CHAPTER 1

ELEMENTS OF THE PHYSICS AND CHEMISTRY OF THE EARTH'S SURFACE

BACKGROUND: SOME BASIC (NON-MATHEMATICAL) PHYSICS RELEVANT TO THE EARTH'S SURFACE

1. Energy

1.1 First you need to feel comfortable about the nature of energy. We have to be concerned with three forms of energy: energy of motion (called ***kinetic energy***), energy of position (called ***potential energy***), and energy of thermal motions of atoms of molecules of a material (called ***thermal energy*** or ***heat energy***). Kinetic energy and potential energy together are often referred to as ***mechanical energy***.

1.2 If you are not already familiar with these concepts of energy, here's a little demonstration that should serve the purpose of giving you the basic ideas. You will need a lump of modeling clay or putty. Throw the lump straight up in the air. When it leaves your hand, it has a certain speed and therefore a certain kinetic energy. It's slowed by the downward force of gravity as it rises, so it loses kinetic energy, but that lost kinetic energy is stored as energy of position, by virtue of being located higher up in the gravity field of the Earth. When it reaches the top of its trajectory, all of its kinetic energy has been stored as potential energy. Then on the way down, the stored potential energy is converted back into kinetic energy. If you were doing this in a vacuum in some enormous evacuated bell jar or on the surface of the Moon, the putty would have the same speed when it lands back in your hand as when you threw it upward. The mechanical energy of the lump, kinetic plus potential, is the same all along the trajectory; the mechanical energy is said to be *conserved*.

1.3 On the real surface of the Earth, of course, the lump is bathed in air, and its motion is retarded by friction both on the way up and on the way down. That friction warms the lump (and the air it passes through), slightly, converting some of the mechanical energy into thermal energy.

1.4 Another thing you can do with the lump is drop it on the floor from some high place. It has some kinetic energy as it lands on the floor, but then it comes to a stop upon impact, without even rebounding. What happened to all of its kinetic energy? It was converted entirely to thermal energy, via the friction involved in the deformation of the lump as it made impact. If you had the right equipment you could actually verify for yourself that the lump was warmer after it landed than before.

2. Electromagnetic Radiation

2.1 All bodies (pieces or regions of matter, in the physicist's parlance) at temperatures above absolute zero radiate energy in the form of *electromagnetic waves*. The subject of electromagnetism goes to the heart of physics, and it's much too complicated for a full treatment here, but all of you are familiar with the existence and effect of electromagnetic waves, in various ways: the radiant heat you receive from your fireplace or electric heater; the light you perceive with your eyes; radio, television, and radar waves; x rays.

2.2 *Electromagnetic waves vary over an enormous range of wavelengths*, from the very short wavelengths of cosmic rays and x rays, through the intermediate range of ultraviolet and visible light, down through the infrared to the long wavelengths of radio waves and the like (Figure 1-1). The shortest wavelength visible to the eye, at the edge of the ultraviolet, is about 0.36 µm; the longest wavelength, at the edge of the infrared, is about 0.76 µm.

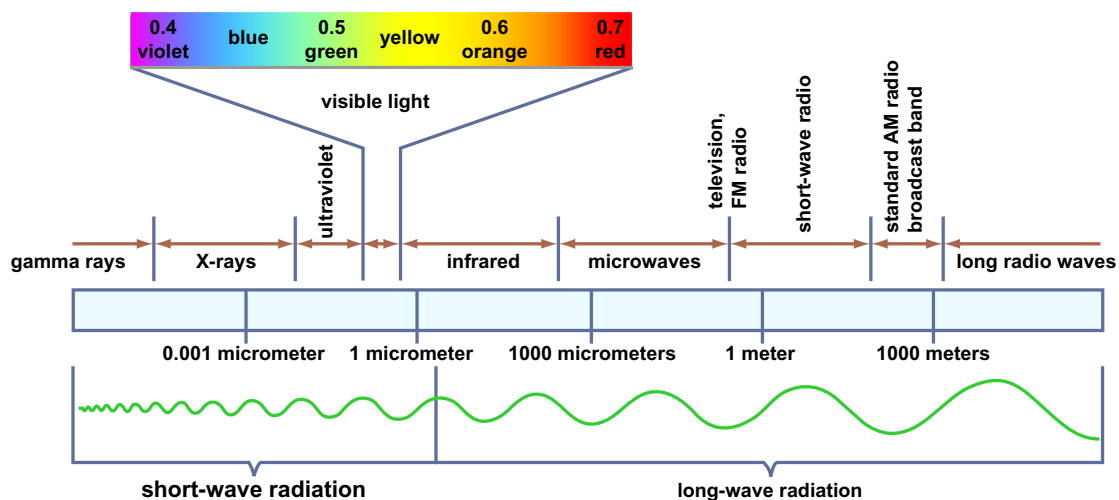Figure by MIT OCW.

Figure 1-1. The electromagnetic spectrum. (From Lutgens and Tarbuck, 2004.)

2.3 Of the various physical laws governing the emission and absorption of electromagnetic radiation, the one that's most relevant for us here is *Wien's law*: *the product of the absolute temperature and the wavelength of the most intense radiation is a constant*. That means that a body with a relatively high surface

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temperature, like the sun, radiates energy at relatively short wavelengths, and a body with a relatively low surface temperature, like the earth, radiates energy at relatively long wavelengths. The maximum intensity of the Sun's radiation is at about 0.5 μm, whereas the maximum intensity of the earth's long-wave radiation is at about 10 μm, well into the infrared range.

2.4 But bodies like the Sun and the Earth don't radiate all of their energy at a single wavelength: they radiate *over a wide range of wavelengths*. Figure 1-2 is a graph of the intensity of solar radiation as a function of wavelength. We see from Figure 1-2 that *the sun radiates most of its energy in the visible and ultraviolet part of the spectrum, but a substantial part also in the infrared part of the spectrum*. A similar graph for the Earth's radiation back to space, also shown in Figure 1-2, would show a similar shape but shifted far toward the long wavelengths.
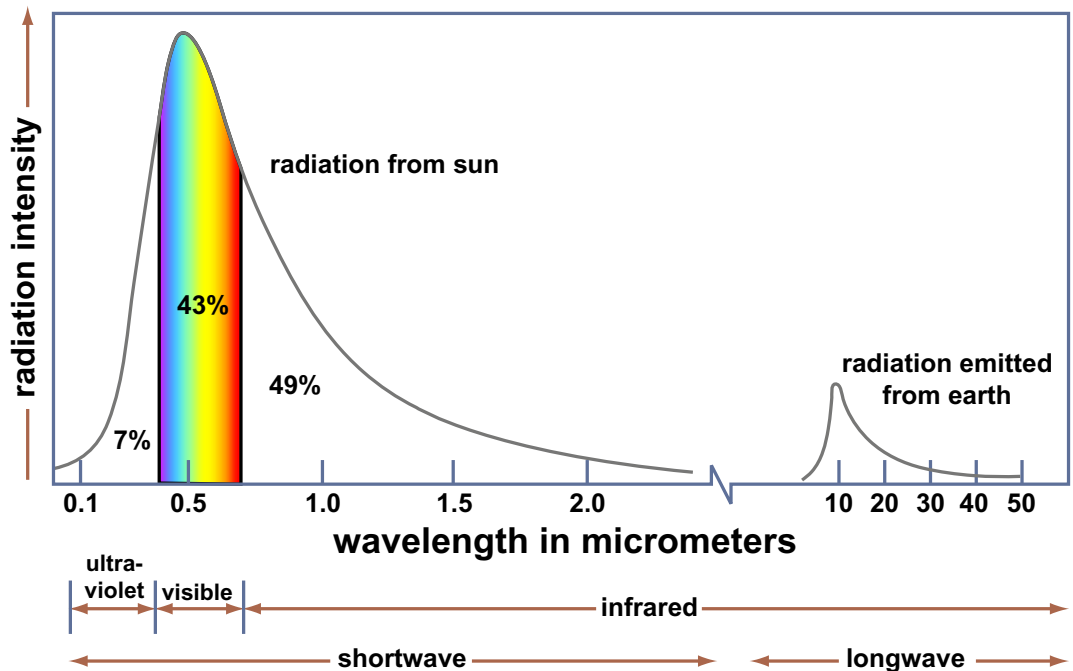
Figure by MIT OCW.

Figure 1-2. Intensity of short-wave solar radiation and long-wave terrestrial radiation as a function of wavelength. (From Lutgens and Tarbuck, 2004.)

2.5 The next time you are out in your yard or garden, or in the park or the countryside, I want you to think about long-wave radiation: you can't see it (although you *can* feel it), but it's operating everywhere, all the time, and it's as

important as sunlight in terms of its effect upon local climate (although obviously not in terms of plant growth, or suntanning, or skin cancer).

3. Temperature and Heat

3.1 All of the atoms or molecules of matter undergo inherent motions. In gases, these motions consist in long, straight trajectories of the atoms or molecules, called *free paths*. If the gas is enclosed in a container, the particles collide with the walls of the container. Macroscopically we sense the aggregate of such collisions as the pressure that the gas exerts on the walls of the container. Now and then, the particles also collide with one another as they fly about. The average distance traveled by a particle between collisions with other particles is called the *mean free path*. The mean free path of air molecules at atmospheric pressure and a temperature of 0°C is about 2×10^{-5} cm (a very small distance, equal to about one thousand molecule diameters). The collision frequency is about 5×10^{9} per second, which is an extremely short time. Each molecule makes about five billion collisions per second!

3.2 In solids, the atoms or molecules are fixed in place, either in the regular array of a crystal structure or in the irregular arrangement of an amorphous (noncrystalline) solid. You will learn more about that in Chapter 2. But the particles do not stand still: they vibrate in place, with a certain amplitude and frequency. In liquids, the atoms or molecules are in close association with one another, and they exert strong forces on one another, but they too undergo the same small-scale random motions that are characteristic of gases and solids.

3.3 What we are dealing with here are called thermal motions, or thermal vibrations. These motions are an inherent feature of all matter. The moving or vibrating particles have some energy of motion, called kinetic energy. The hotter the matter (that is, the higher the temperature of the matter), the more vigorous or energetic are the thermal motions. In fact, what physicists call the **temperature** of the matter is just *a measure of the average kinetic energy of all of the constituent atoms or molecules*. As the temperature of a body of matter is lowered, a point is reached at which the thermal energy of the atoms and molecules is at an absolute minimum. That temperature is called **absolute zero**, about -273°C.

3.4 All of you know about the *Fahrenheit* scale of temperature, which we here in the United States use in our everyday lives. You probably also know that it has been supplanted in most other parts of the world, and by scientists everywhere, by the *Celsius* scale of temperature (earlier called the *centigrade* scale), with the freezing point of water at 0°C and the boiling point of water (at sea-level pressure) at 100°C. What may be less familiar to you is the *Kelvin* scale of temperature, in which the degrees are the same as in the Celsius scale but zero

is fixed at absolute zero. In the Kelvin scale, the degrees are called kelvins (not "degrees Kelvin").

3.5 It's important for you to understand the distinction between temperature and heat: they are related, but they are not the same! ***Heat*** is *the total internal energy of all of the constituent atoms or molecules in a given body of matter*. (By internal energy here, I mean all of the kinetic energy of the atoms and molecules, which is discussed in the preceding paragraphs, together with the energy associated with the forces of attraction among the individual atoms and molecules.) Other things being equal, the bigger a body of matter, the more heat it contains. That's in contrast to the ***temperature*** of the body, which, as you learned above, is *a measure of the thermal energy of the individual atoms or molecules*.

3.6 In contrast to heat, the temperature of the body of matter is independent of how big the body is. Here is an everyday example of this: a small pot of water at nearly 100°C on the stovetop is much hotter (that is, has a much higher temperature) than the water in your almost-full bathtub at 40°C, but the total heat content of the water in the bathtub is much larger than the total heat content of the water in the pot.

3.7 Various units are used to describe heat. The two that are in common use in physics are the *calorie*, which is defined as *the amount of heat that's needed to raise the temperature of one gram of water by one degree Celsius*. Incidentally, there is a lot of potential confusion about calories. What I defined above is sometimes called the *gram calorie*, abbreviated as "cal". There is also the *kilogram calorie* (the amount of heat it takes to raise one kilogram of water by 1°C), abbreviated as "Cal". There are one thousand gram calories ("small calories") in one kilogram calorie ("large calorie"). The calorie that's used to measure the energy content of foods—that is, the dieter's calorie—is the same as the kilogram calorie.

3.8 Heat is also measured in *joules*, the unit of energy in the mks (meter, kilogram, second) system of units in physics. The joule is named in honor of James Prescott Joule, a British physicist (1818–1889), who was the first to demonstrate the equivalence of heat and mechanical energy by means of a classic experiment in which he increased the heat content of water in a large vat by adding mechanical energy to the water by stirring it with a paddle. One gram calorie is equal to about 4.18 joules. Just to confuse you further, in everyday life it's common to measure heat in terms of *British thermal units* (Btu). One Btu is *the amount of heat needed to raise one pound of water one degree Fahrenheit* (technically, from 63° to 64°). One Btu is about equal to 250 gram calories.

3.9 Finally, the concept of heat capacity is an important for anyone who thinks about the Earth's surface. The ***specific heat capacity*** of some given material is *the amount of heat that has to be added to a unit mass of that matter to raise its temperature by one unit*. This could be expressed, for example, as joules

per kilogram or as calories per gram. The importance for the Earth's surface is that the rocks, soil, and waters of the surface all have their own specific heat capacities, so it takes certain amounts of incoming solar energy to raise their temperature, and certain amounts of outgoing terrestrial long-wave radiation to decrease their temperature. Water has a much greater (I'm tempted to say spectacularly greater) specific heat capacity than the multifarious solid materials of the surface. That causes regions that are dominated by the oceans to have much more equable climate, other things being equal, than regions far removed from the oceans.

4. How Heat Is Transported

4.1 So far we've dealt only with radiation. Heat can also be transported by *conduction*, *convection*, and *advection*.

4.2 *Conduction* of heat through a solid is familiar to all: the handle of the pan on the stove heats up by conduction from the hot body of the pan. The same holds true for liquids and gases, although in that case conduction is often overwhelmed by the more efficient processes of convection and advection, by which the fluid, carrying its heat, is moved bodily from place to place.

4.3 The principle behind heat conduction is simple. The heat of a body is a manifestation of the thermal agitation of the constituent atoms and molecules. The hotter the material, the more energetic are the thermal motions of the atoms and molecules. When a difference in temperature from one place to another is imposed upon the body, the differing "intensity of jiggling" of the atoms and molecules from place to place is evened out, thus equalizing the temperature. We say that heat has been transported from the region of higher temperature to the region of lower temperature.

4.4 *Convection* is the term used for *the circulation of a fluid driven by differences in density brought about by differences in temperature*. The familiar example is a room warmed by a radiator on a cold winter day (Figure 1-3): the heating of the air by the radiator decreases its density, causing it to rise, and as it is cooled by the cold walls of the room, it sinks and takes a return path to the radiator, again to be heated. Convection cells of this kind are extremely important in atmospheric processes, on both small and large scales.

4.5 *The horizontal motion of fluid from one region to another, driven by horizontal differences in atmospheric pressure*, is called ***advection***. One can sense the importance of advection on a gloomy winter day when a warm wind blows from the south, melting much of the snow cover. Of course, what a local observer senses as advection might just be one very small part of some gigantic convection cell.
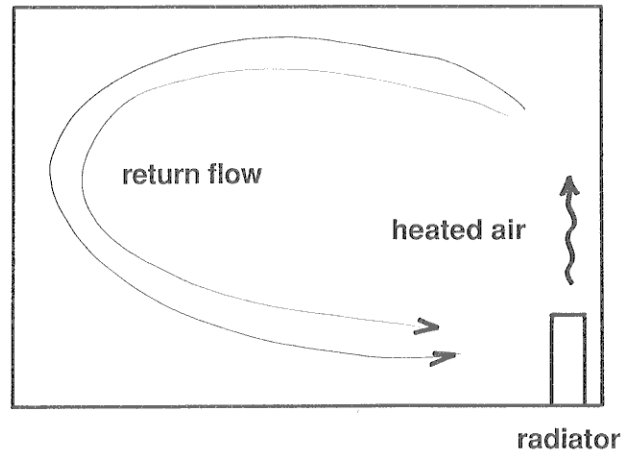
Figure 1-3. A convection cell.

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1. HEATING AND COOLING OF THE EARTH'S SURFACE

1.1 Introduction

1.1.1 There is a branch of climatology, called ***microclimatology***, that deals with *the climate at a particular locality on the Earth*. One important part of microclimatology has to do with what could be described as "the climate near the ground". Does that not seem like a suitable topic for a course on the environment of the Earth's surface?

1.1.2 Most of the standard weather observations made at weather stations are taken a standard height above the ground that's a little greater than the height of the average person. At most times, *the conditions right at the ground surface are rather different*, in terms of wind speed, temperature, and humidity. The climate near the ground, and its effect on the uppermost layer of the soil, is of obvious importance not just for agriculture but also for civil and environmental engineering, architecture, planning, and even medicine.

1.2 The Seasons

1.2.1 I often find myself wondering how much the average person understands about why there are seasons, and why sun height and day length change over the course of a year. Because I don't know much about that (my

basis for judgment is only anecdotal), I risk being either too elementary or too advanced for you in this brief section on the seasons.

1.2.2 First, some facts about the geometry of the Earth–Sun system. The e\Earth revolves around the Sun, once in a full year (that's how a year is defined!), in a plane passing through the earth's orbit, called the ***plane of the ecliptic***. The earth's orbit is nearly, but not quite, a circle; it's actually an *ellipse* with a slight eccentricity. To give you an idea of the degree of non-circularity of the orbit, the maximum Earth–Sun distance is about 152 million kilometers and the minimum distance is about 147 million kilometers.

1.2.3 The only easy way to detect by direct observation that the earth is revolving around the sun is astronomical: *view the stars at the same time every night throughout the year, and see how their position changes*. They make one complete circuit through the heavens in the course of a year.

1.2.4 You know, of course, that the earth rotates about its axis once a day, and that's what causes the difference between night and day. (!) If the Earth's axis of rotation were exactly perpendicular to the plane of the ecliptic, the length of the day and the height of the sun above the horizon at a given time of day (local noon, say) would not change through the year, and things would not be nearly as exciting as they are in reality. (By "day" here I mean the time during the 24-hour day that the sun is above the horizon. The word "day" is rather ambiguous in the English language; think of this aspect of "day" as "daylight day")

1.2.5 The earth's axis of rotation is in fact inclined to the plane of the ecliptic by about 23° 27', usually rounded off to 23-1/2°. This has far-reaching consequences for conditions at the Earth's surface. As you can see from Figure 1-4, there are two times during the year, called the ***equinoxes*** (one in spring, on 20 or 21 March, and one in autumn, on 22 or 23 September), when *the earth's axis of rotation is exactly perpendicular to the line between the earth and the sun*. At those times of the year, and *only* at those times, the daylight day is exactly twelve hours long at every point on the earth.

1.2.6 The earth's north pole and south pole represent special cases, in the sense that at the time of the equinoxes the sun is seen to lie right on the horizon and make a complete circle around the sky every 24 hours!

