Chapter 2
Thermodynamics

Heat

In the last chapter, we defined energy and discussed one method for transferring it (work). In this chapter, we will discuss another method for transferring energy: heat. Much like the terms work and energy, heat is a term that gets used in our everyday language with a meaning that is not technically correct. Heat is often confused with thermal energy or with temperature. While it is connected to these two terms, it is not the same, and its use as such is incorrect.

The most common error, even made by some science textbooks, is to define heat in terms of the total kinetic energy of atoms or molecules in a substance not associated with bulk motion of the substance. This is incorrect, as it is a more appropriate definition of the thermal energy of a system. However, it is easy to see why this misconception holds. While heat is energy, it is not a containable form of energy since, by its very definition, heat is energy that is transferred. In particular, heat is **the energy transferred between objects due to their temperature difference**. The misunderstanding comes from the fact that we often talk about heat leaving a hot object or entering a cold object, which gives people the idea that objects must contain heat. But this is not the case. Once heat enters an object, it increases the internal energy of an object, which is the same result that doing work on the object would produce. The object does not contain the heat or the work; it merely changes its energy because of them.

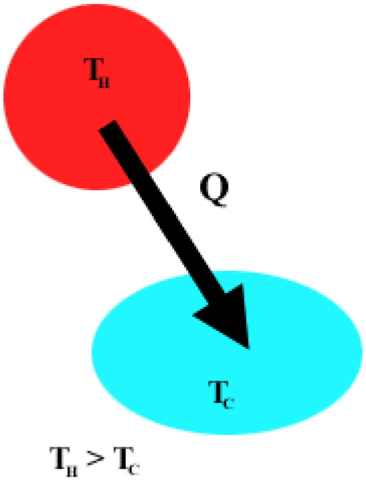

Fig. 1: Heat flows from hot to cold

Heat Versus Temperature

This increase in internal energy can cause numerous things to occur to the object. One of the more common things that it causes is for the temperature of the object to increase. An example of this is when you place a candle flame (hot) in contact with a glass of room-temperature water (cold), which results in the water getting warmer. However, it can cause other things to occur that do not involve any change in temperature, such as a change of state. This would happen in the previous example when the temperature of the water gets so high that it begins to boil and change into steam. The fact that one of the most common experiences is that the temperature changes leads to an erroneous definition for temperature. Many sources define it as "a measure of the speed of motion of a typical atom or molecule in a substance." Again, this is incorrect. While it may be true for an ideal gas, it does not apply to all objects. The best definition for temperature is **the property that two objects have in common when no heat is transferred between them when placed in thermal contact**.

The observant reader is going to note a certain circuitousness about these definitions for heat and temperature, as the definition of one depends on the other. These are the only definitions that truly make sense, though. The best way to illustrate this is to examine what happens when you measure the temperature of a glass of water with a mercury or alcohol thermometer. Upon entering the water, the thermometer does not instantly register the correct temperature. Instead, it takes several seconds for the liquid in the thermometer to settle to the correct reading. During this time, heat is being exchanged between the water and the liquid in the thermometer. As it does so, the temperature of the liquid in the thermometer changes, becoming closer to that of the water. This change in temperature of the alcohol or mercury results in its volume changing, which is what changes the level of the fluid in the thermometer. Once the temperature of the fluid has reached that of the water in the glass, heat stops being transferred between them, and the volume of the fluid stops changing.

Thus, the thermometer is not measuring the average speed of the molecules in the water. The only thing that is being measured is the volume of the liquid in the thermometer. Somebody (or some machine) calibrated the volume of the fluid in the thermometer to a temperature scale that is painted onto its side. Because of this, we are able to read a value for the temperature by merely measuring the height of the liquid in the thermometer. The temperature that we read, though, only tells us which way that heat will flow if the object is put into thermal contact with another object; it does not measure the energy of the substance.

Temperature Scales

The scale that is painted on the side of the thermometer depends upon how it was calibrated and what is the purpose of the thermometer. If you have been through the U.S. K-12 educational system, you know that we in the sciences always talk about the metric system and why it is a better system than the one that is currently used in our country, the English units. Let’s face it: if the English units were good, then why did the British abandon them for the metric system? The metric system is superior because it is so easy to convert between units of different size, such as meters and kilometers (1 kilometer is 1,000 meters). Converting in the English system is a nightmare, as anyone who has ever had to convert from inches to miles knows (1 mile is 5,280 feet, one foot is 12 inches).

The problem is that this idea of “better” is only true when there are different sized units for a particular measurement, such as distance (meters/kilometers versus yards/miles) or weight (newtons/kilonewtons versus ounces/pounds). It is not better when there is only one unit for a particular measurement (As an aside, when are we going to get metric time? What is it with all of this “24 hours to a day, 60 minutes in an hour,…” stuff? Where is my metric day?) This is true in the case of temperature, although you might not realize it.

You have probably been led to believe that the Celsius scale of temperature is superior to Fahrenheit. The Celsius scale is based upon 0 degree being the point at which pure water at standard pressure freezes and 100 degrees being the point at which pure water at standard pressure boils. By implication, the Fahrenheit scale is not as good, since these two situations (freezing and boiling water) are denoted as 32 and 212 degrees in the Fahrenheit scale, which are much harder to memorize. Given this, one has to wonder just how insane Fahrenheit had to be in order to base his scale in such a manner. Really, who would choose a starting point of 32 for their scale?

