13 Evolution of Venus’ Atmosphere

In the previous chapter, we looked at Mars, which is the most Earth-like of the other planets in our Solar System with respect to its potential for supporting life. But, in other ways, Venus is the most Earth-like planet. Venus has nearly the same mass as Earth (Table 13.1) and, as we shall see, similar inventories of volatile elements. But Venus has a very un-Earth-like surface temperature, \(-740\) K, and a vastly different, 93-bar, \(\text{CO}_2\) atmosphere.\(^1\) Venus also has an extremely slow rotation period, 243 Earth days, and it rotates in a retrograde direction with respect to the planet’s orbit – just the opposite of what is observed for Earth and most of the other planets. The combination of this slow retrograde rotation with its orbital period of 224 days gives Venus a solar daylength (noon to noon) of just under 117 Earth days. So, the interesting story about Venus is not how like the Earth it is, but rather how it came to be so different. Before addressing this question, though, we briefly look at what Venus’ atmosphere is like today.

13.1 Current State of Venus’ Atmosphere

Venus is the most-visited planet in our Solar System, having been explored by some 24 different spacecraft, several of which have dropped probes into its atmosphere. These include the Soviet \textit{Venera} spacecraft, ten of which descended to Venus’ surface from 1970 to 1985, and NASA’s \textit{Pioneer Venus}, which made a successful visit in 1978. \textit{Pioneer Venus} consisted of two spacecraft, an orbiter, and a multiprobe mission that included a descent bus, a large descent probe, and three smaller probes. Much of what we know about Venus’ lower atmosphere comes from data obtained by this mission. \textit{Magellan} sent

\(^1\) Values are given at the mean radius of 6051.84 km (Fegley, 2014), noting that temperature varies \(-100\) K and pressure varies several tens of bar across the surface because of topography.

back orbital data from 1990 to 1994, mapping the surface with radar. \textit{Venus Express}, which went into orbit around Venus in 2006, has contributed new atmospheric measurements and also discovered evidence that Venus may be volcanically active. Near-infrared emissivity anomalies around volcanic areas suggest that Venus has been volcanically active in the past 0.25 million years (Shulets et al., 2010) while transient bright spots seen through an atmospheric window at \(\sim 1\) \(\mu\)m are consistent with active lava flows (Shalygin et al., 2015).

13.1.1 Atmospheric Temperature and Composition: the Concept of “Excess Volatiles”

Figure 13.1 shows a composite vertical temperature profile obtained from the four \textit{Pioneer Venus} descent vehicles. The atmospheric temperature increases from about 200 K at the 100-km level to roughly 730 K at the surface. The surface temperature is hot enough to melt lead or tin, and no probe has survived there for more than 2 h. The surface temperature exceeds the critical point of water, 647 K, above which water can only exist in the vapor phase.

Both the \textit{Pioneer Venus Large Probe} and the \textit{Orbiter} contained neutral mass spectrometers, and the \textit{Large Probe} contained a gas chromatograph, as well. Between them, they were able to measure the concentrations of a number of species in Venus’ atmosphere, several of which are shown in Table 13.2. As noted above, \(\text{CO}_2\) is the most abundant gas, comprising some 96.5% of the atmosphere. \(\text{N}_2\), with a mixing ratio of 3.5%, makes up most of the rest.

It is instructive to compare the \(\text{N}_2\) column mass in Venus’ atmosphere with that on Earth. As pointed out in Ch. 1 (eq. (1.19)), the mass of an atmospheric column is equal to the surface pressure divided by the gravitational acceleration. To get the mass of an individual species, one
Table 13.1: Planetary characteristics of Venus. (Source: Fegley (2014).)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Value relative to Earth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>4.8685 x 10^24 kg</td>
<td>0.815</td>
</tr>
<tr>
<td>Mean radius</td>
<td>6052 km</td>
<td>0.95</td>
</tr>
<tr>
<td>Mean density</td>
<td>5243 kg m⁻³</td>
<td>0.95</td>
</tr>
<tr>
<td>Mean surface gravity</td>
<td>8.87 m s⁻²</td>
<td>0.904</td>
</tr>
<tr>
<td>Semi-major axis</td>
<td>108208930 km</td>
<td>0.723</td>
</tr>
<tr>
<td>Orbital eccentricity</td>
<td>0.0067</td>
<td></td>
</tr>
<tr>
<td>Sidereal orbital period</td>
<td>224.701 d</td>
<td>0.615</td>
</tr>
<tr>
<td>Rotation period</td>
<td>243 d (retrograde)</td>
<td>243</td>
</tr>
<tr>
<td>Daylength (noon to noon)</td>
<td>116.75 d</td>
<td>116.75</td>
</tr>
<tr>
<td>Surface temperature at the mean radius</td>
<td>737 K</td>
<td>2.6</td>
</tr>
<tr>
<td>Surface pressure at the mean radius</td>
<td>93.3 bar</td>
<td>93.3</td>
</tr>
<tr>
<td>Bond albedo</td>
<td>0.76</td>
<td>2.53</td>
</tr>
</tbody>
</table>

*Units are in Earth days.

Table 13.2: Composition of Venus’ atmosphere. (Source: Fegley (2014) and references therein.)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Abundance by volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>96.5 ± 0.8%</td>
</tr>
<tr>
<td>N₂</td>
<td>3.5 ± 0.8%</td>
</tr>
<tr>
<td>SO₂</td>
<td>150 ± 30 ppm (22-42 km)</td>
</tr>
<tr>
<td>Ar</td>
<td>30–150 ppm (12–22 km)</td>
</tr>
<tr>
<td>H₂O</td>
<td>66 (40–90) ppm</td>
</tr>
<tr>
<td>CO</td>
<td>30 ± 15 ppm (0–45 km)</td>
</tr>
<tr>
<td>CO₂</td>
<td>17 ± 1 ppm (12 km)</td>
</tr>
</tbody>
</table>

respectively. Thus, Venus has around three times more atmospheric mass of N₂ than Earth. Recall from Ch. 11 that some have used this disparity to argue that Earth once had greater amounts of N₂ in its atmosphere (Goldblatt et al., 2009; Lecuyer et al., 2000). Table 11.1 shows that most of Earth’s nitrogen is locked in minerals.

The CO₂ content of Venus’ atmosphere is, of course, vastly greater than the amount of CO₂ in Earth’s atmosphere or even in Earth’s combined atmosphere–ocean system. Neglecting recent anthropogenic additions, Earth’s atmosphere contains about 300 ppmv of CO₂, and the ocean contains about 60 times this amount, mostly as bicarbonate ions. Together, these yield a CO₂ column mass of ~280 kg m⁻². By comparison, Venus has a column CO₂ mass of ~1.0 x 10⁶ kg m⁻², or more than 3500 times higher. As many authors have pointed out, this discrepancy is easily explained, as most of Earth’s CO₂ is tied up in carbonate minerals and organic carbon in rocks. According to Walker (1985), the total amount of...
carbon in these reservoirs is $-10^{20}$ kg C, which corresponds to $7 \times 10^5$ kg m$^{-2}$ of CO$_2$. If one were to convert all of this stored carbon back into CO$_2$, the resulting CO$_2$ partial pressure would be 70 ± 10 bar. On this basis, Venus and Earth have comparable CO$_2$ inventories. Venus has no water, however, and thus no effective way of forming carbonate minerals, so virtually all of its lithospheric CO$_2$ is present in its atmosphere.

By comparison with the Earth, Venus’ deep interior might retain carbon in elemental form. Earth’s upper mantle contains ~100 ppm C, the lower mantle ~2000 ppm C, and core ~2000-3000 ppm C (as Fe$_2$C), by mass (Wood et al., 1996). If this carbon were released and oxidized, it would constitute an inventory of hundreds of bar.

Sulfur dioxide, SO$_2$, is similar to CO$_2$ in the sense of being much more abundant in the atmosphere of Venus than in Earth’s atmosphere. The SO$_2$ concentration on Venus is ~150 ppmv below the clouds (i.e., below ~45 km altitude), compared to only ~1 ppb or less in Earth’s troposphere. The ~150 ppmv value on Venus was measured by the Pioneer Venus and Venera 11–12 gas chromatographs and is consistent with Venus Express remote measurements (Marçq et al., 2008). According to UV spectroscopic measurements made by the Vega 1 and Vega 2 descent probes, SO$_2$ decreases towards the surface, down to ~25 ppmv (Bertaux et al., 1996). This gradient would require the presence of another major sulfur species, perhaps OCS, to take up the sulfur from SO$_2$, or an unusually large sink for SO$_2$ at the surface. Such a vertical gradient requires confirmation. Above the clouds, the SO$_2$ level drops to ~10 ppbv (Belyaev et al., 2012; Sandor et al., 2010) because of photodissociation, and the SO$_2$ concentration is somewhat variable with altitude, perhaps because of evaporating aerosols (Zhang et al., 2012).

