
The Second Law of Thermodynamics

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- The second law of thermodynamics states that processes occur in a certain direction, not in just any direction.
 - Physical processes in nature can proceed toward equilibrium spontaneously:

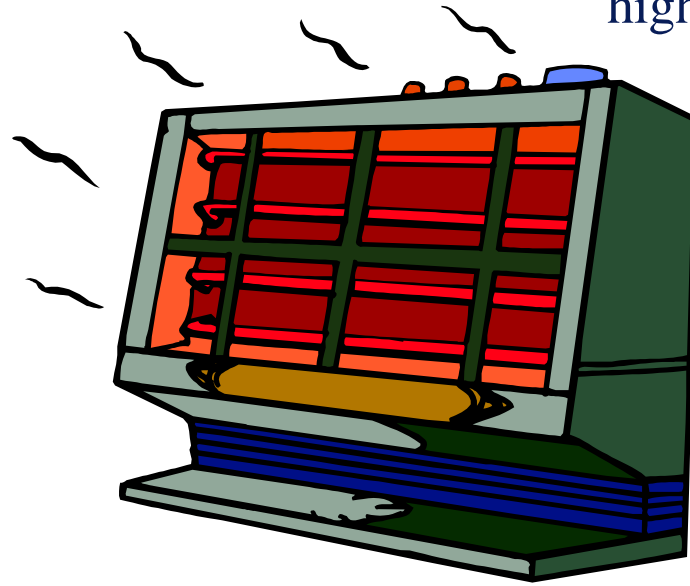
Examples



Water always flows downhill



Gases always expand from
high pressure to low pressure



Heat always flows from high temperature to low temperature

Can We Take Advantage of These Processes?

- Yes!! We can use them to produce work
- Or... we can just let them happen and lose the opportunity.

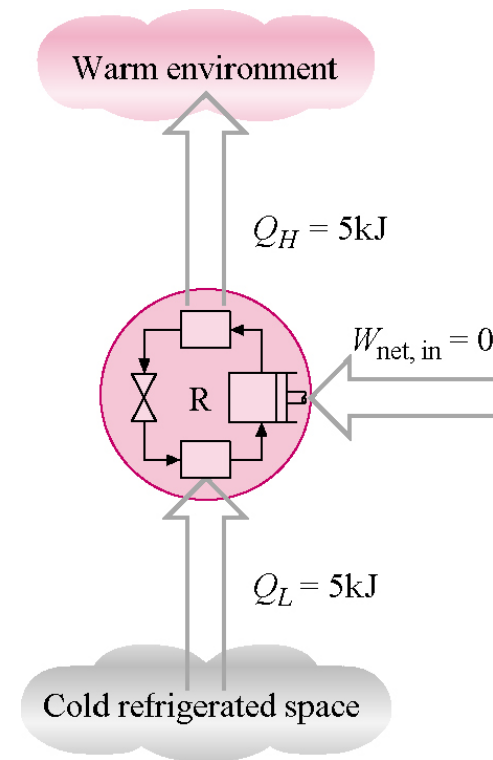
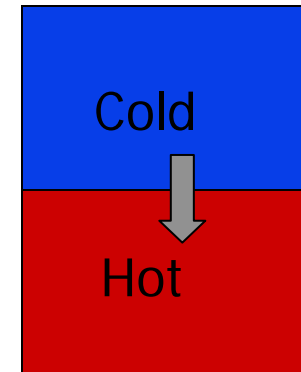
Can we reverse these processes?

- It requires the expenditure of work
- The first law gives us no information about the direction in which a process occurs – it only tells us that energy must balance
- The second law tells us what direction processes occur

Clausius Statement of the Second Law

It is *impossible* to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.

In order to accomplish heat transfer from cold to hot – you need a device, like a heat pump or refrigerator, that consumes work.



