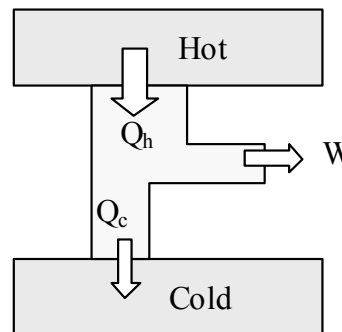
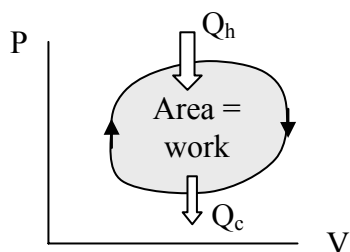


Chapter 22 – Entropy and the 2nd Law of Thermodynamics

This chapter deals with the concept of entropy and the 2nd Law of Thermodynamics.

Heat Engines

A heat engine is a system that converts thermal energy into work. It includes a working substance (e.g., a gas) that goes through a cycle in which it absorbs heat from a high temperature reservoir, converts some of the heat into work, and dumps heat into a low temperature reservoir.



The net change in internal energy during a complete cycle is zero, thus

$$\Delta U = Q + W = 0$$

The work done *by* the substance during the cycle is

$$|W| = Q_{net} = Q_h + Q_c = Q_h - |Q_c|$$

We use absolute values in the above since W and Q_c are negative. The *efficiency* of the heat engine is

$$e = \frac{|W|}{Q_h},$$

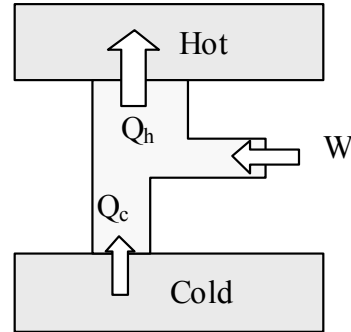
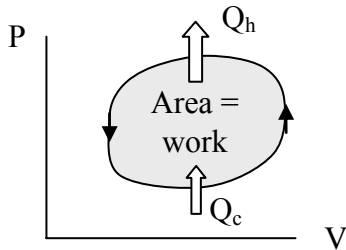
or

$$e = \frac{Q_h - |Q_c|}{Q_h} = 1 - \frac{|Q_c|}{Q_h}.$$

The *Kelvin-Planck* statement of the 2nd law of thermodynamics states that no heat engine can have an efficiency that is 100% ($e = 1$). In other words, a heat engine cannot extract heat from a reservoir and convert it completely to work. Some heat must be dumped at lower temperatures.

Refrigerators and heat pumps

A *refrigerator* is essentially a heat engine operating in reverse. It extracts heat from a cold reservoir (your refrigerator box) and dumps heat into a hot reservoir (your kitchen). Work is done *on* the engine during the cycle.



A refrigerator is rated by its *coefficient of performance* (COP), which is defined as

$$COP(\text{refrigerator}) = \frac{Q_c}{W} = \frac{Q_c}{|Q_h| - Q_c}.$$

A *heat pump* is fundamentally the same as a refrigerator; however, its purpose is to extract heat from outside your house and dump heat into your house. The coefficient of performance of a heat pump is defined as

$$COP(\text{heat pump}) = \frac{Q_h}{W} = \frac{Q_h}{|Q_h| - Q_c}.$$

Note that the above definitions of COP are different for the refrigerator and the heat pump. They are both essentially defined as the ratio of 'what you want' (Q_c or Q_h) divided by 'what you pay for' (work).

The *Clausius* statement of the 2nd law of thermodynamics is that there is no perfect refrigerator (or heat pump). In other words, it is impossible to have a system which transfers heat from a cold to a hot reservoir doing work on the system.

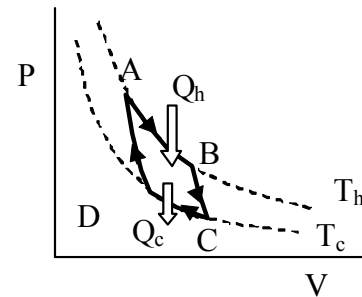
Reversible and Irreversible Processes

A *reversible* process is one such that the system and its environment can be returned to their original state at the end of the process. All real processes are *irreversible*; however, a process can be approximated as reversible if it can be done in small, well-defined steps. An example of a reversible process would be the isothermal expansion of a gas. In reality, if we expand a gas the temperature changes and the process is irreversible; however, if the gas cylinder is in thermal contact with a large thermal reservoir during the expansion and if the expansion is done very slowly, then the gas temperature is always

nearly the same as the reservoir. In example of an irreversible process would be the mixing of hot and cold water.

