3.23 Lecture 6

Last time, the 2nd law was defined. Entropy is an extensive property, and the following equation is true

$$ds \geq dQ / T$$

A process is reversible only when there is an equality sign in this relation. There are heat and work conversion limits and evolution laws. In a reversible process, there is more energy used as work than in an irreversible process.

When an expansion is out of equilibrium, it is irreversible. Work goes to the environment when allowed to expand against the environmental pressure.

Entropy change greater in irreversible process

Calculate the entropy change of the system plus the entropy change to the environment in both the irreversible and reversible case.

$$\Delta S^{irr}_{sys} + \Delta S^{ir}_{env} = \Delta S^{rev}_{sys} + \Delta S^{rev}_{env}$$

In a closed system, the right hand side is equal to zero. Prove that the term ΔS_{env} is different. The system ends in the same state in both processes. Two variables are defined in this state.
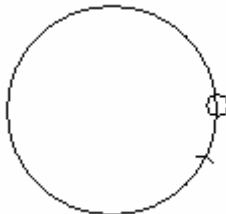
The heat flow along an irreversible path is greater than the heat flow along a reversible path.

$$Q_{rev} + W_{rev} = Q_{irr} + W_{irr}$$
$$W^{rev}_{sys} < W^{irr}_{sys}$$
$$Q^{rev}_{sys} < Q^{irr}_{sys}$$

The entropy change is greater in the case of an irreversible process

Heat to work limits – introduction
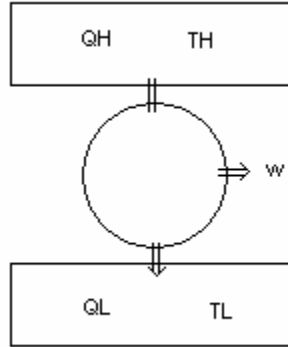
This is an important societal issue. Pick a reversible process

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

When $\Delta S = 0$, the heat flow must be zero, which would mean that there can't be any heat input and no energy out. It is possible to keep the integral zero by doing heat exchange at different temperatures.

Heat and work flow at two temperatures

Relate the efficiency to work and heat flow

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

There is a need for high temperature reservoirs. The Carnot limit is the heat to power conversion limit. When fuel is turned into heat there is a limit. Carnot limit applies to thermalized heat but not to fuel. There is no thermodynamic limit when fuel is converted to power. A fuel cell can run theoretically at 100%

There is an idea of how to exceed the Carnot limit. Combustion results in explosions that produce shock propagations. Use the shock waves directly when converting energy.

Reversible machine

QH   TH

w

QL   TL
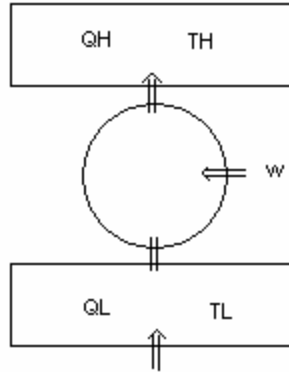
A refrigerator and heat pump are essentially the same. A refrigerator extracts Q_L. Look at the coefficient of performance of a refrigerator

$$\eta = Q_L / W$$

A heat pump is the same as a refrigerator but with different pieces. One construction is to put pipes in the ground for heat exchange. Look at the efficiency of a heat pump.

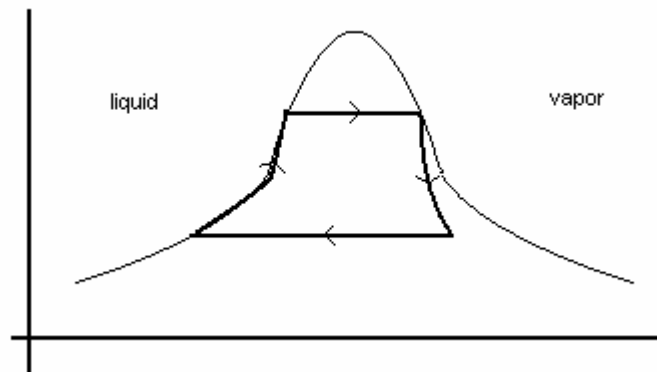$$\eta = -Q_H / W$$
$$\eta = T_H / (T_H - T_L)$$

