Second Law

While his dune buggy is being repaired, Schmedrick decides to take a to the Alps to practice his yodeling up in the mountains. As fate would have it, one of his yodels touches off an avalanche, and thousands of tons of snow crash down in a distant valley. The gravitational potential energy the snow had before falling is now thermal energy, as the 1st Law requires. Is it possible for an avalanche to happen in reverse? *answer:*

The first law does not prohibit the snow from suddenly rising, so long as it the potential energy is regains comes from somewhere, such as the thermal energy of the surrounding air. In other words, the 1st Law allows a "reverse avalanche" if the surroundings become cooler. Thermal energy is converted into potential energy, and energy is conserved. The 2nd Law forbids this, however, since a reverse avalanche would mean a decrease in entropy in the region around the valley. There is more about entropy on upcoming slides.

Entropy: Statistical Approach

Entropy is related to probability. Let’s look at the possible outcomes of flipping four coins, of which there are sixteen ($2^4 = 16$). The outcomes are grouped into macrostates according to the number of heads. Each macrostate is made up a microstates. For example, the 3-heads macrostate is comprised of 4 microstates, because there are 4 combinations that yield 3 heads. One microstate in the 3-heads macrostate is H H T H. The number of microstates in a macrostate determines how likely that state is to exist.

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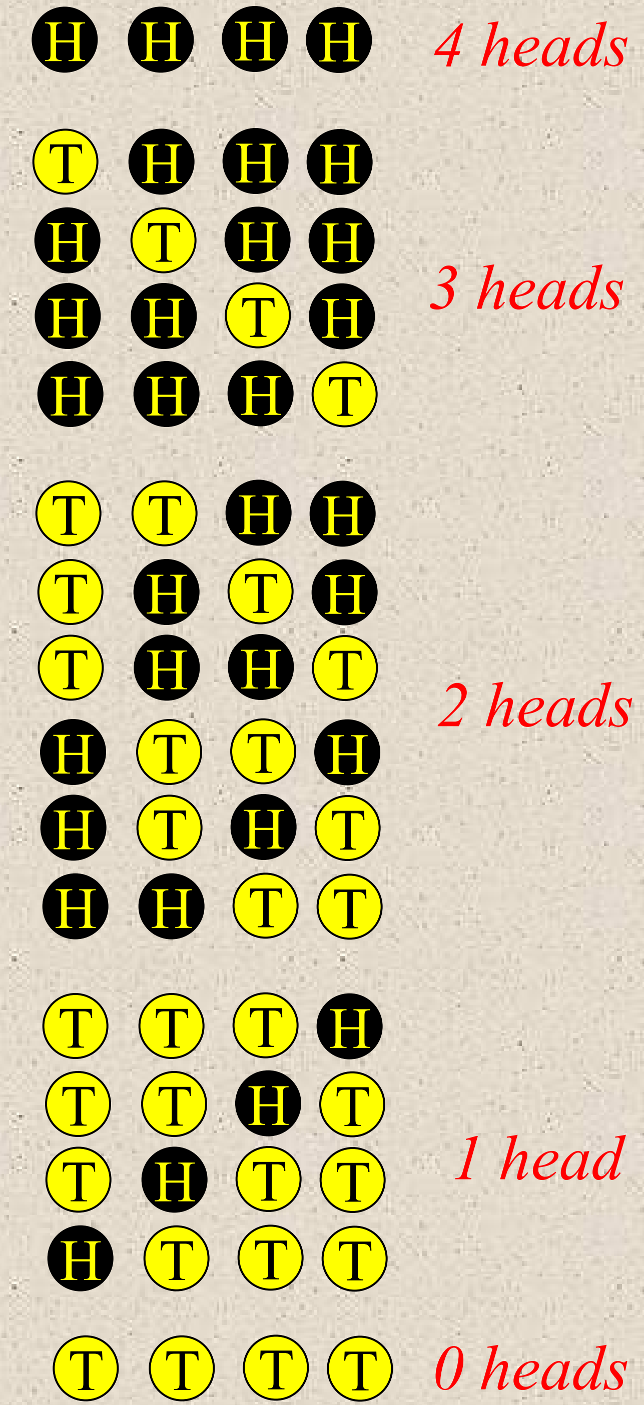

Entropy *(cont.)*

Macrostate	# of Microstates	Probability
0	1	1 / 16
1	4	1 / 4
2	6	3 / 8
3	4	1 / 4
4	1	1 / 16

Macrostate 3 (the group w/ 3 heads) is the most probable since it contains the most microstates (combinations). Macrostate 2 has 6 microstates, so its probability is 6 / 16 = 3 / 8. This macrostate is the most random, or disordered, since there are so many ways 2 heads can come up in 4 flips. Entropy is a measure of disorder, and for this system it's at a max when in macrostate 2. Minimum entropy occurs when the coins are in macrostate 0 or 4, since there is a high degree of order in these states--only one microstate each. These are the least likely microstates to occur.

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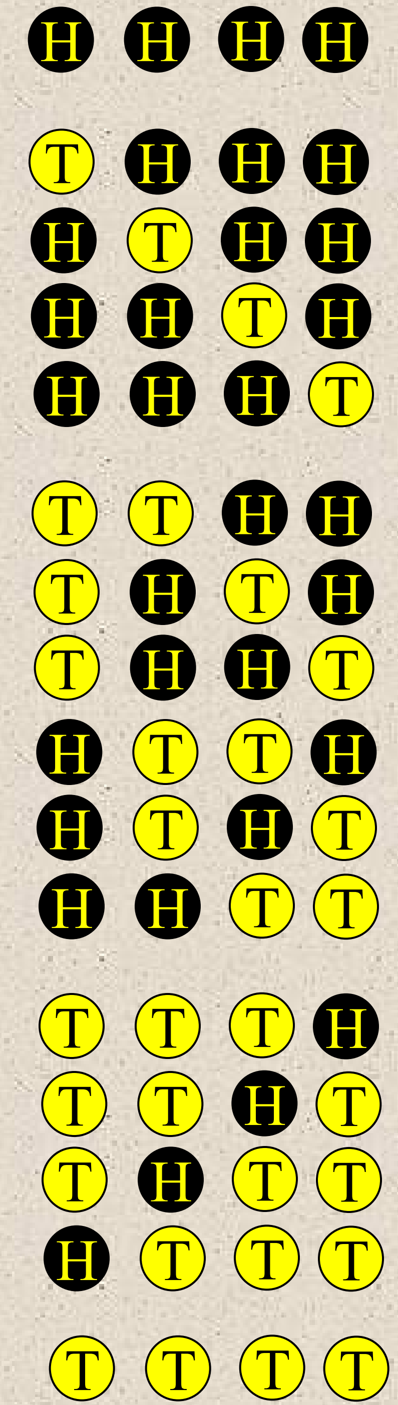


