Thermodynamics!

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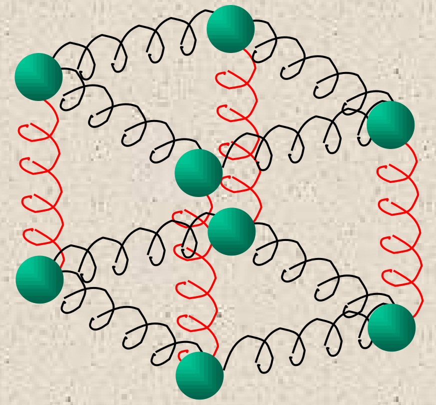
Kinetic-Molecular Theory

It was once common belief that heat was an invisible substance. It even had a name--"caloric," and it was believed that it could be transferred between objects but neither created nor destroyed. To heat up an object this caloric had to flow into it. This, they thought, explained why objects expanded when heated. But this theory could not explain, for example, how heat could emanate from a cold piece of wood once it is set on fire? Where did the caloric come from? If it had been in the wood in the first place, the wood should have been hot all along.

The caloric theory was abandoned in the 19th century and replaced with the kinetic-molecular theory. This new theory stated that all matter is made up of atoms/molecules in constant motion. The faster they move, the hotter an object will be.

Internal Energy

Internal energy (also called thermal energy) is the energy an object or substance is due to the kinetic and potential energies associated with the random motions of all the particles that make it up. The kinetic energy is, of course, due to the motion of the particles. To understand the potential energy, imagine a solid in which all of its molecules are bound to its neighbors by springs. As the molecules vibrate, the springs are compressed and stretched. (Liquids and gases are not locked in a lattice structure like this.)



The hotter something is, the faster its molecules are moving or vibrating, and the higher its temperature. Temperature is proportional to the average kinetic energy of the atoms or molecules that make up a substance.

Internal Energy vs. Heat

The term *heat* refers is the energy that is transferred from one body or location due to a difference in temperature. This is similar to the idea of *work,* which is the energy that is transferred from one body to another due to forces that act between them. Heat is internal energy when it is transferred between bodies.

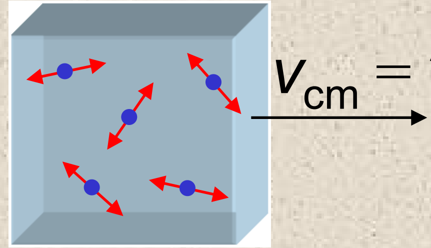
Technically, a hot potato does not possess heat; rather it possesses a good deal of internal energy on account of the motion of its molecules. If that potato is dropped in a bowl of cold water, we can talk about heat: There is a heat flow (energy transfer) from the hot potato to the cold water; the potato's internal energy is decreased, while the water's is increased by the same amount.

Units for Heat

Like any type of energy, the SI unit for heat is the Joule. Another common unit is the calorie, which is approximately the amount of heat energy needed to raise one gram one degree Celsius. 1000 calories are in a Calorie, which is used to measure the energy in foods (that the human body can make use of). The British thermal unit (BTU) is approximately the energy needed to raise one pound of water one degree Fahrenheit.

$$\boxed{1 \text{ cal} = 4.186 \text{ J} \qquad 1 \text{ BTU} = 1055 \text{ J} = 252 \text{ cal}}$$

Internal vs. "External" Energy



Suppose a 1 kg block of ice is sliding at 7 m/s. This is the speed of the center of mass of the block, not the speed of each individual water molecule. To calculate the total kinetic energy of the water molecules of the block directly, we would have to know the speed of each molecule as it vibrates, all 33.4 trillion trillion of them! (In practice we would just measure the temperature & mass of the ice.) The internal energy of the ice does not depend on the motion of the whole body relative to Earth. What matters is the motion of the molecules in the reference frame of the block. Otherwise, it would be impossible for a cold object to move quickly or a hot one to move slowly. Note: If friction is present, it could do work on the ice and convert some of the "uniform" kinetic energy of the block into "random" kinetic energy of its molecules (internal energy). Regardless, the total energy of the block is the kinetic energy of the center of mass + the internal energy: $K_{total} = K_{cm} + E_{int}$

Temperature vs. Internal Energy

Temperature and internal energy are related but not the same thing. Temperature is directly proportional to the average molecular kinetic energy*. Note the word *average* is used, not *total*.

Consider a bucket of hot water and a swimming pool full of cold water. The hot water is at a higher temperature, but the pool water actually has more internal energy! This is because, even though the average kinetic energy of the water molecules in the bucket is much greater than that of the pool, there are thousands of times more molecules in the pool, so their total energy is greater.

It's analogous to this: A swarm of 1000 slow moving bees could have more total kinetic energy than a dozen fast moving, hyperactive bees buzzing around like crazy. One fast bee has more kinetic energy than a slow one, but there are a lot more slow ones.

* *true for gases, approximately true for solids and liquids whose molecules interact with each other more.*

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Temperature vs. Internal Energy (cont.)

Which has more internal energy, a bucket of hot water or a bucket of cold water? *answer:*

The bucket of hot water has more internal energy, at least if the buckets contain the same amount of water.

Internal energy depends on the amount (mass) of substance and the kinetic energy of the molecules of the substance.

Temperature only depends on the molecules' kinetic energy; it is independent of mass.

Temperature Scales

Fahrenheit: water freezes at 32 °F; boils at 212 °F

Celsius: water freezes at 0 °C; boils at 100 °C

Kelvin: water freezes at 273.15 K; boils at 373.15 K

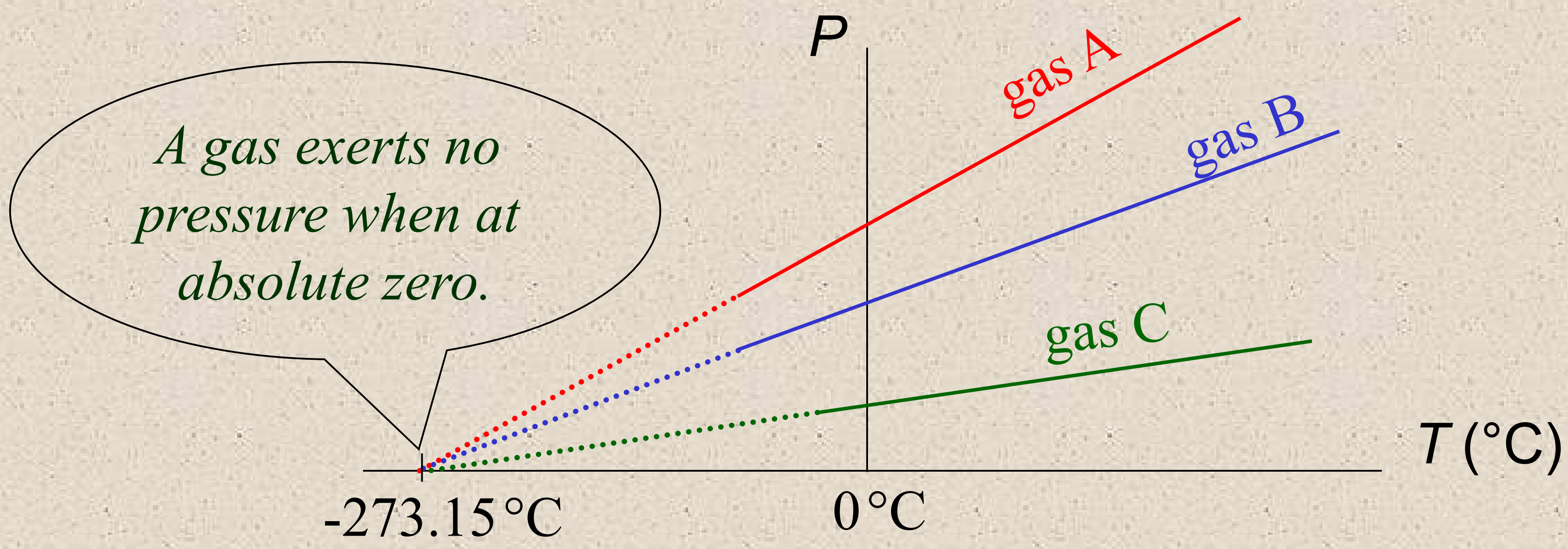
A change of 100 °C corresponds to a change of 180 °F. This means 5 C° = 9 F° or 1 C° = 1.8 F° Note that the degree symbol is on the opposite side of the letter, indicating that we're talking about temperature differences. In other words, five steps on the Celsius scale is equivalent to nine steps on the Fahrenheit scale, but 5 °C is certainly not equal to 9 °F. Since these scales are linear, and they're offset by 32 °F, we get the conversion formula: $F = 1.8C + 32$

One step on the Kelvin scale is the same as one step on the Celsius scale. These scales are off by 273.15 K, so: $K = C + 273.15$

Room temperature is around 293 kelvins, which is 20 °C, or 68 °F.

