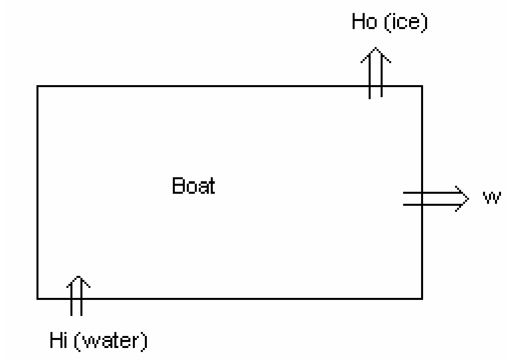
3.23 Lecture 5

Last time there was a brief discussion about heat flow from high to low energy such as in the reverse process of light being emitted from a light bulb. Consider as a review the flow of energy of the party boat.



Write the first law and look at the work the boat can produce. Look at the energy of matter flowing in and out.

$$W = H_{ice(out)} - H_{water(in)}$$
$$W = m(\underline{H}_{ice} - \underline{H}_{water})$$
$$W = -2061\ J$$

Look at the power rate

$$Power\ rate = 1000\ \text{hp}\ (1\ hp = 745\ W)$$

How much ice is produced?

$$Mass\ produced = power\ rate\ /\ -2061$$
$$Mass\ produced = -746{,}000\ /\ -\ 2061$$
$$Mass\ produced = 330\ g\ /\ s$$

There is energy in matter, and it can be small compared to mechanical energy,

The light bulb does not absorb heat and convert electricity. It is known that work is converted into heat. People are interested in turning heat into work and knowing how much work can come from heat.

Second Law

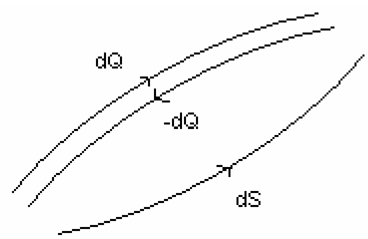
There are many statements of the second law, and it is mostly an empirical observation. It is possible to prove that one statement is equal to another. Below are statements

Kelvin – Planck	It is impossible to convert heat all into work. This is a direct attack on the reverse process of the light – bulb.
Clausius	Heat flows from high to low temperature
Mathematical statement	There exists an extensive state function called entropy $S(U,X_i)$, which is a monotonically increasing function of U, for which its differential is greater than or equal to the heat over temperature

$$ds \geq dQ / T$$

The last statement is the most pragmatic and modern. The other statements follow from a proof of this.

The entropy is an extensive property and is a state function. It describes the state of the system and is a property like volume and internal energy. It sets the direction of the process. The law tells the directionality of processes. Look at the flow of heat.



$$ds \geq dQ / T$$

Multiply by -1 and show that the process is not reversible

$$-ds \geq -dQ / T$$

How do you know if a process is reversible? Look at the mathematical relation. Only when there is an equal sign is the process reversible

$$ds = dQ / T$$
$$-ds = -dQ / T$$

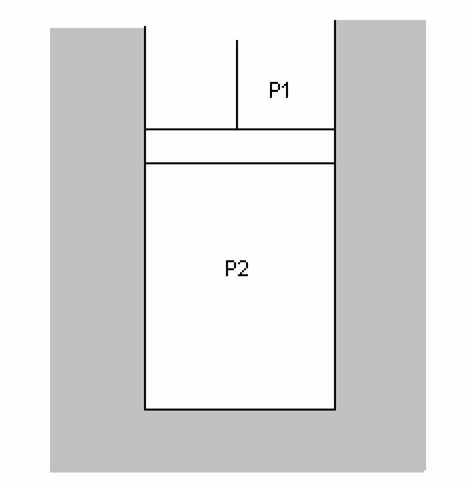
Only with equality is there a truly reversible process. This is a mathematical definition of what is reversible. Calculate the entropy change and heat flow and see if the second law is satisfied. It's easy to see if processes are irreversible. Look for unbalanced forces.