On Earth, SO$_2$ levels are low because SO$_2$ is weakly soluble in water. Furthermore, in the presence of O$_2$ and H$_2$O, sulfur dioxide is quickly oxidized to sulfuric acid, H$_2$SO$_4$, which is highly soluble. Thus, any volcanic SO$_2$ that is outgassed on Earth soon ends up in the oceans as sulfate. From there, it makes its way into the rocks where it forms large reservoirs of gypsum, CaSO$_4$·2H$_2$O, and pyrite, FeS$_2$. The reservoir sizes of these minerals on Earth are each about 2.5 x 10$^{20}$ moles S (Bernier and Raiswell, 1983; Lasaga et al., 1985) for a combined surface sulfur reservoir of 5 x 10$^{20}$ moles S, or ~1.6 x 10$^{19}$ kg S. Canfield (2004) lists a slightly smaller total sulfur inventory of 3.5 x 10$^{20}$ moles S. This terrestrial sulfur inventory vastly exceeds the amount of sulfur stored as SO$_2$ in Venus’ atmosphere which, by the calculation method outlined above, is 114 kg m$^{-2}$ S, or 5.3 x 10$^{16}$ kg S total. So, Earth’s surficial sulfur inventory is 200–300 times larger. As the carbon and nitrogen surface inventories of Earth and Venus are roughly comparable, this suggests that large amounts of sulfur may reside in minerals on Venus’ surface. We return to this question later in the chapter.

This brings us to water. Pioneer Venus was not able to measure the water vapor content of Venus’ lower atmosphere, partly because the inlet leak of the Large Probe mass spectrometer became clogged with a sulfuric acid particle as it descended through the clouds (see below). But H$_2$O has been measured spectroscopically from the Venera 11, 13, and 14 landers (Ignatiev et al., 1997), from ground-based telescopes (Bailey, 2009; Meadows and Crisp, 1996; Pollack et al., 1993), and from Venus Express (Bezard et al., 2009; Marçq et al., 2006) (Fig. 13.2). Seeing through the clouds and dense atmosphere involves taking advantage of various near-IR windows. Based on an analysis of many measurements, the H$_2$O concentration is estimated to be 30 ± 10 ppm from 15–45 km and 30 ± 15 ppm below 15 km (Taylor et al., 1997). Bezard et al. (2009) derive a slightly higher value of 44 ± 9 ppm averaged over the lower atmosphere. A comparison with Earth is again helpful. The 30 ppm of H$_2$O in Venus’ atmosphere is equivalent to a column mass of ~13 kg m$^{-2}$. By comparison, the column mass of Earth’s oceans, which would be roughly 3 km deep if spread out over the entire planet, is about 3 x 10$^8$ kg m$^{-2}$. So, Venus is deficient in water compared to Earth by a factor of 4 x 10$^{-6}$.

We can generalize the discussion above as follows. The American geochemist, William Rubey, defined excess volatiles as compounds at Earth’s surface that cannot be derived simply by weathering of igneous rocks and conversion to sedimentary rocks (Rubey, 1951, 1955). These compounds include H$_2$O, CO$_2$, N$_2$, and SO$_2$, along with Cl. Because these compounds are not present in appreciable quantities in igneous rocks, Rubey assumed that they must have been released from Earth’s interior as constituents of volcanic gases. Alternatively, based on what we believe now about the violent process of planetary accretion, these compounds could have been emplaced directly into the atmosphere by impact degassing (Sec. 6.5). In any case, using Rubey’s terminology, what we have been comparing above are the excess volatile inventories of Venus and Earth. The conclusion is that, based on what are able to directly observe, Earth has much more water and surficial sulfur, and the two planets have comparable inventories of carbon and nitrogen when you account for amounts locked up in the solid Earth.
13.1.2 Cloud Composition and Photochemistry

Venus is entirely shrouded in clouds that make it impossible to see the surface at visible wavelengths, although it is possible to see through them at radio wavelengths and in some near-IR windows. The clouds are found at altitudes of 30–70 km (Fig. 13.3). *Pioneer Venus* measured the cloud composition to be a mixture of 75% sulfuric acid, H$_2$SO$_4$, and 25% water. The sulfuric acid is produced photochemically from photolysis of SO$_2$ and CO$_2$:

\[
\begin{align*}
\text{SO}_2 + h\nu & \rightarrow \text{SO} + \text{O} \quad (13.1) \\
\text{CO}_2 + h\nu & \rightarrow \text{CO} + \text{O} \quad (13.2) \\
\text{SO}_2 + \text{O} + \text{M} & \rightarrow \text{SO}_4 + \text{M} \quad (13.3) \\
\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 \quad (13.4)
\end{align*}
\]

H$_2$SO$_4$ is formed near the top of the cloud deck, around 70 km, where UV photons are available. Because of the low temperatures at these altitudes, H$_2$SO$_4$ condenses out to create particles which gradually fall through the cloud layer. H$_2$SO$_4$ becomes thermodynamically unstable, however, below about 45 km, causing the cloud deck to thin out by evaporation.

The presence of 100% upper cloud cover on Venus illustrates an important distinction between photochemically produced clouds such as these and condensation clouds on Earth. Photochemistry (reactions (13.1)–(13.4)) occurs everywhere where SO$_2$ is exposed to solar UV; hence, clouds form more or less uniformly over the sunlit hemisphere of Venus. By contrast, condensation clouds, such as the H$_2$O clouds on Earth, typically form in updrafts as a result of adiabatic cooling. Updrafts can occur over only a fraction, such as ~50% of Earth’s surface — what goes up must come down — and so condensation clouds typically do not reach 100% cloud cover. Some clouds, e.g., marine stratus clouds, do span large areas, but such clouds do not occur uniformly over Earth’s surface. Extremely thick atmospheres like those of the giant planets are 100% filled with condensation clouds, as viewed from above, but this happens because convection occurs over multiple scale heights and because different constituents condense at different altitudes, thereby producing multiple cloud layers. Saturn’s moon, Titan, is similar to Venus: it is completely enveloped in photochemically produced haze. Titan’s haze, of course, is composed of organic compounds, whereas the Venus haze is composed of sulfuric acid. By contrast, just like water clouds on Earth, the methane condensation clouds that exist in Titan’s troposphere are spotty (e.g., Griffith, 2009).

Unlike the upper cloud layer on Venus, the middle and lower cloud layers appear patchy, based on contrasts in brightness temperatures measured at different near-IR wavelengths (McGouldrick and Toon, 2007). These authors argue that the lower cloud layers on Venus are maintained by radiative-dynamical feedbacks similar to those that maintain stratocumulus clouds on Earth.

Venus’ planet-encircling cloud cover gives it a high planetary albedo of 0.76 ± 0.01 (Moroz et al., 1985). At visible wavelengths, Venus appears through a telescope as a bright, featureless disk. At violet and UV wavelengths, however, cloud markings become visible (Fig. 13.4). The markings are caused by the presence of some compound
that absorbs from 0.32–0.5 nm. In fact, about half of the solar flux received by Venus is absorbed in the upper clouds (58–65 km) by the UV absorber and the CO₂ column (Titov et al., 2007; Titov et al., 2013). The absorber’s identity has remained unresolved for many years.

Early suspicion about the nature of UV absorber centered on various compounds related to elemental sulfur (Toon et al., 1982). SO₂ does not just oxidize to sulfate when it is photolyzed. (This would not make sense, anyway, from a redox standpoint, as little free O₂ is thought to exist in Venus’ atmosphere.) Rather, the SO₂ disproportionate, that is, some of it is oxidized to sulfate by reactions (13.1)–(13.4), while some of it is reduced to elemental sulfur. The reduction is thought to occur by the sequence of reactions described in Ch. 9, Sec. 9.6.3 (reactions (9.32)–(9.36)). The end product of this reaction sequence is S₄, which is the stable form of elemental sulfur at room temperature on Earth. As mentioned in Ch. 9, other sulfur allotropes, such as S, S₂, and S₄, are also formed during this process. In reality, odd-numbered sulfur allotropes should also form, e.g. by the following reaction.

$$S + S₂ + M \rightarrow S₃ + M$$  \hspace{1cm} (13.5)

The sulfur molecules that are created by these reactions can be either linear chains or ring molecules (for S₃ and higher allotropes). Some of this sulfur is present as vapor, while some of it should condense to form particles of amorphous (noncrystalline) sulfur (Toon et al., 1982). Sulfur can also react with hydrogen to form sulfanes (sulfur chains with hydrogen atoms attached to one end). These sulfanes can then play a role in chain growth by way of the following reactions.

$$H₂ + Sₙ \rightarrow HSₙ + H$$  \hspace{1cm} (13.6)

$$HSₙ + S \rightarrow Sₙ₊1 + H$$  \hspace{1cm} (13.7)
Some, or all, of these sulfur chain molecules and sulfanes absorb near-UV radiation and are candidates for the markings in the Venus clouds (Hapke and Nelson, 1975).

Other UV absorbers have also been considered. Photochemical models generate elemental sulfur in the lower atmosphere, which condenses in the middle cloud layer but may have insufficient abundance to account for near-UV absorption at ~60 km (Krasnopolsky and Lefèvre, 2013; Mills et al., 2007; Zhang et al., 2012).