1.2.7 At times midway between the equinoxes, called the ***solstices***, *the earth's axis of rotation lies precisely in the plane that passes through both the sun and the earth and is perpendicular to the plane of the ecliptic* (Figure 1-4). At those times, one of the Earth's poles points closest to the sun and the other pole points farthest from the sun. At the time of the summer solstice in the Northern Hemisphere, on 21 or 22 June, the sun is highest in the sky at a given time of day, as at noon, and the daylight day is longest. Conversely, at the time of the winter solstice in the northern hemisphere, on 21 or 22 December, the sun is lowest in the

sky at a given time of day, and the daylight day is depressingly short, even nonexistent.
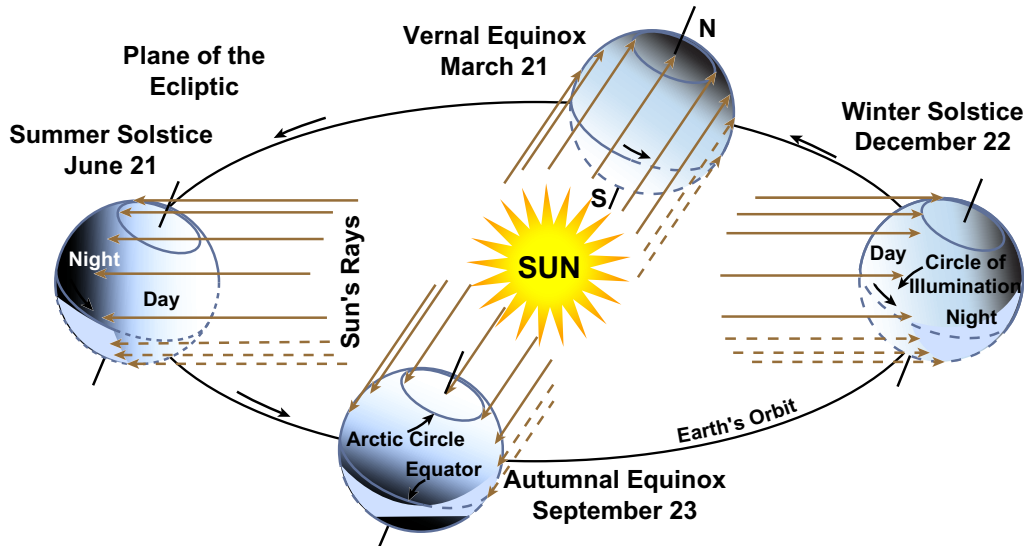
Figure 1-4. The yearly path of the Earth in its revolution around the Sun, showing how the seasons result from the differences in the angle between the Earth's rotation axis and the Earth–Sun line. (From Strahler, 1975.)

1.2.8 (If you think that things around the time of the winter solstice are bad at the latitude of Boston, think about what they are like in the latitude of Scandinavian cities, or Nome or Fairbanks in Alaska. On the other hand, during the legendary "white nights" of St. Petersburg, in early summer, it is said that one can read a newspaper at midnight without artificial light.)

1.2.9 But the angle at which the sun rises above the horizon at sunrise, and the equal angle at which the sun sets below the horizon at sunset, remains the same through the year (Figure 1-5). Think carefully about the geometry of the Earth–Sun system to convince yourself of that fact.

1.2.10 Incidentally, can you think of a reason why the equinoxes and solstices do not fall on exactly the same days, in March and September and in June and December, respectively, every year? It's related to the existence of *leap years*. The astronomical duration of the year—the time it takes for the earth to make on complete revolution around the sun—is close to 365-1/4 days, whereas the calendar year has 365 days, by definition. Every four years they add 29

February to the year, and it makes things come out almost okay, except not quite, so once every century they have to have an extra adjustment of one day, etc., etc. That causes the precise times of the year when the equinoxes and solstices occur to vary depending upon the position of the given year relative to the leap years.
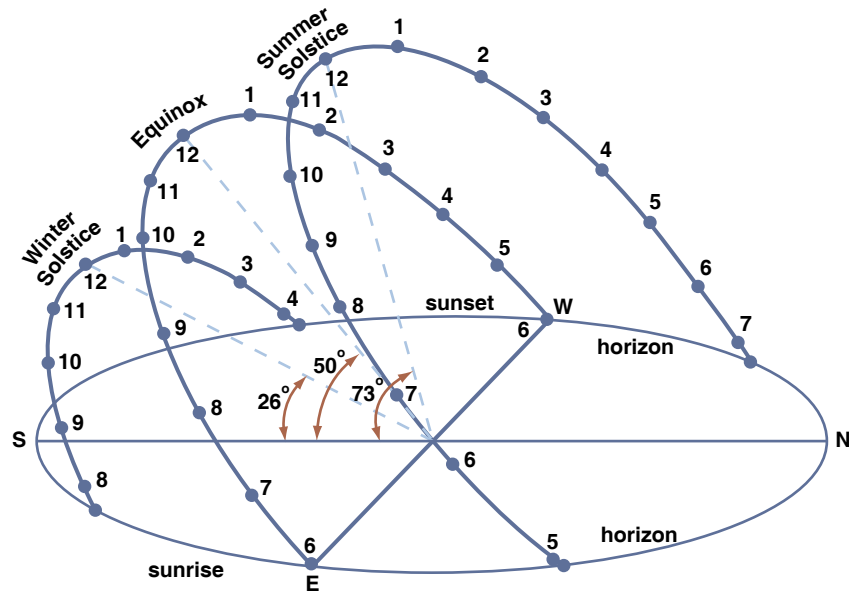

Figure by MIT OCW.

Figure 1-5. The Sun's path in the sky at the equinoxes and at the solstices at latitude 40° N. (Modified from Strahler, 1975.)

1.2.11 One final point: the time of *maximum* distance from the sun to the earth, called **aphelion**, falls on 4 July, and the time of *minimum* distance from the sun to the earth, called **perihelion**, falls on 3 January. Note (Figure 1-6) that (1) these times are out of sync with the seasons and (2) the earth is closest to the sun in the northern-hemisphere winter, by a factor of about 1.03 (152 x 10^6 km divided by 147 x 10^6 km), which because of the inverse-square decrease in the sun's radiant energy with distance from the sun translates to a factor of about 1.07 (or seven percent, in what I think is the conventional way of stating percentages). It's a good thing, too, except perhaps for ski fanatics: if the situation were the reverse, with the Earth farthest from the Sun in the northern-hemisphere winter, winters in New England would be even tougher than they are.

1.3 Sunlight

1.3.1 As you are probably aware, the Sun is fueled by thermonuclear fusion, by which hydrogen is fused to helium with enormous release of energy. The Sun's surface, at a temperature of about 6000°C, radiates energy in all directions over a wide range of wavelengths. The Earth intercepts a tiny fraction of that radiant energy, in the form of sunlight. Most of the ultraviolet part of the radiation

is absorbed before it reaches the Earth's surface, although in recent times the degradation of the ozone layer as a consequence of certain man-made refrigerant gases in the upper atmosphere has led to greater ultraviolet radiation at the surface, especially at high latitudes. The effects of man-made gases on the ozone layer, and its consequences for ultraviolet radiation, is a field of active research by atmospheric chemists and physicists nowadays.
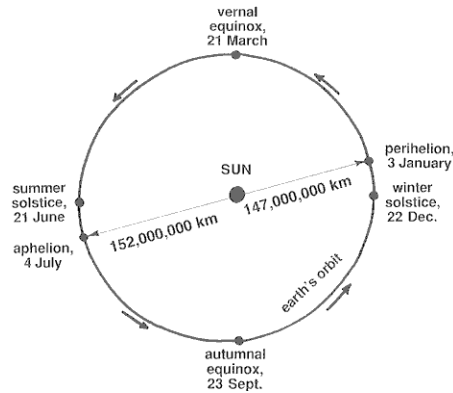

Figure 1-6. The Earth's orbit around the Sun, and the seasons. (Modified from Strahler and Strahler, 1992.)

1.3.2 How much of the Sun's energy reaches the earth? Think about one square centimeter of area, oriented perpendicular to the line between the Earth and the Sun and outside the Earth's atmosphere. The rate of delivery of radiant energy to that square centimeter is very nearly *two gram calories per minute*. This is often referred to as two langleys per minute, a **langley** being *one gram calorie per square centimeter*. This value is called the **solar constant**, although in fact it's not quite constant: it varies slightly depending upon two effects:

- changes in the sun's output, connected with things like solar flares; and
- changes over the course of a year, because the earth's orbit around the sun is not a circle but rather an ellipse with a small eccentricity, as you have already seen.

1.3.3 How can I give you some feel for what the solar constant means in everyday life? First of all, I should point out that the energy flux (by that I mean rate of delivery of energy per unit area perpendicular to the direction of radiation) is at most *about half that just outside the atmosphere*, or about one langley, because of the inevitable absorption and reflection, even on the clearest of days. On cloudy days, or when the sun shines at a low angle through the atmosphere, the value is correspondingly much smaller.

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1.3.4 All of you have some experience with how much energy it takes to heat water. You put a pan of water on the stovetop, turn on the burner, and wait and wait for the water to boil. As you will learn more in a later chapter, water has a very high specific heat capacity: it takes a lot of energy to raise the temperature of water by a given amount.

1.3.5 Suppose that you had a little cube, one centimeter on each side, filled with water and oriented with one face facing directly into the sunlight. The other five faces are perfectly insulated from their surroundings, and the face that catches the sunlight is completely transparent to the sun's incoming energy but can pass no heat back out to its surroundings. How long would it take to heat water contained in the cube from the freezing temperature (0°C) to the boiling temperature (100°C)? Answer: about 100 minutes.

1.4 Heating and Cooling of the Surface

1.4.1 The ground surface is the interface between the atmosphere and the solid and liquid material of the earth. The ground surface is where solar radiation is intercepted and converted to heat. It is also the source of outgoing long-wave radiation. It is where liquid water is evaporated and where incoming rainfall is stored as soil moisture and groundwater. First, in the following two paragraphs, are some very general things about heating and cooling. Then, after some more physics background, there is more detail on the heating and cooling of the Earth's surface.

1.4.2 Low-lying areas are commonly colder at night than higher ground nearby. On clear nights, the ground is chilled as its heat is radiated out to space. The cold ground then chills the air near the ground. The chilled air is slightly more dense than the overlying air, so it tends to flow slowly downhill, in the same way that water flows downhill. The cold air "ponds" in low areas. These are places where the first frosts of autumn are earliest and where the last frosts of spring are latest. If you ever have a chance to plant fruit trees, plant them on the highest ground around!

1.4.3 In hilly areas, north-facing slopes get less sunshine than south-facing slopes. Local temperatures on the north-facing slopes are colder than on south-facing slopes in both summer and winter. In areas with winter snows, the snow melts much later on north-facing slopes. Even over distances of a few meters, the difference in microclimate between a sunny, open area with low herbaceous vegetation and a nearby grove of tall trees can be spectacular.

1.4.4 Everybody knows that the Earth's surface tends to be warmed on a sunny day and cooled on a clear night. Let's look more deeply into how this happens. Many different and interesting effects must be taken into account.

1.4.5 If there were no atmosphere, things would be fairly simple: the Sun radiates energy to the Earth's surface at short wavelengths, most of it absorbed but some of it reflected, and the Earth would re-radiate that energy back out to space at longer wavelengths, and the temperature of the surface would become adjusted so that the outgoing long-wave radiation would balance the incoming short-wave radiation over a long time. (For that statement to make more sense to you, you need to be aware that *the intensity of emission of radiation from a body increases with the temperature of the body—to the fourth power!* That's called the **Stefan-Boltzmann law**.)

1.4.6 A few additional words about the reflection of incoming solar radiation by the Earth's surface back into space are in order here. The local reflectivity varies greatly depending upon what's covering the surface. It ranges from as much as 95%, for fresh snow cover, to as low as just a few percent, for water surfaces at high sun. Figure 1-7 is a table giving approximate values of reflectivity for various kinds of surface. The overall grand average for the entire earth (that is, *the percentage of incoming solar radiation intercepted by the entire earth that's reflected back to space, on a long-term average*), is called the earth's **albedo**; its value is about 30%.

fresh snow cover	75-95
dense cloud cover	60-90
old snow cover	40-70
clean firn snow	50-65
light sand dunes, surf	30-60
clean glacier ice	30-46
dirty firn snow	20-50
dirty glacier ice	20-30
sandy soil	15-40
meadows and fields	12-30
densely built-up areas	15-25
woods	5-20
dark cultivated soil	7-10
water surfaces, sea	3-10

Figure by MIT OCW.

Figure 1-7. The albedo of various kinds of surfaces. (From Geiger, 1965.)

1.4.7 In the real world, with a thick atmospheric cover, the situation at the ground surface is much more complicated, largely by virtue of two effects:

• *The atmosphere reflects and scatters some of the incoming solar radiation.* (**Scattering** is the process whereby the atoms, molecules, and tiny particle in the atmosphere interact with passing electromagnetic waves whose wavelengths are approximately the same as the size of the particles, causing a part of the waves to

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be diverted in a wide range of directions.) What arrives at the surface is a combination of direct radiation and indirect, downscattered radiation. The atmosphere itself absorbs some of the incoming solar radiation, but, perhaps surprisingly, not much. (Incidental note: the shorter wavelengths are more susceptible to scattering than the longer wavelengths, so the indirect downscattered radiation we see at the earth's surface tends to be in the shorter-wavelength part of the visible spectrum—hence the *blue sky* on a clear day. By the same token, the *yellow or orange or even red sun* seen at sunrise or sunset is a consequence of the greater scattering of the shorter wavelengths during the long slanting passage of the Sun's rays through the atmosphere, leaving mainly the longer-wavelength radiation to come through to our eyes.)

• A lot of the long-wavelength back-radiation to space from the earth's surface is absorbed by the atmosphere. Some of the absorbed energy is re-radiated back to the earth's surface, and some is re-radiated out to space. The important effect here is that *there is a net radiation of long-wavelength energy to space, but the almost-equal magnitudes of back-and-forth long-wavelength radiation between the surface and the atmosphere is much larger than the net radiation to space*. This is the famous **greenhouse effect**.

1.4.7 Certain atmospheric gases figure most prominently in the absorption of outgoing long-wave terrestrial radiation by the atmosphere, foremost among them being *water vapor, carbon dioxide, methane, ozone, and certain man-made gases like chlorofluorocarbons*. It's this strengthened greenhouse effect, caused by the increasing concentration of anthropogenic greenhouse gases, that is thought to be the cause of global warming (but the situation is in reality more complicated, in large part because of the still poorly understood potential changes in cloud cover; for such reasons, global warming has its responsible skeptics). Each greenhouse gas absorbs outgoing terrestrial long-wave radiation in different segments of the electromagnetic spectrum; they combine to leave only narrow windows of transparency (Figure 1-8).

1.4.8 Water vapor, because it is an effective absorber of long-wave terrestrial radiation and because it is present in the atmosphere in far greater concentrations than any of the other greenhouse gases, is the number-one greenhouse gas (but the others, most importantly carbon dioxide, humankind has some control over, which is not the case with water vapor). Beware of what you read in the news media about carbon dioxide being the most important greenhouse gas! I could also point out here that the greenhouse effect is much more our friend than our enemy: if it were not for the greenhouse effect, the Earth would be a frozen and lifeless planet.

1.4.9 You need also to be aware of several readily understandable processes specific to the earth's surface, which are important factors in the heat budget of the surface:
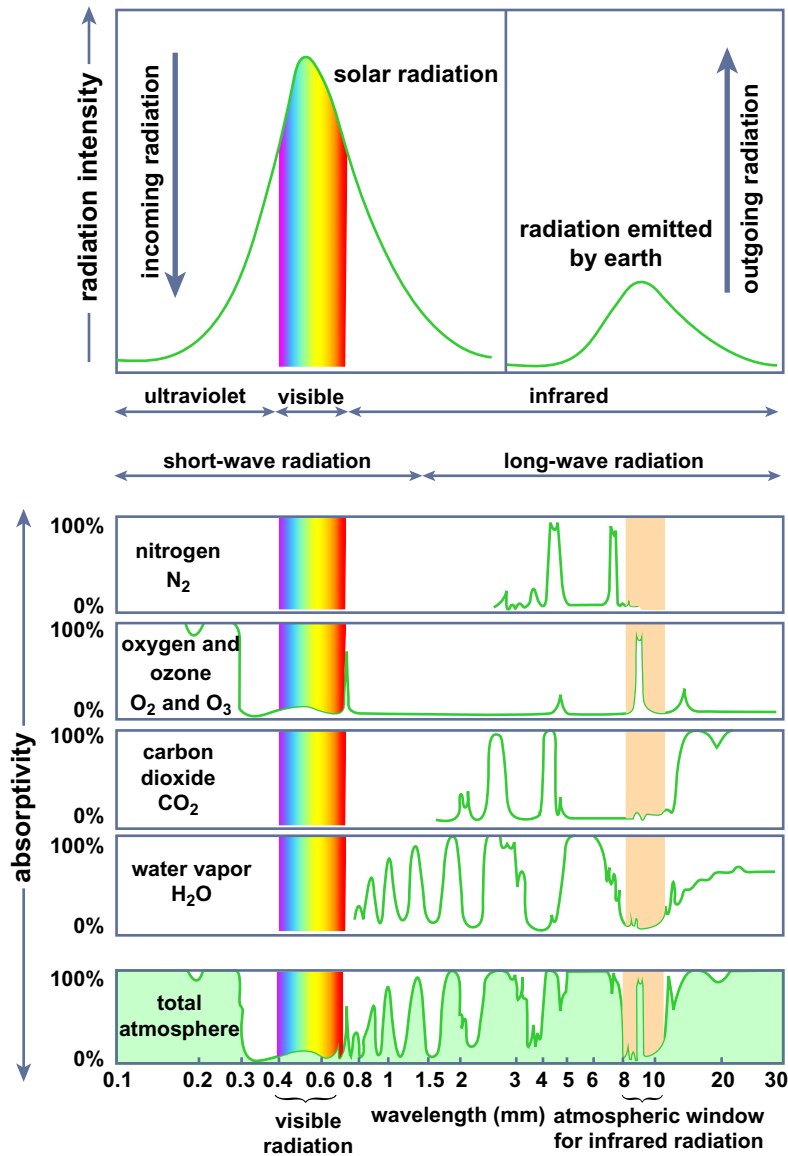
Figure by MIT OCW.

Figure 1-8. The absorptivity of selected greenhouse gases of the atmosphere, and of the atmosphere as a whole. (From Lutgens and Tarbuck, 2004.)

- When the surface is warmer than the immediately overlying atmosphere, heat is conducted from the ground to the atmosphere; when the surface is cooler than the air above, heat is conducted downward from the air to the ground.
- As the ground surface is warmed, heat is conducted downward into deeper levels of the soil; as the ground surface is cooled, heat is conducted upward from the deeper levels.

• Provided that the relative humidity is less than 100%, soil moisture present at the ground surface, or drawn upward to the ground surface by capillary action, is evaporated into the atmosphere, thereby delivering latent heat to the atmosphere. (As you will learn in Section 3 below, it takes a lot of heat energy to evaporate liquid water; that energy is released into the atmosphere when the water vapor condenses to liquid water.)

• Some heat is added to the ground surface by condensation of dew on clear nights, but that's not an important effect; what's more important is delivery of precipitation to the ground surface from above. If the temperature of rain is greater than that of the surface, the surface is warmed, and vice versa.

1.4.10 It's not easy to make any simple statement about the state of the ground surface in terms of heat, because all of the above effects and processes *vary with time of day, state of the weather, time of year, and climatic zone*. But the next time you are outdoors and about, looking at the ground surface, I want you to think about all of the foregoing processes, acting simultaneously to set the temperature of the surface. Just for a summary, look at Figure 1-9, which shows the various processes, and in a qualitative way their typical magnitudes, on a sunny summer day and on a clear summer night. The major effects are: incoming solar radiation absorbed by the ground (S), which is a combination of direct and downscattered radiation; incoming solar radiation reflected from the ground (R); incoming long-wave radiation from the atmosphere (LI); outgoing long-wave radiation to the atmosphere and outer space (LO); conduction of heat from the ground to the overlying air or from the overlying air to the ground (C); and loss (or minor gain) of heat from the ground by evaporation of soil moisture (V).

