SMS-204: Integrative marine sciences.

Chapter 4: Heat and temperature

The study of heat transfer is called <u>thermodynamics</u>. In thermodynamics, we talk about systems, such as a collection of molecules in a container, a slab of material, etc'. Systems are categorized based on whether they are: (1) <u>Open</u>, can exchange energy and mass with their surrounding, (2) <u>closed</u>, can exchange energy but no mass with their surrounding, or (3) isolated, do not exchange energy or mass with their surrounding.

Two bodies have the same <u>temperature</u> if when we put them in contact with each other they do not change energy (they are said to be in thermal equilibrium).

<u>0th law of thermodynamics:</u> if two systems are separately in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other, and they all have the same temperature regardless of the kind of systems they are.

One of the two systems could be an instrument calibrated to measure the temperature - a thermometer. When a calibrated thermometer is put in contact with a system and reaches thermal equilibrium (no change in reading is observed), we then have a quantitative measure of the temperature of the system.

A <u>thermometer</u> is an instrument that measures the temperature of a system in a quantitative way. The easiest way to do this is to find a substance having a property that changes in a regular way with temperature (for example the substance volume). The simplest properties to use as in thermometers have a linear response to temperature, such that:

$$X = aT + b,$$

where X is the property of the substance that changes when the temperature (T) changes.

It turns out that in many cases the response is not linear. For example, thermistors which are made of solids whose electrical resistance changes with temperature, have resistances that do not change linearly with temperature.

Temperature scales

In 1724 that Gabriel Fahrenheit, an instrument maker of Danzig and Amsterdam, used mercury as the thermometric liquid. Mercury's <u>thermal expansion</u> (the change of volume with temperature) is large and fairly uniform (that is, it is close to linear), it does not adhere to the glass (no surface tension issues), and it remains a liquid over a wide range of temperatures.

Fahrenheit calibrated the scale of his mercury thermometer so that the boiling point of water was 212 and the freezing point of water to 32. Thus, the interval between the

boiling and freezing points of water could be represented by 180 degrees. Temperatures measured on this scale are designated as **degrees Fahrenheit (F)**.

In 1745, Carolus Linnaeus of Upsula, Sweden, described a scale in which the freezing point of water at sea level was zero, and the boiling point 100, making it a *centigrade* (one hundred steps) scale. In 1948 the use of the Centigrade scale was dropped in favor of a new scale using **degrees Celsius (°C)**. The Celsius scale is defined by the following:
(i) the triple point of water (the temperature at which water, ice, and water vapor coexist in equilibrium) is defined to be 0.01°C.
(ii) a degree change of one Celsius equals the same temperature change as a degree on the ideal-gas scale (see below).

On the Celsius scale the boiling point of water at standard atmospheric pressure is 99.975 °C in contrast to the 100 degrees defined by the Centigrade scale.

To approximately convert from degrees Celsius to Fahrenheit: multiply by 1.8 and add 32.

$$F = 1.8 \,°C + 32$$

Experiments with gas thermometers have shown very little difference in the temperature scale for different gases. Thus, it is possible to set up a temperature scale that is independent of the thermometric medium if it is a gas at low pressure. In this case, all gases behave like an "Ideal Gas" and have a very simple relation between their pressure (P), volume (V), and temperature (T):

$$PV= (constant)T.$$

This temperature is called the *thermodynamic temperature* and is now accepted as the fundamental measure of temperature. Note that there is a naturally-defined zero on this scale - it is the point at which the pressure of an ideal gas is zero, making the temperature also zero. With this as one point on the scale, only one other fixed point needs be defined. In 1933, the International Committee of Weights and Measures adopted this fixed point as the triple point of water; its value is set as 273.15. The unit of temperature on this scale is called the Kelvin, and its symbol is K (no degree symbol used). To approximately convert from Celsius to Kelvin, add 273.15:

$$K = °C + 273.15.$$

Thermodynamic temperature is the fundamental temperature; its unit is the Kelvin which is defined as the fraction 1/273.15 of the thermodynamic temperature of the triple point of water.

