

## Chapter 8: Planetary atmospheres

- atmospheric composition and evolution
- structure, dynamics, and greenhouse effects
- sample problems

### Compositions and evolution of atmospheres

There are three ways of categorizing the sources of the atmosphere of a planetary body: original gases grabbed from the solar nebula as the planet or moon was forming, constituting the planet's *primitive atmosphere*; volatiles erupted during volcanic activity; or impacts, such as collisions with objects such as comets that have a high volatile content, these latter two providing the *secondary atmosphere*. We will need to distinguish between the elemental composition of an atmosphere and the molecular composition. The most obvious example here is that Earth didn't start out with an atmosphere rich in O<sub>2</sub>; that evolved along with life making use of existing atoms of oxygen.

There are several ways that atmospheres can be lost. The most significant of these is thermal escape: if a substantial fraction of particles have speeds that exceed the escape speed from the planet, the atmosphere will leak. Let's look at the math involved here, starting with reviewing the planet's escape speed:

$$v_{\text{esc}} = \sqrt{2GM/R}$$

where  $M$  and  $R$  are the mass and radius of the planet respectively. For planets such as Earth with a substantial atmosphere it might make sense to use a "radius" that's actually up a hundred kilometers or so above the surface, i.e., up where at a height where atoms or molecules might actually be escaping. For an object with a very tenuous atmosphere, e.g., Ganymede or Mercury, the object's surface radius is fine. Earth's escape speed is ~11 km/sec; Ganymede's is 2.7 and Mercury's is 4.3 km/sec. You should look up their masses and radii and make sure you can calculate escape speeds.

The speed that an atmospheric atom or molecule has is called its thermal speed because the average kinetic energy for any type of particle depends on the temperature. We assume that the particles making up our atmosphere behave as an *ideal gas*. That means that the only interactions between particles are elastic collisions, like collisions of little billiard balls. Being an ideal gas also means that even among particles that are all the same type, e.g., all N<sub>2</sub> molecules in the Earth's atmosphere, there will be a range of particle speeds. The number of particles with various speeds is described by the Maxwell-Boltzmann distribution function. The equation for this distribution is

$$f(v) = 4\pi v^2 \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT}$$

and graphically it looks like this for a gas of hydrogen atoms:

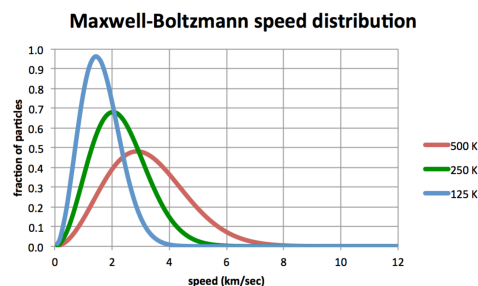


Figure 8.1 — Maxwell-Boltzmann speed distribution

Look at the exponential part of the function: it's a ratio of kinetic energy, i.e.,  $\frac{1}{2}mv^2$ , to available thermal energy, given by  $kT$ , where  $k$  is Boltzmann's constant and has units of J/K. The principle of equipartition of energy among the components of an ideal gas tells us that the speeds of each type of particle in an atmosphere will follow a distribution like this. Since it is equipartition of *energy*, it also tells us that lighter particles will move faster than heavy particles for the same temperature atmosphere.

The area under the curve represents the total number of particles of the type in question. The most probable speed is given by the speed at which the derivative of the above equation equals zero. The most probable speed is given by

$$v_{m.p.} = \sqrt{2kT/m}$$

where  $m$  is the mass (in kilograms if we have  $k$  and  $T$  in mks units) of the type of particle (or the weighted mean of several types of particles) in question.

Example: how fast would a nitrogen molecule likely be moving in an atmosphere of 500 K? One atomic mass unit has a mass of  $1.66 \cdot 10^{-27}$  kg and thus the mass of  $N_2$ , with two atoms, is  $\sim 28$  a.m.u;  $k = 1.38 \cdot 10^{-23}$  J/K. This gives

$$v_{m.p.} = \sqrt{2 \cdot 1.38 \cdot 10^{-23} \text{ J/K} \cdot 500 \text{ K} / 28 \cdot 1.66 \cdot 10^{-27} \text{ kg}} = 545 \text{ m/s.}$$

In other words, the most probable speed of a nitrogen molecule at 500 K is  $\frac{1}{2}$  km/sec.

Note: the most probable speed is not the average, i.e., where half the particles would be going faster and half slower. The average speed is

$$v_{ave} = \sqrt{8kT/\pi m}.$$

Kinetic energy goes as  $v^2$ , so another speed used to describe this distribution is the root mean square (or "rms") speed; this one is

$$v_{rms} = \sqrt{3kT/m}.$$

Many molecules would be going faster than the most probable speed. *Even if* the escape speed is larger than the most probable speed, some particles will leak from the atmosphere. And once the first high-speed particles escape, collisions among the remaining particles will redistribute the thermal energy; in other words, there will continue to be particles in the high-speed tail of the distribution. How large an escape speed is large enough to retain a particular type of atom or molecule in an atmosphere? As a rough approximation, 10 times the thermal velocity is sufficient. If

$$v_{esc} / v_{m.p.} \geq 10$$

there will be so few particles leaking that that species will have been retained over the lifetime of the solar system.

The bottom line for thermal escape vs. atmospheric retention: 1) massive planets with high escape speeds are better at holding on to atmospheres than small planets or moons are, and 2) cold temperatures, so that molecules aren't moving too fast, aid in atmospheric retention.

There are non-thermal ways that atmospheres can be lost. One process that may have been more important earlier in the history of the solar system is impact erosion. A large impactor, something with a size on the order of the scale height (the distance over which the pressure falls by  $1/e$ ) of the atmosphere it's hitting, will shock heat a column of gas high in the atmosphere, boosting much of it to speeds in excess of the escape speed and basically splashing a lot of hot gas off into space. Impacts on a smaller, less dramatic scale can also cause atmospheric loss. The particles in the outermost layers of an atmosphere are being hit by solar ultraviolet photons which often have enough energy to dissociate a molecule, leaving some or all of the fragments with enough energy to escape. Light-weight atmospheric particles on their own way out may hit and drag heavier atoms with them. Fast-moving interplanetary / solar wind particles can

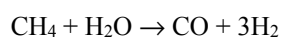
hit atmospheric particles hard enough to knock them off a planet or ionize them and drag them away, similar to the way the gas tail of a comet forms.

These last two possibilities, involving ways the outer atmosphere can interact with the solar wind, seem to have played an important role in the loss of atmosphere from Mars. Mars is small enough to have cooled fast enough that it was unable to maintain a magnetic dynamo and hence rapidly lost any magnetosphere that would have protected it from incoming, charged, solar wind particles. Those particles hit molecules in Mars' outer atmosphere. Some of solar wind particles simply hit Mars' atmospheric molecules hard enough to bounce them out into space, like little billiard balls. Some of the solar wind particles stripped electrons off Mars' atmospheric atoms or molecules; the now-charged atmospheric particle is picked up by the electric and magnetic fields of the solar wind and drawn away from Mars. The Mars Atmosphere and Volatile Evolution (MAVEN) mission, in orbit around Mars since September 2014, finds that Mars is still losing  $\sim 1/4$  kg of atmosphere every second.

