3 Heat, work, energy, and the first law

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Introduction

The science of heat is one of the areas of science where its economic importance was most obvious. Flooded mines led to the introduction of steam engines to pump them dry in the eighteenth century, and the high cost of fuel drove the search for more efficient engines. James Watt increased efficiency greatly by using a separate condenser. Benjamin Franklin, who developed the 'one-fluid' caloric theory of heat, also invented a more efficient wood stove. Benjamin Thompson (Count Rumford), who also came from Massachusetts but chose the wrong side in the war, invented the kitchen range, while working for the Bavarian government, and argued that if paupers were to work for their keep they had to be fed properly. Lazare Carnot, the 'organizer of victory' after the French Revolution, was an engineer who studied the effects of useless work like the creation of turbulence in an engine. His son Sadi Carnot made a theoretical study of engines that founded the science of thermodynamics in the 1820s.

Rumford did not quantify the relation between heat and work, but he tried to disprove the caloric theory, that heat is a conserved component of matter, by showing that boring out a cannon will boil away large quantities of water without breaking down a lot of metal. The idea that heat was simply a form of energy remained just an alternative idea. The general idea of energy conservation was proposed by a ship's doctor, Julius Mayer, around 1842, but he had no convincing evidence, and only a rough estimate of the numerical relation between heat and work. Careful experiments were done by James Joule, a Manchester brewer, in the mid 1840s, who showed the quantitative relation between the loss of potential energy by a falling weight, and the generation of heat in a calorimeter.

3.1 Measurement of heat

Heat can be detected by the rise of temperature that it produces in a body. The specific heat of a material is an intrinsic property of the material, like density or electrical resistivity, characteristic of the material and its composition, but independent of its size and shape. Like these other quantities, the specific heat, per unit mass, per unit volume, or per mole, is dependent on temperature and pressure. The heat capacity of a uniform quantity of

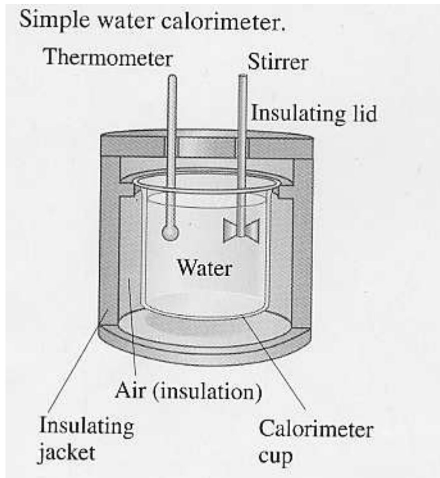

Figure 1: Diagram of a simple water-based calorimeter (from Giancoli)

matter is the specific heat per unit mass multiplied by the mass of the body. The unit of heat, the calorie, was defined as the amount that would heat up a gram of water by one celsius degree, so that the specific heat of water is 1.0 cal/gm C°, or 1.0 kcal/kg C°. In an alternative system of units, used on my gas bill, heat is measured in British thermal units, and then the specific heat of water is 1.0 Btu/lb F°. Just to confuse things further, the Calorie used to evaluate the energy content of food is actually a kilocalorie.

The modern convention is to make use of the first law of thermodynamics, and quantify heat by its energy equivalent, so that it is measured in joules. In these units the specific heat of water at 20 C is 4.18 kJ/kg C°

Quantities such as specific heat, density, and electrical resistivity, that are independent of the shape and size of an object, are known as *intensive* quantities. Pressure and temperature are also intensive quantities, since their meaning does not depend on size or shape. Quantities such as mass, volume, and heat capacity, that are proportional to size and independent of shape, are known as *extensive* properties. Generally I will use small letters, such as p and ρ, for intensive variables, and large letters, such as V, for extensive variables, but, despite that, it is customary to use an upper case T for temperature.

