6 Quasistatic thermodynamic processes

- Quasistatic processes are processes that proceed slowly enough that the system is in internal equilibrium.
- p-V diagrams are a useful way to visualize quasistatic processes.
- You should be able to compute change in internal energy, work done, and changes in entropy over a quasistatic process.
- Reversible vs irreversible processes: reversible processes don't change the total entropy, so $\Delta S = 0$.

6.1 Definition of quasistatic processes

Quasistatic processes are processes that proceed slowly enough that the system is in internal equilibrium. That is, given its macrostate variables such as U, V, N, its entropy has been maximized. The upshot of quasistatic processes is that at all times during the process, we can use our equilibrium conditions. That means that for an ideal gas, we can use the ideal gas law, we can use equipartition, and we can use the first (and second) law of thermodynamics, and the fundamental relation. If the system were changed too quickly then all of our equations from the first few chapters would not be applicable, and we would only be able to use overall conservation of energy, and other much more limited tools. Limiting ourselves to quasistatic processes allows us to compute quite a lot about systems.

6.2 Defining a process

Consider an ideal gas which is enclosed, so that its total number N is constant. We know that the ideal gas law holds so $pV = NkT$. There are many possible values of p, V, T that could satisfy this equation; however, every quasistatic process of an ideal gas must satisfy $pV = NkT$. We thus have three variables and one constraint. To define a process we need one more constraint. What follows is some of the common processes.

Isobaric process In this process the additional constraint is that $p =$constant. In the name, "iso" means same, and "baric" means relating to pressure. An example of an isobaric process might be to heat a gas from T_i to T_f in a piston which is allowed to expand freely. Then as the temperature increases, the volume is given by $V = \frac{Nk}{p}T$, where $\frac{Nk}{p}$ is constant.

Isochoric process In this process, the volume is constant. As you might imagine, "choric" is Greek having to do with volume. An example of an isochoric process might be to heat a gas from T_i to T_f in a container that cannot expand at all. Then as the temperature increases, the pressure is given by $p = \frac{Nk}{V}T$, where now $\frac{Nk}{V}$ is constant.

Isothermal process Shockingly, in this process, the temperature is constant. An example of an isothermal process might be to put a gas into a piston, and slowly expand the piston from V_i to V_f so the gas remains at the same temperature as the surroundings. Then, as the volume increases, the pressure is given by $p = \frac{NkT}{V}$, where NkT is constant.

Adiabatic process This process is a little different from the others; in this process the heat transfer dQ is zero. An example of an adiabatic process might be to put a gas into a piston, and quickly expand the piston from V_i to V_f so that no heat has a chance to flow into or out of the gas. For an ideal gas the derivation is a little tedious but,

$$pV^\gamma = \text{constant}, \tag{1}$$

where $\gamma = 5/3$ for a monatomic ideal gas like He, and 7/5 for a diatomic ideal gas like N_2, O_2 (which make up air).

6.3 Computing work done during a process

$$W_{by} = \int p dV. \tag{2}$$

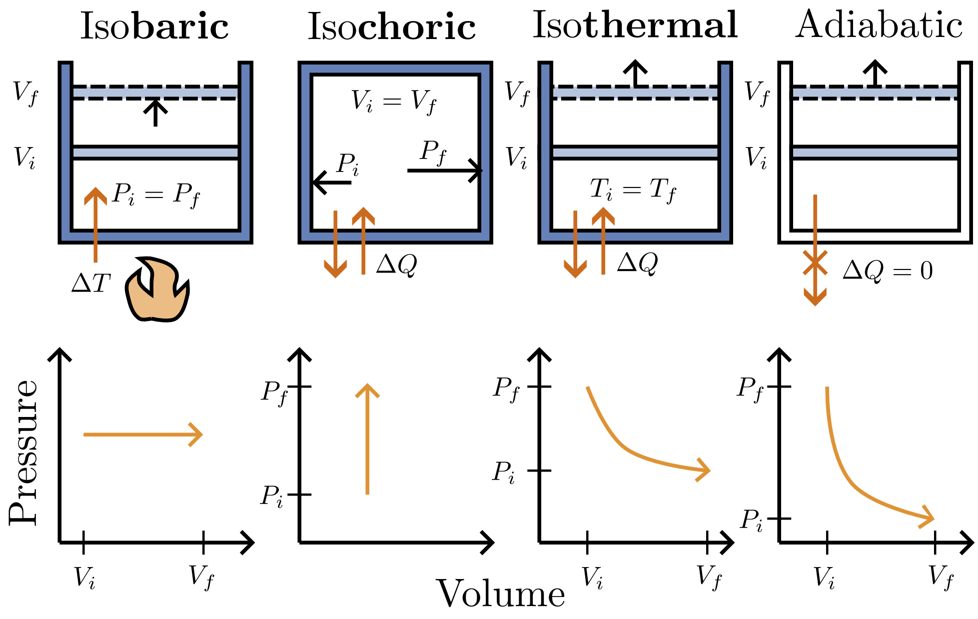

Figure 1: $p-V$ diagrams for common processes.

