

Physics 161: Thermodynamics

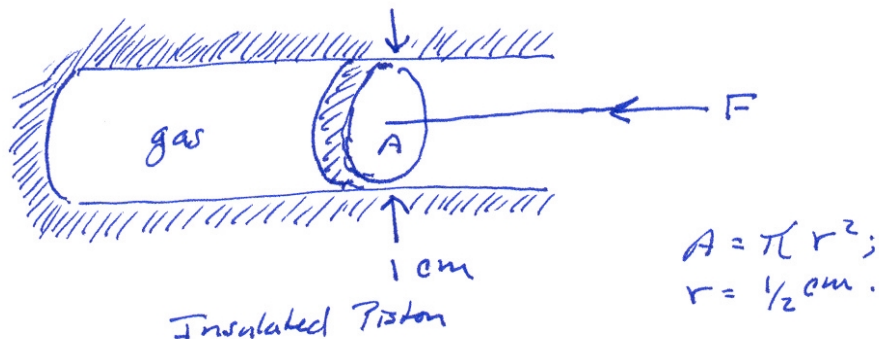
Lecture #5

Adiabatic Processes (Continued)

Consider yet another example of an adiabatic compression.

Example 4:

A cylinder with a diameter of 1.0 cm is fitted with a piston and filled with air. (See Figure 1) The air is initially at room temperature  $T_1$  (70 °F) and ambient pressure  $P_1$  (0.83 atm in Albuquerque). The gas is quickly compressed when the piston is subjected to a constant external force of 23.2 N (5 lbs). The piston is not very well insulated, but because there is little time for heat to escape, let us assume that the compression takes place adiabatically. Find the final temperature  $T_2$  (in Fahrenheit), and the (molar) quantities  $\Delta\bar{U}$ ,  $\Delta\bar{H}$ ,  $\bar{Q}$ , and  $\bar{W}$ . Air has a specific heat  $\bar{C}_P \simeq 7/2R$ , and may be treated as an ideal gas under these



conditions.

We can calculate the external pressure by dividing the applied force by the area of the face of the piston.

$$\begin{aligned} P_{\text{external}} &= \frac{23.2\text{N}}{\pi (5 \times 10^{-3}\text{m})^2} = 2.95 \times 10^5 \text{N/m}^2 \\ &= 2.92 \text{ atm.} \end{aligned}$$

Since the external pressure is held constant, let us first attempt to calculate the

work:

$$\begin{aligned}W &= \int_1^2 P_{\text{external}} dV \\&= P_{\text{external}} (V_2 - V_1) \\&= P_{\text{external}} \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right) \\&= nR \left( \frac{P_{\text{external}} T_2}{P_2} - \frac{P_{\text{external}} T_1}{P_1} \right)\end{aligned}$$

When the piston comes to rest,  $P_2 = P_{\text{external}}$ , so we can make one more reduction to this expression and write,

$$\begin{aligned}W &= nR \left( T_2 - \frac{P_{\text{external}} T_1}{P_1} \right) \\&= nR \left( T_2 - \frac{2.92}{0.83} T_1 \right) \\ \bar{W} &= R(T_2 - 3.52 T_1).\end{aligned}$$

Unfortunately, this is as far as we can go, for we haven't yet determined a value for  $T_2$ .

Let us attempt instead to calculate  $\Delta U$ . Because this is an ideal gas, we know that

$$\left( \frac{\partial U}{\partial V} \right)_T = 0.$$

The important thing here is that this means that  $U$  is a function of only  $T$ , and therefore we can write,

$$\begin{aligned}\Delta U &= \int_{T_1}^{T_2} \left( \frac{\partial U}{\partial T} \right)_V dT \\&= \int_{T_1}^{T_2} C_V dT = \int_{T_1}^{T_2} (C_P - R) dT \\&= \int_{T_1}^{T_2} \left( \frac{7}{2} R - R \right) dT \\&= \frac{5}{2} R (T_2 - T_1)\end{aligned}$$

We can't go any further with this calculation either, again because we don't know  $T_2$ .