Atmospheres also interact with liquid or ices on the surface. Pluto, for instance, has a tenuous atmosphere that's mostly nitrogen ( $N_2$ ) and there's nitrogen ice on the surface. The relative amount of nitrogen vapor depends on the temperature. Because of the tilt of Pluto's axis and its seasons, that's not quite the same as saying that Pluto's atmosphere will be denser at perihelion. Pluto went through perihelion in 1989. At that time its north pole, where there had been quite a bit of frozen nitrogen, had just come into sunlight, so even as Pluto started to get farther from the Sun, the amount of nitrogen in the atmosphere increased for a while, until the south pole got cold enough for more ice to accumulate there. The eccentricity of Pluto's orbit is  $\sim 0.25$ ; its distance from the Sun varies from 29.7 to 49.3 AU, so the amount of sunlight it receives varies noticeably. But there are other Trans-Neptunian Objects whose orbits are considerably more eccentric than Pluto's. In other words, one way to temporarily "lose" an atmosphere is to have it freeze out onto the object's surface at aphelion.

Many of these non-thermal processes could work in either direction, i.e., also at times contributing to an atmosphere. Sputtering could refer to a fast incoming atom or ion hitting an atmospheric atom but it also refers to fast atoms hitting the surface of airless bodies hard enough to eject some atoms from the crust. Meteorite impacts can likewise knock crust atoms loose. These atoms might escape to space but they might alternatively wind up creating a very tenuous atmosphere. The Moon and Mercury have very (*very*) tenuous atmospheres created in part by sputtering. Incoming solar wind ions can get caught, at least temporarily, by planetary bodies that don't have strong intrinsic magnetic fields (which would deflect the charged particles of the solar wind). These interactions contribute to those very tenuous atmospheres of the Moon and Mercury. And, as noted at the beginning of this chapter, large impacts might deliver, or cause to be released on impact, more volatiles than they remove. That, in turn, could modify the planet's climate for a time. Toss that into the hopper of potential reasons Mars might have once been wetter.

The giant planets are massive enough to have captured and retained gases from the solar nebula. Their elemental compositions are roughly solar, with their atmospheres dominated by hydrogen and helium. The next most abundant atmospheric elements, C, N, O, S, and Ne, tend to be found in molecules such as  $CH_4$ ,  $NH_3$ ,  $H_2O$ , and  $H_2S$ . Neon, being a noble gas, hangs out by itself. These conditions are *reducing* (having a large fraction of hydrogen, as opposed to *oxidizing* conditions), and, with the exception of the water, don't look like current conditions in the atmospheres of the rocky / icy planets and moons. Terrestrial atmospheres contain  $CO_2$ ,  $CO$ ,  $N_2$ ,  $H_2O$ ,  $SO_2$ , and  $O_2$ . It could have been the case that terrestrial atmospheres started out looking like giant planet atmospheres but that chemical reactions occurred which favored splitting off, and subsequently losing, hydrogens. As an example, if conditions favor the following reaction



with the subsequent loss of lightweight hydrogen molecules, and further conversion of  $CO$  to  $CO_2$ , a planet that started with a reducing atmosphere could retain many of its primordial atmospheric atoms on the way to acquiring an oxidizing atmosphere.

But the amount of neon, and other noble gases such as argon, krypton, and xenon, suggests that this was *not* the path taken. With the exception of helium, the noble gas atoms are relatively heavy and not readily lost by thermal escape. These atoms are also relatively inert and not likely to be sequestered in rocks. The abundance of neon and the other heavy noble gas elements are too low to support the suggestion that today's terrestrial planets atmospheres are essentially the primordial atmospheres minus only the helium and most of the hydrogen. Terrestrial atmospheres instead must be mostly secondary atmospheres, the result of volcanic outgassing of volatiles entrained in rocks and of impact accretion of volatiles from comets and asteroids. Volcanoes on Earth emit different proportions of gases depending on whether the volcanoes sit over deep-seated hot spots or over subduction zones. Regardless, volcanoes emit H<sub>2</sub>O and CO<sub>2</sub>, as well as some N<sub>2</sub>, S<sub>2</sub>, and lesser amounts of other gases.

The following table lists the major constituents of the atmospheres of Venus, Mars, Earth, and Titan, i.e., the terrestrial objects with the most substantial atmospheres. Minor constituents are often listed with ranges, in part because the composition of the atmosphere may vary with altitude, or latitude, or the seasons.

Table 8.1: properties substantial atmospheres of terrestrial objects

|                                | Venus              | Mars        | Earth                            | Titan                                          |
|--------------------------------|--------------------|-------------|----------------------------------|------------------------------------------------|
| N <sub>2</sub>                 | 0.035              | 0.019       | <b>0.78</b>                      | <b>0.98</b>                                    |
| O <sub>2</sub>                 | < 20 ppm*          | 0.0015      | <b>0.21</b>                      |                                                |
| O <sub>3</sub>                 |                    | 0.01 ppm    | 10 ppm                           |                                                |
| Ar                             | 70 ppm             | 0.019       | 0.0093                           |                                                |
| H <sub>2</sub> O               | ~30 ppm            | < 100 ppm   | < 0.05                           |                                                |
| CO <sub>2</sub>                | <b>0.96</b>        | <b>0.96</b> | 400 ppm                          |                                                |
| CO                             | ~25 ppm            | < 0.001     | 0.2 ppm                          |                                                |
| CH <sub>4</sub>                |                    | trace       | 1.8 ppm                          | 0.14                                           |
| SO <sub>2</sub>                | 20 – 200 ppm       |             | trace (& trace N <sub>2</sub> O) | traces H <sub>2</sub> and various hydrocarbons |
| H <sub>2</sub> S               | 1 – 2 ppm          |             |                                  |                                                |
| H <sub>2</sub> SO <sub>4</sub> | 4 – 10 ppm, clouds |             |                                  |                                                |
| Ne                             | 7 ppm              | 2.5 ppm     | 18 ppm                           |                                                |
| He                             | 12 ppm             |             | 5 ppm                            |                                                |
| surface pressure               | 9200 kPa           | 0.6 kPa     | 101 kPa                          | 147 kPa                                        |

\*Parts per million by volume

Many rocky / icy objects have tenuous &/or transient atmospheres. The following table lists the dominant gases in most of these.

Table 8.2: properties of tenuous atmospheres of terrestrial objects

| Object   | principal gases                                                                      | surface pressure     |
|----------|--------------------------------------------------------------------------------------|----------------------|
| Triton   | N <sub>2</sub> ; CO & CH <sub>4</sub> ~few 10 <sup>-3</sup> N <sub>2</sub> ; Ar, Ne? | ~1.6 Pa              |
| Pluto    | N <sub>2</sub> ; CO & CH <sub>4</sub>                                                | ~0.3 – 1 Pa          |
| Io       | SO <sub>2</sub> ; traces of SO, NaCl, S, O                                           | ~10 <sup>-4</sup> Pa |
| Ganymede | O, O <sub>2</sub> , H                                                                | ~10 <sup>-6</sup> Pa |



|         |                                                                              |                   |
|---------|------------------------------------------------------------------------------|-------------------|
| Europa  | O <sub>2</sub>                                                               | $\sim 10^{-7}$ Pa |
| Rhea    | O <sub>2</sub> , CO <sub>2</sub>                                             | $\sim 10^{-7}$ Pa |
| Dione   | O <sub>2</sub>                                                               | $\sim 10^{-8}$ Pa |
| Mercury | Na, Mg, O <sub>2</sub> , S, H <sub>2</sub> S, Ca, K, H <sub>2</sub> O, He, H | $\sim 10^{-9}$ Pa |
| Moon    | Ar, He, Ne, Na, K                                                            | $\sim 10^{-9}$ Pa |

Any moon with pole caps, even very small moons, will have had some molecules of ices spending some amount of time hopping from warmer subsolar latitudes to the poles.

