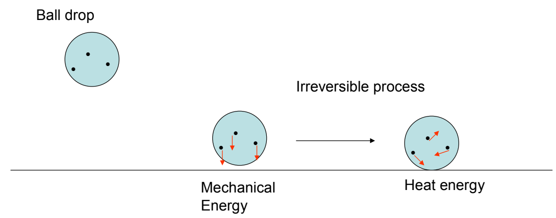
Second Law of Thermodynamics 10.2

Entropy
Quality of Heat
Order / Disorder

Reversible /Irreversible processes



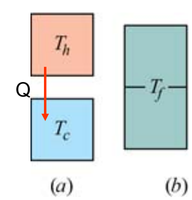
Irreversible process
-proceeds spontaneously
-associated with increasing disorder

The reversal of an irreversible process is improbable (even though it may be possible according to the First Law of Thermodynamics)

Entropy

Heat
Entropy is a state function that governs the availability of heat to do work.
Disorder/Order
The entropy of the system is a measure of the disorder of the system.
The entropy increases for irreversible (spontaneous) processes.
The entropy of the universe is increasing leading to greater disorder.

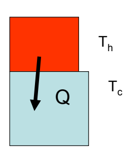
Irreversible Heat Flow



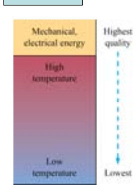
Heat flow from high T to low T is irreversible

The initial (a) and final (b) states have the same energy but have different ability to do work

Quality of Heat



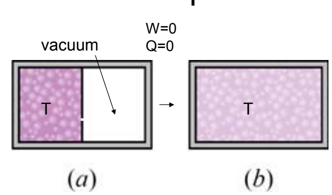
Heat flows from high temperature to low temperature.



High temperature sources of heat can be converted to work with higher efficiency.

High temperature is a measure of the quality of the heat.

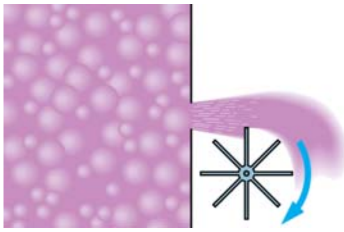
Irreversible free expansion of a gas



The gas is allowed to expand into a vacuum, in an insulated container from a to b without doing work or taking up heat. .
eg by poking a hole in the barrier.

For this case $\Delta U = 0$.
The two states a and b have the same internal energy but have different abilities to do work

Work could be done by the gas



Entropy is a state function

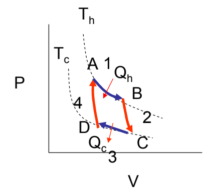
To study the properties of a system we use a reversible Carnot cycle.

Define the change in Entropy

$$\Delta S = \int \frac{dQ}{T}$$

The change in a cyclic process is

$$\oint \frac{dQ}{T} = 0$$

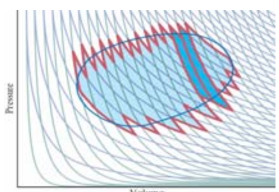


For the Carnot cycle

$$\oint \frac{dQ}{T} = \frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0$$

Here Q_c is negative since heat goes out of the gas.

Any cycle can be constructed from a sum of Carnot cycles.



Therefore, for any arbitrary cycle

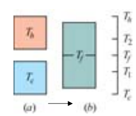
$$\oint dS = \oint \frac{dQ}{T} = 0$$

Entropy S is a state function for any system.

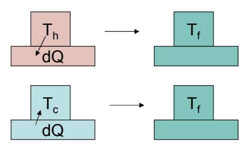
Entropy change in irreversible heat flow

Since S is a state function we can calculate ΔS for irreversible processes from the properties of the initial and final states.

For irreversible heat flow from state (a) to state (b) the change in entropy can be calculated by changing the temperature reversibly.



heat bath
T varies



$$\Delta S_h = \int_{T_h}^{T_f} \frac{dQ}{T} = \frac{\Delta Q}{T_2}$$ average T $T_2 > T_f$

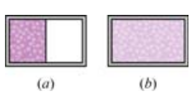
$$\Delta S_c = \int_{T_c}^{T_f} \frac{dQ}{T} = \frac{\Delta Q}{T_1}$$ average T $T_1 < T_f$

$$\Delta S = \Delta S_h + \Delta S_c = \frac{Q_h}{T_2} + \frac{Q_c}{T_1} = \frac{-Q_c}{T_2} + \frac{Q_c}{T_1} = Q_c\left(-\frac{1}{T_2} + \frac{1}{T_1}\right) > 0$$

$\Delta S > 0$ for irreversible heat flow

Entropy change in irreversible free expansion of a gas

Calculate ΔS for transition from (a) to (b). Free expansion, with no heat transfer.



