De Anza College

Thermodynamics
Second Law
Entropy

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Last time

- the Boltzmann distribution (distribution of energies)

- the Maxwell-Boltzmann distribution (distribution of speeds)

- the Second Law of thermodynamics

Overview

- entropy (macroscopic perspective)

- entropy (microscopic perspective) (?)

Reversible and Irreversible Processes
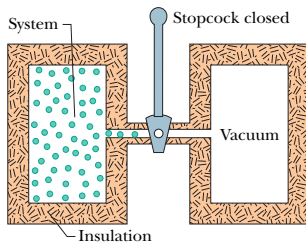
Reversible process

a process that takes a system from an initial state i to a final state f through a series of equilibrium states, such that we can take the same system back again from f to i along the same path in a PV diagram.

Irreversible process

any process that is not reversible.

In real life, all processes are irreversible, but some are close to being reversible. We use reversible processes as an idealization.
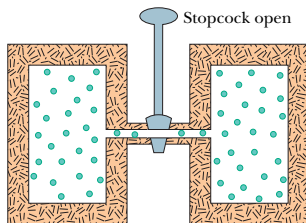
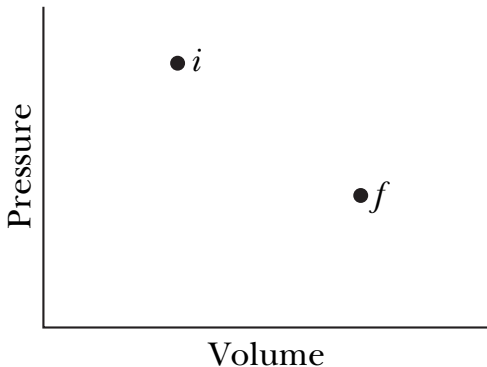# Irreversible Process Example

(a) Initial state i

Irreversible process

(b) Final state f

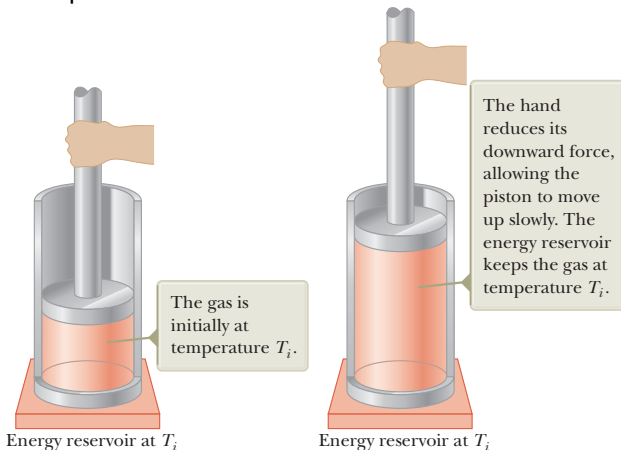# Irreversible Process Example

This process has well-defined initial and final equilibrium states, but during the expansion of the gas is not in equilibrium.

It cannot be plotted on a *PV* diagram. Also, no work is done on the gas in this process.

A Reversible Counterpart

Allow gas to expand very slowly through equilibrium states at constant temperature.

The gas is initially at temperature T_i.

The hand reduces its downward force, allowing the piston to move up slowly. The energy reservoir keeps the gas at temperature T_i.

Energy reservoir at T_i

Energy reservoir at T_i

A Reversible Counterpart

We can plot this isothermal expansion:
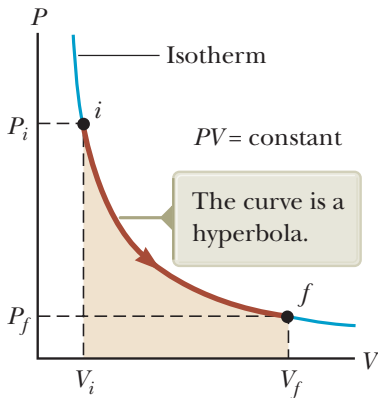
Negative work is done on the gas, heat is transferred in, and the internal energy and the temperature remain constant.

Comparing the Processes

In both of these processes the gas expands into a region it was not in previously.

The energy of the system spreads out.

This corresponds to a change of state, but it is not captured by the internal energy of the gas system, which does not change in either process.

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In both of these processes the gas expands into a region it was not in previously.

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This corresponds to a change of state, but it is not captured by the internal energy of the gas system, which does not change in either process.

Something does change in these processes and we call it *entropy*.

State Variables

State variables of a thermodynamics system are variables that are determined if the system is in thermodynamic equilibrium and you know the system's state.