A repeat note on pressure units: the SI unit of pressure is the pascal;  $1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg / (m s}^2\text{)}$ . We often still use the bar, with  $1 \text{ bar} = 10^5 \text{ Pa}$ , and the atm (or standard atmosphere), roughly a measure of sea level air pressure at mid latitudes;  $1 \text{ atm} \sim 101 \text{ kPa}$ . You may also see barometers that read in mm of Hg (which are approximately equal to Torr) or measure tire pressure in psi (pounds per square inch);  $1 \text{ atm} \sim 760 \text{ mm Hg} \sim 14 \text{ psi}$ . Too many units!? Agreed.

The composition of Earth's atmosphere has been distinctly modified by the presence of life. Some free oxygen, for instance the traces around icy satellites, could be due to splitting water molecules; as much free oxygen as Earth has is indicative of an atmosphere that is not in chemical equilibrium. The following plot illustrates roughly the history of the increase in oxygen in Earth's atmosphere.

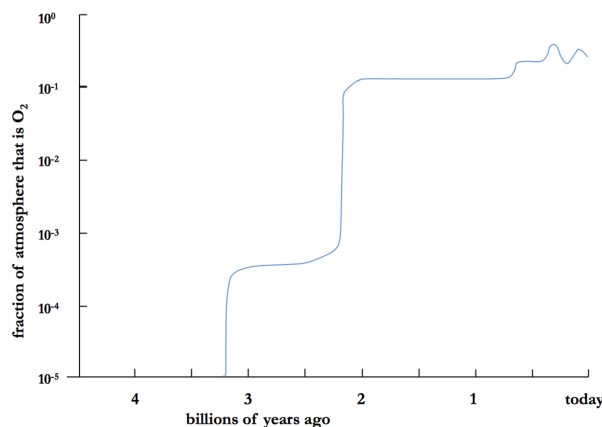


Figure 8.2: Earth's atmospheric oxygen

Life got started in an anerobic environment and the first oxygen early life produced tended to get used up in various chemical reactions – see, for instance, the banded iron formation images in the chapter on endogenic surface processes – so it took a while before the oxygen started to accumulate in the atmosphere.

Note that Earth has as much CO<sub>2</sub> as Venus. Much of our carbon is dissolved in the oceans, locked up in carbonate shells and rocks, much of that to be then carried underground by subduction. Let's elaborate on that process just a bit: Water and CO<sub>2</sub> in the atmosphere mix to form carbonic acid which falls along with rainwater. Earth's surface rocks contain lots of silica along with other elements, including, in particular, calcium. Weathering of rock, aided by the carbonic acid, breaks down the minerals in the rocks. Rivers carry the runoff to the oceans, where various sea critters are adept at using calcium carbonate (CaCO<sub>3</sub>) to make shells. Once their owners are finished using them, the shells sink to the ocean floor; some of this ocean sediment will be compressed to form limestone and some will get scraped up by subducting oceanic plates and carried down into the mantle. There metamorphism happens; the pressure and heat will encourage chemical reactions that produce CO<sub>2</sub>, which will eventually be returned to the atmosphere, mostly by volcanic eruptions or deep sea vents or various smaller springs. This carbonate - silicate cycle plays a significant role in stabilizing the amount of carbon in Earth's atmosphere. (Chemist Harold Urey,

whose interests included pondering what the early terrestrial atmosphere might have been like, was one of the first to consider the importance of the carbonate - silicate cycle, which is why it is sometimes referred to as the Urey cycle.) Of course sea shells are not the only way living things use carbon nor the only way carbon gets sequestered, i.e., locked away out of the atmosphere — think coal or other buried organic material.

Resource note. Earth's climate and climate change may be a topic about which you'd like to learn more. There are many online resources you might want to consult. Here are just a few:

<https://science2017.globalchange.gov/> Climate Science Special Report;

<http://earthguide.ucsd.edu/virtualmuseum/climatechange1/cc1syllabus.shtml> (followed by a second section, replacing both "1"s by "2"s);

<https://unccelearn.org/> from the UN Climate Change Learning Partnership (this requires creating a free account to access course materials);

<https://www.ipcc.ch/> for reports of the UN Intergovernmental Panel on Climate Change (IPCC).

The composition of the atmosphere plays a major role in the color of the sky. Earth's sky is blue because the molecules in our air, and other small particles – aerosols – in the air are smaller than the ~0.5 micron wavelengths of visible light. The blue part of the incoming sunlight is scattered, bouncing around so often that it comes at you from all directions. This kind of scattering process is called Rayleigh scattering and its efficiency has a  $1/\lambda^4$  dependence. In other words, shorter wavelengths are more effectively scattered. At sunset, when the sun is low on the horizon and thus sunlight is travelling through more air than at midday, even some of the green will be scattered. The Sun at sunset looks more orange than at midday. Add some smoke from a forest fire or ash from a volcano and the Sun looks quite red at sunset. But add larger particles, such as the water droplets in fog, and the color effect disappears. Larger particles reflect all colors of light and the fog appears a neutral white. Why do lunar eclipses look reddish? Because the red sunlight gets through the atmosphere and is bent into the Earth's shadow. We don't notice unless there's something in the shadow, such as the Full Moon, for that light to illuminate.

Our atmosphere refracts sunlight. The different colors of the sunlight don't all rise or set at exactly the same time, which permits the phenomenon known as the green flash. At sunset the red disk of sunlight sets first, then orange, etc.; the violet and blue have been scattered, so the last color to set is the green. If you have a still horizon you can catch a tiny flash of green just as the last bit of Sun disappears.

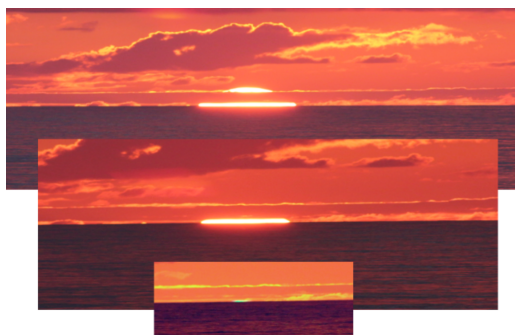


Figure 8.3: Green flash.  
Oregon coast, summer 2011.  
Photo by AKD

The atmosphere of Mars has enough fine grains of dust, larger than the wavelengths of visible light, that the sky is some variation on pink / rust / tan colors. Clouds on Venus filter out blue light and the uncorrected Russian Venera spacecraft images of the surface have a yellowish cast. Titan, with both layers of haze and less sunlight, has dark orange-brown skies.

