

## 13.3: Pressure and Temperature

The way in which the pressure of a material increases with temperature at constant volume is described by  $\left(\frac{\partial P}{\partial T}\right)_V$ .

*Exercise:* By making use of equation 2.4.11, show that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}. \quad (13.3.1)$$

*Exercise:* By making use of equation 10.4.8, show that

$$C_P - C_V = \frac{TV\beta^2}{\kappa} = \frac{9TV\alpha^2}{\kappa}. \quad (13.3.2)$$

Thus we can determine  $C_P - C_V$  from measurements of the expansion coefficient and the isothermal compressibility without knowing the equation of state. We have already shown that the expansion coefficient of an ideal gas is  $1/T$ , and the isothermal compressibility of an ideal gas is  $1/P$ . Note that, for an ideal gas,  $\beta = 1/T$  and  $\kappa = 1/P$ , so that equation 13.3.2 reduces to  $R$ .

Note that, in equation 13.3.2,  $\kappa$  is the isothermal compressibility.  $C_P$  and  $C_V$  may denote the molar heat capacities (in which case  $V$  is the molar volume); or they may denote the specific heat capacities (in which case  $V$  is the specific volume or reciprocal of density); or they may denote the total heat capacities (in which case  $V$  is the total volume).

Recall that the physical reason that  $C_P$  is greater than  $C_V$  is that when a substance is heated and expands at constant pressure, it does work, whereas if held at constant volume it does no work. In the case of an ideal gas expanding reversibly, the work done is all external work. A real gas, or a van der Waals gas, on expanding also does internal work against the intermolecular forces. Therefore  $C_P$  is greater than  $C_V$  by more than  $R$  – but only a little more, because the intermolecular (van der Waals) forces are not very large. In Chapter 10 we developed an explicit expression for  $C_P - C_V$  for a van der Waals gas (equation 10.4.10). When a solid is heated, it expands very little compared with a gas, and hence does very little external work. The intermolecular forces, however, are quite large, and hence an expanding solid does quite a lot of internal work. Thus for a gas, most of the work of expansion is external; for a solid, most of the work of expansion is internal.

Here are order-of-magnitude figures for copper at room temperature (for exact figures, we would have to specify the exact temperature).

Specific heat capacity at constant pressure =  $384 \text{ J K}^{-1} \text{ kg}^{-1}$

Molar mass (“atomic weight”) =  $63.5 \text{ kg kmole}^{-1}$

Molar heat capacity at constant pressure =  $24400 \text{ J K}^{-1} \text{ kmole}^{-1} = 2.93 R$ .

Density =  $8960 \text{ kg m}^{-3}$

Molar volume =  $7.09 \times 10^{-3} \text{ m}^3 \text{ kmole}^{-1}$

Coefficient of linear expansion =  $1.67 \times 10^{-5} \text{ K}^{-1}$

Coefficient of volume expansion =  $5.00 \times 10^{-5} \text{ K}^{-1}$

Isothermal bulk modulus =  $1.40 \times 10^{11} \text{ Pa}$

Isothermal compressibility =  $7.14 \times 10^{-12} \text{ Pa}^{-1}$

Equation 13.3.2 will give us, at a temperature of  $20^\circ\text{C} = 293.15 \text{ K}$ ,  $C_P - C_V$  (molar) =  $728 \text{ J K}^{-1} \text{ kmole}^{-1} = 0.09R$ .  $C_P - C_V$  (specific) =  $11 \text{ J K}^{-1} \text{ kg}^{-1}$ . This is only about 3 percent of  $C_P$ .

Equation 13.3.2 raises an interesting problem concerning water. It will be understood that the reason why  $C_P$  for an ideal gas is greater than  $C_V$  is as follows. When heat is added to an ideal gas at constant volume, all of the heat goes into raising the temperature. When heat is added at constant pressure, however, some of the heat goes into doing external work. Hence  $C_P > C_V$ . That argument is correct. However...

Water at  $2^\circ\text{C}$  (or indeed at any temperature in the range between  $0^\circ\text{C}$  and  $4^\circ\text{C}$ ) contracts upon heating (i.e.  $\beta$  is negative), so that, if we add heat at constant pressure, work is done on the water by its surroundings, and hence (we might argue, though erroneously), for water at  $2^\circ\text{C}$ ,  $C_P < C_V$ . Equation 13.3.2, however, shows that  $C_P \geq C_V$  regardless of the sign of  $\beta$ . (The equality applies where  $\beta = 0$ , which occurs at  $4^\circ\text{C}$ .) Thus we have a paradox.

In fact, equation 13.3.2 is correct, and, at 2 °C,  $C_P > C_V$ . The explanation is as follows. It is true that, when heat is added to an ideal gas at constant volume, all of the heat goes into raising the temperature – but this is true only for an ideal gas in which the internal energy is all kinetic. But for real substances, including water, the correct statement (which is really just the first law of thermodynamics) is that when heat is added to a substance at constant volume, all of the heat goes into raising the *internal energy*, and, for a nonideal substance the internal energy is partly kinetic and partly potential. When we add heat isobarically to water at 2 °C, more of this heat goes into increasing the potential energy than if we add heat isochorically, and hence  $C_P$  is still greater than  $C_V$ . A very clear account of this problem, from both the thermodynamical and statistical mechanical points of view, is to be found in a paper by McDougall and Feistel, *Deep-Sea Research I* **50**, 1523 (2003).

(You may remember a similar apparent paradox in connection with surface tension of a liquid. When we do work adiabatically and reversibly to create new surface, the temperature *drops*. So doing work on a system or adding heat to it doesn't necessarily result in a rise in temperature. It *does* result in an increase of internal energy, which include potential energy.)

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