Suppose, however, that we use the first law to combine our calculations of  $W$  and  $\Delta U$ , and attempt to find the missing temperature  $T_2$ . We have

$$\Delta U = Q - W$$

Since the process is adiabatic,  $Q = 0$ , and it follows that

$$\Delta U = -W$$

Substituting our two equations from above, we have

$$\frac{5}{2}R(T_2 - T_1) = -R(T_2 - 3.52T_1)$$

Solving this for  $T_2$  gives

$$\begin{aligned}T_2 &= T_1 \frac{(3.52 + \frac{5}{2})}{\frac{7}{2}} \\ &= T_1 \left( \frac{2 \times 3.52}{7} + \frac{5}{7} \right) \\ T_2 &= T_1 \times 1.72\end{aligned}$$

Thus the temperature increases by a factor of 1.72. To make use of this, we must first convert 70 °F to Kelvin:

$$\begin{aligned}(70^\circ\text{F} - 32^\circ\text{F}) \frac{5}{9} + 273.15 \\ = 294\text{ K}\end{aligned}$$

The final temperature is therefore

$$T_2 = 294\text{ K} \times 1.72 = 505.7\text{ K}.$$

Converting back to Fahrenheit, we first note that the temperature in Celsius is

$$505.7\text{ K} - 273.15 = 232.5^\circ\text{C}.$$

From this, it follows that

$$T_2 = 232.5^\circ\text{C} \times \frac{9}{5} + 32 = 418.5 + 32 = 451^\circ\text{F}$$

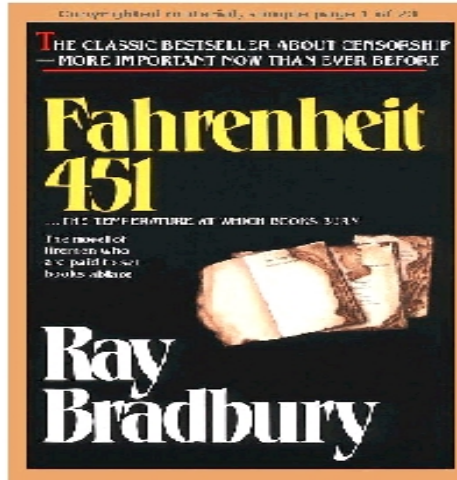
As you probably know, Fahrenheit 451 is the name of a science fiction book by Ray Bradbury which expounds upon the fact that 451 °F is the temperature at which paper will spontaneously burst into flame. (The actual temperature at which this occurs depends on the density and type of the paper, and on the pressure of the air, but experience suggests that it is not a good idea to have paper in an oven when the temperature is set above 450 °F!) See Figure 2.

We can now go back and evaluate some of the missing quantities. The work is

$$\begin{aligned}\bar{W} &= R(505.7\text{ K} - 3.52 \times 294\text{ K}) \\ &= -8.314 \frac{\text{J}}{\text{mole K}} \times 529.2\text{ K} \\ &= -4.40\text{ kJ/mole}\end{aligned}$$

Since  $Q = 0$ , the change in energy per mole is

$$\Delta\bar{U} = -\bar{W} = 4.40\text{ kJ/mole}$$



The change in enthalpy per mole is

$$\begin{aligned}
 \Delta \bar{H} &= \Delta \bar{U} + \Delta (P\bar{V}) \\
 &= 4.40 \text{ kJ/mole} + R\Delta T \\
 &= 4.40 \text{ kJ/mole} + 8.314 \frac{\text{J}}{\text{mole K}} \times (505.7 \text{ K} - 294 \text{ K}) \\
 &= 4.40 \text{ kJ/mole} + 1.76 \text{ kJ/mole} = 6.16 \text{ kJ/mole}
 \end{aligned}$$

Example 5:

Let us consider the same adiabatic compression as in Example 4, but this time, let us compress the piston reversibly, from the same initial state,  $P_1 = 0.83 \text{ atm}$  and  $T_1 = 70 \text{ }^\circ\text{F}$  to the same final pressure of  $P_2 = 2.92 \text{ atm}$ . In this case, what is the final temperature  $T_2$ , and what are  $\Delta \bar{U}$ ,  $\Delta \bar{H}$ ,  $\bar{Q}$ , and  $\bar{W}$ ?