A *calorimeter* typically consists of a known mass of water in a container made of a good conductor of heat, such as copper, of measured heat capacity. There is a thermometer in the water, and the whole system is insulated.

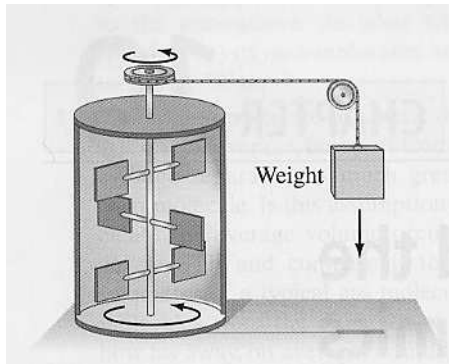

Figure 2: Diagram of Joule's apparatus for measuring the heat generated from gravitational potential energy by a paddle wheel in a water-based calorimeter (from Giancoli)

Heat is measured when an object comes to equilibrium with the calorimeter by noting the initial temperatures of the object and the calorimeter, and measuring the change in temperature when equilibrium is reached.

The transfer of heat to a system does not necessarily change its temperature. Where two phases coexist at the same temperature and pressure, heat must be transferred to change the proportion of the two phases. This is known as the *latent heat of fusion* in the case that the heat is required to melt a solid on the solid–liquid phase boundary, and as the *latent heat of evaporation* when it is required to evaporate a solid or liquid on the solid–vapor or liquid–vapor phase boundaries. These latent heats can be very large in comparison with specific heats. The latent heat of fusion of ice at 0 C is 333 kJ/kg, while the latent heat of vaporization of water at 100 C is 2256 kJ/kg. The latent heat of vaporization is what is used to heat up your latte when steam is bubbled through it.

3.2 First law of thermodynamics

All the ideas presented in the last section, except for the choice of the joule as a unit of heat, are independent of whether heat is energy or a separately conserved fluid. Mayer estimated the energy value of heat by using the difference between the specific heat at constant volume of a gas, when the gas is heated without allowing it to do work, and the specific heat at constant pressure, when the gas does work while it is heated. Joule made careful measurements by using falling weights to drive a paddle wheel in the water of a well insulated calorimeter. By careful lubrication of the bearings he tried to convert as much as possible of the gravitational potential energy loss of the weights into heat released inside the calorimeter. The result he obtained was within 1% of the 4.18 J/cal accepted today, although he called it 782 ft lb/Btu.

The first law of thermodynamics states the conservation of energy, in the form "**The increase of internal energy ΔU of a body is equal to the sum of the work W done on it and the heat Q that flows into it".** We can write this as

$$\Delta U = W + Q \ . \tag{1}$$

For the case of a gas or liquid we can write the work as $W = -p\delta V$ for small changes of volume, or, in general,

$$W = -\int p\, dV \ . \tag{2}$$

For a solid work can also be done by shear forces. For any materials work can also be done by electromagnetic fields, as in a microwave oven, or in a light bulb.

Actually this statement must be modified a little, since the internal energy is not usually taken to include the center of mass kinetic energy or potential energy, nor the rotational energy of a solid, so such other forms of energy must be added to the left side of Eq. (1) if the center of mass is in motion.

The internal energy U is another extensive property of a uniform body. When the body is kept at constant volume, so that no work is done, the first law for small changes of temperature at constant volume takes the form $\delta U = Q$, so we can write the heat capacity as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \ . \tag{3}$$

where I have started using the useful convention that when we write a partial derivative the subscript or subscripts show what variable is being kept constant.

Heating under constant pressure conditions gives a different result, since the gas expands and so does work. For a small temperature change we can write Eq. (1) in the form

$$\delta U = -p\, \delta V + Q \ . \tag{4}$$

We can divide this by δT and take the limit $\delta T \to 0$, to get

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p . \tag{5}$$

Differentiation of the ideal gas law gives $p(\partial V/\partial T)_p = nR$. As we shall discuss later, the internal energy of an ideal gas is a function of temperature only, so $(\partial U/\partial T)_p = (\partial U/\partial T)_V$ for an ideal gas. In this case Eqs. (3) and(5) give the relation

$$C_p = C_v + nR \tag{6}$$

for an ideal gas.

