Physics 161: Thermodynamics

Lecture #2

Thermodynamics was developed in the 1800s originally as the study of the utilization and conversion of energy. It is concerned with placing bounds on and establishing relations between macroscopic observables. What is special about thermodynamic relations is that they are not based on the underlying microscopic mechanisms which may give rise to the macroscopic behavior of interest. Thus it is an important tool for the study of the frontiers of science such as cosmology, e.g. wherever microscopic system details such as the interactions between particles, or planets, or galaxies, etc. are not fully understood. Thermodynamics provides important constraints for the development of new ideas and models.

We will be focusing on two fundamental *laws* of thermodynamics:
1) Energy is conserved when heat is taken into account. (Joule, 1840).
2) No cyclic process is possible whose sole result is the transfer of heat from a colder body to a hotter body (Clausius, 1850).

The first law tells us that energy cannot be created or destroyed. Although it is not obvious at this point, we shall see that the second law can be used to determine whether or not a process will occur spontaneously, and it gives the direction in which a change will occur.

We will be concerned with equilibrium properties of systems consisting of solids, liquids, and gases. What is meant by a *system*? A system is that part of the universe on which we focus our attention. The remainder of the universe is called the *surroundings*. While it is easy to separate the system from the surroundings in theory, it can be very difficult to achieve comparable separation in the laboratory.

system

surroundings
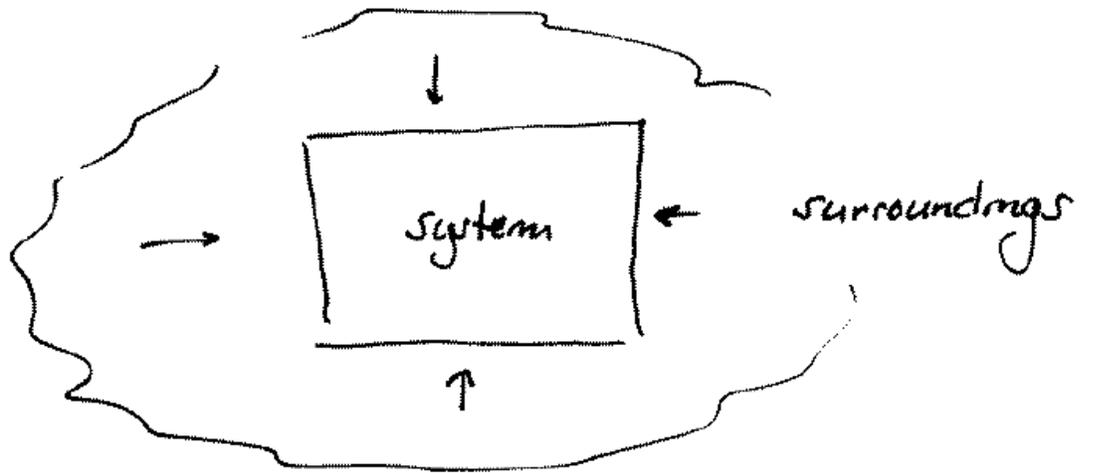
Just as the laws of nature are based on certain general facts of experience, so two are the laws of thermodynamics. For example:

•It is a fact of experience that the state of a fluid in a single phase depends on only two parameters, pressure P, and volume V.

The idea that the *state* of a fluid can be determined by the two quantities P and V means that two fluids that are identical in chemical composition, one at P_1 and V_1, and the other at P_2 and V_2, will be indistinguishable from one another when $P_1 = P_2$ and $V_1 = V_2$. You are all familiar with the equation of state for the ideal gas,

$$PV = nRT,$$

where T is temperature, n is the number of moles, and R is the gas constant

$$
\begin{aligned}
R &= 0.082 \, \frac{\text{liter-atm}}{\text{mole-K}} \\
&= 8.314 \, \frac{\text{J}}{\text{mole-K}}.
\end{aligned}
$$

The quantities P, V, and T are referred to as thermodynamic variables, system variables, state variables, or state functions. Note that while there are clearly three thermodynamic variables in the equation of state, specifying any two determines the third.