So, another leading candidate for the UV absorber is ~1% FeCl₃ dissolved in sulfuric acid (Markiewicz et al., 2014; Zasova et al., 1981).

### 13.1.3 Atmospheric Circulation

Our brief tour of the modern Venus atmosphere would be incomplete without commenting on its atmospheric circulation (e.g., see reviews by Limaye and Rengel, 2013; Read, 2013). Long ago it was noticed that the markings in the clouds—for example, a characteristic sideways “Y” pattern that can be seen in Fig. 13.4—persist for long enough to allow a measurement of the wind velocities near the cloud tops. The wind velocities at this level are directed in a retrograde sense, like the planet’s rotation, but much faster. The apparent rotation period at cloud-top level is about 4 days, which corresponds to wind velocities of ~120 m s⁻¹. Atmospheric rotation at equatorial latitudes that exceeds the rotation of the surface is superrotation, which is a basic feature of Venus’ atmospheric circulation (see Sec. 4.5).

The Pioneer Venus probes made it possible to measure wind velocities as a function of altitude (Fig. 13.5). Doppler tracking of the probes by Earth-based radar gave their velocities as they descended through Venus’ atmosphere. According to these measurements, wind velocities decrease monotonically with decreasing altitude, reaching values of 1–2 m s⁻¹ near the surface, which is consistent with similar Doppler tracking of Venera and Vega entry probes. At all locations where it has been observed, however, the atmosphere appears to be superrotating. This rotation extends up to high latitudes and so is readily observed in images taken by Venus Express as it went over Venus’ poles (e.g., Taylor, 2010, his Sec. 8.3). There, the superrotation produces a strong polar vortex that carries air downward at its center, much as the wintertime circumpolar vortex does in Earth’s polar stratosphere.

As discussed in Sec. 4.5, why the atmosphere circulates in this way is not entirely understood, even though numerous papers and book chapters have been written about this topic (see, e.g., Gierasch et al., 1997; Lellouch et al., 1997; Schubert, 1983). Below the clouds the circulation should be dominated by large Hadley cells in each
hemisphere caused by preferential heating of air near the equator and cooling near the poles (Sec. 4.2.5). Support for the existence of a planet-wide Venus Hadley circulation comes from observations of CO abundance made by Venus Express and summarized by Taylor and Gнихспен (2009). Above the cloud tops, Venus’ atmospheric circulation is different: evidence suggests that both subsolar-to-antisolar and equator-to-pole circulations are present. In between, within the clouds, the circulation appears to be driven primarily by strong thermal tides (Giersch et al., 1997). In general, as discussed in Sec. 4.5, some mechanism, either thermal tides or eddies associated with atmospheric waves, must transfer angular momentum to the 65–70 km level of maximum wind speed in the equatorial atmosphere.

13.2 The Solid Planet: Is Plate Tectonics Active on Venus?

As discussed in Ch. 11, a critical aspect of Earth’s long-term climate control system is its ability to recycle carbonate rocks back into gaseous CO₂. On Earth, this recycling occurs largely because of plate tectonics. Carbonate sediments on the seafloor, and carbonate veins that form within mid-ocean ridge hydrothermal vent circulation systems, are carried down into the upper mantle when seafloor is subducted. Volatilization of those carbonate minerals as they are heated up leads to outgassing of CO₂ through volcanoes, thereby resupplying CO₂ to the atmosphere and helping to stabilize climate over long timescales.

Do other rocky planets within our Solar System show evidence for plate tectonics? One way to tell is through hypsometry—measuring the relative elevation of surfaces. Hypsometric curves for the Moon and three terrestrial planets are shown in Fig. 13.5. The distribution of surface elevation on Earth is distinctly bimodal. Roughly 30% of the surface lies at elevations of 2 ± 1 km, measured with respect to sea level. This, of course, represents the continents. The other 70% of Earth’s surface—the seafloor—lies at elevations of −4 ± 2 sea-level difference in elevation between continents and seafloor is a direct consequence of the action of plate tectonics. Indeed, granitic continents might not even exist if plate tectonics were not active (Campbell and Taylor, 1993).

According to Fig. 13.6, Mercury, the Moon, Venus, and Titan have unimodal elevation distributions. The data for Venus were collected by radar altimetry from NASA’s Magellan Mission. This, by itself, suggests that plate tectonics is not active on these bodies. (The topography of Mars was discussed in Sec. 12.1.1.)

Other data from Magellan support the idea that plate tectonics does not operate on Venus today. Magellan used synthetic aperture radar, or SAR, to map surface features on Venus down to a spatial resolution of ~120–280 m. SAR makes images by bouncing radar beams off the surface and combining signals from different points along the spacecraft’s orbit. The effective aperture of the radar becomes the distance between these points, rather than the diameter of the antenna itself, thereby allowing the SAR system to achieve high spatial resolution. With SAR, Magellan mapped about 900 impact craters on Venus, all of them over 2 km in diameter (Herrick et al., 1997; Schaber et al., 1992). The reason for the lack of smaller impact craters is easy to determine: incoming bolides smaller than ~1 km are unable to penetrate Venus’ dense atmosphere, so they fragment and produce airbursts rather than craters. Intriguingly, impact craters on Venus appear to be randomly spaced over Venus’ surface (but see further discussion below). Since impacts occur sporadically over long periods of time, this implies that the mean age of Venus’ surface is approximately the same everywhere, initially estimated as 0.5 ± 0.3 billion years (Schaber et al., 1992). Subsequent models that take account of
the deceleration and flattening effects of Venus’ dense atmosphere on impactors put the age at 0.73 ± 0.1 billion years (Korycansky and Zahnle, 2005).

Unlike Venus, the age distribution of Earth’s surface, like its elevation, is bimodal. The seafloor has a mean age of 60 million years, whereas the continents exhibit a variety of ages but are typically about 1 billion years old. The difference is caused by the fact that the seafloor is continually being subducted, whereas the continents are not.

The fact that plate tectonics does not operate on Venus does not necessarily imply that its surface is volcanically inactive. Time-dependent changes in the measured SO₂ concentration above the clouds have been interpreted as evidence of periodic emission of volcanic gases (Epstein, 1984). Alternative explanations include time-dependent changes in dynamical transport of SO₂ from the lower atmosphere (Mills et al., 2007). As mentioned earlier, anomalously high near-IR emissivities measured in volcanic regions, including transient brightening, support the idea that Venus is volcanically active (Shalynin et al., 2015; Smrekar et al., 2010).

What happens inside Venus’ interior if plate tectonics is not active? Upward transport of heat by conduction through the crust is inefficient, so heat released by radioactive decay of elements within Venus’ mantle should cause it to become extremely hot. One suggestion is that Venus experiences episodic, planet-wide volcanism (Turcotte, 1993). Instead of releasing its interior heat more or less continuously, as Earth does by creating new seafloor, Venus stores it up until the upper mantle becomes so hot that it melts over wide regions. Global volcanism results, resurfacing much or all of the planet’s surface, and thereby accounting for the uniform surface age inferred from crater counts. Once the heat is released, the upper mantle freezes solid again and volcanism slows or stops until the cycle is repeated.

Not all authors agree that Venus experiences episodic global resurfacing. Phillips et al. (1992) argue that the distribution of impact craters is not completely random; rather, some areas have slightly fewer craters, and these craters are partially embayed (filled) with material that could represent fresh lava flows. But they acknowledge that the hypothesis of random crater spacing for Venus cannot be ruled out. Recent crater density studies remain consistent with global resurfacing scenarios (Kreslavsky et al., 2015).

If the catastrophic resurfacing hypothesis is correct then one must ask why Venus behaves this way, while Earth does not, given that Venus is almost the same size as Earth. The difference between the two planets is probably related to Venus’ lack of water (Morris and Solomonov, 1998). On Earth, the presence of water in the upper mantle lowers the viscosity of rocks, thereby helping to create the ductile asthenosphere on which the lithospheric plates ride. Without water, the asthenosphere would be much more viscous, making it more difficult for plates to slide around. On Earth, water weakens rock and lowers the strength of the lithosphere (Stern, 2007), and water substantially lowers the melting point below areas from ~1400 to 800 °C (Till et al., 2012). Finally, on Earth, the presence of liquid water helps remove CO₂ from the
atmosphere, limiting the magnitude of the greenhouse effect, and keeping the surface relatively cool. On Venus, the dense CO₂ atmosphere that built up in the absence of water (see discussion below) creates such high surface temperatures that the temperature distribution within the mantle is affected. The conversion of seafloor basalt into eclogite, which occurs once subducting slabs reach ~35 km depth on Earth, may not occur on Venus. Eclogite is denser than basalt, and so this transition is thought to increase “slab pull,” which is one of the forces driving plate motions on Earth. For all of these reasons, the lack of water on Venus could be the reason why plate tectonics does not operate there. Thus, how Venus lost its water, which we discuss below, may be the key to understanding the operation of the entire planet.

13.3 Formation of Venus' Atmosphere: Wet or Dry?

As already discussed, a key difference between Venus and Earth is that Earth has large oceans on its surface, while Venus is extremely dry. Most of the remaining parts of this chapter are concerned with why that is the case. The first question, obviously, is: Did Venus form dry, or did it form wet and then lose its water over time? This question was debated vigorously during the 1960s and 1970s (see, e.g., Donahue et al., 1982; Lewis and Prinn, 1984).