Measuring temperature

The earliest devices used to measure the temperature were called thermoscopes. They consisted of a glass bulb having a long tube extending downward into a container of

colored water (we will make one in the class). Some of the air in the bulb was expelled before placing it in the liquid, causing the liquid to rise into the tube. As the remaining air in the bulb was heated or cooled, the level of the liquid in the tube would vary reflecting the change in the air's temperature. An engraved scale on the tube allowed for a quantitative measure of the fluctuations. The air in the bulb is referred to as the *thermometric medium*, i.e. the medium whose property (here volume) changes with temperature.

In 1641, the first sealed thermometer that used liquid rather than air as the thermometric medium was developed for Ferdinand II, Grand Duke of Tuscany. His thermometer used a sealed alcohol-in-glass device, with 50 "degree" marks on its stem but no "fixed point" was used to zero the scale. These were referred to as "spirit" thermometers.

Robert Hook, Curator of the Royal Society, in 1664 used a red dye in alcohol in his device. His scale, for which every degree represented an equal increment of volume equivalent to about 1/500 part of the volume of the thermometer liquid, needed only one fixed point. He selected the freezing point of water. By scaling it in this way, Hook showed that a standard scale could be established for thermometers of a variety of sizes. Hook's original thermometer became known as the standard of Gresham College and was used by the Royal Society until 1709 (The first intelligible meteorological records used this scale).

T. J. Seebeck, in 1826, discovered that when wires of different metals are fused at one end and heated, a current flow from one to the other. The electromotive force generated can be quantitatively related to the temperature and hence, the system can be used as a thermometer - known as a thermocouple. The thermocouple is used in industry and many different metals are used - platinum and platinum/rhodium, nickel-chromium and nickel-aluminum, for example.

Thermistors, resistors whose resistance change with temperature, were invented in 1930 by Samuel Ruben (the founder of Duracell). Dependent on the composition, their resistance may increase or decrease with temperature. They are usually made of a ceramic or polymer semiconductor.

For the measurement of very low temperatures, the magnetic susceptibility of a paramagnetic substance is used as the thermometric physical quantity. For some substances, the magnetic susceptibility varies inversely with temperature. Crystals such as ferrous magnesium nitrate and chromic potassium alum have been used to measure temperatures down to 0.05 K; these crystals are calibrated in the liquid helium range.

Temperature and heat

Temperature is a number that is related to the average kinetic energy of the molecules of a substance. If temperature is measured in degrees Kelvin, then this number is directly proportional to the average kinetic energy of the molecules. This is an example in which

a microscopic characteristic (the energy of molecules) of a system is measurable macroscopically (by a thermometer).

Heat is a measurement of the total microscopic energy in a substance. That total energy is also made up of the potential energies of the molecules. When heat goes into a substance one of two things can happen:

1. The substance can experience a rise in temperature. 2. The substance can change state. For example, if the substance is ice, it can melt into water.

Perhaps surprisingly, this change in phase does not cause a rise in temperature. The moment before melting the average kinetic energy of the ice molecules is the same as the average kinetic energy of the water molecules a moment after melting. Although heat is absorbed by this change of state, the absorbed energy is not used to speed up the molecules. The energy is used to change the bonds between the molecules. Changing the manner in which the molecules bond to one another constitutes a change in potential energy. Heat comes in and there is an increase in the potential energy of the molecules. Their kinetic energy remains unchanged.

Most materials have two state transitions: from solid to liquid and from liquid to gas. Each change in state requires an investment in energy (or a release of energy, when transitioning back).

Conservation of energy implies that in order to heat material (raise the kinetic energy of the molecules, without change in state) we need to do work. The heat capacity of a system is the amount of thermal energy needed to raise the temperature of the system by one K. The specific heat (C_p) is the heat capacity per unit mass, describing how much heat per unit mass will raise the temperature of a given material by 1 K. The heat needed to raise the temperature of a mass m of material by ΔT without changing its state is $C_p m \Delta T$. The fundamental unit of energy in the metric system is the joule (J).