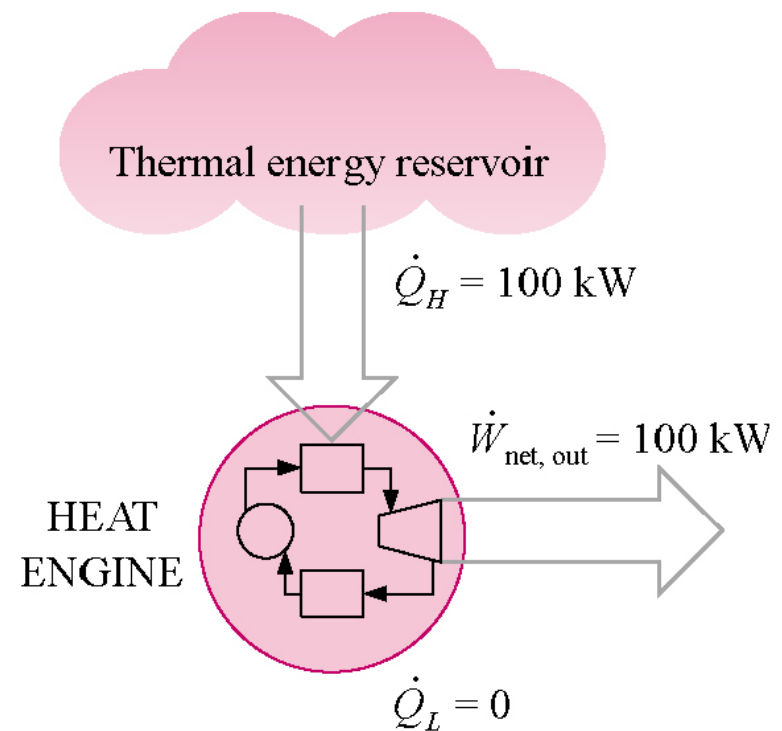
Energy from the surroundings in the form of work or heat has to be expended to force heat to flow from a low-temperature media to a high-temperature media. Thus, the COP of a refrigerator or heat pump must be less than infinity.

$$COP_R = \frac{Q_L}{W_{net}} < \infty$$

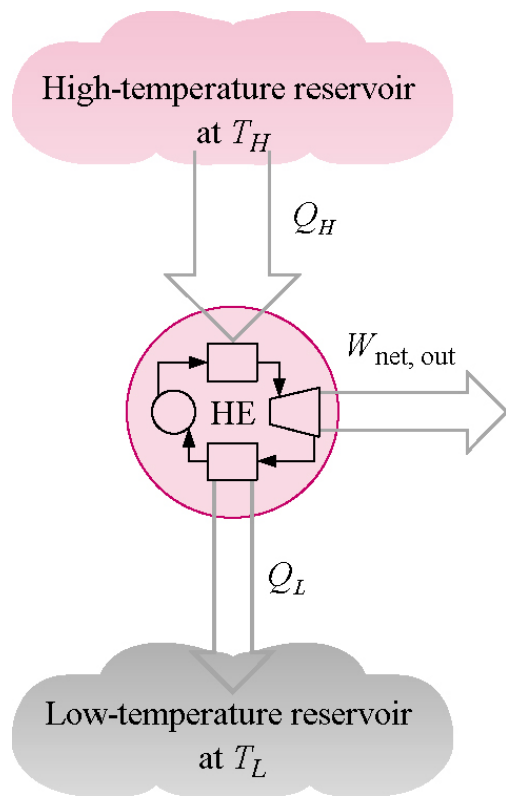
$$COP_{HP} = \frac{Q_H}{W_{net}} < \infty$$

Kelvin-Planck Statement of the Second Law

It is *impossible* for any device that operates on a cycle, to receive heat from a single reservoir and produce a net amount of work.



The Kelvin-Planck statement of the second law of thermodynamics states that no heat engine can produce a net amount of work while exchanging heat with a single reservoir only. In other words, the maximum possible efficiency is less than 100%.



$$\eta_{th} = \frac{W_{net, out}}{Q_{in}} < 100\%$$

So What is the Best You Can Do?