Reversible process

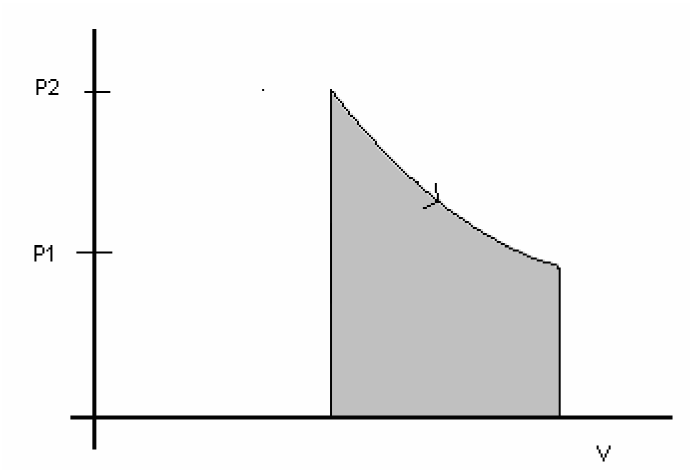
A reversible process is a process in which the system and surroundings are restored to the initial state without a change in surroundings

Sources of irreversibility

The lack of mechanical equilibrium is a source of irreversibility. Consider the experiment of a gas in a cylinder.



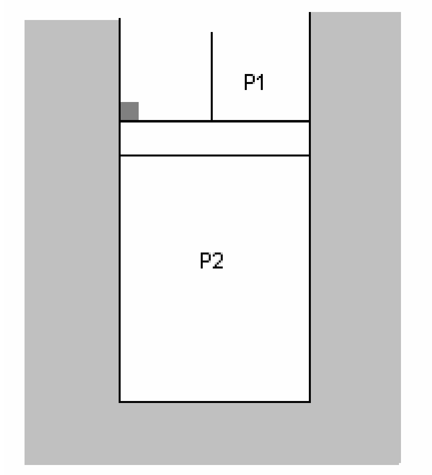
In an isolated process, there is heat flow. In a reversible process, at all times there must be a balance of forces on both sides of the piston. There needs to be a device that adjusts force, which may require pulleys and levers. Look at the *P-V* curve.



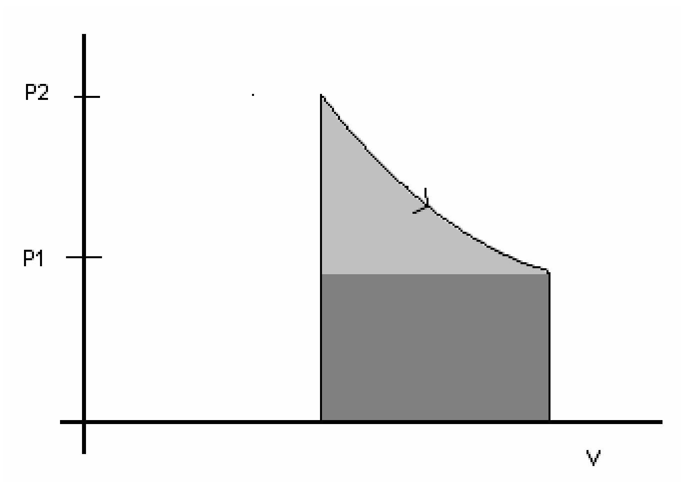
The gas does work below the curve

$$W = -Integral[pdV]$$

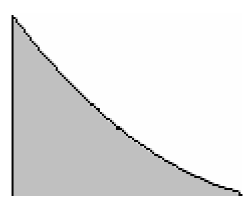
This is true in the case of the back pressure being the same as the gas. Consider the case of clamping the piston in place and then displacing the clamp. The piston accelerates after the displacement with no devices to absorb.



The final temperature and pressure are set, so the system ends in the same state.

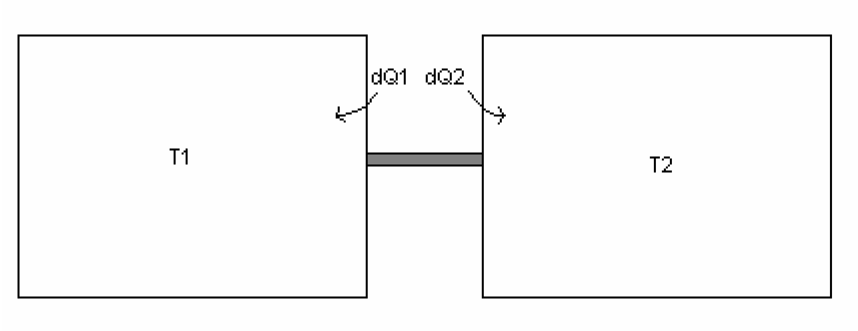


There is work to the environment against P_1. There is a source of irreversibility. The following portion of the curve is work that cannot be retrieved.



