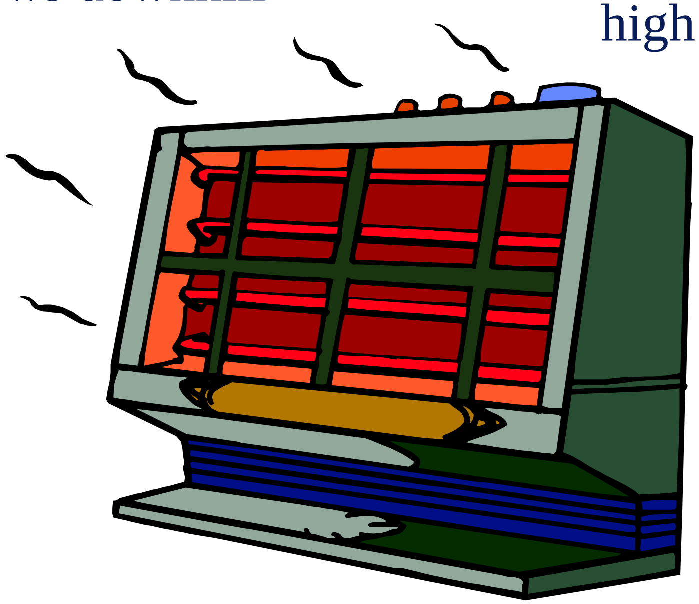
The Second Law of Thermodynamics

- 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?

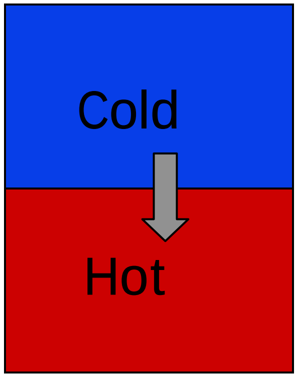
- Yes!! We can use them to produce work
- Or… we can just let them happen and lose the opportunity.

Can we reverse these processes?

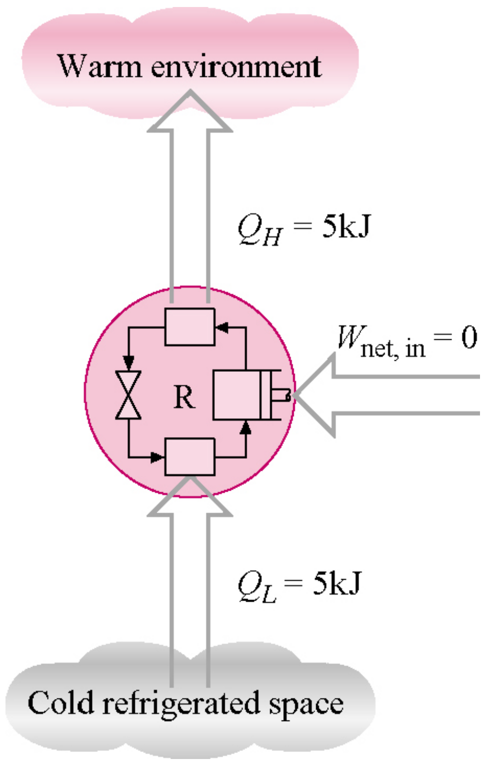
- It requires the expenditure of work
- The first law gives us no information about the direction in which a process occurs – it only tells us that energy must balance
- The second law tells us what direction processes occur

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.