1.4.11 On average, over the course of a year, there is a net gain of heat by **insolation** (the term used to describe *the totality of solar radiation reaching the Earth's atmosphere*) at low latitudes and a net loss at high latitudes. That imbalance has to be made up somehow, because the Earth's average surface temperature changes only very slowly with time. That happens by net transport of heat from low latitudes to high latitudes by the Earth's wind systems and ocean currents. One consequence of the existence of seasons is that the solar energy received by the Earth varies not only with latitude, as described above, but also with the seasons. Does it surprise you to learn that around the time of the summer solstice insolation at the north pole is even greater than at the equator at that same time, because the sun shines there twenty-four hours a day! Figures 1-10 and 1-11 show, in two different ways, how insolation varies as a function of both latitude and season.

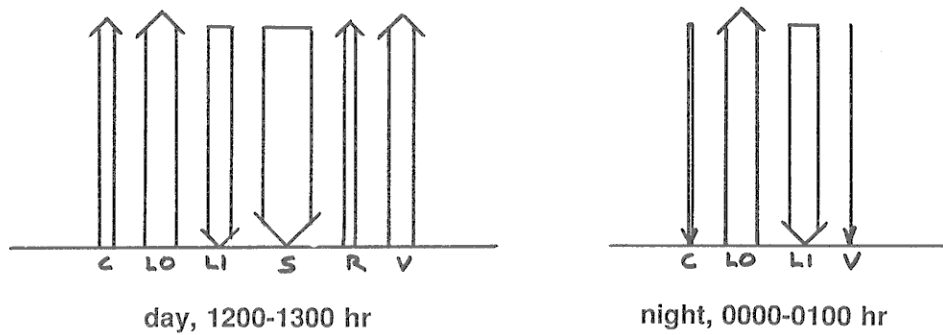day, 1200-1300 hr   night, 0000-0100 hr

Figure 1-9. Elements of the heat budget of the ground surface. Left: clear summer day. Right: clear summer night. The thickness of the arrows show very approximately the relative magnitudes of the effect. (Modified from Geiger, 1965.)
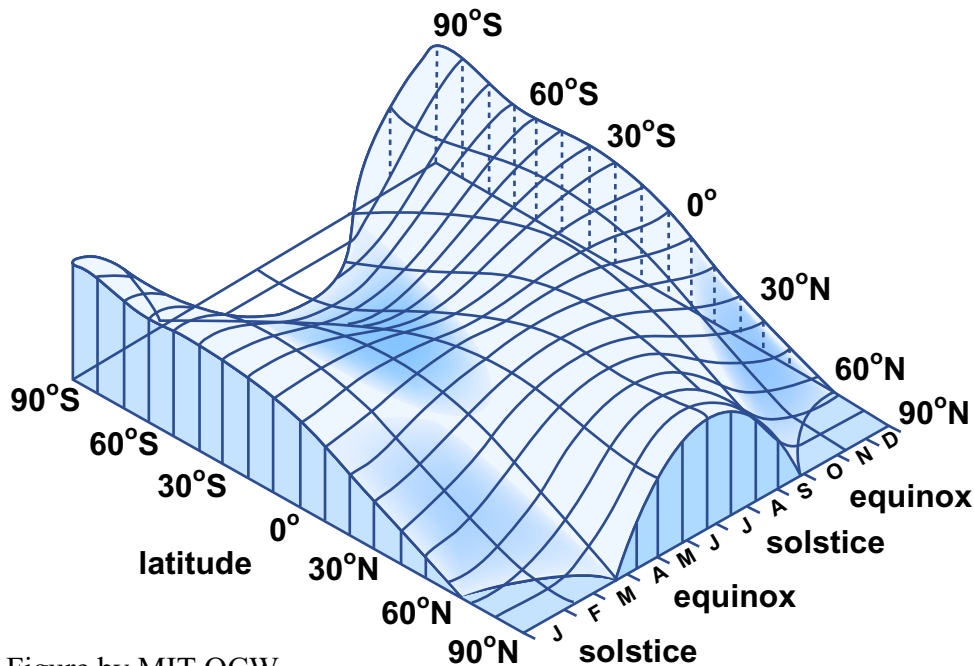

Figure by MIT OCW.

Figure 1-10. Insolation as a function of latitude and season. (From Strahler, 1975.)

1.4.12 What about the temperature of the soil (or, more generally, regolith and bedrock) beneath the ground surface? Despite songs about the cold, cold ground, the substrate is not necessarily colder than the ground surface. *The vertical distribution of temperature as a function of depth below the surface depends upon a multitude of factors*:

- ambient temperature of the air above the surface
- clarity of the sky

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- state of the ground surface, especially moisture content and vegetative cover
- composition of the substrate
- moisture content of the substrate
- past history (because the temperature profile does not adjust instantaneously to changing surface temperature: there's a long time lag)
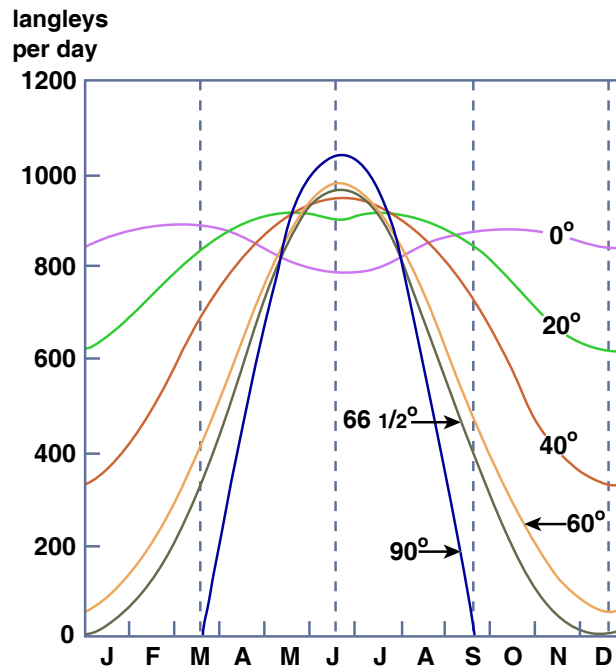

Figure by MIT OCW.

Figure 1-11. Insolation as a function of latitude and season in the northern hemisphere. (From Strahler, 1975.)

1.4.13 When the Sun shines on the Earth's cool land surface and heats it, that heat is conducted downward into the Earth, at a rate that depends on the temperature difference between the surface and the subsurface and also on the heat capacity and the thermal conductivity of the Earth's soil and rock materials. Likewise, when the Earth's surface cools by radiation of energy back out to space, heat from the still-warm subsurface materials is transferred by conduction back out to the surface. Such changes are mainly on time scales of day to night and of winter to summer seasons. Figures 1-12, 1-13, and 1-14 show some interesting results of actual measurement of the cyclic changes in temperature with depth.

1.4.14 Obviously the temperature near the surface is greatest in summer and least in winter, but there are two significant effects below the surface:

- The changes in temperature over one diurnal (that is, daily) cycle or over one yearly cycle decrease with depth in the Earth. Below a depth of about a meter, the day-to-day changes are negligible, and below a depth of about ten meters the temperature is almost the same year-round.

- The timing of the change in temperature at some depth lags behind the timing of the change in temperature at the surface. That's because it takes time for the heat to be conducted downward. The time lag increases with depth. At a certain depth, the cycle is out of phase with the surface by a whole half cycle: that is, the maximum temperature attained at depth happens at the time of minimum temperature at the surface, and vice versa!
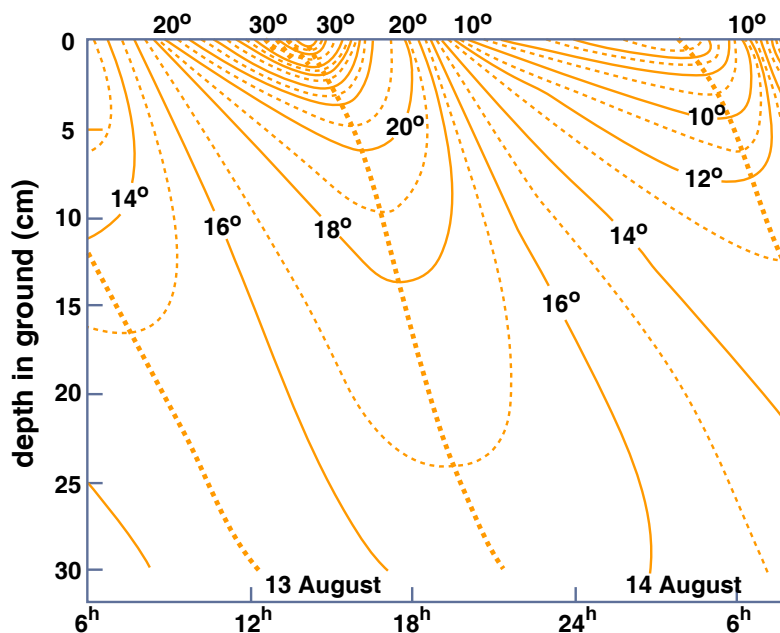

Figure by MIT OCW.

Figure 1-12. Penetration of the daily temperature wave (in degrees Celsius) into the ground on a clear summer day in Finland in mid-August. (From Geiger et al., 2003.)

1.4.15 In colder climates the effects would be qualitatively the same, but the temperatures would be lower. In such areas, as in New England, the upper layer of the substrate, to a significant depth, becomes frozen for quite some time in the winter. Building codes in cold regions are specified to ensure that footings for

foundations are placed at a depth great enough to be below the deepest freezing level to be expected in the given climate.
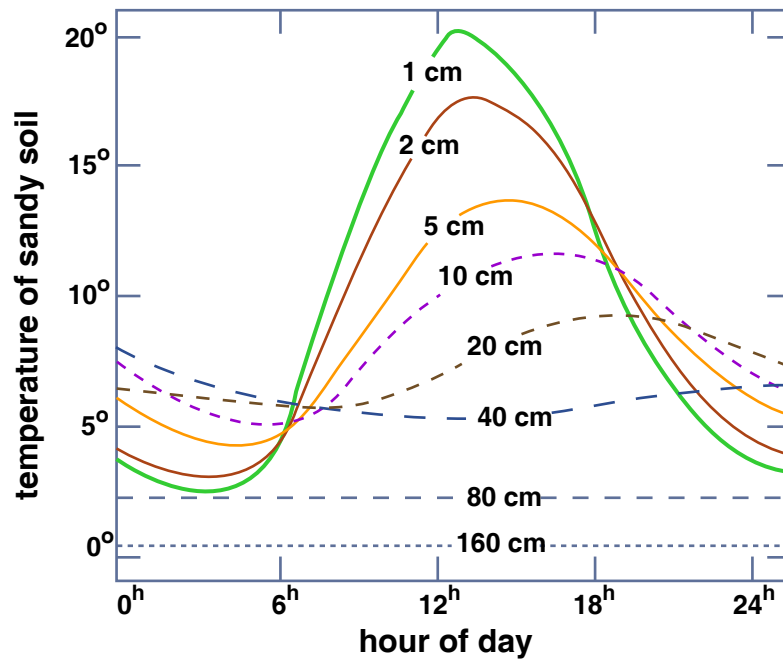
Figure by MIT OCW.

Figure 1-13. Daily sequence of temperature in sandy soil in May (ten-year averages). (From Geiger et al., 2003.)
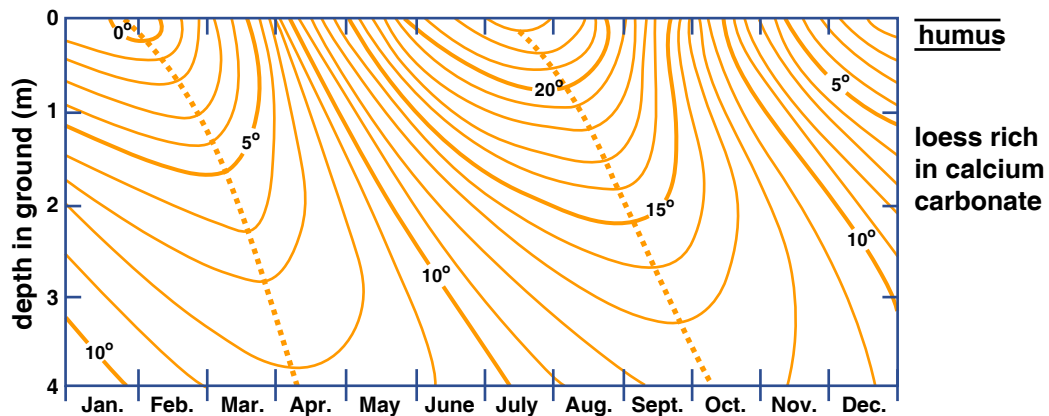
Figure by MIT OCW.

Figure 1-14. Annual sequence of soil temperature (in degrees Celsius). (From Geiger et al., 2003.)

BACKGROUND: SOME ELEMENTARY CHEMISTRY RELEVANT TO THE EARTH'S SURFACE

1. Atoms

1.1 Atoms are the building blocks of matter. Do I need to define for you what an atom is? One way of doing that is to say that an atom is the smallest unit of matter that reflects the chemical characteristics of the matter, in respect to its interactions with the atoms of other kinds of matter. In other words, atoms are units of matter that cannot be split up further without losing the chemical behavior of the matter, in terms of bonding with other atoms to form chemical compounds. If you're going to understand why various kinds of atoms bond together the way they do to form the important minerals, you have to know what atoms are like and why the atoms of the various chemical elements behave differently.

1.2 The simplest cartoon for an atom (Figure 1-15) has a number of electrons orbiting a nucleus consisting of closely packed protons and neutrons.
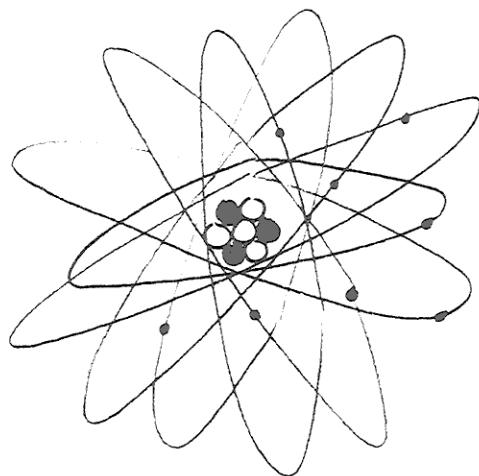

Figure 1-15. Extremely oversimplified cartoon of an atom.

1.3 Basic facts (don't worry about how we know them, and don't worry about remembering them for exam purposes):

mass of proton: 1.7×10^{-24} g
mass of neutron: 1.7×10^{-24} g

mass of electron: about 1/1840 of the above

electric charge on neutron: zero

electric charge on electron (one "unit" of negative charge (smallest amount possible!)

electric charge on proton: one "unit" of positive charge (just the opposite of that of the electron)

size of atom: about 10^{-10} m

size of nucleus: about 10^{-15} m

1.4 Note right away that for an atom to be electrically neutral is must have the same number of protons and electrons. So the nucleus is much heavier than the electron cloud around it, but also much smaller, by a factor of about 10^5.

1.5 What's the best way for you to visualize the actual size of an atom? Think about the very tiniest dust particle you can see with your unaided eye under the best lighting conditions. Assume this to be one hundredth of a millimeter, or 10^{-5} m. About how many atoms would stretch across that distance? See Figure 1-16 for a computation.

(diameter of atom) (no. of atoms across particle) = diameter of particle

$$\text{no. of atoms} \quad = \quad \frac{\text{diameter of particle}}{\text{diameter of atom}} \quad = \quad \frac{10^{-5}\text{m}}{10^{-10}\text{m}} \quad = \quad 10^5$$

or 100,000 atoms

Figure by MIT OCW.

Figure 1-16. Computation to give you an idea how big an atom is.

1.6 What are electrons really like, and what are their orbits around the nucleus really like? These are complicated questions, difficult to answer in a simple way. To get a good idea you need to know something about quantum mechanics, a branch of physics, which has grown up since the early decades of the Twentieth Century, that deals with the behavior of very small particles.

1.7 Particles that are very small and very fast-moving behave in ways our common sense doesn't cover. Electrons aren't just little solid spheres, like billiard balls or mini-planets; they are both particles and little packets of waves at the same time, in that in some ways they behave like particles and in other ways they behave like waves. In this respect, electrons are just like light, which also shows

this particle–wave duality. If this doesn't make much sense to you, don't worry about it. Also, we have no way of knowing where the electrons are in their orbits around the nucleus: all we can say is what the probability is that they will be found in a given place. So it's a little better to cartoon the atom as a smeared-out "probability cloud" of electrons around the nucleus (Figure 1-17), although even that is still not very satisfactory.
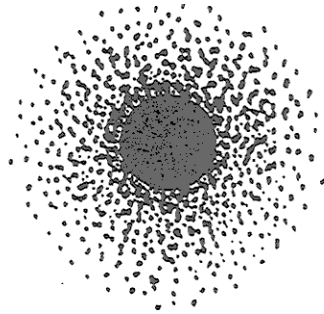

Figure 1-17. An atom schematized as a smeared-out probability cloud around the nucleus. The denser the shading, the more likely you are to find the electron there.

   1.8 But with all this said, in order to get somewhere studying minerals we will make some simplifications about electrons and think of them as "ordinary" little particles traveling in "ordinary" little orbits around the nucleus.

2. *The Chemical Elements*

   2.1 There are many different kinds of atom, depending upon the number of electrons, protons, and neutrons in the atom. In terms of the chemical behavior of atoms, which is what we're interested in here, the important thing is the number of electrons (and the equal number of protons), because that's what determines how the atom bonds (or fails to bond) with other atoms. Each distinctive kind of atom, in terms of the number of electrons and protons it has, is called a ***chemical element*** (or just an ***element***).

   2.2 Let's investigate the structure and behavior of the elements by starting with the lightest and simplest kind of atom: hydrogen. The nucleus of the hydrogen atom consists of one proton, and the electrically neutral atom has one electron orbiting the proton nucleus. The next lightest and next simplest atom is helium. Its nucleus consists of two protons, and the electrically neutral atom has two electrons orbiting it—et cetera. We can build up a picture of all of the

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elements in this way, by adding one proton (and therefore one electron) at a time—with some neutrons thrown into the nucleus also.

	1	2	3	4	5	6	7	8
1	H 1							He 2
2	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20						

Figure 1-18. The first part of the periodic table of the elements.

2.3 Figure 1-18 is a chart of the first twenty or so elements. This covers most of the important elements that go into the most important rock-forming minerals. Why have I arranged the elements in this way? You might remember from some chemistry course that this represents the first three rows of what is called the ***periodic table of the elements***, plus a little of the fourth row.

2.4 This grouping of the elements corresponds very closely to the chemical behavior of atoms of these elements, when it comes to combining, or bonding, with atoms of other elements to form chemical compounds. (Remember that minerals are just chemical compounds.)

2.5 This kind of grouping (more complete than shown here) was first perceived by the Russian scientist Dmitrii Mendeleev in 1869. His insight into the nature of organization of the elements in terms of their chemical behavior paved the way for people after him to actually discover new elements his table predicted. It was not until the early 1900s, with the advent of the quantum theory of matter, however, that people realized why the elements are arranged in this way.

2.6 Electrons are present in atoms in group of orbits called ***shells***. That is, electron orbits occur in groups. A filled shell (all the electron orbits of the shall

are occupied by electrons) is a very stable configuration of electrons—stable in the sense that the electrons are tightly bound, and it takes a lot of energy to remove one, and also the atom has no tendency to take on electrons to try to fill a shell. Elements with filled-shell electron configurations are very inert and almost totally nonreactive.

