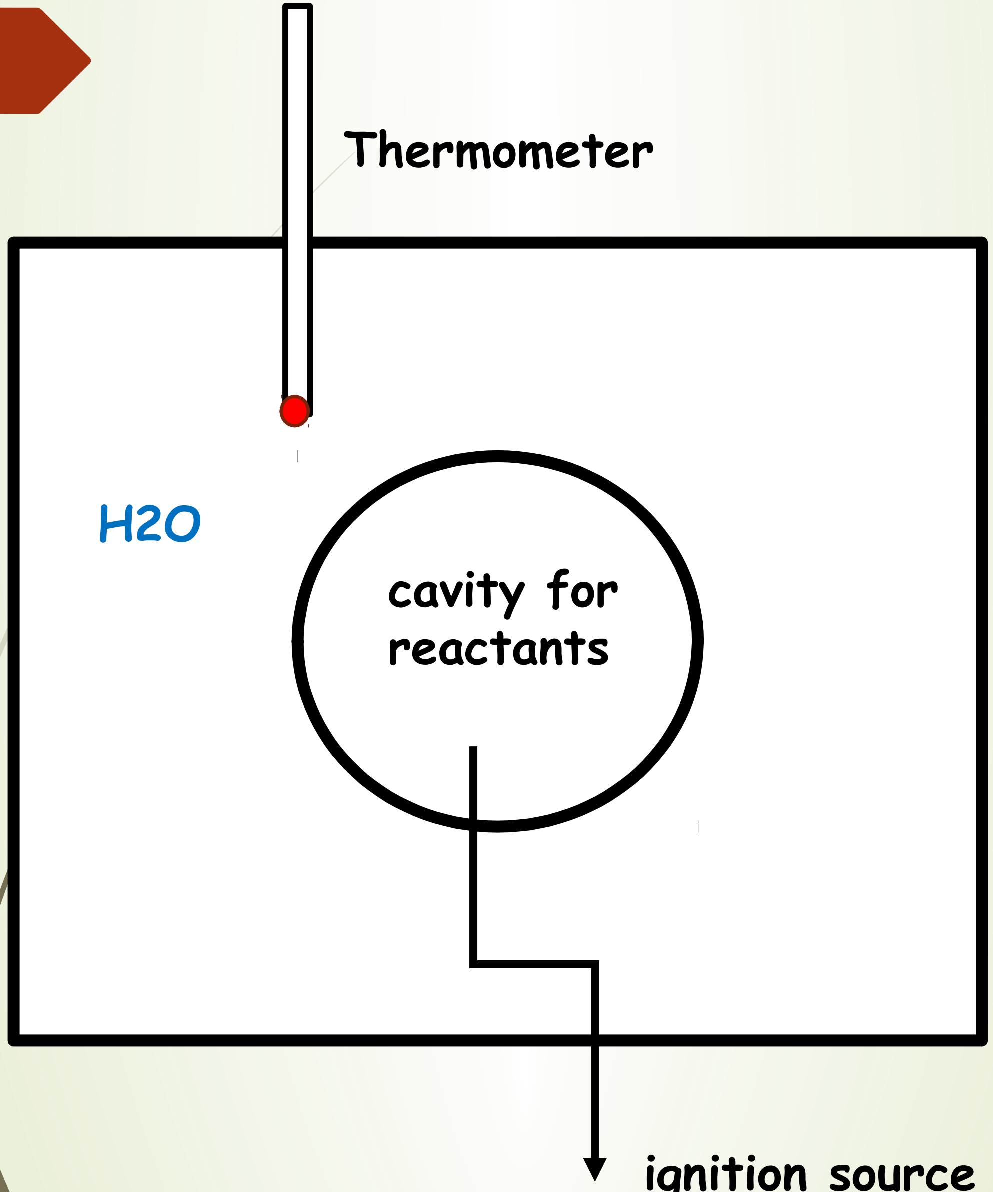
For the closed calorimeter system, $\Delta U = 0$

If $\Delta V = 0$, then no work is done ($w = 0$).