$$T_L = 273\ K$$
$$T_H = 298\ K$$
$$\eta = 11.9$$

The engineering is hard but the conversion is better than a space heater. A space heater involves a pure dissipative process. The conversion of energy is 100 % with a space heater.
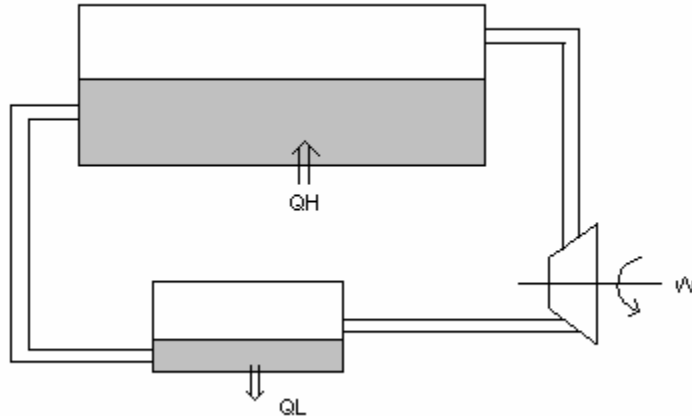
How to make a Carnot Machine

Circulate a fluid in a coexistence region.

liquid   vapor

The machine absorbs heat and the fluid is boiled. There is a volume discontinuity.

Build a boiler

It's possible to get work out by running a reversible process. Run the process adiabatically, for there is a desire not to lose heat.

Run the process as efficiently as possible. Water under 1 atm boils at 100º C, and the efficiency at this temperature and pressure is only 20 %. Put under pressure to increase the boiling point. During evaporation there is a high temperature and pressure. The limit to high temperature comes from the materials used.

It is bad to end in a mixed state. The mixed state is a vapor with liquid bubbles. The small bubbles are very hard. Expanding into the coexistence phase can destroy the machine.

Refrigerator
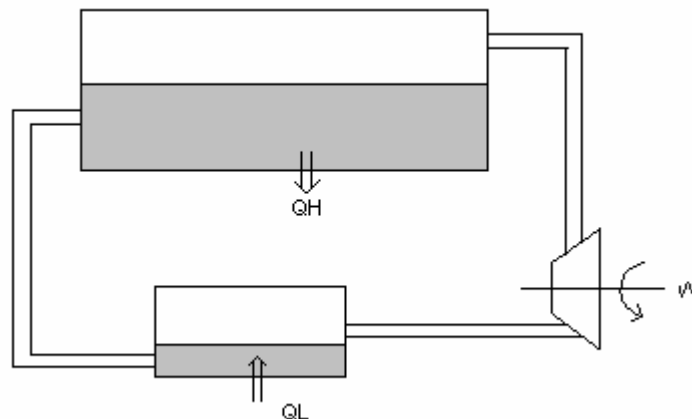
Heat moves in at low temperature and out at high temperature. In order to boil at a temperature below condensing, there needs to be a large pressure gradient. Move the boiling point down at Q_L and up at Q_H. This is again a materials issue. In order to separate the boiling point and condensing point by 20 – 30 °, there needs to be much pressure. This relates to the enthalpy of evaporation and is how Freon was born. The boiling point of Freon shows a strong dependence on pressure.

Where does the Second Law come from?

It's easy to come up with the second law. The first law states that heat and work both contribute to the internal energy, and it doesn't matter which is added. The second law makes a distinction between flows. There is a property that depends on heat flow.

Why is the following expression written with an inequality sign?

$$ds \geq dQ / T$$

When heat is added to a material, the change of entropy is essentially dQ / T. The inequality results from heat flows that are not seen. Work is dissipated as heat. Identify all heat flows.
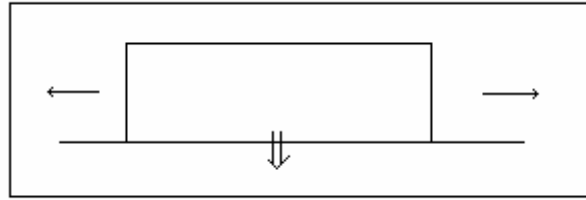
Consider the experiment of rubbing a block on a table.

Look at the entropy change of the table. Rubbing generates heat. Consider the case of the boundary as the table. Heat goes in as $dS = dQ / T$
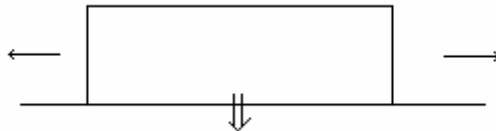
Consider the case when the table and block are both part of the system.