2.7 The first shell has positions for two electrons. This corresponds to the first row of the periodic table. Hydrogen doesn't have a filled-shell configuration, so it enters into an enormous number of chemical compounds in its search for the extra electron, from some other atom willing to give it up, to attain the filled-shell configuration. But helium, which has two electrons already, is an inert gas. The second shell contains eight electrons, corresponding to the second row of the periodic table. Neon has both of the first two shells filled and, like helium, is an inert gas. The third shell also contains eight electrons, and corresponds to the third row of the periodic table. Argon is the inert gas with all three first shells filled.

3. *Ions*

3.1 How about the elements with unfilled shells? There is a strong tendency for an atom to end up with a filled shell, by either giving up electrons (to another atom) or taking on electrons donated from another atom (or by sharing electrons with another atom; see below). Atoms that have attained a filled-shell configuration by either giving up or taking on electrons are called ***ions***. The characteristic thing about ions is that have an electric charge.

3.2 Those elements (near the left side of the periodic table) with only a few electrons in their outer shell can fairly easily be stripped of those electrons so as to have a filled-shell configuration. Examples are sodium (Na), magnesium (Mg), potassium (K), and calcium (Ca). Ions like these have a positive charge, because they have lost electrons (which are negatively charged).

Na atom minus 1 electron $\rightarrow$ Na^+ ion (single positive charge)

Mg atom minus 2 electrons $\rightarrow$ Mg^{2+} ion (double positive charge)

Figure 1-19 shows some examples of positively charged ions.

3.3 Elements that are near the right side of the periodic table, with almost enough electrons in the outer shell to produce a filled-shell configuration, can easily take on enough electrons to fill the shell. Examples are oxygen (O), fluorine (F), sulfur (S), and chlorine (Cl). Ions like these have a negative charge, because they have gained electrons.

Cl atom plus 1 electron $\rightarrow$ Cl^- ion (single negative charge)

O atom plus 2 electrons $\rightarrow$ O^{2-} ion (double negative charge)

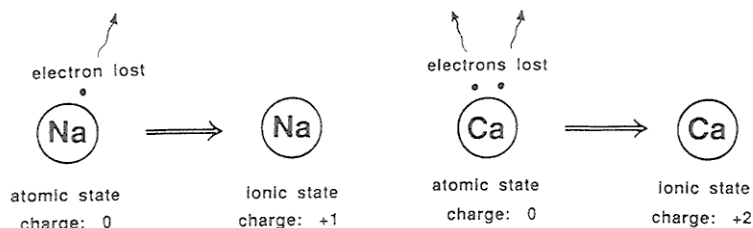Figure 1-20 shows some examples of negatively charged ions.
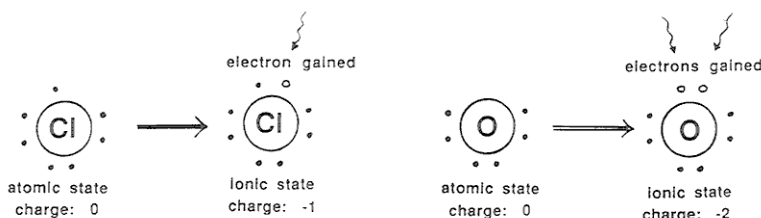

Figure 1-19. Examples of positively charged ions.

Figure 1-20 Examples of negatively charged ions.

3.4 For reasons that need not concern us here, positively charged ions are called ***cations*** and negatively charged ions are called ***anions***.

4. Ionic Bonds

4.1 All of you know that there are such things as electric charges and that these can be moved around from place to place. (Think about hair and clothes on dry days. Or get under the synthetic-fiber bedspread in the dark when the humidity is low and run your hands over its surface, and watch the sparks.) Benjamin Franklin recognized that there can be positive and negative charges (incidentally, the assignment of "positve" and "negative" is arbitrary) and that charges of the same sign repel one another and charges of opposite sign attract one another. This is expressed by ***Coulomb's law***, one of the basic laws of physics:

$$F = K\frac{Q_1\,Q_2}{R^2}$$

the two charges

the force

a constant

distance between charged particles

Figure by MIT OCW.

If Q_1 and Q_2 are of the *same* sign, F is *repulsive*

If Q_1 and Q_2 are of *opposite* sign, F is *attractive*

4.2 All of this applies to ions! Two ions of opposite charge can become bonded to one another by this Coulomb attractive force. This kind of bond is called an ***ionic bond***. Most minerals are held together by just this kind of bond. (Now we're getting somewhere on the basic nature of minerals.) Crystals that are held together by ionic bonding are called ***ionic crystals***.

5. *Ionic Crystals*

5.1 The mineral halite (NaCl, sodium chloride, also known as table salt) is a good example of an ionic crystal—and an important rock-forming mineral as well. The structure of halite involves equal numbers of positive ions (sodiums) and negative ions (chlorides) arranged in a cubic array, each sodium surrounded by six chlorides and each chloride surrounded by six sodiums. (See Figure 1-21.)

5.2 Think of three mutually perpendicular lines, and along each line there's a regular alternation of sodium and chloride ions. If you draw lines connecting all of the six chlorides that are the nearest neighbors to any given sodium, you get a regular geometric solid, called an octahedron, made up of eight equilateral triangles. For this reason we say that there is *octahedral coordination* of chlorides around sodiums. You can show for yourself that the same holds true for the six nearest-neighbor sodiums around any given chloride.

5.3 The picture in Figure 1-21 is in one sense a fake, because, for reasons of good visibility, I've drawn it with too much space between adjacent ions. To get the "true" picture you have to imagine that all of the spheres, of both kinds, expand (in such a way that the relative sizes of the two kinds stay the same) until they are all in contact; this is difficult for me to draw intelligibly.
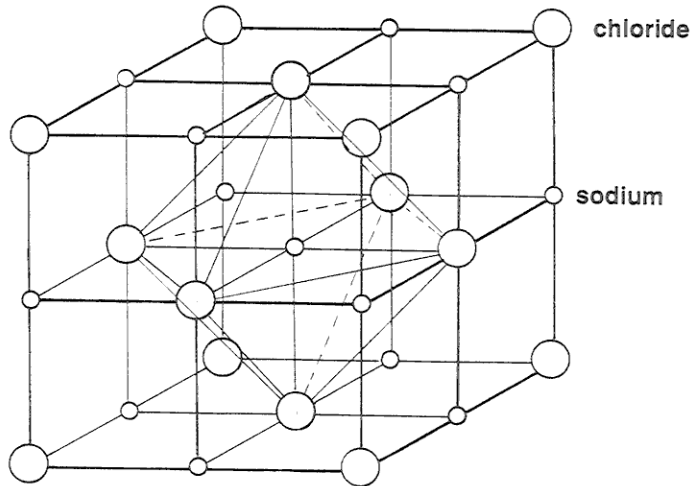
Figure 1-21. Blown-up sketch of the arrangement of sodium ions (small) and chloride ions (large) in the structure of halite.

5.4 It turns out that the relative sizes of Na and Cl ions are just about right for this kind of "cubic" packing—just right in the sense that they all come out to be just about touching. In fact, if they were of different relative sizes the packing would have come out to be of some different kind.

5.5 Look at the central sodium in the figure. The strongest forces on it are attractive, exerted by its six nearest neighbors, which are chlorides. (Keep in mind the strong, inverse-square dependence of the force on the separation distance in Coulomb's law.) The next strongest forces are repulsive, exerted by its twelve next-nearest neighbors, which are sodiums. And so on outward. The structure likes to form because the overall picture of forces, summed over all of the ions, near and far, surrounding that ion is attractive. Other structures with different kinds of atoms, which might seem okay at first thought, don't form because the overall picture of forces comes out to be repulsive. To get such a structure to hold together, you would have to deep squeezing it hard from all directions.

5.6 There are two other factors that determine whether a given mineral forms (i.e., is stable) in a given situation:

  • All atoms are in a state of continual jiggling, because of their thermal energy. Only at absolute zero does all movement cease. This jiggling

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may be so strong that, even though the picture of inter-ionic forces is attractive, the crystal flies apart because of the thermal jiggling. This is why crystals (ice is an everyday example) melt as the temperature rises.

• The greater the concentration of Na and Cl ions in the medium surrounding the crystal, the higher the temperature at which the crystal melts, because ions from the surroundings tend to diffuse into the crystal and keep it together.

6. Covalent Bonds

6.1 There's another kind of bond that's especially important in silicate minerals, called a ***covalent bond***. It's not as easy to understand than the ionic bond. Atoms can fill their electron shells by *sharing electrons with other atoms*.

6.2 The simplest example is the bond in the H_2 molecule (Figure 1-22). This is very schematic, and it doesn't give you a good picture that both electrons orbit both nuclei. It's as if each nucleus gets something for nothing. Figure 1-23 is a slightly better way of looking at it, in terms of the shape of the electron cloud.
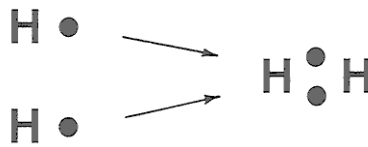

Figure 1-22. Very schematic representation of a hydrogen molecule.
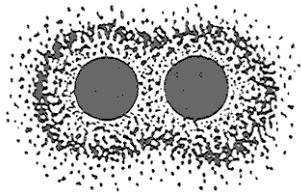

Figure 1-23. A slightly better way of representing the hydrogen molecule.

6.3 Comments:

• Covalent bonds (if they are favorable in the first place because of electron-orbit considerations) tend to be found between atoms of elements that are

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in the same or almost the same position in the periodic table, in terms of columns.

- Many bonds are purely ionic or purely covalent, but many are intermediate in character: there is partial sharing of electrons, but the density of electron distribution is shifted so that one component atom tends to be negatively charged and the other positively charged. This is called *partial ionic character* of the bonds.

- Covalent bonds are inherently more complicated to understand than ionic bonds, and I've been much more superficial about them. They depend upon certain intricacies of electron orbit structure that are understandable only on the basis of quantum mechanics. Covalent bonds actually have a directional property that's governed by the nature of electron distributions around the atoms, not just packing geometry as in the case of ionic bonds. It's as if the atoms had little hooks on them in certain positions.

7. Solids, Liquids, and Gases

7.1 Most chemical compounds can exist in all of three different *states of aggregation*—as a *solid*, a *liquid*, or a *gas*—depending on temperature and pressure. This was known, of course, long before the molecular theory of matter was developed in the late eighteenth century and the early nineteenth century. In the past hundred and fifty years, great effort has gone into developing theories to account for the nature of solids, liquids, and gases on the molecular level. (Here, I'll use the term *molecule* for atoms, ions, or molecules indiscriminately.)

7.2 You probably already know well the fundamental macroscopic distinctions among gases, liquids and solids:

    gas:
- has relatively low density
- cannot withstand applied shearing forces without continuing deformation
- expands to attempt to fill its container uniformly

    liquid:
- has relatively high density
- cannot withstand applied shearing forces without undergoing continuing deformation
- maintains a definite volume within a well-defined bounding surface

solid:

- has relatively high density

- withstands applied shearing forces without undergoing continuing deformation

- maintains a definite volume within a well defined bounding surface

7.3 On a more fundamental level, the basic picture of a **gas** is that its constituent molecules are widely separated relative to their diameter, except for occasional close encounters, and are moving in free trajectories with only occasional collisions with the walls of the container and with each other. If you could somehow travel on a gas molecule, most of the time you would be having a boring ride, because the molecule would be in a state of uniform straight-line motion at constant speed, with neighboring molecules so far away you'd have to use binoculars to see them. Every now and then, however, another molecule or the wall of the container would come rushing toward you, and your molecule would rebound elastically from the encounter.

7.4 This state of motion, with its well-defined elastic collisions and negligible mutual forces among molecules in the meantime, lends itself to successful modeling of the gaseous state—especially because many-body (that is, three-plus) collisions or interactions are so rare. Such modeling has led to the *kinetic theory of gases*, by which most of the properties of gases can be accounted for or predicted.

7.5 At the other end of the line, on a molecular level a **solid** is characterized by fixed and ordered positions of the constituent molecules, with packing so close that there are strong forces at all times between any given molecule and all of its near neighbors. At temperatures above absolute zero the molecules oscillate or vibrate in various ways about their fixed mean positions, but only rarely do molecules trade places in their ordered arrangement.

7.6 If you could occupy one of the molecules in the solid structure, you would feel as if you had been consigned forever to one of those vibratory-massage beds they used to have in motels, and if you looked over at the strictly regular pattern of neighboring molecules looming near you, they would be vibrating too, but maintaining their mean positions for extremely long times before trading places with a neighbor. And you would have the same picture for as far as you could see through the structure.

7.7 Despite the complexity of the mutual forces, the ordered and permanent arrangement in crystalline solids has allowed successful modeling, and the solid state is by now well understood.

7.8 Liquids, however, have presented much greater problems than gases and solids. As with solids, the molecules are always close enough together that they exert strong forces on one another, but the degree of ordering (or, more precisely, the time scale for the existence of ordering) is much less than for solids.

7.9 If you were to occupy a molecule in a liquid, your vibratory movement would be about the same as when you were in the solid, and your neighbors would loom almost as close. But the arrangement of your neighbors would stay the same only for a short time and then change to some different arrangement by a combination of just shifting in position and actually trading places. You might or might not get a sense of regular arrangement of the neighbors, but even if you did you wouldn't be able to follow that regularity very far outward, and anyway it would be transitory.

7.10 Various kinds of conceptual models of the liquid state, partly geometric and partly kinematic, have been devised. These models can be massaged, by supplying somehow the constants or parameters that must go along with them, to predict the properties of the liquid. None of these models comes close to accounting well for all of the important properties of liquids. Knowledge of the liquid state is therefore still far from perfect.

8. *Chemical Reactions*

8.1 In case your knowledge of chemistry is scanty, here is some basic stuff. Chemical reactions, like Reaction 1 above, are processes by which certain substances react with one another to produce other substances. (That includes situations in which a single substance undergoes a change by which it is transformed into one or more different substances, or by which two or more substances are transformed chemically into a single substance.) The beginning substances are called the *reactants*, and the ending substances are called the *products*. The substances involved might be solids (crystalline or amorphous), or ions or molecules dissolved in a liquid medium, or even just the atoms and molecules of a gas.

8.2 The details of chemical reactions involve usually complex interactions among the atoms that constitute the substances involved, and they need not concern us here. In the case of solid substances, you can think in terms of the atoms of the reactants being disengaged from the crystal structure of the reactant(s) and then added to the crystal structure of the product(s). Or, in the case of the *dissolution* of a solid substance in a liquid, what's going on is that the ions or molecules of the solid are being detached from the surface of the solid, to roam around freely in solution in the liquid. The reverse of a dissolution reaction like that is the addition of the dissolved ions or molecules onto the growing surface of the solid by removal from solution—a process called *precipitation* (not to be

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confused with the meteorological term, which is used for liquid or solid water particles falling through the atmosphere).

8.3 In the case of dissolution or precipitation, mentioned above, what's really going on is that ions or molecules are continually being added to and removed from the solid surface. Whether the solid is shrinking (dissolution) or growing (precipitation) depends on the relative rates of removal and addition of atoms or molecules.

8.4 Chemical reactions can go both ways. That's why Reaction 1, shown above, has the double arrow in the middle of it. If you pump up the concentration of the substances on the left side of the reaction, that drives the reaction to the right, producing the substances on the right (then called the products) at the expense of the substances on the left (then called the reactants). But if instead you pump up the concentration of the substances on the right, that drives the reaction to the left—and then you have to use the terms "reactant" and "product" in reverse!

10. Oxidation

9.1 The business about oxidation, and the difference between iron in the ferrous state and in the ferric state, is likely to be mysterious to you unless you have some sophistication in chemistry. Here's some background material on such matters. You probably have heard of *oxidation*, and you may also have heard of *reduction*. These two processes go hand in hand, and are often combined into the term **redox**.

9.2 Many chemical reactions we deal with in and on the earth involve transfer of the actual nuclei of the atoms involved. The dissolution and precipitation of soluble salts like NaCl are good examples. A large and important class of chemical reactions, however, involve only *transfer of electrons*. This is the stuff of a field of chemistry called **electrochemistry**. The practical applications of electrochemistry include batteries, electrical smelting of ores, and electroplating of one metal upon another.

9.3 A simple example should help to give you the basic idea. Suppose you mixed up an aqueous solution that contains ferric ions, Fe^{3+}, and another solution that contains stannous ions, Sn^{2+}. (Iron can exist in solution as two kinds of ions, with different electric charges: *ferric* ions, Fe^{3+}, and *ferrous* ions, Fe^{2+}; tin can exist in solution as two kinds of ions also: *stannic* ions, Sn^{4+}, and *stannous* ions, Sn^{2+}). If you then mix the two solutions together, the Fe^{3+} ions take electrons away from the Sn^{2+} ions, and in the process they become Fe^{2+} ions and make the Sn^{2+} ions into Sn^{4+} ions. (Remember that, by convention, electrons have a unit negative electric charge.)

9.4 *The Fe^{3+} ions have stolen electrons from the Sn^{2+} ions.* Why? A "deep" answer would require a lot of explanation, but an adequate ("shallow") answer here might be that the details of the electron structure of the two kinds of ions makes that "want" to happen, and so it does, spontaneously. The chemical reaction can be written, simply, as

$$2Fe^{3+} + Sn^{2+} \; \rightarrow \; 2Fe^{2+} + Sn^{4+}$$
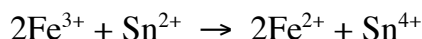
The reaction proceeds until all of one or the other reacting ions gets used up.

9.5 If you made up two separate aqueous solutions, one containing Fe^{3+} ions and the other containing Sn^{2+} ions, and then connected them with a conducting wire, electrons would flow from the one with the Sn^{2+} ions to the one containing the Fe^{3+} ions, to make the reaction happen, even though the two kinds of ions are not in contact! You could then measure the voltage on the wire, at the start of the process. The voltage is a measure of what is called the ***electrical potential*** between the two solutions. Think of voltage as an "electrical pressure", analogous to the water pressure that drives the flow of water in your home water pipes.

9.6 It would be nice to be able to measure, separately, the electrical potential associated with the removal of electrons from the Sn^{2+} ions and the addition of electrons to the Fe^{3+} ions. You can think of those two processes as "half-reactions", which add together to produce the whole reaction, written above. You could then use such results to figure out, directly, which substances steal electrons from which other substances.

9.7 Unfortunately, there's no way of doing that: all you can do is *measure the electrical potential associated with the whole reaction*. Chemists have gotten around that problem in a neat and convenient way: they characterize reactions of the kind described above that involve a wide variety of different substances *with reference to a solution that contains molecular hydrogen* (which could be bubbled, as a gas, through an aqueous solution). To make that concrete, you can imagine putting either the Fe^{3+} ions or the Sn^{2+} ions into a solution into which molecular hydrogen is added. The electrical potential of the reaction that takes place (called the ***redox potential***, denoted by Eh) can then be measured. Then they tabulate all of the half-reactions relative to the hydrogen standard.

9.8 Substances, like oxygen, that tend to steal electrons away from other substances are called ***oxidizing agents***; substances, like metallic iron, that tend to lose electrons to other substances are called ***reducing agents***. The word "oxidizing" here, however, is misleading, because a great many other substances can act as oxidizing agents, in the sense that they tend to steal electrons away from

other substances. The rationale, I suppose, is that oxygen is the most important oxidizing agent in so many natural chemical systems. Likewise, there are many other reducing agents besides metallic iron, but because iron and its compounds are so important in natural chemical systems, it's natural to think in terms of metallic iron, or ferrous iron ions (Fe^{2+}), as reducing agents.