There is more energy delivered as work in the first process. In the second process there is more energy being sent out as heat. There is a difference in entropy generation. The change in internal energy is the same since the initial and final state are the same.

Irreversible process, heat flow over a temperature gradient



Assume that the heat conductor is of negligible mass and that there are no significant work terms.

$$\delta Q = -\delta Q_2$$

What direction does heat flow? Calculate the entropy change of both systems.

$$dS_{total} = dS_1 + dS_2$$

What is dS_1? The expression is below, and the inequality signs are not useful.

$$dS_1 \geq \delta Q_1 / T$$

Use the idea that dS_1 is a state function. Calculate the change of state, and the entropy will be defined. What change of state does the heat flow cause? Look at the change of temperature when heat is added to a body under constant pressure.

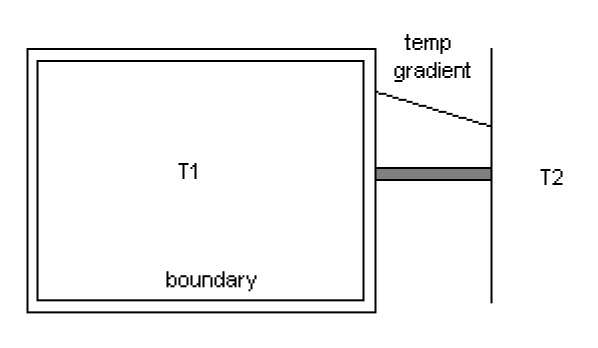
$$dT = \delta Q / (n_1 \, Cp_1)$$

There is an entropy difference between the states with temperature T_1 and $T_1 + dT_1$ (p = constant) This is well-defined. Look at the change of state under a reversible process. Break the process into a series of reversible paths.

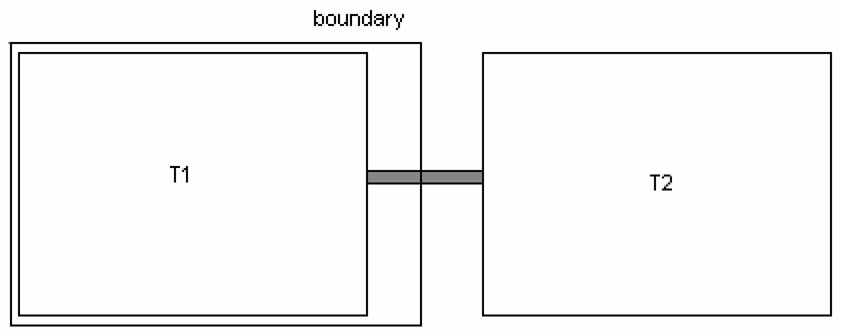
$$\begin{aligned} dS_{total} &= \delta Q_1 / T_1 + \delta Q_2 / T_2 \\ &= \delta Q_1 \,(1 / T_1 - 1 / T_2) \\ &= \delta Q_1 \,((T_2 - T_1)/ T_1 T_2) \end{aligned}$$

This is a statement of the direction of heat flow. When $T_2 > T_1$, $\delta Q_1 > 0$ for the entropy to increase. In this case heat flows from right to left.

Two reversible processes were added and the irreversible part comes from the connector. Look at the boundary.



The heat flow over the gradient is an irreversible process. The reversible statement of the second law is not true with different boundaries. Define the boundary to be between the two bodies.



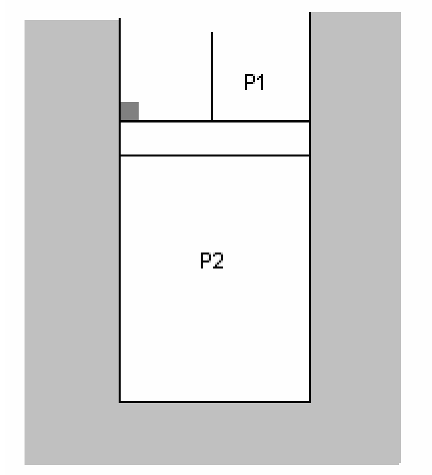
If $T_2 > T_1$, the temperature T' at the boundary is higher than T_1. There is heat flow at a higher temperature than T_1.

$$dS \geq \delta Q / T'$$

The associated entropy change is smaller in this case than with the previous boundaries. The placement of boundaries defines the temperature of heat exchange.