There is work done when rubbing with the eraser.   There is no visible heat flow, but dS must be the same.

The part that can't be measured is from inefficiencies. The lost work is the additional term that creates an inequality.

When a system is made smaller, there is less opportunity to include irreversibilities. Looking at the system closer results in treating it more reversibly.

Systems are limited to materials from this point on.

Entropy of Materials – Temperature Dependence

Two states are connected through a heat flow through a reversible path. The heat flow is path dependent and the constraint defines the constraint on heat capacity. There can be complex paths, and the heat capacity is defined by keeping variables constant. There can be complex paths, and below is the definition of heat capacity

$$TdS = (\ \delta Q_{rev}\ )_{constraint}$$
$$TdS = n(C)_{constraint}dT$$
$$T(\delta S/\delta T)_{constraint} = C_{constraint}$$

S(T) **at constant** *P*
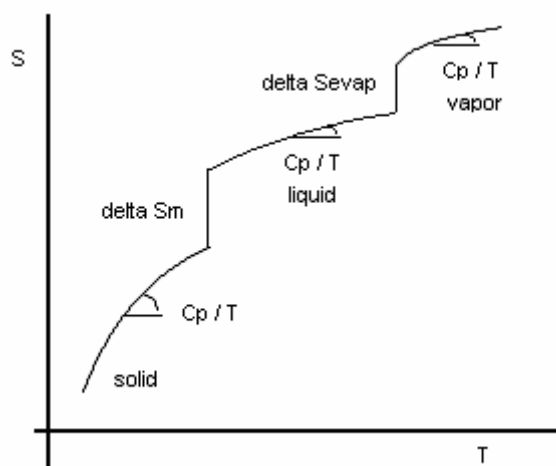
At a phase transition, there is a discontinuity, and the heat flow divided by the temperature is equal to ΔS.

$$\Delta S_{melting} = \Delta H_{melting} / T_{melting}$$

The temperature is constant under melting processes. In general, under constant P,

$$\Delta S_{transformation} = \Delta H_{transformation} / T_{transformation}$$

Richard's rule is a statement of the increase in entropy being universal at a phase transformation.

$$\Delta H_m \text{ (J)} = 9\ T_m(K) \qquad \text{Richard's rule}$$
$$\Delta S_m \text{ (J)} = 9\ [J/(mol\ K)]$$
$$\Delta H_{evap} \text{ (J)} = 90\ T_{evap}(K) \qquad \text{Trouton's rule}$$
$$\Delta S_{evap} \text{ (J)} = 90\ [J/(mol\ K)]$$

In statistical mechanics, there will be an explanation where the rules come from. Entropy is a measure of disorder. The increase in disorder that results during the transition from solid to liquid is about constant. The change in enthalpy is a measure of disorder and is not chemistry dependent. For atomic-like species enthalpies are constant. This is not true for large molecules; entropy is considered differently.

Reference state for entropy

Pick stable states at 298 K for enthalpy. For entropy the stable states are chosen to be at 0K. The entropy of elements in equilibrium states at 0K is zero. From reaction enthalpies, the reference states for compounds could be tabulated. This is not needed for entropy based on the third law of thermodynamics.

Third Law of Thermodynamics

The magnitude of any entropy change goes to zero as the temperature approaches zero. As the temperature approaches zero, the entropy change in any irreversible process tends to zero. This was first postulated by Nernst in 1906. There was not yet knowledge of thermodynamics or the atomistic nature. He was awarded the Nobel Prize in 1920 for the postulate, which is a rather short time from the year it was postulated.

Combine reference states of compounds from elements in processes associated with zero entropy change. Everything is in the equilibrium state at 0K. Most things at equilibrium are crystalline, but not everything. Due to quantum mechanical effects, helium is a liquid at 0K. In general, there can be movement without disorder.

Zero K is unattainable

Attaining 0 K is not possible. Generally, things are cooled by putting something in contact with something cool. It is not possible to do this and attain 0 K. Extracting heat also does not work.