Water has one of the highest values of specific heat: C_p=4186 Joule K^{-1} Kg^{-1} (or 1000 calories, at 288K. Food related Calories are equal to one thousand calories or one kilocalorie). For air C_p=1006 Joule K^{-1} Kg^{-1}. Because the density of water is about 1000 the density of air it means that, for a fixed *volume*, it takes approximately 4000 times more energy to heat water than air. Similarly, when water cools it releases 4000 more energy than air, for the same *volume*. The mass of a column of the atmosphere approximately equals that of a column of 10m of water, so the total heat capacity of the atmosphere is contained in 3.6m of the world's oceans (adjusted of 70% of the planet being covered by water). The contrast in heat capacity and mass also explains why in areas where the weather is influenced by large bodies of water the weather is temperate (temperature does not change much between day and night, and across seasons) while inland we observe large fluctuations in temperature. This is not the only reason for the differences; another important one is that heating of the Earth is done by absorption at the surface, while the Oceans absorb heat over a significantly deeper layer that is also is actively mixed (by wind and night-time convection) with layers below.

The heat needed to change the state of a material is called latent heat of fusion (for changing from solid to liquid) and latent heat of vaporization (for changing from liquid to gas). For water, the latent heat of vaporization is approximately 2.4×10^6 J Kg^{-1}. The large size of this number has many important consequences of which we will name a few. Suppose we have a fluid at a mammal body temperature ~38°C. If we let 6% of it evaporate, the amount of heat invested equals to the amount of heat stored by the rest of the fluid if we cooled it to 0°C. Thus, a small amount of evaporation can cool a body substantially, as done by human when they sweat. Evaporation is also the primary reason why large lakes and the ocean rarely exceed 28-30°C.
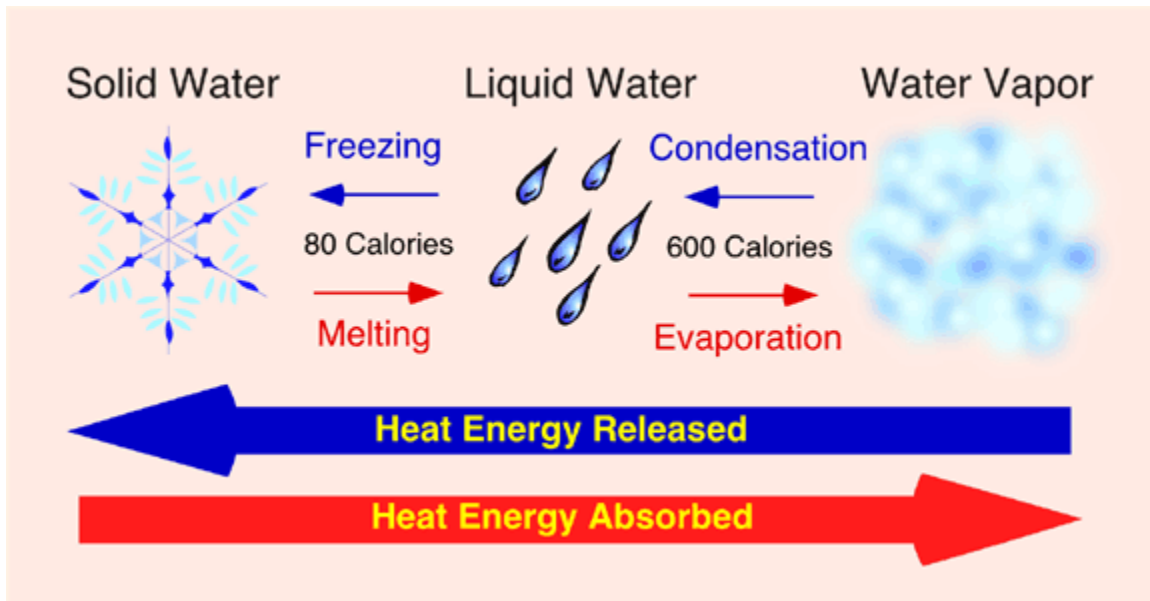

Figure 1. Heat released/absorbed by water in the process of changing state. The Numbers listed are calories per gram of water needed to change state, not food Calories. From: http://www.geog.ouc.bc.ca/physgeog/contents/images/latent.GIF

1st law of thermodynamics (conservation of energy): when heat is transformed into any other form of energy, or when other forms of energy are transformed into heat, the total amount of energy (heat plus other forms) in the system is constant.

