

## Physics 161: Thermodynamics

### Lecture #6

Before moving on, let us summarize the first law. There are two parts to the first law of thermodynamics. First is the postulate that energy  $U$  is a state function. Second is the postulate that the energy of the universe is constant. Any increase in the energy of the system can be accounted for by a loss of energy from the surroundings. These things cannot be proved, but we believe that they are rational postulates. If we know the means by which a system is mechanically and electrically connected to the surroundings, then we understand the work  $W$ . The first law,

$$\Delta U = Q - W,$$

is then a definition of heat  $Q$  as that part of the energy transfer between the system and surroundings which is not  $W$ .

#### Aside: Reversible Heat Transfer

We have already discussed the idea of reversible work, when  $P_{\text{system}} \Rightarrow P_{\text{external}}$ . This hypothetical situation obtains when a mechanical process takes place slowly, so that the system stays in equilibrium with the surroundings every step of the way. The transfer of heat can be described in the same manner. If very little heat is transferred, so that the system remains in equilibrium, then the transfer is said to have taken place reversibly. Such a condition will be satisfied when  $T_{\text{system}}$  is close to  $T_{\text{surroundings}}$ . The system takes on heat reversibly when these two temperatures differ by an infinitesimal amount, i.e., in the limit when

$$T_{\text{system}} - T_{\text{surroundings}} \rightarrow 0.$$

#### Aside on Surroundings

The surroundings are an enormous heat reservoir. After all, the surroundings are the “rest of the universe” which is not the system. It is convenient to imagine that all parts of the surroundings are in contact with the system simultaneously. The way to approximate this situation in the lab is to attach large cooling fins onto the system. These distribute any heat which is given up or extracted from the surroundings as broadly as possible. Since the surroundings are infinite, any amount of heat which is transferred to the surroundings from a finite system is insufficient to change the temperature of the surroundings, or to take the surroundings out of equilibrium. Hence, due to their infinite size, the surroundings *always* take on heat reversibly, even when  $T_{\text{system}} \rightarrow T_{\text{surroundings}}$ .

## The Heat Engine

Energy is stored in the environment surrounding us. Think of the total energy content of the Earth's atmosphere, for example. If the heat capacity of the atmosphere is roughly

$$C_V = \frac{5}{2}nR,$$

then, at 273 K, there is tremendous energy stored in such a large *heat reservoir*. We would like to extract energy from such a heat reservoir and use it to do useful work. For example, we could extract heat  $Q$  from the atmosphere and use it to drive a turbine to generate electricity. Such a machine is called a *heat engine*. It is a fact of experience, however, that a heat engine requires two heat reservoirs, one at a high temperature and one at a low temperature.

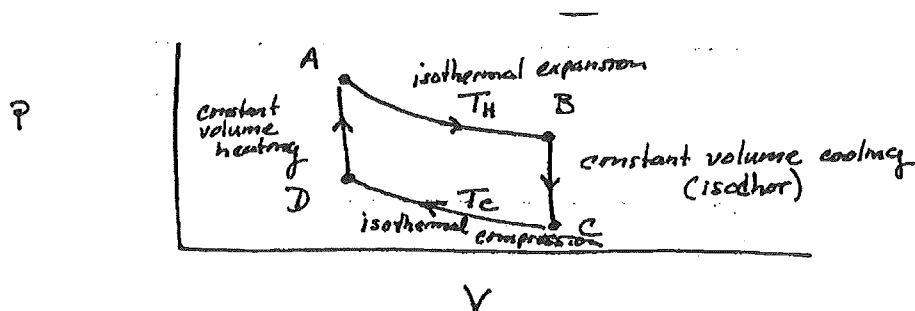
The Stirling engine (Robert Stirling, patented 1816) is an example of a heat engine. It consists of a piston with air as the *working fluid*. (See Figure 1) The air is alternately heated and cooled as the piston moves in and out. After each cycle, the working fluid returns to the same state;

$$\Delta U_{\text{cycle}} = 0$$

Stirling's idea was that a piston could be driven in this manner without producing any exhaust gases, and as such, it would be excellent for powering the propellers of underwater torpedoes.