History does not show that Fahrenheit was mentally deranged or impaired. Instead, he based his scale on other standards which were and are harder to repeat. His scale starts at 0 degrees, but instead of being the point at which pure water freezes, it is the point at which the saltiest water freezes. This starting point makes a tremendous amount of sense if you are involved in traveling the ocean, as England was in the early 1700's. If the temperature is 0 degrees in the Fahrenheit scale for an extended period of time, then you can expect to see ice forming on the ocean, which means that your ships will not be able to get out of harbor. If you use the Celsius scale, you are going to have to remember where this point is.

Far from being inferior, one could make the case that the Fahrenheit scale is superior to Celsius as one degree of temperature change in the Fahrenheit scale is smaller than that on the Celsius scale. This means that the Fahrenheit scale has greater resolution than the Celsius scale. However, one could also make the claim that a third scale, the Kelvin scale, is superior to both of these since it starts at absolute zero. This means that there is no such thing as negative temperatures on the Kelvin scale, which is good for use in equations.

The fact is that inferior or superior is merely a value judgment and holds little sway in science. We use all three depending upon which is most expedient and makes most sense for the application. When we are measuring things in our homes in the U.S., we will use the Fahrenheit scale. When we are measuring energy changes due to heat exchanges, we will use the Celsius scale. When we are discussing energy changes due to electromagnetic radiation, we will use the Kelvin scale. This will not be a problem, as we will not ask you to convert between the scales.

Calorimetry

As we stated earlier, when heat enters or leaves a substance, it can cause the temperature to change. The amount of the temperature change is determined by the calorimetry equation

$$Q = m\,c\,\Delta T \qquad \textbf{(Equn. 2.1)}$$

where Q is the amount of heat leaving or entering the substance, m is the mass of the substance, c is the **specific heat** of the substance, and ΔT is the temperature difference experienced by the substance. The specific heat of the substance is a constant that is determined by the substance and its state of matter. For example, the specific heat of water is 1 calorie per gram per degree Celsius (1 cal/(gm ^{o}C)). Another way of stating this is that it requires 1 calorie of energy to raise the temperature of 1 gram of water 1 ^{o}C (Note: this calorie is not the food calorie that is listed on every box of processed food in the U.S. There are 1,000 calories to a food calorie). Table 1 has a list

Compound	Specific Heat (cal/gm K)	Heat of Fusion (cal/gm)	Heat of Vaporization (cal/gm)
Water	1.00	79.7	540
Steam	.475	-	540
Iron	.108	63.7	
Sodium	.295	27.4	944
Aluminum	.215	94.5	

Table 1: Specific and latent heats (*Source: CRC, 63rd Edition*)

of some common substances and their specific heats.

As a convention, heat entering a substance is taken to be positive, which will result in a positive value for ΔT. If heat is leaving a substance, Q is negative, as is the ΔT that will result from the equation. This convention makes sense, since an increase in energy in the substance will usually result in the molecules in the substance moving faster, which will correspond to an increase in temperature.

This is true except when a change of state in the substance occurs. When this happens, the energy entering the substance is used to break intermolecular bonds and not to increase the kinetic energy of the molecules. In other words, this heat goes toward increasing the potential energy of the molecules in the substance instead of the kinetic energy. When a substance reaches a temperature at which a change of state will occur, then the temperature of the substance stops changing until an amount of energy is exchanged to complete the change. The amount of energy required for the change is given by the formula

$$Q = m\ L \qquad \textbf{(Equn. 2.2)}$$

where L is either the latent heat of vaporization or the latent heat of fusion, depending upon whether it is at the gas-liquid interface or the liquid-solid interface (Table 1).

To illustrate both of these equations, let us look at an example. Suppose a 700-gram pot of water needs to go from 20 ^{o}C to 105 ^{o}C. As heat is added to the substance, its temperature will increase until it reaches 100 ^{o}C. At this point, the temperature will stop increasing, as all heat added will go toward vaporizing the water. After all of the water vaporizes, the temperature will once again increase until it reaches 105 ^{o}C. In these three stages, the amount of heat that enters the water is

$$Q_1 = (700\ \text{gm})\ (1\ \text{cal/gm}^{o}\text{C})\ (80\ ^{o}\text{C}) = 56{,}000\ \text{cal}$$
$$Q_2 = (700\ \text{gm})\ (540\ \text{cal/gm}) = 378{,}000\ \text{cal}$$
$$Q_3 = (700\ \text{gm})\ (.475\ \text{cal/gm}^{o}\text{C})\ (5\ ^{o}\text{C}) = 1{,}663\ \text{cal}$$

for a total of 435,663 calories.

Energy Transfers and the First Law of Thermodynamics

While we have been discussing energy transfers, we have yet to discuss if there are any limits to how energy transfers take place. In the 1800's, scientists found, empirically, that rules do exist that limit energy transfers. The first of these rules is called the First Law of Thermodynamics. This law is usually stated as, "Energy can neither be created nor destroyed; it can only be transferred from one form to another." This can lead to the re-titling of this law as the Conservation of Energy Principle since it says that energy must be conserved. However, this is not technically correct, as the Conservation of Energy Principle is a very limited case of the First Law when the energy within a system is kept constant, i.e. the system does not exchange energy with its surroundings. The First Law applies to all systems, even those exchanging energy with their surroundings.