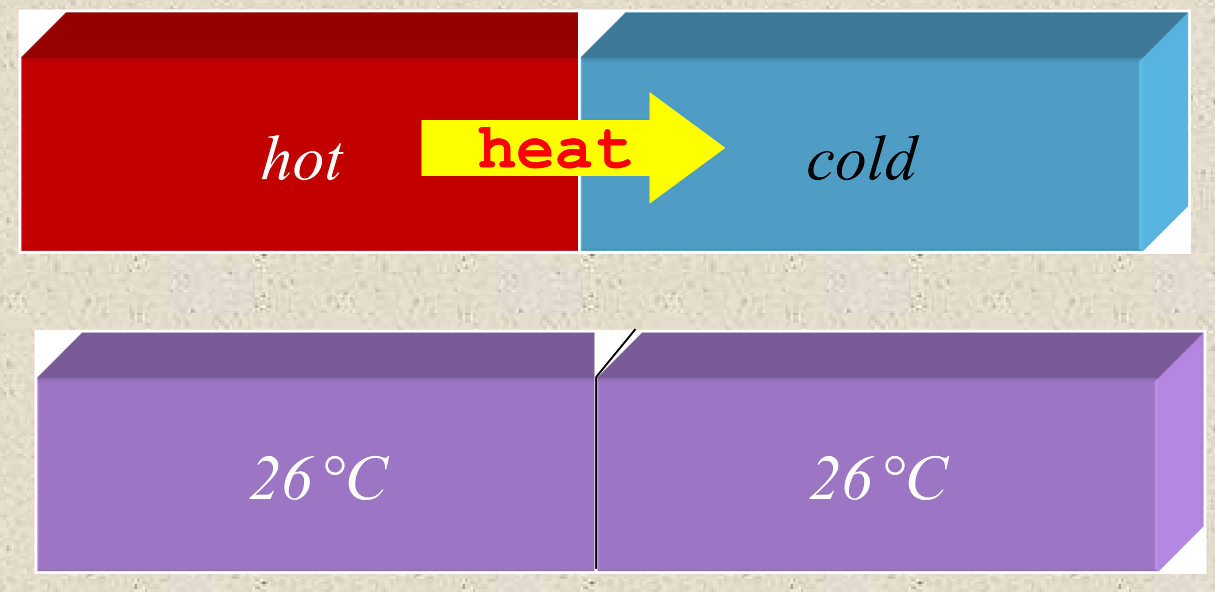
Absolute Zero & the Kelvin Scale

The Kelvin scale is setup so that its zero point is the coldest possible temperature--absolute zero, at which point a substance would have zero internal energy. This is -273.15 °C, or -459.69 °F. Absolute zero can never be reached, but there is no limit to how close we can get to it. Scientists have cooled substances to within 10^{-5} kelvins of absolute zero. How do we know how cold absolute zero is, if nothing has ever been at that temperature? The answer is by graphing Pressure vs. Temperature for a variety of gases and extrapolating.



Thermal Equilibrium

Two bodies are said to be at thermal equilibrium if they are at the same temperature. This means there is no net exchange of thermal energy between the two bodies. The top pair of objects are in contact, but since they are at different temps, they are <u>not</u> in thermal equilibrium, and energy is flowing from the hot side to the cold side.



No net heat flow

The two purple objects are at the same temp and, therefore are in thermal equilibrium. There is no net flow of heat energy here.

Heat Transfer Processes

Heat energy can be transferred from one body to another in three different ways. Upcoming slides will give an example of each.

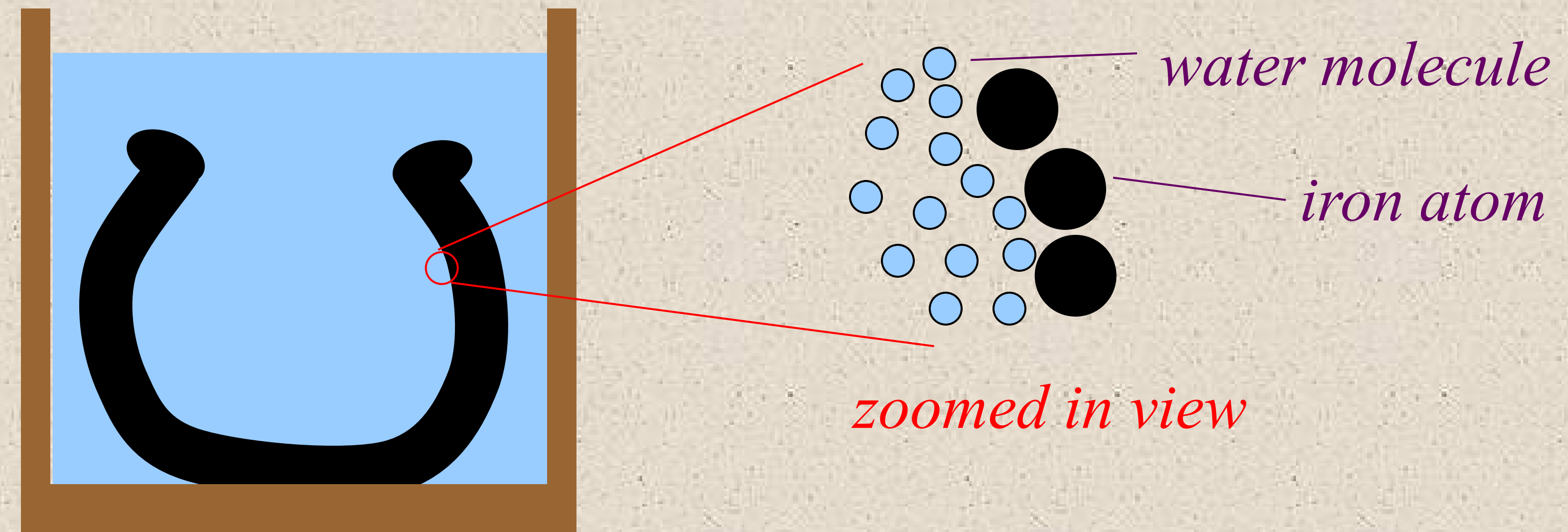
- Conduction: Energy is transferred when two objects are in direct contact. Molecules of the hotter object bump into molecules of the colder object and cause them to speed up, warming the colder object.

- Convection: Energy is transferred from one body to a cooler one via currents in a fluid (a gas or liquid).

- Radiation: All objects, at any temperature, radiate electromagnetic radiation (light of visible and invisible wavelengths). Unlike conduction & convection, no medium (matter of any type) is necessary for heat transfer through radiation. Objects absorb radiation as well. At thermal equilibrium it will absorb as much as it radiates.

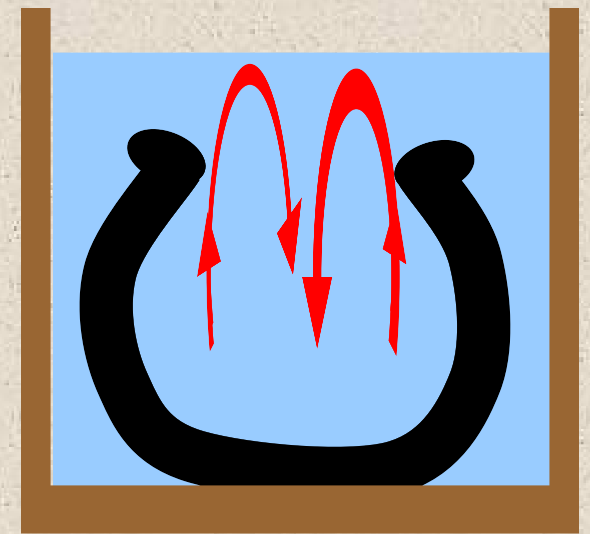
Conduction

Schmedrick decides to become a blacksmith. In order to forge a horse-shoe for his horse, Bucephalus, Scmedrick heats up the shoe in a fire, pounds on it with a mallet to shape it, and then cools it by dipping it in a bucket of water. Because the water is colder, heat flows from the shoe to the water--quickly at first, and more slowly as the shoe cools. The water molecules, with little kinetic energy, are in direct contact with the iron atoms, which are jiggling rapidly and have lots of kinetic energy. When an iron atom bumps into a water molecule, the iron atom slows down a bit, while the water molecule speeds up (an elastic collision). In this way water gains the heat energy that the iron loses.



