

8.1: Heat Capacity

Definition: The heat capacity of a body is the quantity of heat required to raise its temperature by one degree. Its SI unit is J K^{-1} .

Definition: The specific heat capacity of a substance is the quantity of heat required to raise the temperature of unit mass of it by one degree. Its SI unit is $\text{J kg}^{-1} \text{K}^{-1}$.

Definition: The molar heat capacity of a substance is the quantity of heat required to raise the temperature of a molar amount of it by one degree. (I say "molar amount". In CGS calculations we use the mole – about 6×10^{23} molecules. In SI calculations we use the kilomole – about 6×10^{26} molecules.) Its SI unit is $\text{J kilomole}^{-1} \text{K}^{-1}$.

Some numerical values of specific and molar heat capacity are given in Section 8.7.

One sometimes hears the expression "the specific heat" of a substance. One presumes that what is meant is the specific heat capacity.

The above definitions at first glance seem easy to understand – but we need to be careful. Let us imagine again a gas held in a cylinder by a movable piston. I choose a gas because its volume can change very obviously on application of pressure or by changing the temperature. The volume of a solid or a liquid will also change, but only by a small and less obvious amount. If you supply heat to a gas that is *allowed to expand at constant pressure*, some of the heat that you supply goes to doing external work, and only a part of it goes towards raising the temperature of the gas. On the other hand, *if you keep the volume of the gas constant*, all of the heat you supply goes towards raising the temperature. Consequently, more heat is required to raise the temperature of the gas by one degree if the gas is allowed to expand at constant pressure than if the gas is held at constant volume and not allowed to expand. Thus the heat capacity of a gas (or any substance for that matter) is greater if the heat is supplied at constant pressure than if it is supplied at constant volume. Thus we have to distinguish between the *heat capacity at constant volume* C_V and the *heat capacity at constant pressure* C_P , and, as we have seen $C_P > C_V$.

If the heat is added at constant volume, we have simply that $dU = dQ = C_V dT$.

One other detail that requires some care is this. The specific heat capacity of a substance may well vary with temperature, even, in principle, over the temperature range of one degree mentioned in our definitions. Therefore, we really have to define the heat capacity at a given temperature in terms of the heat required to raise the temperature by an infinitesimal amount rather than through a finite range. Thus it is perhaps easiest to **define** heat capacity at constant volume in symbols as follows:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (8.1.1)$$

(Warning: Do not assume that $C_P = (\partial U / \partial T)_P$. That isn't so. The correct expression is given as equation 9.1.13 in Chapter 9 on Enthalpy.)

As with many equations, this applies equally whether we are dealing with total, specific or molar heat capacity or internal energy.

If heat is supplied at constant pressure, some of the heat supplied goes into doing external work PdV , and therefore

$$C_P dT = C_V dT + PdV. \quad (8.1.2)$$

For a mole of an *ideal gas at constant pressure*, $P dV = R dT$, and therefore, for an ideal gas,

$$C_P = C_V + R, \quad (8.1.3)$$

where, in this equation, C_P and C_V are the molar heat capacities of an ideal gas.

We shall see in Chapter 10, Section 10.4, if we can develop a more general expression for the difference in the heat capacities of *any* substance, not just an ideal gas. But let us continue, for the time being with an ideal gas.

In an ideal gas, there are no forces between the molecules, and hence no potential energy terms involving the intermolecular distances in the calculation of the internal energy. In other words, the internal energy is independent of the distances between molecules, and hence the internal energy is independent of the volume of a fixed mass of gas if the temperature (hence kinetic energy) is kept constant. That is, for an ideal gas,