This statement of the First Law does not say anything about how energy can be transferred, though. It turns out that there are only two ways. This was discovered in 1850 by the English scientist James Joule, who found that heat and work are equivalent methods for changing the energy of an object. In his experimental work, Joule was able to show that he could increase the thermal energy of a pot of water by either placing it over a flame (adding heat), or by stirring it with a paddle (doing work). Using this, we can re-write the First Law mathematically as

$$\Delta E = W + Q \qquad \textbf{(Equn. 2.3)}$$

where ΔE is the change in the energy of an object, W is the work done on the object, and Q is the heat added to an object. In laymen's terms, this means that the only way to change the energy of an object is to either do work on it or add heat to it (it should be noted that having the object do work on its surroundings, or allowing the object to give off heat, are equivalent to having negative values for W or Q). For his work in this area, the SI unit of energy is called a joule (1 J = 1 kg m^2/sec^2).

As an example, suppose that a person compresses a balloon filled with air while putting the balloon in a warmer room. In order to compress the balloon, a force through a distance is applied, which means that work is done on the gas in the balloon. By putting the balloon in a warmer room, the gas is being heated. If the total amount of work done is equal to 200 J and 300 J of heat enter the balloon, then the First Law states that the energy change in the balloon is

$$\Delta E = W + Q = 200\ J + 300\ J = 500\ J$$

If we had placed the balloon in a colder room, then heat would have left the air in the balloon, which would decrease the energy of the air. In that case, we would subtract the heat from the work done.

Conduction

As you can see from the example, understanding how heat can be transferred is very important to understanding the energy in a substance. Heat can be transferred in one of three ways: conduction, convection, and radiation. All that is required is that there be a temperature difference between two objects. In many situations, heat will flow by a combination of all three of these. The importance of one to the overall flow varies depending upon the situation under consideration. Between the Sun and Earth, radiation is most important, as the virtual vacuum of space limits conduction and convection. In a well-sealed home, conduction will usually be the most important, followed quickly by convection. As we previously stated in last chapter, homeowners, on average, spend almost 50% of their energy budget for heating and cooling. This means that understanding and finding ways to control heat flow can be very cost effective.

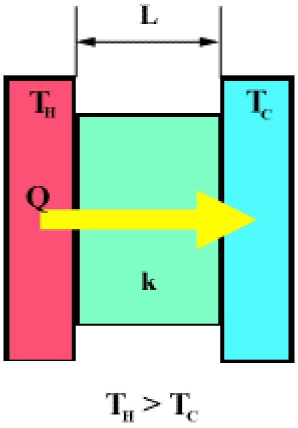

Fig. 2: Conduction, single layer

Conduction occurs when two regions of different temperature are put into direct contact, but are not allowed to mix. As an example, the inside temperature of a home in the winter is hotter than the exterior temperature if the home is being heated. The walls, doors, and windows are all conducting heat to the outside since they are in direct contact with both reservoirs of air. The exchange takes place as air molecules in the warm air collide with the particle making up the walls. These air molecules give some of their kinetic energy to the particles in the wall, which causes them to move faster. The particles then collide with their nearest neighbors, which transmits the energy deeper into the wall. Eventually, the particles on the other side of the wall receive this energy delivered by collisions and spread it to the air molecules in the cool air outside. Through all of these collisions, heat has flowed from the warm interior to the cool exterior.

The rate at which heat gets transferred (see Figure 2) depends upon (1) the thickness of the material L, (2) the thermal conductivity k (this depends on the composition of the material), (3) surface area of the material A, and 4) the temperature difference between the reservoirs. If you understand the description above, this makes sense. If the wall is thicker, then it will take longer for the energy to get from one side to the other. If there is more surface area, then there are more collisions and paths for the heat to flow, which will increase the rate of heat flow. If the temperature difference is greater, then there will be more energy to flow across the material.

In particular, the rate of heat transfer by conduction is given by

$$Q/t = A\ k\ (T_H - T_C)/L. \qquad \textbf{(Equn. 2.4)}$$

This equation shows that the thicker the material separating the two reservoirs (L larger), the smaller the surface area that is contact (A larger), or the smaller the temperature difference, the slower the rate of heat transfer through the substance, just as we stated above. When it comes to heating and cooling our homes, this is exactly what we will need to strive for in order to reduce our energy bills.

We need to stress that this equation is for the rate of heat transfer and not for the amount of heat transfer. This rate can be very important, especially to heat transfers that are occurring into and out of our bodies. The way that we perceive objects as hot or cold has a lot to do with the rate at which heat is conducted from our skin. For example, consider two chairs that have been sitting in a 70 ^oF for several hours. One of the chairs is made of steel, while the other is made of wood. You are asked to sit on one of the chairs while you are wearing short pants. All other things being equal, most people in this situation will choose the wood chair to sit on. The reason given for this choice is usually, “The steel chair is too cold.” However, as both chairs have been in the room for a long enough time to come to equilibrium with it, they will both be at the exact same temperature of 70 ^oF. The reason for the differences in the feel of the chairs is that steel has to do with the fact that steel has a much higher thermal conductivity than wood. When you sit on it, it draws heat away from your body much faster than the wooden chair, even though both are at the same temperature. It is this rate of heat transfer that you experience as colder.