Carnot Engine

A Carnot engine is a hypothetical engine that operates in a reversible cycle between hot and cold reservoirs. A Carnot engine could be an ideal in which the cycle consists of isothermal and adiabatic process, as illustrated to the right. The individual processes are:



A-B: Isothermal expansion. Heat Q_h is absorbed from the high temperature reservoir at T_h .

B-C: Adiabatic expansion. Temperature drops from T_h to T_c .

C-D: Isothermal compression. Heat Q_c is released to the low temperature reservoir at T_c .

D-A: Adiabatic compression. Temperature increases from T_c back to T_h .

It can be shown that $|Q_c/Q_h| = T_c/T_h$. Thus, the efficiency is

$$e = 1 - \frac{T_c}{T_h}$$

Example:

A heat engine absorbs heat at 500°C and dumps heat at 25°C . What is the maximum efficiency?

$$e = 1 - \frac{T_c}{T_h} = 1 - \frac{25 + 273}{500 + 273} = 0.386$$

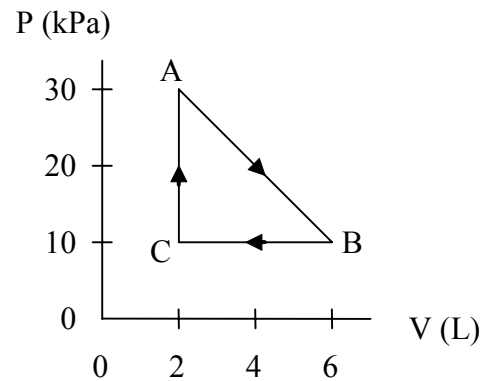
If the engine takes in heat at the rate of 10 kW, what is the power output?

$$W = eQ_h$$

$$\text{Power} = \frac{dW}{dt} = e \frac{dQ_h}{dt} = (0.368)(10\text{kW}) = 3.68\text{kW}$$

Example:

An ideal monatomic gas goes through the cyclic process A→B→C→A as shown to the right. The temperature of the gas at A is 600K. Calculate the work done on the gas, the heat absorbed by the gas, and the change in internal energy for each process and for the total cycle.



From the ideal gas equation, $PV = nRT$, we can calculate that $T_B = 600\text{K}$ and $T_C = 200\text{K}$. Since this is a monatomic gas, then we have $U = 3/2 nRT$. We keep in mind that 1 liter = 10^{-3} m^3 .

A→B:

Since the gas is expanding, then the work done *on* the gas is negative and

$$W_{AB} = -\text{area under PV curve} = -(2 \times 10^4 \text{ Pa})(4 \times 10^{-3} \text{ m}^3) = -80 \text{ J}$$

$$\Delta U_{AB} = 3/2 nR\Delta T_{AB} = 0 \quad (T_A = T_B)$$

$$\text{From the 1}^{\text{st}} \text{ law, } Q_{AB} = \Delta U_{AB} - W_{AB} = 0 - (-80 \text{ J}) = 80 \text{ J (heat is absorbed)}$$

B→C:

Since the gas is being compressed, the work done *on* the gas is positive and

$$W_{BC} = \text{area under PV curve} = (1 \times 10^4 \text{ Pa})(4 \times 10^{-3} \text{ m}^3) = 40 \text{ J}$$

$$\begin{aligned} \Delta U_{BC} &= 3/2 nR\Delta T_{BC} = 3/2 nR(T_C - T_B) = 3/2 P_C V_C - 3/2 P_B V_B \\ &= 3/2 (1 \times 10^4 \text{ Pa})(2 - 6) \times 10^{-3} \text{ m}^3 = -60 \text{ J} \end{aligned}$$

$$Q_{BC} = \Delta U_{BC} - W_{BC} = -60 \text{ J} - 40 \text{ J} = -100 \text{ J}$$

C→A:

This is an isovolumeric process, so $W_{CA} = 0$.