How does T change? T remains unchanged

How can we go reversibly from a to b? By an isothermal expansion.

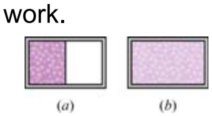
Calculate ΔS. since Q=W for isothermal expansion

$$\Delta S = \frac{Q}{T} = \frac{W}{T} \quad \text{and} \quad W = nRT\ln\frac{V_2}{V_1}$$

$$\Delta S = nR\ln\frac{V_2}{V_1}$$ since $V_2 > V_1$ $\Delta S > 0$

Entropy Increases for the irreversible process

The change in entropy reflects the loss of ability to do work.



Work that could have been done by (a) -> (b) is

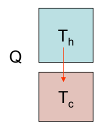
$$W = nRT\ln\frac{V_2}{V_1} = T\Delta S$$

$$E_{unavailable} = T_{min}\,\Delta S$$

During an irreversible process in which the entropy of the system increases by ΔS, the energy $E = T_{min}\,\Delta S$ becomes unavailable to do work. T_{min} is the coolest temperature available to the system.

Loss of available energy in irreversible heat transfer.

Suppose a quantity of heat Q flows from T_h to T_c. The quantity of heat is much smaller than the heat capacity of the reservoirs so that the temperatures of the reservoirs don't change. Find the change in the ability to do work.



ΔS

$$\Delta S = \Delta S_h + \Delta S_c = -\frac{Q}{T_h} + \frac{Q}{T_c} = Q\left(-\frac{1}{T_h} + \frac{1}{T_c}\right) > 0$$

$E_{unavailable}$

$$E_{unavailable} = T_{min}\Delta S = T_c Q\left(-\frac{1}{T_h} + \frac{1}{T_c}\right) = Q\left(1 - \frac{T_c}{T_h}\right)$$

Lowering the temperature lowers the Carnot efficiency of the heat

Question

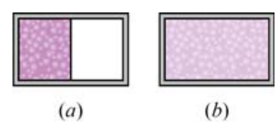
A 250 g pot of water is heated from 10°C to 95°C. How much does the entropy of the water change? (c_{water} =4184 J/kg K)

Question

In an adiabatic free expansion 8.7 mol of an ideal gas at 450 K expands 10-fold in volume. How much energy becomes unavailable to do work?

Entropy and Disorder

free expansion of a gas



The gas molecules have a larger accessible volume in b than in a.

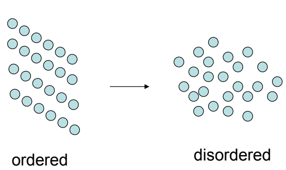
The state (a) is more improbable than (b) - How probable is it to go from b to a by random motion of the gas molecules?

Increased entropy in a -> b is due to an increased disorder.

$$\Delta S > 0$$

Entropy and disorder

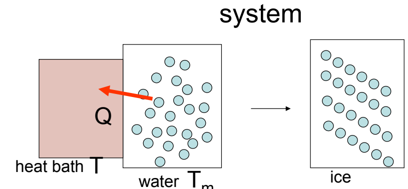
ice melting



$$\Delta S_{ice} = \frac{Q}{T_m} > 0$$

The increase in entropy upon ice melting is due to the disordering in the liquid state.

Decreased in entropy for one system must be coupled to an entropy increase in another system



$$\Delta S_{heatbath} = \frac{Q}{T} > 0 \qquad \Delta S_{water} = \frac{Q}{T_m} < 0$$

but $T \leq T_m$

$$\Delta S = \Delta S_{water} + \Delta S_{heat\ bath} > 0$$

The change in entropy for the total system must increase.

Entropy statement of the second law of thermodynamics

The entropy of a closed system can never decrease.

$$\Delta S \geq 0$$

A closed system does not exchange heat or energy with its environment.

This is equivalent to the statement that heat does not flow from low to high temperatures and that heat cannot be converted to work with 100% efficiency since these would result in a decrease in entropy.

Living things are open systems

The decrease in entropy in growth is driven by coupling to energy inputs.

The earth is an open system

The decrease in entropy is driven by energy from the sun.