As often as not, the material through which heat is being conducted is made up of more than one substance (Figure 3). In our homes, the exterior surfaces are usually comprised of several types of building material. For instance, a wall can be composed of 3 1/2 inches of fiberglass insulation which is covered by 1/2 inches of sheetrock on the inside and plywood and brick on the exterior. When two or more different materials are between the hot and cold reservoirs, the equation on the previous page can become quite messy since there will be various thermal conductivities and thicknesses with which to deal.

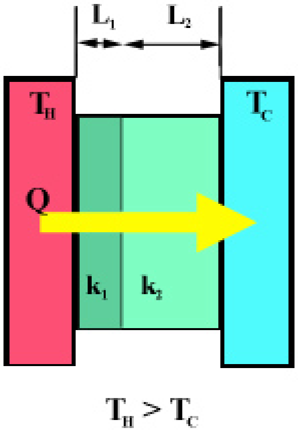

Fig. 3: Conduction, multiple layers

The equation is greatly simplified if we consider the **R-value** of objects instead of their thermal conductivity. This is a measure of how well the material resists the flow of heat through it, and it combines the thermal conductivity and thickness into one term (R-value = thickness/thermal conductivity = L/k). While the common units for the R-value are ft^2 hr ^{o}F/Btu, these are often not quoted. If you visit any hardware store, you are likely to just see the R-value of a substance to just be quoted as a number, as in "Fiberglass R-value = 13."

From Equation 2.4, we can see that the equation for conductive heat transfer through a single substance is given by

$$Q/t = A\,(T_H - T_C)\,k/L = A\,(T_H - T_C)/R \qquad \textbf{(Equn. 2.5)}$$

If there are multiple materials that comprise the surface, then the equation becomes

$$Q/t = A\,(T_H - T_C)/R_T$$

where R_T = sum of all of the individual R-values. As an example, in the wall that we proposed above, the R-value for the fiberglass is 13, for the plywood and brick is 4, and for the sheetrock is 0.5. Therefore the total R-value for the wall is 17.5, which is what would be placed in the denominator of the heat transfer equation.

R-Factors for Common Materials

The R-factor of a surface determines how quickly heat is conducted across it. The values below are some of the more common R-factors for surfaces found on homes in the U.S.

Windows and Sliding Glass Doors:

Glass	Factor	Low Emissivity	Drapes	Quilts
Single pane	0.9	1.1	1.4	3.2
Single w/storm window	2.0		2.5	4.2
Double pane, 1/4" air space	1.7		2.2	4.0
Triple pane, 1/4" air space	2.6		3.0	4.8

Other Household Materials

Doors	**Factor**
1 1/2" wood no storm door	2.7
1 1/2" wood with 1" storm door	4.3
1 2/3" solid core wood door	3.1
1 3/4" steel insulated door	16
Roof/Ceiling	
No insulation	3.3
3 1/2" fiberglass	13
6" fiberglass	20
6" cellulose	23
12" fiberglass	43
12" cellulose	46
Walls	
Brick with 4" uninsulated stud wall	4
Brick with 4" insulated stud wall	14
Wood frame, uninsulated with 2" x 4" construction	4.6
Wood frame with 3 1/2" fiberglass; studs 16" o.c.	12
Wood frame with 3 1/2" fiberglass and 1" foam	20
Floor	
Over vented basement/crawl space, uninsulated floor	4.3
Over vented basement/crawl space,6" fiberglass insulation	25
Over sealed, basement/crawl space, uninsulated floor	8
Over sealed, basement/crawl space,3 1/2 fiberglass on basement walls	20
Concrete slab, no insulation	11
Concrete slab, 1" foam perimeter insulation	46

Convection

Another method by which heat can be transferred is via convection. This occurs when hot and cold materials mix. This mixing can occur naturally, as when hot air rises into cold air. It can also happen via forced methods, such as a fan blowing hot air around in a convection oven. Convection only occurs naturally in fluids like gases and liquids. It is possible for convection to happen in a forced manner in a granular solid, but it is not common.

Convection can be an extremely important type of heat flow. It is what allows the entire pot of water to come to boil rather than just the bottom. It is what makes you feel colder on a windy day. In our homes, it can cause our energy bills to go through the roof. Air flowing into or out of our homes is convection. When we open the doors to our homes, hot and cold air are allowed to mix, and heat is convected. Even when doors or windows are not open, there is convection occurring through any cracks or breaks in our windows, walls, doors, ceilings, and floors. We often notice this convection occurring on very cold, windy days. You will find a blast of cold air hitting you when you walk by electrical outlets or windows on such days, a sign that your house is not airtight.

Of course, as air from the outside is coming into your home, the air inside of your home is going outside. Over time, the total volume of air in your home will be completely replaced with air from the outside. While this is good from the standpoint that stale, possibly toxic air is leaving your home, it is bad from an energy standpoint since your heating/cooling system will have to come on to bring this air temperature back to the prescribed setting. In a new, well-built home, the number of openings in your home allows this air exchange to occur over a period of about 2 hours. In older homes that have developed more cracks, this amount of time can be much shorter. For instance, in very old, poorly maintained homes, it might take as little as 15 minutes for all of the air in your home to be replaced by air from the outside. The number of **air exchanges per hour**, therefore, is a measure how much energy you will need to use in order to counter the effects of heat transfer via convection.