Another situation to which we can apply the first law in the form (1) is when a gas is allowed to expand in a a thermally insulated enclosure without doing any work. This can be done by having the gas in one side of an enclosure separated from the other side by a partition which can be suddenly moved out of the way, with the partition moving parallel to itself, so that there is no motion in the direction of the pressure force; in practice care has also to be taken to minimize the viscous force on the partition. In this case no work is done on the gas, and no heat is transferred to it, so Eq. (1) now says that the internal energy is unchanged. For dilute gases the temperature change is found to be small. A zero temperature change implies that the internal energy depends only on temperature:

$$\delta T = 0 \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0 . \tag{7}$$

The sign of the temperature change, if it is nonzero, gives the sign of the derivative of the internal energy U with respect to volume at constant temperature. The fact that there is little change of temperature resulting from free expansion for most of the gases or vapors we think of as close to ideal shows that for these gases the internal energy is primarily a function of temperature, and not of pressure. This is an example of an *irreversible process.* You cannot suddenly compress a gas at constant temperature without doing work on it.

A quite different situation is the reversible *adiabatic expansion* of a gas. In this case the gas is expanded slowly, for example by moving a piston of low thermal conductivity on which the pressure of the gas acts, while the gas remains thermally insulated. Since it is thermally insulated, the heat Q is zero, and the work $-p\delta V$ done on the gas must equal the change δU of the internal energy. For an ideal gas the internal energy depends only on the temperature, so we have

$$0 = \delta U + p\delta V = C_v\delta T + p\delta V . \tag{8}$$

From differentiation of Avogadro's Law we have

$$p\delta V + V\delta p = nR\delta T \ ,$$

which gives, with Eqs. (8) and (6),

$$\left[\frac{C_v}{nR} + 1\right] p\delta V + \frac{C_v}{nR} V\delta p = 0 \ .$$

If we use the relation (6) here we get

$$C_p \frac{\delta p}{p} + C_v \frac{\delta V}{V} = 0 \ ,$$

which gives the law for the adiabatic expansion of an ideal gas

$$pV^\gamma = \text{constant}\,, \quad \text{where} \ \ \gamma = C_p/C_V \ . \tag{9}$$

One important application of this is to the speed of sound c_s. Newton derived the formula for the speed of sound in a fluid, $c_s^2 = K/\rho$, where K is the bulk modulus and ρ the density. This works well for liquids, but is 15% or 20% too low for many gases. The reason for this is that the period of oscillation is too short, or the wavelength too long, for heat to flow from the compressed regions to the rarefied regions, so the compressions and rarefactions are adiabatic, not isothermal. For an ideal gas the isothermal bulk modulus is just p, but under adiabatic conditions it is $p\gamma$, so the sound speed is given by

$$c_s^2 = \gamma p/\rho \ , \tag{10}$$

which gives the correct sound speed, or can be used to determine the ratio γ of the specific heats.

There is another important application of adiabatic expansion, which is to the cooling of air as it rises in the atmosphere. This is discussed in section 3.9.

3.3 Transfer of heat

There are four main methods by which heat is transferred from one place to another. These are:

1. Conduction through a stationary medium, which occurs at a rate that depends on the nature of the medium. Metals are better heat conductors than nonmetals, and solid nonmetals and liquids are better

conductors than gases or porous materials. Heat conduction is quite fast over small distances, but much slower over longer distances. Temperature changes between day and night penetrate about 0.1 m into the ground, but changes between winter and summer only penetrate about 2 meters – the depth of penetration is proportional to the square root of time. This is typical of a *diffusion process.*

2. Convection involves the bodily transfer of heat by a moving medium, usually fluid. This convection can be forced, like the transfer of hot air from the heater of a car to the interior by means of a fan, or natural, as when hot air produced in the neighborhood of a radiator circulates round the room, because its lower density causes it to flow upwards. Convection is the main mechanism by which heat is moved over large distances in the atmosphere, in the oceans, and deep in the earth's interior.

