0Lapse Rate. Prof. Ruiz (Doc), UNC-Asheville (1978-2021), DoctorPhys on YouTube.
Prerequisites: Chemistry, Physics I, II. Calculus I, II, III. Thermodynamics.

Chapter G. Specific Heat at Constant Volume. A very important concept in atmospheric science is the specific heat.

1. Heat Capacity. The heat capacity C of a substance is defined as

$$C \equiv \lim_{\Delta T \to 0} \frac{Q}{\Delta T},$$

where Q is the heat pumped into the substance and ΔT is the change in its temperature.

The heat capacity is a physical quantity that indicates the ability of a substance to absorb heat. You put in heat and see how much the temperature rises. If you add heat and the temperature goes up just a little, then the capacity to absorb heat is great since you are dividing by a small ΔT. But remember that heat is not a variable of the state of the gas. You cannot say a gas contains heat. A gas contains energy and it may pass some of this energy off in the form of heat. Think of heat as energy in transfer.

If you add heat and the substance's temperature goes up a lot as if the substance is "going crazy," we say that the substance has a small heat capacity. Since ΔT is large in this case, you divide by a larger value, making the ratio $\frac{Q}{\Delta T}$ smaller. To be better at absorbing heat, the substance must not be affected very much when the heat is added.

We can write $C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T}$ with infinitesimal changes.

$$C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T} \quad \Rightarrow \quad C = \frac{\delta Q}{dT}$$

$$\boxed{C = \frac{\delta Q}{dT}}$$

2. Specific Heat Capacity. The However, it is not fair to compare two substances unless they have equal mass. The specific heat is found by dividing the heat capacity by the mass of the substance. We use lowercase for the specific heat.

$$C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T} = \frac{\delta Q}{dT} \qquad c = \frac{1}{m} C$$

In chemistry and thermodynamics we often encounter molar specific heat, where one divides by the number of moles n instead of the mass m .

$$c_n = \frac{1}{n} C$$

I include a subscript n for molar specific heat.

The equation $C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T}$ looks like some kind of broken derivative.
We can fix this situation by invoking the first law of thermodynamics

$\Delta U = Q - W$, where $W = p\Delta V$.

$$\Delta U = Q - p\Delta V$$

Solve for Q .

$$Q = \Delta U + p\Delta V$$

We now return to $C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T}$.

$$C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T} \quad \Rightarrow \quad C = \lim_{\Delta T \to 0} \frac{\Delta U + p\Delta V}{\Delta T}$$

Now we have regular derivatives.

$$C = \lim_{\Delta T \to 0} \frac{\Delta U + p\Delta V}{\Delta T} \quad \Rightarrow \quad C = \lim_{\Delta T \to 0} \frac{\Delta U}{\Delta T} + p \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T} \quad \Rightarrow \quad C = \frac{dU}{dT} + p\frac{dV}{dT}$$

Summary $\boxed{C = \frac{\delta Q}{dT} = \frac{dU}{dT} + p\frac{dV}{dT}}$

3. Heat Capacities at Constant Volume. Let's work through calculating some specific heats for an ideal gas of point particles. We will focus on a gas held at constant volume and in the next section we will address constant pressure. For constant volume $C = \frac{dU}{dT} + p\frac{dV}{dT}$ becomes

$$C_V = \left.\frac{dU}{dT}\right|_V + p\left.\frac{dV}{dT}\right|_V .$$

where the subscript V reminds us that the volume is fixed, i.e., held constant ($dV = 0$).

$$C_V = \left.\frac{dU}{dT}\right|_V + p\left.\frac{dV}{dT}\right|_V \quad \Rightarrow \quad C_v = \left.\frac{dU}{dT}\right|_v$$

Recall our energy equations for a gas. Remember that we earlier found the following equations.

$$\boxed{U = N\frac{1}{2}m\overline{v^2}} \qquad \boxed{U = \frac{3}{2}NkT} \qquad \boxed{U = \frac{3}{2}nR^*T}$$