How do we determine atmospheric compositions? If we are doing it remotely, we have to look at absorption lines in spectra. In other words, as electromagnetic radiation from a background source passes through the gases of the atmosphere, the gases absorb wavelengths that correspond to the energy transitions the particular atoms or molecules can make. We see dark lines in the spectrum. The background source

could be the infrared emission from the surface of the planet, a background star, or the Sun, which works for outer planets as long as we are making our observations from a distant spacecraft. (There are a few paragraphs about molecular spectra in the Intro chapter.)

Some of the spacecraft that have visited other planets have carried with them instruments capable of performing gas chromatography and / or mass spectrometry. In gas chromatography a sample is run through a thin tube, the inner walls of which are coated with a compound with which molecules in the gas sample are likely to interact, slowing their passage through the tube. Different molecules interact more or less strongly and are thus slowed by different amounts. Mass spectrometry works by ionizing a gas sample and then directing the ions through a region with an electric or magnetic field, either of which will cause moving charged particles to be deflected. The amount of deflection depends on the mass of the particles. Often both of these techniques are used together (a GC-MS), increasing the chances of clearly identifying the components of the atmospheric sample. The Huygens probe carried a GC-MS to aid in the analysis of the atmosphere of Titan, for instance.

### Structure and dynamics of terrestrial atmospheres

Air temperatures and pressures vary over the course of the day, the year, and with location on a planet. That said, it's possible to average over these quantities so as to isolate the variations in temperature and pressure as a function of altitude. Let's consider the structure of the Earth's atmosphere first. Nearest the surface, temperature drops with altitude. This is a region of convection, mixing, and weather. As such, it's appropriately called the *troposphere* (tropos means "turning"). The troposphere extends to about 12 km; it's a bit less at the poles and as much as ~20 km at the equator. Above the troposphere, in the *stratosphere*, the temperature turns around and starts to rise with increasing altitude, heated in large part by the ultraviolet portion of the incident sunlight being absorbed by the ozone (O<sub>3</sub>) layer. The stratosphere extends up to about 50 kilometers. Above 50-55 km molecules such as CO<sub>2</sub> which are efficient at radiating away energy to space help cool the atmosphere and the temperature starts to decline again, in a middle atmospheric layer called the *mesosphere* that extends up to ~85 km. Above this is the *thermosphere*, where temperatures climb again. High-energy photons and charged particles from the Sun dissociate molecules and ionize many of them. Here is where the majority of auroral emission occurs. The temperatures in the thermosphere vary over the day; the extent of the thermosphere varies with the solar activity cycle, puffing up at times when the flux of particles from the Sun is relatively high. The orbit of the International Space Station, at ~330 – ~410 km, lies in the thermosphere; particle densities are low enough that there's not too much drag on spacecraft in low Earth orbits.

Above the thermosphere is an extended region called the *exosphere*. It starts several hundred km up, depending on the extent of the thermosphere, and just keeps going, out to about 10,000 km where it's no longer reasonable to talk about particles being part of our atmosphere. Here the temperature is relatively constant with height in large part because there are too few particles to radiate away energy. The density of particles is so low that they rarely run into each other – a particle's mean free path, i.e., the distance between collisions, is approximately equal to the scale height. The exosphere is the region from which atmospheric loss takes place.

The *ionosphere*, the region that contains the majority of the electrically charged atmospheric particles, isn't quite coincident with the thermosphere. During the day, mesospheric atoms and molecules may be ionized as well, and since the base of the exosphere varies, the lower exosphere usually counts as part of the ionosphere as well. Electrons in the ionosphere interfere with some fraction of radio waves from space but the atmosphere is still relatively transparent at wavelengths from ~1 mm to ~10 m wavelength. Lower frequency radio transmission from the ground can reflect off layers in the ionosphere and bounce to receivers potentially thousands of kilometers away. The ionospheric layers change with sunlight; at night you may be able to pick up AM radio stations many hundreds of miles away but lose them when the Sun rises.

The ionosphere is home to STEVE, mauve-colored ribbons of light stretching roughly east-to-west that were only in 2016 recognized as a form of skyglow that's distinct from auroral emissions. The latter are associated with the interactions of solar wind particles, Earth's magnetic field, and excitation of atmospheric molecules; aurorae are usually seen at relatively high latitudes, in ovals around Earth's magnetic poles. STEVE is often visible in conjunction with aurorae, but may also be seen at lower latitudes. The nickname "Steve" came first, as auroral photographers and scientists started to realize that this was a distinct phenomenon. The name stuck and it now stands for Strong Thermal Emission Velocity Enhancement. The current view (pun intended) is that a flowing stream of plasma leads to particle collisions, friction, heat, and arcs of light that last for a few tens of minutes.

The following figure is a sketch of the temperature structure of the Earth's atmosphere. The next panels show the approximate structure for Venus, Mars, and Titan.

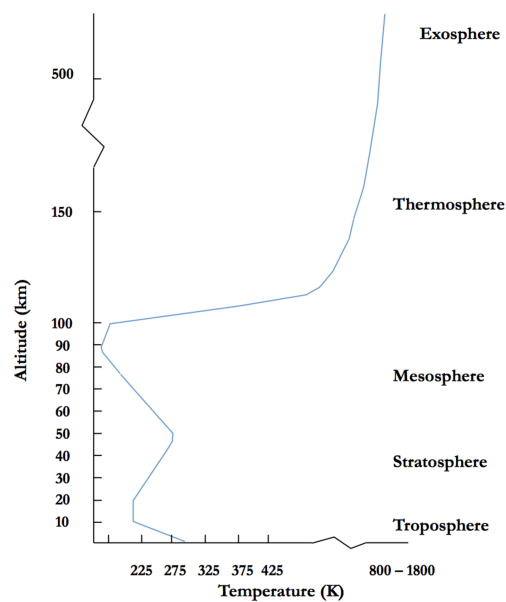
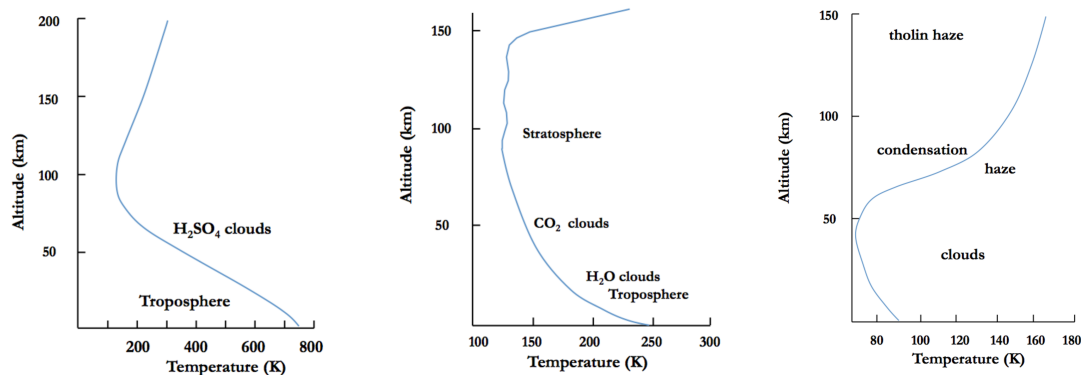


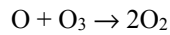
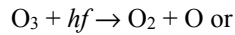
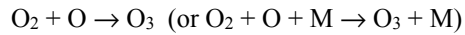
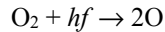
Figure 8.4: Earth's atmospheric structure

Figure 8.5: Atmospheres of a) Venus (left), b) Mars (center), and c) Titan (right).