$$\left(\frac{\partial U}{\partial V} \right)_T = 0. \quad (8.1.4)$$

Let us think now of a *monatomic* gas, such as helium or argon. When we supply heat **to** (and raise the temperature of) an ideal monatomic gas, we are increasing the translational kinetic energy of the molecules. If the gas is *ideal*, so that there are no intermolecular forces then *all* of the introduced heat goes into increasing the translational kinetic energy (i.e. the temperature) of the gas. (Recall that a gas at low pressure is nearly ideal, because then the molecules are so far apart that any intermolecular forces are negligible.) Recall from Section 6.5 that the translational kinetic energy of the molecules in a mole of gas is $\frac{3}{2}RT$. The molar internal energy, then, of an ideal monatomic gas is

$$U = \frac{3}{2}RT + \text{constant.} \quad (8.1.5)$$

From equation 8.1.1, therefore, the molar heat capacity at constant volume of an ideal monatomic gas is

$$C_V = \frac{3}{2}R. \quad (8.1.6)$$

The molar heat capacities of real monatomic gases when well above their critical temperatures are indeed found to be close to this.

When we are dealing with *polyatomic* gases, however, the heat capacities are greater. This is because, when we supply heat, only some of it goes towards increasing the translational kinetic energy (temperature) of the gas. Some of the heat goes into increasing the *rotational* kinetic energy of the molecules. (Wait! Some of you are asking yourselves: "But do not atoms of helium and argon rotate? Do they not have rotational kinetic energy?" These are very good questions, but I am going to pretend for the moment that I haven't heard you. Perhaps, before I come to the end of this section, I may listen.)

When two molecules collide head on, there is an interchange of translational kinetic energy between them. But if they have a glancing collision, there is an exchange of translational and rotational kinetic energies. If millions of molecules are colliding with each other, there is a constant exchange of translational and rotational kinetic energies. When a dynamic equilibrium has been established, the kinetic energy will be shared equally between each degree of translational and rotational kinetic energy. (This is the *Principle of Equipartition of Energy*.) We know that the translational kinetic energy per mole is $\frac{3}{2}RT$ - that is, $\frac{1}{2}RT$ for each translational *degree of freedom* ($\frac{1}{2} m \overline{u^2}$, $\frac{1}{2} m \overline{v^2}$, $\frac{1}{2} m \overline{w^2}$). There is an equal amount of kinetic energy of rotation (with an exception to be noted below), so that the internal energy associated with a mole of a polyatomic gas is $3RT$ plus a constant, and consequently the molar heat capacity of an ideal *polyatomic* gas is

$$C_V = 3R. \quad (8.1.7)$$

It takes twice the heat to raise the temperature of a mole of a polyatomic gas compared with a monatomic gas.

The exception we mentioned is for *linear* molecules. These are molecules in which all the atoms are in a straight line. This necessarily includes, of course, all diatomic molecules (the oxygen and nitrogen in the air that we breathe) as well as some heavier molecules such as CO₂, in which all the molecules (at least in the ground state) are in a straight line. (The molecule H₂O is not linear.) In linear molecules, the moment of inertia about the internuclear axis is negligible, so there are only two degrees of rotational freedom, corresponding to rotation about two axes perpendicular to each other and to the internuclear axis. Thus there are five degrees of freedom in all (three of translation and two of rotation) and the kinetic energy associated with each degree of freedom is $\frac{1}{2}RT$ per mole for a total of $\frac{5}{2}RT$ per mole, so the molar heat capacity is

$$C_V = \frac{5}{2}R. \quad (8.1.8)$$

Summary: A monatomic gas has three degrees of translational freedom and none of rotational freedom, and so we would expect its molar heat capacity to be $\frac{3}{2}RT$.

A diatomic or linear polyatomic gas has three degrees of translational freedom and two of rotational freedom, and so we would expect its molar heat capacity to be $\frac{5}{2}RT$.

A nonlinear polyatomic gas has three degrees of translational freedom and three of rotational freedom, and so we would expect its molar heat capacity to be $3R$.

