

Calorimetry Concepts

The whole point of calorimetry is to “trap” the heat that is entering/exiting the system and get a quantitative measure of it (how many joules?). Water is an excellent absorber of heat. It has one of the highest specific heats (C_s) there is at $4.184 \text{ J/g}^\circ\text{C}$. Unfortunately water must be in a container and we must therefore account for the heat entering/exiting the container (the hardware) as well as the water. You can treat the water and the container as one whole unit – the calorimeter. As a unit the whole calorimeter (water + hardware) will have a definite heat capacity, C_{cal} which will have units of J°C or kJ/K . The key thing here is there is only energy per degree temperature for units. All heat capacities have that for units and all heat capacities are extensive properties – meaning the bigger the calorimeter, the bigger the heat capacity will be.

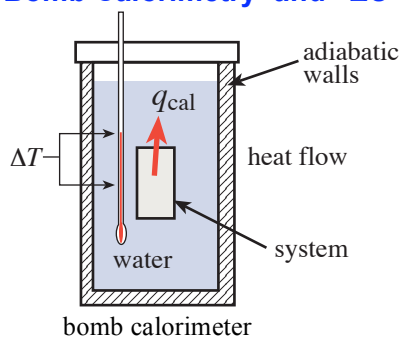
Heat capacities of calorimeters must be measured. You *calibrate* your calorimeter *before* you use it. How? Put a known amount of heat (q_{cal}) into it via a standard reaction of some sort or a precise electric heater. Then measure the temperature response, ΔT . The heat capacity will simply be

$$C_{\text{cal}} = q_{\text{cal}}/\Delta T$$

Now you can turn that equation around and use C_{cal} and ΔT to get q_{cal} . The heat from the chemical reaction you are studying (q_{rxn}) is equal to but opposite in sign from the value of q_{cal} . That is

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

Bomb Calorimetry and ΔU



Bomb calorimetry is conducted under constant volume (isochoric) conditions. This is shown explicitly by writing q_v for the heat term. The subscript “v” means conducted at constant volume. Because the volume is held constant and ΔV is forced to be zero, no expansion work can be done throughout the process ($w = 0$). This means that all heat flow is now equal to the internal

energy change, ΔU . The calculations are as follows for the heat flow in/out of the calorimeter.

$$q_{\text{cal}} = C_{\text{cal}}\Delta T$$

Where C_{cal} is the heat capacity of the entire calorimeter (both water and hardware). A bomb calorimeter has lots of hardware (stirring blade, stainless steel reaction chamber, walls of container, etc...) and the heat capacity of just the hardware can be significant. It is a common practice to split up the overall calorimeter heat capacity into two components, the water part and the hardware part. This leads to the following equation.

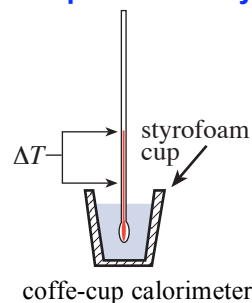
$$q_{\text{cal}} = (C_{\text{water}} + C_{\text{hardware}})\Delta T$$

The water part of this can be further split into the specific heat of water and its mass.

$$C_{\text{water}} = C_{s,\text{water}} \cdot m_{\text{water}}$$

The specific heat for water (an intensive property) times the mass of the water (extensive property) equals the heat capacity of the water (an extensive property).

Coffee-Cup Calorimetry and ΔH



Coffee cup calorimetry is conducted under constant pressure (isobaric) conditions. This means that work is allowed to be done if necessary and the heat flow is equal to the enthalpy change, ΔH . As with all calorimetry,

$$q_{\text{cal}} = C_{\text{cal}}\Delta T$$

where C_{cal} is the heat capacity of the entire calorimeter (both water and hardware). However, since the “hardware” of a coffee cup calorimeter is really just a Styrofoam cup, you can assume the hardware heat capacity is zero and only consider the water. And using the specific heat of water and its mass you get

$$q_{\text{cal}} = C_{s,\text{water}} \cdot m_{\text{water}} \cdot \Delta T$$

Here we assume that the cup itself does not contribute to the overall heat absorption. We are treating the walls of the cup as perfectly adiabatic walls. Remember that an adiabatic process is one where $q=0$. An adiabatic wall is a perfect insulator.