Is it possible to completely convert the heat energy into work, making it a 100% efficient machine? The 2nd law of thermodynamics states that it is not possible to fully convert heat energy into mechanical energy.

The 2nd law of thermodynamics introduces the concept of <u>entropy</u>. Entropy is a quantity proportional to the logarithm of the likelihood (probability) of a given state of a system. If the state if very likely (i.e. all the molecules are randomly distributed) the entropy is high. When the state is very unlikely (e.g. all the molecules are arranged in a neat pattern on one side of the box and 10 of them are at the other end) the entropy is low. The 2nd law of thermodynamic states that entropy in a *closed system* cannot decrease. Systems move from organized to less organized states and not *vice versa*. The only way to keep things

organized is by investing more energy. Ever wondered why it is so hard to keep your room organized? The 2nd law of thermodynamics explains it!

Heat transfer

With this understanding of the concept of temperature, it is possible to explain how heat (thermal energy) flows from one body to another. Thermal energy is carried by the molecules in the form of their kinetic energy and some of it, through molecular collisions, is transferred to molecules of a second object when put in contact with it. This mechanism for transferring thermal energy by contact is called **conduction**. Conduction occurs when two object at different temperatures are in contact with each other. Net heat flows from the warmer to the cooler object until they are both at the same temperature. Conduction is the movement of heat through a substance by collision of molecules. Some substances conduct heat more easily than others. Solids are, in general, better conductors than liquids and liquids are better conductors than gases. Metals are very good conductors of heat, while air and blubber are very poor conductors of heat. You experience heat transfer by conduction whenever you touch something that is hotter or colder than your skin *e.g.* when you wash your hands in warm or cold water.

A second mechanism of heat transport is illustrated by a pot of water set to boil on a stove - hotter water closest to the flame will rise to replace cooler water near the top of the pot which sinks next to the pot's sides. **Convection** involves the movement, or flow, of the more energetic molecules in a liquid or gas as they expand (and thus become more buoyant – less dense). In liquids and gases, convection is usually the most efficient way to transfer heat. You have probably heard the expression "Hot air rises and cool air falls to take its place" – it aptly describes convection in our atmosphere. In the oceans, the 'thermohaline' circulation is the circulation which results when heavy, salty cooled seawater sinks down in the North Atlantic and near Antarctica forcing less dense fluid to rise. Relative motion within the fluid during convection creates shear (large changes in velocity over short distances) which promotes turbulence (formation of energetic small-scale motion) that in turn enhances mixing (the exchange of properties between adjacent water parcels). In fluids, the last step of change of temperature is done at the molecular level through diffusion. Mixing does not change the diffusion coefficient but enhances the gradients in temperature within the fluid on which diffusion acts enhancing the heat exchange. Think of where people place heaters or air conditioners. For effective heating, it is best to put the heater low so that the rising air will generate circulation and enhance mixing. Similarly, placing an air conditioner high in a room will most effectively cool it.

Both conduction and convection require matter to transfer heat. **Radiation** is a method of heat transfer that does not rely upon any contact between the heat source and the heated object. For example, we feel heat from the sun even though we are not touching it. Heat can be transmitted though empty space (vacuum) only by thermal radiation. Thermal radiation is a type electromagnetic radiation. Radiation is a form of energy transport consisting of electromagnetic waves traveling at the speed of light. No mass is exchanged and no medium is required.

Objects emit radiation when high energy electrons at a high atomic level fall down to lower energy levels. The energy lost is emitted as light or electromagnetic radiation. Energy that is absorbed by an atom causes its electrons to "jump" up to higher energy levels. All objects absorb and emit radiation. When the absorption of energy balances the emission of energy, the temperature of an object stays constant. If the absorption of energy is greater than the emission of energy, the temperature of the object rises. If the absorption of energy is less than the emission of energy, the temperature of the object falls.