- We know that Coefficients of Performance for refrigerators and heat pumps must be less than infinity, but how much less?
- We know that thermal efficiencies for heat engines must be less than 100%, but how much less?

It Depends on... Irreversibility

Reversible Process

- A process is *reversible* if both the system and its environment can be returned to their states before the process.
- Only ideal situations are ever reversible. Example: a frictionless roller coaster.
- Any process that happens spontaneously is irreversible. Examples: friction turning mechanical energy into heat; a drop of ink spreading out when it falls into a bucket of water.

Reversible Processes

- Heat pumps, refrigerators and heat engines all work best reversibly
- Reversible processes don't have any losses such as
 - *Friction*
 - *Unrestrained expansion of gases*
 - *Heat transfer through a finite temperature difference*
 - *Mixing of two different substances*
 - *Any deviation from a quasi-static process*
- The internally reversible process is a quasi-equilibrium process, which once having taken place, can be reversed without any changes in the system. This says nothing about what happens to the surroundings around the system.
- The externally reversible process is a quasi-equilibrium process, which once having taken place, can be reversed without any changes in the system or surroundings.

Reversible processes represent the best that we can do.

Carnot Cycle

- Named for French engineer *Nicolas Sadi Carnot* (1769-1832)
- One example of a *reversible* cycle
- Composed of four *reversible* processes
 - 2 adiabatic heat transfer
 - 2 reversible isothermal heat transfer

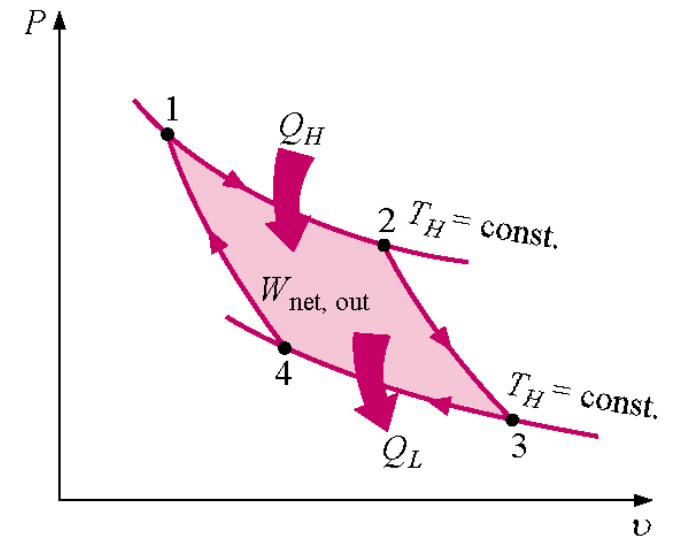
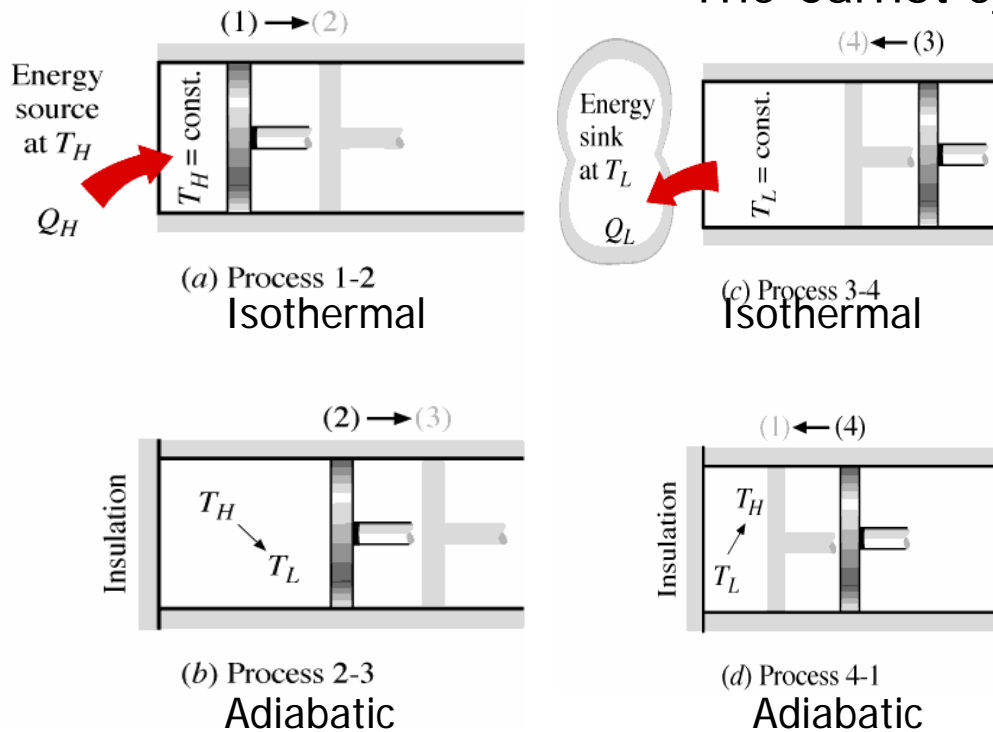
Carnot Cycle