Convection

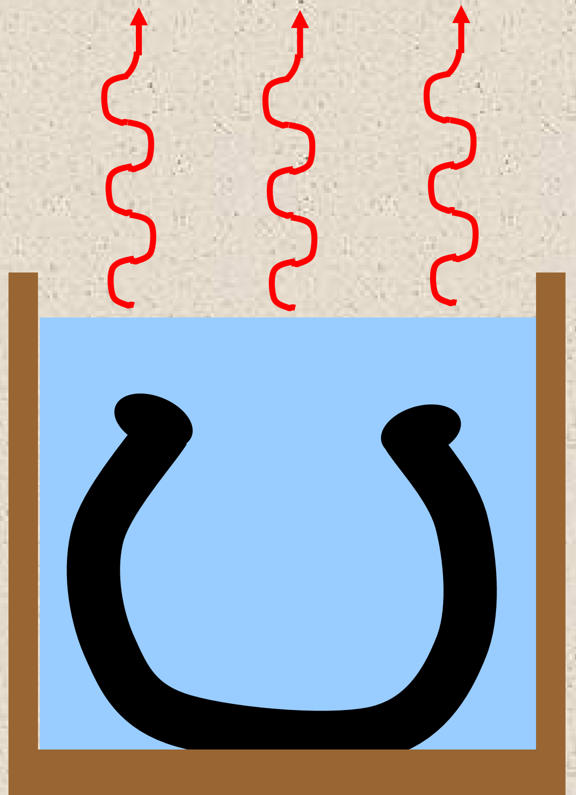
The water near the hot horseshoe is warmer than the water further from the shoe. This warm water is lower in density than the cooler water, since its molecules are moving faster and taking up more space. With lower density, the warm water begins to float to the surface, carrying its heat energy with it. As it rises to the surface it cools and becomes denser. Then it begins to sink, warmer water from below taking its place. These convection currents transfer heat from the horseshoe to the air via the water, which is the convection medium.



If the water were surrounded by something solid or too viscous to flow, heat could only be transferred to the air via conduction, and it would take much longer. Convection plays a big role in determining global weather patterns.

Radiation

The molecules of warm water cooling the horseshoe at the surface of Schmedrick's bucket bump into air molecules and transfer heat to the air via conduction. The water can also transfer energy to the air by emitting electromagnetic radiation. This is simply light, but usually it's light of a wavelength that is too long for us to see--infrared. Bodies also continually absorb radiation, but when a body is warmer than its surroundings, it emits more than it absorbs. Night vision technology takes advantage of this fact by detecting infrared light in order to "see in the dark." Radiation can cool or warm objects even if they are surrounded by a vacuum. (Even a perfect Thermos bottle full of hot chocolate will eventually cool down.) When Schmed's bucket cools long enough, it will be in thermal equilibrium with the air, and the net radiation (emission - absorption) will be zero.



Radiation: Power & Temperature

The rate at which a hot object emits radiation is its power output. Recall, power, P, is the rate at which work is done or energy is expended or absorbed. P depends on the body's temp (in kelvin) and on the amount of surface area it has. Power is directly proportional to the surface area and proportional to the 4th power of absolute temperature:

$$P \propto A\,T^4$$

Note that the closer the radiating body gets to absolute zero, the lower its power output of electromagnetic radiation, meaning the amount of internal energy it is radiating out in a unit of time is low. Also, an object with lots of surface area will radiate at a greater rate.

Don't forget that bodies radiate and absorb energy at the same time. The same equation describes absorption, except we use the temp of the surroundings. $P_{net} = 0$ when a body is in thermal equilibrium.

Black Body

A black body is an ideal absorber. It absorbs any radiation that is incident upon it (any light that hits it). It exists only in theory.

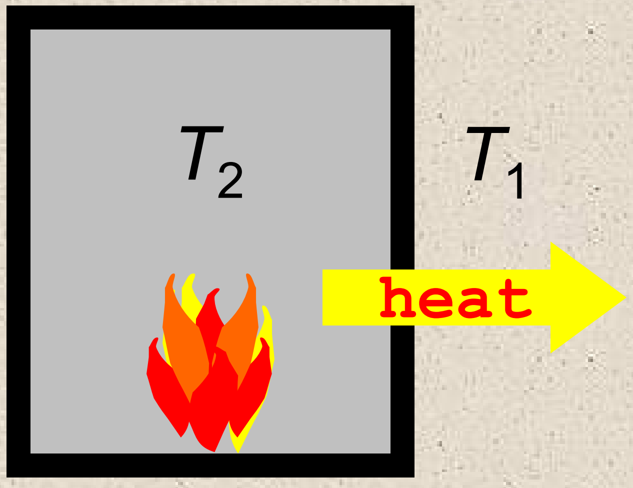
Suppose Schmedrick has Bucephalus is all shoed up and ready to run. Schmed hops on the back of his trusty steed, and with a mighty "Hi ho Bucephalus! Away!" he heads off into the sunset. Before falling off, Schmedrick ponders the sunlight streaming through the atmosphere from 93 million miles away. Not all of the light that reaches Earth makes it to the surface. The atmosphere reflects some of it back into space and absorbs some of it. (It scatters away more of the blue light than the red, which is why sunsets look red.) It is the same story for the light hitting Bucephalus: his coat absorbs some of it (and warms him); and some is reflected (otherwise he would be called Bucephalus the Invisible Horse).

All real-world objects interact this way with light. Only a black body would absorb all light, including wavelengths we can't see.

Thermal Conductivity, k

Heat transfer via conduction was described a few slides back. Thermal conductivity, k, refers how easily heat can move through a material. Metals have high thermal conductivity, meaning heat passes through them readily. Wood is a fairly good insulated of heat, and styrofoam is even better. These materials have low thermal conductivities. k is very low for air as well. (Attic insulation and styrofoam cups trap air, making them good insulators.) Heat from a boiler passes through all sides of its metal enclosure. The rate at which heat is transferred is given by:

$$H = \frac{kA}{L}(T_2 - T_1)$$



A = area of side wall

L = thickness of wall

k = thermal conductivity of the metal

$T_2 - T_1$ = temperature difference

H is simply power, and its SI unit is the Watt.

SI Units for Thermal Conductivity

$$H = \frac{kA}{L}(T_2 - T_1)$$

k must have units that cancel out all the units on the right, leaving only the units for *H*. The units are:

$$\frac{\mathrm{W}}{\mathrm{m \cdot K}} \quad \text{or equivalently,} \quad \frac{\mathrm{W}}{\mathrm{m \cdot {}^\circ C}}$$

Since one kelvin is as big a change in temp as one degree Celsius, these units are equivalent.

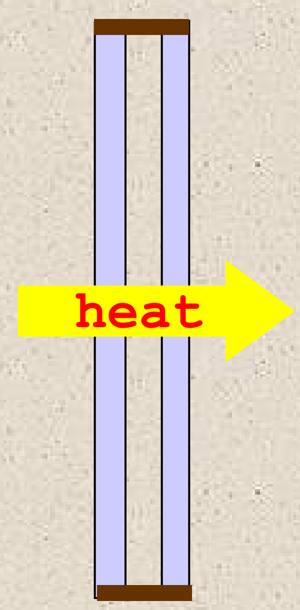
Note: *k* for thermal conductivity is not the same as the *k* in Hooke's Law in which it represents the spring constant!

Cold Tootsies

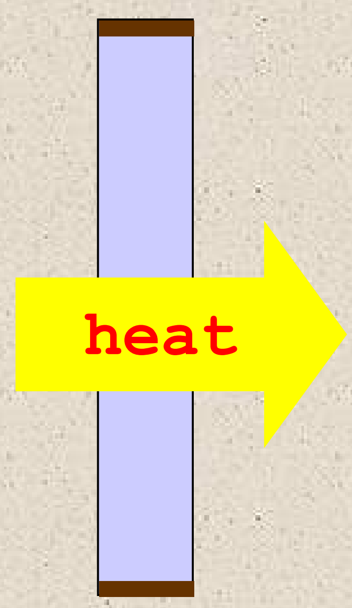
Have you ever gotten out of bed in the wintertime and walked barefoot from a carpeted floor to a tile bathroom floor? The carpeting feels much warmer than the tile. But, assuming the house is in thermal equilibrium, the carpet and tile are at the same temp. So why does the tile feel colder? *answer:*

The tile has a greater thermal conductivity constant than the carpeting does. That is, the carpet is a better insulator. So, even though their temps are the same, the tile draws body heat away from your tootsies more quickly than the carpet does. Thus, it feels as if the tile is colder.