The electromagnetic spectrum covers an enormous range in wavelengths, from very short waves to very long ones.
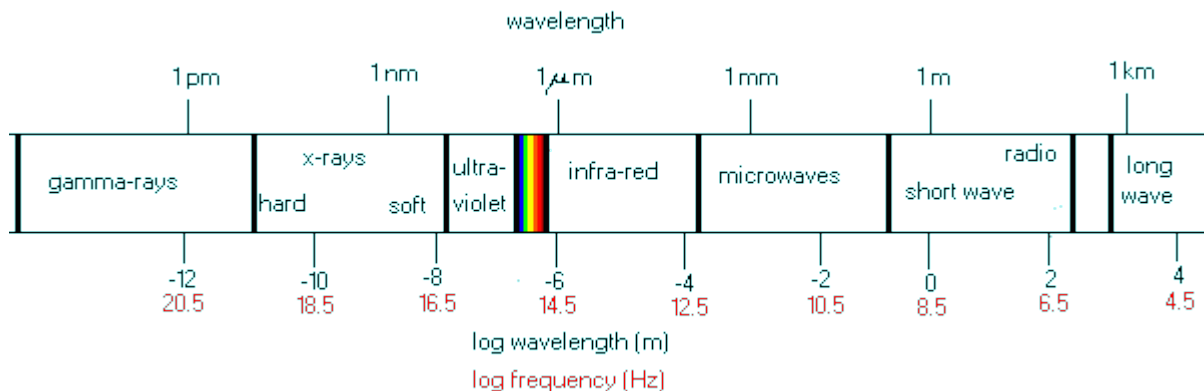

Figure 2. The EM spectrum. The only region of the electromagnetic spectrum to which our eye is sensitive is the "visible" range identified in the diagram by the rainbow colors.

The sun is not the only object that provides radiant energy; any object whose temperature is greater than 0 K will emit some radiant energy. If an object is placed in a container whose walls are at a uniform temperature, the object will come into thermal equilibrium with the walls of the enclosure and would emit radiant energy just like the walls of the container. Such an object absorbs and radiates the same amount of energy. A black surface absorbs all visible incident radiation. **Black-body radiation** is the term applied to the quantity and spectrum of radiation emitted by such a perfect absorber.

The relation between temperature and radiant energy (Stefan-Boltzmann's law) states that the energy radiated by a black body per unit of area per unit of time is proportional to its temperature (T, in K) raised to the 4th power, $E = \sigma T^4$ where $\sigma = 5.7 \times 10^{-8} W\ m^{-2}\ K^{-4}$.