- Process 1-2 Reversible isothermal heat addition at high temperature, $T_H > T_L$ to the working fluid in a piston--cylinder device which does some boundary work.
- Process 2-3 Reversible adiabatic expansion during which the system does work as the working fluid temperature decreases from T_H to T_L .
- Process 3-4 The system is brought in contact with a heat reservoir at $T_L < T_H$ and a reversible isothermal heat exchange takes place while work of compression is done on the system.

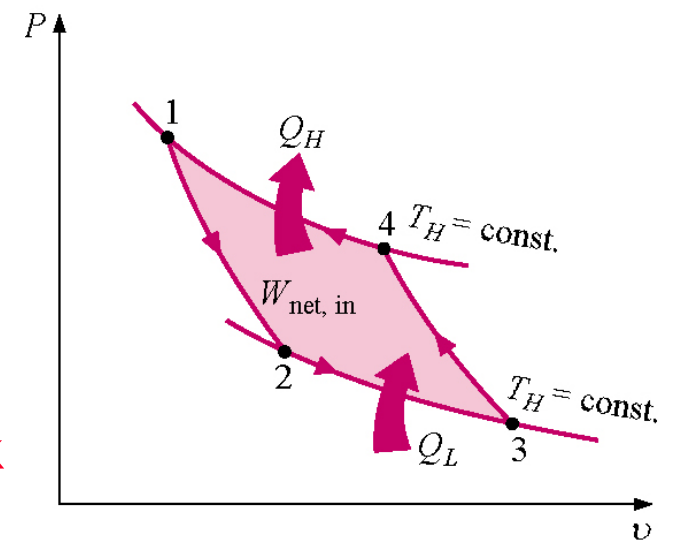
Process 4-1 A reversible adiabatic compression process increases the working fluid temperature from T_L to T_H

Carnot Cycle

The Carnot cycle is a reversible heat engine



A reversed Carnot Cycle is a refrigerator or a heat pump



The area inside these figures represent the work

The *Carnot principles* state that the thermal efficiencies of all reversible heat engines operating between the same two reservoirs are the same, and that no heat engine is more efficient than a reversible one operating between the same two reservoirs.

- These statements form the basis for establishing a thermodynamic temperature scale related to the heat transfers between a reversible device and the high- and low-temperature reservoirs by

$$\left(\frac{Q_H}{Q_L} \right)_{rev} = \frac{T_H}{T_L}$$

- Therefore, the Q_H/Q_L ratio can be replaced by T_H/T_L for reversible devices, where T_H and T_L are the absolute temperatures of the high- and low-temperature reservoirs, respectively.