Entropy *(cont.)*

Suppose our coin system is in macrostate 4 (all heads). This represents maximum order, minimum entropy. Every so often one of the coins is chosen at random and flipped. With each flip there is a 50-50 chance that the macrostate will change. With time (after enough flips), it is doubtful that the system will still be in the minimum entropy state. It is much more likely to be in macrostate 2, the state with the most entropy.

The 2nd Law states that during any process the universe moves toward more probably states--states with more entropy. It is possible to decrease the entropy of our coin system by physically turning all tails over so that there are all heads, but in doing this we must expend energy. This energy expenditure increases the entropy of our surroundings more than it decreases the entropy of the system. Thus the entropy of the universe is increased.

continued on next slide

Entropy *(cont.)*

In our coin example we only dealt with four coins. In real life even a quadrillion atoms or molecules might not be very much. (A single bacterium contains about 100 billion atoms.) How much more likely is it for a system to be in its highest entropy state than in its lowest? It depends on how big the system is:

Number of Coins	Ratio of Probabilities
4	6 : 1
10	252 : 1
20	184,756 :1
50	$\sim 10^{14}$: 1
100	$\sim 10^{29}$: 1

This means that if 100 coins were dumped on the floor it is about 100 billion billion billion times more likely for half the coins to come up heads than for all of them to be heads!

See next slide to see how these ratios are calculated.

Entropy: Statistics Formula

We've seen that there are six ways to get exactly two heads in four flips. There were only sixteen combinations of four heads and tails, so we just listed them and counted how many had exactly two heads. But you wouldn't want to have to list all the combinations in fifty flips, since there are 2^{50} combos—over a quadrillion lines of 50 H's and T's! So we'll use some math instead. The number of ways to place 50 H's in 100 spots is "100 choose 50," which is written like this: $\binom{100}{50}$

In general, $\binom{n}{r} = \dfrac{n!}{r!\,(n-r)!}$

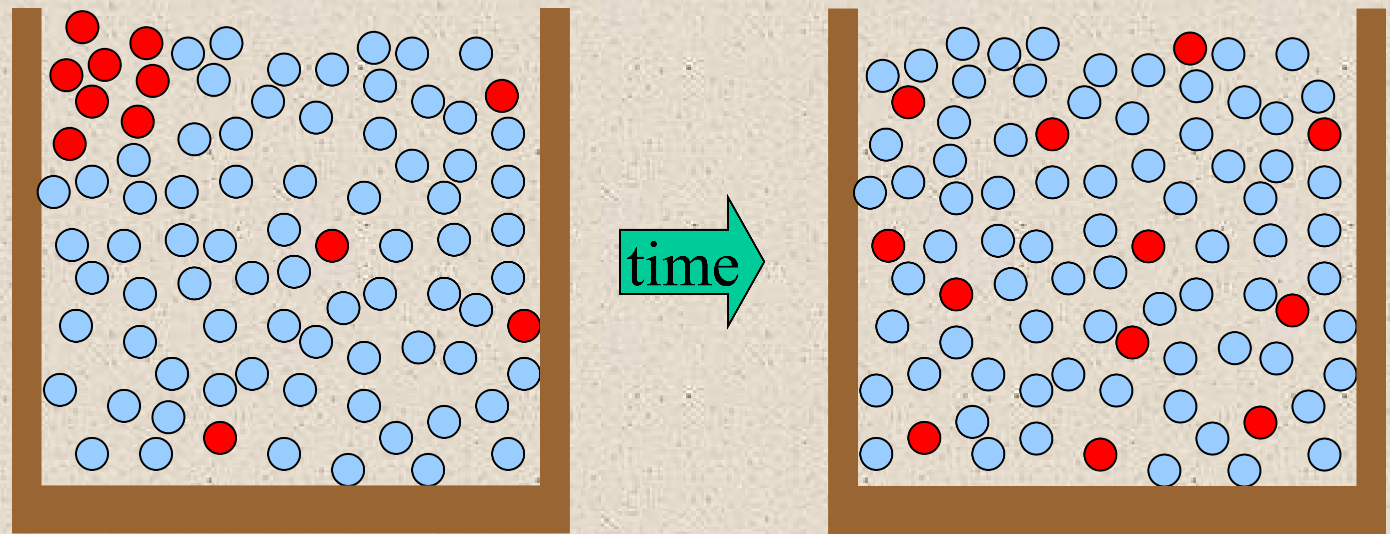
Let's try out the formula with 2 heads in 4 flips:

$$\binom{4}{2} = \frac{4!}{2!\,(4-2)!} = \frac{4\cdot 3\cdot 2\cdot 1}{(2\cdot 1)\,(2\cdot 1)} = 6,$$