The proper way to measure the number of air exchanges per hour in your home is somewhat involved. It requires using air flow meter readings from various locations in your home. Since very few people have the necessary equipment to measure it exactly, we have developed a set of guidelines for estimating this factor. The table below gives you some idea as to the value for your home. You may need to interpolate between the values below to get the correct estimate for your home. For instance, if you have an average, insulated home that has been caulked and weather stripped in the last 4-5 years, you should probably select 1.0 as your value. However, if it has been about 8-10 years since you caulked or weatherstipped, you might want to choose something between 1.0 and 2.0 as the value.

Type of home	Air exchanges per hour
Old, uninsulated, weatherstripping not maintained	4.0
Old, uninsulated, weatherstripping maintained	2.0
Avg. insulated house, well maintained	1.0
New, well insulated house	0.5
New, superinsulated (12" walls)	0.2

Radiation

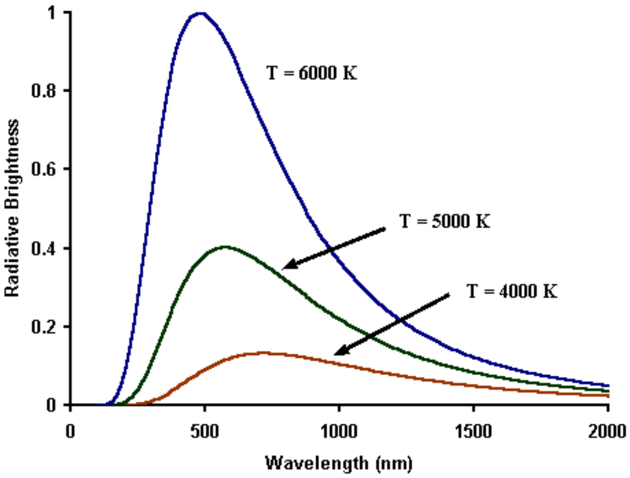

Fig. 4: Radiation brightness vs. wavelength

The last form of heat transfer is via electromagnetic radiation. This occurs because of the vibration of electrons and protons in a substance because of the thermal energy that it contains. As long as a substance has a temperature above absolute zero (0 Kelvin or –273 ^{o}C), it will radiate energy. At absolute zero, not even the electrons in the atoms are moving.

Given the origin of the radiation, it makes sense that the type and amount of radiation depends upon the temperature of the substance. Figure 4 shows a plot of the different types of radiation that are emitted by an object at different temperatures. As you can see, the position of the wavelength at which the most radiation is emitted changes as the temperature of the object changes. In particular, the peak wavelength decreases in value as the temperature increases. This relationship is given by the equation

$$\lambda_{max} = .003 \text{ m K}/T \qquad \textbf{(Equn. 2.6)}$$

where λ_{max} is the wavelength at maximum brightness, .003 m K is a constant, and T is the temperature in Kelvin. For an object like our Sun that is at about 6,000 K, λ_{max} occurs at 5 x 10^{-7} m, which is near the middle of the visible part of the spectrum. For objects that are as hot as the human body (about 300 K), it occurs at about 1 x 10^{-5} m, which is in the infrared. Thus, to see humans when there is no external light, one needs to use infrared goggles or infrared film.

Figure 4 also shows that the shape and the height of the curves change as the temperature changes. In particular, the height increases as the temperature increases. The total amount of heat that is emitted is just the sum of all of the energy that is below the curve. Thus, as the temperature increases, the amount of heat emitted increases. The exact form of this increase is given by the Stefan-Boltzmann law, which states that the rate of heat flow away from the object is

$$Q/t = e\,\sigma\,A\,T^4 \qquad \textbf{(Equn. 2.7)}$$

where e is the emissivity of the surface of the object ($0<e<1$), σ is a constant, A is the surface area, and T is the temperature in Kelvin. The first term shows that the amount of heat radiated depends upon what the surface is constructed. The third term means that a larger object will emit more heat.

The last term in the Stefan-Boltzmann equation shows a heavy dependence of the heat on the temperature. Since this term is to the fourth power, it means that small variations in the temperature can greatly change the amount of heat radiated. As an example, if the temperature were to double, the amount of heat would increase by a factor of 16. A change in the temperature of only 1% results in a change in the heat emitted by 4%.

While the object is emitting radiation, its surface will also be absorbing radiation. The amount of radiation that it absorbs depends upon the temperature of the objects around it that are emitting radiation. The net heat rate that is radiated is given by the formula

$$Q/t = = e \sigma A (T_{obj}^4 - T_{env}^4)$$

where T_{env} is the temperature of objects in the environment around it. If the temperature of objects around it are hotter than it is, then this rate will be negative, which means that the object is absorbing more radiation than it is emitting.