Let's consider the Earth's layer of ozone,  $O_3$ , in the stratosphere in a bit more detail. Most of it is concentrated between about 30 – 35 km altitude; 90% of the ozone is found between 10 km and 50 km

altitude. Ultraviolet photons split (photodissociate) some  $O_2$  molecules; individual oxygen atoms combine with oxygen molecules to form  $O_3$ . This step is aided by the presence of a third molecule to carry away some of the energy associated with the reaction. Additional ultraviolet can then split the ozone molecules or an oxygen atom can join the ozone, which then splits into two  $O_2$  molecules. Written in reaction form, these processes look like:



The ionizations that occur out in the thermosphere prevent most solar radiation with wavelengths shortward of  $\sim 100$  nm from reaching the Earth's surface. Oxygen chemistry removes more ultraviolet, out to  $\sim 330$  nm, in particular by photodissociation. Wavelengths shortward of  $\sim 175$  nm can dissociate  $O_2$  molecules; short of 310 nm will split  $O_3$  molecules. High-energy photons can damage cells, so ozone up in the stratosphere is a good thing. Ozone can be destroyed by various molecular reactions, making it unavailable for absorbing UV. CFCs, molecules with chlorine, fluorine, and carbon, are among the molecules that humans produce that are capable of reaching the stratosphere and splitting ozone. The most apparent ozone hole lies over the South Pole, where a growing region of substantial ozone degradation has been monitored since 1979. The ozone hole extends far enough from the South Pole to affect people living on southern continents. For instance, between about 1980 and 2010 the incidence of skin cancers in Australia jumped by  $\sim 60\%$ . Various environmental protection measures have been put in place to reduce the use of ozone-depleting chemicals but many of these chemicals are very stable and have long lifetimes in the stratosphere, meaning ozone depletion is not going to be stopped rapidly.

Recall that the scale height is the distance over which the pressure or density falls by a factor of  $e$ . We may write the idea gas law as

$$P = \frac{\rho kT}{\mu m_{\text{amu}}},$$

where  $\mu$  is the mean molecular weight; the product of the mean molecular weight times the weight of one atomic mass unit (approximately the weight of one hydrogen atom),  $\mu m_{\text{amu}}$ , is the average particle mass in kilograms. If our atmosphere is in hydrostatic equilibrium we also have that

$$dP/dr = -\rho g$$

describing the way the pressure must fall with height. If our atmosphere, or at least the region under consideration, is roughly isothermal and not so extensive that  $g$  or the composition are changing, recall that the pressure will fall exponentially as

$$P = P_0 e^{-r/H}, \text{ where } H = kT/(\mu m_{\text{amu}} g)$$

is the scale height. Near Earth's surface the scale height is  $\sim 8.5$  km. Titan, which also has an atmosphere of nitrogen, has a lower surface temperature but a much lower surface gravity; its scale height is  $\sim 20$  km.

Having just considered an ideal atmosphere that is stable, let us consider weather. Most terrestrial weather occurs in the troposphere. Convection occurs because the planet's surface is heated by sunlight, warms up and radiates in the infrared, which heats the air near the surface. That surface air expands, becomes less dense, and, because it is now buoyant, rises. As it rises and expands it will cool, even if it doesn't radiate away any of its excess heat. When this bubble of air rises, it leaves behind a lower pressure region into which nearby surface air flows; we experience that flow as wind. Let's look at this combination of events in a bit more detail.

Here is a somewhat idealized schematic of the locations of the convective cells in our atmosphere and the resulting wind directions.

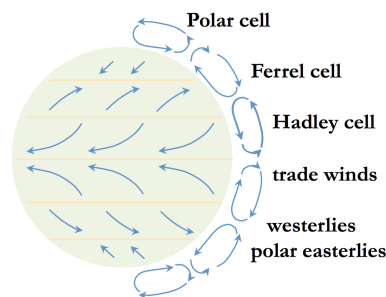


Figure 8.6: Convective cells in Earth's atmosphere and ground-level wind directions.

The assumption is that the sunlight is hitting the equator fairly straight on, as if the Earth were not tilted. Given that, look at the Hadley cell circulation for the northern hemisphere: Sunlight warms the ground at the equator; that air expands and rises and cools and moves north out of the way. Eventually it runs into the air at the top of the mid-latitude Ferrel cell moving southward and together they sink back toward the surface of the Earth. At the ground, following the Hadley cell, air will move back toward the equator where some other rising parcel of air has left a region of low pressure into which our first parcel can move.

The winds, though, don't blow north / south, because the ground underneath these air parcels is moving toward the east at a rate that depends on latitude. The surface of the Earth rotates as a solid; the angular speed of all places on Earth is the same and every location is carried around the rotation axis in  $23^{\text{h}}56^{\text{m}}$ . But locations near the equator have farther to go in that day than locations at higher latitudes. The linear ground speed is higher at the equator. The sinking air at the north end of the Hadley cell, at about  $30^{\circ}$  north latitude, is moving toward the east less fast than the ground near the equator is moving toward the east. As that air flows along the ground toward the south, anyone living near the equator and being carried along toward the east with the fast speed of the ground, will run into the air flowing toward the equator at the base of the Hadley cell. They will experience a wind coming from the east. These are the trade winds, useful for carrying trade westward in the days of sailing ships. At the latitudes where the air is either rising or sinking back toward the ground, the ground-level winds are light and variable. At the top of the Hadley cell, the air moving northward is moving faster than the ground and high-flying jets experience westerly winds.

This is an example of the apparent deflection of objects relative to a moving reference frame. Imagine sitting near the edge on a merry-go-round that is not rotating. A friend at the center of the merry-go-round throws a ball toward you. No problem; assuming your friend can throw straight, the ball will go straight to you. But what happens if you try this while the merry-go-round is rotating? The ball still makes a straight path relative to someone standing on the ground watching, but it does not make a straight path relative to you because you are now in a rotating frame of reference.

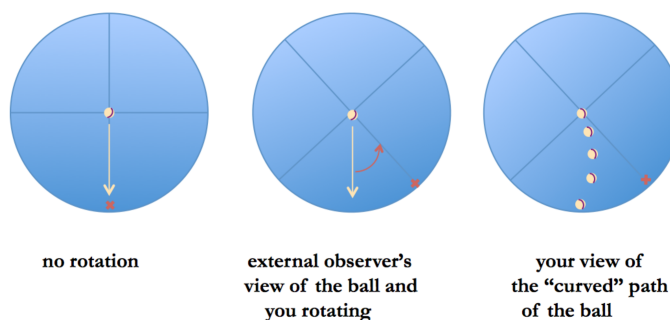


Figure 8.7: Deflection in a rotating reference frame

In the first frame, the merry-go-round is not rotating and you and an external observer both agree that the ball moves in a straight line toward the edge of the platform. In the middle frame, with the merry-go-round rotating, the person standing on the ground continue to observe the ball moving in a straight line toward the edge of the platform. Your view, shown in the third frame, riding on the merry-go-round, is that the ball curves away from you.