9.9 Finally, here are some comments on oxygen vs. the two kinds of iron ions. In a solution containing oxygen, ferrous (Fe^{2+}) ions are inevitably oxidized to ferric (Fe^{3+}) ions, which have a strong tendency to combine with oxygen to form insoluble ferric iron oxides or hydroxides. If, on the other hand, the solution has no free oxygen (perhaps all of the available oxygen had already been used up in the oxidation of organic matter, which is a reducing agent), then the ferrous ions (Fe^{2+}) remain happily in the solution.

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2. THE NATURE OF WATER

2.1 Introduction

2.1.1 Human beings in general, and often even scientists in particular, are inclined to take water for granted: it's almost literally everywhere, and we can't live without it. It's difficult to cite a process—physical chemical, or biological—operating on or near the Earth's surface that doesn't involve water in a substantial if not essential way. Because water seems so ordinary, we tend to judge the behavior of so many other substances with reference to it. In reality, however, *water is a highly unusual compound*, greatly different in many (but by no means all) of its properties and aspects of behavior than what one would expect in view of its apparently simple composition and low molecular weight. Just one example should suffice here: the *expansion when solid water thaws to liquid water*. This is *close to being unique*, and it has profound implications for processes and life on the Earth's surface.

2.1.2 This section attempts a survey of the nature and properties of water. Its goal is to show you the most important facts about the nature and relationships among water in its solid, liquid, and gaseous states, and how these can be explained on the molecular level. The latter endeavor will necessarily be somewhat superficial, because a fundamental approach to the behavior of water is heavily quantum-mechanical, and also because there is still much that's not well understood.

2.2 The Water Molecule

2.2.1 The unusual properties of water are a direct consequence of the structure of the H_2O molecule, so I'll give you some facts about its *geometry*, *structure*, and *electrical state* before looking at the behavior and properties of water.

2.2.2 It is well established that the water molecule consists of two atoms of hydrogen and one atom of oxygen arranged as an isosceles triangle. The H–O–H angle is about 104.5°, and the O–H bond length is very close to 0.1 nm (nanometers; 10^{-9} meters). Assuming the effective atomic radius of the oxygen to be 0.14 nm and that of the hydrogens to be 0.12 nm, one way of schematizing the water molecule is shown in Figure 1-24. It's known that this basic geometry is little affected by the changing environment of the molecule in the gas, liquid, or solid form over a wide range of temperatures and pressures.
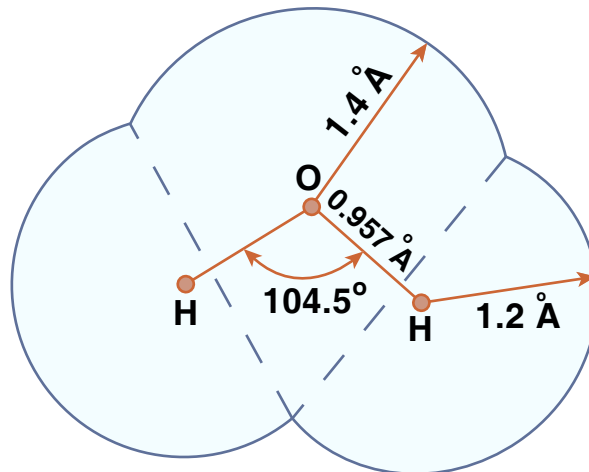
Figure by MIT OCW.

Figure 1-24. Cartoon of the water molecule, showing O–H distance, H–O–H angle, and effective radii of the hydrogen and the oxygen.

2.2.3 Keep in mind, however, that the picture in Figure 1-24 is something of a fake, because what really governs what the molecule looks like to the outside world is the electron distribution around the three nuclei, because that's what determines how close you can get to the molecule from any given direction before enormous repulsive forces build up as you try to penetrate the electron field.

2.2.4 The three nuclei of the water molecule are always undergoing vibrations, of three kinds (Figure 1-25): the two hydrogens oscillate back and forth along the oxygen–hydrogen directions in phase (this is called the **symmetric stretching vibration**); the two hydrogens oscillate back and forth along the

oxygen–hydrogen directions a half cycle out of phase (this is called the *asymmetric stretching vibration*); and the two hydrogens move in phase in opposite directions along circular arcs lying in the plane of the molecule (this is called the *bending vibration*). These are the fundamental or normal modes of the vibration; the actual vibration is a linear superposition of these (in other words, they all add up together, without any one affecting either of the others). The periods of the oscillations are extremely small—of the order of 10^{-14} s!
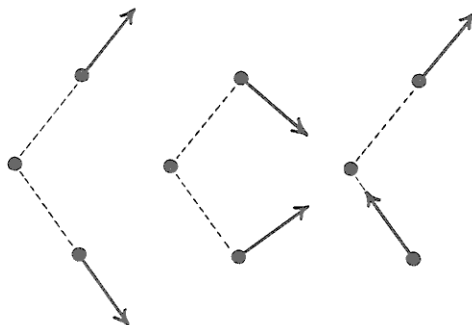
Figure 1-25. Modes of vibration of the water molecule.

2.2.5 The distribution of the electrons, in space, in and around the water molecule—the most important feature of the molecule in terms of bonding—is not what you might guess. Because oxygen is near the right side of the periodic table and hydrogen is at the left side, it should seem reasonable that the electrons tend to be more in the vicinity of the oxygen than in the vicinity of the hydrogens. The molecule is thus what is called a *polar molecule*: the oxygen "end" or "side" has a negative electric charge, and the hydrogen "end" or "side" has a positive electric charge (Figure 1-26).
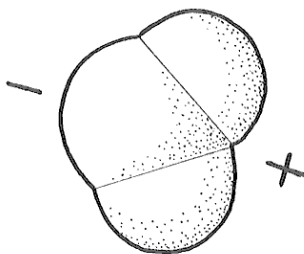

Figure 1-26. Overall distribution of electric charge on the water molecule.

2.2.6 But a more fundamental way of viewing the electron distribution of the water molecule (a way that is beyond the scope of this course) has to do with the quantum-mechanical structure of the electron "orbits", or, more properly, electron *orbitals*. The six electrons in the outermost electron shell of the oxygen (those are the ones involved in bonding with other atoms) turn out to be in *equivalent* orbitals, and the way you can arrange four directions in space in the most equivalent or non-preferential way is *tetrahedrally*—that is, starting from the center of a tetrahedron, in the directions toward the four vertices of the tetrahedron (Figure 1-27). Two of these tetrahedral positions are associated with the bonding with the two hydrogens, and the other two are what I'll call very unofficially here the *open positions*. Figure 1-28 is a crude sketch of the geometry of the bonding directions.
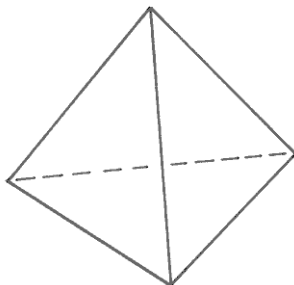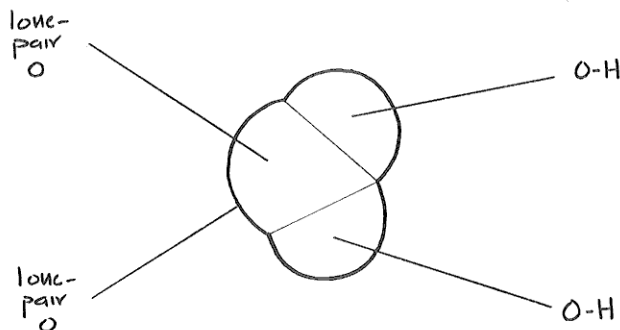

Figure 1-27. A tetrahedron.

Figure 1-28. Geometry of bonding directions in the water molecule.

2.3 Ice

2.3.1 We'll look at the structure of ice before worrying about liquid water, because its structure is well known, thanks to the technique of x-ray diffraction.

The ice that you and I are familiar with is known as ***ice I*** (or, more precisely, *ice Ih*). This is the form of ice that's found at room pressures and low temperatures. At higher pressures several other polymorphs of ice make their appearance, but they never occur under the conditions of the earth's surface and atmosphere. (Minerals that have the same composition but different crystal structure are called ***polymorphs*** of one another.)

    2.3.2 The most striking and very unusual thing about ice Ih is *the openness of its structure*. This arises from the way water molecules are bonded to one another. Water molecules are bonded by what are called ***hydrogen bonds*** (Figure 1-29): one of the hydrogen atoms of one molecule is bonded electrostatically to the oxygen atom of the other molecule, in such a way that the hydrogen is attached to the oxygen at one of the open positions—of which there are two, remember, in tetrahedral relationship to each other.
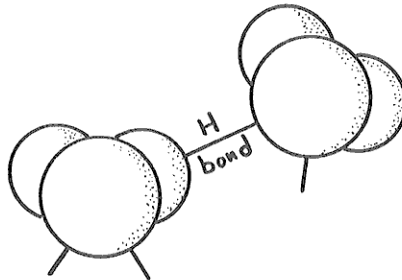
Figure 1-29. The hydrogen bond. (the atoms at the ends of the bond should be touching.)

    2.3.3 The hydrogen bond is not nearly as strong as the very strong oxygen–hydrogen bonds within the water molecule itself, but it's strong enough to promote bonding to form a stable crystal structure (and, as you will see soon, liquid water too) at temperatures much higher than we have any right to expect.

    2.3.4 In the ice structure, each water molecule is surrounded by, and hydrogen-bonded to, four water molecules, arranged tetrahedrally around that given water molecule. Two of these nearest-neighbor water molecules have one of their hydrogens bonded at the open positions of the oxygen of the given water molecule, and each of the other two nearest-neighbor water molecules have one of the open positions of its oxygen bonded to one of the hydrogens of the given water molecule.

2.3.5 Does that sound too complicated? Read the last paragraph through again, and then look at Figure 1-30, which is a blown-up view of this tetrahedral hydrogen-bonding arrangement, the best I can draw it for you. When looking at Figure 1-30, keep in mind that *all the water molecules should really be touching*.
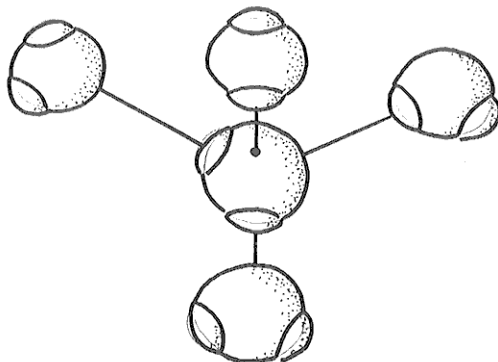
Figure 1-30. Blown-up view of the tetrahedral hydrogen-bonding arrangement in ice.

2.3.6 To build up the ice structure, I want you now to imagine starting with the top four of the five-molecule tetrahedral arrangement in Figure 1-30 and adding water molecules in all horizontal directions, to form a kind of *puckered sheet* (unofficial term). Then stack puckered sheet upon puckered sheet and bond them together by means of the vertically upward-directed and downward-directed fourth bonds extending from each molecule in each puckered sheet. Figure 1-31 is a sketch of just one little segment of two adjacent puckered sheets, viewed from the side.
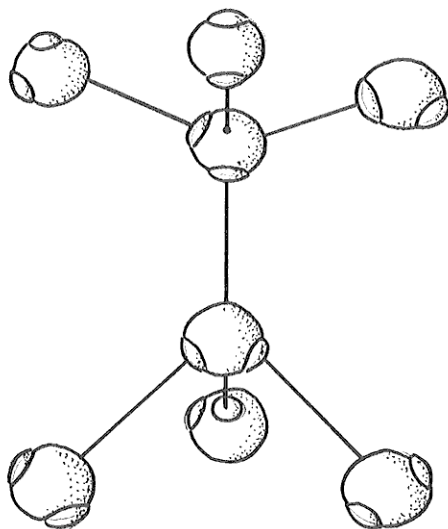
Figure 1-31. Blown-up sketch of one small segment of two adjacent "puckered sheets" in the ice structure.

2.3.7 If you stretch your powers of three-dimensional visualization a little more, you'll see that *the puckered sheets have hexagonal symmetry when viewed normal to the sheets*. Figure 1-32 shows schematically the arrangement of the water molecules in one of the puckered sheets. The water molecules in the sheet are alternately high and low, and are so labeled *H* and *L* in Figure 1-32.
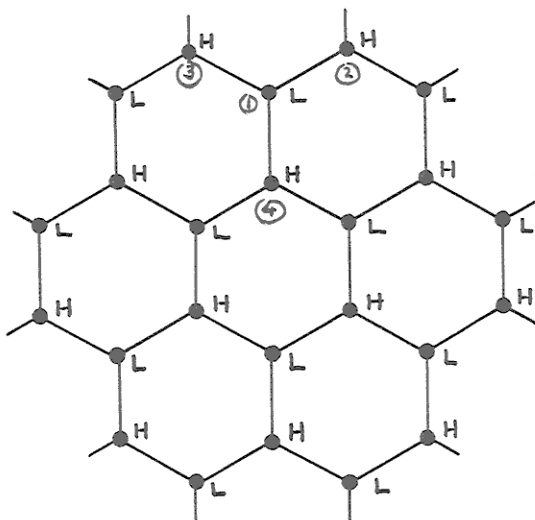

Figure 1-32. Schematic arrangement of water molecules in a "puckered sheet" in the ice structure. The circled numbers correspond to those shown in Figure 1-31.

2.3.8 So the ice structure is one of hexagonal symmetry, with big columns of empty space down the middles of the hexagons. A view from the side (Figure 1-33) suggests (but does not show too well in the figure) *open tunnels running normal to the hexagonal axis* also. The hexagonal symmetry axis is called the ***c axis***, and the plane parallel to the puckered sheets is called the ***basal plane***.

2.3.9 What is striking about this hexagonally symmetric ice structure is its *openness*. If the hydrogen bonding did not happen, and the water molecules were close packed, each would be surrounded by *twelve* nearest neighbors instead of *four*, and the structure of ice would be much denser than it actually is. This is the fundamental reason why *the solid phase, ice, is less dense than the liquid phase*. (That seemingly simple little statement has profound implications for water on the

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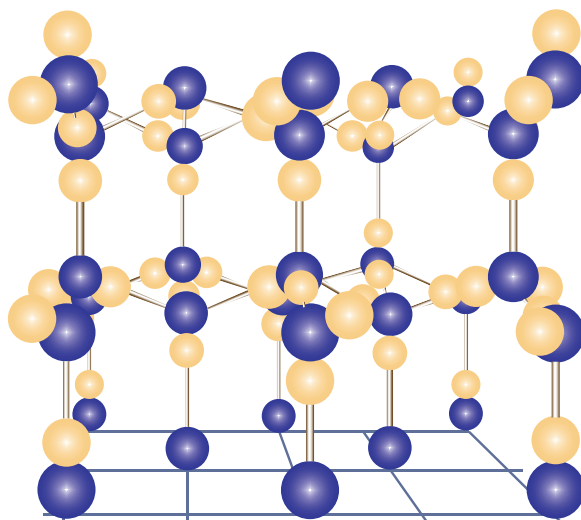Earth.) Only a handful of other substances, germanium and silicon among them, show this behavior.

Figure 1-33. Side view of the ice structure.

2.4 Liquid Water

2.4.1 I said in an earlier section that the liquid state is complicated and relatively poorly understood. This is true even more so for water, *because of the existence of those unusual hydrogen bonds*. Here I will concentrate on some of the unusual properties of liquid water and make some qualitative comments on how they might be explained.

2.4.2 First off, think about *the density of water as a function of temperature and pressure*. The pressure dependence of the density is not out of the ordinary: water has a certain small compressibility, not out of line with other liquids. But the temperature behavior is astounding (Figure 1-34): at constant pressure *the density of liquid water actually increases with increasing temperature from 0°C to about 4°C and then slowly decreases with increasing temperature above that magic 4°C temperature*.

2.4.3 Keep in mind also that *the density increases in the transition from ice to liquid water upon melting at room pressures*, from about 0.92 g/cm^3 to 1.00 g/cm^3. When most solids melt to their liquid phase, the structure opens up a little, as the molecular ordering decreases and the molecules become partially free to wander relative to their nearest neighbors. But the opposite is true for water: *the packing of the molecules in liquid water is actually greater than in ice*.

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2.4.4 The best way to explain the behavior of water density with temperature is to postulate that the melting of ice involves breakage of some of the hydrogen bonds, so that there is a partial collapse to closer packing. Models of the liquid water state tend to assume that there are transient and local ice-like structural regions with complete hydrogen bonding (called, expressively, "flickering clusters"), and other transient and local regions in which the water molecules are more closely packed. As the temperature of the liquid increases, a greater and greater percentage of the molecules are in a close-packed state, leading to the amazing increase in density from 0°C to 4°C.
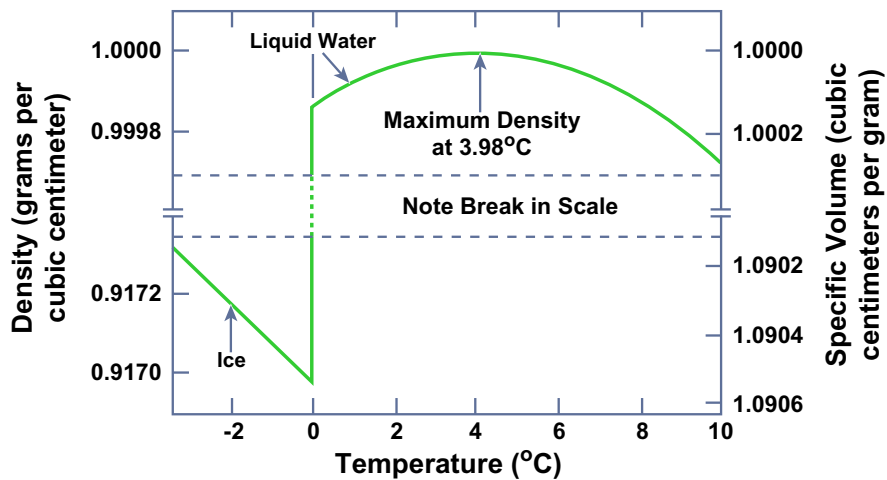

Figure by MIT OCW.

Figure 1-34. Graph of density against temperature for ice and pure liquid water. (From Gross, 1990.)

2.4.5 Counteracting the hydrogen-bond-breaking tendency is the normal tendency for overall increase in the separation distance of all the molecules in the aggregate due to increase in thermal agitation of the molecules as the temperature increases. At temperatures greater than 4°C, this expansion effect more than counteracts the condensation effect due to breaking of hydrogen bonds.

2.4.6 Another outstanding feature of liquid water is its *extremely high heat of vaporization*, about 540 cal/g. This is almost an order of magnitude higher than what might be expected for normal liquids of the same molecular weight. Why so high? Again one can invoke the progressively smaller percentage of hydrogen bonds per unit mass of water. It takes energy to break the hydrogen bonds, and that's what shows up as additional heat of vaporization, in addition to the usual

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contribution that goes into detaching molecules of the liquid from the liquid–vapor interface, where they are held tightly by the attractive forces of the subjacent molecules.

2.4.7 The specific heat capacity of liquid water is extremely high, for the same reason: as heat is added to liquid water, not only does it go toward increasing the thermal energy of vibrations of the water molecules; it also has to go toward breaking more and more of the remaining hydrogen bonds, which takes energy.

2.4.8 Finally, it's worth pointing out that many important properties of liquid water are not out of the ordinary. Properties that involve molecular transport, like the coefficient of viscosity and the coefficient of diffusion are in line with what would be expected of a normal liquid.

