

Lecture # 5

Reverse and Irreversible process

$S(N, U, V)$ – If number of particles is fixed the entropy can change as a result of two process (1) small change of energy, (2) small change of volume

$$(1) dS = \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV = \frac{1}{T} dU + \frac{P}{T} dV$$

We may rearrange the terms and write

$$(2) dU = TdS - PdV \text{ - The thermodynamic identity}$$

The equation is true for any infinitesimal change in any system provided that T and P are well defined and no other relevant variables are changing. Please memorize it. From the thermodynamic identity you may get equations for pressure and temperature.

The thermodynamic identity looks very much like the 1st law of thermodynamics

$$dU = dQ - dW$$

So it is tempting to say that

$$(3) dQ = TdS$$

$$(4) dW = +PdV$$

Equation (3) and (4) are not always valid, (4) is valid only if any change in volume taken place quasistatically (so the pressure is uniformly distributed through the system). That is also what we mean when we say that pressure becomes well or well defined. Temperature also has to behave well and has to be uniformly distributed through the system. If we know for sure that $dW = +PdV$ we have quasistatic process.

A special case when $Q = 0$ (adiabatic process) and $dW = +PdV$ (quasistatic) is called isentropic, isentropic = quasistatic + adiabatic

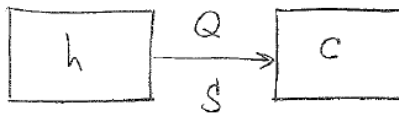
Equilibrium of mechanically applied pressure usually occurs with the speed of sound, so quasistatic process can be rather fast.

So if $dW = +PdV$ we have $dQ = TdS$

$$dU = TdS - PdV \quad dS = dU + PdV / T = dQ/T$$

$dS = dQ/T$ Thermodynamic definition of entropy (1860...)

Recall our example with copper blocks



So we may say that we have the heat flow and this heat flow changes the energy.

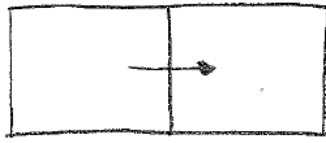
We may also say that we have an entropy “flow”. Entropy leaves the hotter body and enters colder body if $T_h > T_c$ the heat exchange generates extra entropy.

$$dS = \frac{-dQ}{T_h} + \frac{dQ}{T_c}$$

Once we transfer the amount of dQ from hotter body to colder body we can not retract it back, because that would mean a decrease in entropy and the second law prohibits us to conduct such processes.

The above example is an example of irreversible process.

- Irreversible process is a process in which total entropy of a system plus surroundings increases!!!
- Reversible process is a process in which total entropy of a system plus surroundings is constant.



$$T_h \approx T_c \quad \text{infinitesimally small difference}$$

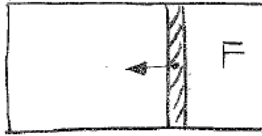
$$dS = 0$$

Another example of reversible process is a heat exchange with negligibly small difference between temperatures of “hot” and “cold” bodies.

$$\Delta S = 0$$

Questions

Does entropy of the system increase in adiabatic process?



Does the entropy of the system increase (decrease, stay constant) in isothermal compression?

In any stage of compression temperature of the surroundings and the system is the same.

$$dS = dQ/T$$

Does entropy of whole universe (system + surroundings) change?

Example: Not quasistatic (sufficiently fast) compression. There is some pressure “build up” in front of the piston.



$$dW = PdV \text{ – quasistatic process}$$

$$|dW| > |PdV| \text{ – fast compression} \quad (\text{here } P \text{ is equilibrium pressure})$$

Let's get signs right. Upon compression work done by the system is negative (from $dW = PdV$, dV is negative) = in fast compression we have

$$dW < PdV$$

(Is the above expression correct for fast expansion?)

So we compress the system, wait till equilibrium is settled. Now we want to compute the change in the entropy of the system and universe.

