University of Washington
Department of Chemistry
Chemistry 452
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Lecture 10 7/16/14
ERD: 5.11
DeVoe: 4.3.1, 4.3.3

A. Work and the Second Law of Thermodynamics: Efficiency of Heat Engines

One of the most important consequences of the Second Law is the limitation it places on the efficiency with which an energy transformation can produce useful work.

- Question. What is a condition required for the production of work?
  Answer. A thermal gradient, a gradient in the electrical potential, a gravitational potential that causes a mass to fall, etc. When these conditions exist, useful work may be produced.
- The flow of energy in the biological work is initiated by radiant energy from the sun, which enables photosynthesis, which in turn produces carbohydrates. The respiratory systems of animals utilize oxygen, carbohydrates and other foodstuffs to produce biologically useful work…and lots of entropy. How efficient is the production of useful work in the biological world and in general?

Consider a simple work production scheme. An "engine" (i.e. the system) exploits a thermal gradient in the surroundings…consisting of a heat reservoir at a high temperature T_h and a low temperature reservoir at T_l. See diagrams below…

- If the two heat reservoirs are brought into direct contact (left, above) a quantity of heat q is transferred from the high temperature reservoir to the low temperature reservoir. Because the temperatures T_H and T_C are very, very different the heat transfer is irreversible and the entropy change is $\Delta S = q\left(\frac{1}{T_l} - \frac{1}{T_h}\right) > 0$. No work is produced by this process.

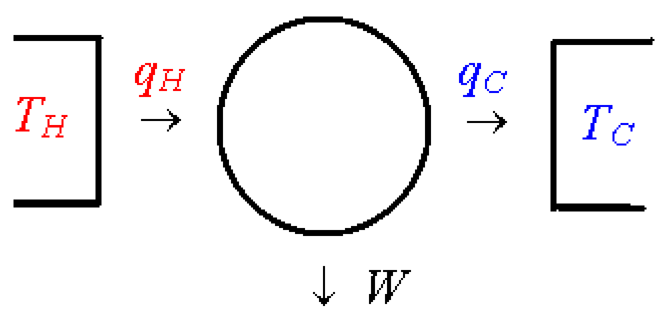


Figure 1: Schematic of a heat engine.

- Suppose the two reservoirs are not allowed to come into direct contact. Instead, an engine transfers heat q_H, *reversibly* (see Figure 1) from the high temperature reservoir. The engine converts some of the heat to work and exhausts the remaining heat q_C to the low temperature reservoir.
- Man-made engines are cyclic devices. This means at the end of a work cycle the moving parts of the engine are restored to their original thermodynamic states…ready to work again. A piston in a car is a good example. After firing, hot gases in the piston cylinder of a car increase their volume pushing the piston outward. But at the end of the cycle the piston must be restored to its original thermodynamic state to the work cycle can be repeated.
- A heat engine is an engine that converts heat absorbed from a heat reservoir into work. A key property of any heat engine is the efficiency with which it converts the heat which is input to the engine into work. This efficiency is given by:

$$\varepsilon = \frac{-w_{net}}{q_H} = \frac{q_H - (-q_C)}{q_H} = \frac{q_H + q_C}{q_H} \qquad (10.1)$$

- In equation 10.1 the net amount of work performed by the engine is a positive number. But by convention work performed by an engine is negative. Therefore the amount of work performed is $-w_{net}$.
- The amount of net work $-w_{net}$ is the difference between the amount of heat absorbed q_H and the amount of heart exhausted $-q_C$. Note again use of the negative sign because heat given off by the engine $q_C<0$. Equation 10.1 is general for any heat engine and states that the efficiency is the ratio of the amount of work performed by the engine divided by the heat input to the engine.
- How high can the efficiency of a heat engine be? To determine the upper limit of efficiency for heat engines, a hypothetical heat engine, which runs reversibly was proposed by a French scientist Sadi Carnot. This reversible heat engine is now called a Carnot engine. A Carnot engine cannot be realized in reality because it runs reversibly.
- The Carnot engine consists of an ideal gas is confined to a cylinder by a frictionless piston. A Carnot engine consists of a 4-step work cycle, shown in Figure 2…