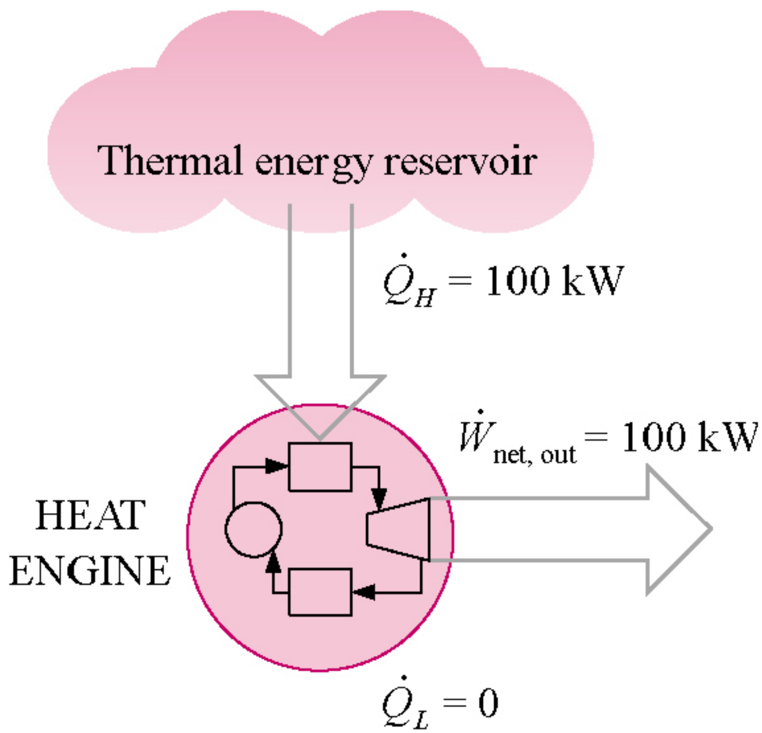


Energy from the surroundings in the form of work or heat has to be expended to force heat to flow from a low-temperature media to a high-temperature media. Thus, the CP of a refrigerator or heat pump must be less than infinity.

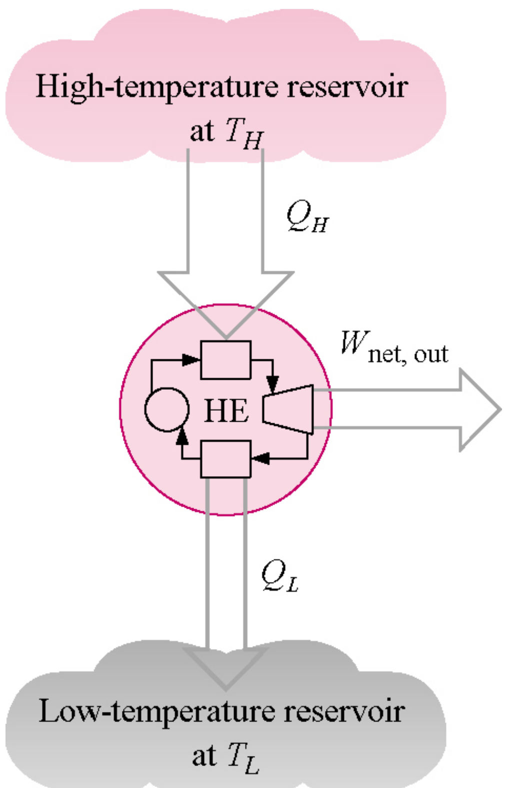
$$CP_R = \frac{Q_L}{W_{net}} < \infty \qquad CP_{HP} = \frac{Q_H}{W_{net}} < \infty$$

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 surroundings can be returned to their initial states.
- 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