A black-body does not radiate all of its energy at one wavelength (or frequency) of light, but in a certain distribution of frequencies (Planck's distribution). The surface temperature of the sun is 6000 K, and its Planck curve peaks in the visible wavelength range. For bodies cooler than the sun, the peak of the emission spectrum shifts to longer wavelengths, until a temperature is reached such that very little radiant energy is emitted in the visible range. While most objects are not strictly black, the radiation they emit can be modeled well using black-body radiation.
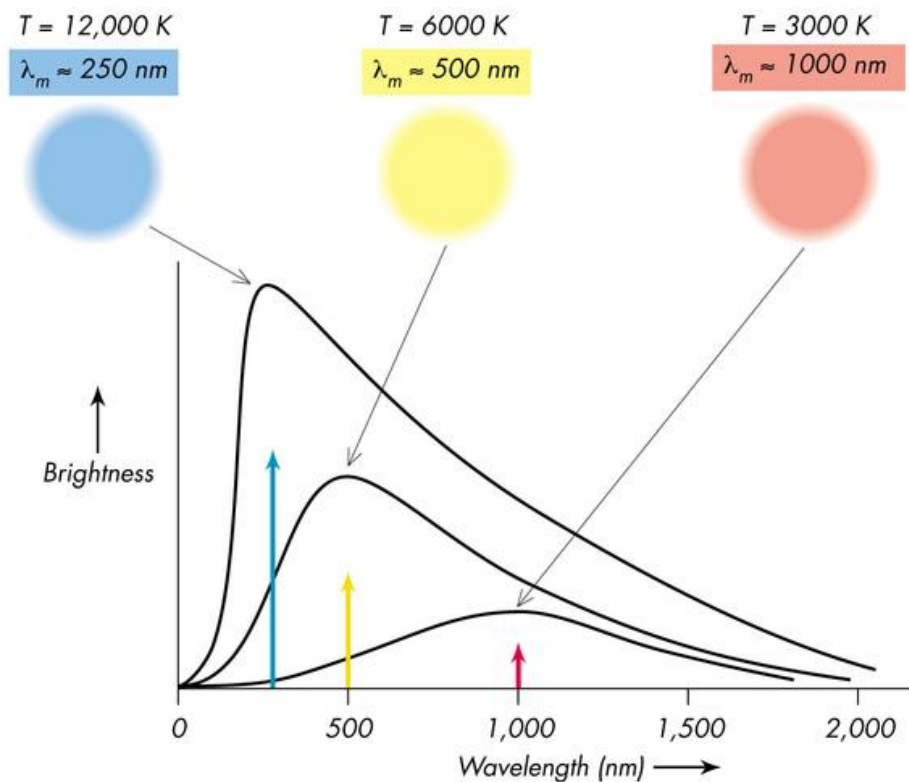
Figure 3. blackbody radiation of object of varying temperature From:
http://pegasus.phast.umass.edu/a101/images/light_bb_spectra.jpg

The position of the maximum emission is given by Wien's law, which states that the wavelength of maximum brightness of emission [nm] is related to the temperature of the body [T in K] by $\lambda_{max} \sim 3 \times 10^6 \; T^{-1}$. The human body has a temperature of about 310 K and radiates primarily in the far infrared ($\lambda_{max} \sim 10 \; \mu m$).

Some snakes have evolved 'eyes' with which they can sense the infrared black-body radiation emitted by their prey. In water, infrared radiation is absorbed very efficiently by the water itself, making IR radiation an ineffective way to sense one's environment. Satellite IR estimates of sea-surface temperature are based on the temperature of the upper 1mm of the ocean (aptly named skin temperature).

A few important concepts associated with heat and temperature

Heat flux – conduction (conductive heat flux): The rate of passage of heat from one body to another. When we touch a cold metal, it feels colder than a wooden object because it conducts heat better away from our hand. Our hand does not warm only the part we touch as the heat spreads fast to the rest of the metal. With the wooden object, only the part we touch warms up quickly (with much slower conduction), and thus the wood feels warmer than the metal. Conversely, hot metal feels much hotter than hot

wood for the same reason; wood conducts heat to your hand much more poorly. Fluids also conduct heat, but conduction and convection typically occur simultaneously.

Heat flux – advection (advective heat flux): Right next to the object the fluid velocity is zero and the only way heat is transferred to the fluid is through conduction (which in a fluid we call diffusion). The thickness of the layer where diffusion is the dominating heat flux process depends on the fluid flow around the body. The faster the flow the smaller the diffusive layer. Since the heat flux to or from the body depends on the gradient (that is the difference) between the temperatures of the body to that of the surrounding fluid (on the other side of this boundary layer), the thinner the boundary layer the sharper the gradient and thus the flux of heat to or from the object.

Wind chill: This phenomenon is a direct result of the reduction of the boundary layer around a body due to the wind and the associated increase in heat loss due to it. Due to the wind, the difference between a body's temperature and that of the environment per unit distance increases (that is the temperature gradient increases). The body loses heat faster to its surrounding, making us feel that the air around the body is colder (that is, we lose heat faster than if there is no wind, temperature of the air being the same). Wind chill cannot cause the body to cool below the air temperature (assuming no evaporation) but it causes the body to cool faster.

