Q. What is specific heat at constant volume, \( c_v \)?

To answer this question, we should start with a more basic question: What is internal energy, and how do you measure it?

Internal energy is the molecular activity of a substance – the vibrational, translational, and rotational kinetic energy of the molecules of the substance. You can imagine that this would be difficult to measure, but fortunately this energy results in something that we can easily measure: a change in the temperature of the substance.

This leads us to the next step: measuring the internal energy change of a substance. (Note that we are more interested in the change in internal energy, not the absolute value. We will find that the change in internal energy is all we really need.) To measure this change, we turn to the 1st Law of Thermodynamics for a closed system:

\[
\delta q - \delta w = \delta e = du + \Delta (KE) + \Delta (PE)
\]

I’ve written the differential form above, and divided through by the mass of the system since it is closed, and therefore the mass doesn’t change. Now, we are interested in measuring \( du \), the change in specific internal energy, so let’s set up a system that eliminates boundary work, as well as changes in kinetic and potential energy. We’ll choose a rigid container that does not move during the process, as shown below. The resulting analysis is shown below.

In the system we’ve chosen above, the change in energy is equal to the heat we add. What do you think will happen to the system when heat is added? You’d expect the temperature to rise. In fact, it turns out that for small amounts of heat added, the temperature change is proportional to the amount of heat added:

\[
\delta q (= du) \propto dT
\]

To make this an equality, we can add a proportionality constant to the relationship above:

\[
\delta q (= du) = c_v dT,
\]

so

\[
c_v = \left( \frac{du}{dT} \right).
\]

We call the proportionality constant \( c_v \), the “specific heat at constant volume,” and has dimensions of Energy/(mass·ΔT). You may have heard of the term heat capacity; this is just the specific heat times the mass.
Q. What does $c_v$ mean, physically?

The specific heat of a substance physically represents how much the energy of a substance takes in or gives off when its temperature changes. For example, if you heat ten kilograms of water from 25 °C to 100 °C, it takes more energy than to raise the temperature of an equal mass of air. This implies that the specific heat of water is larger than that of air.

We call (lower-case) $c$ the specific heat because it is the heat capacity of a substance divided by its mass, and all “specific” properties are properties per unit mass, or mass-specific properties.

Why call it constant-volume? Because the specific heat is defined when the system was held at constant volume.

Q. If $c_v$ assumes constant volume, how can we use $c_v$ if the system isn’t at constant volume?

Technically, we can’t. If the volume of the system changes, the internal energy may be affected. So let’s generalize the above approach. First, let’s assume that internal energy is a function of both temperature and volume:

$$u = u(T, v).$$

Assuming that $u$ is a function of two variables instead of one makes more sense, considering that the State Principle (see Chapter 2) dictates that we need two independent variables to fix the state of a simple system.

Given that $u$ is a function of $T$ and $v$, the derivative of $u$ would be as follows,

$$du = \left( \frac{\partial u}{\partial T} \right)_v dT + \left( \frac{\partial u}{\partial v} \right)_T dv .$$

Remember that the subscripts $v$ and $T$ on the derivatives mean that the subscript variable is held constant. Like before, we’ll call the first derivative the specific heat at constant volume,

$$c_v \equiv \left( \frac{\partial u}{\partial T} \right)_v .$$

(The other partial derivative isn’t given a name.) So $u$ is, in general, a function of temperature and pressure.

But wait. Under certain conditions the specific internal energy is approximately a function only of temperature. This is true when the substance can be approximated as either an incompressible substance or an ideal gas. In these cases the partial derivative, $\left( \frac{\partial u}{\partial v} \right)_T$, is negligible, and so
\[ \frac{du}{dT} \] 

and 

\[ c_v \equiv \left( \frac{du}{dT} \right). \]

Note that the partial derivatives have been replaced by ordinary derivatives because \( h \) is now a function only of \( T \). We also drop the subscript \( v \) because it doesn’t matter anymore whether the system is at constant volume. Then we can write,

\[ du = c_v dT. \]