as we showed by listing combinations

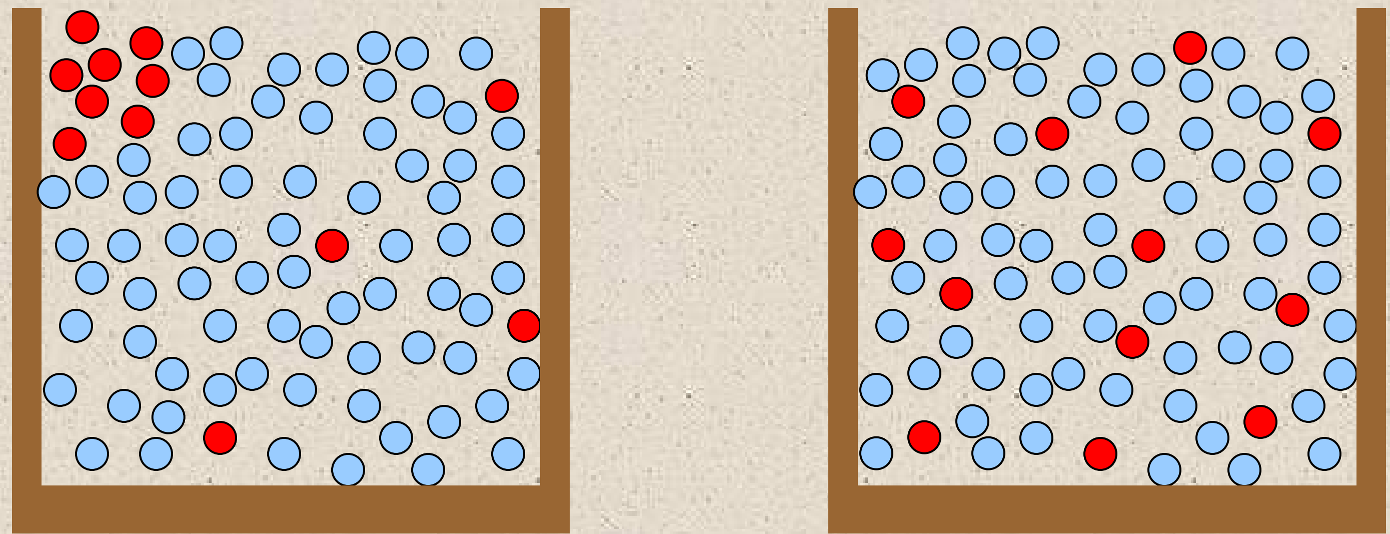
Entropy & Fluids

Suppose a beaker of very hot water is poured into an aquarium of cool water. Conservation of energy would not be violated if all the hot water remained right at the spot where it was poured. But the 2nd Law demands that the thermal energy eventually become evenly distributed. The cool water has molecules moving at a wide range of speeds (red = fast; blue = slow). Since the water is cool, there are more blues than reds. The hot water poured in has mostly red. The aquarium has less disorder (entropy) when all the fast molecules are in one spot than when they are mixed in. With time a much more likely situation exists, with a much higher entropy. *continued*



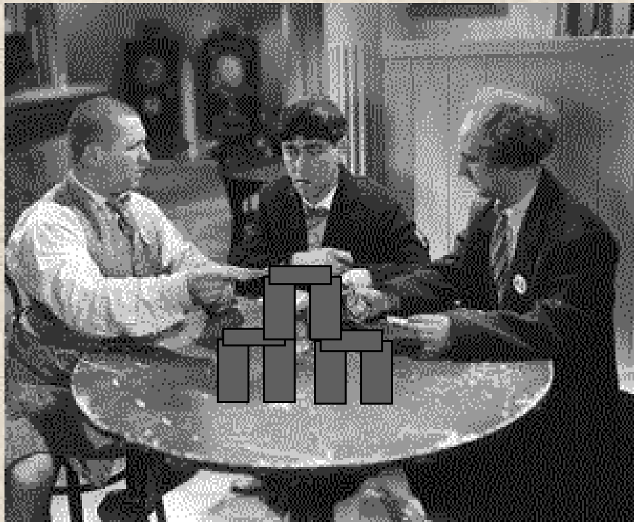
Entropy & Fluids (cont.)

Imagine how many different ways you could take 100 blue balls and paint 8 of them red. There are about $1.86 \cdot 10^{11}$ ways to do this. Many, many more of those ways look like the picture on the right than on the left. The diffusion of perfume from an open bottle throughout a room is also a consequence of the 2nd Law. Unlike diffusion, though, the "hot" water molecules don't necessarily have to move so that they are spread out evenly. Convection currents will allow some to move, but it is really the heat energy rather than the molecules themselves that must distribute itself equally throughout the aquarium.



Entropy Example 1

Stooges build a card house. Inevitably, Moe smacks Curly upside the head, and Curly bumps the table, knockings down the cards. The potential energy the cards had before falling is converted into thermal energy, and the room is warmed up ever so slightly. The 2nd Law prohibits the room from cooling a little so that the card house can spontaneously rebuild itself, even though energy would be conserved. As a card house the cards are very organized. They're in a low entropy state. In a jumble on the table, they are very unorganized and in a high entropy state. Moreover, the air in the room has more entropy when heated because thermal energy is just the random motions of molecules. The hotter the air, the more random motion the molecules have. The stooges could decrease the entropy of the cards by rebuilding the house, but in doing so they would expend energy, which would heat up the room a little. The cards' entropy would decrease, but the air's would increase even more. Overall, entropy goes up!



Entropy Example 2

Moe kicks a football in quintessential Stooge fashion. While the ball is flying through the air, its got kinetic as well as thermal energy. When it lands on the ground the ball no longer has kinetic energy, which goes into increasing the thermal energy of the air, ground, and ball. Energy is conserved, but there is a net gain of entropy for the universe. The kinetic energy the ball had was very organized: All the molecules in the ball were pretty much moving in the same direction. The thermal energy, on the other hand, is not organized at all, since it is a consequence of random molecular motions. The 2^{nd} Law guarantees that the ball won't suddenly absorb heat from its surroundings and come flying back at Curly's head, since this would mean a decrease in the total entropy of the universe.

Most Probable = Least Useful

Kinetic energy, with many molecules moving in the same direction, represents an "organized form of energy." Chemical potential energy, such as that contained in oil, is organized as well, since oil is comprised of long hydrocarbons with very specific arrangements of atoms. Gravitational potential energy is organized too, as in the card house. All of these energies can be used to do useful work, such as lifting objects, generating electricity, etc. Thermal energy is always disordered unless there is a separation of temperatures. If hot water is separated from cold water, heat can flow and work can be done.