Efficiency of a Carnot Engine

For a **reversible** cycle the amount of heat transferred is proportional to the temperature of the reservoir

$$\eta_{rev} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

Only true for the reversible case

COP of a Reversible Heat Pump and a Reversible Refrigerator

$$COP_{HP,rev} = \frac{1}{1 - Q_L/Q_H} = \frac{1}{1 - T_L/T_H}$$

Only true for the reversible case

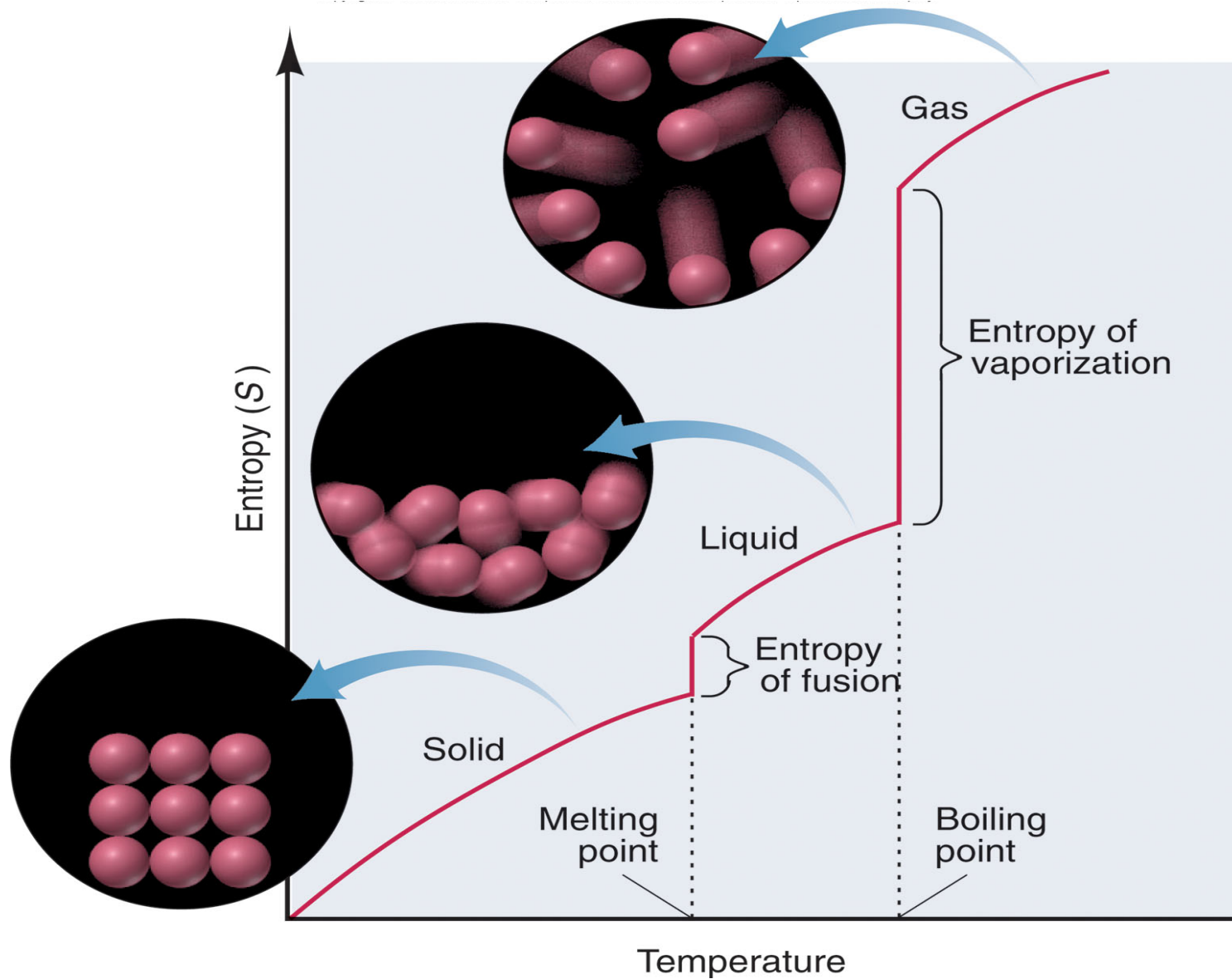
$$COP_{R,rev} = \frac{1}{Q_H/Q_L - 1} = \frac{1}{T_H/T_L - 1}$$