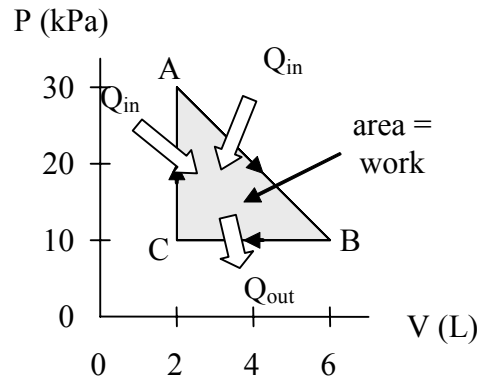
$$\begin{aligned} \Delta U_{CA} &= 3/2 nR\Delta T_{CA} = 3/2 nR(T_A - T_C) = 3/2 P_A V_A - 3/2 P_C V_C \\ &= 3/2 (3 \times 10^4 \text{ Pa} - 1 \times 10^4 \text{ Pa})(2 \times 10^{-3} \text{ m}^3) = 60 \text{ J} \end{aligned}$$

$$Q_{CA} = \Delta U_{CA} - W_{CA} = 60 \text{ J}$$

Summary results:

	A→B	B→C	C→A	Total
W (J)	-80	40	0	-40
Q (J)	80	-100	60	40
ΔU (J)	0	-60	60	0

Note that the total work done in the cycle is the enclosed area. The negative value means that the gas does work on its environment during the cycle. Since the gas returns to its original state, the net change in internal energy is zero. The net heat absorbed is equal to the net work done *by* the gas. Heat is absorbed during the processes A→B and C→A and rejected during the process B→C.



For the above cyclic process, the efficiency can also be calculated:

$$Q_{in} = Q_{AB} + Q_{CA} = 80J + 60J = 140J$$

$$W(\text{net}) = 40J \text{ (done by the gas)}$$

$$e = \frac{W}{Q_{in}} = \frac{40J}{140J} = 0.286 = 28.6\%$$

Entropy

The entropy of a system is a measure of its disorder. The higher the disorder, the higher the entropy. Specifically, if a system absorbs heat at a fixed temperature, then the change in entropy is given by

$$\Delta S = \frac{Q}{T} \quad \text{units} = \text{J/K or cal/K}$$

If heat is absorbed, then $\Delta S > 0$. If heat is lost, then $\Delta S < 0$.

If the temperature changes during a reversible process, then the entropy change is

$$\Delta S = \int_i^f \frac{dQ}{T}$$

The change in entropy in a reversible process depends only on the initial and final states and not how the change takes place. For a complete cycle, $\Delta S = 0$.

Example:

50 g of water melts at 0°C . What is the change in entropy of the water?

$$\Delta S = \frac{Q}{T} = \frac{mL_f}{T} = \frac{(50\text{g})(80\text{cal/g})}{273\text{K}} = 14.7 \text{ cal/K} = 61.3 \text{ J/K}$$

Example:

100 cal of heat is transferred from a reservoir at 100°C to a reservoir at 0°C . Assuming that the reservoirs are large enough so that their temperatures don't change, what is the total change in entropy of the two reservoirs?

$$\begin{aligned} \Delta S &= \Delta S_{hot} + \Delta S_{cold} = \frac{Q_{hot}}{T_{hot}} + \frac{Q_{cold}}{T_{cold}} = \frac{-100\text{cal}}{373\text{K}} + \frac{100\text{cal}}{273\text{K}} \\ &= 0.098 \text{ cal/K} \end{aligned}$$

Note that $\Delta S > 0$, which means that the total disorder has increased. If heat flowed from the cold to the hot, then ΔS would be negative. This cannot occur spontaneously. Another way of stating the 2nd law of thermodynamics is to say that **the total entropy of a closed system increases in all natural processes**.

Example:

100 g of water at 20°C is mixed with 100 g of water at 80°C . What is the net change in entropy?

Although this is an irreversible process, we could get the same final result (200 g of water at 50°C) by slowly warming the cool water from 20°C to 50°C and slowly cooling the warm water from 80°C to 50°C . Thus,

$$\begin{aligned} \Delta S &= \Delta S_{hot} + \Delta S_{cold} = \int_{293\text{K}}^{323\text{K}} \frac{dQ}{T} + \int_{353\text{K}}^{323\text{K}} \frac{dQ}{T} = \int_{293\text{K}}^{323\text{K}} \frac{mcdT}{T} + \int_{353\text{K}}^{323\text{K}} \frac{mcdT}{T} \\ &= (100\text{g})(1\text{cal/g}^\circ\text{C}) \ln\left(\frac{323}{293}\right) + (100\text{g})(1\text{cal/g}^\circ\text{C}) \ln\left(\frac{323}{353}\right) \\ &= 9.75 \text{ cal/}^\circ\text{C} - 8.88 \text{ cal/}^\circ\text{C} = \underline{0.87 \text{ cal/}^\circ\text{C}} \end{aligned}$$