An object or fluid with uniform temperature has uniformly distributed thermal energy and can't do any useful work. Unfortunately, this high entropy state is the most probable. Many scientists believe that the ultimate fate of the universe is a "heat death" in which the whole universe is at one uniform temp. This would represent maximum entropy. No life could exist, since life requires energy uptake and expenditure. This can't happen if the universe has only thermal energy.

Change in Entropy Equation

Because most systems are many up of so many particles, calculating entropy via probabilities would be very difficult. Fortunately, we are normally concerned only with changes in entropy. If we have a system in which energy is not changing forms, the change in entropy is defined as:

$$\Delta S = \frac{\Delta Q}{T}$$

ΔS = change in entropy

ΔQ = change in internal energy (heat flow)

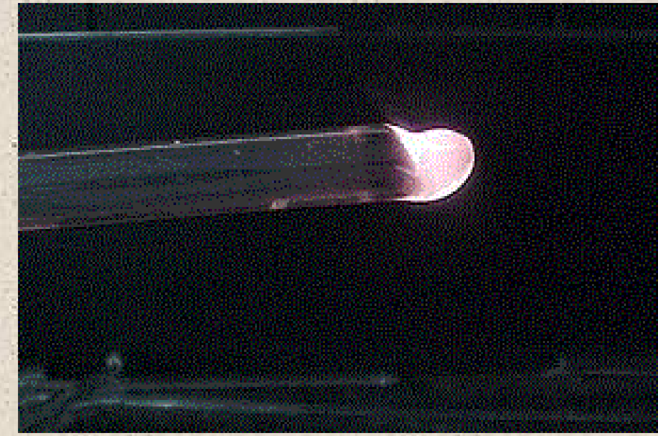
T = absolute temperature

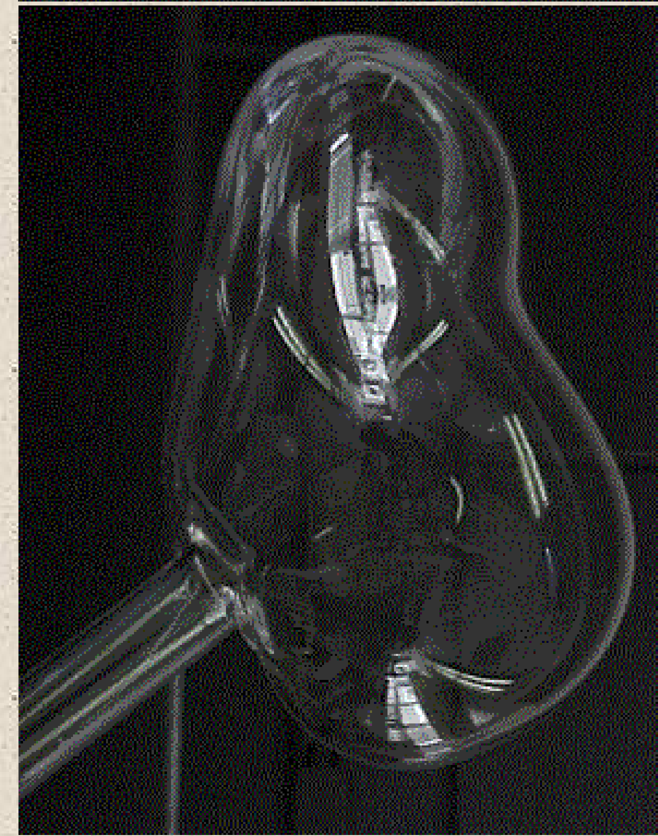
The 2nd Law of Thermodynamics says that during any process:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$

Change in Entropy Example

A glass rod is heated and then blown by a glassblower. When it is at 185°C it is brought outside to cool. 3200 J of heat are transferred from the glass to the air, which is at 18°C. Find the change in entropy of the universe:





$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

$$= \Delta S_{glass} + \Delta S_{air}$$

$$= \frac{\Delta Q_{glass}}{T_{glass}} + \frac{\Delta Q_{air}}{T_{air}}$$

$$= \frac{-3200\text{ J}}{458\text{ K}} + \frac{3200\text{ J}}{291\text{ K}}$$

$$= -7\text{ J/K} + 11\text{ J/K} = +4\text{ J/K}$$

Change in Entropy Example *(cont.)*

As the glass cooled we assumed that the air temp didn't go up appreciably due after the heat transfer, which would have complicated the problem. Important points:

- The temps were converted to kelvins.
- The glass lost as much thermal energy as air gained, as the 1st Law requires.
- ΔQ_{glass} is negative since the glass lost thermal energy so ΔS_{glass} is also negative.
- ΔQ_{air} is positive since the air gained thermal energy so ΔS_{air} is also positive.
- Even though the ΔQ's are the same size, the ΔS's aren't, since the temps are different.
- The positive ΔS is greater than the negative ΔS, as the 2nd Law requires.

Second Law Consequences

- Heat will not flow from a cold body to a hot body.
- “Reverse diffusion” is a no-no (such as smoke from a fire isolating itself in a small space).
- An object or fluid of uniform temperature (no matter how hot) cannot do useful work. (There must be temperature difference so that there will be a heat flow, which can be used to do work.)
- The various forms of energy tend to degrade over time to thermal energy. This represents useful, low probability forms of energy converting into an unusable, high probability form.
- Without input of energy, bodies tend to reach thermal equilibrium. (We can maintain temperature differences via refrigerators or heating units, but this requires energy.)

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Second Law Consequences (cont.)