Reversible and Real Systems Comparison

- The efficiency of a reversible heat engine, such as a Carnot engine, is always higher than a real engine
- The COP of a reversible heat pump is always higher than a real heat pump
- The COP of a reversible refrigerator is always higher than a real refrigerator

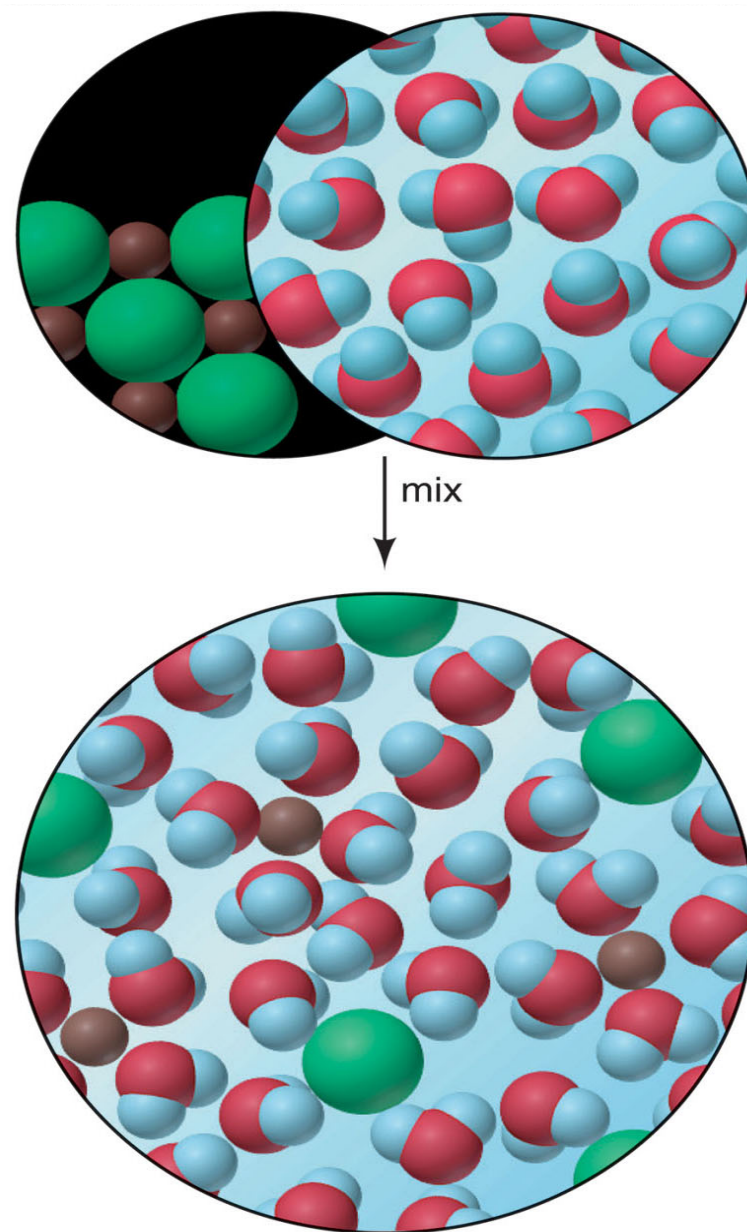