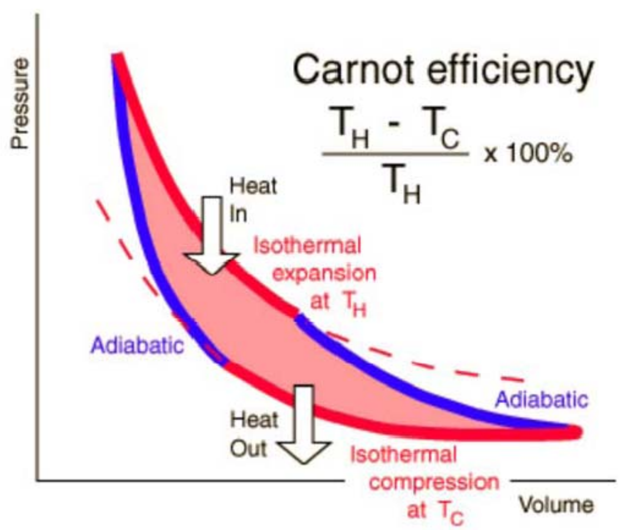


Figure 2: Schematic of a Carnot Engine Cycle.

Step 1: The engine is designed so the first step of the cycle is an isothermal expansion, $T=T_H$ from V_1 to V_2. Therefore $\Delta U_1=0$ and the work done is

$$w_1 = -q_H = -RT_H \ln\left(\frac{V_2}{V_1}\right) \tag{10.2}$$

- Step 2: The engine is designed to continue the reversible expansion from V_2 to V_3, but to do so *adiabatically*, This means no further heat is absorbed from the reservoir, i..e. $q_2=0$. . Because the engine is doing work as the gas expands, the energy of the gas must decrease and because the gas is ideal this means the temperature must decrease to T_l. Because the process is reversible

$$w_2 = \Delta U_2 = C_V\left(T_C - T_H\right) = C_V \Delta T \tag{10.3}$$

- Step 3: The engine now reverses the piston movement. The piston compresses the gas isothermally and reversibly from V_3 to V_4, giving off heat q_C at $T=T_C$ The work is

$$w_3 = -q_C = -RT_C \ln\left(\frac{V_4}{V_3}\right) \tag{10.4}$$

- Step 4 is a adiabatic, reversible compression from V_4 back to V_1. Because work is done in compressing the gas with the piston, the temperature of the gas must increase from T_C back to T_H. The system, i.e. the gas in the cylinder and the piston, is restored to its original state. Because this step is adiabatic and reversible work is

$$w_4 = \Delta U_4 = -C_V\left(T_C - T_H\right) = -C_V \Delta T \tag{10.5}$$

Comments:

- The net work is

$$\begin{aligned} w_{net} &= w_1 + w_2 + w_3 + w_4 = -RT_H \ln\left(\frac{V_2}{V_1}\right) + C_V\Delta T - RT_L \ln\left(\frac{V_4}{V_3}\right) - C_V\Delta T \\ &= -RT_H \ln\left(\frac{V_2}{V_1}\right) - RT_C \ln\left(\frac{V_4}{V_3}\right) \end{aligned} \tag{10.6}$$

- Steps 1 and 3 are adiabatic and reversible so the volume changes are related by

$$\begin{gathered} \left(\frac{T_C}{T_H}\right)^{C_V} = \left(\frac{V_2}{V_3}\right)^{R} \text{ and } \left(\frac{T_H}{T_C}\right)^{C_V} = \left(\frac{V_4}{V_1}\right)^{R} \\ \therefore \frac{V_1}{V_2} = \frac{V_4}{V_3} \text{ and } w_{net} = -R\left(T_H - T_C\right)\ln\left(\frac{V_2}{V_1}\right) \end{gathered} \tag{10.7}$$

- Using equation 10.1 the engine efficiency is defined as:

$$\varepsilon = \frac{-w_{net}}{q_H} = \frac{R\left(T_H - T_C\right)\ln\left(\frac{V_2}{V_1}\right)}{RT_H \ln\left(\frac{V_2}{V_1}\right)} = \frac{T_H - T_C}{T_H} \tag{10.8}$$

- Equation 10.8 states that 100% efficiency cannot be achieved because there will always be some exhausted heat. But what basic feature of a heat engine limits the efficiency in this way.?