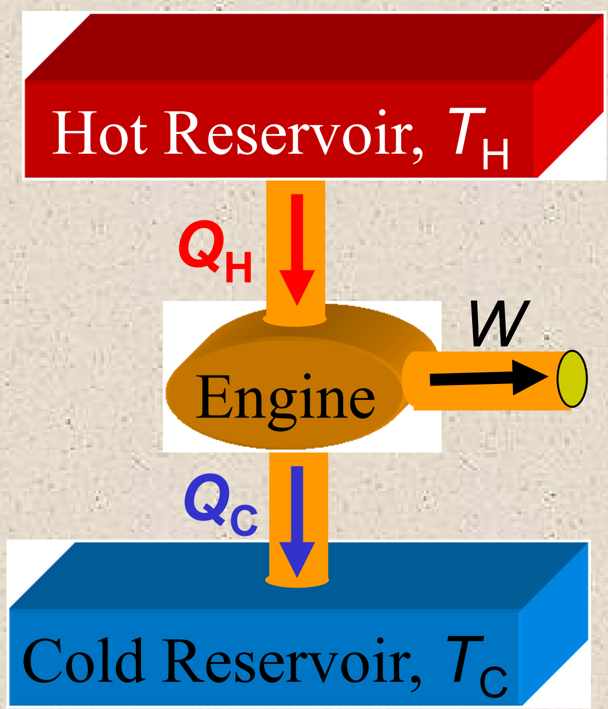
• Any time we do something that decreases the entropy of a system, the energy we expend in doing it increases the entropy of the surroundings even more.

• A perpetual motion machine is impossible to make. A perpetual motion machine is a device that would absorb thermal energy from a hot body and do as much work as the energy it absorbed. (See pics on next slide.)

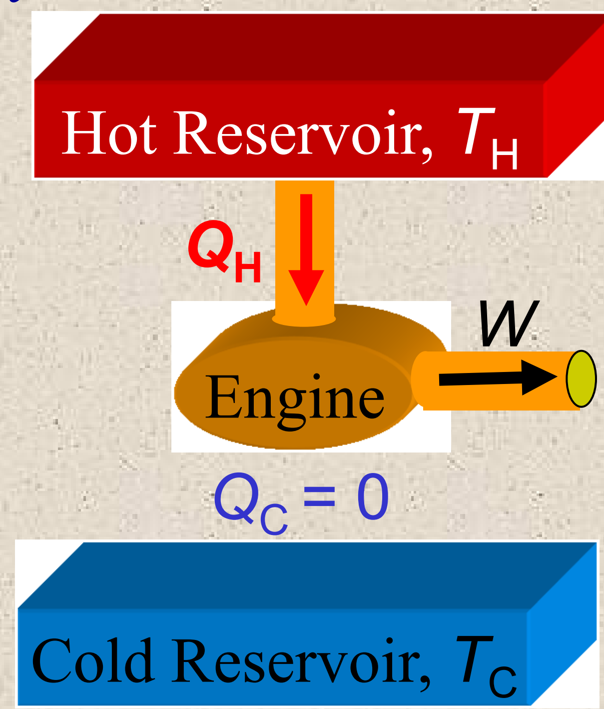
• During any process the entropy of the universe cannot decrease. Expending energy to decrease the entropy of a system will lead to an increase in entropy for the surrounding by a greater amount.

Heat Engines

A heat engine takes advantage of temp differences to produce useful work. The amount of work done depends on the size of the reservoirs, engine efficiency, and the temp difference (T_H - T_C). Q_H is the heat that flows from the hot region; Q_C is the heat flowing into the cold region. W is the useful work done by engine. The smaller Q_C is, the more efficient the engine is. The engine on the right satisfies the 1st Law but violates the 2nd Law, i.e., 100% efficiency is unattainable.



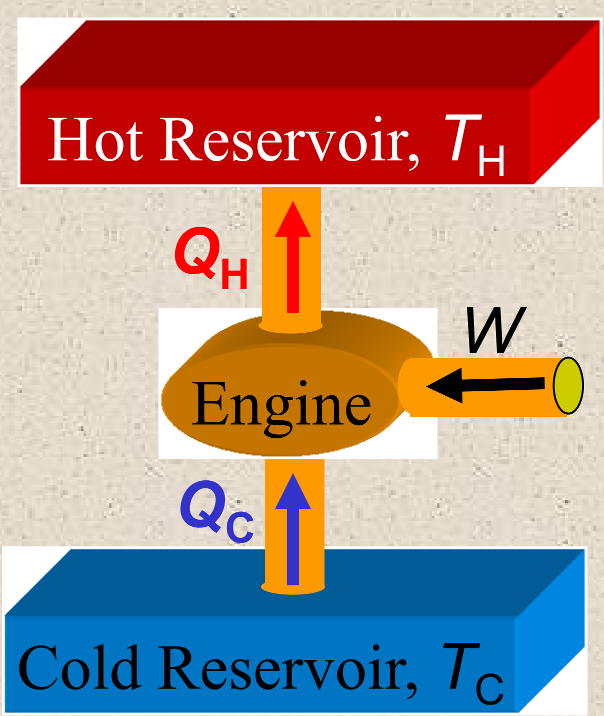
Real engine. $Q_H = Q_C + W$



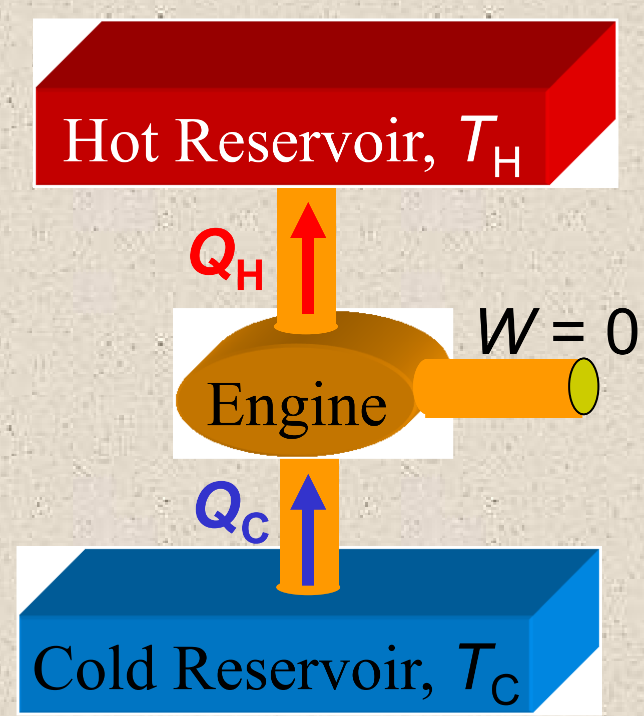
Impossible engine. $Q_H = W$

Refrigerators

A refrigerator forces heat from a cold region into a warmer one. It takes work to do this, otherwise the 2nd Law would be violated. Can a fridge be left open in the summer to provide a make shift air conditioner? Nope, since all heat pumped out of the fridge is pumped back into the kitchen. Since $Q_H > Q_C$ because of the work done, leaving the refrigerator open would actually make your house hotter!