1) Cooling by extracting energy does not work.
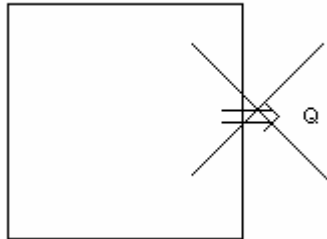
2) Deliver work to the environment. Consider the adiabatic expansion of a gas in the tire. Energy goes out, and internal energy decreases

$$W < 0 \rightarrow \Delta U < 0$$

In an adiabatic process, there is no heat flow. The most efficient process is when $Q = 0$. Consider an isentropic process. Consider a work delivery process. Start at a high volume. The system gives off heat and lowers in temperature. Do compression at a constant temperature, and there is a change of state. Compressing results in giving off heat.

     Do an isentropic expansion, and the system goes to a higher value of X. The temperature goes down, but this can only be done once. It's possible to give off heat once. It's possible to divide the system in two. Heat is given off to another system, but the system never travels down to 0 K.
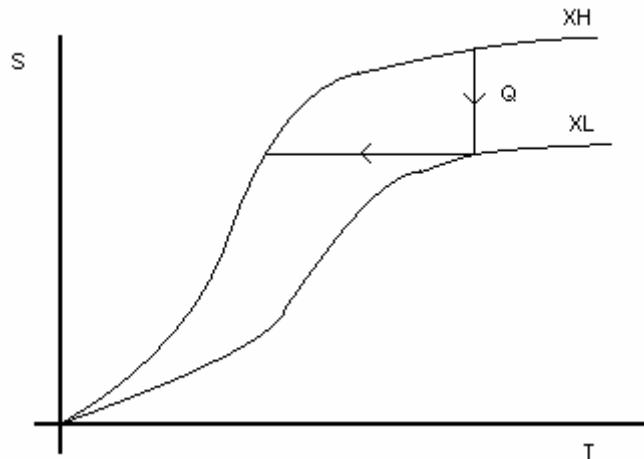
If the third law were not true, the isentropes would look like what is shown below. Believing in the third law means believing in the unattainability of reaching 0 K.
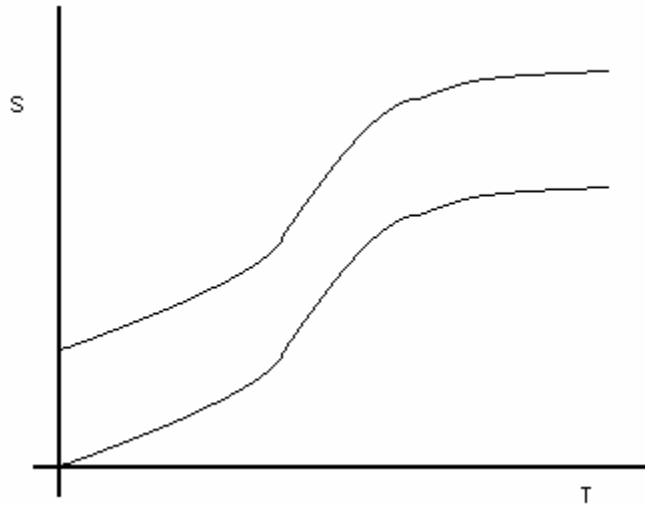
Calculations of ideal gas

1) Entropy change for adiabatic reversible expansion

$$\delta Q = 0$$

$$dS = \delta Q / T = 0$$

The process is isentropic

$$T (\delta S / \delta T)_P = C_P$$
$$dS = C_P \, dT / T$$

2) Isothermal reversible expansion

The derivative of entropy is not much use. Consider an isothermal process.

$$\delta W = - \delta Q$$

Calculate dS

$$dS = \delta Q / T$$
$$dS = - \delta W / T$$
$$dS = p dV / dT$$

$$\Delta S = Integrate[p dV / dT]$$
$$\Delta S = Integrate[n R dV / V]$$
$$\Delta S = n R \ln V_2 / V_1$$

$$\Delta S = -nR\ln P_2 / P_1$$

Consider an arbitrary change. The change is not path dependent. Consider the combination of an isothermal and isobaric process

$$dS = dS_{isobar} + dS_{isotherm}$$

$$dS = nC_p \, dT / T - n \, R \, dP / P$$

The entropy change is in terms of two state variables. For an ideal gas, the entropy change can be described with two variables.

Consider when $dS = 0$

$$C_p \, dT / T = R \, dP / P$$

Look back to lecture 2 and 3