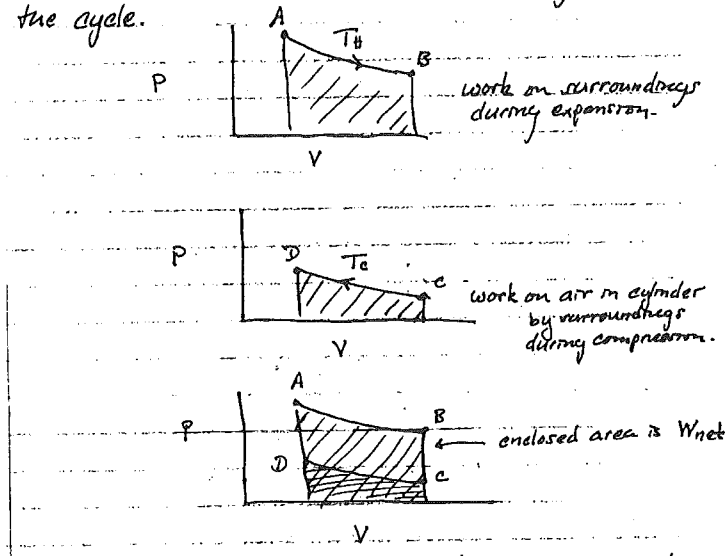


As an idealization, the Stirling cycle can be thought of as consisting of an isothermal expansion at a high temperature  $T_H$  followed by an isochoric (constant volume) cooling to a low temperature  $T_C$ , followed by an isothermal compression at  $T_C$ , followed by an isochoric heating back to  $T_H$ . (See Figure 2)



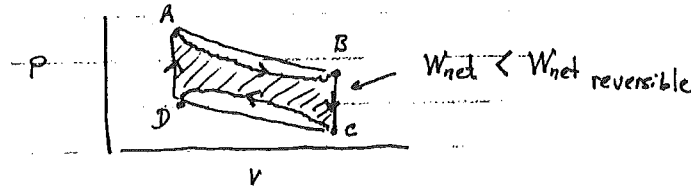
The work which is performed in going around the cycle can be calculated from the area on a  $PV$  diagram. (See Figure 3) The work on the surroundings during the expansion is greater than the work on the system during compression. The difference between them,  $W_{\text{net}}$ , is the net work output of the machine per cycle.

Notice the work which is performed in going around the cycle.



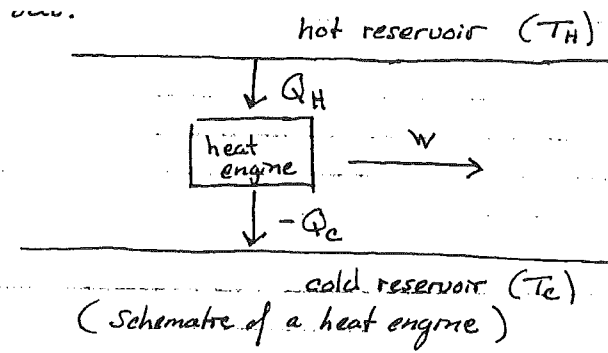
This is, of course, an idealization of the cycle, for the true cycle does not follow reversible isotherms. It is obvious from the area in the PV diagram in Figure 4 that

$$W_{\text{net (actual)}} < W_{\text{net (reversible isotherms)}}$$



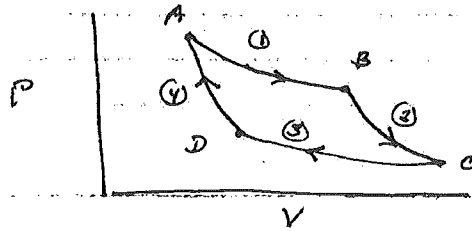
It is important to note that even if the isothermal expansion and the isothermal compression were to be carried out reversibly, the Stirling cycle cannot really be conceived as a reversible cycle, because heat is transferred to and from the surroundings irreversibly during the two isochors. When the isochoric cooling begins, the gas is still at the temperature  $T_H$ , and it loses heat to the reservoir at  $T_C$ . This is an irreversible process since cooling at a finite temperature difference  $\Delta T$  takes the gas temporarily out of equilibrium.