Real fridge. $Q_C + W = Q_H$



Impossible fridge. $Q_C = Q_H$

Specific Heat

Specific heat is defined as the amount of thermal energy needed to raise a unit mass of substance a unit of temperature. Its symbol is *C*.

For example, one way to express the specific heat of water is one calorie per gram per degree Celsius: $C = 1\ \text{cal}/(\text{g}\cdot{}^{\circ}\text{C})$, or $4.186\ \text{J}/(\text{g}\cdot{}^{\circ}\text{C})$. This means it would take 20 cal of thermal energy to raise 4 grams of water 5 ºC.

Water has a very high specific heat, so it takes more energy to heat up water than it would to heat up most other substances (of the same mass) by the same amount. Oceans and lake act like “heat sinks” storing thermal energy absorbed in the summer and slowing releasing it during the winter. Large bodies of water thereby help to make local climates less extreme in temperature from season to season.

Specific Heat Equation

$$Q = mC\Delta T$$

Q = thermal energy
m = mass
C = specific heat
ΔT = change in temp

Ex: The specific heat of silicon is 703 J/(kg · ºC). How much energy is needed to raise a 7 kg chunk of silicon 10 ºC?

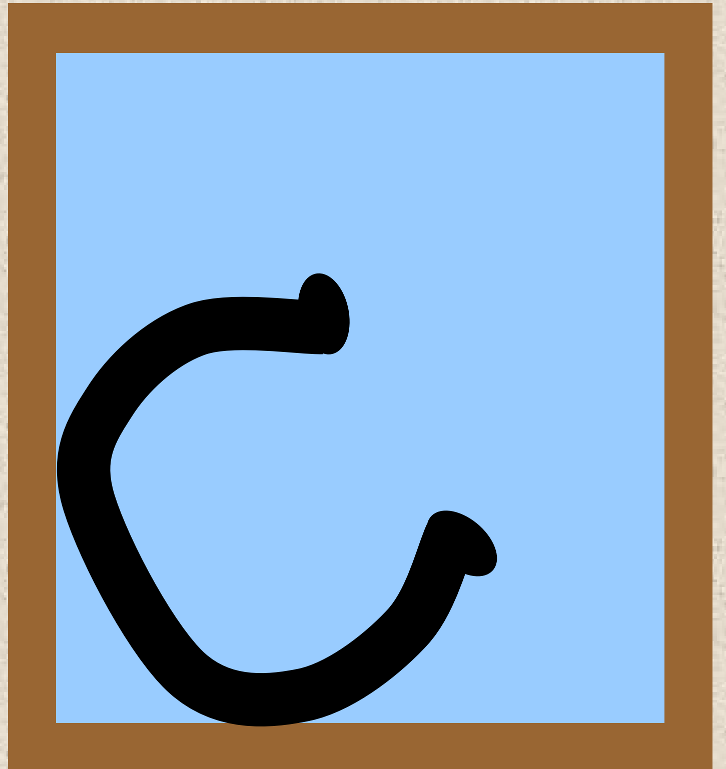
answer:

$$Q = 7\text{ kg} \cdot \frac{703\text{ J}}{\text{kg} \cdot {}^{\circ}\text{C}} \cdot 10\,{}^{\circ}\text{C} = 49\,210\text{ J}$$

Note that the units do indeed work out to be energy units.

Calorimetry

Schmedrick takes another horseshoe out of the fire when it's at 275 ºC, drops in his bucket of water, and this time covers the bucket. The bucket and cover are made of an insulating material. The bucket contains 2.5 L of water originally at 25 ºC. The 1.9 kg shoe is made of iron, which has a specific heat of 448 J/(kg·ºC). Let's find the temp of the horseshoe and water once equilibrium is reached.



Let's assume that the container allows no heat to escape. Then the 1st Law implies that all heat the shoe loses is gained by the water. Since one milliliter of water has a mass of one gram, the bucket contains 2.5 kg of water. At thermal equilibrium the water and shoe are at the same temp. The total thermal energy in the bucket does not change, but it is redistributed.

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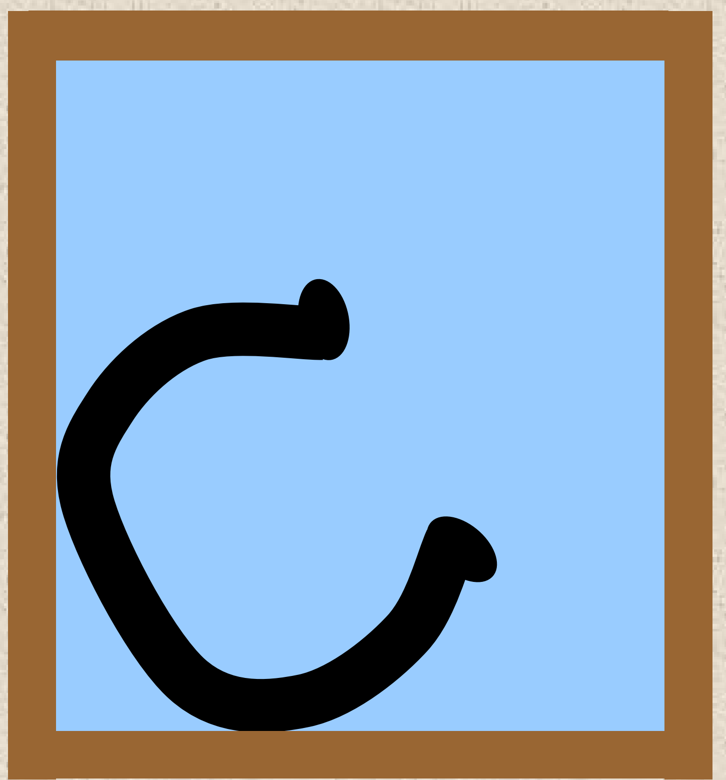
Calorimetry (cont.)