Thermopane Windows



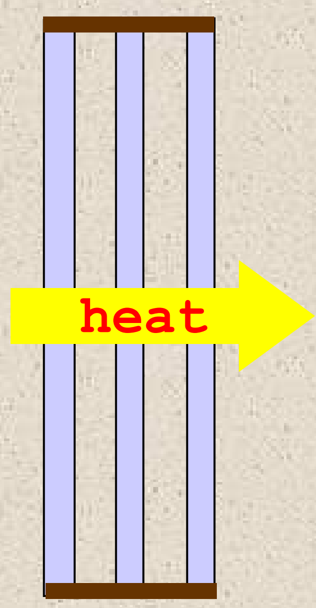
In a house we often want to prevent heat from getting in or getting out. Windows can be problematic. Thermopane windows have two or more panes of glass with air or some other gas between the panes. Which type of window, a double pane or a thick single pane, is better for minimizing heat transfer, if the total thickness is the same?



answer:

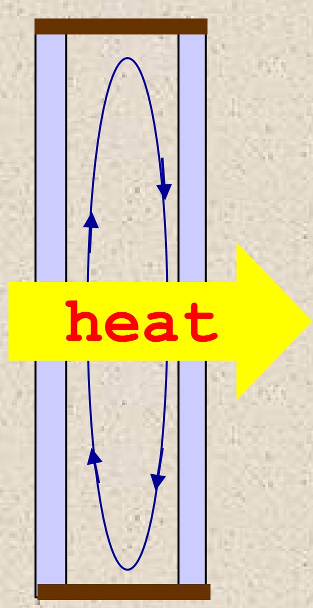
There is more glass in the single pane window to block the heat, but the air in between the panes of the double pane window has thermal conductivity that is about 35 times lower than that of the glass itself. So much more heat would be transferred through the single pane.

Triple pane vs. Double pane



If they are of the same total thickness and pane thickness, which is better at minimizing heat transfer, a double or triple pane window?

answer:



The double pane window has more air between the outer panes, so its thermal conductivity is lower. However, air is a mobile medium, and convection currents can shuttle warm air from the warm side to the cold side. On the warm side the air rises, moves across the the cold side, and sinks, moving in a loop and carrying its energy from the warm side to the cold side. The middle pane in the triple pane window reduces the energy transfers due to convection and is the better window (but probably more expensive).

R Value

The R value of a material is its "thermal resistance" and refers to how good an insulator is. Here's how it's defined:

$$R = \frac{L}{k}$$

As in previous equations:
L = the thickness of the material
k = thermal conductivity of the material

Note that the R value is inversely proportional to thermal conductivity, meaning good heat conductors have a low R value and are poor insulators. Also, the R value is directly proportional to the thickness of the material, meaning the thicker it is, the better it insulates. Thus, more insulation in the attic can save energy.

Wind & Heat Loss

A breeze can cool us off in the summer, and wind can make us feel colder in the winter. Why is this?

answer:

When we sweat the perspiration absorbs body heat, and when it evaporates, it takes this heat with it. This is called evaporative cooling. A steaming cup of hot chocolate cools in the same way.

The reason a coat keeps us warm in the winter is because it traps air that is heated by our bodies. (Wearing layers is like having a triple pane window.) A thin layer of stagnant air also surrounds the outside walls of buildings and helps insulate them. Wind tends to blow this warm air away, along with its heat. The windier it is, the colder it feels to us, and the greater the heat loss from a building.

Trees around you home can save energy in two ways: blocking wind in the winter; and shielding your home from excess solar radiation in the summer.

Laws of Thermodynamics

(examples upcoming)

- Zeroth Law: If object A is in thermal equilibrium with object B, and if object B is in thermal equilibrium with object C, then objects A and C are also in equilibrium. This is sort of a "transitive property of heat."

- First Law: Energy is always conserved. It can change forms: kinetic, potential, internal etc., but the total energy is a constant. Another way to say it is that the change in thermal energy of a system is equal to the sum of the work done on it and the amount of heat energy transferred to it.

- Second Law: During any natural process the total amount of *entropy* in the universe always increases. Entropy can be defined informally as a measure of the randomness or disorder in a system. Heat flows naturally from a hot to cooler surroundings as a consequence of the second law.

Zeroth Law

In math we have a transitive property of equality: If $a = b$ and $b = c$, then $a = c$. The zeroth law of thermodynamics works the same way with temperature.

Suppose some firewood is brought in from the cold and an apple pie is removed from a hot oven. Both are placed in the same room. With time the firewood and the room with reach thermal equilibrium, as will the pie and the room. This means the firewood and the room are at the same temp. The pie and room are at the same temp too. Therefore, by the zeroth law, the firewood and pie are at the same temp, meaning they too are in thermal equilibrium.

First Law

Schmedrick is cruising around in dune buggy daydreaming about thermodynamics. When he hits the gas, a mixture of fuel and air is injected into a cylinder and ignited by a spark-plug. The gasoline contains chemical potential energy, meaning when it is burned by combining it chemically with O_2, the products of the reaction are mainly small molecules (CO_2, H_2O, & pollutants) that contain less potential energy than the reactants. Some of this energy goes into kinetic energy of the dune buggy. The wheels have both rotational & translational kinetic energy. Some may go into gravitational potential energy, if Schmed drives up hill. Most of the energy is actually wasted. The exhaust gas is very hot, and thus contains internal energy that Schmed would have preferred to have gone into propelling his vehicle. Some of the energy also heated up the engine. The 1st Law guarantees that all the original chemical potential energy is accounted for.

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First Law *(cont.)*

As Schmedrick cruises around, he becomes too engrossed in his daydream and crashes into a street light and putting a big, ole dent in it. The 1st Law has something to say about the crash too:

In order to dent the pole, work has to be done on it. That is, a force must be applied to the pole over some distance. The force is from the dune buggy. The work done on the pole is energy transferred to it by the buggy, which quickly dissipates as heat. If the pole were made of some material that could spring back into its normal shape after impact, it would store some energy during the collision as elastic potential energy, rather than simply generating heat.

Here's the point: If you need to do work, the 1st Law demands that you have at least as much energy available as the amount of work you need to do. If Schmed had been going slower, his kinetic energy would have been less, and he wouldn't have been able to do as much work on the pole, and the dent would have been smaller.

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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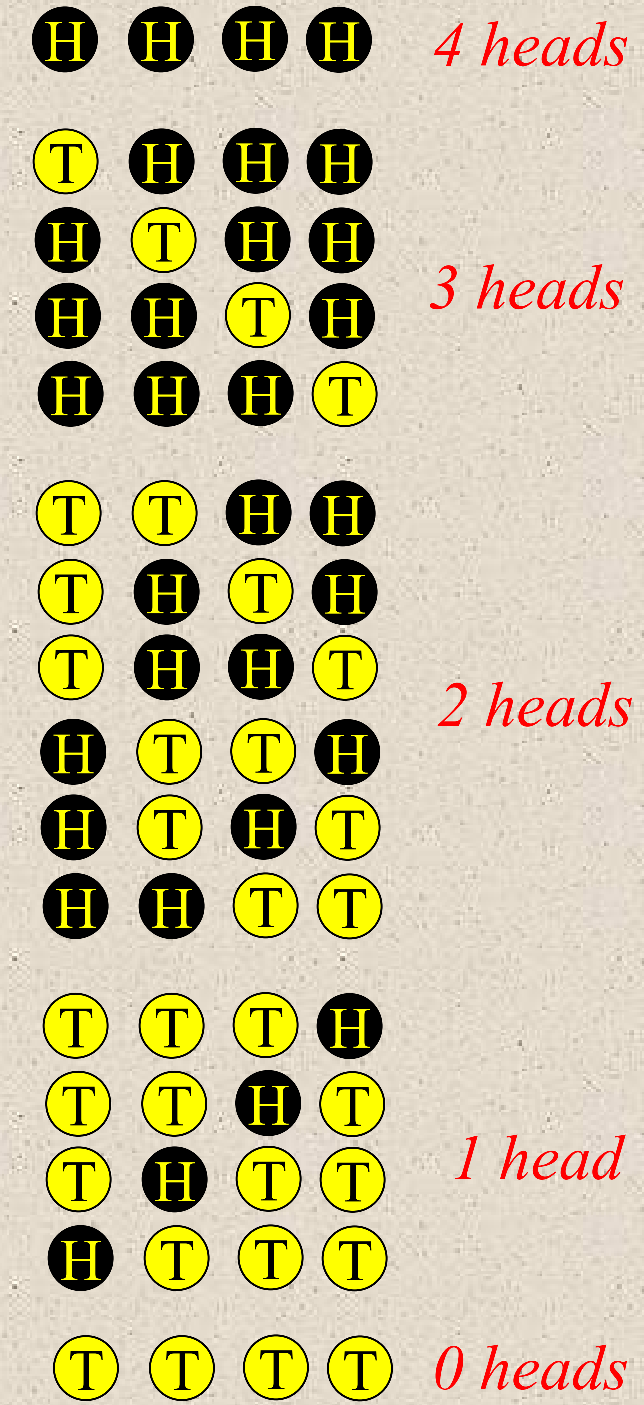
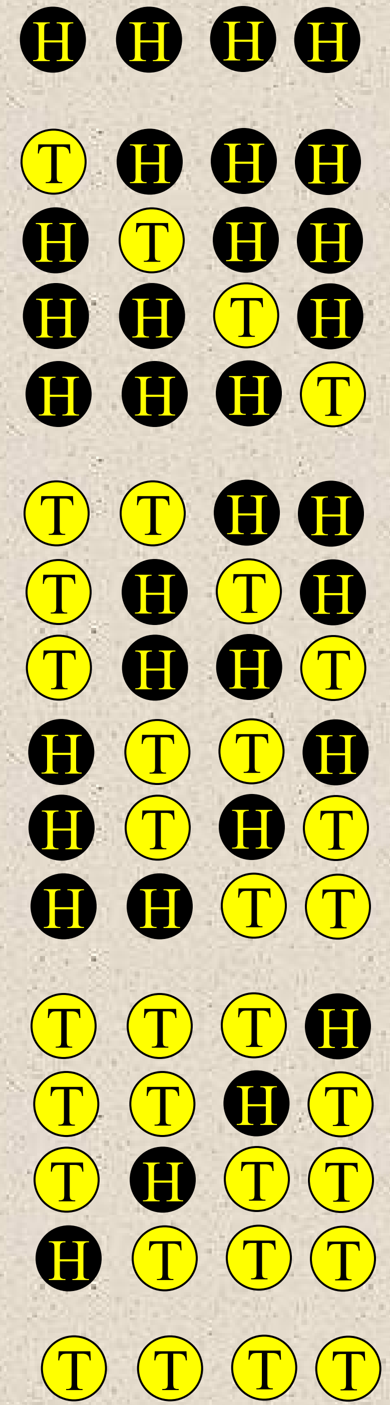