Heat balance on the Earth

The Earth receives its energy from the sun unevenly as function of latitude. Its distribution is due to the change in angle between the incoming rays of the sun and the surface of the Earth as function of latitude; the angle increases with distance north or south from the equator (Fig. 4). This unevenness results in a temperature and heat gradient on the Earth from equator to poles, which , ultimately, drives both ocean currents and winds. The currents and wind advect (that is take heat with them) heat from equator to poles. The Gulf stream is a prime example of a current that transfers heat poleward.
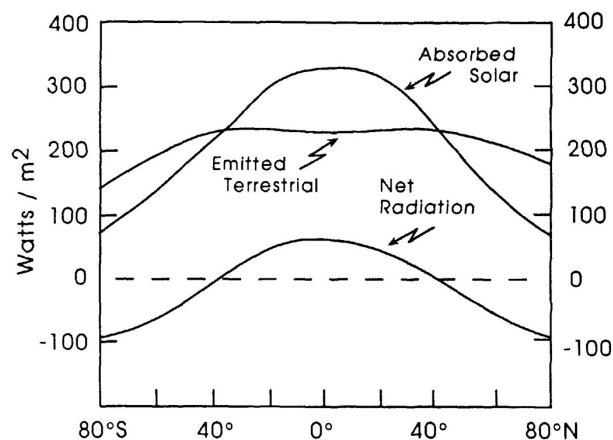
The seasons: as the earth rotate around the sun it changes its tilt relative to the plane on which the Earth rotate around the sun. This results in the change of radiative heat flux from Sun to a specific location on Earth as function of the time of the year. The heat flux changes because both the day length *and* the angle of the sunlight to the ground change. The lower the sun is on the horizon (the larger its zenith angle, i.e. the farther it is from directly overhead) the lower is the heat flux, as it is spread over a lager area (the decrease in radiation intensity per area is proportional to the cosine of the angle between the sun and zenith). Another (smaller) effect is that the lower the sun is in the sky the more its radiation is attenuated by the atmosphere as the pathlength through the atmosphere is longer before reaching the Earth. The time of maximum radiative heat flux in the Northern hemisphere (around the longest daylight time of the year, e.g. June 21st) is NOT the time of maximal temperature there. From that time, onward the temperature keeps increasing as long as the total heat flux is positive (e.g. more is gained than lost). Once the heat flux changes sign (sometime in late August for land in Maine, and early September of the waters of the Gulf of Maine) temperatures start to drop. Similarly, the maximum heat loss occurs near Christmas but temperatures continue to decrease until early February (air) or late February (water) when the heat flux changes sign and start becoming positive.

The 'greenhouse' effect

The greenhouse effect describes the fact that the Earth has a different temperature than it would have if it had no atmosphere; this is similar to the way greenhouses operate. A greenhouse[1] is warmer than the surrounding due to the properties of the glass or plastic it is made of (when it is not heated independently). The equivalent to the glass and plastic for the Earth are clouds (water droplets) and gases within the atmosphere (primarily, Methane, CH_4, Carbon dioxide, CO_2, and water vapors).

This process begins with the absorption of visible (or shortwave) radiation from the sun on the Earth's surface. This absorption converts the light into heat. Some of this heat is transferred to the lower atmosphere by conduction and convection. Following the absorption driven heating, the ground and the lower atmosphere emit infrared (or longwave) radiation due to their own temperature (blackbody radiation discussed above). This emission of energy is directed to space and results with the ground maintaining a near thermal equilibrium state (heat gained = heat lost). However, only a portion of this energy is transferred through the atmosphere. About 70 % of the long-wave radiation emitted from the Earth's surface is absorbed by the atmosphere's greenhouse gases (Methane, carbon dioxide and water vapor), that are much more transparent to the shortwave radiation coming in from the sun (much like your car's windshield or the glass or plastic in a greenhouse). Absorption of this energy warms the Earth's atmosphere

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[1] Note: the analogy to greenhouse fails somewhat due to the fact that in a greenhouse advection and convection are suppressed by the glass and walls. If we open the doors and windows the greenhouse will be much closer in temperature to its surrounding.