2.5 Phase Equilibrium in Water

2.5.1 Now that we have surveyed the structure of solid and liquid water, it's time to look at *the equilibrium among the solid phase, the liquid phase, and the vapor phase*. The best way to do this is by means of a ***phase diagram***, which shows the ranges of pressure P and temperature T characteristic of each phase and the sets of pressures and temperatures for which two (or even all three) phases can coexist with one another at equilibrium. Figure 1-35 shows such a diagram for water—but only for very low pressures, much less than atmospheric. Figure 1-36 is a simplified "cartoon" version of Figure 1-35.

2.5.2 What are the important features of the phase diagram in Figures 1-35 and 1-36? Note first that way down near the lower left corner there is an unobtrusive ***triple point*** among the vapor, liquid, and solid phases. At that particular set of values of T and P (at a temperature of about 0.1°C and a pressure of about 4.6 mm Hg, or about 6 x 10^{-3} atmospheres), *all three phases can coexist at equilibrium*, each with a different value of density.

2.5.3 Another interesting thing about the *P-T* diagram in Figures 1-35 and 1-36 is the narrowing and eventual termination of the vapor–water equilibrium cylinder as the phase boundaries join at what is called the ***critical point***. This means that the distinction between the densities of liquid and vapor, which is great at the familiar Earth-surface temperatures and pressures, diminishes with increasing temperature and increasing pressure and finally vanishes at the triple point! At even greater temperatures and pressures, water exists in a single fluid phase, rather dense, with no distinction between the vapor state and the liquid state. (This is not relevant to this course, but I couldn't resist including it, because it's so fascinating—to science nerds like me, anyway.)

2.5.4 With reference to Figures 1-35 and 1-36, you can see that it's possible to convert liquid water to water vapor continuously, without the catastrophic phase change involved in crossing the boundary directly by the shortest route. You could do this by changing the *P–T* conditions by a roundabout route like that shown in Figure 1-37. Along that route, all the properties of the water vary continuously from the liquid phase to the vapor phase.
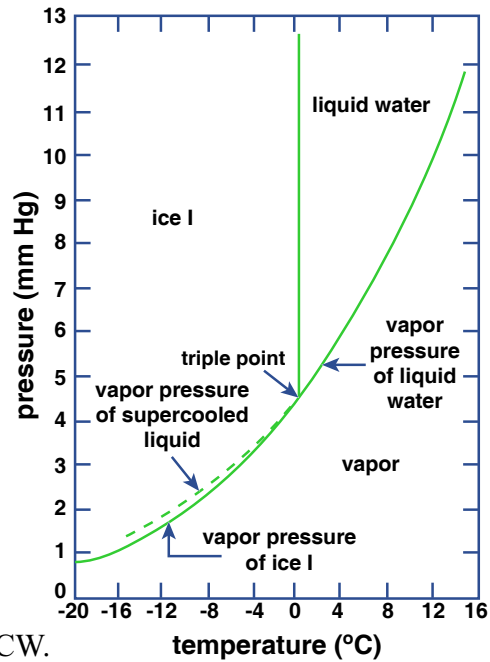

Figure by MIT OCW.

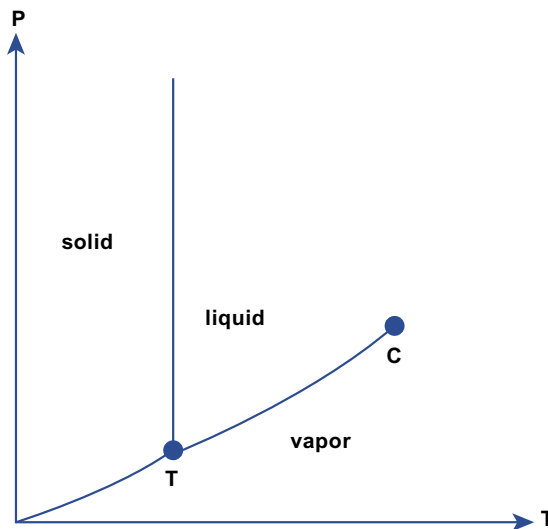Figure 1-35. P–T diagram for water in the region of the triple point.

Figure by MIT OCW.

Figure 1-36. Cartoon *P–T* diagram with axes distorted to show qualitatively both the triple point and the critical point clearly. (Not to scale!)

Figure by MIT OCW.

Figure 1-37. How you can pass from the liquid phase to the vapor phase, or vice versa, by continuous change in temperature and pressure around the critical point. (Not to scale!)

2.5.5 When you boil water, you are converting liquid water into water vapor. That process can be shown very simply on the *P–T* diagram for water (Figure 1-38). You start with room-temperature water at atmospheric pressure (Point A in Figure 1-38). As you heat the water, it follows a path in the *P–T* diagram horizontally to the right, until it reaches the liquid–vapor phase boundary, whereupon it boils. The water then stays at the boiling temperature until all of the liquid water is used up.

2.5.6 You can also account nicely for the formation of dew and frost by use of the *P–T* diagram. In that case, however, you have to think more carefully about what to use for the pressure. The atmosphere consists of several gases, which together account for the atmospheric pressure, by virtue of their weight in the column of air that overlies the given locality. The contributions of each gas to the total pressure is called its ***partial pressure***.

2.5.7 Water vapor in the atmosphere ranges in concentration from considerably less than one percent, in the coldest and driest air, to more than four percent, in the warmest and most humid air. In the *P–T* diagram in Figure 1-39, start with a point (Point A) well to the right of the liquid–vapor phase boundary, at a temperature above freezing. On a clear night, as the ground surface cools, by loss of heat by radiation to outer space, the water vapor takes a path horizontally to

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the left in the *P–T* diagram. When it reaches the liquid–vapor phase boundary it condenses as dew on the cold surfaces.
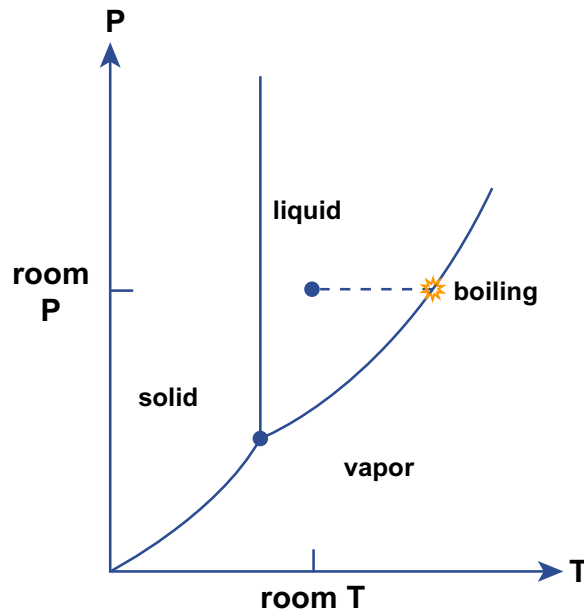

Figure by MIT OCW.

Figure 1-38. The boiling of water, as expressed in the *P–T* phase diagram for water.
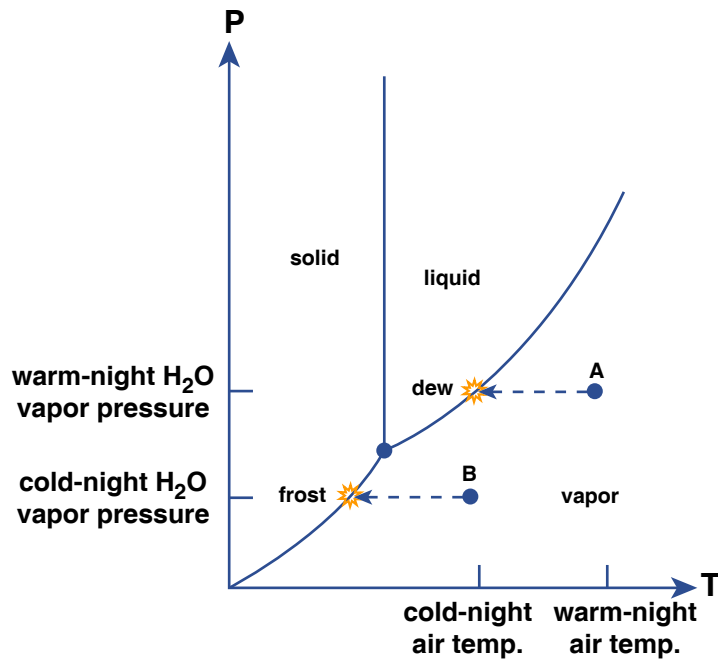

Figure by MIT OCW.

Figure 1-39. The formation of dew and frost, as expressed in the *P–T* phase diagram for water.

2.5.8 You can do the same thing for the formation of frost, by starting at a temperature below freezing. Then the path leads horizontally left, from, say, Point B in Figure 1-39, to reach the ice–vapor boundary, at which point little ice crystals grow on the cold surfaces, fed directly from the water vapor in the air. (You can conclude from this that frost is not just frozen dew—although dew itself can freeze, as the air temperature decreases during the night.)

2.6 The Chemistry of Water

2.6.1 The water molecules in liquid water have a slight tendency to dissociate into H^+ ions and OH^- ions. The H^+ ions are called (naturally!) ***hydrogen ions***. They are basically just protons. (Actually, they tend to be hydrated by attachment to a water molecule, giving the formula H_3O^+, but conventionally they are written as, and treated as, just H^+ ions.) The OH^- ions are called ***hydroxyl ions***.

2.6.2 This dissociation of water molecules into hydrogen ions and hydroxyl ions is expressed by the following simple chemical reaction, with which you are probably all familiar:

$$H_2O \Leftrightarrow H^+ + OH^-$$
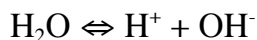
Keep in mind that, as with all such chemical reactions, water molecules are all the time dissociating into hydrogen ions and hydroxyl ions, while at the same time hydrogen ions and hydroxyl ions are recombining to form water molecules.

2.6.3 The balance between dissociation and recombination is such that only a very small proportion of the water molecules, at any given time, are dissociated. In pure water that is contained in a completely insoluble container and is not in contact with any gas, proportion of water molecules that are dissociated at any given time is one in 10^7—a very small proportion. Moreover, the numbers of hydrogen ions and hydroxyl ions are equal, simply because the dissociation of one water molecule produces one H^+ ion and one OH- ion. The concentrations of both the H^+ ions and the OH^- ions is said to be 10^{-7}. (But beware: I am being somewhat superficial here because I am not telling you the units of the concentrations. That would take a lot more explanation than this course permits.)

2.6.4 If, now, we allow some H^+ ions from outside to be added to the water, somehow, there will be a corresponding and one-for-one decrease in the numbers of OH^- ions. Conversely, if we allow some OH^- ions to be added to the water,

somehow, there will be a corresponding and one-for-one decrease in the numbers of H^+ ions. That leads to the idea of *a scale of concentration of H^+ ions*. That scale is called the ***pH scale***.

2.6.5 All of you probably have heard of the pH of aqueous solutions and know that it is somehow connected with the acidity of the water. The pH of an aqueous solution is defined as *the negative of the logarithm to base ten of the concentration of hydrogen ions in the aqueous solution.* (For those of you who are unfamiliar with the concept of logarithms, all you need to keep in mind that the base-ten logarithm of the number 10^7 is 7 and that the base-ten logarithm of the number 10^{-7} is -7). So the pH of pure water, in which, as discussed above, the hydrogen-ion concentration is 10^{-7}, is 7. Aqueous solutions with greater concentrations of hydrogen ions have smaller pH values and are said to be *acidic*; aqueous solutions with lesser concentrations of hydrogen ions have larger pH values and are said to be *alkaline*.

3. SOME ESSENTIALS OF THE CHEMISTRY OF THE SURFACE ZONE OF THE EARTH

3.1 Introduction

3.1.1 I think that a good case can be made that the three outstanding characteristics of the chemical environment of the near-surface zone of the Earth are that

(1) it is pervaded with water;

(2) it is largely oxygenated, and

(3) it involves the chemical element carbon in various important ways.

3.2 The Role of Water

3.2.1 Almost all of the chemical reactions that are important in the surface zone of the Earth take place in an aqueous medium. Water is the great reaction medium for near-surface chemical processes on the Earth. (The important exceptions are certain gaseous reactions in the Earth's lower atmosphere, which will not concern us in this course. That brings in a whole other field of science: atmospheric chemistry.)

3.2.2 Water is often described as the universal solvent. More specifically, water dissolves far more substances than any other liquid, largely because the hydrogen ions and hydroxyl ions, as well as the polar water molecules themselves, can insinuate themselves into the ionic crystals of which most of the solid Earth is composed.

3.2.3 Chemical reactions of the kind that are important in the Earth's near-surface solid materials just don't happen in a waterless medium. All you need to do to convince yourself of that is to compare the rates of weathering processes on Earth (there will be a long section on that in the following chapter) with weathering processes on a dry planetary body like the Moon. All of the important reactions by which the primary minerals of igneous and metamorphic rocks are broken down into other minerals, which are sable under Earth-surface conditions, along with dissolved materials, are hosted by water.

3.3 The Role of Oxygen

3.3.1 The geologic evidence is good that the Earth's atmosphere has contained abundant oxygen for about the latter half of geologic time. At present, the Earth's atmosphere consists of about twenty percent oxygen, by volume. You know, of course, that oxygen is essential to animal life on Earth. What is probably less obvious to you is that the presence of that oxygen means that chemical compounds in the reduced state which become exposed to the Earth-surface conditions are very susceptible to oxidation. This is especially true of rock-forming minerals that contain ions ferrous iron (Fe^{2+}). When such rocks undergo weathering at the Earth's sauce, about which you will learn in the next chapter, the ferrous iron is oxidized to ferric iron (Fe^{3+}).

3.3.2 Also, organic material (the tissues of plants and animals), which consists of a great variety of chemical compounds made up largely of carbon and hydrogen, become oxidized back to carbon dioxide and water when they are exposed to the oxygen-rich waters of the Earth's surface. Only in places where ferrous-iron-bearing material and organic material are sealed off from the oxidizing environment can these materials survive in the reduced state. This happens, for example, in places like lake bottoms or the sea floor where the materials are rapidly buried under fine-grained sediments (muds), which are largely impermeable to the passage of surface waters. Under such conditions, all of the oxygen is consumed during oxidation, leaving variable amounts of the reduced materials intact. With regard to organic materials, the consequences for human society are enormous: that's the origin of all of the fossil fuels we burn in today's world!

3.3 The Role of Carbon

3.1 This is a good place for some comments on the important role of carbon dioxide in the Earth's surface environment. Carbon dioxide, a gas, CO_2, is a minor—but extremely significant—constituent of the Earth's atmosphere. The average concentration of CO_2 in the modern but pre-industrial atmosphere is (was!) about 280 parts per million (ppm), or about three percent, by volume. As a

consequence of our burning of fossil fuels, it's now up around 370 ppm, and climbing rapidly.

3.2 Carbon dioxide has an essential role in the Earth's atmosphere: after water vapor, it is the most important greenhouse gas, as described in an earlier section of this chapter. (And, in contrast to water vapor, which is a dependent variable in the sense that its concentration in the atmosphere is itself a function of variety of atmospheric processes, the concentration of carbon dioxide is, nowadays at least, an independent variable, in the sense that humankind is acting to raise its concentration independently of atmospheric processes.)

3.3 Carbon dioxide, like the other atmospheric gases, dissolves in water. For a given concentration of carbon dioxide in the atmosphere, there is a corresponding equilibrium concentration of dissolved carbon dioxide in waters exposed to the atmosphere. Incidentally, that concentration depends on the temperature of the carbon dioxide–water system: the higher the temperature, the lower the equilibrium concentration. It also depends strongly on pressure, as anyone who has opened a bottle of champagne knows well, but that's not a major factor in the behavior of carbon dioxide in the Earth's surface environment because the atmospheric pressure varies over only a small range.

3.4 The carbon dioxide dissolved in water reacts with the water to form a weak acid, carbonic acid, H_2CO_3, according to the reaction

$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$
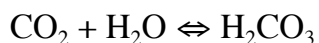
In turn, the carbonic acid dissociates to form hydrogen ions and bicarbonate ions, according to the reaction

$$HCO_3 \Leftrightarrow H^+ + HCO_3^-$$
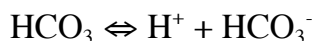
The consequence is that the Earth's natural waters in contact with the atmosphere are mildly acidic, with a pH between 5 and 6. That natural acidity plays a major role in the chemical weathering of rock, as you will see in the following chapter.

4. THE FLOW OF WATER

4.1 Introduction

4.1.1 Much of what happens by way of natural processes on the earth's surface involves the flow of water or air. Just think about it: the obvious examples are streams and rivers, ocean currents, and the wind. Less obvious, but

extremely important, is the flow of groundwater beneath the Earth's surface. The topic of fluid flow is of central importance in this course, and I would be remiss in not subjecting you to some basic ideas in the dynamics of fluid flow. Of course, whole courses can be devoted to fluid dynamics, and a genuinely deep understanding necessitates much more math and physics than is appropriate for this course. I know, however, from my own experience in teaching fluid dynamics that most of the really important concepts can be made clear without heavy mathematics.

4.1.2 In this section we'll concentrate in a qualitative way on some of the most important physical effects, those you need to be aware of in dealing with any situation in which a gas or liquid is flowing past a solid boundary. This section will be cursory but not overly superficial.

4.2 Variables

4.2.1 Two of the most important physical properties of fluids are density and viscosity. The *density* of a fluid, denoted by ρ, is *the mass of fluid per unit volume of fluid*. The density of water is very close to one gram per cubic centimeter (1 g/cm^3) or one thousand kilograms per cubic meter (10^3 kg/m^3). The density of air at sea level and room temperature is far smaller, by a factor of about 800.

4.2.2 The *viscosity* of a fluid, usually denoted by μ, is *a measure of the resistance of the fluid to deformation*. Here's a great kitchen experiment to introduce you to the concept of viscosity. Obtain two big sheets of plate glass, about the size of home window sashes. You will have to attach a couple of handles to the top surface of one of them, perhaps with suction cups of some kind. Lay one of them flat on your kitchen table or counter and slather it with a "thick" (read "viscous") liquid, like honey, molasses, corn syrup, or motor oil (your choice). Right away, before the liquid starts to ooze off the glass, place the other piece of plate glass, the one with the handles, on top of the surface of the liquid (Figure 1-40). Be sure there are no trapped air bubbles.
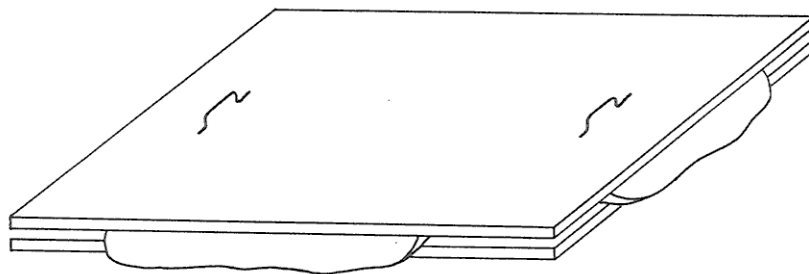

Figure 1-40. Shearing a viscous fluid between two parallel plates

4.2.3 Now grip the handles and shift the upper plate horizontally at constant speed parallel to the lower plate, being careful to maintain constant spacing between the two plates. You will easily sense that the greater the relative speed of the plates, the greater the force needed to maintain the shearing of the fluid. The viscosity is just the coefficient associated with the ratio between the rate of shearing and the force (measured per unit area in the planes of shear) that resists the shearing:

$$\text{viscosity} = \frac{\text{resisting force per unit area}}{\text{rate of shearing}}$$

Here, the rate of shearing is measured by the speed of the upper plate relative to the stationary lower plate, divided by the spacing between the plates (Figure 1-41). For most common fluids, air and water included, this ratio is the same whatever the rate of shearing; such fluids are called ***Newtonian fluids***.
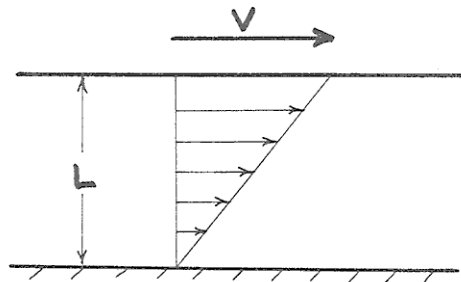
Figure 1-41. Cross-section view through the kitchen-table-top experiment on shearing of a viscous fluid, showing the spacing *L* of the plates and the speed *V* of the upper plate relative to the lower plate. Also shown is the distribution of local fluid speed you would measure along a line between the two plates.