Over the past 30 years, a consensus has emerged that Venus probably started wet, for two reasons. The first was discussed in Sec. 6.2.1: John Lewis’s equilibrium condensation model – which had predicted that Venus formed dry – is no longer accepted as a viable model for planetary formation. Although large portions of Earth’s mass may indeed have been derived from volatile-poor material that condensed at or near 1 AU, significant quantities of volatile-rich material are thought to have come from the asteroid belt region or beyond. If these volatile-rich planetesimals were hitting the early Earth, then Venus must have gotten hit, too. Venus need not have received the same amount of water as Earth, but forming Venus with as little water as we observe there today is considered to be highly unlikely, given that Venus has roughly similar inventories of other volatiles, such as carbon and nitrogen.

It was a fortuitous measurement of the deuterium/hydrogen (D/H) ratio from Pioneer Venus, though, that finally seemed to clinch the argument for a wet early Venus (Donahue et al., 1982). During its descent through the clouds, the inlet leak on the Large Probe mass spectrometer became clogged with a sulfuric acid particle. While this meant that the mass spectrometer results below cloud deck were largely useless, it provided a great enhancement in the hydrogen abundance (because H₂ is included in H₂SO₄), enough to enable the detection of deuterium. The D/H ratio returned from the mass spectrometer was 0.019, or about 120 times higher than the ratio in Earth’s oceans (1.56×10⁻⁴). Since then, the D/H ratio in Venus’ atmosphere has been measured even more accurately using near-IR spectroscopic observations from Earth (DeBergh et al., 1991), which yield an estimate of 150 times the terrestrial value. A similar D/H ratio was obtained from the ion mass spectrometer aboard the Pioneer Venus Orbiter (McElroy et al., 1982). The investigators from the latter instrument reported the presence of a mass-2 positive ion in Venus’ ionosphere, which was initially considered to be H₂⁺. After some thought, and following comparison with the probe data, it was realized that the ion must be D⁺.

How can the high D/H ratio on Venus be explained? As discussed in Sec. 6.2.3, both Venus and Earth are thought to have received most of their water from the outer asteroid belt. Water-rich carbonaceous chondrites, which are believed to originate from that region, have D/H ratios that scatter widely, but that are on average about the same as that of Earth’s ocean (Robert, 2001). As described in detail in Sec. 6.2.3, the D/H values in Oort Cloud and Kuiper Belt comets range from around one to three times the terrestrial ocean value. So, neither comets nor asteroids could have provided water with a D/H ratio as high as that observed on Venus. The only plausible mechanism for producing such an enhancement is by having an initially much larger H₂O endowment, and then by enriching D/H by way of preferential escape of the lighter hydrogen isotope. Not only is this idea plausible, but the mechanisim to enable it – the runaway greenhouse – had already been proposed some 13 years before Venus’ D/H ratio was measured (Ingersoll, 1969; Rasool and DeBergh, 1970). Thus, the dry early Venus model quickly lost support after the D/H data were published.

Before leaving this discussion, it should be acknowledged that the D/H data do not by themselves require a large initial water endowment on Venus. In theory, if only H atoms escaped to space, and all D atoms were left behind, the required initial inventory of water is just 150 times the present inventory, which is still less than 0.1% of Earth’s oceans. Furthermore, it is possible that Venus’ water has been resupplied by comet impacts (Grinspoon, 1987; Grinspoon, 1993), in which case the present D/H ratio tells us little about the initial water inventory. But it is also possible that Venus was endowed with much larger quantities of water. If the initial escape of hydrogen was hydrodynamic, as seems likely (Kasting
and Pollack, 1983; Kumar et al., 1983), deuterium should have been carried away along with hydrogen. In this case, the fractionation between the two isotopes would have been small (Sec. 5.11), leaving little or no signature, and so the amount of water lost could have been very large.

### 13.4 The Runaway Greenhouse

This brings us to the runaway greenhouse hypothesis. Before getting into the details of this theory, we should say what we mean by *runaway greenhouse*, as various definitions have been used. A useful review is given in Goldblatt and Watson (2012) and briefly summarize some of their discussion here.

Gold (1964) defined a runaway greenhouse as a positive feedback loop that causes surface temperatures to increase almost without bound. That feedback loop was described earlier in the book (Sec. 2.3) and is illustrated in Fig. 13.7. An increase in surface temperature causes an increase in atmospheric water vapor, which then increases the greenhouse effect, causing a further increase in surface temperature. This feedback loop amplifies perturbations, e.g., those caused by CO₂ increases, by about a factor of two in Earth’s present climate system, but it does not destabilize the system. The feedback becomes more powerful, though, as the climate warms, and can eventually reach a point at which it makes the climate system unstable.

We can define the runaway greenhouse more precisely by identifying what happens when the temperature “runs away.” A consequence of wet atmospheres is that spectral atmospheric windows close up, and thermal infrared radiation cannot escape to cool the planet. In this case, a limit to the outgoing radiation is set by the physics of water vapor, as pointed out initially by Simpson (1927) and later by Komabayashi (1967, 1968) and Ingersoll (1969). If the absorbed solar flux exceeds the outgoing infrared limit, then the planet’s surface heats up until rocks melt. The glow of the hot atmosphere at near-infrared wavelengths, where water vapor is more transparent, shines through to space and restores balance in incoming and outgoing fluxes. The temperature of molten rocks, ~1500 K, is well above the critical temperature for water, 647 K, and so in this state liquid water cannot exist on the planet’s surface. This distinction is important because one can also identify climate states in which surface liquid water is present, but in which the stratosphere is moist, so that water vapor is rapidly photodissociated and the hydrogen is lost to space. Kasting et al. (1994a) termed this a *moist greenhouse* state, following an earlier suggestion by Towe (1981). As we will see, this latter mechanism is how Venus may actually have lost its water, although the topic is debated (Hamano et al., 2013; Kurosawa, 2015).

To summarize, we define the *runaway greenhouse effect* as an upper limit on the outgoing thermal infrared radiation flux from a dense atmosphere dominated by water vapor, which is set by the physics of water vapor, so that under an incoming solar flux that exceeds the outgoing limit, all water enters the vapor state and a planet’s surface melts. We note, parenthetically, that such runaway states could apply to other condensable species (e.g., methane on a Titan-like planet), as well. However, we restrict our discussion here to water on Earth-like planets because our interest is in habitability.

#### 13.4.1 The Classical Runaway Greenhouse

One of the earliest papers on the runaway greenhouse, and conceptually one of the easiest to understand, was by Rasool and DeBergh (1970). These authors performed a simple climate calculation for three young planets, Venus, Earth, and Mars, as they formed atmospheres from volcanic outgassing. The planets were assumed to begin their existence as airless bodies with their present masses, and variations in solar luminosity were neglected. (This should not be surprising, as Sagan and Mullen had not yet published their 1972 paper on the faint young Sun.)

In Rasool and DeBergh’s model, H₂O and CO₂ were assumed to have been outgassed in a 4:1 ratio. A slightly simpler, pure-H₂O model was published later by Goody and Walker (1972), also without consideration of solar luminosity changes. Their model illustrates the point well and is easier to understand, so we use it as our example.

Both Rasool and DeBergh and Goody and Walker assumed gray, radiative-equilibrium atmospheres, and they used the Eddington approximation to obtain an analytic solution to the radiative transfer equations. This approach is a variation of the two-stream method described in Sec. 2.4.5.3. The key step is to assume that the specific intensity, I, in Schwarzschild’s equation of
radiative transfer in a plane parallel atmosphere, eq. (2.81), is independent of zenith angle (Goody, 1964, p.52). In Sec. 2.4.5.3, we used a diffusivity factor \( D \), of 1.66, whereas in this treatment, it is 3/2. When this approximation is used, the temperature within the atmosphere is given by

\[
\sigma T^4(\tau) = \frac{F_S}{2} \left( 1 + \frac{3}{2} \tau \right)
\]

(13.8)

This is just eq. (2.106) with \( D = 3/2 \). Similarly, the surface temperature is given by

\[
\sigma T^4(\tau_{ground}) = \frac{F_S}{2} \left( 2 + \frac{3}{2} \tau_{ground} \right)
\]

(13.9)

In these equations, \( \tau \) represents vertical thermal infrared optical depth at an arbitrary altitude, \( \tau_{ground} \) is the total atmospheric optical depth, and \( F_S \) is the absorbed solar flux, \( S(1 - A)/4 \), which (in equilibrium) is equal to the outgoing infrared flux at the top of the atmosphere.