which itself radiates long-wave energy in all direction, about half of it directed back to Earth. Heating of the ground by this long-wave radiation causes the ground surface to heat a little more than if it were absent. Repeated absorption and reemissions results in an Earth with a higher temperature than it would have had without atmosphere (Fig. 5).
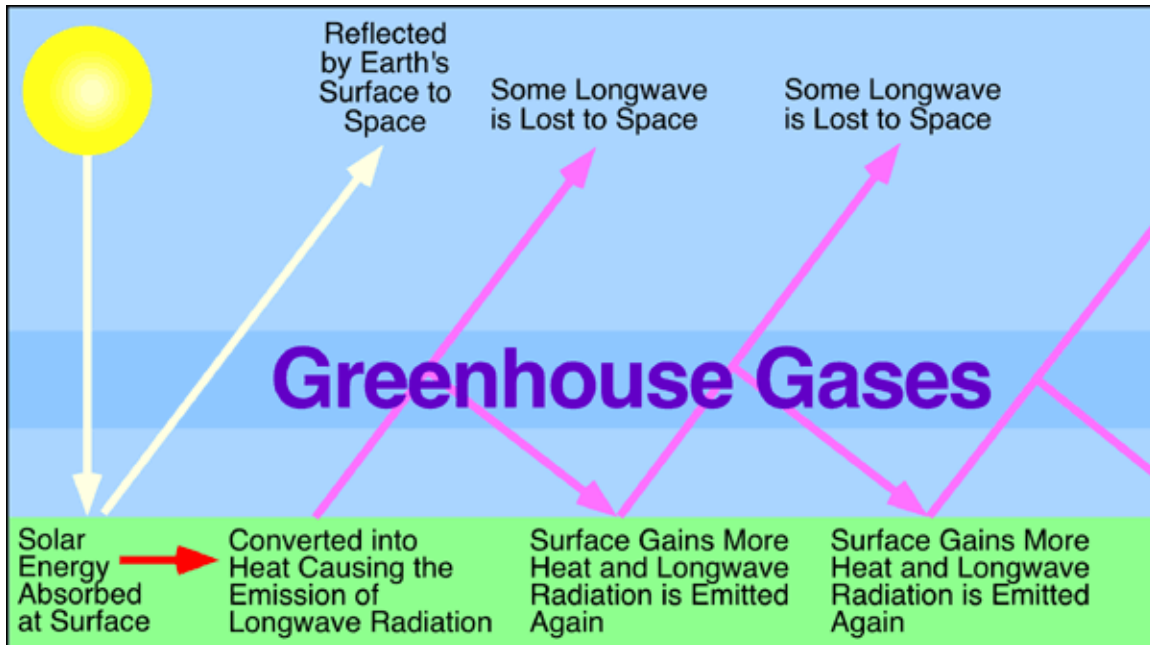

Figure 5. The greenhouse effect. From: www.geog.ouc.bc.ca/physgeog/contents/images/greenhouse.GIF

Not all the light arriving to the Earth's surface is absorbed. Some is reflected back. The fraction of the impinging radiation that is reflected to is called the <u>albedo</u>. The mean albedo of the Earth is 0.3. The albedo of snow and ice is about 0.6-0.8 while that of vegetated land is about 0.15. The ocean has an average albedo between 0.15-0.3 (that means that 0.7-0.85 of light impinging on the oceans get absorbed by it).

Global observing systems of ocean temperature

Sea surface temperature (often abbreviated as SST) is typically measured by observing the thermal emission of the Earth at long infra-red wavelength (near 10 micrometer). Resolution is typically ~1km^2. An example is NOAA's advanced very high resolution radiometer (http://noaasis.noaa.gov/NOAASIS/ml/avhrr.html). SST data are available freely for example from NASA's Giovanni portal.
For subsurface temperature distribution, the Argo fleet provides measurement nearly every degree, with a ~4000 strong fleet of floats profiling approximately every 10 days. Data is available freely from http://www.coriolis.eu.org/.

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