How do real gases behave compared with these predictions? The monatomic gases (helium, neon, argon, etc) behave very well. The diatomic gases quite well, although at room temperature the molar heat capacities of some of them are a little higher than predicted, while at low temperatures the molar heat capacities drop below what is predicted. Indeed below about 60 K the molar heat capacity of hydrogen drops to about $\frac{3}{2}RT$ - just as if it had become a monatomic gas or, though still diatomic, the molecules

were somehow prevented from rotating. The molar heat capacities of nonlinear polyatomic molecules tend to be rather higher than predicted.

First let us deal with why the molar heat capacities of polyatomic molecules and some diatomic molecules are a bit higher than predicted. This is because the molecules may *vibrate*. When we add heat, some of the heat is used up in increasing the rate of rotation of the molecules, and some is used up in causing them to vibrate, so it needs a lot of heat to cause a rise in temperature (translational kinetic energy). The possibility of vibration adds more degrees of freedom, and another $\frac{1}{2}RT$ to the molar heat capacity for each extra degree of vibration. To be strictly correct, the "number of degrees of freedom" in this connection is the number of squared terms that contribute to the internal energy. Each vibrational mode adds two such terms – a kinetic energy term and a potential energy term. This means that the predicted molar heat capacity for a nonrigid diatomic molecular gas would be $\frac{7}{2}RT$. Polyatomic gases have many vibrational modes and consequently a higher molar heat capacity.

So – why is the molar heat capacity of molecular hydrogen not $\frac{7}{2}RT$ at all temperatures? Why is it about $\frac{5}{2}RT$ at room temperature, as if it were a rigid molecule that could not vibrate? True, at higher temperatures the molar heat capacity does increase, though it never quite reaches $\frac{7}{2}RT$ before the molecule dissociates. Why does the molar heat capacity decrease at lower temperatures, reaching $\frac{3}{2}RT$ at 60 K, as if it could no longer rotate?

Let us ask some further questions, which are related to these. We said earlier that a monatomic gas has no rotational degrees of freedom. Why not? True, the moment of inertia is very small, but, if we accept the principle of equipartition of energy, should not each rotational degree of freedom hold as much energy as each translational degree of freedom? Also, we said that a linear molecule has just two degrees of freedom. It is true that the moment of inertia about the internuclear axis is very small. This is not the same thing as saying that it cannot rotate about that axis. If all degrees of freedom equally share the internal energy, then the angular speed about the internuclear axis must be correspondingly large.

Now I could make various excuses about these problems. The fact is, however, that the classical model that I have described may look good at first, but, when we start asking these awkward questions, it becomes evident that the classical theory really fails to answer them satisfactorily. In truth, the failure of classical theory to explain the observed values of the molar heat capacities of gases was one of the several failures of classical theory that helped to give rise to the birth of quantum theory. Quantum theory in fact accounts spectacularly well and in detail for the specific heat capacities of molecules and how the heat capacities vary with temperature. This topic is often dealt with on courses on statistical thermodynamics, and I just briefly mention the explanation here. The solution of Schrödinger's equation for a rigid rotator shows that the rotational energy can exist with a number of separated discrete values, and the population of these rotational energy levels is governed by Boltzmann's equation in just the same way as the population of the electronic energy levels in an atom. At temperatures of 60 K, the spacing of the rotational energy levels is large compared with kT , and so the rotational energy levels are unoccupied. Thus, in that very real sense, the hydrogen molecule does indeed stop rotating at low temperatures. The spacing of the energy level is inversely proportional to the moment of inertia, and the moment of inertia about the internuclear axis is so small that the energy of the first rotational energy level about this axis is larger than the dissociation energy of the molecule, so indeed the molecule cannot rotate about the internuclear axis. Vibrational energy is also quantised, but the spacing of the vibrational levels is much larger than the spacing of the rotational energy levels, so they are not excited at room temperatures. This has been only a brief account of why classical mechanics fails and quantum mechanics succeeds in correctly predicting the observed heat capacities of gases. It is a very interesting subject, and the reader may well want to learn more about it – but that will have to be elsewhere.

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