For these pure water vapor atmospheres, the optical depth, measured vertically downwards, is given by

\[
d\tau = -\kappa_\nu \rho_\nu \frac{dP}{g}
\]

(13.10)

Here, \( \kappa_\nu \) is the absorption coefficient of water vapor (assumed to be 0.01 \( m^2 \ kg^{-1} \)), \( \rho_\nu \) is mass density of water vapor, \( g \) is gravity, \( z \) is altitude, and \( P \) is pressure. We have used the barometric law, \( dP/dz = -\rho \), to change from altitude to pressure coordinates. The absorption coefficient is one that is relevant to the 8–12 \( \mu \)m window region where water vapor is most transparent (Goody, 1964, p. 195). This is a reasonable assumption, as most of the outgoing radiation should escape from within that interval. The optical depth at the surface is found by integrating equation (13.10) downward starting from \( \tau = 0 \) at the top.

\[
\int_{\tau_{ground}}^{0} d\tau = \int_{P_{ground}}^{P_0} \frac{\kappa_\nu P}{g} \Rightarrow \tau_{ground} = \frac{\kappa_\nu P_{ground}}{g}
\]

(13.11)

The above equations can be used in the following way. A given temperature defines a saturation vapor pressure, according to the Clausius–Clapeyron equation (Sec. 1.1.3.5). If we vary the vapor pressure, assumed to be \( P_{ground} \), we can calculate an optical depth from eq. (13.11) and a surface temperature from eq. (13.9), if we specify the solar flux, \( F_S \). The results of such calculations are shown in Fig. 13.8. The dark, solid curve represents the saturation vapor pressure curve for water. The three dashed curves show the mean surface temperatures of the three terrestrial planets, as calculated from eq. (13.9). All three planets were given surface albedos of 0.17, similar to that of Mars today. Mars itself, being furthest from the Sun, starts out the coldest, \( \sim 220 \) K. As vapor pressure is increased, which we can think of as water being outgassed, one moves from left to right in the diagram. Once the surface pressure of Mars’ atmosphere reached about 2 \( \text{Pa} \) (0.02 mbar), where the solid and dashed curves intersect, water vapor began to exceed its saturation vapor pressure, and so it condensed out to form ice. To a first approximation, this explains what we see today: Mars is basically a frozen desert with a very thin atmosphere.

Earth, being somewhat closer to the Sun, started out a little warmer than Mars, about 270 K, which is fairly warm because the model used an assumed surface albedo that’s low and a modern solar luminosity. Hence, water vapor was able to accumulate to higher concentrations before it began to condense. In Earth’s case, enough water vapor accumulated to produce an optical depth in eq. (13.11) greater than unity and a greenhouse effect. That is why the curve for Earth bends slightly upwards as one follows it towards the right. As a result, when water vapor began to condense on Earth, the surface temperature was \( >0 \) °C, and so it formed liquid water instead of ice. Once again, to a first approximation, this is what we observe. Earth’s large inventory of surface water is almost all contained in its oceans.

For Venus, the calculated surface temperature evolution is quite different. Because Venus is even closer to the Sun than is Earth, its surface started out hotter still, \( \sim 315 \) K. This allowed large amounts of water vapor to
accumulate in Venus’ atmosphere – enough so that the greenhouse effect became large well before saturation was reached. Thus, the surface temperature curve for Venus bends sharply upwards at pressures above about 0.01 bar, and so it never intersects the saturation vapor pressure curve. According to this calculation, all of the water released from Venus’ interior would have remained in the vapor phase, forming a dense steam atmosphere. If one assumes that Venus started out with the same amount of water as did Earth, the surface pressure of this atmosphere would have been about 270 bar. Once in the atmosphere, the water vapor would have been lost by photodissociation followed by escape of hydrogen to space. We have not yet described that process in detail but will do so below. The net result would be a dry planet similar to the one we observe today.

Although the calculation described above illuminates the basic idea of a runaway greenhouse very well, in other ways it is unsatisfying. As described in Ch. 6, we no longer believe that planets begin their lives as airless bodies; instead, they form atmospheres and oceans as they accrete. The variation in solar luminosity with time was ignored, whereas in reality the Sun was approximately 30% less bright when the planets formed. And the climate model used was a gray, radiative-equilibrium model, which ignores convection and offers only a crude approximation of the detailed line absorption in a real CO$_2$–H$_2$O atmosphere. We will describe more complicated atmospheric models in Section 13.4.4. For now, though, let’s retain the gray atmosphere approximation and look at the problem from a different perspective.

### 13.4.2 A Simple Approximation to the Outgoing Infrared Flux from a Runaway Greenhouse Atmosphere

Another way to approach the runaway greenhouse problem is to treat it as a static phenomenon and to calculate the solar flux needed to trigger it. This is the approach that has been taken historically by most authors. Two different types of static radiation limits have been derived: one based on emission of radiation from the convective troposphere (Simpson, 1927); the other based on emission from a radiative-equilibrium stratosphere (Ingersoll, 1969; Komabayashi, 1967, 1968). The tropospheric limit was the first one to be studied and is actually the more physically relevant limit, so we discuss it first. The treatment is approximate. A more rigorous calculation is described in the next section.

We consider a pure H$_2$O atmosphere, as before. As explained in Sec. 2.4.4, most of the outgoing infrared radiation should be emitted from the region around optical depth unity. Let’s start by assuming that the mass absorption coefficient depends on pressure linearly, as follows.

\[ \kappa_v = \kappa_0 \left( \frac{P}{P_0} \right) \]  \hspace{1cm} (13.12)

Here, \( P_0 \) is a reference pressure where the opacity is \( \kappa_0 \). Such pressure-dependence of the mass absorption coefficient is appropriate for pressure-broadened or collision-induced absorption, which is the situation in the tropospheres (see Sec. 2.5.7). The vertical optical depth at any height in a pure H$_2$O atmosphere is given by eq. (13.10) at some pressure, \( P \), within the atmosphere, as follows.

\[ d\tau = -\kappa_r \rho_v \, dz = \kappa_0 \left( \frac{P}{P_0} \right) \frac{dP}{g} \Rightarrow \tau = \kappa_0 \frac{P^2}{2gP_0} \]  \hspace{1cm} (13.13)

In the last step, we have done a simple integration. Remember that the subscript “\( r \)” stands for “vapor”, not frequency. There is no frequency dependence because the atmosphere is gray.

Now, assume that thermal-infrared radiation is being emitted from within the saturated troposphere. Then, \( P = P_v \), the saturation vapor pressure. Most of the radiation emerges from the region where the optical depth along a slant path is equal to unity, i.e., \( \tau^* \approx D\tau = 1.66 \tau = 1 \). The diffusivity factor \( D = 1.66 \) accounts for the increase in pathlength along an average slant path from Rodgers and Walshaw (1966). The vapor pressure at the \( \tau^* = 1 \) radiation level will therefore be:

\[ P_v (\text{at } \tau^* = 1) \approx \sqrt{\frac{2gP_0}{\kappa_0 D}} \]  \hspace{1cm} (13.14)

But, the vapor pressure \( P_v \) is uniquely defined by temperature through the Clausius–Clapeyron equation (1.49). Combining this equation with eq. (13.14) yields

\[ P_v = \left( \frac{2gP_0}{\kappa_0 D} \right)^{1/2} = P_{\text{ref}} \exp \left[ \frac{L_c}{R_c} \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \]  \hspace{1cm} (13.15)

Here, \( P_{\text{ref}} \) and \( T_{\text{ref}} \) are the triple point values for water of 611 Pa and 273.15 K, and \( L_c \) and \( R_c \) are the latent heat of vaporization and the specific gas constant for H$_2$O. Inverting the previous equation and solving for \( T \) gives

\[ T (\text{at } \tau^* = 1) = \frac{T_{\text{ref}}}{1 - T_{\text{ref}} \frac{L_c}{R_c} \ln \left( \frac{2gP_0}{\kappa_0 D} \right)^{1/2} \frac{1}{P_{\text{ref}}}} \]  \hspace{1cm} (13.16)

We can think of \( T \) as the temperature of an infrared “photosphere” for a planet in a runaway greenhouse.
We can write the outgoing infrared radiation from the planet as \( F_{IR} = \sigma C T^4 \), where \( \sigma \) is the Stefan–Boltzmann constant and \( C \) is a constant of order unity, which accounts for the fact that the blackbody temperature of emission will be slightly less than that found at optical depth of unity and that the ratio \( l_c/\tau_r \) (which is dimensionally a temperature) in eq. (13.16) is not really constant but depends on temperature and pressure. We take \( R_e = 462 \text{ J K}^{-1} \text{ kg}^{-1} \), \( l_c = 2.425 \times 10^8 \text{ J kg}^{-1} \), and \( g = 9.8 \text{ m s}^{-2} \).

The gray body water vapor absorption coefficient is less certain. A reasonable fit to non-gray numerical 1-D modeling results is given by \( \kappa_0 = 0.05 \text{ m}^2 \text{ kg}^{-1} \) at \( P_0 = 10^4 \text{ Pa} \). This gives \( C T = 266.3 \text{ K} \) from eq. (13.16), and a limit on the outgoing radiative flux of \( F_{IR} = \sigma (CT^4) = 285 \text{ W m}^{-2} \), where \( \sigma \) is the Stefan–Boltzmann constant.

The value of \( \kappa_0 = 0.05 \text{ m}^2 \text{ kg}^{-1} \) approximately matches the absorption around 10 \( \mu \text{m} \) at a temperature of \( \sim 320 \text{ K} \) in the mid-runaway troposphere at a saturation pressure \( \sim 10^4 \text{ Pa} \).