$\Delta U = q + 0 = q_v$ (q_v = heat at constant volume)

$q_v = C\Delta T$, where C is the heat capacity of the bomb calorimeter and $\Delta T = T_f - T_i$

Bomb Calorimetry

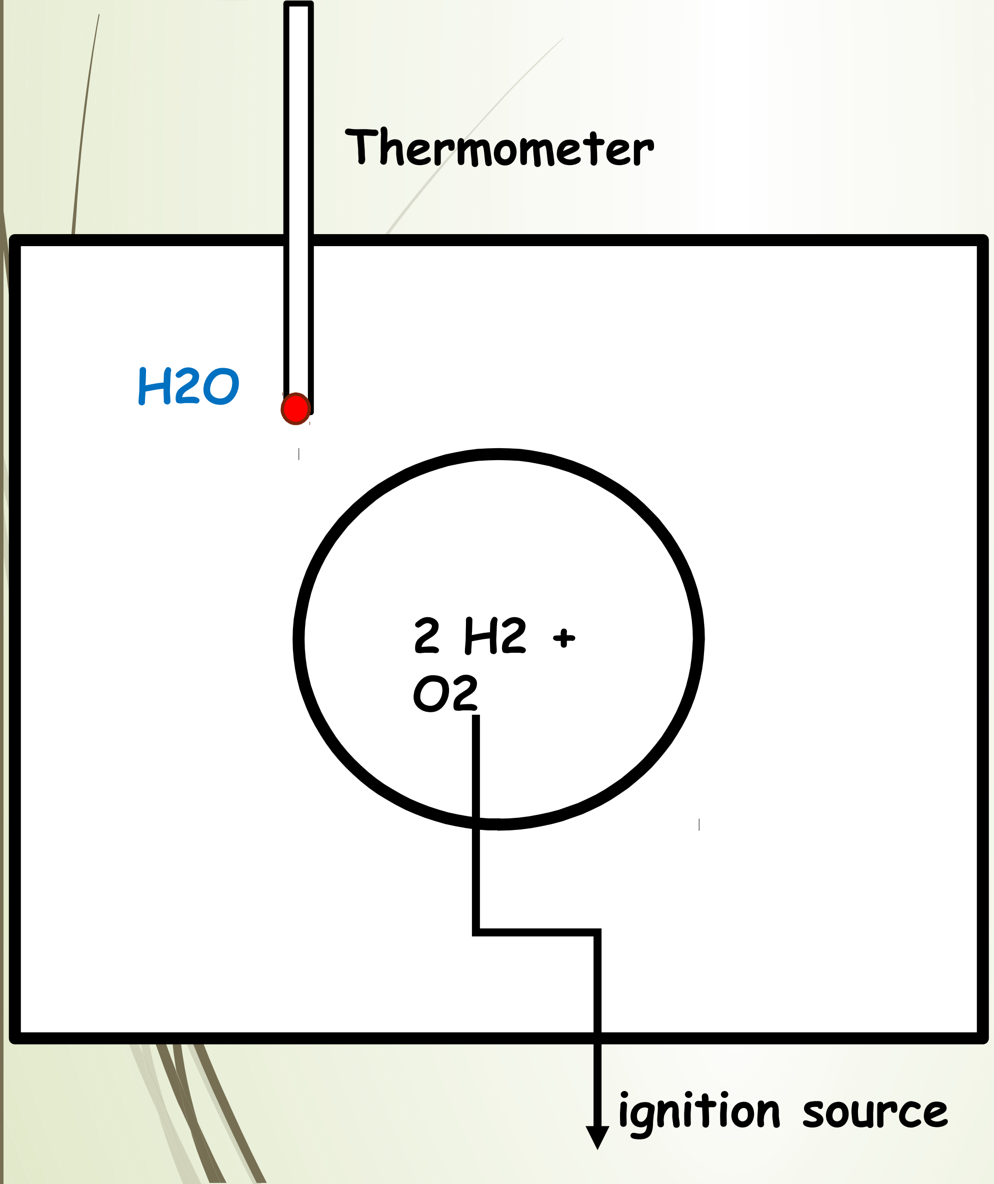

Thermometer
H2O
cavity for reactants
ignition source

Bomb calorimeters are used in reactions where one or more of the reactants is a gas. The “bomb” is made of rigid materials, such as steel, and includes a cavity (for reactants) surrounded by a water bath.

$$q = C\Delta T$$

where C is the heat capacity of the whole calorimeter (water and steel, etc.)