Let T = the equilibrium temperature.

Q lost by iron = Q gained by water

$$m_{iron}\, C_{iron}\, \Delta T_{iron} = m_{water}\, C_{water}\, \Delta T_{water}$$

$$(1.9 \text{ kg})(448 \text{ J/kg}\cdot{}^{\circ}\text{C})(275\ {}^{\circ}\text{C} - T) = (2.5 \text{ kg})(4186 \text{ J/kg}\cdot{}^{\circ}\text{C})(T - 25\ {}^{\circ}\text{C})$$



Note how the ΔT terms are written so that each side is positive. We've got a simple linear equation with T on both sides. Solving it gives us T = 43.8 ºC. This is the equilibrium temp--the final temp for both the shoe and water. If T had come out over 100 ºC, the answer would have been invalid, since the specific heat for steam is different than that of water.

Latent Heat

The word "latent" comes from a Latin word that means "to lie hidden." When a substance changes phases (liquid ↔ solid or gas ↔ liquid) energy is transferred without a change in temperature. This "hidden energy" is called latent heat. For example, to turn water ice into liquid water, energy must be added to bring the water to its melting point, 0 ºC. This is not enough, however, since water can exist at 0 ºC in either the liquid or solid state. Additional energy is required to change 0 ºC ice into 0 ºC water. The energy increases the internal energy of the water but does not raise its temp. When frozen, water molecules are in a crystalline structure, and energy is needed to break this structure. The energy needed is called the *latent heat of fusion*. Additional energy is also needed to change water at 100 ºC to steam at 100 ºC, and this is called the *latent heat of vaporization*.

Latent Heat Formula

$$Q = mL_f \quad \text{or} \quad Q = mL_v$$

Q = thermal energy
m = mass
L = heat of fusion or vaporization

L is the energy per unit mass needed to change the state of a substance from solid to liquid or from liquid to gas. Ex: L_f (the latent heat of fusion) for gold is 6440 J/kg. Gold melts at 1063 ºC. 5 grams of solid gold at this temp will not become liquid until additional heat is added. The amount of heat needed is:

(6440 J/kg) (0.005 kg) = 32 J. The liquid gold will still be at 1063 ºC.

Latent Heat / Specific Heat Example

Superman vaporizes a 1800 kg ice monster with his heat ray vision. The ice monster was at -20 ºC. After being vaporized he is steam at 135 ºC. How much energy did Superman expend?

Substance	Specific Heat (in J/kg·ºC)
ice	2090
liquid water	4186
steam	1970

For water: $L_f = 3.33 \cdot 10^5$ J/kg; $L_v = 2.26 \cdot 10^6$ J/kg

$Q = (1800 \text{ kg})(2090 \text{ J/kg}\cdot\text{ºC})(20 \text{ ºC})$ *heating ice to melting pt.*

$+ (1800 \text{ kg})(3.33 \cdot 10^5 \text{ J/kg})$ *ice to water, const. temp of 0 ºC*

$+ (1800 \text{ kg})(4186 \text{ J/kg}\cdot\text{ºC})(100 \text{ ºC})$ *heating water to boiling pt.*

$+ (1800 \text{ kg})(2.26 \cdot 10^6 \text{ J/kg})$ *water to steam, const. temp of 100 ºC*

$+ (1800 \text{ kg})(1970 \text{ J/kg}\cdot\text{ºC})(35 \text{ ºC})$ *heating steam to 135 ºC*

$= 5.62 \cdot 10^9 \text{ J}$ *total energy expended by Superman*

Latent Heat & Entropy

Schmedrick is enjoying a cool glass of soy milk while relaxing on a cot on a winter morning in his backyard. Suddenly his dog, Rover, barks at a squirrel and startles Schmed, who drops his drink. A 10 g ice cube at 0 ºC falls to the ground and melts. The temp outside is 10 ºC. Calculate the change in entropy of the universe due to the melting of the ice only. *answer:*

For the cubie: $Q = m L_f = (0.01 \text{ kg})(3.33 \cdot 10^5 \text{ J/kg}) = +3330 \text{ J}$. This is the energy absorbed by the ice from the surroundings.

$\Delta S_{ice} = \Delta Q_{ice} / T_{ice} = +3330 \text{ J} / 273 \text{ K} = +12.198 \text{ J/K}$.

For the surroundings: $Q = -3330$ J, since the surroundings lost as much thermal energy as the cubie gained. The temperature of the backyard does not decrease significantly, though, with such a small energy loss. $\Delta S_{surr} = \Delta Q_{surr} / T_{surr} = -3330 \text{ J} / 283 \text{ K} = -11.767 \text{ J/K}$.