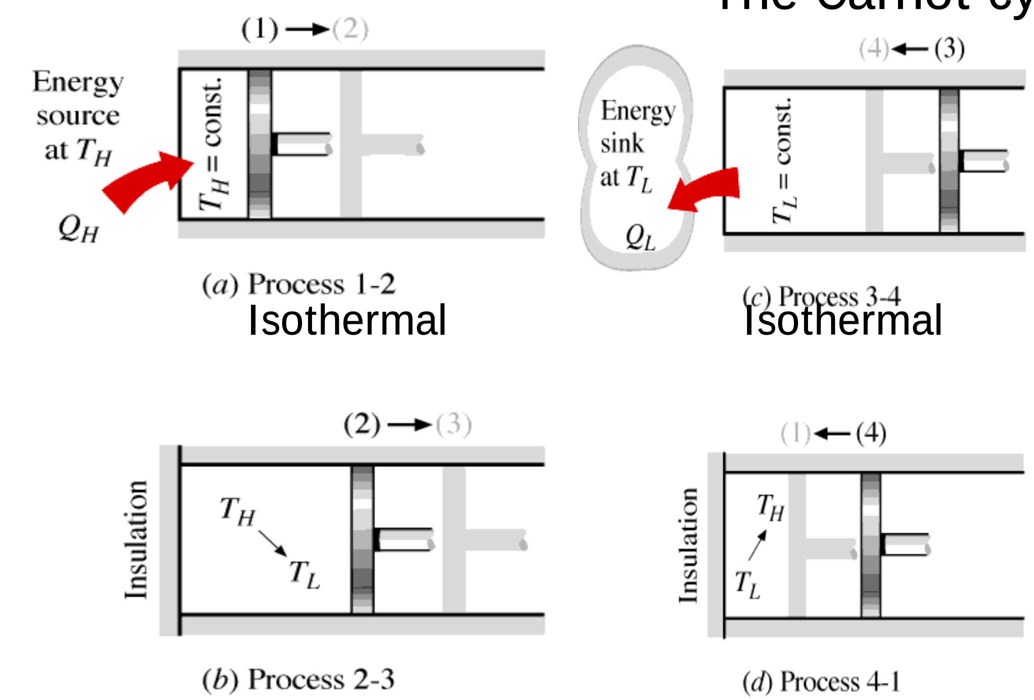
Carnot Cycle

- 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

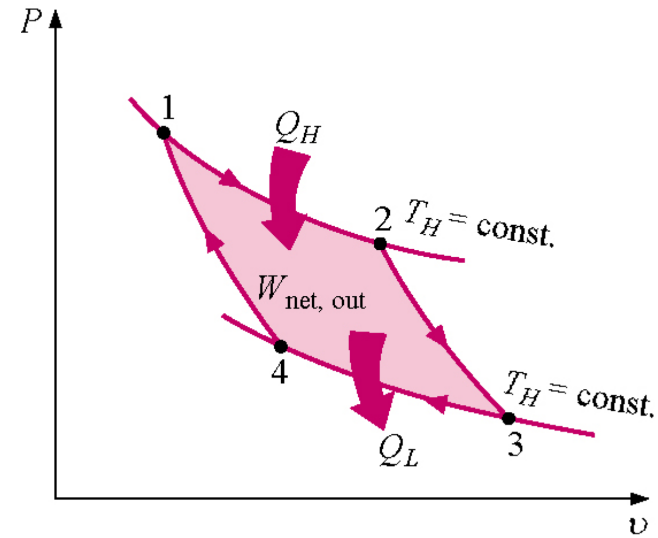


Isothermal

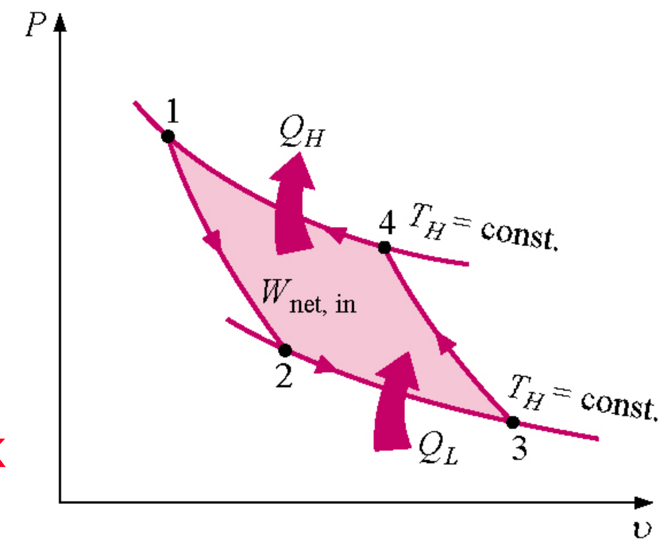
Isothermal

Adiabatic

Adiabatic



A reversed Carnot Cycle is a refrigerator or a heat pump



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Carnot Cycle