Let us look at this first in general. For a reversible process, we may write the first law as

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV = \delta Q - PdV,$$

where we have substituted  $P$  for  $P_{\text{external}}$ . The heat  $\delta Q$  will be zero for an adiabatic process. Substituting  $C_V = \left( \frac{\partial U}{\partial T} \right)_V$ , and putting all of the terms which multiply  $dT$  on one side of the equation and all of the terms which multiply  $dV$  on the other side of the equation, we have the following connection between  $dT$  and  $dV$ :

$$C_V dT = - \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] dV$$

If we know  $C_V$  as a function of  $T$  and  $V$ , and if we know  $P$  and  $(\frac{\partial U}{\partial V})_T$  as functions  $T$  and  $V$ , we ought to be able to integrate this equation to find a connection between the initial state variables  $T_1$  and  $V_1$  and the final state variables  $T_2$  and  $V_2$ . Our job is relatively easy for the case of the ideal gas because  $C_V$  is a constant, and  $(\frac{\partial U}{\partial V})_T = 0$ . This we have

$$C_V dT = -PdV = -\frac{nRT}{V}dV$$

Dividing both sides of this equation by  $T$ , we have

$$\frac{dT}{T} = -\frac{nR}{C_V} \frac{dV}{V}.$$

Integrating from the initial state to the final state, we have

$$\begin{aligned} \int_{T_1}^{T_2} \frac{dT}{T} &= -\frac{nR}{C_V} \int_{V_1}^{V_2} \frac{dV}{V}; \\ \ln(T_2) - \ln(T_1) &= -\frac{nR}{C_V} [\ln(V_2) - \ln(V_1)]; \\ \ln\left(\frac{T_2}{T_1}\right) &= -\frac{nR}{C_V} \ln\left(\frac{V_2}{V_1}\right) \end{aligned}$$

Thus we have a general result for an ideal gas which undergoes an adiabatic reversible compression (or expansion). Exponentiating both sides, we have,

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_1}\right)^{-\frac{R}{C_V}} \quad (\text{reversible adiabatic expansion of ideal gas}).$$

There are two other permutations of this result which may be useful. We may substitute  $PV = nRT$ , to write

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

This can be used to eliminate volume;

$$\begin{aligned} \left(\frac{T_2}{T_1}\right) &= \left(\frac{T_2}{T_1}\right)^{-\frac{R}{C_V}} \left(\frac{P_1}{P_2}\right)^{-\frac{R}{C_V}}; \\ \left(\frac{T_2}{T_1}\right)^{1+\frac{R}{C_V}} &= \left(\frac{P_2}{P_1}\right)^{\frac{R}{C_V}}; \\ \frac{T_2}{T_1} &= \left(\frac{P_2}{P_1}\right)^{\frac{R}{R+C_V}}; \end{aligned}$$

which gives the direct connection between  $T$  and  $P$ ,

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}} \quad (\text{reversible adiabatic expansion of ideal gas}).$$

We could also have eliminated temperature using

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

in order to write

$$\begin{aligned}\frac{P_2 V_2}{P_1 V_1} &= \left(\frac{V_2}{V_1}\right)^{-\frac{R}{C_V}}; \\ \frac{P_2}{P_1} &= \left(\frac{V_1}{V_2}\right)^{1+\frac{R}{C_V}}; \\ \frac{P_2}{P_1} &= \left(\frac{V_1}{V_2}\right)^{\frac{C_V+R}{C_V}} = \left(\frac{V_1}{V_2}\right)^{\frac{C_P}{C_V}}.\end{aligned}$$

This can be factored to give the relation

$$P_2 V_2^{\frac{C_P}{C_V}} = P_1 V_1^{\frac{C_P}{C_V}},$$

so that it may be said that, for an adiabatic *reversible* expansion of an ideal gas, the path followed in a  $PV$  diagram must be such that

$$PV^\gamma = \text{const.} \quad (\text{reversible adiabatic expansion of ideal gas}).$$

where the exponent

$$\gamma = \frac{C_P}{C_V}$$

is greater than unity since  $C_P = C_V + nR$ .

Returning now to the problem at hand, let us first calculate the final temperature  $T_2$ . Using the expression

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}}$$

we have

$$\begin{aligned}T_2 &= T_1 \left(\frac{2.92 \text{ atm}}{0.83 \text{ atm}}\right)^{\frac{2}{7}} \\ &= 294 \text{ K} \times (3.52)^{\frac{2}{7}} \\ &= 294 \text{ K} \times 1.43 \\ &= 421 \text{ K}\end{aligned}$$

This means that the final temperature of the gas after a reversible compression is only

$$(421 \text{ K} - 273.15 \text{ K}) \times \frac{9}{5} + 32 = 298^\circ \text{F}$$

Although the gas reaches the same final pressure, apparently it does not reach the same final state. The temperature is lower, which means that the volume will be smaller - the gas will be more tightly compressed.