Thermodynamics applies to systems which have been left alone sufficiently long so that their physical and chemical properties are no longer evolving in time. Such systems are said to be in thermodynamic equilibrium. The manner in which a system comes to equilibrium is easily illustrated by considering the example of two sub-systems that are originally isolated but which are then placed in contact with each other. Equilibrium between the two may be established via movement which allows one sub-system to do work on the other, or via the flow of heat between one sub-system and the other, or even via the flow of material across the boundary between the two. Let us distinguish between these processes as follows:

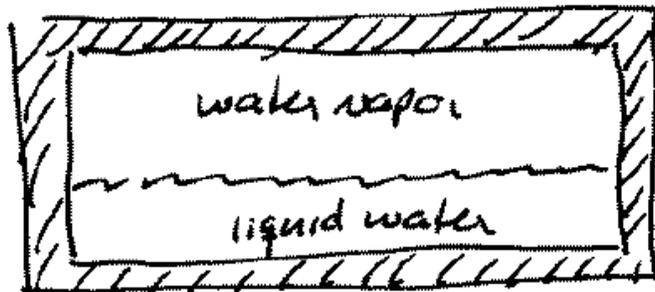1) Mechanical equilibrium (movement of piston occurs until the **pressures** are the same).
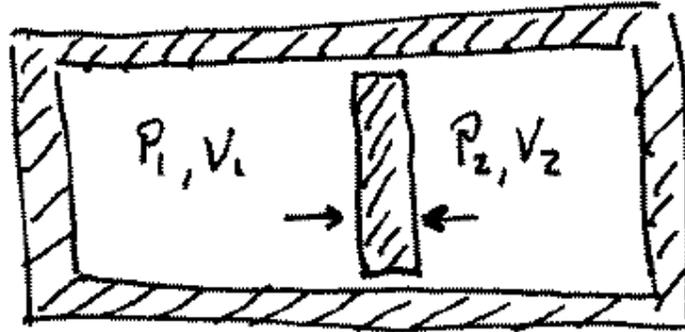
$$P_1 = P_2$$

2) Thermal equilibrium (heat flows from one to the other until **temperatures** are the same.).
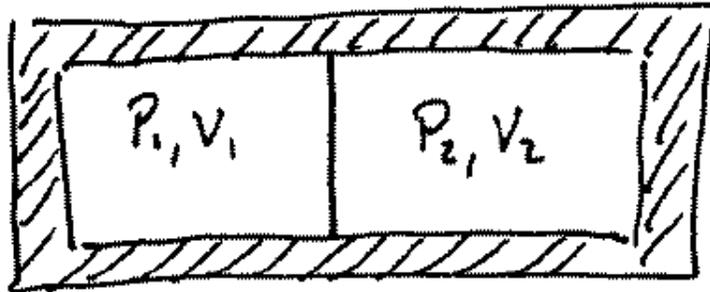

$$T_1 = T_2$$

3) Material equilibrium (material moves from one phase to another until **chemical potentials** are the same).

$$\mu_{liquid} = \mu_{vapor}$$

When two systems are in mechanical equilibrium, their pressures must be equal. When two systems are in thermal equilibrium, their temperatures must be equal. When systems are in material equilibrium, their chemical potentials must be equal.

If we plot the relation between P and V for an ideal gas, we have a curve $P = \frac{nRT}{V}$ whose height depends on the value of the constant T. Such a curve is called an *isotherm*.
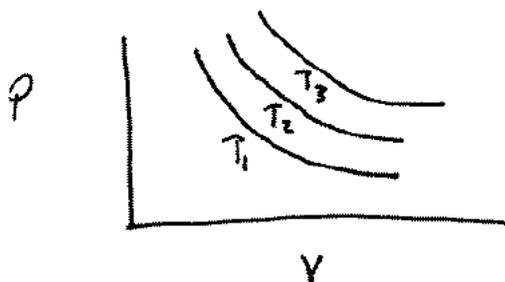
Different temperatures correspond to different isotherms. In fact, by mapping out the different isotherms, the ideal gas provides a way of defining a temperature scale, namely

$$T \equiv \lim_{P \to 0} \left(\frac{PV}{nR} \right)$$

This defines an absolute temperature scale, for the lowest possible temperature is obviously zero for an infinitely dilute gas in any finite volume. This can be determined in practice by extrapolation of the product PV for a constant volume gas thermometer. The temperature at which water will exist in equilibrium in all three phases simultaneously is used as a second reference point, and is defined to be

$$T_{\text{triple point}} = 273.16 \text{ (exactly)}.$$

The two points $T = 0$ and $T = 273.16$ define the temperature in Kelvin. The scale is related to the (modern) Celsius scale as follows:

$$0\,^{\circ}\text{C} = 273.15 \text{ K}$$
$$100\,^{\circ}\text{C} = 373.15 \text{ K}$$