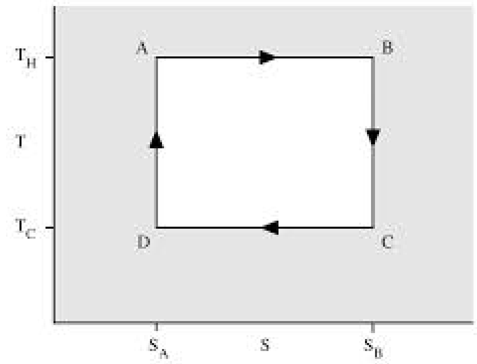


Figure 3; The Carnot Cycle shown on a T-S diagram.

- If the Carnot Cycle is diagramed as a T-S diagram, the result is a simple rectangular diagram, where the horizontal lines are the isotherms (ΔT=0) , and the vertical lines are the adiabats (q=0 and ΔS=0)
- Now the entropy is a state function so the entropies of the four steps must sum to zero:

$$\Delta S_{cycle} = 0 = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = \frac{q_H}{T_H} + 0 + \frac{q_C}{T_C} + 0$$
$$\therefore \frac{q_H}{T_H} + \frac{q_C}{T_C} = 0 \qquad (10.9)$$

- Combining 10.1 with 10.9 we again obtain the efficiency equation 10.7 $\varepsilon = \frac{T_H - T_C}{T_H}$

  This means that the necessity for the entropy to sum to zero over the engine cycle requires that q_C be non-zero and expelled at T_C.
- Real engine do not performed work with a working fluid in the gas pahse over the entire cycle. For example, real heat engines include steam engines, which convert liquid water to steam which is used to drive a piston. The upper limit for the Carnot efficiency of steam engines (i.e. the Rankin Engine) is about 63%.
- Piston-driven steam engines are called reciprocating engines. Steam turbines are generally more efficient than reciprocating steam engines because they produce rotary motion and shaft work directly. About 90% of the electricity in the U.S. is produced by steam turbines which have thermodynamics efficiencies in the 70-80% range.

B. Refrigerators and Heat Pumps

- A Carnot refrigerator simply reverses the cycle shown in Figure 2. Instead of heat q_H being withdrawn into the engine from the high temperature reservoir, partly converted to work with balance of the heat q_L the expelled into the low temperature reservoir, a refrigerator

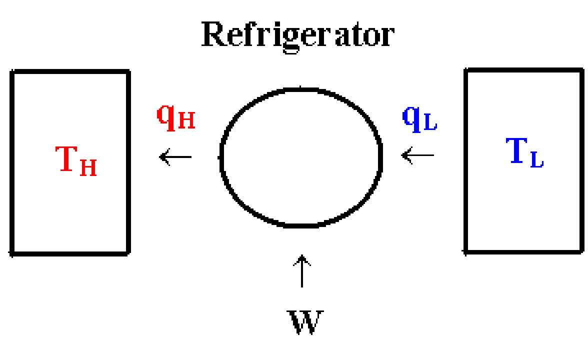


Figure 4: Carnot Heat Pump (Refrigerator)

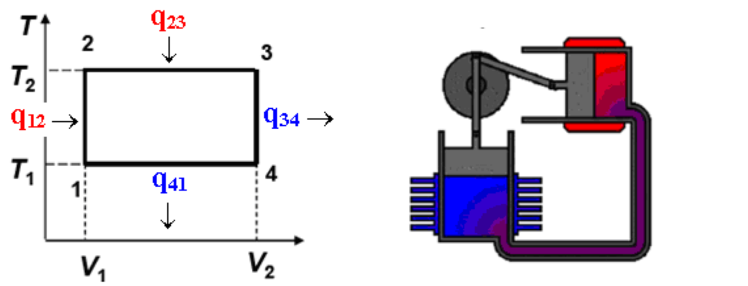
transfers heat from the low temperature reservoir it into the high temperature reservoir. In analogy to a water pump which transports water uphill, a refrigerator is sometimes called a heat pump. In order for heat to be transferred from low to high temperatures work must be done on the heat pump.