Example: Bomb Calorimetry


Thermometer
H2O
2 H2 +
O2
ignition source

0.05 mol $H_2(g)$ and 0.025 mol $O_2(g)$ react to produce $H_2O(l)$ according to the reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

The heat capacity of the calorimeter is 90.6 kJ/°C and the initial temperature is 25.000°C. The reaction is ignited and the temperature increases to 25.155 °C. Calculate q for this reaction.

Example: Bomb Calorimetry

0.05 mol $H_2(g)$ and 0.025 mol $O_2(g)$ react to produce $H_2O(l)$ according to the reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

The heat capacity of the calorimeter is 90.6 kJ/°C and the initial temperature is 25.000°C. The reaction is ignited and the temperature increases to 25.155 °C. Calculate q for this reaction.

$$\Delta T = 25.155 - 25.000°C = 0.155°C$$

$$q_{cal} = C\Delta T = (90.6\ kJ/°C)(0.155°C) = 14.0\ kJ$$

Was heat absorbed or released by the reaction (i.e., is the reaction endo- or exothermic)?

Example: Bomb Calorimetry

$H_2(g)$ and $O_2(g)$ react to produce $H_2O(l)$ according to the reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $q_{cal} = 14.0$ kJ

Was heat absorbed or released by the reaction (i.e., is the reaction endo- or exothermic)?

The temperature of the calorimeter increased.

Heat was released by the reaction and absorbed by the calorimeter.