The schematic for a heat engine is often drawn as shown in Figure 5. Heat  $Q_H$  is extracted from a hot reservoir at  $T_H$ , and heat  $-Q_C$  is deposited in a cold reservoir at  $T_C$ , producing a net amount of work  $W$  in each cycle.

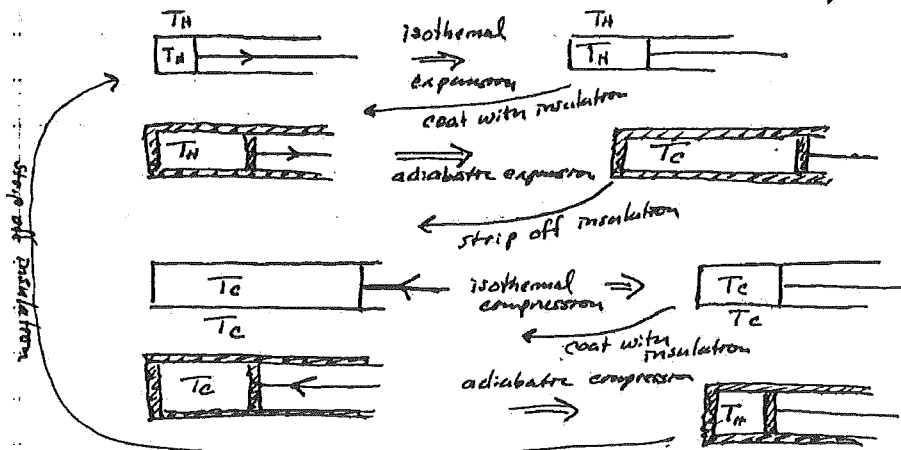


In 1820, Sadi Carnot invented a hypothetical cycle of operations for a heat engine which would allow the engine to be operated reversibly between two heat reservoirs. The Carnot cycle consists of two isotherms and two adiabats, working between a reservoir at  $T_H$  and a reservoir at  $T_C$ . By alternately placing insulation on and off the cylinder (awkward in practice) we can alternate between adiabats and isotherms.

The Carnot cycle consists of two isotherms and two adiabats, working between a reservoir at  $T_H$  and a reservoir at  $T_C$ .



- ①  $A \rightarrow B$  Isothermal reversible expansion at  $T_H$
- ②  $B \rightarrow C$  Adiabatic reversible expansion lowers  $T$  from  $T_H$  to  $T_C$
- ③  $C \rightarrow D$  Isothermal reversible compression at  $T_C$ .
- ④  $D \rightarrow A$  Adiabatic reversible compression raises  $T$  from  $T_C$  to  $T_H$



Let us calculate the efficiency of this reversible cycle. We will do so for the special case where the

working fluid is an ideal gas, because the equation of state is easy to work with. First, let us define efficiency

$$\varepsilon = \frac{W_{\text{net}}}{Q_H}$$

the ratio of the net work per cycle to the heat extracted from the hot reservoir. Notice, because  $\Delta U_{\text{cycle}} = 0$ , it follows that  $W_{\text{net}} = Q_H + Q_C$ . Using this, one can write the efficiency of *any* heat engine running between two reservoirs as

$$\varepsilon = \frac{Q_H + Q_C}{Q_H}.$$

The question we ask here is how  $Q_H$  and  $Q_C$  will be related to the temperatures  $T_H$  and  $T_C$  for the reversible (Carnot) engine running between two reservoirs when the working fluid is an ideal gas.

Let us determine the work by explicitly going around the cycle, one leg at a time.