4.2.4 One more fluid property, the ***specific weight*** (in other words, weight per unit volume), usually denoted by γ, is important when the fluid is in a gravitational field, as on the earth's surface. The specific weight is *the weight of the fluid per unit volume of fluid*. It's not the same as the density of the fluid, which is the mass per unit volume. For us earthbound beings, the ratio of the density to the specific weight is almost exactly constant, because the two are

related by virtue of the acceleration due to gravity, g: $\gamma = \rho g$. You can "uncouple" the density and the specific weight only by taking a trip in a space ship to another planet!

4.2.5 Now I want you to concentrate on what the fluid dynamicists call an *open-channel flow*. As the term implies, it's just *a flow in some kind of channel that's open to the air above, rather than being enclosed within a pipe or conduit* as in your home plumbing system. To study open-channel flow you can play in the gutter after a brief heavy rainstorm, or park yourself next to a stream or river, or nail a channel together in your back yard and supply it by means of a hose. Such examples of channel flows, although rather different in scale and geometry, share most of their essential features.

4.2.6 Incidental but important note: It turns out that these open-channel flows differ from their pipe-flow cousins only in the presence of the so-called "free surface", not in their essential behavior. Most of the flows we will touch upon in this course are open-channel flows, but when we deal with groundwater flow, you'll see that pipe flow is the closer analogy.

4.2.7 There's a wealth of variables you can use to describe the flow. Some are more concrete and easy to understand than others. On the one hand, you can think about the velocity of the flow, and on the other hand, you can think about the force per unit area the flow exerts on its boundary.

4.2.8 With regard to velocity, if you occupied any point in the flow that's fixed relative to the boundaries and used a magic little velocity meter to measure the local fluid velocity, you would get some stable local *time-average velocity* if you continued your measurement for a fairly long time. This time-average local velocity varies continuously from point to point all over the cross section of the flow (Figure 1-42); more on what that distribution of local velocity looks like presently.
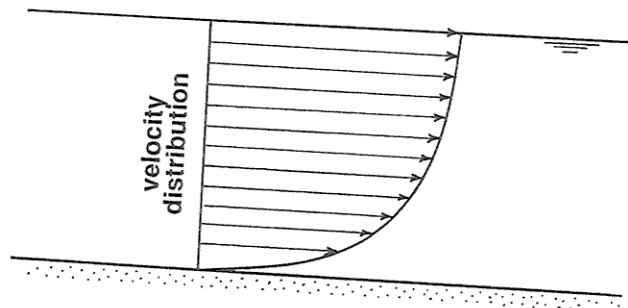

Figure 1-42. Time-average local velocity varies continuously from point to point all over the cross section of the flow

4.2.9 You can take the average of all the local velocities all over the flow cross section to get a ***mean flow velocity*** *U* (Figure 1-43). In real rivers this is how it's actually done, but in laboratory channels, where it's easy to know the water discharge (the volume rate of flow), you can use the relationship $Q = UA$, where *Q* is the discharge and *A* is the area of the flow cross section, to find *U*.
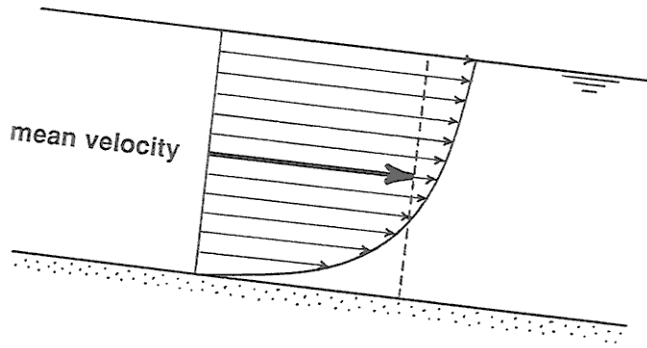

Figure 1-43. Averaging all the local velocities all over the flow cross section to obtain the cross-section mean flow velocity

4.2.10 You could also measure the surface velocity U_s along the centerline of the flow (Figure 1-44). This is greater than the mean velocity, by a factor of something like 1.2 or 1.3; it's related to *U* in a rather complex way that needn't concern us here. Incidentally, unless the channel is very wide compared with the depth of flow the position of maximum velocity on the cross section lies a little below the surface.
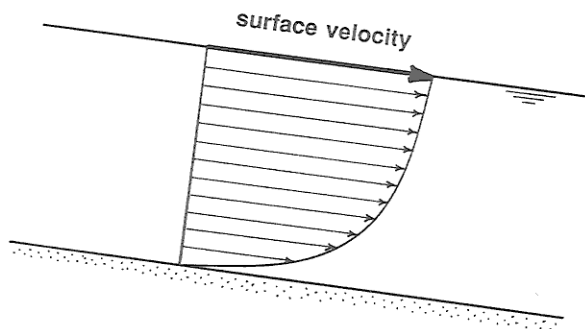
Figure 1-44. The surface velocity, shown along with the velocity distribution in the interior of the flow.

4.2.11 The average force per unit area the flow exerts on its boundary, called the boundary shear stress, denoted by τ_o (read "tau sub zero" or "tau naught") is a little trickier to deal with than velocity, and is less concrete to visualize, but it's important for the obvious reason that it's what exerts forces on the sediment particles on the bed of a stream or river or on the surface of a sand dune under the wind.

4.2.12 Let me backtrack a little to point out something about the flow near the boundary that will probably seem very counterintuitive to you, but stands as a firmly established fact of observation: *fluid in direct contact with a solid boundary has exactly the same velocity as that solid boundary*. That's called the **no-slip condition**. In the context of our open-channel flow, it means that the water right at the bed has zero velocity! But of course there is an increase in velocity upward from the bed, so all the water above the bed, no matter how small a distance above, generally has a nonzero velocity.

4.2.13 The reason I have brought in the no-slip condition here is this: the origin of shear stresses in fluids is just the existence of shearing itself. If that doesn't make sense to you at first thought, go back to your sticky, messy kitchen-table-top experiment on shearing of a viscous fluid. The stronger the shearing, the greater the shear stress that's generated, other things being equal. And foremost among those other things is the viscosity, introduced earlier.

4.2.14 So, back to the boundary shear stress τ_o. It's true that if you could get right down close to any point on the channel bottom, you could (with the right instrument, which doesn't actually exist!) measure a local shearing force per unit area the flow exerts on the solid boundary. That fits the term "boundary shear stress" well, but it's not what's conventionally meant by the boundary shear stress. What you have to do is take a spatial average of the local shear stress (that is, the average of a large number of "point values" of the local shear stress) over an area large enough to include a large number of representative "roughness elements" (sand grains, or boulders, or even larger protuberances, whatever "non-planarities" happen to be present on the channel bottom).

4.3 More on Forces Exerted by Moving Fluids

4.3.1 So far you have learned that a fluid moving past a solid body exerts frictional ("viscous") forces on the surface of the body. These are friction forces in the true sense of the term, even though the detailed nature of the force is not quite the same as the friction between a sliding brick and surface upon which it's sliding. Aerodynamicists have developed a very expressive term for such frictional forces: **skin friction** (by reference to the "skin" of an airplane wing). But there's another important kind of force exerted by moving fluids: **pressure forces**. These

are forces exerted by the flow on what might be called blunt bodies or bluff bodies: those that present a "frontal surface" to the oncoming flow (Figure 1-45).
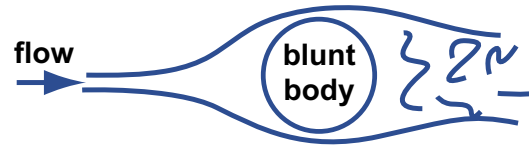

Figure by MIT OCW.

Figure 1-45. Flow around a blunt body.

4.3.2 It will probably seem obvious to you that the fluid pressure (by *pressure* I mean *force per unit area directed normal to a surface*) on the upstream side of a blunt body is greater on the upstream side than the downstream side. What is much less obvious, but nonetheless true, is that, in absolute terms, the pressure on the front is greater than the "free-stream pressure" (the pressure in the fluid at some point far away from the body) but the pressure on the back is less than the free-stream pressure. It would take a lot more background work than we have time for to satisfy you that that's true; you will have to take my word for it.

4.3.3 If you are inclined to doubt the foregoing statement, here's a home experiment which (in contrast to many of my proposed home experiments) would actually be easy to do. All you need is a barometer, of the kind they now peddle as part of "home weather stations". You would need a windy day for this experiment, and a single-family home. Close all of the doors and windows tightly, so there's no throughgoing wind in the house. Stand next to the upwind side of your house and read the barometer. Now go around to the downwind side of the house and take a reading there too. You would find, of course, that the local atmospheric pressure on the downwind side is noticeably less than on the upwind side. That's the real origin of the wind force that tends to blow your house down. But now walk far away from your house and take a barometer reading in an open and unobstructed area (you are now in that "free stream" I mentioned earlier). That reading will lie between the first two—showing that the local atmospheric pressure on the downwind side of the house is indeed lower than the free-stream pressure!

4.3.4 The pressure difference, fore and aft, means that the fluid pressure is exerting a net force in the downstream or downwind direction on the bluff body; it's just a matter of adding a larger downstream-directed force (call that the positive direction) and a smaller upstream-directed force (call that the negative

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direction); the result is a positive downstream force. This kind of force is very expressively called *pressure drag* or *form drag*.

4.3.5 Except for very small-scale flows and very slow velocities, *the pressure drag is likely to be much larger than the skin friction*. Does that make sense to you? Probably not, because I don't think it's "intuitively obvious". If not, then here's still another experiment, another one that would be easy in real life, that you can do for yourself to demonstrate the truth of that proposition. It's probably the simplest experiment I'll propose all semester: all you would need is a pizza pan and a swimming pool! Stand in water up to your chest, and move the pan through the water in the direction parallel to itself. It slips easily through the water, right? Now turn it so that the surface of the pan is normal to the direction of movement. It takes a far greater force on your part to move the pan through the water in that orientation than before. That's because the front-to-back pressure difference adds up to a much greater force than just the frictional forces on the two surfaces of the pan when it's moved parallel to itself (Figure 1-46).

all skin friction

mostly pressure drag
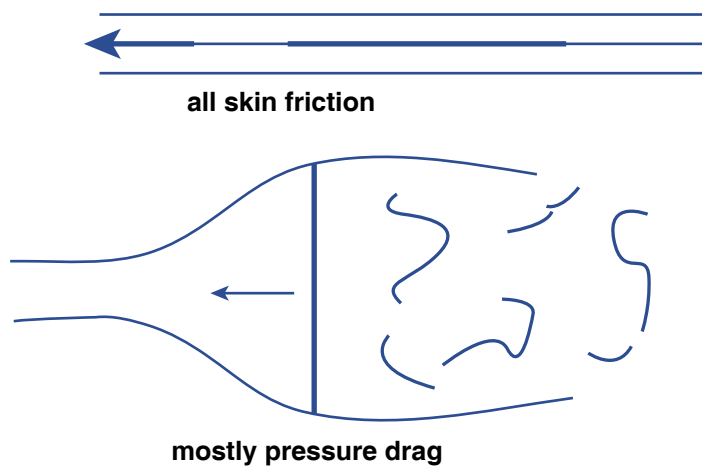
Figure by MIT OCW.

Figure 1-46. Skin friction and pressure drag on a pizza pan moved through still water.

4.4 Why Do Fluids Move?

4.4.1 The movement of fluids is part of the experience of our daily lives. But it's valuable to think for a moment about why fluids move. According to Newton's first law of motion, a body moves in a state of uniform motion (changing neither speed nor direction) unless it is acted upon by some force.

Moving fluids are always acted upon by friction, so they come to rest unless some other force is available to offset the friction and keep them in motion.

4.4.2 Two important kinds of forces drive fluid motions:

• **The force of gravity.** In a flow down a sloping channel, the weight of an element of fluid has a downslope component (Figure 1-47). This downslope component of fluid weight counterbalances the frictional resistance exerted on the fluid by the bottom boundary.

• **Pressure gradients.** In a flow in a horizontal pipe or conduit, the fluid moves only if there is a downstream decrease in fluid pressure. To see why this causes the fluid to move, look at an element of fluid in the pipe (Figure 1-48). If there is a downstream pressure gradient (that is, the pressure decreases in the downstream direction), then the force on the upstream face of the element is greater than the force on the downstream face. The difference in forces on the upstream and downstream faces is a force directed downstream. This downstream force counterbalances the frictional resistance exerted on the fluid by the walls of the pipe.
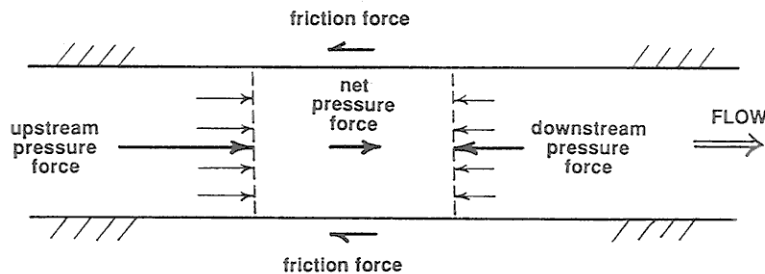
Figure 1-47. In a flow in a horizontal pipe or conduit, the fluid moves only if there is a downstream decrease in fluid pressure.

4.4.3 In a general fluid flow, both of these kinds of forces (downslope gravity components and downstream pressure gradients) can be present at the same time, and the fluid moves under their combined effect.

4.5 Channel Flows

4.5.1 Now let's think about what the flow really looks like in a large channel flow like a river. The basic picture is as shown in Figure 1-48: there's a balance between the downchannel pull of gravity on the fluid, which acts throughout the flow, and the resistance force the bed and banks exert on the

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flowing fluid, which is equal and opposite to the boundary shear stress we discussed above. A natural consequence of the action of these two different forces—gravity acting throughout the fluid and the resistance force acting only at the boundary—is that *the velocity increases upward in the flow*, from zero at the boundary, by the no-slip condition, to a maximum at or near the surface.
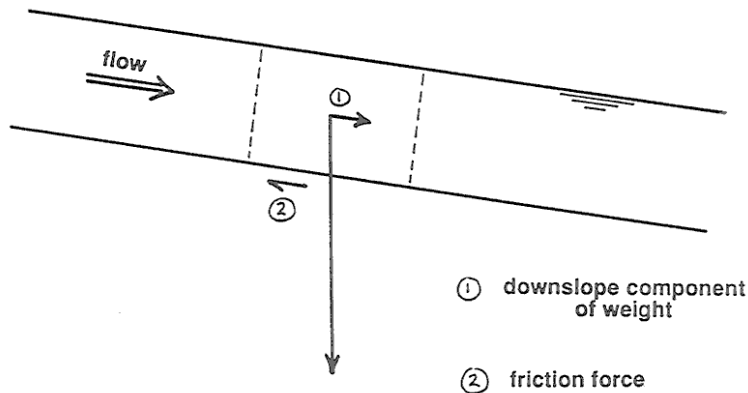

Figure 1-48. In a flow down a sloping channel, the weight of an element of fluid has a downslope component that's balanced by the friction force the boundary exerts on the flow.

4.5.2 That's only the crudest first-order picture, though: the question comes naturally to mind: what are the details of the distribution of time-average local flow velocity over the entire cross section of the flow? That's much too intricate a question for us to pursue here, so I will just hit the high points.

4.5.3 It's simplest to think about a river with a large width-to-depth ratio, which is usually the case. Then we can forget about the effect of the banks. A straightforward application of Newton's laws, which I'll have to skip over here, shows that the distribution of velocity should be parabolic (Figure 1-49A), with the vertex of one limb of a parabola located at the surface. (If you are inclined to pursue this matter further, look me up, and I will set the problem for you to work on.)

4.5.4 But if you went out and measured the local time-average velocity at a series of points along a vertical from the surface down to the bottom, you would find the actual distribution to be far from parabolic: the distribution would be much more uniform over most of the flow depth, and the necessary decrease to zero at the boundary would be in a very thin zone right next to the boundary. The distribution would closely approximate a logarithmic distribution (Figure 1-49B). The reason why the distribution is close to being logarithmic is beyond the scope

of this course, but you can readily understand why the qualitative shape of the curve is the way it is, with a much smaller velocity change throughout most of the flow depth but a sharply greater velocity change right near the bottom. To see why, however, we have to do a little more preparatory work; read on.
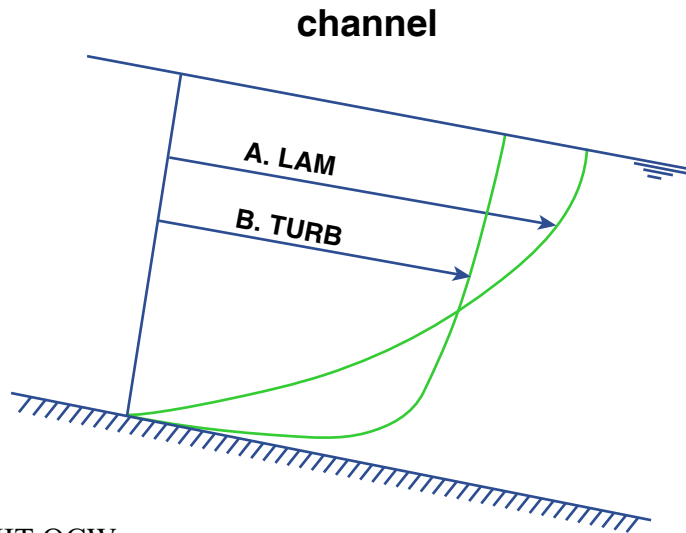
channel

Figure by MIT OCW.

Figure 1-49. Laminar and turbulent velocity profiles in open-channel flow.

4.5.5 This difference in velocity profiles has to do with the difference between laminar flow and turbulent flow, which I am sure you have all heard about one way or another. Channel flows that are very shallow and/or very slow-flowing (like sheet flow or overland flow on the land surface during and after a rain) are characterized by the regular and locally rectilinear flow trajectories of *laminar flow* (Figure 1-50A), whereas channel flows that are deeper and/or faster-moving (almost all channelized flows fall into this category) show the irregularly sinuous flow trajectories characteristic of *turbulent flow* (Figure 1-50B).
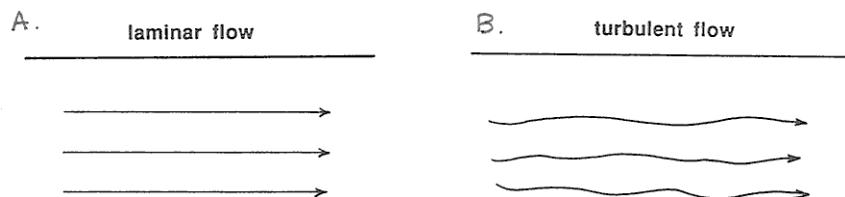

Figure 1-50. Paths of fluid elements in A) laminar flow and B) turbulent flow.