3. Evaporation is one of our body's main methods of cooling. The sweat on our skin evaporates, and the latent heat of evaporation of the water cools us very effectively. When water evaporates from the surface of the ocean and is deposited as rain elsewhere a similar transfer of the latent heat is taking place. This is a common mechanism used for moving heat from the inside of a refrigerator to the outside, or from the inside of a house to the outside with an air conditioner.

4. Radiation is the only means by which heat is carried across a vacuum, and the visible radiation from the sun is the ultimate source of most of the energy that is available to us. Colder bodies also radiate, although we cannot see the radiation without infrared detectors. Radiation occurs over large distances with great speed, but is less important than conduction over short distances.

Thermal conduction and forced convection obey Newton's empirical law of cooling, that the rate at which heat flows away from or into a body is proportional to the temperature difference from the environment, and so does radiative transfer if the temperature differences are small compared with the Kelvin temperature.

3.4 Conduction of heat

Thermal conduction occurs at a rate that is proportional to the area normal to the direction of heat flow (the direction of the temperature gradient). In a bar of cross-sectional area A in which the temperature $T(x)$ depends on position the heat δQ flowing in time δt is given by

$$\frac{\delta Q}{\delta t} = -kA\frac{dT}{dx} , \tag{11}$$

where the thermal conductivity k is a characteristic property of the medium. There is a minus sign because the heat flows from the high temperature region to the low temperature region. The left side of this equation has dimensions joules per second, or watts, so k must have dimensions of watts per meter kelvin.

In steady state situations there is no accumulation of heat in the material, so, for a uniform slab the temperature gradient is constant. If there are two slabs of thickness d_1, d_2 in series the heat flow across each of them must be the same, so the temperature gradient has to be inversely proportional to the thermal conductivity. If T_1 is the temperature on the outside of the first slab, T_2 is the temperature on the outside of the second slab, and T_m is the temperature where the two slabs join, the heat flow per unit area is

$$k_1\frac{T_1 - T_m}{d_1} = k_2\frac{T_m - T_2}{d_2} . \tag{12}$$

The ratio of the temperature drops is therefore $(d_1/k_1)/(d_2/k_2)$, and the rate of heat flow per unit area is $(T_1 - T_2)/(d_1/k_1 + d_2/k_2)$, so that we can think of d/k as the thermal resistance per unit area. Clothes to keep you warm in winter or building materials to keep the house well insulated are designed to have a high thermal resistance. Since air is a poor conductor, one of the best ways of getting a good thermal insulator is to trap air in the material. Air needs to be trapped, because, although it has low thermal conductivity, it is very effective at convecting heat away.

To get the general equation for heat flow in a slab or bar of area A, where the temperature depends on time t as well as position x, we consider that slice of the slab that lies between the coordinates x and $x + \delta x$. The heat flowing in from the left of this slice is equal to $-kA\partial T(x,t)/\partial x$, while the heat flowing out at the right is $-kA\partial T(x+\delta x, t)/\partial x$, so that the total rate of change of heat in this slice is

$$\frac{dQ}{dt} = -kA\frac{\partial T(x,t)}{\partial x} + kA\frac{\partial T(x+\delta x,t)}{\partial x} \approx kA\delta x\frac{\partial^2 T(x,t)}{\partial x^2} . \tag{13}$$

The heat capacity of the slice is $A\delta x\rho c$, where ρ is the density and c the specific heat capacity per unit mass, so the temperature of the slice changes as

$$\frac{\partial T(x+\delta x/2,t)}{\partial t} = \frac{1}{A\delta x \rho c}\frac{dQ}{dt} \ . \tag{14}$$