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

CP of a Reversible Heat Pump and a Reversible Refrigerator

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

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

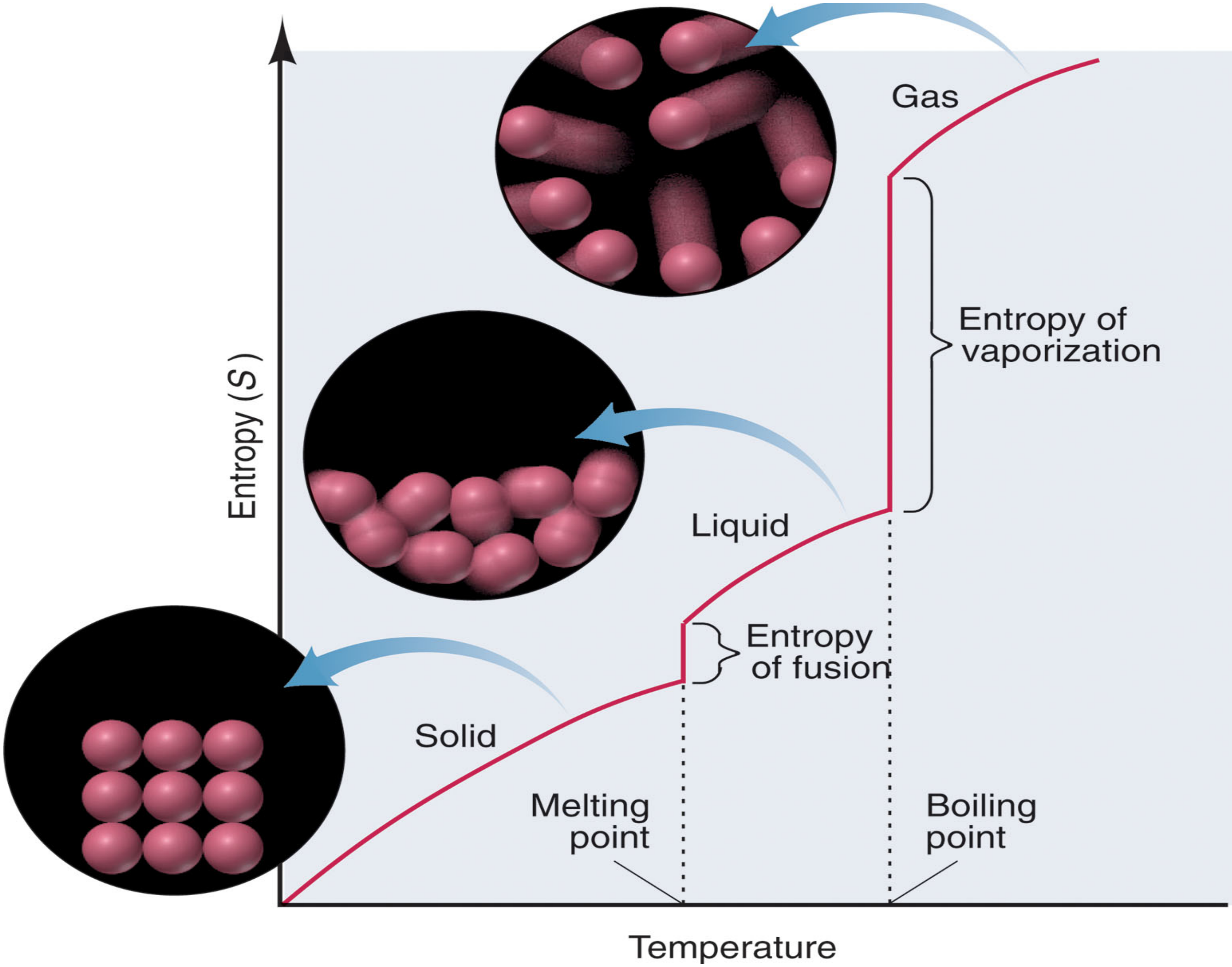
Only true for the reversible case