We can gain a better appreciation of this limit by comparing it to the radiative fluxes in Earth’s present atmosphere. In equilibrium, the outgoing infrared flux, \( F_{IR} \), must equal the absorbed solar flux, \( S(1 - \Delta)/4 \). For Earth’s present albedo of 0.3, the absorbed solar flux is about 239 \text{ W m}^{-2}. The runaway greenhouse limit derived above is higher than this by a factor of 1.2. So, this analysis predicts that a pure water vapor atmosphere on Earth (assuming a gray opacity and no change in planetary albedo) would turn into a runaway greenhouse if solar luminosity were to increase by \( \sim 20\% \).

The analytical form of eq. (13.16) allows us to generalize this result to planets other than Earth. The dependence on \( g \) indicates that a planet that is more massive than Earth will have a higher runaway limit, while low-mass planets will have smaller limits and be more susceptible to runaway greenhouses. The reason is that the atmospheres of high-mass planets are more compressed. The level at which the emitting optical depth is unity occurs at higher pressure, according to eq. (13.14). It must lie along the saturation vapor curve, as well, so the emitting temperature must be higher, along with the emitted flux. To give an example, a 10-Earth-mass, water vapor-saturated planet with a surface gravity of \( \sim 18 \text{ m s}^{-2} \) should have a runaway greenhouse limit of 305 \text{ W m}^{-2}, about 7% higher than a 1-Earth-mass planet. This prediction is borne out by non-gray numerical models, which show that the runaway greenhouse threshold changes by about \( \pm 8\% \) for planets that are, respectively, 10 times more massive or 10 times less massive than Earth (Kasting et al., 1993b, Table 1; see also Pierrehumbert, 2010, his Fig. 4.37).

### 13.4.3 More Rigorous Limits on Outgoing Infrared Radiation from Gray Atmospheres

Kombayashi (1967, 1968) and Ingersoll (1969) independently developed another way of illustrating the runaway greenhouse mathematically. Their analyses focused on the radiative-equilibrium stratosphere. Their approach is elegantly explained by Nakajima et al. (1992), who also showed how the radiation limit derived in this manner is related to the one derived by considering emission from the convective troposphere. Hence, we follow Nakajima et al.

The simplest version of the story once again concerns a pure water vapor atmosphere. Assume further that the atmosphere consists of a stratosphere, which is in radiative equilibrium, along with a convective troposphere. By the same logic as used for eq. (13.11), the opacity at the tropopause is

\[
\tau_{TP} = \frac{\kappa_0 P_{TP}}{g} = \frac{\kappa_0 P_{TP} (T_{TP})}{g}. \tag{13.17}
\]

Here, we have set the pressure at the tropopause equal to the saturation vapor pressure, \( P_s(T_{TP}) \), at the tropopause temperature. But \( P_s \) is given by the Clausius–Clapeyron equation, as before; hence, eq. (13.17) gives \( \tau_{TP} = \tau_{TP}(T_{TP}) \). Meanwhile, evaluating eq. (13.8) at the tropopause gives \( T_{TP} = T_{TP}(\tau_{TP}) \). These two equations are displayed graphically in Fig. 13.9. The dashed curve represents eq. (13.17), while the solid curves represent eq. (13.8) for three different values of \( F_{IR} \), the outgoing flux at the top of the atmosphere. It can be seen immediately that the curves do not intersect for \( F_{IR} > 385 \text{ W m}^{-2} \), meaning that there is no solution in this region. Physically, that’s because if the outgoing flux is to be any higher, the tropopause temperature must also be higher. But this, in turn, would increase the amount of water vapor in the stratosphere, and thus its opacity, which would make it even harder for the radiation to get out.

This is the Komabayashi–Ingersoll (KI) limit on the outgoing infrared radiation flux (name coined by Nakajima et al.). Note that it is about 35% higher than the approximate radiation limit derived in the previous section. The KI limit would be achieved for a net absorbed solar flux increase by a factor of 1.61, relative to today’s value of 239 \text{ W m}^{-2}.

One can do more with the gray atmosphere approximation. A real atmosphere would contain not just water vapor, but also one or more non-condensable components. It would also have a convective troposphere linking the stratosphere with the surface. Both Ingersoll and Nakajima et al. have treated this more general case. In a
Figure 13.9 Diagram illustrating the Komabayashi–Ingersoll limit on the runaway greenhouse outgoing thermal infrared flux, $F_{IR}$. The dashed line represents the saturation vapor pressure of water. The three solid curves show the variation of temperature with altitude calculated from eq. (13.8). A gray atmosphere is assumed. (From Nakajima et al. (1992). Reproduced with permission. Copyright 1992, American Meteorological Society.)

For a two-component model, the opacity along a vertical path is given by

$$d\tau = (\kappa_\alpha x_\alpha m_\alpha + \kappa_n x_n m_n) \frac{dP}{mg}$$

(13.18)

Here, $m_\alpha$ and $m_n$ are the molecular masses of water vapor and the non-condensable species, $m$ is the mean molecular mass, and $x_\alpha$ and $x_n$ are the respective volume mixing ratios. The variation of temperature with pressure in the troposphere is assumed to be given by the moist adiabatic lapse rate (eq. (1.56)). In the model considered here, $m_n = m_\alpha = m$, and $x_n = 0$, i.e., the non-condensable component has the same molecular mass as water vapor and does not absorb radiation. Results of two separate calculations are shown in Fig. 13.10. The lower curve shows the outgoing infrared flux as a function of surface temperature for a pure water vapor atmosphere, while the middle curve shows the flux for an atmosphere with a non-condensable gas partial pressure of 1 bar, similar to modern Earth. The flux from a blackbody, $\sigma T^4$, is shown for comparison. In neither case does the outgoing infrared flux reach the Komabayashi–Ingersoll limit (dashed line). Other model atmospheres with larger non-condensable components can reach this limit, but in thin atmospheres this does not happen. Instead, the radiation being emitted to space comes mostly from the troposphere. This tropospheric radiation reaches an asymptotic limit of $\sim 393 \text{ W m}^{-2}$ at surface temperatures $>400 \text{ K}$. The physical reason for this behavior is straightforward: As the surface temperature becomes higher and higher, the lower atmosphere becomes increasingly opaque to infrared radiation. Eventually, none of the outgoing radiation comes from the surface; rather, it all comes from the upper troposphere. The amount of radiation being emitted depends on the absorption coefficient of water vapor, along with the slope of the moist adiabat. This same asymptotic behavior is exhibited in non-gray models, as well (Abe and Matsui, 1988; Kasting, 1988; Pollack, 1971; Watson et al., 1984). Although all of these models preceded the paper of Nakajima et al. (1992), it was the latter authors who most clearly elucidated the physics behind this tropospheric emission limit and, as mentioned earlier, it was Simpson (1927) who discovered it. Hence, following Goldblatt and Watson (2012), we will term this the Simpson–Nakajima (SN) radiation limit.

The SN limit on the outgoing infrared flux is substantially lower than the KI limit and similar to the approximate runaway greenhouse threshold derived in the previous section. Under the same assumptions as above (no albedo change) the calculated value of 293 W m$^{-2}$ corresponds to an increase in solar flux by a factor of 1.23 compared to present Earth. This result depends on the assumed atmospheric composition because one needs to get over the “hump” in the middle curve in Fig. 13.10, and that hump can be as high as the KI limit. As we shall
see, however, the SN limit shown here is probably closer to the real limit for triggering a runaway greenhouse.

Finally, Fig. 13.10 provides a visual way of thinking about feedback loops, or lack thereof, in the runaway greenhouse calculation. As discussed in Ch. 1, the feedback loop that stabilizes Earth’s climate on short time scales (months to years) today is that between surface temperature and the outgoing infrared flux. An increase in the outgoing infrared flux always cools the planet, so that coupling is always negative. And, under normal circumstances, an increase in surface temperature causes an increase in the outgoing infrared flux, so that coupling is positive. Once one gets over the hump in Fig. 13.10, though, this coupling changes sign, becoming strongly or weakly negative, depending on how much background gas is present and how well that gas absorbs in the infrared. As a result, the stabilizing negative feedback loop disappears, and the system is free to “run away” to very high surface temperatures.

13.4.4 Radiation Limits from Non-Gray Models

The runaway greenhouse has been studied with non-gray atmospheric models, as well. Two early studies were those by Abe and Matsui (1988) and Kasting (1988). Abe and Matsui looked at possible steam atmospheres that might have existed during Earth’s accretion. They found that a runaway greenhouse was caused when the accretional heat flux exceeded 150 W m\(^{-2}\). Their model included solar energy, as well, and with a little effort, one can calculate that the SN limit in their model\(^2\) was \(304\) W m\(^{-2}\). This is slightly higher than the SN limit calculated by the gray model in the previous section (293 W m\(^{-2}\)), but it shows that the same atmospheric physics is coming into play;

\(^2\) Abe and Matsui (1988) assumed a solar constant of 960 W m\(^{-2}\), appropriate for early Earth. Parameters for their E150 model, which is just slightly below the runaway greenhouse threshold, are given in their Table 4. They used spherical geometry, and they listed global fluxes, which we normalize here to Earth’s surface area of \(5.1\times 10^{14}\) m\(^2\). The outgoing infrared flux in their E150 model, \(F_{\text{IR}}\), was \(155.1\times 10^{15}\) W, which is equivalent to a flux per unit area of

namely, most of the emitted infrared flux is coming from the convective troposphere. One can also calculate that their planetary albedo was \(~0.37\). As we will see, both the outgoing IR flux and the planetary albedo are close to values derived independently by Kasting (1988) (discussed below), but both have now been superseded by more up-to-date calculations.

