



# **Thermodynamics**

## **Second Law**

### **Entropy**

Lana Sheridan

De Anza College

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## Last time

- the Maxwell-Boltzmann distribution (distribution of speeds)
- the Second Law of thermodynamics

# Overview

- entropy (macroscopic perspective)

# Reversible and Irreversible Processes

## Reversible process

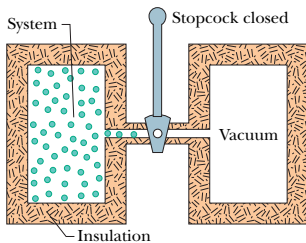
a process that takes a system from an initial state  $i$  to a final state  $f$  through a series of equilibrium states, such that we can take the same system back again from  $f$  to  $i$  along the same path in a  $PV$  diagram.

## 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.

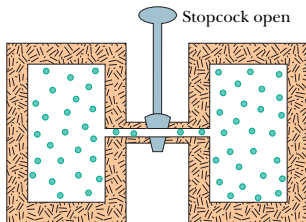
# Irreversible Process Example



(a) Initial state  $i$



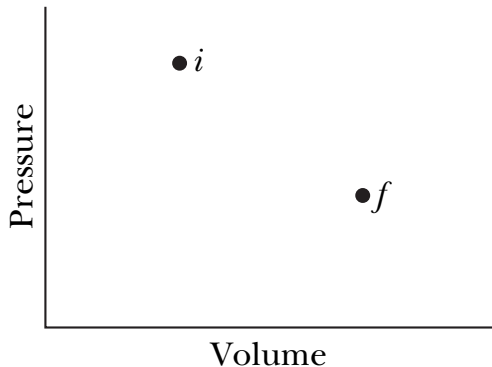
Irreversible  
process



(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.

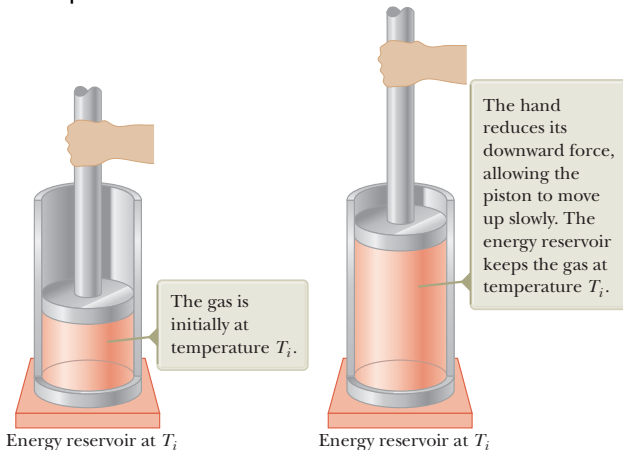


It cannot be plotted on a  $PV$  diagram. Also, no work is done on the gas in this process.

## A Reversible Counterpart

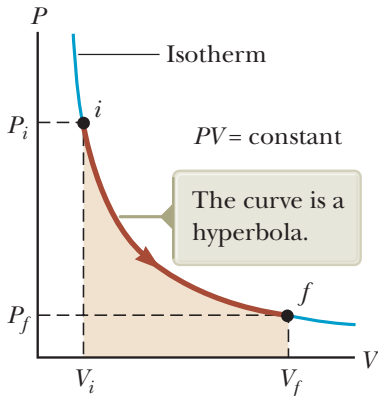
This process has the same starting and ending points.

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



# 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.

## Comparing the Processes

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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. (They are transfer 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:

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Can we find the entropy change for an irreversible process?

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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,

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

Rearranging, we can find an expression for  $dQ_r$ , using

$$\Delta E_{\text{int}} = nC_V \Delta T:$$

$$dQ_r = nC_V dT + P dV$$

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**<sup>1</sup> True or False: The entropy change in **any** adiabatic process must be zero because  $Q = 0$ .

- (A) True
- (B) False

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<sup>1</sup>Serway & Jewett, page 673.

## Question

**Quick Quiz 22.6**<sup>1</sup> True or False: The entropy change in **any** adiabatic process must be zero because  $Q = 0$ .

- (A) True
- (B) False ←

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<sup>1</sup>Serway & Jewett, page 673.

# Summary

- entropy as a thermodynamic variable (macroscopic perspective)

**Test** next week on Ch 21 & 22.

## Homework

- new WebAssigns