Entropy *(cont.)*

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.

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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.

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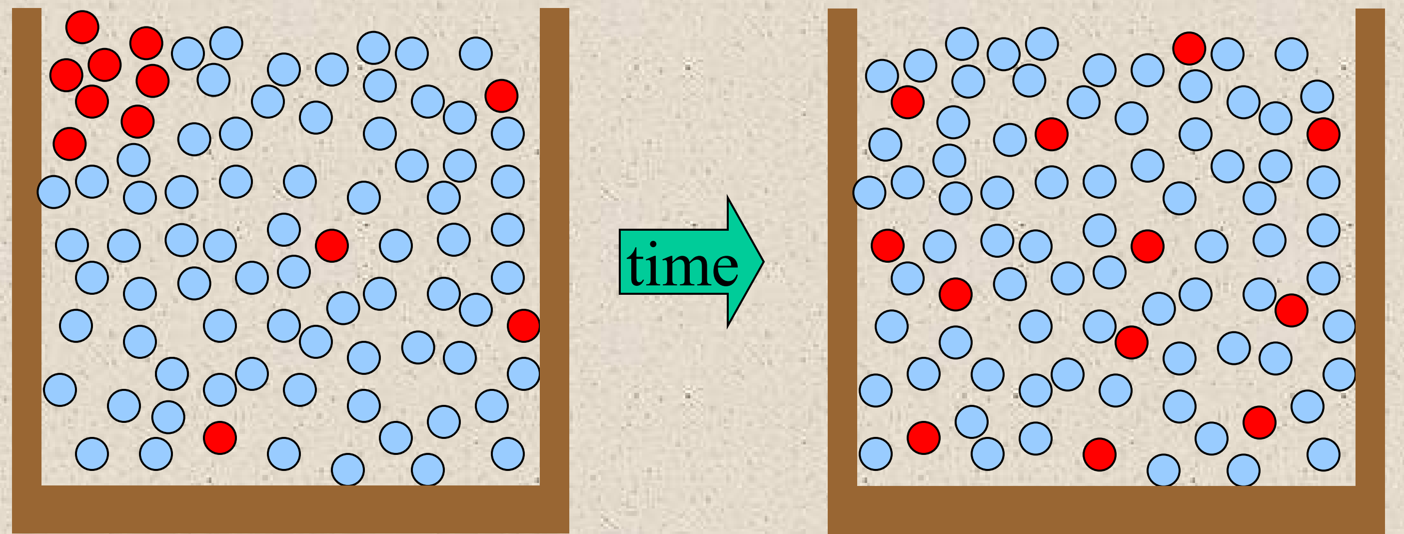
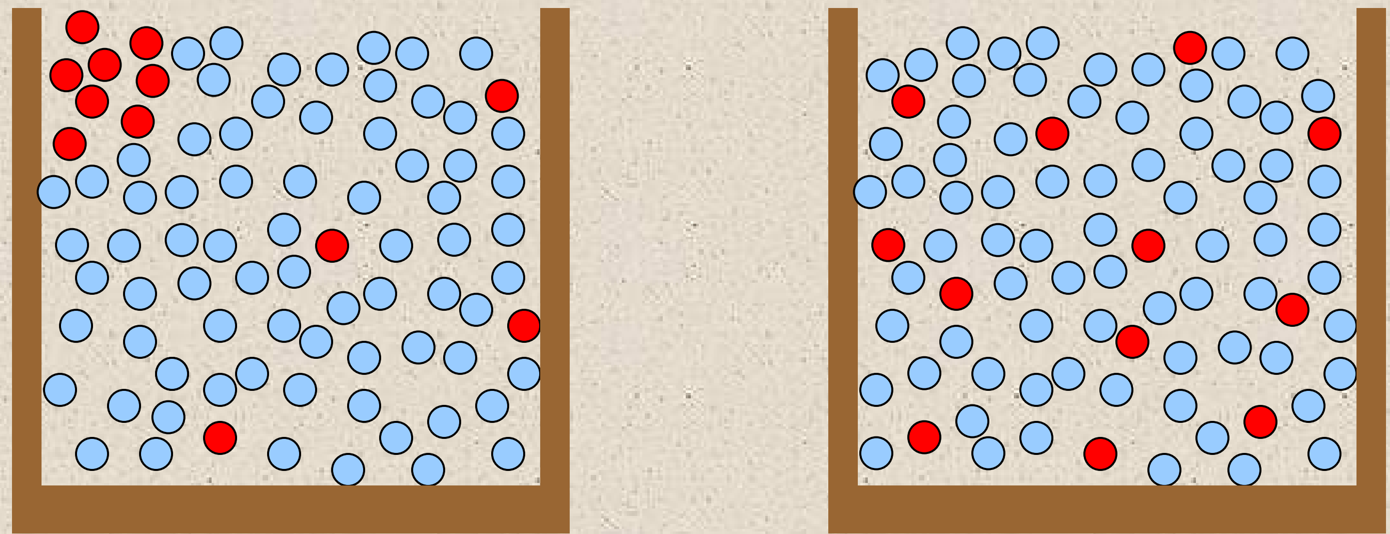


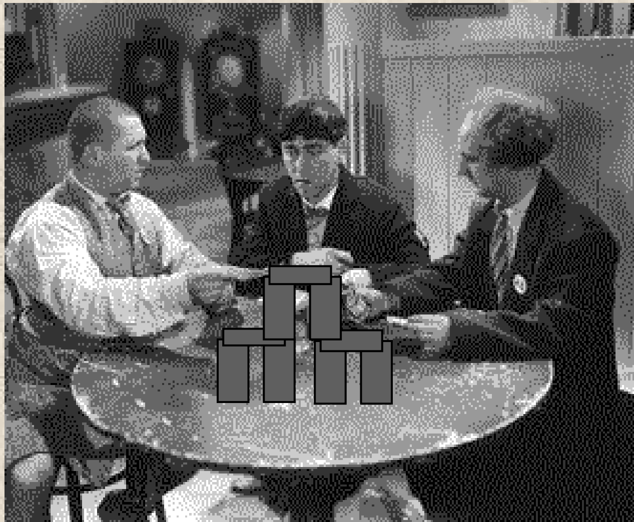
Entropy & Fluids (cont.)