The non-gray model of the runaway greenhouse by Kasting (1988) was driven by solar radiation only. The calculation that he performed was equivalent to taking the present Earth, with its existing atmosphere and ocean, and sliding it slowly in toward the Sun. Like the Rassol and DeBergh simulation discussed earlier, this calculation does not correspond directly to how a real runaway greenhouse atmosphere might evolve. But it demonstrates under what conditions an Earth-like atmosphere can become unstable.

Because of the strong positive feedback from water vapor, climate model calculations can be difficult to control once the critical threshold for a runaway greenhouse is passed. Kasting avoided this problem by performing inverse calculations. The stratospheric temperature was fixed at \(200\) K, a value appropriate for Earth without an ozone layer, and the surface temperature, \(T_s\), was raised sequentially to higher and higher values. By-products of \(H_2O\) photolysis would presumably catalytically destroy an ozone layer if \(H_2O\) became a major constituent in the stratosphere. The surface pressure was set equal to 1 bar of non-condensable gas (\(N_2 + O_2\)) plus the saturation vapor pressure of water. The tropospheric temperature profile was assumed to follow a moist pseudo-adiabat as long as the surface temperature was below the critical point for water, \(647\) K (Fig. 13.12(a)). As discussed in Sec. 1.1.3.6, the pseudo-adiabat is one in which the condensed water is assumed to immediately rain out. The formulation of Ingersoll (1969), which remains valid in the region near the critical point, was used to calculate the pseudo-adiabatic lapse rate. This assumption makes physical sense, because the vapor pressure of (pure) water at the critical point, 220.6 bar, is lower than the pressure of a fully vaporized ocean, \(~270\) bar. In Kasting’s model, once the surface temperature exceeded \(647\) K, the surface pressure immediately jumped to \(271\) bar (\(= 270\) bar \(H_2O + 1\) bar \(N_2/O_2\)), and the lower atmosphere became unsaturated. The tropospheric lapse rate was assumed to follow a dry adiabat up to the point where water vapor began to condense, after which it followed a moist adiabat up to the tropopause (Fig. 13.12(b)).

Temperature and water vapor profiles for the low-temperature simulations (\(T_s < 420\) K) are shown in Fig. 13.13. As the surface temperature is increased, the convective troposphere extends to higher and higher
altitudes, reaching values $>150$ km for surface temperatures above 400 K. The reason, as explained originally by Ingersoll (1969), is because of the large amount of latent heat released when water vapor condenses. At high surface temperatures, the atmosphere becomes water-dominated, and so the tropospheric $P-T$ profile approaches the saturation vapor pressure profile given by the Clausius–Clapeyron equation (1.49). The lapse rate in this water-dominated regime can be derived from the differential form of this eq. (1.48). If, for clarity, we replace the meteorologists' symbol for saturation vapor pressure, $e_v$, with the symbol we have been using in this chapter, $P_v$, eq. (1.48) becomes

$$\frac{dP_v}{dT} = \frac{\rho g}{R} \frac{T^2}{T_s^2}$$

Inverting this equation and using the barometric law and the perfect gas law gives

$$\frac{dT}{dz} = \rho g \frac{dP_v}{dT} \frac{R}{\rho g} \frac{T_s^2}{l_c P_v} = \frac{gT}{l_c}$$

The latent heat of condensation, $l_c \approx 2.5 \times 10^6$ J kg$^{-1}$, so at 288 K the predicted lapse rate from eq. (13.20) is $\approx 1.1$ K km$^{-1}$. By comparison, the dry adiabatic lapse rate for Earth's present atmosphere is $T_{dry} = g/c_p \approx 10$ K km$^{-1}$. The moist adiabatic lapse rate for a water-dominated atmosphere is clearly very much smaller, so the troposphere must extend to very high altitudes before the temperature drops to the assumed stratospheric temperature ($T_{strat}$) of 200 K. One could argue that it is artificial to keep $T_{strat}$ fixed during such a calculation. However, by analogy to the gray atmosphere solution, as the tropopause moves higher and higher, $T_{strat}$ should approach the skin temperature of the planet, which is given by eq. (2.97) as $T_{skin} = T_{eq}/2^{1/4}$, where $T_{eq}$ is the effective radiating temperature. Thus, $T_{strat}$ varies only as the fourth root of the outgoing infrared flux. As the stratosphere becomes higher and thinner it emits less radiation, and so any deviations in $T_{strat}$ make little difference to the overall planetary radiation balance (Kasting, 1988).

The assumption that an upper stratosphere approaches the skin temperature has been challenged. Lecante et al. (2013) point out (following Pierrehumbert, 2010, p. 289 ff.) that the temperature at low optical depths in a non-gray atmosphere can be much lower than the gray
atmosphere skin temperature. In their 3-D numerical model, the temperature at the top of the troposphere reaches 115 K. This produces a much more effective cold trap and may limit the amount of water that can be lost from such planets. However, Venus does seem to have lost lots of water, so this prediction may be in conflict with observations. The tropopause moves up to high altitudes (low pressures) in all of these models, so non-LTE effects may also become important, which need to be considered with further models.

The water vapor profiles corresponding to the vertical temperature profiles of Fig. 3.13(a) are shown in Fig. 3.13(b). At low surface temperatures, $T_s$, the water vapor mixing ratio, $f_{H_2O}$, drops off rapidly with altitude, as it does in Earth’s troposphere today. As a consequence, the stratosphere is dry (<10 ppmv for $T_s = 280$ K). The 1-D model overestimates stratospheric water vapor slightly because it lacks a cold, high, equatorial tropopause. The actual stratospheric H$_2$O mixing ratio is 3–5 ppmv.

As $T_s$ rises above about 320 K, a dramatic change takes place: the water vapor mixing ratio in the upper troposphere and stratosphere increases dramatically, reaching values near unity for $T_s > 400$ K. Once again, Ingersoll (1969) predicted such behavior. He pointed out that the critical transition occurs when the volume mixing ratio of water vapor at the surface exceeds ~0.2. The saturation vapor pressure of water at 340 K is ~0.3 bar, and so for the Kasting (1988) model, with its 1 bar of non-condensable gas, this is about where the critical transition to a wet stratosphere occurs.

The calculated outgoing infrared flux, $F_{IR}$, and absorbed solar flux, $F_S$, for these simulations are shown in Fig. 13.14. Here, $F_S$ is the absorbed solar flux for the present solar constant. In reality, of course, the outgoing infrared flux must equal the absorbed solar flux. This is true at only one particular surface temperature in the figure, $T_s = 288$ K, the present value for Earth. So, at other surface temperatures, the required, or “effective,” solar flux, $S_{eff}$, would be either higher or lower than the present flux, according to

$$F_{IR} = S_{eff} \cdot F_S$$  \hspace{1cm} (13.21)

Turning this relationship around, $S_{eff} = F_{IR} / F_S$. The significance of $S_{eff}$ will be discussed below.

Let’s focus on the behavior of $F_{IR}$ and $F_S$. The outgoing infrared flux, $F_{IR}$, is similar to that shown in the gray atmosphere model of Nakajima et al. (1992) (Fig. 13.10), except that the “hump” is much smaller. According to Nakajima et al., this is probably because the non-condensable gas in this model contains CO$_2$, which is an infrared absorber, whereas the calculations shown in Fig. 13.10 assume that the background gas is transparent in the infrared. The asymptotic limit on the outgoing infrared flux, termed the SN limit above, is about 310 W m$^{-2}$ (versus 293 W m$^{-2}$ for the gray model). More recent models put the SN limit at 282 W m$^{-2}$ (Goldblatt et al., 2013) to 290 W m$^{-2}$ (Kopparapu et al., 2013; Pierrehumbert, 2010, his Fig. 4.37).

Whereas the gray atmosphere was assumed to be completely transparent in the visible, the non-gray Kasting model atmosphere absorbs and scatters incident solar radiation. As seen from Fig. 13.14(a), the absorbed solar flux $F_S$ first increases slightly then decreases as the surface temperature is raised. The initial increase in $F_S$ is caused by the presence of more water vapor in the model atmosphere. As mentioned in Sec 2.4.2, water vapor has several strong absorption bands in the visible/near-IR region, which absorb some of the incident solar flux. At higher surface temperatures, the atmospheric density increases because of the additional H$_2$O, and this causes
increased Rayleigh scattering. More sunlight is reflected back to space, causing $F_S$ to decrease. The behavior of the solar radiation is easier to visualize if one realizes that $F_S = S_0(1-A)/4$, where $S_0$ is the present solar constant, 1360 W m$^{-2}$ in this particular calculation. Turning this relationship around allows one to calculate the albedo from the following.

$$A = 1 - \frac{4F_S}{S_0} \quad (13.22)$$

The albedo can be seen to dip slightly at first and then increase to an asymptotic value of 0.35 as the surface temperature increases and the atmosphere becomes water-dominated (Fig. 13.14(b)). The dashed line in the figure shows the assumed surface albedo of 0.22. The surface albedo was adjusted in this cloud-free model to yield the correct surface temperature for modern Earth, given the present solar constant.