Changes in State Functions

Consider an ideal gas at temperature T_1 and pressure P_1 that is heated and compressed to a temperature T_2 and pressure P_2. What is the relation between the final volume V_2 and the initial volume V_1?

$$V_2 = V_1 \times \frac{T_2}{T_1} \times \frac{P_1}{P_2}$$

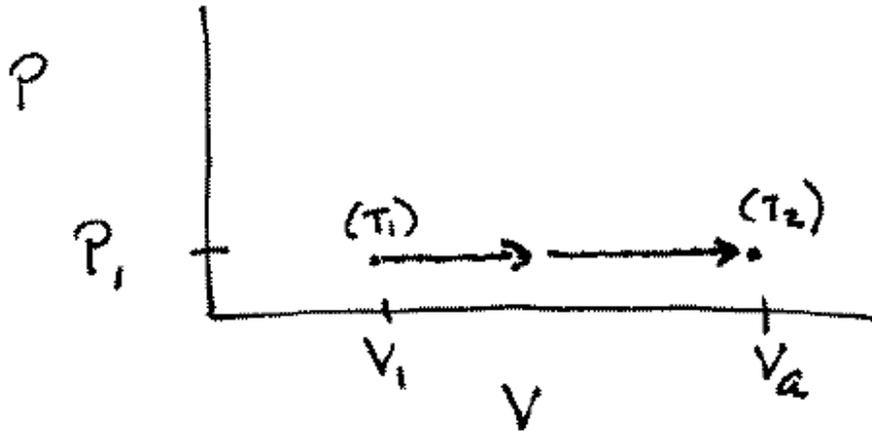We can get this directly from the equation of state,

$$\frac{P_2 V_2}{T_2} = nR = \frac{P_1 V_1}{T_1}$$

and multiplying both sides by T_2/P_2,

$$\frac{P_2 V_2}{T_2} \times \frac{T_2}{P_2} = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}$$
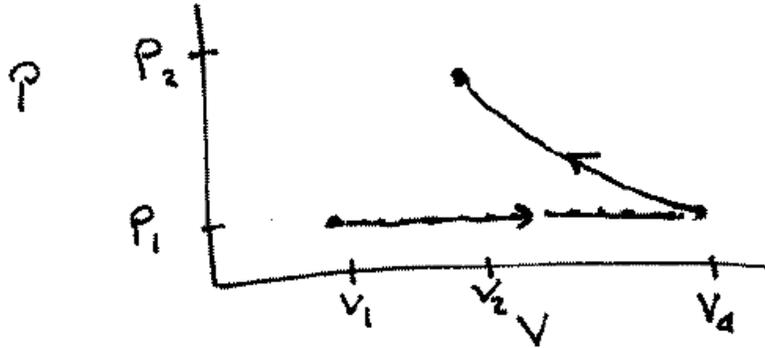$$V_2 = V_1 \frac{P_1 T_2}{T_1 P_2}$$

We can also consider the process as being carried out in two steps:

Step 1) Heat the gas from T_1 to T_2 at constant P_1 (isobaric expansion) so that it expands to a new volume V_a;

$$V_a = V_1 \frac{T_2}{T_1}$$

Step 2) Increase the pressure from P_1 to P_2 at constant temperature (isothermal compression) to reduce the volume to V_2;

$$V_2 = V_a \frac{P_1}{P_2}$$

The final relation is found by eliminating the intermediate volume V_a;

$$\frac{P_2}{P_1} V_2 = V_a = V_1 \frac{T_2}{T_1}$$

Rearranging terms, we obtain the same expression we found above,

$$V_2 = V_1 \frac{T_2}{T_1} \frac{P_1}{P_2}.$$

The point here is that you can obtain an expression for the final volume without thinking about a physical process that would achieve this - you just the ideal gas law. Or you can think about a physical process that follows a *particular path* in the PV diagram.