Putting eqs. (13) and (14) together we get the partial differential equation

$$\frac{\partial T}{\partial t} = \frac{k}{\rho c}\frac{\partial^2 T(x,t)}{\partial x^2} \ , \tag{15}$$

which is the *diffusion equation* that governs the spread of temperature differences. The constant $D_T = k/\rho c$ is the thermal diffusion constant, and has dimensions of m^2/s; this indicates that the distance a temperature change travels is proportional to the square root of time. This thermal diffusion constant comes out at about 1.2×10^{-4} m^2/s for fairly pure copper, 2.1×10^{-5} m^2/s for iron, and about the same for air, 1.1×10^{-6} m^2/s for ice, and 1.4×10^{-7} m^2/s for water. I do not know what the typical figure is for building materials and for the soil, as I have not found values for their specific heats, but I think it comes out at about 5×10^{-7} m^2/s, which would be consistent with my figures for the penetration distances of diurnal and annual temperature variations (there are 3.1×10^7 seconds in a year, and 86400 s in a day).

3.5 Convection

Natural convection is driven by the changes in density that occur when a fluid changes temperature. If the surface of a lake in summer cools down at night, the colder water is denser than the water just below it, so it can sink down, bringing more warm water to the surface in its place. This process stops when the water reaches its maximum density at 4 C. When the surface is heated in summer the warmer water naturally floats on the colder water, so it does not mix, and the surface can get reasonably warm, even in Puget Sound.

Convection is a complicated process to describe in detail. There is a famous type of experiment devised by Bénard in which a fluid is heated uniformly from below. At a very low rate of heating there is just conduction through the fluid, but at a faster rate the fluid circulates from top to bottom of the container, setting up regularly spaced rolls of circulation, such as are illustrated in fig. 3. At a higher rate of heating still these regular patterns break down, and a 'chaotic' turbulent system is set up. one can sometimes see such convection rolls in cloud formations when one is flying over them.

Forced convection is complicated in a different way. When a fluid passes over a solid there will be a thin layer of the fluid close to the solid which is

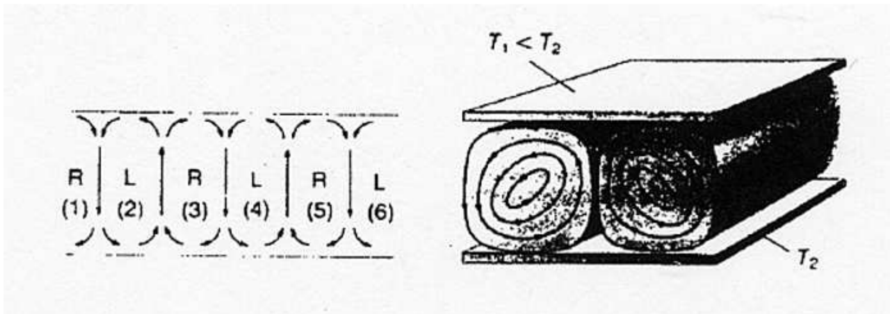

Figure 3: Steady convection in a fluid heated from below

not moving fast, and through which the heat must be conducted. You can see this if you look at a gas flame under a test-tube or a saucepan – the air in contact with the test-tube or pan is far below the very high temperature of the flame.

3.6 Evaporation and condensation.

It is perhaps unfair to class evaporation and condensation as a separate mechanism of heat transfer from convection, but I want to emphasize the fact that latent heat is involved. It is this fact that enables you to go into a sauna at a temperature of 100 C without discomfort – your skin is kept far cooler than the ambient air temperature because sweat evaporates from your skin so rapidly. For this mechanism to be effective the relative humidity of the air must be low.