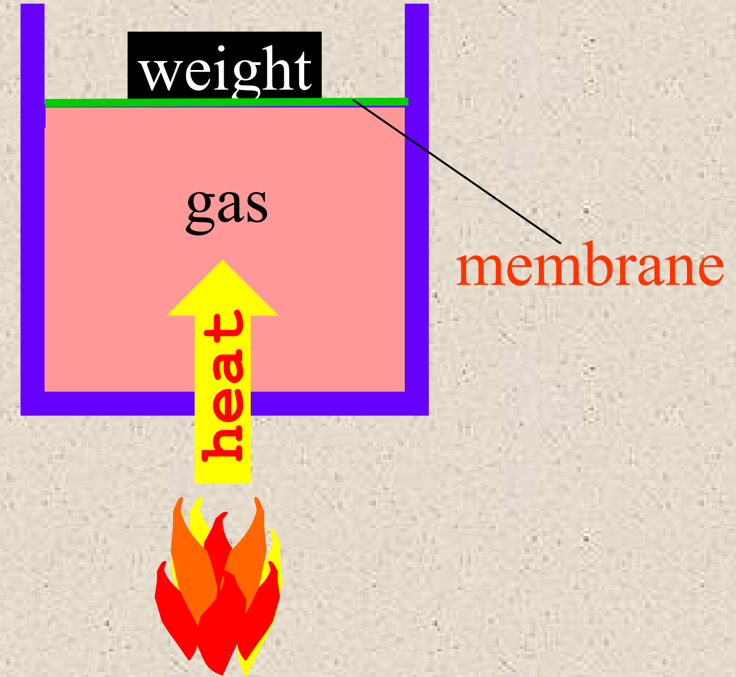
For the universe: $\Delta S_{univ} = \Delta S_{surr} + \Delta S_{ice} = 12.198 \text{ J/K} - 11.767 \text{ J/K} = +0.431 \text{ J/K}$. Thus, the 2nd Law is satisfied.

Internal Energy, Work, & Heat

The internal energy, ΔE_{int}, of a substance or object can be changed in two ways:

1. by letting heat flow in or out of the substance, Q
2. by the substance doing work or having work done on it, W

In summary: $\Delta E_{int} = Q - W$, which is one way to state the 1st Law.



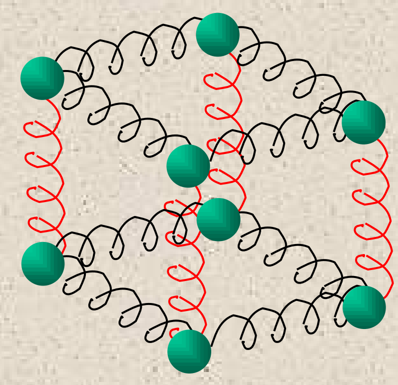
Q is positive if heat flows in. W is the work done <u>by</u> the substance. If the gas expands because of the added heat, it will do work by lifting the weight up. Then W would be positive, and the work the gas does would decrease its internal energy.

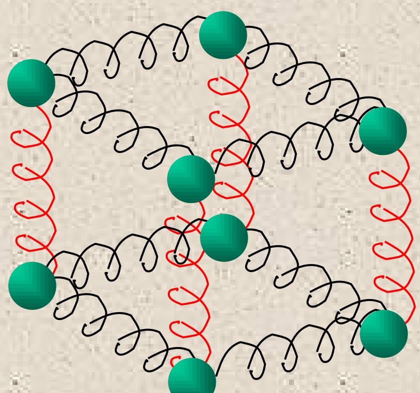
Internal Combustion Engine

In the carburetor of your car, air and fuel are mixed. The gaseous mixture is injected into a cylinder, compressed by a piston, and ignited by a spark plug. (If your car has fuel injection, which is more efficient, there is no carburetor; instead fuel is sprayed into the cylinders at appropriate times, where it vaporizes.) The fuel mixture contains internal as well as chemical potential energy. After burning most of the potential energy is released. This energy heats the gas in the cylinder, raising its internal energy. The burning gas also does work on the piston as it expands. The force applied to the piston causes the crankshaft to rotate. The crankshaft is hooked up to the transmission. The exhaust gases are expelled from the cylinder so that the cycle can begin again. Cars are very inefficient, since most of the chemical potential energy in the gasoline goes into heating the exhaust gases, which pollute our atmosphere and contribute to global warming. Only a small amount of the chemical potential energy does useful work.

Thermal Expansion

As a material heats up its atoms/molecules move or vibrate more vigorously, and the average separation between them increases. This results in small increases in lengths and volumes. Buildings, railroad tracks, bridges, and highways contain thermal expansion joints to prevent cracking and warping due to expansion. The amount of expansion depends on the original length/volume, the type of material, and the change in temp. L is length, V is volume, T is temp, α is the coefficient of linear expansion, and β is the coef. of volume expansion. When a solid of a single material expands, it does so proportionally in all directions. Since volume has 3 dimensions and length is only 1, $\beta = 3\alpha$.


cold solid


hot solid

Length expansion:

$$\frac{\Delta L}{L} = \alpha \, \Delta T$$

Volume expansion:

$$\frac{\Delta V}{V} = \beta \, \Delta T$$

Thermal Expansion & The Concorde

The Concorde is a supersonic jet made of a heat tolerant aluminum alloy. Its nose tilts down on takeoff and landing so the pilot can see the runway. In flight the nose comes up to reduce drag, but at a speed of around 1,350 mph, friction with the air causes significant heating of the plane, enough to make the Concorde grow in length by 7 inches! (To maintain this speed for one hour, the Concorde must burn over 6,700 gallons of fuel.)

$\frac{\Delta L}{L} = \alpha \Delta T$

Thermal Expansion Example

$\frac{\Delta V}{V} = \beta \Delta T$

Schmedrick takes his dune buggy to the gas station and fills it up to the very brim. His tank is a steel cylinder of radius 23 cm and height 45 cm (big enough to hold about 20 gallons). He burns a liter of gas getting to the beach, where both the tank and the gas heat up by 20 ºC. Both the tank and the gas expand. For steel $\alpha = 1.1 \cdot 10^{-5}$ / ºC. For gasoline $\beta = 9.6 \cdot 10^{-4}$ / ºC. Does the tank overflow? *Hints:*

1. Use the linear expansion formula to calculate the increase in radius of the tank: *$5.06 \cdot 10^{-3}$ cm*
2. Use the linear expansion formula to calculate the increase in height of the tank: *$9.9 \cdot 10^{-3}$ cm*
3. For a cylinder, $V = \pi r^2 h$. Calculate the increase in volume of the tank: *49.3694 cm^3*
4. Calculate the volume of gasoline at the beach before expansion. (1 cm^3 = 1 mL): *73 785.613 cm^3*
5. Use the volume expansion formula to calculate the increase in volume of the gasoline: *1 416.684 cm^3*
6. Conclusion: *Schmed will be kicked out for spilling gas at the beach!*