Example: what happens if you fire a rocket straight north from the equator? will it land straight north of you or somewhat east or west?

Answer: it will land to the east of your line of longitude. The rocket when launched shares the ground speed of the equator, which is faster than the ground speed at higher latitudes. The rocket gets ahead, i.e., east, of the ground it's flying over and its path relative to the ground curves toward the east.

In reality the Earth is tilted and, except at the equinox, sunlight is not falling directly onto the ground at the equator. Our winds are more complicated than the model above would suggest.

Circulation in the atmosphere of Venus is dominated by one set of Hadley cells, rather than three cells in each hemisphere as on Earth. In the atmosphere of Venus the Hadley cells extend from the equator to latitudes of about  $60^\circ$ , with smaller belts around the poles. Venus rotates slowly, but its atmosphere doesn't. The ground-level winds are not fast,  $\sim 10$  km/hour, but the upper atmosphere is moving very fast, with wind speeds over 300 km/hour. (Some 2018 simulations suggest that the fast, dense atmosphere, consistently flowing faster than the planet's rotation speed, could hit the mountains hard enough to speed up Venus' rotation slightly!) The following image was taken in ultraviolet light by the Pioneer Venus spacecraft. Multiple images show the cloud patterns moving east-to-west; there are often bright clouds near the poles.

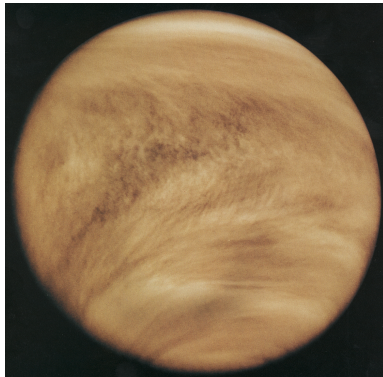


Figure 8.8: Venus upper-atmosphere clouds in UV, Feb. 1979.

NASA – Pioneer Venus spacecraft

[http://nssdc.gsfc.nasa.gov/photo\\_gallery/photogallery-venus.html](http://nssdc.gsfc.nasa.gov/photo_gallery/photogallery-venus.html)

Surface conditions on Venus, Earth, and Mars are clearly very different. One significant difference is the extent to which each planet experiences a *greenhouse effect*. Consider an atmosphere that is initially relatively transparent to visible wavelengths of light. Sunlight hits the planet's surface and a fraction ( $1 - \text{albedo}$ ) of that light will be absorbed. Much of what is absorbed will go into heating the surface, which will radiate in the infrared. It emits infrared because the surfaces emit approximately like blackbodies with temperatures ranging from a few tens of kelvin for icy outer solar system objects to a few hundred kelvin for inner rocky objects. Even though the atmosphere was transparent in the visible we can't assume that it will be transparent in the infrared. Many molecules, such as  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$ , have vibrational energy transitions in the infrared, meaning that they can absorb and re-emit many wavelengths of the infrared passing upward through the atmosphere from the warm surface below. Some of what is re-emitted is emitted downward, back into the lower layers of the atmosphere. Effectively some fraction of the IR gets trapped. (Actual greenhouses work by blocking the warmed air from escaping.) If you've been out in the desert on a clear night you know that it can get quite chilly. The ground was warmed by the Sun during the

day and continues to radiate for a while after sunset, but the dry clear air just lets that IR escape. You stay warmer on cloudy nights (although you lose out on seeing the stars!).

If Earth didn't have a bit of a greenhouse effect it would be a tough place to live. We are far enough from the Sun that Earth's surface could have frozen over; ice is reflective, the albedo would have gone up, and the planet could have stayed frozen. This scenario is called the "snowball Earth". Too large a concentration of greenhouse gases is also clearly problematic. The average temperature on Earth is increasing in synch with increasing levels of CO<sub>2</sub>. Perhaps more scary is the amount of ice — polar and glacial — that's melted in recent years. You may recall from a chemistry class (or from practical experience trying to use snow to get water for tea while out backpacking) that when you heat a mix of water and ice the temperature rises only slowly at first because it takes so much energy to get water to change phase from solid to liquid compared to the amount it takes to raise the temperature of liquid water. We're melting the ice.

Conditions on Venus and Mars are both related to a greenhouse effect that got out of balance. The surface temperature on Venus is ~735 K, everywhere, all the time. Carbon dioxide in the early atmosphere of Venus raised the temperature. Venus had water — the ratio of deuterium to hydrogen (D / H or <sup>2</sup>H / <sup>1</sup>H) is ~100 times higher for Venus than for Earth. Heavier isotopes are more likely to get left behind and lighter isotopes to escape. The fact that Venus had more hydrogen in the past implies that Venus had water. It doesn't tell us whether Venus had oceans, but if it had, they would have boiled away, perhaps fairly early in the planet's history, perhaps upwards of two billion years on, but sooner or later, they boiled. UV splits the water molecules, the hydrogen escapes, no more water. The crust gets dry and brittle, too hot and dry for carbonate minerals, which drives even more CO<sub>2</sub> into the atmosphere. Sulfate clouds increase the albedo a little but more importantly they reflect IR back toward the surface of Venus. Venus becomes a runaway greenhouse.

Mars is a runaway freeze-dried desert. Nitrogen isotope ratios show that Mars lost a lot of atmosphere; here again, we are assuming that its nitrogen isotope ratios looked like Earth's initially and that the heavier isotope, <sup>15</sup>N, preferentially gets left behind and the lighter one preferentially escapes. Without the protection of a magnetosphere, the solar wind played a major role in stripping Mars' early atmosphere. Without enough greenhouse action, Mars cooled. The liquid water froze into the surface. The occasional planet-wide dust storms on Mars temporarily warm the surface by several degrees, which encourages the winds, which kick up more dust. When the dust settles, Mars is still a freeze-dried desert. (One such planet-wide months-long dust storm, in the middle of 2018, darkened the skies too much for the rover Opportunity, with which NASA was unable to reestablish contact after the skies cleared.)

When Mars became a freeze-dried desert is an active research question. The surface of Mars shows indications that point to liquid water, present both as floods and possibly also as standing water. The latter would suggest an atmosphere warm enough and dense enough to support stable liquid water, in other words, an atmosphere with much more CO<sub>2</sub> than is present today. As one piece of evidence possibly favoring water, the Opportunity rover found hematite concretions a few millimeters in size resembling terrestrial structures formed in water. The Curiosity rover, examining ~3.5-billion-year-old mudstone sediments drilled from the near surface (to about 5 cm depth) in regions that appear to be ancient lakebeds in Gale Crater, has detected organic molecules. (For those with a bit of chemistry background, detected molecules include aliphatic compounds, aromatics such as benzene, and thiophenes; the sulfur in the latter may have aided in the preservation of the organic material.) Curiosity has also detected intriguing seasonal variations (from a minimum of ~0.2 to a maximum of ~0.7 parts per billion by volume) in the methane level in Mars' atmosphere, with the abundance peaking near the end of the northern hemisphere summer. On the other hand, Curiosity has not detected the carbonate minerals we would expect to find if the atmosphere of Mars three to four billion years ago had had a sufficient amount of CO<sub>2</sub> to provide the necessary greenhouse effect for stable liquid water. Neither the atmospheric methane nor the more complex organic molecules in the soil require a biological explanation, but they are intriguing nonetheless. Clearly the detailed evolution of Mars' atmosphere remains to be deciphered.