3.7 Radiation

Electromagnetic radiation is understood in great detail, but I am not giving a lot of details here. Two basic results of the detailed theory are that the rate of radiation per unit area is proportional to T^4, and that the peak frequency of the radiation is proportional to T. The sun, with a surface temperature of 6000 K has its main emission in the visible wavelengths. A colder star like Betelgeuse radiates more at the red (low frequency) end of the spectrum, while a blue star is hotter than the sun. A piece of iron that looks red-hot to us is radiating predominantly in the infrared, since its temperature is down on that of the sun's surface by a factor of 5 or 6.

Such radiation is not confined to things that appear hot. Even outer

space is filled with the remains of radiation that was emitted during the early stages of the universe, when the universe was still quite hot. Initially the radiation is in equilibrium, but when the universe cooled down to around 3000 K, as a result of the universe's expansion, the ions mostly became neutral atoms and molecules, and the radiation no longer interacted much with matter. This is the *cosmic background radiation*, which in recent measurements has been studied in considerable detail and with great precision. By now the continued expansion has caused the background radiation to cool down to a temperature of 2.7 K. Not only can the 600 km/s motion of the local cluster of galaxies relative to the rest of the universe be detected from the 0.2% Doppler shift of the background radiation, but the different speeds of the different parts of the universe where the radiation that is detected now originated produce further Doppler shifts of the order of 0.01%. For details of this look at the NASA web site http://map.gsfc.nasa.gov/m_uni/uni_101bbtest3.html, or the University of Tennessee site
http://csep10.phys.utk.edu/astr162/lect/cosmology/cbr.html.

The Stefan-Boltzmann Law says that the power radiated from a surface of area A at temperature T is equal to

$$e\sigma AT^4 \ , \tag{16}$$

where σ is the Stefan-Boltzmann constant, equal to 5.67×10^{-8} $\mathrm{Wm}^{-2}\mathrm{K}^{-4}$, and e is the emissivity of the surface, which has a value between zero and unity. The ideal black body has an emissivity of unity, and it emits radiation at the maximum rate; it also absorbs all radiation that falls on it. If the emissivity were zero no radiation would be emitted, and all incident radiation would be reflected from the surface. The silver coating on the inside of a vacuum flask is designed to cut the emissivity of the surface, so that there is little radiation across the vacuum enclosed between the inside and the outside of the flask.

If the sun occupied the whole sky the earth would soon heat up to the temperature of the sun. Fortunately the sun occupies a small fraction of the sky, about 5.4×10^{-6} if you average over day and night, so, to keep in balance with the radiation it receives from the sun, the earth should radiate at this fraction 5.4×10^{-6} of the rate it would have if it had the 6000 K temperature of the sun's surface. If we write

$$e_e\sigma T_e^4 = 5.4 \times 10^{-6} e_s\sigma T_s^4 \ , \tag{17}$$

and assume that the emissivities are the same, then we get $T_e = 0.048T_s$, which gives the very reasonable figure $T_e = 290$ K. It is not as simple as that, of course, for a number of reasons. There is not a complete balance, but the earth does seem to give off a little more heat than it receives. Also the emissivity that determines what proportion of the sun's radiation is absorbed and how much is reflected refers primarily to the visible spectrum, while the emissivity that determines the amount that is radiated from the earth refers to the far infrared frequencies that are characteristic of thermal radiation at 300 K. The discussion of greenhouse gases such as carbon dioxide and methane is related to this issue. These gases do not stop visible light from getting to the earth's surface, but they can make it difficult for the infrared radiation emitted from the earth's surface to escape from the atmosphere.

On a clear night very little heat is radiated from the sky, but the ground and objects open to the sky are radiating heat out towards the sky. As a result, the ground can get colder than the air. Some of the heat lost by radiation is replaced by conduction of heat from lower down, but objects such as the deck of a house or the roof of a car which are not in good thermal contact with anything warmer can get very cold. This is the main reason for the formation of frost or dew on such exposed surfaces. Seattle is not a great place to observe this, as the sky is rarely very clear; it can be much more obvious under desert or mountain conditions.