Since the energy is a function of the temperature only we drop the subscript V .

$$C_V = \left.\frac{dU}{dT}\right|_V \quad \Rightarrow \quad C_V = \frac{dU}{dT}$$

I will use the form $U = \frac{3}{2}nR^*T$.

$$C_V = \frac{dU}{dT} \quad \Rightarrow \quad C_V = \frac{d}{dT}\left(\frac{3}{2}nR^*T\right) \quad \Rightarrow \quad C_V = \frac{3}{2}nR^*$$

Chemists like to find the molar specific heat by diving the specific heat by the number of moles n .

$$c_{V,n} = \frac{C_V}{n} = \frac{1}{n}\frac{3}{2}nR^* = \frac{3}{2}R^*$$

I include the subscript n so we do not confuse the molar specific heat $c_{V,n} = \frac{C_V}{n}$ with the specific heat where we divide the heat capacity by the mass m of the gas instead of the number of moles n . By dividing the heat capacity by the mass m we obtain the default specific heat for the meteorologist, where we leave the subscript only as v . But be careful whose book you are reading since chemists and some others will consider the molar specific heat as the default. The default specific heat for us will therefore be

$$c_V = \frac{C_V}{m} = \frac{1}{m}\frac{3}{2}nR^* = \frac{3}{2}\frac{R^*}{m/n} = \frac{3}{2}\frac{R^*}{M} = \frac{3}{2}R\,.$$

We have used our formulas $M = \frac{m}{n}$ and $R = \frac{R^*}{M}$ from earlier in our course.

Note that the chemists ideal gas constant R^* is a true constant, i.e., constant for all gases.

The meteorologist's $R = \frac{R^*}{M}$ depends on the specific gas due to the molar mass factor.

I would like to mention a nice formula to memorize that helps us go back and forth between meteorologists and chemists. Take the relation $R = \frac{R^*}{M}$ and the formula $M = \frac{m}{n}$. From these we find

$$R = \frac{R^*}{M} \quad \Rightarrow \quad R = \frac{R^*}{m/n} \quad \Rightarrow \quad R = \frac{n}{m} R^* \quad \Rightarrow \quad mR = nR^*$$

The last equation is a good one to remember.

$$\boxed{mR = nR^*}$$

4. Heat Capacity at Constant Volume Formula. Let's return to

$$C = \frac{\delta Q}{dT} = \frac{dU}{dT} + p\frac{dV}{dT}.$$

For constant volume $dV = 0$ and

$$C_V = \frac{\delta Q_V}{dT} = \frac{dU}{dT}.$$

Divide by the mass m.

$$\frac{C_V}{m} = \frac{1}{m}\frac{\delta Q_V}{dT} = \frac{1}{m}\frac{dU}{dT}$$

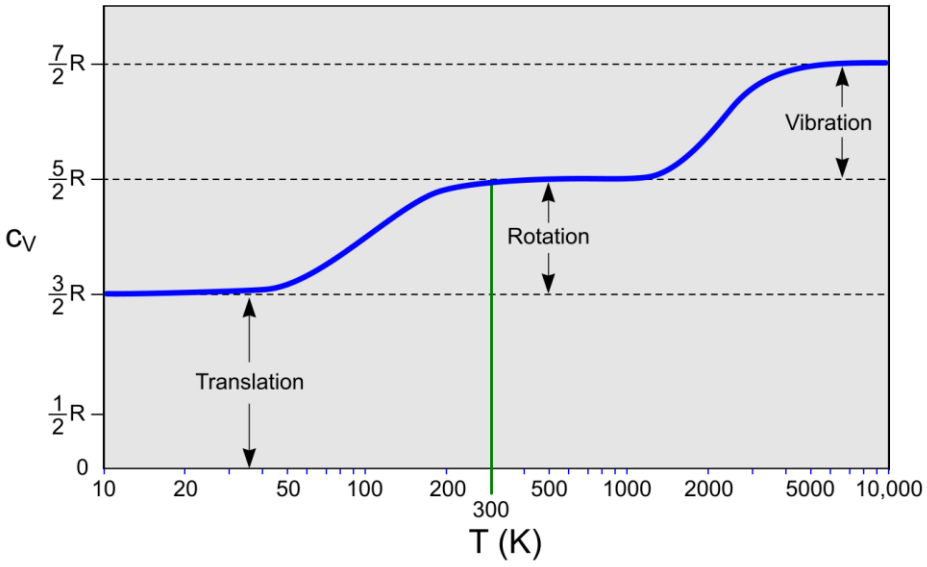
With our usual definitions when we divide by the mass, we set lowercase $c_V = \frac{C_V}{m}$ and