Some atmospheric particles can have an anti-greenhouse effect. On Titan, both effects are in play. Greenhouse gases raise the surface temperature by  $\sim 21$  K over the radiative equilibrium value. But the small haze particles in Titan's stratosphere block shorter-wavelength incoming solar radiation. Those particles are mostly transparent to outgoing infrared from Titan's surface, which helps us map the surface using infrared detectors, but which ultimately act to cool Titan's surface by  $\sim 9$  K. Titan's surface temperature is  $\sim 94$  K, which is only  $\sim 12$  K warmer than it would be if it were in equilibrium with the sunlight at its distance from the Sun. Pluto's atmosphere is even more extreme: its haze particles, hydrocarbons tens of nanometers in size, are so effective at radiating away infrared that the atmospheric temperature measured by the New Horizons spacecraft is roughly 70 K, rather than the 100 K that had been predicted prior to the flyby.

Air moving rapidly upward combined with solid condensates such as ice crystals and larger particles such as graupel (snow crystals heavily rimed from meeting supercooled water droplets) can lead to particle collisions that result in electric charge separation. Volcanic eruptions accompanied by sufficient ash can accomplish a similar charge separation. If the voltage thus produced is large enough a discharge of electrostatic energy is produced and we have lightning. There is clear evidence for lightning in the atmospheres of Jupiter and Saturn; lightning also seems possible in the atmosphere of Venus.

Atmospheric circulation involving upward motion of air containing moisture, often provided by evaporation of liquid from a planet's surface, can lead to precipitation as the rising air cools, becomes saturated, and droplets too large to remain suspended form and fall. In other words, it rains. Rain doesn't have to be water and doesn't just happen on Earth. Titan's surface features suggest that it probably experiences rain of methane and other organic compounds. In the upper atmosphere of Venus, droplets of sulfuric acid fall; they evaporate long before they reach the ground (perhaps 25 km elevation), a phenomenon known as *virga*. Relatively heavy elements are likely to rain down in the low-density atmospheres of the giant planets. And exoplanets? we don't know for sure but it's not impossible for conditions that would favor exotic raindrops of iron or tiny diamonds.

We are just beginning to understand atmospheres of exoplanets: which exoplanets have atmospheres, what are those atmospheres composed of, what sort of structure or features do they have, and so forth. How can we tell? If an exoplanet with an atmosphere transits in front of the disk of its star, light from the star will temporarily pass through the planet's atmosphere. There are absorption lines in the spectrum of the star, but those should be at least somewhat different from absorption lines caused by molecules in the exoplanet's atmosphere. Molecular lines are often in the infrared and telescopes that are sensitive to infrared (e.g., JWST) can look for those lines. There might also be emission from the planet's atmosphere itself, which will be blocked when the planet is in eclipse behind its star. Exoplanets that are close to their stars can be considerably hotter than any planets in our solar system, so it makes sense that we may detect atmospheric gases on "hot Jupiters" that we wouldn't see in planetary atmospheres in our solar system. We have positive detections for several exoplanets, including detecting  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ ; some (e.g., HD 209458b, WASP 19-b) seem to have sodium in their atmospheres and at least a couple (e.g., WASP-33b, WASP-19b) show the presence of titanium oxide. The latter implies a very hot atmosphere — this is a molecule that shows up in the spectra of cool stars. Planets close to their stars may also be tidally locked, like our Moon is on us, meaning that one side of the planet would be continually in sunlight and the other side continually in darkness. There might be winds on such planets, redistributing energy to the night side, but it's also probable that the weather (haze? clouds?) on the night side is different from that on the daytime side of the planet.

Addendum: more on winds.

There are four principal forces at work in the consideration of which way the wind is going to blow: the pressure gradient (which may be vertical as well as horizontal), Coriolis, centripetal, and friction. Let's add them into the mix one by one.

First the pressure gradient. In the following sketch, the clouds on the right are cooling the air beneath them; that air becomes denser and sinks, creating a region of higher air pressure near the surface. The unshaded ground warms up and air above it rises, creating a region of lower air pressure near the surface. Air flows from the higher pressure to the lower.

Figure 8.9: Pressure gradient wind

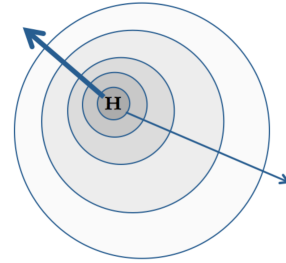
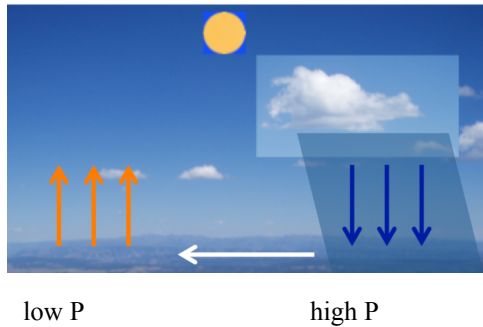


Figure 8.10: isobars

The pressure gradient =  $\Delta P / \Delta r$ . Recall that

$$F = P \cdot \text{area} = (P / r) \cdot \text{volume}; \text{ also}$$

$$F = m \cdot a = (\rho \cdot \text{volume}) \cdot a.$$

Therefore we may express the acceleration due to the pressure gradient as

$$a = (1/\rho) \cdot \Delta P / \Delta r.$$

A plot of isobars (line of constant pressure), shown in the right-hand panel above, gives us a top view of a region of high or low pressure. A pressure gradient wind will flow most strongly in the direction of the steepest pressure gradient and much less strongly in other directions.

Second we have the Coriolis effect, the deflection of moving air in a rotating system. The magnitude of the Coriolis force (or pseudo-force, since it is an effect of rotation) is

$$F_{\text{Coriolis}} = 2 m \Omega v \sin(\varphi),$$

where  $m$  is the mass of the parcel of air moving with speed  $v$  at a latitude  $\varphi$  on a planet rotating with angular speed  $\Omega$ . We can divide out the mass to obtain an expression for the acceleration. In the Earth's northern hemisphere winds are deflected to the right. Here is a sketch of the magnitude of the Coriolis acceleration as a function of latitude and wind speed. The Coriolis effect doesn't change the speed of the wind, only its direction.