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 2nd 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:

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

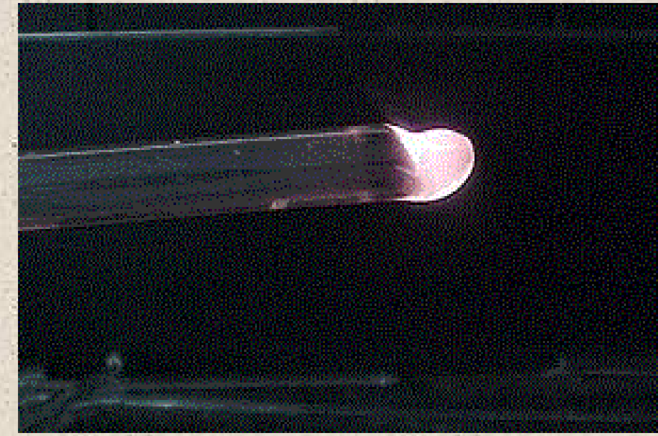
ΔS = change in entropy
ΔQ = change in internal energy (heat flow)
T = absolute temperature

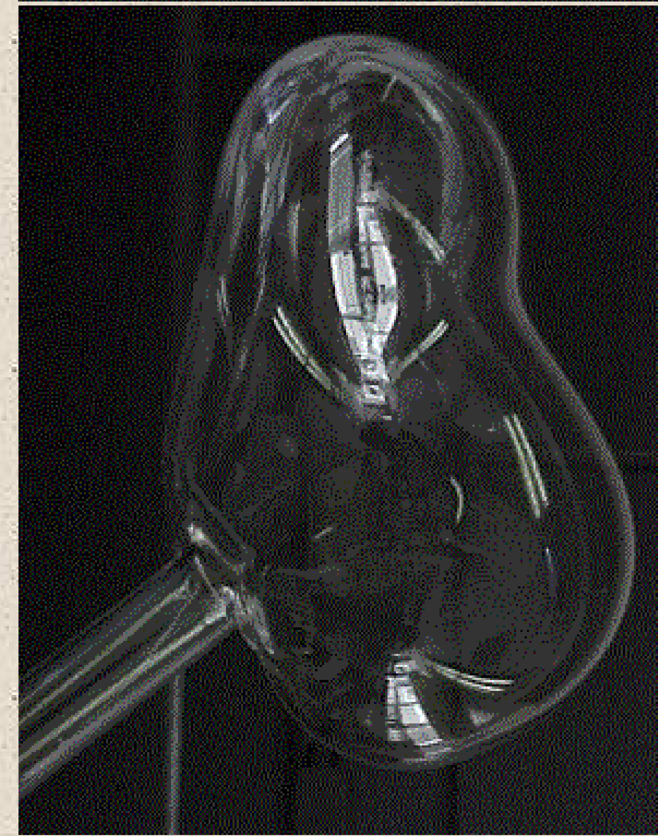
The 2nd Law of Thermodynamics says that during any process:

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

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.)*

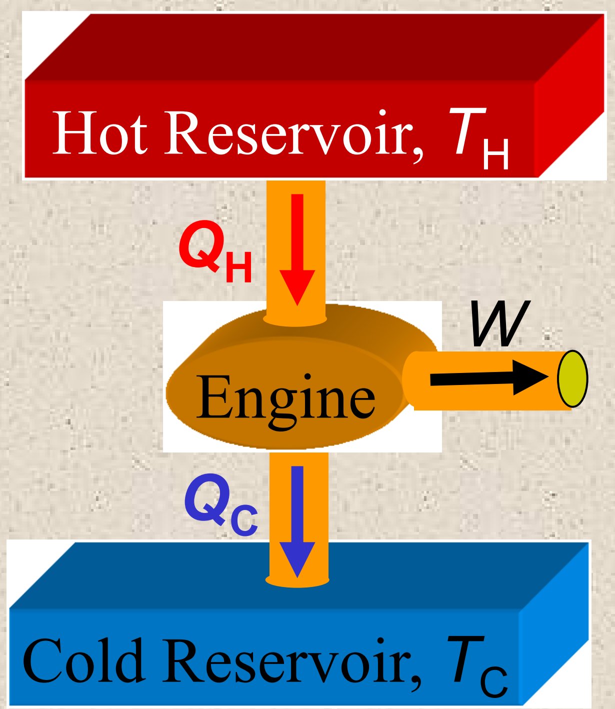
• Any time we do something that decreases the entropy of a system, the energy we expend in doing it increases the entropy of the surroundings even more.

• 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.)

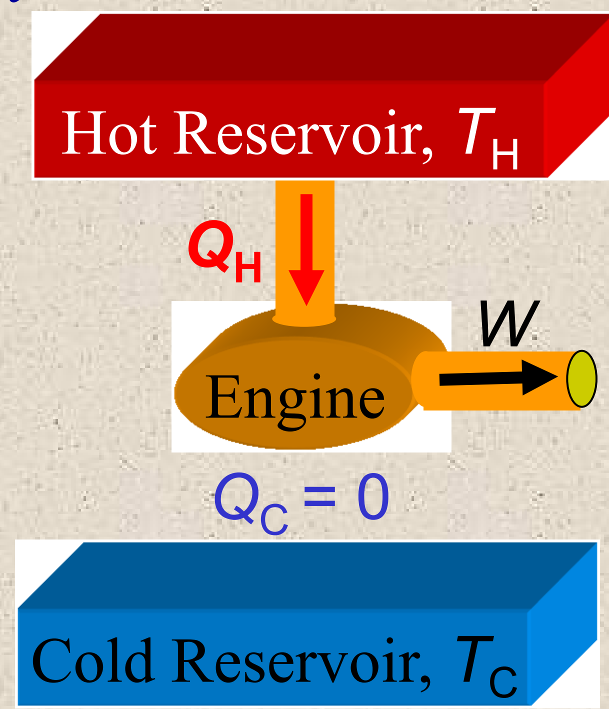
• During any process the entropy of the universe cannot decrease. Expending energy to decrease the entropy of a system will lead to an increase in entropy for the surrounding by a greater amount.

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.



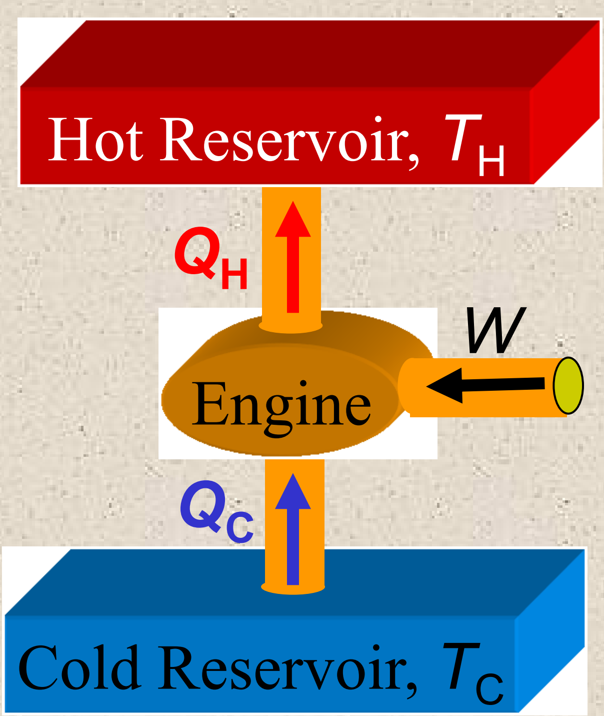
Real engine. $Q_H = Q_C + W$



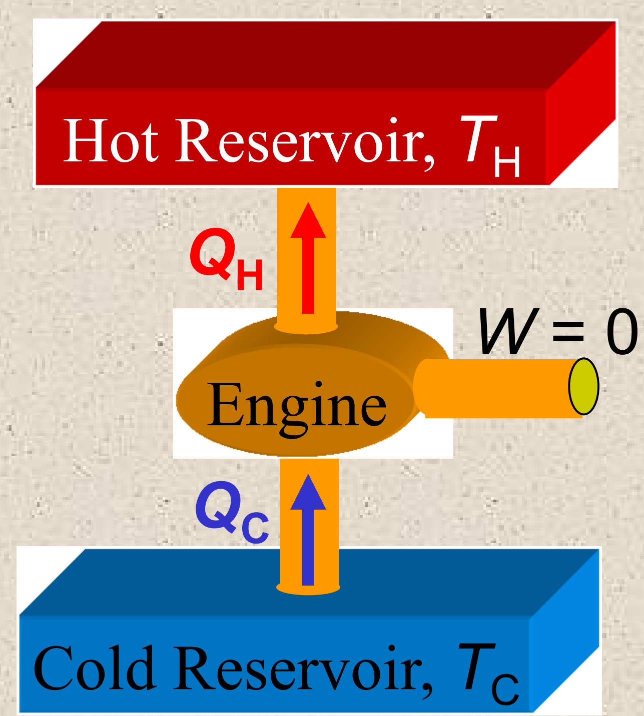
Impossible engine. $Q_H = W$

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?