Modern window glass is designed to cut down heat loss by radiation. It is transparent to the visible light from the sun, but opaque to the infrared, so that heat comes in from outside during the day, but not much radiates directly to the outside from inside the room. Even modern windows are a major path for heat loss from a house, partly because they conduct heat to the outside, but also because the glass itself is emissive, and radiates to the outside, even if it blocks radiation coming from further in.

3.8 Cooking

Cooking is one of the oldest of human arts, and its primary function is to raise food to a temperature high enough to destroy bacteria and parasites. It also converts indigestible material, such as potatoes, wheat flour, or tough lean meat, into a more digestible form, but again reaching a suitable temperature is a large part of the story. Transfer of heat is therefore what cooking is all about.

If you broil fish on a standard electric cooker you have a red-hot element above the fish. This transfers heat to the top surface of the fish primarily by radiation. The heat then penetrates the interior of the fish by conduction, so you turn it over when you think that nearly half the fish is heated through.

If you are boiling potatoes in a saucepan, the bottom of the pan is heated by the cooker. This heat is conducted through the bottom of the pan. Strong convection currents are set up, so that the water in the pan is uniformly at about 100 C (a little more if you have added salt to the water). This heat has to be transferred to the middle of each potato, and this occurs slowly by conduction. Heat is lost by radiation from the sides of the pan, and by evaporation out past the lid of the pan. If you are at a high altitude, so that the boiling point of water is lower, it can be a long time before the potatoes get to a high enough temperature in the middle.

Steaming food is an alternative to boiling it. Water is boiled at the bottom of a pan, and then condenses on the surface of the food that is being steamed, giving up its latent heat again. This leads to fairly uniform heating of the surface of the food, but may wash away less of the nutrients and flavor into the water.

Convection in an oven can be by natural convection, as when heating is from a gas flame or hot element at the bottom of the oven, or there may be a fan to drive a forced convection current. In a microwave oven the heating is directly by radiation of microwaves into the interior of the food. The microwaves are tuned to be strongly absorbed by the water molecules in the food, so that the heating occurs directly in the interior of any food that contains water, and it is quicker than cooking that relies on heat conduction into the interior.

3.9 Weather

Radiation from the sun is the main source of energy that powers weather patterns. Thermal conduction does something to distribute heat locally, but convection, evaporation and condensation are the most important mechanism for distributing heat on anything but the shortest length scales and longest time scales. In fine weather there is a typical pattern during the day of air over the land being warmed and rising, and air over the sea which has been kept cool and moistened by evaporation moving inland to replace it. At night the land is cooler, because it radiates more efficiently than the water, so the wind may reverse and blow from the land towards the sea if there are no larger scale movements to disturb it.

There is another factor, which is that air cools as its pressure is reduced. Hot columns of air are generated over the land in summer, and these rise to great heights where the pressure is much lower. This is approximately an adiabatic expansion, governed by Eq. (9), since the rising air is doing work as it expands. The temperature drops as the pressure is reduced, so that it falls below the dew point, where the water vapor pressure is equal to the saturated vapor pressure, and then cumulus clouds are formed at the head of these rising columns of air. They may go high enough that ice begins to form, and falling ice particles can lead to electric charge separation in the clouds, so that thunderstorms are produced. Air moving in from the side to replace the rising air may develop a rotational motion, so that small scale whirlwinds or large scale tornados develop. If the mixing of air at lower altitudes was completely adiabatic, the temperature would drop by about 1 °C in each 100 m increase in height, but actually some of the work is expended internally, creating turbulence, which then gets converted back to heat, so the temperature drop in 100 m is about 0.65 °C. At higher altitudes, in the *stratosphere*, this mixing of air from different levels no longer takes place, and the temperature depends on the balance between absorption of ultraviolet light by ozone and the emission of infrared by CO_2 and other gases.