Examples: pressure, volume, internal energy, temperature. Also, **entropy**.

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Each variable on it's own is not enough to determine the state of the system. (Many systems in different states might have the same volume.)

Once the current state is known, we do know all of these variables' values.

How the system arrived at its current state, does not affect these values. Heat and work are *not* state variables.

Entropy

Sadi Carnot discovered that the most efficient possible engine must be reversible (more on this to come).

Rudolph Clausius interpreted this as being due to the behavior of a new quantity (entropy).

The change in entropy moving between two states i and f is:

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

where dQ_r is an infinitesimal heat transfer when the system follows a reversible path.

(T can be a function of Q!)

Entropy Example # 42

An ice tray contains 500 g of liquid water at 0 degrees C. Calculate the change in entropy of the water as it freezes slowly and completely at 0 degrees C.

Entropy

When a reversible path is followed:

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

Can we find the entropy change for an irreversible process?

Entropy

When a reversible path is followed:

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Can we find the entropy change for an irreversible process?

Yes! Since entropy is a state variable, we can consider the entropy change in **any reversible process with the same initial and final states**.

Then:

$$\Delta S_{irr} = \int_i^f \frac{dQ_r}{T}$$

The entropy change in that process will give us the entropy difference between those two states, regardless of the process.

Entropy Change

Consider an initial state i and final state f.

We can find the entropy change moving between those two states (for any process, reversible or irreversible), by finding the entropy change along an arbitrary reversible path.

First law,

$$dE_{int} = dW + dQ_r$$

Rearranging, we can find an expression for dQ_r, using $\Delta E_{int} = nC_V \Delta T$:

$$dQ_r = nC_V \, dT + P \, dV$$

To find entropy, we multiply by $1/T$ and integrate:

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \int_i^f \frac{nC_V}{T} \, dT + \int_i^f \frac{P}{T} \, dV$$

Entropy Change

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \int_i^f \frac{nC_V}{T}\, dT + \int_i^f \frac{P}{T}\, dV$$

Finally, replace $\frac{P}{T} = \frac{nR}{V}$ (ideal gas):

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \int_i^f \frac{nC_V}{T}\, dT + nR \int_i^f \frac{1}{V}\, dV$$

The entropy difference is:

$$\Delta S = nC_v \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

Question

Quick Quiz 22.6[1] True or False: The entropy change in any adiabatic process must be zero because $Q = 0$.

(A) True
(B) False

[1]Serway & Jewett, page 673.

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Example (Macroscopic Entropy Analysis)

What is the entropy change during an adiabatic free expansion of an isolated gas of n moles going from volume V_i to volume V_f? (Note: such a process is not reversible.)

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In an adiabatic free expansion $Q = 0$, and since its isolated, $W = 0$, and therefore $\Delta E_{int} = 0$ and $T_f = T_i$.

$$\Delta S = nC_v \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

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$$\Delta S = nC_v \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

using $\ln 1 = 0$ becomes

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

Example

Exercise for you:

What is the entropy change the same n moles of gas (a diatomic gas around room temperatures) in an constant volume process, with temperature going T_i to T_f?

What is the entropy change when the pressure is constant and the volume goes V_i to V_f?

Question

Quick Quiz 22.5[2] An ideal gas is taken from an initial temperature T_i to a higher final temperature T_f along two different reversible paths. Path A is at constant pressure, and path B is at constant volume. What is the relation between the entropy changes of the gas for these paths?

(A) $\Delta S_A > \Delta S_B$
(B) $\Delta S_A = \Delta S_B$
(C) $\Delta S_A < \Delta S_B$

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(B) $\Delta S_A = \Delta S_B$
(C) $\Delta S_A < \Delta S_B$

Clausius Equality

Clausius found that the entropy change around any reversible cycle (closed path) is zero.

This is called the Clausius Equality:

$$\Delta S = \oint \frac{dQ_r}{T} = 0$$

And moreover that since real engines can never quite conform to this ideal, for all engines the Clausius Inequality holds:

$$\Delta S = \oint \frac{dQ_r}{T} \geqslant 0$$

Entropy in an isolated system

This gives us another way to state the second law:

2nd Law

In an isolated system, entropy does not decrease. $\frac{dS}{dt} \geqslant 0$

In a non-isolated system (either closed or open) entropy can decrease, but only by increasing the entropy of the environment at least as much.

Summary

- entropy as a thermodynamic variable (macroscopic perspective)
- entropy (microscopic perspective) (?)

Homework Serway & Jewett:

- Ch 22, onward from page 679. CQs: 9; OQs: 9, 11; Probs: 43, 45, 47, 53 (entropy problems)