The reaction is exothermic. $q_{cal} = -q_{rxn}$

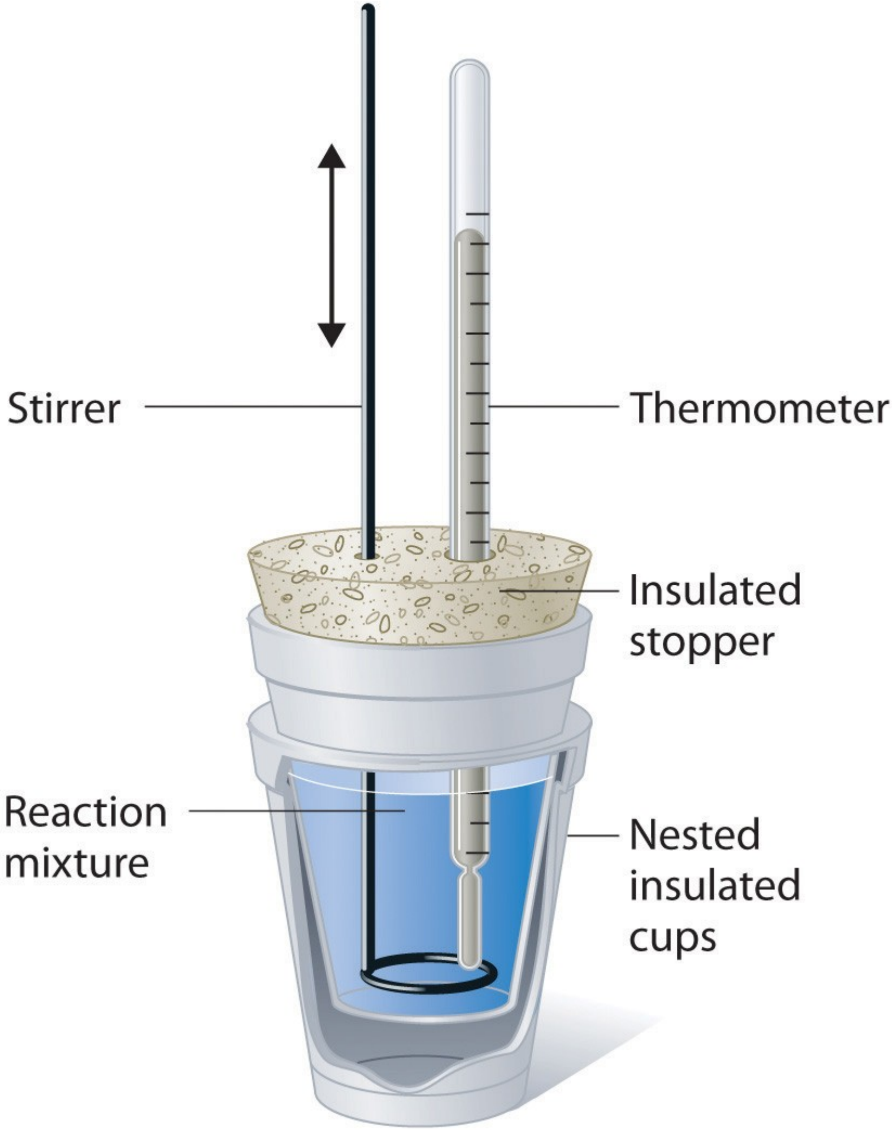
Constant Pressure Calorimetry

- Recall: ΔH is the heat at constant pressure.

$$\Delta H = \Delta U + P\Delta V = q_P$$

Therefore, constant pressure calorimeters measure ΔH directly.

Calorimeter (Const P)


Stirrer
Thermometer
Insulated stopper
Reaction mixture
Nested insulated cups

- Measuring heat transfers during a chemical reaction (e.g., coffee cup calorimeter)

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimeter} = -mc_s\Delta T$$

$$q_{rxn} = -mc_s\Delta T$$

Where m is the mass of water (or solution)

c_s is the specific heat capacity of water (or solution)

ΔT is the temperature change of the water during the reaction.

This book (and image) is licensed under a Creative Commons by-nc-sa 3.0 license.
http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0m/s09-03-calorimetry.html

Example: Constant P Calorimetry

A student built a coffee cup calorimeter using 100.0 mL of water. 4.95 g solid KOH was then added to the water. As the KOH dissolved into solution, the temperature of the solution increased from 23.0°C to 34.5°C. Calculate ΔHrxn. You may assume the density of water is 1.0g/mL and its specific heat capacity is 4.184 J/g°C.

Example: Constant P Calorimetry

A student built a coffee cup calorimeter using 100.0 mL of water. 4.95 g solid KOH was then added to the water. As the KOH dissolved into solution, the temperature of the solution increased from 23.0°C to 34.5°C. Calculate ΔHrxn. You may assume the density of water is 1.0g/mL and its specific heat capacity is 4.184 J/g°C.

Before we start with calculations, let's think about where we are going and the concepts involved…

First: What is the reaction? The dissolution of KOH in H2O.

Second: The temperature of the solution (in the calorimeter) increased…so heat was absorbed by the solution in the calorimeter.

Knowing this; is the *dissolution reaction happening in the calorimeter* releasing or absorbing heat?

Example: Constant P Calorimetry

A student built a coffee cup calorimeter using 100.0 mL of water. 4.95 g solid KOH was then added to the water. As the KOH dissolved into solution, the temperature of the solution increased from 23.0°C to 34.5°C. Calculate ΔHrxn. You may assume the density of water is 1.0g/mL and its specific heat capacity is 4.184 J/g°C.

The reaction is releasing heat, and the calorimeter absorbs it.

Therefore, $q_{calorimeter} = mc_s\Delta T$ $q_{calorimeter} = -q_{rxn}$

So, $q_{calorimeter} = -q_{rxn} = -\Delta H_{rxn}$ (recall that $q_p = \Delta H$)

Example: Constant P Calorimetry

- A student built a coffee cup calorimeter using 100.0 mL of water. 4.95 g solid KOH was then added to the water. As the KOH dissolved into solution, the temperature of the solution increased from 23.0°C to 34.5°C. Calculate ΔH_{rxn}. You may assume the density of water is 1.0g/mL and its specific heat capacity is 4.184 J/g°C.

Now, we're ready to start calculating. Let's find the heat absorbed by the calorimeter first.

$$q_{cal} = mc_s\Delta T = mc_s(T_f - T_i)$$

The mass of the calorimeter solution is the mass of the water plus the KOH dissolved, so

$$m = 100\text{ mL}\left(\frac{1.0\text{ g}}{1\text{ mL}}\right) + 4.95\text{g} = 104.95\text{ g solution}$$

Example: Constant P Calorimetry

- A student built a coffee cup calorimeter using 100.0 mL of water. 4.95 g solid KOH was then added to the water. As the KOH dissolved into solution, the temperature of the solution increased from 23.0°C to 34.5°C. Calculate ΔH_{rxn}. You may assume the density of water is 1.0g/mL and its specific heat capacity is 4.184 J/g°C.