Step #1: Reversible Isothermal Expansion

This expansion takes place while the piston is in contact with the hot reservoir. Since it is a reversible expansion, the work is given by

$$W_1 = \int_{V_A}^{V_B} P_{\text{external}} dV = \int_{V_A}^{V_B} P dV = nRT_H \ln \frac{V_B}{V_A}$$

In this step, the temperature  $T = T_H$ , and therefore the change in energy

$$\Delta U_1 = C_V \Delta T = 0,$$

is therefore zero for an ideal gas. It follows from the first law that  $Q_1 = W_1$ . Consequently, the heat

$$Q_H = Q_1 = nRT_H \ln \frac{V_B}{V_A}$$

taken in from the hot reservoir in this process is equal to the work output.

Step #2: Reversible Adiabatic Expansion

In this expansion the piston is insulated. The piston is withdrawn until the temperature of the gas is reduced to  $T_C$ . Since it is adiabatic,  $Q_2 = 0$ , and

$$\Delta U_2 = -W_2$$

But for an ideal gas, the change in energy depends on the heat capacity and the change in temperature,

$$\Delta U_2 = C_V(T_C - T_H)$$

It follows that

$$W_2 = -C_V(T_C - T_H).$$

Step #3: Reversible Isothermal Compression

For this step the gas, which is now at temperature  $T_C$ , is placed in thermal contact with the cold reservoir, which is also at temperature  $T_C$ . The gas is compressed isothermally, and hence  $\Delta U_3 = 0$  and  $Q_3 = W_3$  for an ideal gas. The work can be calculated by integrating,

$$\begin{aligned}
 W_3 &= \int_{V_C}^{V_D} P_{\text{external}} dV = \int_{V_C}^{V_D} P dV \\
 &= nRT_C \int \frac{dV}{V} = nRT \ln \frac{V_D}{V_C}
 \end{aligned}$$

It follows that the heat added to the system from the cold reservoir is

$$Q_C = Q_3 = nRT \ln \frac{V_D}{V_C}$$

Step #4: Reversible Adiabatic Compression

In this step,  $Q_4 = 0$ , and

$$\Delta U_4 = C_V(T_H - T_C) = -W_4$$

Combining the work and heat for the full cycle, we have

$$\begin{aligned}
 W_{\text{net}} &= W_1 + W_2 + W_3 + W_4 \\
 &= nRT_H \ln \frac{V_B}{V_A} - C_V(T_C - T_H) \\
 &\quad + nRT_C \ln \frac{V_D}{V_C} - C_V(T_H - T_C) \\
 W_{\text{net}} &= nRT_H \ln \frac{V_B}{V_A} + nRT_C \ln \frac{V_D}{V_C}
 \end{aligned}$$

$$Q_H = nRT_H \ln \frac{V_B}{V_A}$$

This is enough to determine the efficiency,

$$\begin{aligned}
 \varepsilon &= \frac{nRT_H \ln \frac{V_B}{V_A} + nRT_C \ln \frac{V_D}{V_C}}{nRT_H \ln \frac{V_B}{V_A}} \\
 &= 1 + \frac{T_C}{T_H} \left( \frac{\ln \frac{V_D}{V_C}}{\ln \frac{V_B}{V_A}} \right)
 \end{aligned}$$

The ratios of volumes can be related to the ratio of temperatures for the reversible adiabatic expansion, according to

$$\begin{aligned}
 \frac{V_C}{V_B} &= \left( \frac{T_C}{T_H} \right)^{-\bar{C}_V/R} \\
 \frac{V_A}{V_D} &= \left( \frac{T_H}{T_C} \right)^{-\bar{C}_V/R}
 \end{aligned}$$

This means that

$$\frac{V_C}{V_B} \frac{V_A}{V_D} = 1$$

or that

$$\frac{V_C}{V_D} = \frac{V_B}{V_A}$$

and hence that

$$\frac{\ln \frac{V_D}{V_C}}{\ln \frac{V_B}{V_A}} = \frac{-\ln \frac{V_C}{V_D}}{\ln \frac{V_B}{V_A}} = -1$$

Consequently, the efficiency of a Carnot cycle with an ideal gas as the working fluid is

$$\varepsilon = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H}.$$