Heat flow across a gradient is an irreversible process. Tighten the boundaries and treat the system as reversible.

Consider the case of the piston with a clamp and then slow acceleration.



If the boundary is below the plunger, the gas is considered to be expanding reversibly. If the plunger is inside the system, it is an irreversible process.

Comments about entropy

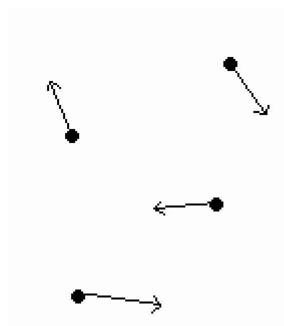
1) Local process can be reversible but the overall process can be irreversible. The flow of heat is an example
2) Entropy is not a conserved quantity like energy. When rubbing a table, heat is generated, and there is not a decrease in entropy of anything.
3) The entropy of adiabatic systems always increases

$$dS \geq \delta Q / T > 0$$

The entropy of the universe must increase. In a closed system, there is no heat flow across boundaries, and $dS_{universe} \geq 0$. Entropy provides the arrow of time. There is a one way evolution that travels to a maximum. With this law, not all processes are permissible. There is an increase in entropy with even the slightest process. This leads to the idea of entropy death.

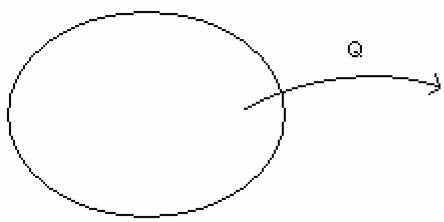
Entropy is odd. It is not a property we are accustomed to measuring.

Consider particles moving at a particular velocity.



Is it possible to reverse velocities? Is going in the other direction equally likely? According to Newtonian mechanics and quantum mechanics, this is a reversible process. The state in the forward and reverse direction is not equally likely. The arrow comes from the fact that the probability distributions are not symmetric.

4) Entropy can go down. This occurs when a body is cooled.



This heat flow, Q, is not negative. The entropy of a system can decrease, but the entropy change of a system, environment, and universe always increases.

Publishing the second law

The second law was fist published by Carnot, who was an engineer. He wrote on two sheets of paper, and it was not published in a journal. Kelvin heard of the 2nd law and looked for the paper for 15 years. Hemholtz gave a copy to him.

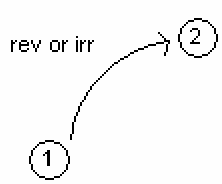
Consequences of the 2nd law

Below are consequences of the 2nd law.

1) $\delta W_{rev} < \delta W_{irr}$
2) limits of conversion of Q to W
3) evolution

$\boldsymbol{\delta W_{rev} < \delta W_{irr}}$

Look at the change of state under two different paths



Apply the first law to both paths

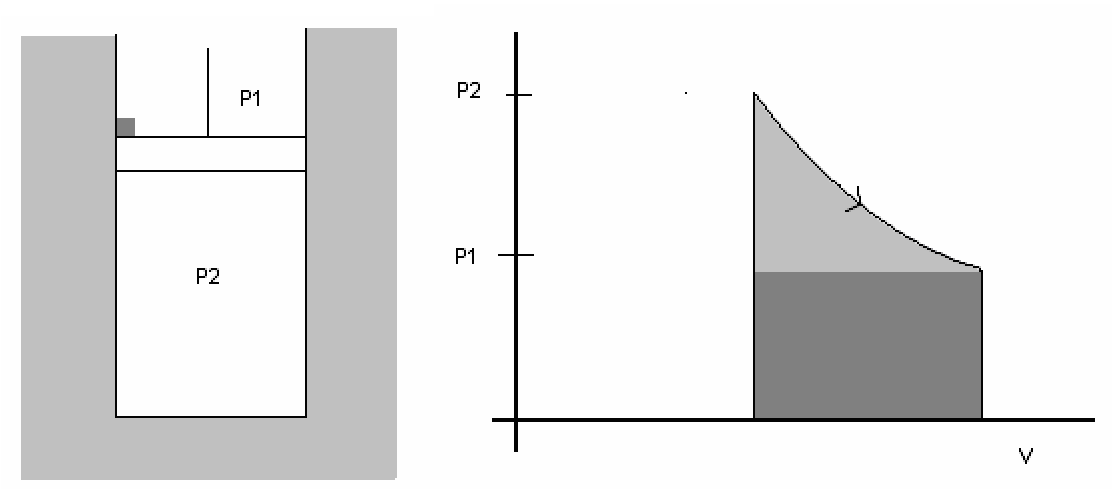
$$dU_{syst} = \delta W_{rev} + \delta Q_{rev}$$
$$dU_{syst} = \delta W_{irr} + \delta Q_{irr}$$