Because  $U$  for an ideal gas depends only on temperature, and because for  $Q = 0$ ,

$$\Delta U = -W,$$

it is obvious that less work was done by us in compressing the gas reversibly than was done by us in compressing the gas irreversibly. In the reversible case,

$$\begin{aligned}\Delta \bar{U} &= \frac{5}{2} R (421 \text{ K} - 294 \text{ K}) \\ &= \frac{5}{2} \times 8.314 \frac{\text{J}}{\text{mole K}} \times (421 \text{ K} - 294 \text{ K}) \\ &= 2.64 \text{ kJ/mole}\end{aligned}$$

so that

$$\bar{W} = -2.64 \text{ kJ/mole}$$

and

$$\begin{aligned}\Delta \bar{H} &= 2.64 \text{ kJ/mole} + 8.314 \frac{\text{J}}{\text{mole K}} \times (421 \text{ K} - 294 \text{ K}) \\ &= 3.70 \text{ kJ/mole}.\end{aligned}$$

#### Comparison of the Reversible and Irreversible Compressions from Examples 4 and 5

It is instructive to compare the reversible and irreversible processes on a  $PV$  diagram. The starting point for both processes is

$$\bar{V}_1 = \frac{R \times 294}{.83} = 29 \text{ liters/mole},$$

$$P_1 = 0.83 \text{ atm},$$

Taking  $\bar{V}$  in liters/mole, and  $P$  in atmosphere, the reversible process can be sketched as a curve following

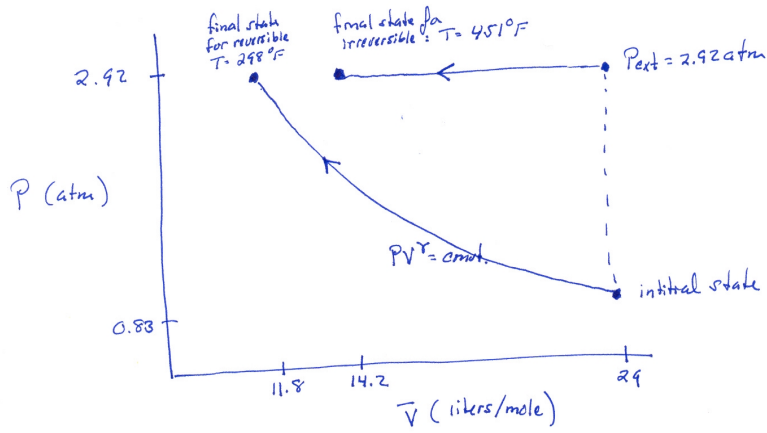
$$P = \frac{92.6}{\bar{V}^{5/7}}$$

and ending when the pressure is

$$P_2 = 2.92 \text{ atm}$$

and the volume is

$$\bar{V}_2 \text{ (reversible)} = \left( \frac{92.6}{2.92} \right)^{5/7} = 11.8 \text{ liters/mole}.$$



Let us now sketch the irreversible compression on the same graph. (See Figure 3) Let us take  $P$  to be the external pressure for the irreversible process; this is fixed at 2.92 atm. We will draw a straight line which connects the initial volume to the final volume. As we mentioned above, the final volume for the irreversible compression is greater than it is for the reversible compression:

$$\begin{aligned}
 \bar{V}_2 \text{ (irreversible)} &= \frac{R \times 505.7 \text{ K}}{2.92 \text{ atm}} \\
 &= \frac{0.082 \frac{\text{liter-atm}}{\text{mole-K}} \times 505.7 \text{ K}}{2.92 \text{ atm}} \\
 &= 14.2 \text{ liters/mole}
 \end{aligned}$$



As a final note, suppose we were to re-expand the gas to 0.83 atm. If we did this reversibly, the system would return to the same initial state,  $P = 0.83$  atm and  $T = 70$  F. But if we did this irreversibly (say, by expanding against a constant external pressure of 0.83 atm), the system would be left in a state of higher temperature, and therefore in a state of higher volume than it was initially. When taken in a cycle, the irreversible adiabatic expansion considered in this example will not return the system to its initial state. We shall see later that, according to the second law of thermodynamics, this must always be so.

(I wish to emphasize once again that the pistons in our illustrations are assumed to move without friction. The differences between the irreversible processes and the reversible processes you have seen above are related to properties of the gas alone, and have nothing to do with the lubrication of the piston.)