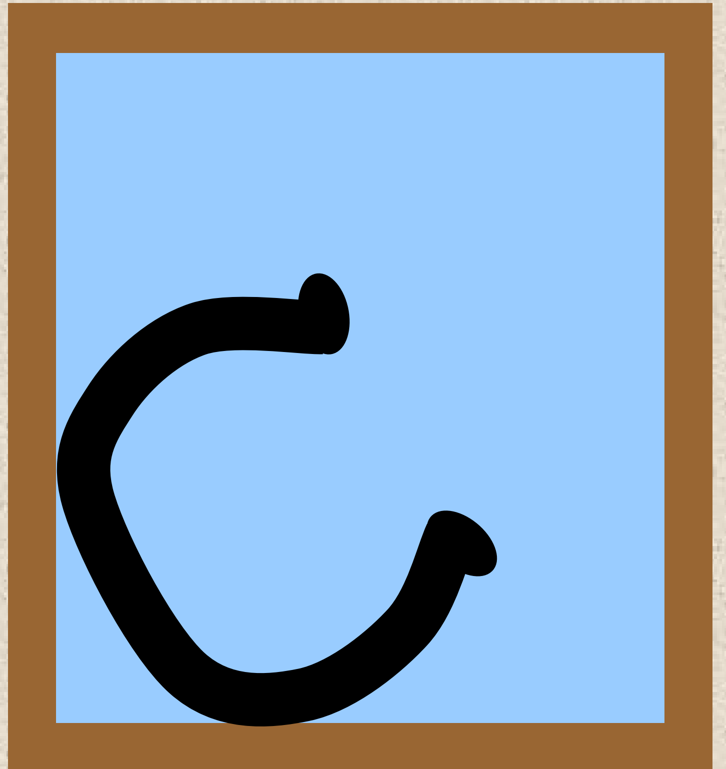
answer:

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

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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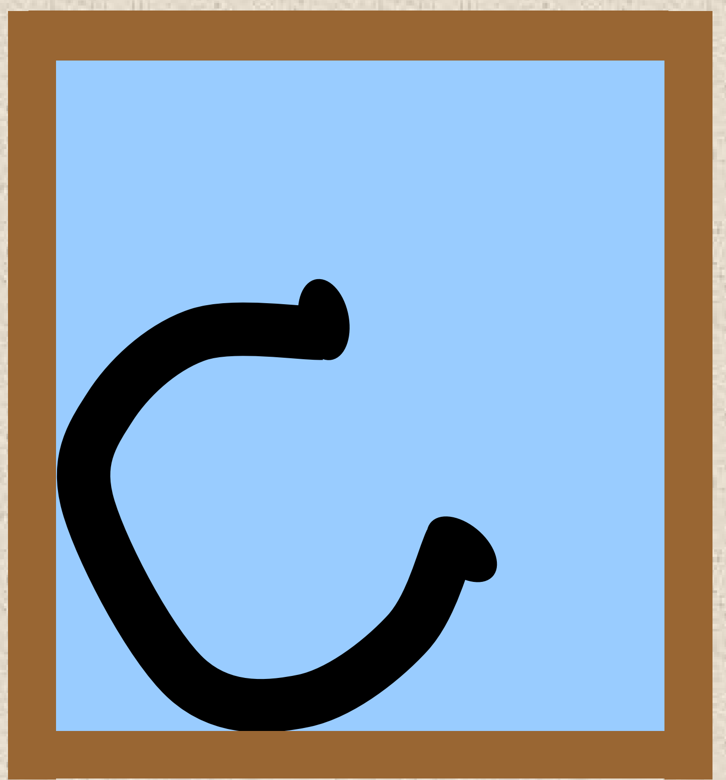
Calorimetry (cont.)

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 $\leftrightarrow$ solid or gas $\leftrightarrow$ liquid) energy is transferred <u>without</u> 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*.

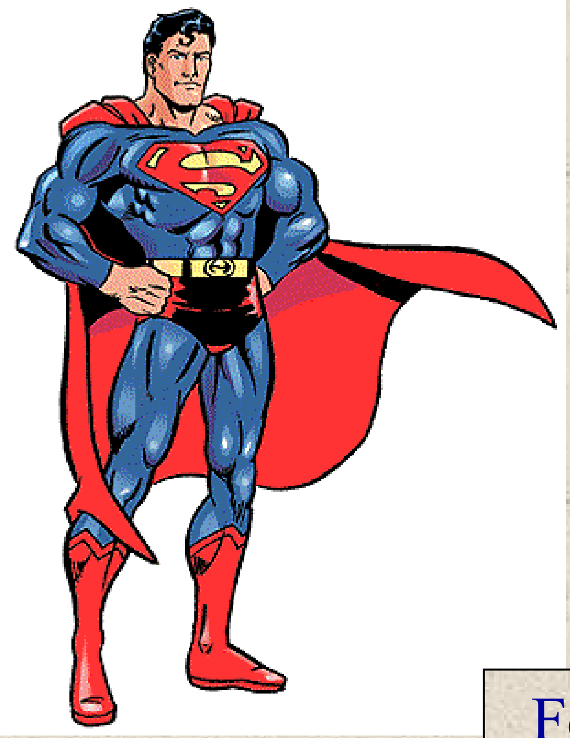
Latent Heat Formula

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

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

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

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

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

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

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

$= 5.62 \cdot 10^9$ 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. $\Delta S_{surr} = \Delta Q_{surr} / T_{surr} = -3330 \text{ J} / 283 \text{ K} = -11.767 \text{ J/K}$.

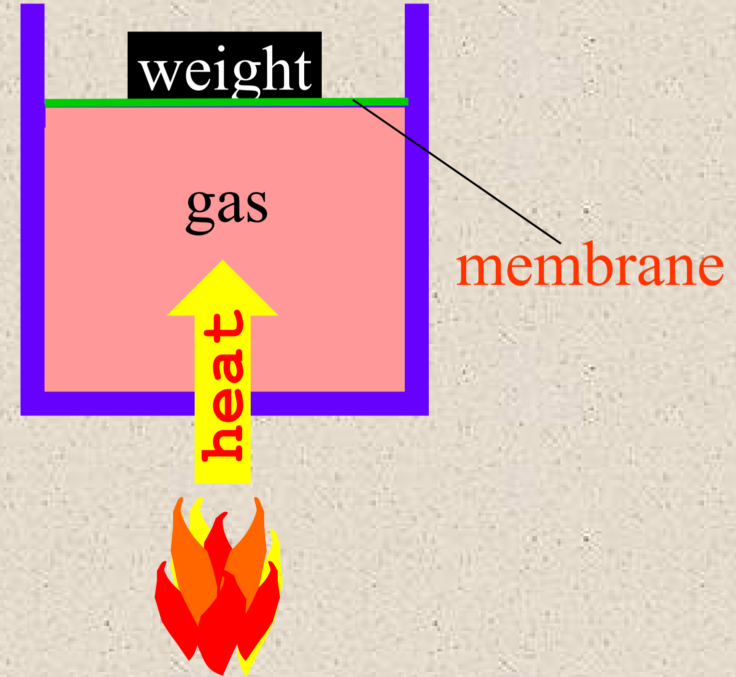
For the universe: $\Delta S_{univ} = \Delta S_{surr} + \Delta S_{ice} = 12.198 \text{ J/K} - 11.767 \text{ J/K} = +0.431 \text{ J/K}$. Thus, the 2nd Law is satisfied.

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

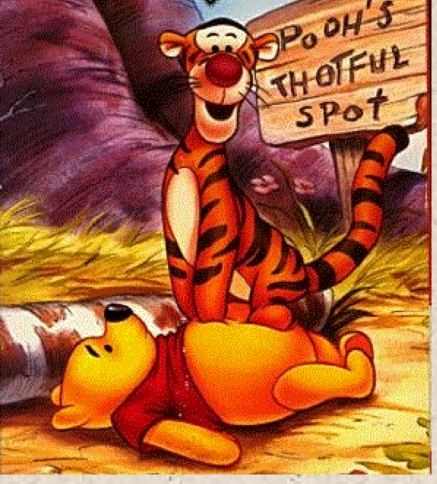
In summary: $\Delta E_{int} = Q - W$, which is one way to state the 1st Law.



Q is positive if heat flows in. W is the work done by 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.



