

7.13: Heat Capacities for Gases- C_V , C_P

If we heat or do work on any gas—real or ideal—the energy change is $E = q + w$. When we investigate the energy change that accompanies a temperature change, we can obtain reproducible results by holding either the pressure or the volume constant. With volume held constant, we measure C_V . With pressure held constant, the energy change we measure depends on both C_P and the relationship among the pressure, volume, and temperature of the gas. If we know an equation of state for the gas and the values of both C_V and C_P , we can find the energy change between any two states of the gas, because the same change of state can be achieved in two steps, one at constant pressure and one at constant volume.

To see this, we recognize that the state of any pure gas is completely specified by specifying its pressure, temperature, and volume. Any change of state necessarily involves changing at least two of these state functions. Any change of state that changes all three of them can be achieved in an alternate way that involves two changes, each of which occurs with one variable held constant. For example, the change

$$(P_1, V_1, T_1) \rightarrow (P_2, V_2, T_2)$$

can be achieved by the constant-pressure sequence

$$(P_1, V_1, T_1) \rightarrow (P_1, V_2, T_i)$$

followed by the constant-volume sequence

$$(P_1, V_2, T_i) \rightarrow (P_2, V_2, T_2)$$

where T_i is some intermediate temperature. Note that this sequence has to be possible: with P held constant, specifying a change in T is sufficient to determine the change in V ; with V held constant, specifying a change in T is sufficient to determine the change in P .

Let us consider how the energy of one mole of any pure substance changes with temperature at constant volume. The rate of change of E with T is

$$\left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial q}{\partial T}\right)_V + \left(\frac{\partial w}{\partial T}\right)_V = C_V + \left(\frac{\partial w}{\partial T}\right)_V$$

where we use the definition of C_V . For any system, and hence for any substance, the pressure–volume work is zero for any process in which the volume remains constant throughout; therefore, we have $(\partial w / \partial T)_V = 0$ and

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V$$

(one mole of any substance, only PV work possible)

When we develop the properties of ideal gases by treating them as point mass molecules, we find that their average translational kinetic energy is $3RT/2$ per mole or $3kT/2$ per molecule, which clearly depends only on temperature. Translational kinetic energy is the only form of energy available to a point-mass molecule, so these relationships describe all of the energy of any point-mass molecule. In particular, they describe all of the energy of a monatomic ideal gas. Since the energy of a monatomic ideal gas is independent of pressure and volume, the temperature derivative must be independent of pressure and volume. The ordinary derivative and the partial derivatives at constant pressure and constant volume all describe the same thing, which, we have just seen, is C_V .

$$\frac{dE}{dT} = \left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V = C_V = \frac{3}{2}R$$

(one mole of a monatomic ideal gas)

It is useful to extend the idea of an ideal gas to molecules that are not monatomic. When we do so, we have in mind molecules that do not interact significantly with one another. Another way of saying this is that the energy of the collection of molecules is not affected by any interactions among the molecules; we can get the energy of the collection by adding up the energies that the individual molecules would have if they were isolated from one another. In our development of statistical thermodynamics, we find that the energy of a collection of non-interacting molecules depends only on the molecules' energy levels and the temperature. The

molecules' energy levels are fixed. This means that if we extend our idea of ideal gases to include non-interacting polyatomic compounds, the energies of such gases still depend only on temperature. For any ideal gas, we have

$$\frac{dE}{dT} = \left(\frac{\partial E}{\partial T} \right)_P = \left(\frac{\partial E}{\partial T} \right)_V = C_V$$

(one mole of any ideal gas)

However, for polyatomic molecules it will no longer be true that $C_V = 3R/2$. Let us see why. Recall that we construct our absolute temperature scale by extrapolating the Charles' law graph of volume versus temperature to zero volume. (Figure 2-2.) By experiment, we find that this graph is the same for one mole of a polyatomic ideal gas as it is for one mole of a monatomic ideal gas. Evidently, our definition of temperature depends only on the translational energy of ideal gas molecules and *vice-versa*. At a fixed temperature, the average translational kinetic energy is the same for any ideal gas; it is independent of the mass of the molecule and of the kinds of atoms in it. To increase the temperature by one degree requires that the translational kinetic energy increase by $3R/2$, and *vice versa*.

Consider what happens when we add energy to a polyatomic ideal gas. Polyatomic gas molecules have energy in rotational and vibrational modes of motion. When we add energy to such molecules, some of the added energy goes into these rotational and vibrational modes. To achieve the same increase in translational kinetic energy, the total amount of energy added must be greater. We find that we need a larger ΔE to achieve the same ΔT , which means that the heat capacity (either C_V or C_P) of the polyatomic ideal gas is greater than that of a monatomic ideal gas.

Now let us consider the rate of change of E with T at constant pressure. For one mole of any substance, we have

$$\left(\frac{\partial E}{\partial T} \right)_P = \left(\frac{\partial q}{\partial T} \right)_P + \left(\frac{\partial w}{\partial T} \right)_P = C_P + \left(\frac{\partial w}{\partial T} \right)_P$$

This equation is as far as we can go, unless we can focus on a particular situation for which we know how work varies with temperature at constant pressure.

For one mole of an ideal gas, we have this information. From $PV = RT$ at constant P , we have $PdV = RdT$. If reversible work is done on the ideal gas,

$$w = \int -P_{\text{applied}} dV = \int -PdV \quad \text{and}$$

$$\left(\frac{\partial w}{\partial T} \right)_P = \left[\frac{\partial}{\partial T} \int -PdV \right]_P = \left[\frac{\partial}{\partial T} \int -RdT \right]_P = -R$$

(any ideal gas)

That is, when enough heat is added to increase the temperature of one mole of ideal gas by one degree kelvin at constant pressure, $-R$ units of work are done on the gas. This is the energy change that occurs because of the increase in volume that accompanies the one-degree temperature increase. Since, for any ideal gas,

$$C_V = \left(\frac{\partial E}{\partial T} \right)_P = \left(\frac{\partial q}{\partial T} \right)_P + \left(\frac{\partial w}{\partial T} \right)_P = C_P - R$$

we have

$$C_P = C_V + R$$

(one mole of any ideal gas)

For a monatomic ideal gas,

$$C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$$

(one mole of a monatomic ideal gas)

The heat capacity functions have a pivotal role in thermodynamics. We consider many of their properties further in the next section and in later chapters (particularly §10-9 and §10-10.) Because we want to use these properties before we get around to justifying them all, let us summarize them now:

1. For monatomic ideal gases, C_V and C_P are independent of temperature.
2. For polyatomic gases, real or ideal, C_V and C_P are functions of temperature.
3. C_P is always greater than C_V , but as the temperature decreases, their values converge, and both vanish at absolute zero.
4. At ordinary temperatures, C_V and C_P increase only slowly as temperature increases. For many purposes they can be taken to be constant over rather wide temperature ranges.
5. For real substances, C_V is a weak function of volume, and C_P is a weak function of pressure. These dependencies are so small that they can be neglected for many purposes.
6. For ideal gases, C_V is independent of volume, and C_P is independent of pressure.

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