2.1: Work and the Inexact Differential

2.1 Changes of energy: work and heat

Now that we are content with measuring changes in energy, we can start by defining it with:

$$\partial U = \partial w + \partial q \tag{2.1.1}$$

where the change in energy (∂U) is equal to the change in heat (∂q) plus the change in work (∂w). The symbol "∂" indicates a partial differential, which should be familiar to you from your first Calculus class. It represents a change so small that it is essentially $\sim$0; as a result, partial quantities must be integrated to build up a "body" so that the difference can actually be measured. Throughout this course, we will often see that calculus equations can be described using physical actions, which must be true as the variables are real things. For example, integrating moles: $\int_{0\ mol}^{n\ mol} \partial n$ physically corresponds to leaking **n** moles of a gas into a vacuum chamber. Likewise integrating volume: $\int_{0\ m^3}^{X\ m^3} \partial V$ is akin to filling a hole. We will point out such analogies when possible, and hopefully it will help you understand the calculus equations we will work with throughout the remainder of the book. Last, you should know that partials have units. Thus, $\partial n sim\ 0\ mol$ and $\partial V sim\ 0\ m^3$, not just "0".

There is a small complication that we run into when performing thermodynamic integrations. Specifically, the partial differential "∂" may represent a change along a particular path and integrating that partial will have to take the path into account. But before we start losing everyone in "math-speak", note that you are already familiar with paths! For example, you can work efficiently or inefficiently; these are different paths. The integration along an inefficient path will reveal that less work comes out of the system compared to the efficient one.

Heat is rather boring, except to pyromaniacs. It represents energy transfer, like lighting a match under a metal can when you were learning calorimetry in Freshman chemistry (Figure 2.1A). This was rather inefficient due to irreversible losses to the environment; however, heat can be provided to a system very efficiently as shown in Figure 2.1B. Like work, efficient heating is the best, and for the purposes of this class, heat is mostly expressed as the addition of "X" Joules of energy into a gas in a piston or a water cup. Like we said, boring. Now take the same thing and divide by temperature, as discussed in Chapter 4, and you will understand why everything in the Universe works the way it does. Including cats.

Let's calculate the work ∂w due to a change in volume of a piston inside your car engine. This occurs immediately after the exterior pressure increases after the spark plug ignited the fuel/air mixture:

$$\partial w = -P_{ext} \cdot \partial V \tag{2.1.2}$$

This is the IUPAC definition of volume work, whereby the piston is considered the system (alternatively, some view the exterior vehicle as the system- we don't do that here!). Work done ***on the system*** requires lowering the interior volume. This would occur by increasing the exterior applied pressure P_{ext}, as this is the driver of the volume decrease. Note that the piston compression will stop when the interior and exterior pressures are equal. Work done ***on the system*** is positive energy, because the "–" sign in $-P_{ext} \cdot \partial V$ negates the loss of volume ∂V, which is negative. No work is done if there is no change in volume, even if the external pressure is significantly higher than the piston's internal pressure. Negative work performed ***by the system*** occurs when the piston expands; both positive (compression) and negative (expansion) work by a piston are diagrammed in Figure 2.2 above.

Work is path-dependent because it can be performed efficiently or inefficiently. Just like how we can raise a weight using a simple machine such as a pulley, or by brute force pushing the same weight with our bare hands and legs. There is a mathematical representation of this path dependence, and to demonstrate let's analyze two different ways for work to be done on a piston. This is usually referred to as "PV-work". Step 1 of figure 2.3 represents inefficient compression whereby the external pressure jumps immediately from 1 to 2 bar. As in our previous example, a model for such a dynamic is the interior of a car engine piston that experiences a sudden pressure jump due to the spark plug igniting gasoline; however, we will assume that the temperature is constant since this significantly simplifies the analysis. After the exterior pressure increase, the system "catches up" in step 2 by compressing the piston. Since the equation for work: $\partial w = -P_{ext} \cdot \partial V$ has two partials (∂w and ∂V), we need to integrate both to define a finite, measurable value for work:

$$\int \partial w = \Delta w = \int -P_{ext} \cdot \partial V \tag{2.1.3}$$

First, we must make sure the units are consistent with Joules. Since volume is often expressed in Liters (equivalent to cubic decimeters), we must change the pressure to kPa since kPa$\times$L=J. Next, we have to use definite integrals by applying limits, and note that there are two steps in the compression. In these situations, the total work is the sum of the integrations along each step. In the first, we see that the exterior pressure increases while the volume is constant. As a result the work is:

$$\Delta w_1 = \int_{2L}^{2L} -P_{ext} \cdot \partial V = -P_{ext} \times (2L - 2L) = 0\ J$$

There is no work done in the 1^{st} step because it doesn't matter what the pressure is doing if it gets multiplied by $\Delta V_1 = 0\ L$. Now the second step where the volume does change the work is integrated as:

$$\Delta w_2 = -P_{ext} \int_{2L}^{1L} \partial V = -200\ kPa \times (1L - 2L) = +200\ J$$

where the exterior pressure comes out of the integral because it is constant. The total work is the sum of these two steps, which is a positive 200 Joules.

Let's see what happens if we do the work efficiently, which means that we slowly increase the exterior pressure from 1 to 2 bar. This allows the internal pressure enough time to equalize incrementally to the rising exterior pressure as shown in Figure 2.4. We will describe this using a "phenomenological" model, which is a mathematical expression that makes sense. In this case, we will say that the interior volume decreases from 2 L to 1 L as the exterior pressure increases from 100 kPa to 200 kPa as: $V = 2L \cdot \frac{100\ kPa}{P_{ext}}$. The change in volume is now a smooth function of the exterior pressure, although we actually need to solve this model for the exterior pressure: $P_{ext} = 100\ kPa \cdot \frac{2\ L}{V}$ because the exterior pressure explicitly appears in the equation for work: $\partial w = -P_{ext} \cdot \partial V$. What is interesting is that P_{ext} is now "hiding" a factor of V which is our integrand ∂V. As a result, we must include this volume factor in the evaluation of the integral, which we do by solving:

$$\Delta w = \int_{2L}^{1L} -P_{ext} \cdot \partial V = \int_{2L}^{1L} \frac{-100\ kPa \cdot 2\ L}{V} \cdot \partial V$$

This integral is more complicated than in the previous example, but fortunately we know enough Calculus to solve this by taking out constant factors and using the identity: $\int x^{-1} \partial x = \ln(x)$:

$$\Delta w = -100\ kPa \cdot 2L \cdot \int_{2L}^{1L} \frac{\partial V}{V} = -100 kPa \cdot 2L \cdot \ln\left(\frac{1L}{2L}\right) = 138\ J$$

Consequently, the efficient transition involves slowly increasing the exterior pressure to allow the interior pressure to adjust accordingly, which requires less positive work ($\Delta w = 138$ J). In contrast, the inefficient transition has such a sudden increase in the exterior pressure that the system doesn't have time to respond, which ultimately necessitates greater, more positive work ($\Delta w = 200\ J$). Hence, there is a path dependence to work. Note that, in either case the piston reached the same final state, although the efficient path required less work to achieve it.