These equations show that the heat rate depends upon what the surface of the object is made and how it appears. Special coating can be applied to objects to change the emissivity of its surface. This factor will also be affected by the color of the object. However, one has to be careful about this. We must remember that the object is emitting in all wavelengths, and not just in the visible. Therefore, the emissivity depends upon the "color" of the object in all wavelengths. However, we can generalize this situation for good and poor emissivities. Objects with a low emissivity generally appear white in color, while high emissivity objects are normally black. An object with an emissivity of 1 is called a "blackbody radiator".

Heat Pumps Versus Heat Engines

Understanding heat flow is also important to the operation of two devices that make our current way of life possible: the heat engine and the heat pump. A heat engine is a device that is able to extract useful work out of heat that is flowing from a hot reservoir to a cold reservoir. There are numerous examples of these devices, everything from the engine in your car to the steam-operated turbines at a power plant. A heat pump reverses this process, taking useful work to move heat from a cold reservoir to a hot one, going against the natural flow from hot to cold. The air conditioner that gives you relief in the middle of the summer is a prime example, as is the refrigerator that you use to store your food.

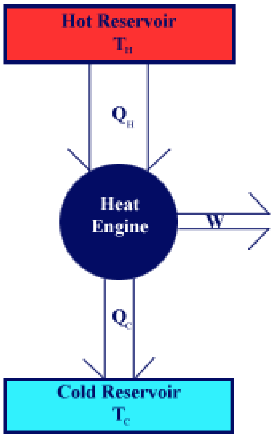

Fig. 5: Heat engine diagram

The methods by which both of these devices operate depend upon what the two reservoirs are and the expense of performing the operation. For example, gasoline is a fluid, which means that it can be easily transported and piped to many different locations without too much oversight. It is also highly flammable when mixed with oxygen. Because of this, it can operate in an internal combustion engine very easily, as opposed to a solid fuel source like coal. By spraying it into a piston chamber, mixing it with air, and igniting it, you can create a very hot reservoir. The heat from this reservoir causes the gas in the chamber to expand as its temperature increases, which applies pressure to the piston head. This force pushes the piston back, thus performing work (force times distance). To allow the piston to come back to its initial starting position so that further work can be done, the gas in the chamber needs to be cooled. This is done by allowing the heat to escape to the cold reservoir through a valve, which lets the heat go out the tailpipe into the cold reservoir (the atmosphere).

One important aspect of this process is that heat must be allowed to flow to the cold reservoir. This heat is energy from which no useful work can be extracted. Therefore, we call this waste heat. How much heat is wasted is a very important value to know for a heat engine, as it is a measure of how good or poor the engine is at transferring energy. Because of this, we have developed the concept of the **efficiency** of an engine, which is a measure of the useful work out as a ratio of the energy that is input. If we use the designation of Q_H for the heat from the hot reservoir, Q_C for the waste heat going to the cold reservoir, and W as the useful work out, we get that the efficiency is given by

$$\text{Efficiency} = W/Q_H \qquad \textbf{(Equn. 2.8)}$$

The First Law tells us that there is a relationship between these three factors. Since energy cannot increase or decline in the engine over time (lest it blow up or freeze solid), we know that

$$Q_H = W + Q_C$$

If we use this in equation 2.8, we get an alternative expression for the efficiency of

$$\text{Efficiency} = (Q_H - Q_C)/Q_H = 1 - (Q_C/Q_H) \qquad \textbf{(Equn. 2.9)}$$

Most heat engines in operation today are fairly inefficient. An automobile engine is about 25% efficient, while the steam turbine of a coal power plant is about 35%. There are some natural gas-powered power plants in operation today that use the heat from the exhaust of a turbine engine (connected to a generator) to power a steam turbine (also connected to a generator). The efficiency of these heat engines is as high as 60%.

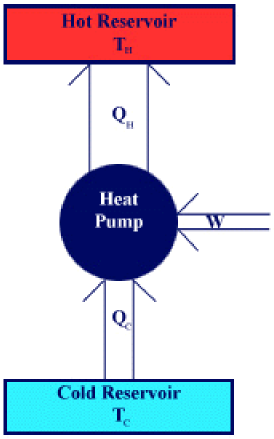

Fig. 6: Heat pump diagram

The operation of a heat pump also depends upon the reservoir and the expense of performing a particular operation. The vast majority of heat pumps in operation today look very similar: two heat exchanger coils, a pump, some valves, and fluid that is able to change from gas to liquid and back over the range of pressures over which the pump operates. Here is a quick synopsis of how one works. The pump pressurizes the gas and sends it to the heat exchanger in the hot reservoir (condenser). By pressurizing the gas (doing work on it), it becomes hotter than its surroundings (you can do the same thing with a bicycle pump and air) in the hot reservoir. Naturally, heat will flow from the gas to the hot reservoir, and cool the gas to the temperature of the reservoir. The gas is then allowed to leave the condenser through a series of valves that allows it to expand rapidly. This causes the gas to cool (the gas does work on its surroundings, losing energy in the process; feel an aerosol can after spraying it for some time to get firsthand experience with this) immensely and condense to a temperature lower than the cold reservoir once it gets there. The colder liquid in the heat exchanger (vaporizer) then absorbs heat from the cold reservoir, causing it to vaporize back into a gas, which goes to the pump and starts the cycle again.