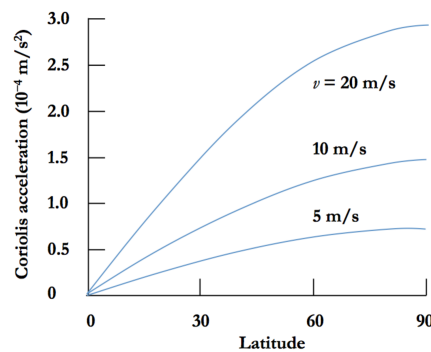


Figure 8.11: Coriolis acceleration

If we put together the accelerations due to the pressure gradient and the Coriolis effect the result is called the *geostrophic wind*. In this sketch a parcel of air initially has velocity toward the north; that velocity is curved toward the right by the Coriolis effect until the pressure gradient and Coriolis

accelerations are in balance. It may seem odd, but the wind really can blow perpendicular to the direction the pressure is changing.

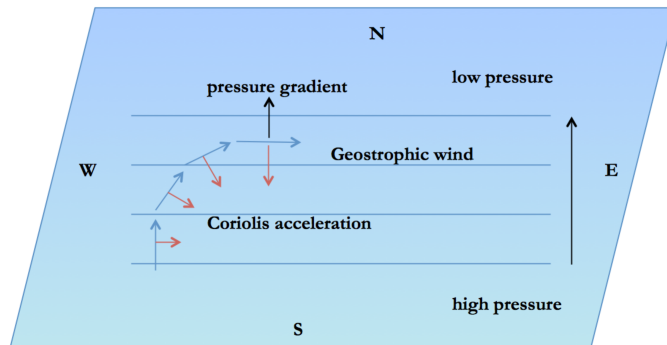


Figure 8.12: Geostrophic wind

Setting these two accelerations equal and solving for the speed gives us

$$v = \Delta P / (\Delta r \rho \, 2\Omega \sin(\varphi) ) .$$

The third effect to consider, the centripetal acceleration, arises when the isobars are curved rather than straight. Centripetal acceleration for circular motion is given by

$$a = v^2 / r .$$

Here is a sketch of what happens around a low in the Earth's northern hemisphere. The Coriolis force acts to deflect the wind to the right. The pressure gradient and centripetal forces are both directed inward toward the low pressure center. If the Coriolis acceleration balances the sum of the gradient and centripetal accelerations, the wind direction is bent around into a circle, counterclockwise. This is called a gradient wind. Around a high pressure center in the northern hemisphere the winds blow clockwise. In the southern hemisphere the Coriolis force deflects the wind to the left, so the wind directions are reversed compared to the northern hemisphere. In the right-hand panel is an image of Hurricane Ivan in September 2004.

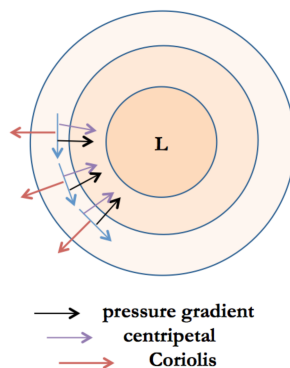


Figure 8.13: The gradient wind.

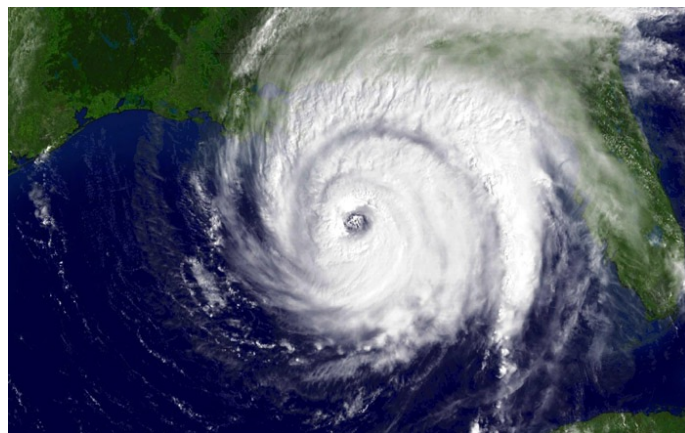


Figure 8.14: Hurricane Ivan, 2004; NOAA image

<http://www.noaanews.noaa.gov/stories2005/s2438.htm>

The fourth acceleration to consider is that at ground level there will be friction. This has the effect of reducing the wind speed which in turn reduces the Coriolis acceleration. In our gradient wind sketch, above, the Coriolis acceleration would no longer balance the pressure gradient and centripetal accelerations. Around a low pressure the wind will thus be directed more inward and may cross the isobars, as in this sketch.

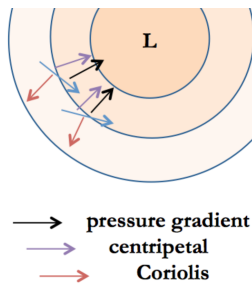


Figure 8.15: Gradient wind + friction

One more point about winds: we've been looking at various patterns of isobars and wind directions lying in a plane. If we add a vertical dimension we often find that the winds get stronger with altitude because of thermal effects. If we added a vertical dimension and considered planes of equal pressure, we would find those planes are farther apart above warm ground than above cool ground. The result is a vertical shear to the geostrophic wind. In the next figure we start again with our initial picture of air rising above warm ground, setting in motion a cycle as air from a cooler region flows toward the ground-level low and air sinks into the cool below the clouds. This time we've added 3 lines to represent the isobars. The separation between isobars is larger over the warm updraft. The result of this tilt in the isobars is that as we go up in altitude the acceleration due to the pressure gradient at that altitude (i.e., go back to thinking about flat slices of atmosphere at a given height) gets larger and the geostrophic wind gets stronger.

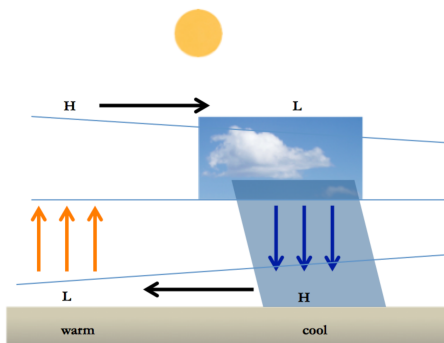


Figure 8.16: Thermal wind.

### Sample problems

1. Triton's surface temperature is about 38 K and it has an atmosphere of  $N_2$ .
  - a) Assuming Triton radiate as a blackbody, calculate the wavelength of the peak of its radiated spectrum.
  - b) Calculate the most probable speed for a nitrogen molecule in the atmosphere of Triton.
  - c) Calculate the escape speed from the surface of Triton.
  - d) Calculate the scale height for Triton's atmosphere.

2. What's the mass of air above you? Assume  $10^5$  Pa atmospheric pressure and calculate the mass of air in a column above 1 square meter of Earth's surface. Hint: a lot of the air is close to the surface so you could assume  $g$  to be constant.

3. Briefly define / explain

- a) Why the terrestrial sky is blue.
- b) Why the path of a projectile shot straight north from the equator will curve toward the right.
- c) Why a relatively high  $^{15}\text{N} : ^{14}\text{N}$  ratio for Titan suggests that Titan has lost atmosphere over time.
- d) Why it is harder to detect  $\text{N}_2$  in a planetary atmosphere than to detect  $\text{CO}$ .
- e) The ozone hole.
- f) How  $\text{CO}_2$  etc. act as greenhouse gases.

Answers to selected problems are on the next page:

1.
  - a) 76 microns
  - b) 150 m/s
  - c) 1453 m/s
  - d) 14.5 km

2.  $\sim 10,000$  kg.