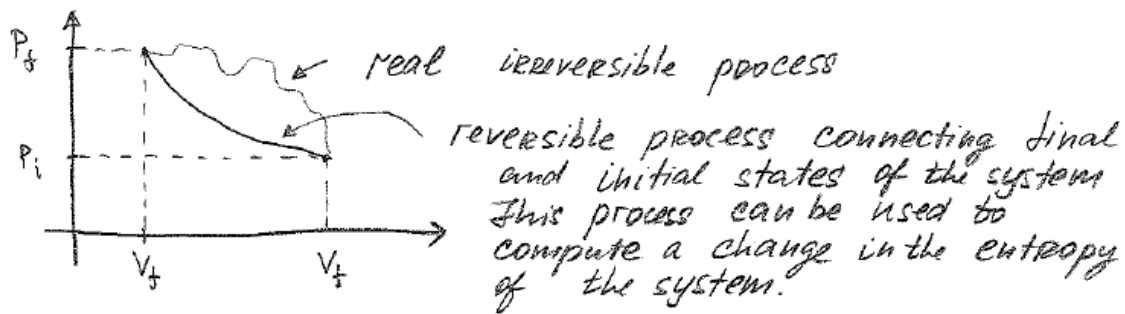
Is dS a total (exact) differential?

$$dS = \frac{dQ}{T} \text{ for reversible processes}$$

dS is an exact differential

$$S(U, N)$$

S characterizes the state, not the process.



Reversible process connecting final and initial state of the system, this process can be used to compute a change in the entropy of the system.

* Isothermal process $T = \text{constant}$, $\Delta U = 0$

So from 1st law $dQ = PdV$ ($dU = dQ - PdV$)

$dS_s = \frac{PdV}{T} < 0$ - The change of the entropy (of the system) is negative

(dS) total must be zero at best or positive. To find it we need to compute the entropy change of surroundings.

Real work $dW < PdV$

The heat $dQ_s = dW$ (from 1st law)

$dQ_{ex} = -dQ_s$ (The heat added to surroundings (dQ_{ex}) is the same as the heat released by the system or mathematically is minus heat added to the system, that is what we have written.

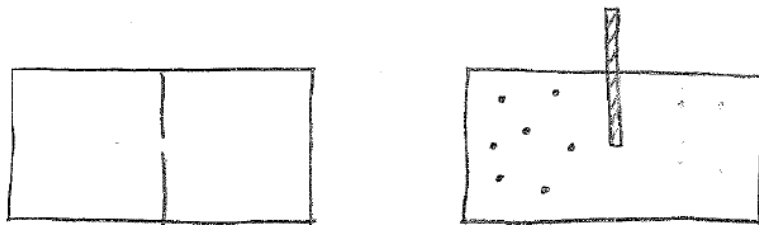
$$dS_t = dS_s + dS_{ext} = \frac{1}{T} (+PdV - dW) = \frac{|dW| - |PdV|}{T} > 0$$

Problem 3.28 (text book)

A liter of air, initially at room temperature and atmospheric pressure, is heated up at constant pressure until it doubles in volume. Calculate the increase in its entropy during this process.

What is the change in the universe entropy?

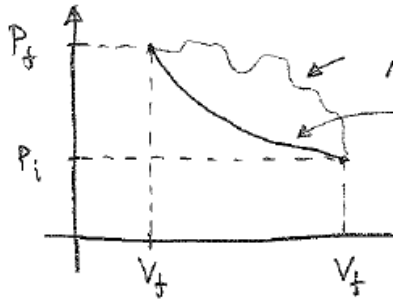
Expansion into vacuum



- 1) Energy of the system did not change
- 2) No work was done by system
- 3) There are no heat exchange

What happened to entropy? Of course it increased. Expansion into Vacuum is irreversible process. There is no way all molecules of gas collect themselves in the right portion of a chamber.

How do we find the change in entropy? Our initial and final states are well defined.



Entropy is a function of the state system, $S = k \ln g$. Entropy is defined by U , P , V , N or $P_1 V_1$ and $T_1 N$ (ideal gas considered here is a special case when U depends only on T).
Let us compute it as a problem