While it is tempting to calculate the efficiency for this device using our previous model, it would be erroneous to do so. There are two energy inputs into the heat pump, and only one output. Instead of the efficiency, we calculate a coefficient of performance, which measures how much energy we want moved versus the amount of energy for which we pay. If we are operating the heat pump as a refrigerator, then we want to know how much heat gets removed from the cold reservoir for each unit of energy that is paid for doing the moving. In other words,

$$COP_{refrigerator} = Q_C/W \qquad \textbf{(Equn. 2.10)}$$

If we are operating the heat pump as a heater, then we want to know how much heat goes to the hot reservoir for every unit of energy we pay for,

$$COP\ heater = Q_H/W = (W + Q_C)/W = 1 + (Q_C/W) \qquad \textbf{(Equn. 2.11)}$$

Refrigerators usually have a COP of about 5-6, while air conditioners run in the 2-3 range under normal conditions (20-30 ^oF temperature difference between inside and outside). Equation 2.11 shows that the COP of a heat pump heater is always greater than 1. How much greater, though, depends greatly upon the temperature difference between inside and outside. A difference of 20-30 ^oF results in COP’s of about 2-3, while temperature differences much greater than this can move the COP down closer to two. This why most heat pump heaters that people have installed in their homes have a back up electrical resistance heater that kicks in when the temperature is too great for efficient operation.

Second Law of Thermodynamics

The First Law of Thermodynamics tells us that the energy involved in any transfer must be conserved. This would seem to mean that we should never run out of energy and should pay no heed to anybody talking about energy being lost. The problem is that this is not the only law that governs energy transfers. While the total amount of energy does not change, the Second Law of Thermodynamics puts limits on the amount of **usable energy** that can be transferred. Before we proceed to this, let us first look at what the Second Law states.

There are many equivalent statements of the Second Law of Thermodynamics. Most often, people write about the consequences of the Second Law (Ex. "Heat will flow spontaneously from hot to cold", "The useful energy output will be less than input", "A heat engine and a heat pump both require a hot and a cold reservoir"). An increasingly more uncommon way to write it is in mathematical terms. For example, old textbooks usually write it something like

In a closed system, the total entropy either increases or stays the same

The reason why most authors today are loathe to write this is that it is not particularly useful in this form and it requires a lot of explanation. First, one has to define the term "entropy", which is a fairly non-standard word. Entropy is actually the logarithm of the number of states accessible to a system and is defined by the equation

$$1/T = (dS/dU)_N$$

where T is the temperature, S is the entropy, U is the total energy of the system and $(dS/dU)_N$ is the partial derivative of the entropy with respect to energy while holding particle number fixed. If your brain has not exploded by reading this definition, and you are still reading, then you realize why most scientist just say "Entropy is a measure of the chaos of a system", which, in a way, it is (a chaotic system usually has more states accessible to it than a non-chaotic one).

Even if you are able to get past the entropy difficulty, you then have to explain what a closed system is (there are no real closed systems in the universe, just ones that are close) and why entropy would only increase or stay the same in such a system. After you have spent a great deal of time doing this, you realize that you might have just as well written one of the consequences of the Second Law (which are understandable by most people) and have called it a day. Which is exactly what we are going to do.

The Second Law and Efficiency

The Second Law does imply the consequences stated above. The one that is of most use to us right now is that the total amount of usable energy that comes out of any process will be less than the total amount of energy that went into the process. The difference between the total amount of energy input and the usable energy output is expended as waste heat. What this means is that no efficiency will ever be equal to 100%.

Knowing that the efficiency will be less than 100% does not mean that you know just how efficient a device can be. In 1824, a French engineer by the name of Sadi Carnot applied the Second Law to the generalized designs of heat engines to see what would be the most efficient engine he could devise. In doing so, he was able to calculate what the theoretical maximum efficiency for a heat engine would be. If T_H is the temperature of the hot reservoir and T_C is the temperature of the cold reservoir, then the maximum efficiency of the heat engine is

$$\text{Maximum efficiency} = 1 - (T_C/T_H) \quad \textbf{(Equn. 2.12)}$$

where both temperatures are expressed in Kelvin. This equation shows that the maximum efficiency can be increased by increasing the difference between the temperatures of the reservoirs. As an example, if T_H = 400 K and T_C = 300 K, then the maximum efficiency is 1 – (300 K/400 K) = 1 - .75 = .25, or 25%. If, however, T_H = 600 K and T_C = 300 K, then the maximum efficiency is 1 – (300 K/600 K) = 1 - .5 = .5, or 50%.

A well-designed heat engine usually gets about half of its maximum efficiency. This is why this equation is so important. It is also why many proposed alternative energy sources never see the light of day. For instance, there is a temperature difference in equatorial oceans between water at the surface and water that is several hundred feet below the surface. Surface waters will usually be about 27 ^{o}C (300 K), while deeper waters will be about 7 ^{o}C (280 K). One could operate a heat engine between these two reservoirs, and not have to pay a dime for input energy. However, the maximum efficiency of such a device would be about

1 – (280 K/300 K) = 1 - .93 = .07 = 7%

Even though the energy is free, the costs of construction, power transfer to land, and maintenance will make the cost of energy from such a system much more than what one can get by buying coal and burning it.