the equation $\frac{C_V}{m} = \frac{1}{m}\frac{\delta Q_V}{dT} = \frac{1}{m}\frac{dU}{dT}$ becomes $c_V = \frac{\delta q_V}{dT} = \frac{du}{dT}$.

(15) $\boxed{c_V = \frac{\delta q_V}{dT} = \frac{du}{dT}}$

When we apply the concept of specific heat to air we need to consider diatomic molecules. Air consists mainly of nitrogen (78%) and oxygen (21%). Both of these gases exist in diatomic form. If we

plot by experiment the specific heat for air across a wide spectrum of temperatures, we obtain something like the figure below. The figure is somewhat idealized and schematic.



At low temperatures we obtain the expected

$$c_V = \frac{3}{2}R$$

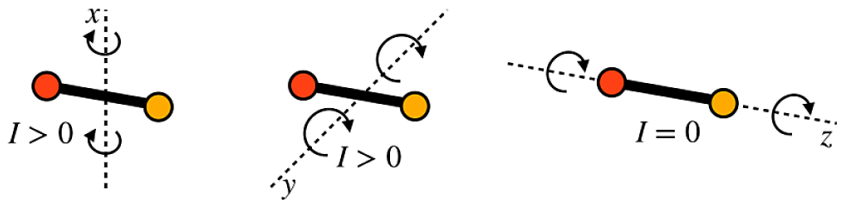
since

$$c_V = \frac{du}{dT}$$

and

$$u = \frac{3}{2}RT\,.$$

But when the temperature gets higher, the diatomic molecules start rotating.



Courtesy Tom Weideman
University of California, Davis
LibreTexts, License: CC BY-SA 4.0

The left figure shows the diatomic molecule rotating about the three axes in space. The first two cases can absorb significant heat energy rotating, while the third case has very small rotational inertia energy since mass hugs the axis. Here we see that we add $\frac{1}{2}RT$ to the energy for each way to express energy. So rotation has two significant ways as shown in the figure. The I represents rotational inertia. It is important for the first two cases.

Classical Model of Diatomic Molecule
Courtesy Elizabeth Johnson, Analytical Methods in Geosciences
License: CC BY-SA 4.0

When you get to the very high temperatures, you kick the molecule into vibration. The table below gives ways the molecule can absorb energy as the temperature goes up to excite it more. But doesn't the vibrational mode just give one more mode of energy absorption and would only make $c_v = \frac{5}{2}R$

jump by $\frac{1}{2}R$ due to the kinetic energy of the vibration? No! We must remember that the potential energy counts as an energy mode too. Refer to the table below.

Specific Heats for a Diatomic Molecule

Temperature	Available Modes	Contributes to Molar Specific Heat	Total Molar Specific Heat
Low	3 Translational Modes	$3 \cdot \frac{1}{2}R$	$\frac{3}{2}R$
Medium	2 Rotational Modes of Significance	$2 \cdot \frac{1}{2}R$	$\frac{5}{2}R$
High	1 Vibrational Kinetic Energy Mode 1 Vibrational Potential Energy Mode	$2 \cdot \frac{1}{2}R$	$\frac{7}{2}R$

Adding $\frac{1}{2}R$ for each degree of energy absorption or expressions is called the *equipartition theorem*. The energy gets partitioned into these modes of expression.