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 CP of a ***reversible*** heat pump is always ***higher*** than a real heat pump
- The CP of a ***reversible*** refrigerator is always ***higher*** than a real refrigerator

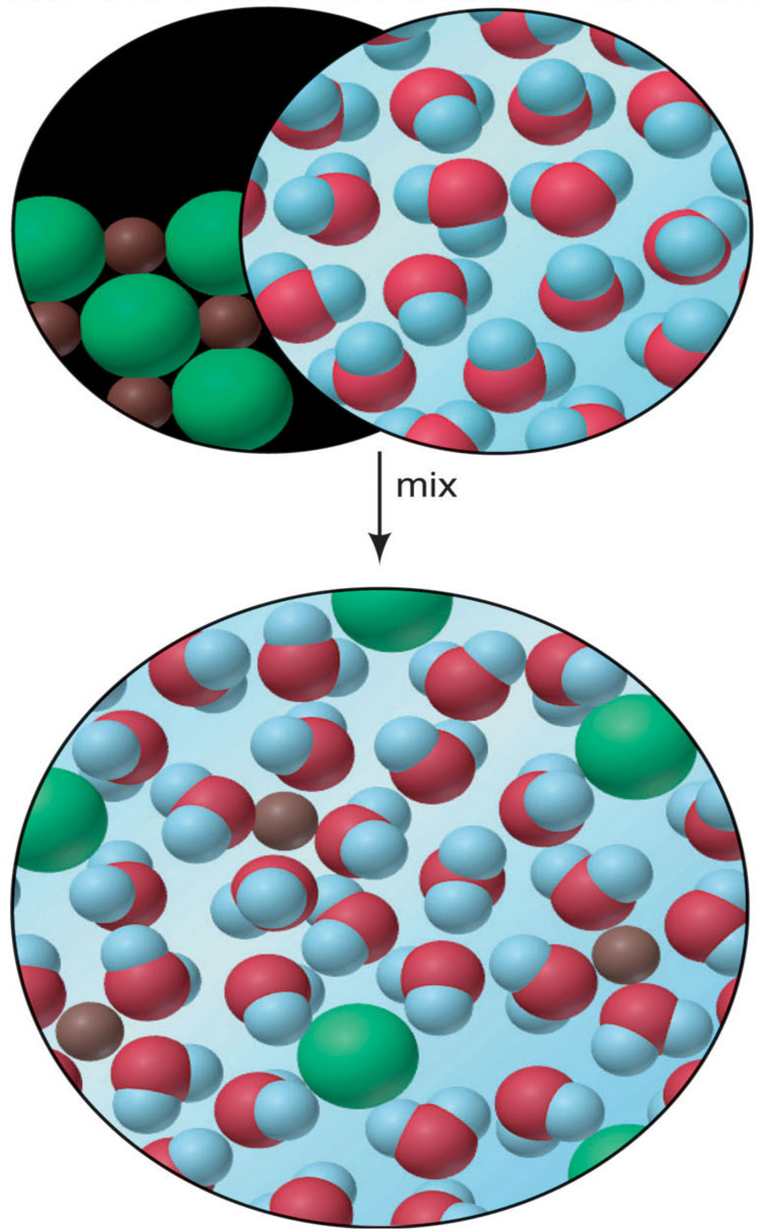
Entropy

Gases have more entropy than liquids which have more than solids.



