7.7: Measuring Pressure-Volume Work

By definition, the energy of a system can be exploited to produce a mechanical change in the surroundings. The energy of the surroundings increases; the energy of the system decreases. Raising a weight against the earth's gravitational force is the classical example of a mechanical change in the surroundings. When we say that work is done on a system, we mean that the energy of the system increases because of some non-thermal interaction between the system and its surroundings. The amount of work done on a system is determined by the non-thermal energy change in its surroundings. We define work as the scalar product of a vector representing an applied force, $\overrightarrow{F}_{applied}$, and a second vector, $\overrightarrow{r}$, representing the displacement of the object to which the force is applied. The definition is independent of whether the process is reversible or not. If the force is a function of the displacement, we have

$$dw = \overrightarrow{F}\left(\overrightarrow{r}\right)_{applied} d\overrightarrow{r}$$

Pressure–volume work is done whenever a force in the surroundings applies pressure on the system while the volume of the system changes. Because chemical changes typically do involve volume changes, pressure–volume work often plays a significant role. Perhaps the most typical chemical experiment is one in which we carry out a chemical reaction at the constant pressure imposed by the earth's atmosphere. When the volume of such a system increases, the system pushes aside the surrounding atmosphere and thereby does work on the surroundings.

When a pressure, $P_{applied}$, is applied to a surface of area A, the force normal to the area is $F = P_{applied}A$. For a displacement, dx, normal to the area, the work is $Fdx = dw = P_{applied}A\,dx$. We can find the general relationship between work and the change in the volume of a system by supposing that the system is confined within a cylinder closed by a piston. (See Figure 4.) The surroundings apply pressure to the system by applying force to the piston. We suppose that the motion of the piston is frictionless.

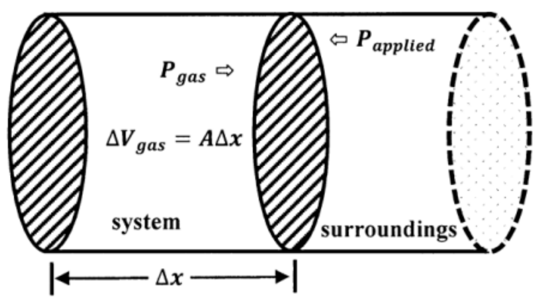

Figure 4. Pressure–volume work.

The system occupies the volume enclosed by the piston. If the cross-sectional area of the cylinder is A, and the system occupies a length x, the magnitude of the system's volume is $V = Ax$. If an applied pressure moves the piston a distance dx, the volume of the system changes by $dV_{system} = A\,dx$. The magnitude of the work done in this process is therefore

$$\begin{aligned} \left|dw_{system}\right| &= \left|P_{applied}A\,dx\right| \\ &= \left|P_{applied}dV_{system}\right| \end{aligned}$$

work is positive if it is done on the system

We are using the convention that work is positive if it is done on the system. This means that a compression of the system, for which $dx < 0$ and $dV_{system} < 0$, does a positive quantity of work on the system. Therefore, the work done on the system is $dw_{system} = -P_{applied}dV_{system}$ or, using our convention that unlabeled variables always characterize the system,

$$dw = -P_{applied}dV$$