- The effectiveness of a refrigerator is related to its ability to remove heat from the low temperature reservoir (i.e. the food) and expel it to the outside. The coefficient of effectiveness is the ratio of the heat transferred from the low temperature reservoir to the work performed to accomplish this transfer:

$$\varepsilon_{eff} = \frac{q_L}{w} = \frac{q_L}{q_H + q_L} = \frac{T_L}{T_H - T_L} \qquad (10.10)$$

C. Real Engines: the Stirling Engine

- Real engines will have efficiencies less than a carnot engine. A Stirling engine is a real heat engine which like a Carnot Engine uses a gas as a working fluid. The cycle for a Stirling Engine is shown in Figure 5.



A: Stirling Engine Cycle **B: Schematic of a Stirling Engine**

Figure 5 a) The Stirling Engine Cycle shown as a T-V plot , b) A Stirling Engine uses a “displacer” piston (top) to move gas from the hot (red) zone through a long tube or cylinder to a cool zone (blue). A “power” piston changes the volume as the gas expands and contracts as its temperature changes.

- A Stirling Engine Cycle is most easily visualized on a T-V plot (Figure 5A)
  - Step 1: The displacer piston drives gas into the hot zone where the gas absorbs heat q_{12} at constant volume (isochoric) raising the temperature from T_1 to T_2
  - Step 2: Gas absorbs heat q_{23} isothermally at T_2 and power piston moves to expand the volume from V_1 to V_2 .
  - Step 3: Gas gives off heat q_{34} and cools to T_1 at constant volume V_2.
  - Step 4; Contraction of gas moves power piston downward decreasing the volume back to T_1 and giving off more hear q_{41}.

- The efficiency of the Stirling engine is

$$\varepsilon_{Stirling} = \frac{-w_{net}}{q_{12} + q_{23}} = \frac{q_{12} + q_{23} - \left(-q_{34} - q_{41}\right)}{q_{12} + q_{23}} = \frac{q_{23} + q_{41}}{q_{12} + q_{23}} \qquad (10.11)$$

  - Equation 10.11 uses the fact that because step 1 is the exact reverse of step 3, q_{12}=-q_{34}. Now because Step 1 is isochoric

$$q_{12} = \Delta U_{12} = nC_V\left(T_2 - T_1\right) = \frac{3nR}{2}\left(T_2 - T_1\right) \qquad (10.12)$$

  - Steps 2 and 4 are isothermal so

$$q_{23} = -w_{23} = nRT_2 \ln\left(\frac{V_2}{V_1}\right) \quad and \quad q_{41} = -w_{41} = nRT_1 \ln\left(\frac{V_1}{V_2}\right) = -nRT_1 \ln\left(\frac{V_2}{V_1}\right) \qquad (10.13)$$

- Put equations 10.12 and 10.13 into the efficiency equation 10.11:

$$\varepsilon_{Stirling} = \frac{q_{23}+q_{41}}{q_{12}+q_{23}} = \frac{(T_2 - T_1)\ln\left(\frac{V_2}{V_1}\right)}{\frac{3}{2}(T_2 - T_1) + T_2 \ln\left(\frac{V_2}{V_1}\right)} < \frac{T_2 - T_1}{T_2} \qquad (10.14)$$

- Equation 10.14 means that the efficiency of a Stirling Engine is less than the efficiency of a Carnot engine i.e. $\varepsilon_{Carnot} = \frac{T_2 - T_1}{T_2}$

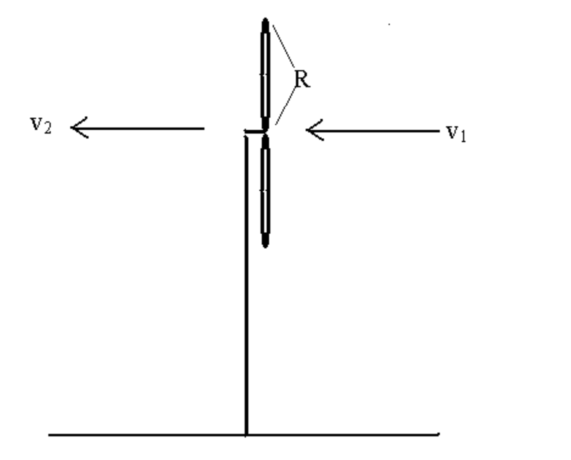
D. Efficiency of a Wind Turbine:

- Wind turbines are now recognized as useful devices for power generation. Wind turbines of various types are wide-spread in the U.S. and Europe and are bound to become more common in the future. Consider an ideal wind turbine. The blades of the wind turbine sweep out an area $S = \pi R^2 = \pi\left(\frac{d}{2}\right)^2$ where R is the length of the blade and d=2R is the rotor diameter . Assume the turbine blade rotates without friction. Assume the wind blows axially into the turbine blade (i.e. parallel to the rotor blade shaft) with velocity v_1, and exists the rotor area with velocity $v_2<v_1$. Assume no drag exists between the wind and the turbine blades.
  - Under these circumstances the turbine will convert the kinetic energy of the wind into rotational motion of the turbine blades. Suppose the mass transport $\dot{m}$ is the mass of air that crosses an area S in a unit time, assuming the air mass moves at a uniform velocity of v. Then the wind's mass transport is $\dot{m} = \rho S v$ where ρ is the density of the air, and we assume the wind crosses an area the size of the turbines rotor.
  - By the conservation of energy, the power of the turbine is given by

$$P_{turbine} = \tfrac{1}{2}\dot{m}\left(v_1^2 - v_2^2\right) = \tfrac{1}{2}\rho S v\left(v_1^2 - v_2^2\right) \qquad (10.15)$$

where v is the velocity of the wind at the rotor

Figure 4; Idealized wind turbine with frictionless rotor blades of length R. The wind is assumed to blow axially into the rotor blade with velocity v_1 and exits the rotor area A with velocity $v_2<v_1$. The velocity of the wind at the rotor blade is assumed to be the average $v=(v_1+v_2)/2$.



- It can be shown that v is the mean of the incoming and outgoing velocities: $v=\frac{1}{2}(v_1+v_2)$. Using this fact:

$$P_{turbine}=\tfrac{1}{2}\rho S v\left(v_1^2-v_2^2\right)=\tfrac{1}{4}\rho S\left(v_1+v_2\right)\left(v_1^2-v_2^2\right)$$
$$=\tfrac{1}{4}\rho S v_1^3\left(1+\tfrac{v_2}{v_1}-\left(\tfrac{v_2}{v_1}\right)^2-\left(\tfrac{v_2}{v_1}\right)^3\right)=\tfrac{1}{4}\rho S v_1^3\left(1+\tfrac{v_2}{v_1}\right)\left(1-\left(\tfrac{v_2}{v_1}\right)^2\right) \quad (10.16)$$

- By way of comparison, if wind moving at v1 crosses the same area the power would be:.

$$P_{wind}=\tfrac{1}{2}\dot{m}v_1^2=\tfrac{1}{2}\rho S v_1^3 \quad (10.17)$$

- The efficiency of the wind turbine is the ratio of these two powers;

$$\varepsilon=\frac{P_{turbine}}{P_{wind}}=\tfrac{1}{2}\left(1+\tfrac{v_2}{v_1}-\left(\tfrac{v_2}{v_1}\right)^2-\left(\tfrac{v_2}{v_1}\right)^3\right)=\tfrac{1}{2}\left(1+\tfrac{v_2}{v_1}\right)\left(1-\left(\tfrac{v_2}{v_1}\right)^2\right) \quad (10.18)$$

- In analogy to the heat engine where the efficiency is only a function of T_H and T_L, the efficiency of a wind turbine only depends of the ratio of v_1 and v_2.
- What is the maximum turbine efficiency? To find this maximize the efficiency with respect to $x=v_1/v_2$. Then for a maximum…

$$\frac{d\varepsilon}{dx}=0=\tfrac{1}{2}\frac{d}{dx}\left(1+x-x^2-x^3\right)=\tfrac{1}{2}\left(1-2x-3x^2\right) \quad (10.19)$$

- Solving this simple quadratic equation we find that the efficiency is maximum if $x=\frac{v_2}{v_1}=\frac{1}{3}$. Substituting this value of x into the efficiency equation:

$$\varepsilon_{\max}=\tfrac{1}{2}\left(1+\tfrac{1}{3_1}-\left(\tfrac{1}{3}\right)^2-\left(\tfrac{1}{3}\right)^3\right)=\tfrac{16}{27}\approx 0.59 \quad (10.20)$$

- This means that an ideal wind turbine can convert at most 59% of the incoming wind power into rotary motion of the turbine blade. This is called Betz' Law. Most real wind turbines operate with efficiencies in the range 10-30%.