The general strategy is to write p as a function only of V and then do the integral.

For example, suppose we consider an isothermal process, in which a monatomic gas at high pressure is allowed to slowly push a piston out from V_i to V_f, which then rotates a crank and moves a car forward. Then $p(V) = \frac{NkT}{V}$, and the total work done by the gas is

$$W_{by} = \int_{V_i}^{V_f} \frac{NkT}{V} dV = NkT \ln \frac{V_f}{V_i}. \tag{3}$$

On the other hand, if the expansion is done suddenly so no heat could come in or out, that would be an adiabatic process and

$$W_{by} = \int_{V_i}^{V_f} \frac{C}{V^\gamma} dV = -\frac{C}{\gamma}\left(\frac{1}{V_f^{\gamma-1}} - \frac{1}{V_i^{\gamma-1}}\right), \tag{4}$$

since $\gamma > 1$, where typically we will find the constant C from the initial conditions by using $p_i V_i^\gamma = C$.

The cases of isochoric and isobaric processes are much simpler than adiabatic and isothermal; try to apply the principles above to those cases.

6.4 p–V diagrams

As we saw in the previous section, for a given process it is very helpful to know $p(V)$, pressure as a function of volume, for a given process, since the area under that curve tells us the work done by the thermodynamic system. We will use p–V diagrams to understand multiple processes chained together, and ultimately we will use p–V diagrams to understand engines and other thermodynamic machines. In Fig 1 we show $p(V)$ curves for the main four types of processes we consider in this class. Note that almost any function $p(V)$ is technically possible, so long as the temperature changes accordingly so the ideal gas law (or equivalent for non-ideal systems) is satisfied.

6.5 Entropy and reversible processes

The basic equation is

$$\Delta S = \int \frac{1}{T} dQ = \int \frac{1}{T} dU + \int \frac{p}{T} dV. \tag{5}$$

We use the same strategy as for work to compute changes in entropy: write the integrand as a function of the integration variables, and perform one-dimensional integration.

For an ideal gas, the entropy change is fairly easy: from the ideal gas law $\frac{p}{T} = \frac{Nk}{V}$, and from equipartition $U = \frac{3}{2}NkT$. So

$$\Delta S = \frac{3}{2}Nk \int_{T_i}^{T_f} \frac{1}{T} dT + \int \frac{Nk}{V} dV = \frac{3}{2}Nk \ln \frac{T_f}{T_i} + Nk \ln \frac{V_f}{V_i}. \tag{6}$$

Here for the first integral, we substituted $dU = \frac{3}{2}NkdT$ since usually we know the temperature but not the internal energy. Hopefully this makes sense; if the temperature is raised, then the entropy increases because the gas particles are moving faster, and therefore have more velocities and directions that they could be moving in. Think about the surface of a sphere with radius $|v|$, v being the velocity of the particles; as $|v|$ increases, there is more surface area. Similarly, if the volume increases, then the gas particles have more locations they could be in the volume, which increases the entropy as well.

Independent of the ideal gas law, we can also say something about the entropy change of two of our processes: adiabatic and isothermal. Neither of these processes change the total entropy, and so we call them **reversible**. They are called reversible because due to the second law, only processes that increase the entropy or keep it the same can proceed forward. So if a gas undergoes, for example, isobaric expansion, the entropy increases. That means that isobaric compression, which would decrease the entropy of the gas, cannot occur unless the entropy of something else increases more than the entropy of the gas decreased. On the other hand, a reversible process can be run either way and still satisfy the second law of thermodynamics.

One can show that the isothermal and adiabatic processes have zero change in entropy. For the adiabatic process, dQ is zero, so according to Eqn 5, ΔS is zero. For the isothermal process, some amount of heat Q is transferred from the environment to the system during the process (negative Q means that the heat goes the other way). We have:

$$\Delta S = \Delta S_{system} + \Delta S_{env} = \frac{Q}{T} - \frac{Q}{T} = 0. \tag{7}$$

Because the temperature was constant, the integral becomes very simple, and because in an isothermal process the environment and the system are at the same temperature, the entropy change is equal in magnitude and opposite in sign for the environment and system. As it turns out, *only* isothermal and adiabatic processes are reversible.