The Second Law implication that all energy transfers be less than 100% efficient applies to non heat pump devices, as well. All appliances and energy transfer devices, from motors to generators to natural gas heaters, all will fall short of 100%. For example, a fluorescent light bulb converts about 20% of the electrical energy that runs through it into visible light energy. While this may not sound like a very efficient transfer, it is much better than the 5% efficiency of an incandescent light bulb, which most people use.

When discussing the efficiency of a process, we have to make sure and not forget all of the transfers that might need to take place in order to get to the one under investigation. A great example of this occurs when comparing the efficiencies of electric and internal combustion engine powered cars. The efficiency of the electric motor in a car is about 90%, while the efficiency of the internal combustion engine is only about 25%. However, these efficiencies are not the only things that need to be considered when comparing the two devices. How is the electricity that charges the car created? Where does the gasoline come from that powers the internal combustion engine? What types of transmission systems does each car have? There are many steps and energy transfers that take place in getting each type of car to move, and each one of these has its own individual efficiency. For instance, the average electric plant is only about 30-35% efficient in generating electricity (some newer natural gas plants are closer to 50-60%). This fact greatly reduces the overall efficiency of an electric car. When we consider the total efficiency, from getting the energy from its natural source to the car moving down the highway, we find that the electric car is only about 20% efficient, while the internal combustion engine automobile is about half that at 10%.

Appliances

The efficiency of all of the appliances in our homes affects how much money we spend and energy we use. While heating/cooling does consume the largest single amount of the energy budget of the average household, it does not consume the majority. Other appliances in the home consume over 50% of all of the energy. Almost every American home has some type of stove or range, while about 75% of them have a washer and dryer, 50% have a dishwasher, and 33% have a separate freezer from their refrigerator. All of these appliances, plus the heating/cooling systems, amounted to over 100 million Btu's of energy being consumed in the homes of America in the last year. Considering the inefficiencies of transporting energy to homes, the total amount of energy that had to be consumed in order to power our houses was over 170 million Btu's.

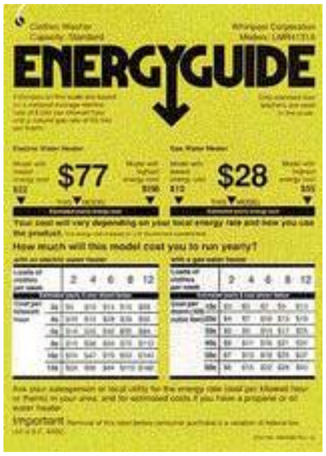

Fig. 7: Efficiency sticker

The amount of money consumed by an appliance depends on the type of fuel used by the appliance, the power of the appliance, and the length of time that the appliance is allowed to run. For instance, the average electric oven uses an average of about 2,000 watts of power to heat itself to a temperature of 350 ^oF. If it is run for 1 hour, then it will use an amount of energy equal to

Energy = Power x Time = 2,000 watts x 1 hour = 2,000 watt-hour = 2 kilowatt-hour

At the current rate of about $.08 per kWhr, this corresponds to a cost of about 16 cents. The average natural gas stove uses about 11,000 Btu/hr to maintain the same temperature. If you ran it for the same amount of time as the electric stove, it would consume an amount of energy equal to

Energy = Power x Time = 11,000 Btu/hr x 1 hour = 11,000 Btu

The current cost of natural gas is about $.70 per therm. One therm is equivalent to 100,000 Btu. Thus, the natural gas costs about $.000007 per Btu. This means that the cost of running the natural gas stove for 1 hour is about 7 cents.

Further Reading:

" Residential Energy Consumption Survey", Dept. of Energy,http://www.eia.doe.gov/emeu/recs/contents.html.

Objectives

1. State and discuss the implications of the first and second laws of thermodynamics.
2. Differentiate between heat and temperature.
3. Differentiate between the Fahrenheit, Celsius, and Kelvin scales. Describe scenarios under which each would be useful.
4. Describe the three methods of heat transfer and be able to calculate flow rates for each one.
5. Differentiate between a heat pump and a heat engine.
6. Define efficiency and coefficient of performance and be able to calculate them for different scenarios.
7. Define the Carnot efficiency and discuss its significance.
8. Discuss energy usage in the United States both in the private sector and in industry.

Problems

1. If 350 J of work are done on a gas and 200 J of heat are added to it, by how much does its internal energy change?
2. An ice cube at 0 ^oC is put into a drink that is at 15 ^oC. Which way does heat flow, and what will be the final state of the system?
3. A car takes in 20,000 J of gasoline energy and outputs 3,000 J of kinetic energy. What is the efficiency of the car?
4. What are 3 things that you could do to your home to improve its energy usage? Are these changes economically feasible?
5. If heat is conducting between two reservoirs, what would happen to the rate of transfer if the temperature difference between the two doubled? What would happen to it if the thickness of the barrier between them doubled?

6. The element on an electric stove is at 500 K. What is the wavelength at which the most energy is radiated?
7. Which has a higher insulation value: an insulated brick wall or a ceiling with 6 inches of fiberglass insulation?
8. What is the total efficiency of an incandescent light bulb if the power plant that makes the electricity is 35% efficient, the transmission of electricity to your house is 90% efficient, and the conversion of electricity to light in the bulb is 5% efficient?
9. Using pressure, the steam in a turbine generator is heated to 600 K. If the cooling water used to turn the steam back to water is at 350 K, what is the maximum efficiency of the generator?