The δQ_{rev} and δQ_{irr} terms are both equal to TdS.

$$\delta Q_{rev} + \delta W_{rev} = \delta Q_{irr} + \delta W_{irr}$$
$$TdS + \delta W_{rev} \leq TdS_r + \delta W_{irr}$$
$$\delta W_{rev} < \delta W_{irr}$$

In a process that produces work, the work flow is negative. In a reversible process there is more work out. Imagine a machine that does work on a fluid (pump). The work flow is positive. An irreversible process is wasteful

Look back at the example of the source of irreversibility in the expansion of gas.



Look at the heat flows in an irreversible process. The final state of the system is the same as the initial state.

$$\Delta S^{rev}{}_{rev} = \Delta S^{irr}{}_{rev}$$

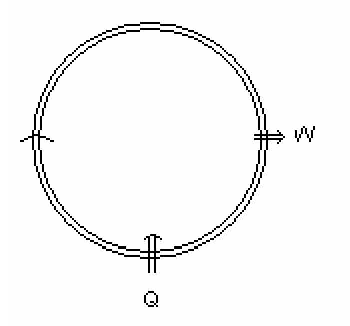
The temperature and pressure are defined and the change in internal energy must be the same.

$$Q_{rev} + W_{rev} = Q_{irr} + W_{irr}$$
$$W_{rev} < W_{irr}$$
$$Q_{irr} < Q_{rev}$$

In an irreversible process, there is less heat flow in and more heat flow into the environment. This is an irreversible process and there is more entropy generation.

Limits of heat to work conversion

Imagine a cyclic process that absorbs heat and generates work



Prove that there are limits to the conversion to work and that most of the work produced is with a reversible process.

$$Integrate[dS] = Integrate[\delta Q / T]$$
$$\Delta S = 0$$
$$\Delta S = Q / T$$
$$Q / T = 0$$

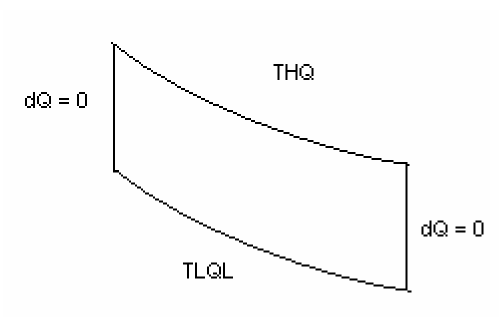
In a reversible process, heat can't be put in.

$$\Delta U = Q + W$$

When $\Delta U = 0$, and $Q = 0$, the work term must zero.

Heat into work

How is heat converted into work? Do heat and work flow at multiple temperatures.



Look at a relation with heat flows.

$$\Delta S = Q_H / T_H + Q_L / T_L$$
$$Q_L = -T_L / T_H \, Q_H$$

There are two heat flows with opposite sign and different magnitude. There is net energy into the system.

$$W = \Delta U - Q_H - Q_L$$
$$W = - (1 - T_L / T_H) \, Q_H$$

The temperatures are positive and there is work out.

Efficiency of process (economic concept)

What you want / what you pay for

$$\eta = W / Q = (1 - T_L / T_H)$$

For efficiency to be high, T_H approaches infinity

Typical efficiencies

$T_H = 100^\circ$ C
$T_L = 25^\circ$ C

Make the temperature as high as possible. A lower temperature is better, but it is hard to lower.

$$\eta = 1 - 298 / 373$$
$$= 20\ \%$$

If a machine is run with 100 J of heat, 20 J of energy will come out. The higher the value of T_H there is, the more power that results. Consider another example.

$T_H = 550^\circ$ C
$T_L = 25^\circ$ C
$\eta = 63$ %

A real machine operates under an irreversible process and will do less. It's easier to increase efficiency at a larger scale. Novel materials will help increase T_H. The temperature resulting from the combustion of methane is 3000ºC. Fuels do not limit T_H. Limitations arise from materials operating and the need to contain the combustion.

Consider the efficiency of a jet. The walls are air and water cooled. When running with super alloys, the material is stronger at 1000ºC.