Entropy

Gases Have More Entropy Than Liquids Which Have More Than Solids



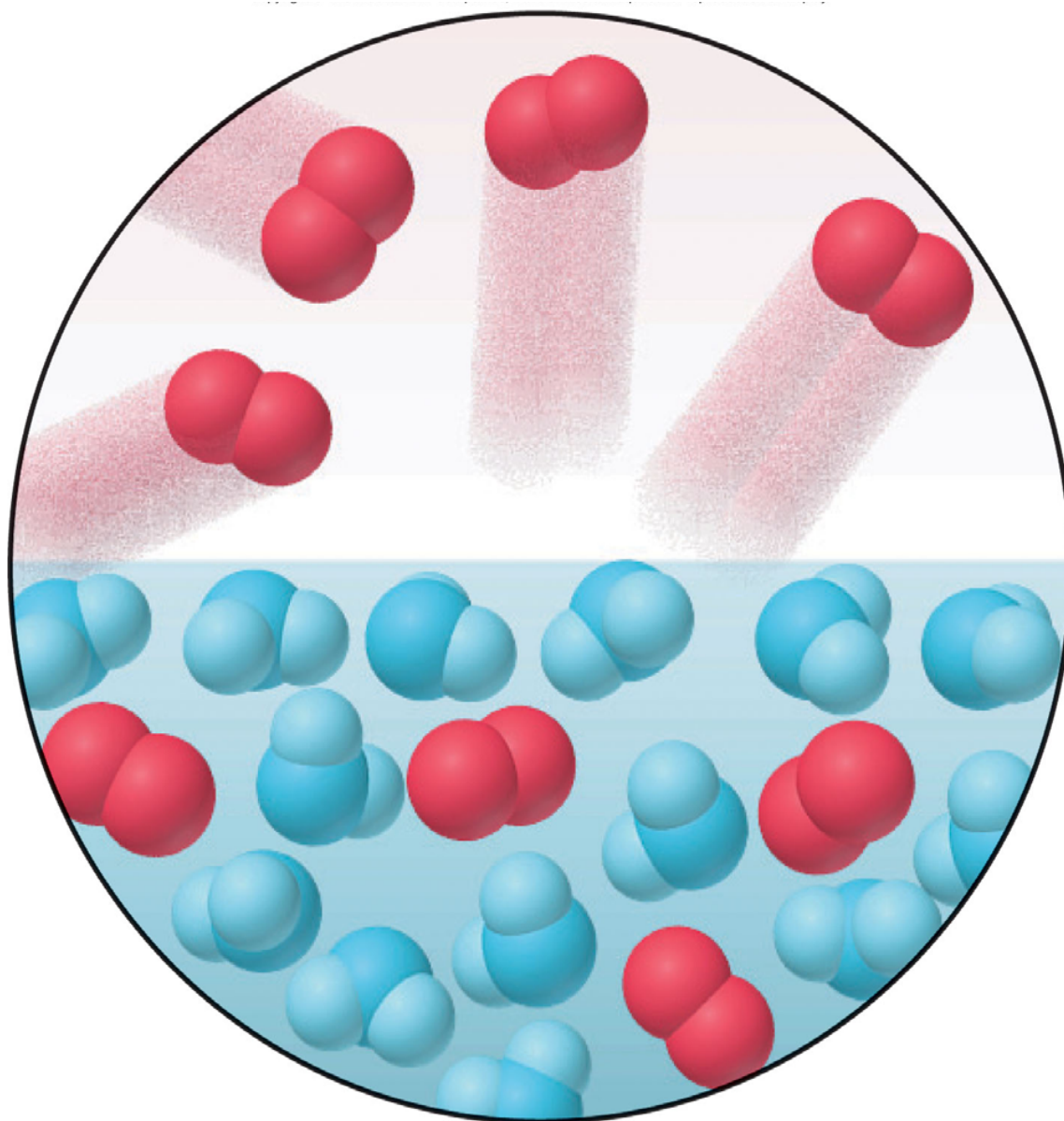
Entropy

Entropy always favors making solutions because there are more possible arrangements of the atoms or molecules



Entropy

Entropy decreases
when a gas dissolves
in a liquid



Entropy

Entropy increases during these processes