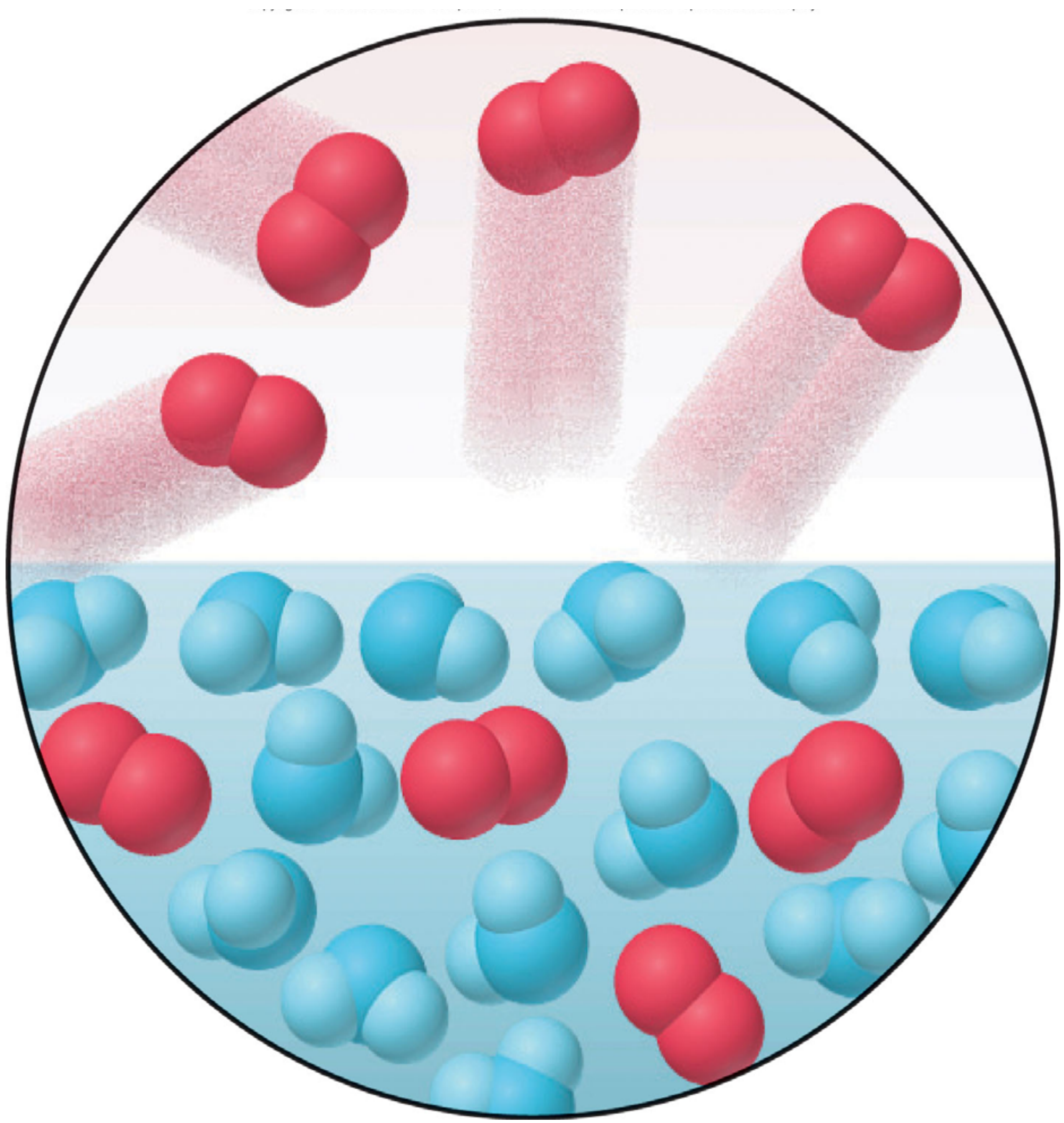
Entropy

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