Calorimetry & Tigger

Tigger greets Pooh in his usual enthusiastic manner. When he realizes that Pooh is storing a large vat of honey, Tigger bounces around the Enchanted Forest, and with one last, mighty bounce propels himself

into the vat. Tigger's mass is m. His tail has a spring constant k and compresses a distance x. The honey's mass is M, and its specific heat is C. Assuming the honey gains all of Tigger's energy, how much does the honey's temperature rise? *answer:*

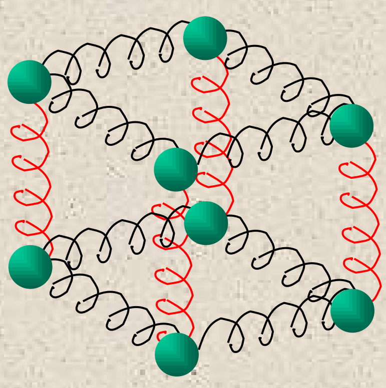
The elastic potential energy stored in Tigger's tail is converted to thermal energy in the honey:

$$E_0 = E_f \Rightarrow \tfrac{1}{2} k x^2 = M C \Delta T \Rightarrow \Delta T = \tfrac{1}{2} k x^2 / MC$$

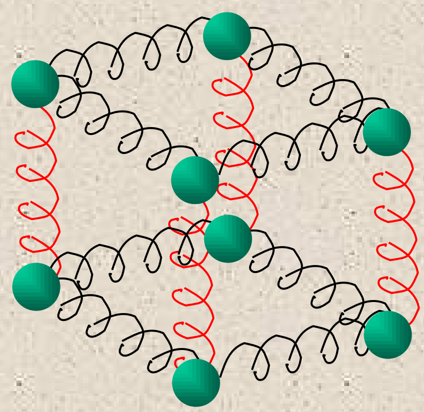
In real life ΔT would be slightly less since some of Tigger's original energy would have gone into heating the air and Tigger himself. Note that Tigger's mass and the height of his bounce matter not.

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

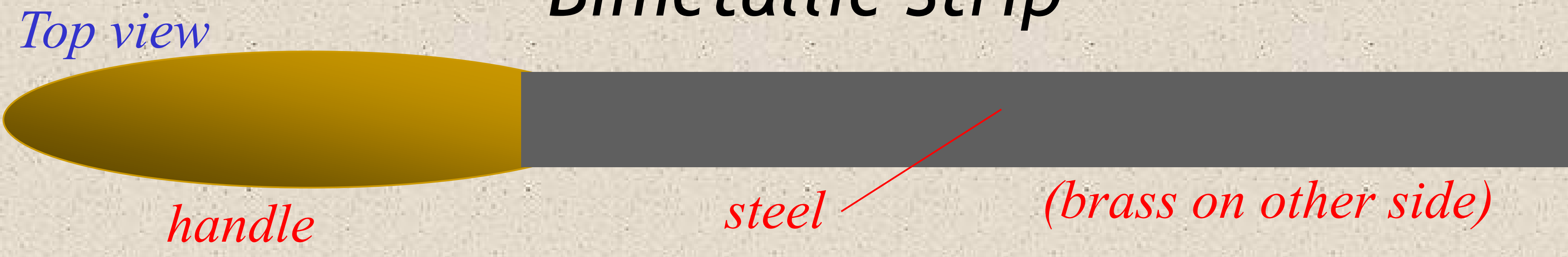
Length expansion:

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

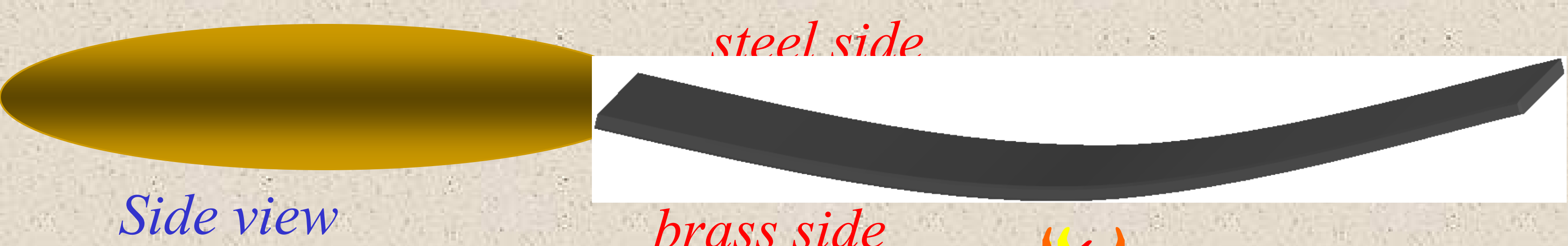
Volume expansion:

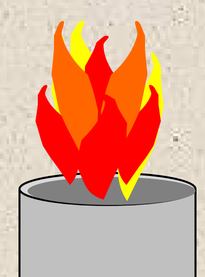
$$\frac{\Delta V}{V} = \beta\,\Delta T$$

Bimetallic Strip



A bimetallic strip is a strip of two different metals—often steel on one side and brass on the other. When heated the strip curves because the metals have different coefficients of thermal expansion. Brass's coefficient is higher, so for a given temperature change, it expands more than steel. This causes the strip to bend toward the steel side. The bending would be reversed if the strip were made very cold.

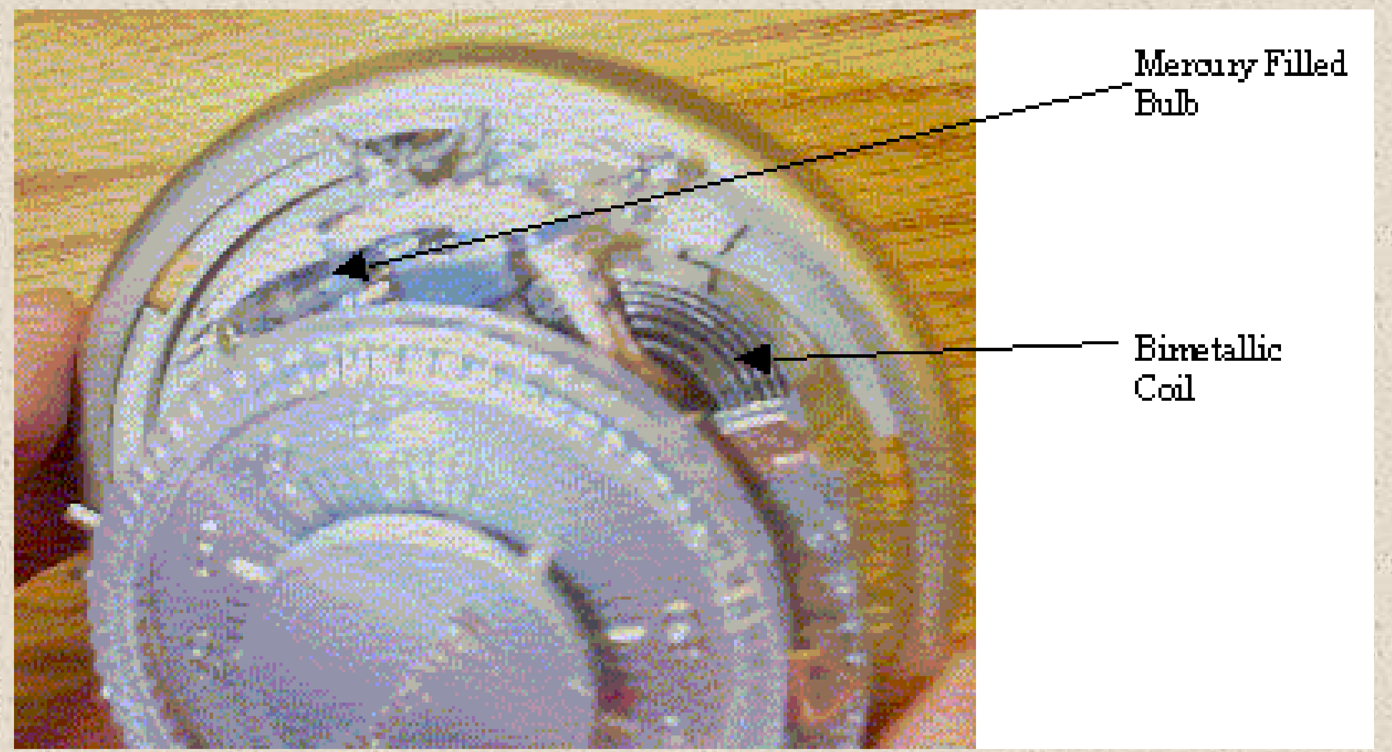




Click for Internet Demo

Thermostats

Bimetallic strips are used in thermostats, at least in some older ones. When the temperature changes, the strip bends, making or breaking an electrical circuit, which causes the furnace to turn on or shut off. In this model when the strip bends it tilts a bulb of mercury, which then bridges two wires and allows current to flow.



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!*

Credits

Thermostat: http://www.phys.virginia.edu/Education/outreach/8thgradesol/ThermostatFrm.htm