Hey, where's the system?

You'll notice in the diagram for the coffee-cup calorimeter that there is no system pointed out. Where is the system? We only do solution chemistry in coffee-cup calorimetry. The system is dissolved in the water. So the system and the water are occupying the exact same space. This is important for thermodynamics. Boundaries for the system/surroundings can sometimes be very abstract. In a solution with water as the solvent, I can define the system as only those species that are reactants and products – all of which are dissolved in water (the surroundings). This is what is so nice about a coffee-cup calorimeter. It is incredibly simple and cheap. Pull a cup off a stack and you have a perfectly good adiabatic container to do calorimetry in. The thermometer itself can be used as the stirring rod. The trick is keeping your reactants separate from one another before you're ready for them to react. This is typically done by having a solution of reactant A in your coffee-cup, and a solution of reactant B in a separate container. When you're ready, you pour the solution of B in with A and the reaction starts. You can weigh the whole thing afterwards to get the weight of the water. You'd be surprised just how accurate this cheap setup can be.

OK, I've got q_{cal} . Now what?

OK, so you've done the work and solved for q_{cal} , what now? Are you done? Not quite. Most heat transfer processes that are measured are recorded as an intensive property and not extensively. So even though you have a value for ΔU or ΔH , those values happen to be for the amounts you happened to use – typically NOT standard amounts mind you. You'll need to DIVIDE by the amount of substance used. That amount can be in grams or in moles. Make sure you calculate the version that is asked for.

So to summarize, just getting q_{cal} will give you the extensive answer which is just plain ol' joules or kJ. ALL tabulated thermodynamic values all listed as intensive values which are J/mol or J/g. And if those joules are really big, then they'll be reported as kJ/mol or kJ/g.

Can I get ΔH with a bomb calorimeter?

Yes, although you don't get ΔH directly like you do ΔU . The fact is that ΔH and ΔU are related and if you get one, you can calculate further to get the other. The most useful relationship between the two for this purpose is

$$\Delta H = \Delta U + \Delta nRT$$

You WILL need to have a balanced chemical equation in order to figure out what Δn is. Δn is the change in the number of moles of gas in going from reactants to products. Specifically,

$$\Delta n = \sum n_{\text{gas products}} - \sum n_{\text{gas reactants}}$$

The reason this works is because any change in volume must be due to a change in the total number of moles of gas. Reactions can produce more moles of gas (volume increases and work is done BY the system) or they can produce less (volume decreases and work is done ON the system). We are basically exploiting the ideal gas law and the definition of work.

$$w = -P_{\text{ext}}\Delta V = -\Delta nRT$$

So yes, you can get ΔH and ΔU from one another. Just know when and how to do it.

Calibration of a Calorimeter

So how DO you deliver an exact known amount of heat to a calorimeter? There are two basic ways to do this.

1. Use some standard reaction that is very well defined. A specific amount of a combustible material will give a specific amount of heat out per gram (or mole). Measure carefully the amount and you'll know the amount of heat. In general,

$$q = \Delta H \cdot n$$

Where ΔH is the enthalpy change for some process – most likely an exothermic chemical reaction such as a combustion. The units on ΔH will be kJ/mol, therefore you will need to multiply by the number of moles actually used to get the specific amount of heat generated.

2. Use an electric heater with a known power rating (the wattage). Put the heater into the water bath of the calorimeter and turn it on for an exact amount of time.

$$\text{energy (joules)} = \text{power (watts)} \cdot \text{time (seconds)}$$

Remember that a watt is defined as a J/s. Another electric heater version is measuring the current and potential used by the heater over a specified time.

$$\begin{matrix} \text{energy} & = & \text{potential} & \cdot & \text{current} & \cdot & \text{time} \\ \text{(joules)} & & \text{(volts)} & & \text{(amps)} & & \text{(seconds)} \end{matrix}$$

An amp (A) is equal to a coulomb per second (C/s) and a volt-coulomb (V·C) is equal to a joule.

You now have learned more than enough to fully conquer all calorimetry questions.