4.5.6 Turbulence isn't easy to describe, but because it's such an important aspect of fluid flows on the earth's surface I'll attempt to give you a qualitative picture of what turbulence is like, with channel flow as the example. One way of studying turbulence is to make a continuous measurement of velocity as a function of time at a fixed point in the flow. You would obtain a record that looks something like the graph shown in Figure 1-51: velocity fluctuations with a range of magnitudes and time scales would be present around the time-average velocity. Another way of seeing the turbulence is to release small neutrally buoyant markers from some fixed point in the flow and watch them move downstream (Figure 1-52). The trajectories would be irregularly sinuous, with angles of deviation from the downstream direction amounting to no more than several degrees. Each trajectory would be different in detail from all of the others.
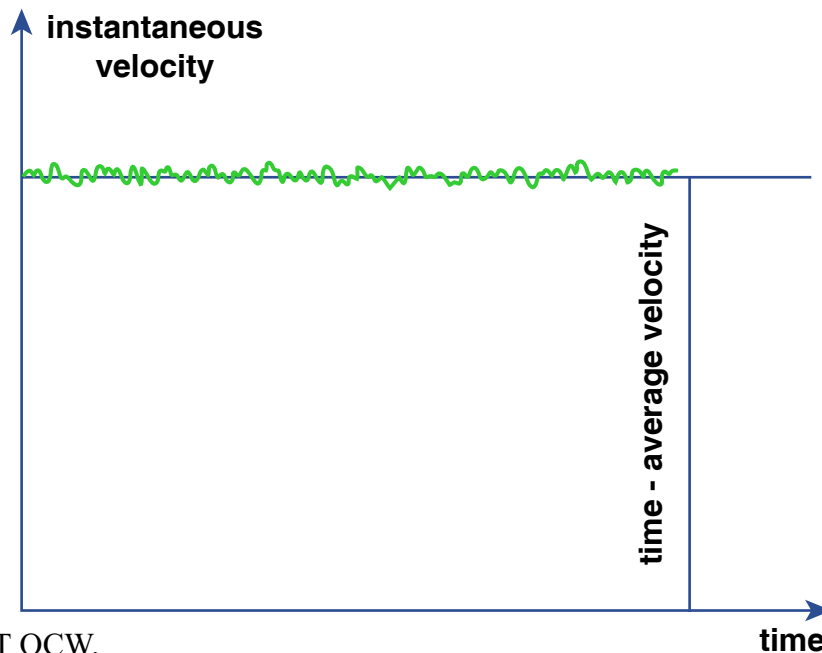

Figure by MIT OCW.

Figure 1-51. Typical record of a continuous measurement of velocity as a function of time at a fixed point in a turbulent flow.

4.5.7 The best way to see the turbulence, however, is to sprinkle the flow with magic powder that allows you to see the *turbulent eddies* (Figure 1-53). You would see rotating swirls of fluid that grade continuously into one another and that change their shape continuously with time. Individual eddies retain their identity for a certain period of time (larger eddies live longer than smaller eddies). but any given eddy eventually becomes unrecognizable and is replaced with newly

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developed swirls. The flowing surface of a river carrying fine sediment in suspension shows eddies moving up to the water surface to spread out and flatten themselves. You might also watch smoke or steam issuing from a smokestack to see the production and decay of eddies as the plume of hot stack gases rises through the still ambient air.
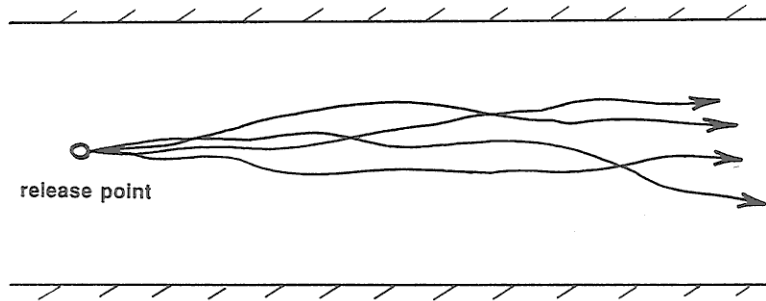
Figure 1-52. Trajectories of small neutrally buoyant marker particles released from some fixed point in a turbulent channel flow.
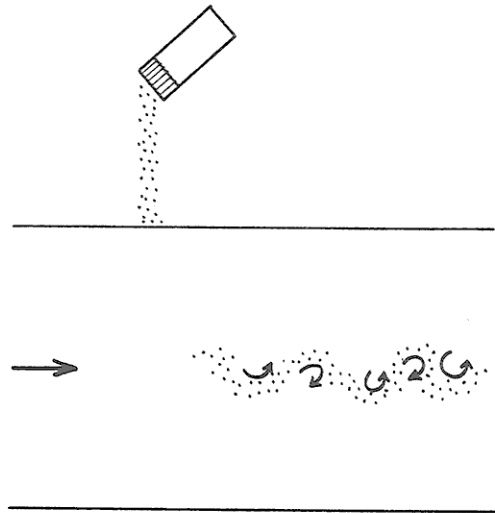
Figure 1-53. Sprinkling the flow with magic powder that allows you to see the eddies.

4.5.8 The maximum vertical scale of eddies in the flow is not much smaller than the depth of the flow, and the maximum cross-flow scale is even larger. There's a continuous range of sizes down to very small eddies, of the order

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of fractions of a millimeter. The smaller eddies are superimposed on the larger eddies. As the large eddies sweep along the boundary they cause periods of stronger flow and weaker flow. When you're standing on a broad plain or on the deck of a ship at sea, the wind gusts you feel are a manifestation of these large eddies affecting the flow boundary. Have you ever watched a broad field of tall grass or grain in a strong wind from a point high above? You would see a striking pattern of wind gusts moving along in the direction of the wind as they sway the grass.

4.5.9 Returning now to the important qualitative difference between laminar and turbulent velocity distributions, in turbulent flow the velocity distribution is much more uniform over most of the thickness of the flow but changes much more sharply very close to the boundary. It's easy to understand why this is so (Figure 1-54). In turbulent flow, over most of the flow depth the lateral motions of eddies tend to even out the differences in time-average velocity from layer to layer. Here's how this works (keep in mind the overall average upward increase in flow speed): upward-moving eddies tend to arrive at their new surroundings with a speed slower than their new surroundings, so they tend to slow those new surroundings down. Conversely, downward-moving eddies tend to arrive in their new surroundings with a speed faster than their new surroundings, to they tend to speed those new surroundings up.
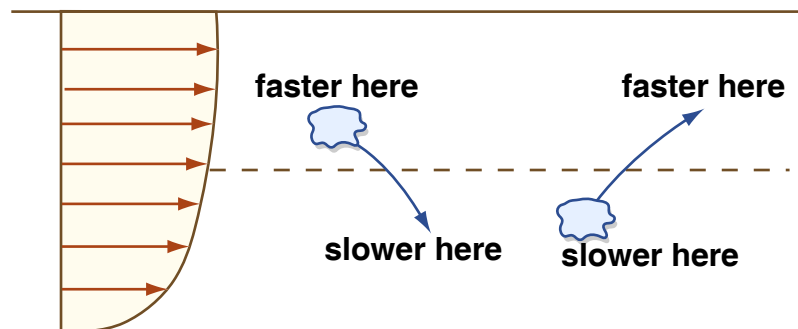

Figure by MIT OCW.

Figure 1-54. Why the velocity profile in turbulent flow is blunter over most of the profile than in laminar flow.

4.5.10 As we move closer and closer to the boundary, however, the fluid motions perpendicular to the boundary are more and more restricted—because remember that right at the boundary the fluid velocity must match that of the boundary, so there can be no component of velocity normal to the boundary there. In a thin layer next to the boundary, therefore, the turbulence can't even out the differences in velocity from layer to layer, so the gradient of velocity is very steep.

This layer next to the boundary, where viscous shearing is more important than turbulence, could be called the *viscosity-dominated layer* (Figure 1-55). Its thickness is typically a very small percentage of the flow depth, no more than millimeters to at most a few centimeters. The next time you're sitting in a window seat in the jetliner, look out at the surface of the wing and think about that viscosity-dominated layer. The air speed, relative to the surface of the wing, decreases from its free-stream value of several hundred miles per hour to zero over a thickness of centimeters, and the viscosity-dominated layer is a small fraction of a millimeter. Incidentally, the cross-section shape of the wing (the "airfoil") is designed to minimize pressure drag, so in this case the body (the wing) is not really a blunt body at all! The reason the plane stays in the air is that the local air pressure on the upper surface of the wind is less than on the lower surface, but the aerodynamic reason for this would require a lot more work on your part.
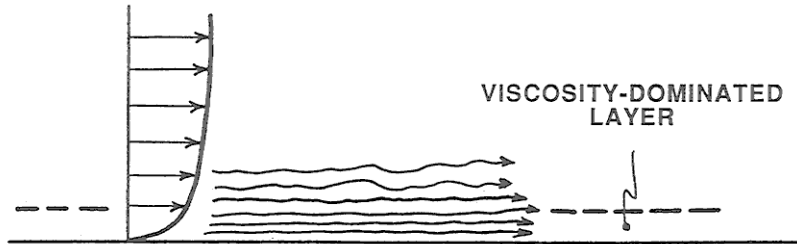

Figure 1-55. The viscosity-dominated layer at the base of a turbulent channel flow.

4.6 Oscillatory Flows

4.6.1 Everything in the preceding sections is relevant to unidirectional flow: a current that moves in one direction only, with velocity either unchanging with time (steady flow) or changing somehow with time (unsteady flow). Also important in the transport of sediments is oscillatory flow: a current that reverses its direction periodically with time. The approach in this section will be somewhat different from the approach in the preceding sections: I'll concentrate more on the origin and description of oscillatory flows than on their dynamics.

4.6.2 Except for reversing tidal currents, which technically are oscillatory flows with very long oscillation periods but which are better considered as reversing unidirectional flows, almost all of the important oscillatory flows in nature are caused by surface gravity waves which propagate on the surfaces of oceans and large lakes. Such waves are called *surface waves* because they are associated with the water surface, and they're called *gravity waves* because the

dominant force involved in their propagation (the force which attempts to restore the deformed water surface to a planar condition) is the force of gravity.

4.6.3 The generation of wind waves is a complex process, even now not fully understood, that involves both the shear stress of the moving air on the water surface and on the unequal distribution of air pressure over the windward and leeward sides of geometrical irregularities on the water surface. I'll note here only that the size of the waves depends on three factors: the speed of the wind, the duration of time the wind acts on the water surface, and the downwind distance (called the *fetch*) over which the wind acts on the water surface.

4.6.4 The best way to obtain an idea of the basic nature of the water motions produced by surface gravity waves is to watch the propagation of a single train of waves in a wave tank (Figure 1-56). You can imagine building a long tank with rectangular cross section, perhaps several meters long, open at the top. Put a wave generator at one end. A board hinged to the bottom of the tank can be rocked or oscillated back and forth to produce a train of waves. It's best to install some porous material at the other end of the tank to absorb the waves, so that they're not reflected to interfere with the propagating wave train.
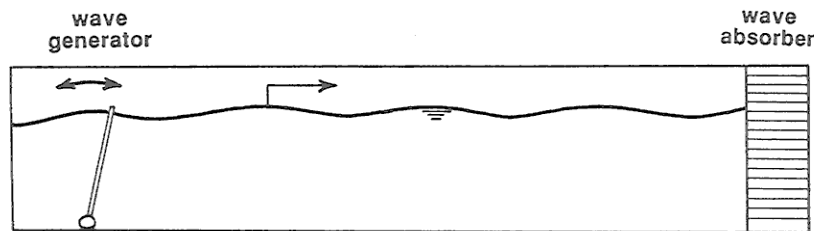
Figure 1-56. Making waves in a backyard wave tank.

4.6.5 Here are some terms used to describe the waves in a simple train of waves (Figure 1-57). The *crest* of the wave is the highest point on the wave profile, and the *trough* is the lowest point on the wave profile. The *period* of the wave is the time needed for one complete wave form to pass a point that is fixed relative to the bottom of the tank. Surface gravity waves in natural environments have periods that range from less than a second to almost twenty seconds. The *wavelength* of the waves is the distance from crest to crest or from trough to trough. The *height* of the waves is the vertical distance from trough to crest. The heights of large waves generated by major storms are commonly in the range of five to fifteen seconds

4.6.6 If you place a floating cork on the water surface and watch its motion through the wall of the tank as the waves pass by, you see that the cork

travels in an almost perfectly circular orbit, making one circle during the passage of each wave (Figure 1-58). The sense of motion is such that the cork moves in the direction of wave propagation while the crest of the wave is passing, and opposite to the direction of wave propagation while the trough of the wave is passing.
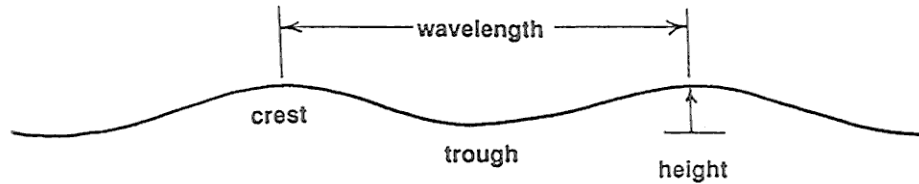

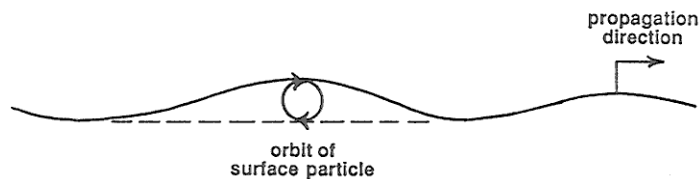Figure 1-57. Some terms used to describe the waves in a simple train of waves.

Figure 1-58. The circular orbit of a particle floating on the water surface as a wave passes.

4.6.7 The water below the surface also moves as the waves pass, but the size of the orbits of the water particles decreases very rapidly with depth below the surface (Figure 1-59). The size of the orbits at a depth equal to half a wavelength is only about ten percent of the size of the orbits at the surface, and the size of the orbits at a depth equal to one full wavelength is negligible. Such waves are called *deep-water waves*. If the wavelength of the waves is much greater than the water depth, however, the size of the orbits is still appreciable at the bottom (Figure 1-59). Such waves are called *shallow-water waves*, and they are common during storms. Downward from the surface the orbits become flattened into ellipses with greater and greater eccentricity, until at the very bottom the orbits are back-and-forth straight lines. This should make sense to you, because at the bottom there can be no fluid motion perpendicular to the bottom—if the slight flow into and out of the porous sediment is ignored.
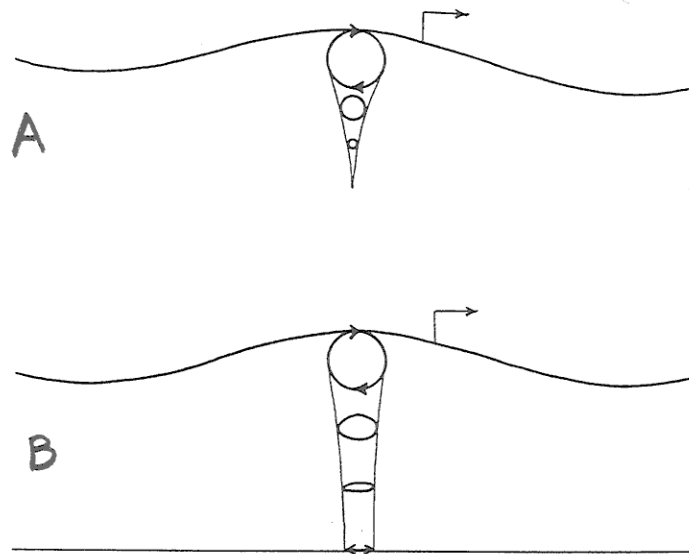
Figure 1-59. A) Decrease in orbital diameter with depth beneath a deep-water wave. B) Decrease in orbital diameter beneath a shallow-water wave.

4.6.8 Now examine more closely the nature of the oscillatory water motion at the bottom. If you measured the fluid velocity near the bottom as a function of time at a point which is fixed relative to the bottom, you would obtain a record that looks like the graph in Figure 1-60: the velocity varies sinusoidally with time. The nature of the motion can be characterized by its period T, or by the maximum velocity U_m that is attained during one oscillation cycle (this happens when the water is at the central point of its oscillation path), or by the distance d_o moved by a water particle during one full oscillation (this is called the *orbital diameter*).

4.6.9 It's part of the physical nature of waves that different trains of surface gravity waves can be superimposed on each other in such a way that the water-surface height and water motion at a given point is the sum of contributions from each superimposed wave train. You might know from watching storms at sea or on large lakes that the sea state produced by a strong wind is complicated, because it's a superposition of a large number of separate trains of waves with slightly different periods, propagation directions, and heights. Also, when the wind direction changes as a storm passes, the waves adjust their direction of propagation in response. In such cases, the pattern of water movement at the bottom is no longer a simple back-and-forth movement. Even the relatively

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simple case of two regular trains of waves moving in different directions, the water movement on the bottom can be surprisingly complicated, to say nothing of the really complicated wave conditions produced during storms.
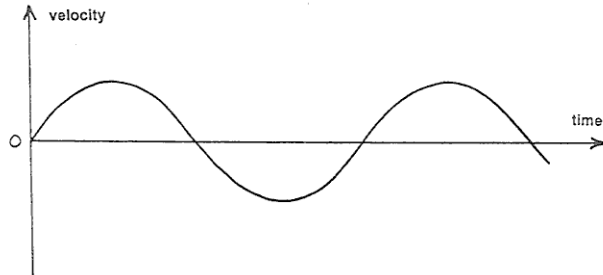

Figure 1-60. Fluid velocity near the bottom as a function of time at a point that's fixed relative to the bottom, as a shallow-water wave passes by overhead.

4.7 The Wind

4.7.1 The large-scale structure of the lower part of the atmosphere is obviously much different from that of even the largest river. The most obvious difference is the absence of a free surface in the atmosphere. An equally important difference has to do with the much larger scale of wind systems. This is important because the Earth's rotation plays a dominant role in determining wind direction (but this is not the course in which to pursue that very counterintuitive but fascinating matter) but is a minor aspect of even the largest of rivers. A third important difference is related to the easy compressibility of air, in contrast to the incompressibility of water. This means that the thermodynamics of compressibility plays an essential role in the behavior of the atmosphere.

4.7.2 Despite these far-reaching differences, it's fortunate for us as earthbound creatures that the structure of the wind in the near-surface layer, up to hundreds or even a few thousands of meters above the surface, is usually not greatly different from that of large-scale channel flows, in terms of such things as velocity distribution, turbulence structure, and boundary forces. Most of what I said in earlier sections of this chapter for channel flows of water is applicable to the wind. This is especially true of eolian sand transport and the shaping of sand dunes.

4.7.3 You might complain that the wind is so much more gusty than the ordinarily turbulent flow of rivers. I would counter that by saying that your conception of the gustiness of the wind is shaped by observations made for the most part down in among large and very irregularly shaped and irregularly distributed roughness elements like trees, hills, and buildings. To the extent that

things like that occupy river bottoms (hills are certainly there, and we'll have to deal with them as a really important part of this course), and you sensed turbulence down at their level, flow in rivers would seem pretty "gusty" too. (There will be more on that later, when we talk about flow over subaqueous bed forms.) If you have ever experienced a strong wind at sea, you know that the wind unimpeded by large roughness elements is surprisingly steady.