$$q_{cal} = mc_s\Delta T = mc_s(T_f - T_i)$$

$$m = 104.95 \text{ g}, \qquad c_s = 4.184 \, {}^{J}/_{g°C}$$

$$\Delta T = T_f - T_i = 34.5 - 23.0 \text{ °C} = 11.5 \text{ °C}$$

$$q_{cal} = (104.95 \text{ g})\left(4.184 \, {}^{J}/_{g°C}\right)(11.5 \text{ °C}) = 5049.8 \text{ J}$$

5050 J

Example: Constant P Calorimetry

- A student built a coffee cup calorimeter using 100.0 mL of water. 4.95 g solid KOH was then added to the water. As the KOH dissolved into solution, the temperature of the solution increased from 23.0°C to 34.5°C. Calculate ΔH_{rxn}. You may assume the density of water is 1.0g/mL and its specific heat capacity is 4.184 J/g°C.

$$q_{cal} = 5050 \text{ J} \qquad q_{cal} = -\,\Delta H_{rxn} = -5050 \text{ J (or } -5.050 \text{ kJ)}$$

$$\Delta H_{rxn} = -5050 \text{ J (or } -5.050 \text{ kJ)}$$

We need 3 significant figures, so $\Delta H_{rxn} = -5.05$ kJ

This experiment showed that 5.05 kJ was released when 4.95 g KOH was dissolved into 100 mL of water.

Example: Constant P Calorimetry

- This experiment showed us that 5.05 kJ was released when 4.95 g KOH was dissolved into water.

How could use our result to figure out how much heat is released when 1 mol of KOH is dissolved into solution?

Let's use our result as a conversion factor (4.95 g KOH releases 5.05 kJ as heat)

The molar mass of KOH is 56.11g/mol.

$$56.11\,\frac{\mathrm{g}}{\mathrm{mol}}\left(\frac{-5.05\ \mathrm{kJ}}{4.95\ \mathrm{g\ KOH}}\right) = -57.2\ \mathrm{kJ/mol}$$ **KOH dissolved** (ΔH_{soln})

Summary of Calorimetry Concepts

Calorimetry is a means to measure **heat transfer** during a reaction.

Calorimeters minimize heat loss to the surroundings making it possible to **relate the observed temperature change in the calorimeter to the reaction occurring inside.**

The amount of heat absorbed by the calorimeter is the same as the amount of heat released during the reaction, if we assume no heat is lost to the surrounding environment, or vice versa.

Summary of Calorimetry Concepts

$q_{calorimeter}$ is equal in magnitude to q_{rxn}, with opposite sign.

For an exothermic reaction at const P (heat is released by the reaction and absorbed by the calorimeter):

$$q_{cal} = -\Delta H_{rxn}$$

For an endothermic reaction at const P (heat is absorbed by the reaction from the calorimeter):

$$-q_{cal} = \Delta H_{rxn}$$

For an endothermic reaction, would the temperature of the *calorimeter* increase or decrease?

Summary of Calorimetry Concepts

$q_{calorimeter}$ is equal in magnitude to q_{rxn}, with opposite sign.

For an exothermic reaction at const P (heat is released by the reaction and absorbed by the calorimeter):

$$q_{cal} = -\Delta H_{rxn}$$

For an endothermic reaction at const P (heat is absorbed by the reaction from the calorimeter):

$$-q_{cal} = \Delta H_{rxn}$$

For an endothermic reaction, would the temperature of the *calorimeter* increase or decrease?

Summary of Calorimetry Concepts

In a constant pressure calorimetry experiment, we can measure the heat transfer for a small amount of reactant, then use our result to calculate the molar enthalpy, which is the amount of heat released or absorbed by a mole of the substance.

The heat under constant volume conditions is equal to ΔU. $q_v = \Delta U$

The heat under constant pressure conditions is equal to ΔH. $q_p = \Delta H$

What You Should Be Able to Do

Describe how a calorimetry experiment is used to measure heat transfer.

Describe the differences between bomb and constant pressure calorimetry, and which thermodynamic state function they measure (ΔU or ΔH).

Be able to perform calculations involving calorimetry.

Be able to identify and justify whether energy (heat) was released or absorbed by the reaction during a calorimetry experiment.