The planetary albedo of an H$_2$O-dominated atmosphere has also changed in newer models. Goldblatt et al. (2013) calculate an asymptotic value of 0.17 at high surface temperatures, and Kopparapu et al. (2013) calculate 0.19. As explained by Goldblatt et al., the reason why these albedos are much lower than previously found is because the absorption coefficients for H$_2$O are being calculated from the new HITEMP database, which includes weak absorption lines shortward of 500 nm that are not found in the older HITRAN database.

13.4.5 Evolution of Venus’ Atmosphere: the “Moist Greenhouse”

Figure 13.15 summarizes the Kasting (1988) results. The runaway greenhouse threshold is determined by the relationship between surface temperature $T_s$ and a solar flux $S_{\text{eff}}$, normalized to the solar constant. Although $S_{\text{eff}}$ was calculated as a function of $T_s$ in the model, the axes have been inverted in Fig. 13.15 to show $T_s$ as a function of $S_{\text{eff}}$ (solid curve). Again, imagine that the Earth is slowly sliding toward the Sun, $S_\text{eff}$ will of course increase according to the inverse square law, $S_\text{eff} \propto \frac{1}{S_0} \propto (\frac{T_s}{T_{\text{Earth}}})^2$.

As this happens, $T_s$ increases, slowly at first, then more rapidly, as the atmosphere becomes more and more water-dominated. At $S_\text{eff} \approx 1.4$, $T_s$ shoots up sharply from ~600 K to ~1600 K. The critical temperature is 647 K, so any surface temperature in excess of this is too hot to allow liquid water. The reason that $T_s$ levels out around 1600 K is that the moist convective layer is now sufficiently optically thin that radiation from the dry convective region below it can now radiate to space. Note that 1600 K is above the melting temperature for typical silicate rocks, so a planet in this state should have a magma ocean at its surface, similar to that predicted for the accretional models of Matsui and Abe (1986a, b), Abe and Matsui (1988), and Zahnle et al. (1988). This runaway greenhouse threshold occurs at $S_\text{eff} \approx 1.06$ in the newer model of Kopparapu et al. (2013).

Figure 13.15 shows something else, though, that is even more important in terms of planetary habitability. The dashed curve in the figure, which goes with the scale on the right, shows the stratospheric water vapor mixing ratio as a function of $S_{\text{eff}}$. Stratospheric water vapor increases rapidly with surface temperature, as we have already seen in Fig. 13.13(b). When expressed in terms of $S_{\text{eff}}$, the behavior is quite dramatic: the stratosphere goes from being dry to water-dominated as $S_{\text{eff}}$ increases beyond 1.1 (or 1.015 in the Kopparapu et al. (2013) model). Once this happens, the planet is likely to become
uninhabitable, for two reasons. (1) If the planet had oxygen and ozone in its atmosphere, the ozone layer would be destroyed by catalytic cycles involving the byproducts of H₂O photolysis. (2) More importantly, the presence of large amounts of H₂O in the stratosphere would overcome the "cold-trap bottleneck" for hydrogen escape (described in Sec. 5.8.4). Photodissociation of this water vapor, followed by escape of hydrogen to space, could lead to loss of the planet's oceans on time scales of tens to hundreds of millions of years (Kasting, 1988; Kasting and Pollack, 1983; Kasting et al., 1984a). This "water loss" limit on planetary habitability is much more stringent than the runaway greenhouse limit. According to the inverse square law, the (non-gray) runaway greenhouse limit corresponds to an orbital distance of \( \frac{1}{(1+1.4)^{1/2}} \approx 0.85 \) AU in the Kasting (1988) model. By comparison, the water loss limit corresponds to a distance of \( \frac{1}{(1+1.1)^{1/2}} \approx 0.95 \) AU in that model. In the Kopparapu et al. (2013) model, the corresponding limits are 0.97 AU and 0.99 AU. In reality, these limits derived from 1-D models are probably too pessimistic, because clouds could provide negative feedback and because real tropospheres are not fully saturated.

A 3-D climate model has tested how clouds may affect the runaway greenhouse limit (Leconte et al., 2013). As mentioned earlier, these authors do not predict a wet stratosphere because their cold trap temperatures are very low. However, they do compute a runaway greenhouse limit of 0.95 AU, or \( S_{\text{eff}} \approx 1.1 \). Their model includes H₂O absorption coefficients from HITEMP, so it should in principle give similar results to Kopparapu et al. (2013) except for 3-D effects. Decreased relative humidity is indeed a stabilizing influence in this model, causing the runaway greenhouse limit to move in slightly. Surprisingly, clouds give positive feedback in this model, contrary to previous predictions (Kasting, 1988). It remains to be seen whether other 3-D climate models produce the same result.

What do these calculations imply for the evolution of Venus' atmosphere? Venus' orbital radius is 0.723 AU, so the solar flux at Venus' orbit today is 1.91 times that of Earth. Taken at face value, this should put present Venus well into the runaway greenhouse regime, according to any of the published 1-D or 3-D calculations. But the solar flux in Venus' early history was about 30% lower, yielding \( S_{\text{eff}} \approx 1.34 \). That is below the (older) runaway greenhouse limit, but well above the (older) water loss limit (\( S_{\text{eff}} = 1.1 \)). This led Kasting (1988) to conclude that early Venus should have been in a moist greenhouse state in which liquid water remained present at the surface while at the same time water was being rapidly depleted by photolysis and hydrogen escape. The newer calculations, however, suggest that Venus was always well inside the runaway greenhouse limit, so that it never had liquid water on its surface. This prediction is consistent with other recent studies, which predict that Venus formed a steam atmosphere during accretion, and that this steam atmosphere persisted until almost all of Venus' water was lost (Hamano et al., 2013; Kurosawa, 2015).

Finally, let's consider how Venus' atmosphere and surface might have evolved from an early water-rich state to its present condition. As water was lost, any ocean at its surface - if it existed at all - would have become smaller and smaller until it eventually disappeared. H₂O photolysis and hydrogen escape would have continued, however, until some other process limited it. On Venus, that process was probably the buildup of SO₂ and the formation of the hygroscopic sulfuric acid clouds. These would have locked up H₂O, severely limiting the H₂O vapor pressure above the clouds and thereby shutting down hydrogen escape. SO₂ would have built up in the atmosphere because volcanoes were still active at this early stage in Venus' history - indeed, they may still be active today, as discussed earlier in Sec. 13.2. However, loss of SO₂ to the surface would have become slow once the liquid water disappeared. The same statement holds true for CO₂. Formation of carbonate minerals on Earth requires liquid water. So, once Venus lost its water, volcanic CO₂ should have accumulated, leading to the very dense CO₂ atmosphere that we observe today. And, of course, if water was important to plate tectonics, as suggested in Sec. 13.2, then plate tectonics would have shut down, as well.

One last, but important, question is: what happened to the oxygen that was left behind, as H₂O was lost? This question has several possible answers. If much of the hydrogen loss occurred early in Solar System history when the solar EUV flux was very high, then some of the oxygen may have been dragged off to space along with the escaping hydrogen (see Sec. 5.10.4). Quantifying this loss would require better models of hydrodynamic escape than currently exist. Some oxygen is being lost to space today by interactions with the solar wind (Barabash et al., 2007), although not enough to explain the loss of an entire ocean. Some oxygen could have combined with outgassed CO to form CO₂. How much oxygen could have been lost depends on how much of Venus' CO₂ was initially outgassed as CO. If the Earth is a good analogy (see Ch. 7, eq. (7.12)), the CO should only have been a small amount, ~5% of the outgassed carbon. That is enough to soak up only a small amount of oxygen, less than 1% of the amount contained in water in Earth's oceans.
A more likely sink for the oxygen is crustal oxidation. This has previously been considered to be a major issue for water loss (Lewis and Prinn, 1984, p. 190). Suppose that Venus started off with a 3 km-deep ocean. That is equivalent to \(5 \times 10^7\) g \(H_2O\) cm\(^{-2}\), or \(1.7 \times 10^6\) moles \(H_2O\) cm\(^{-2}\). Assume that crustal density is 2.5 g cm\(^{-3}\), the crust is 10% FeO, and that the FeO is oxidized to magnetite.

\[
3 \text{ FeO} + \frac{1}{2} \text{O}_2 \rightarrow \text{Fe}_3\text{O}_4
\]

(13.23)

Three moles of FeO are required for each mole of water, so the total FeO demand is \(5 \times 10^4\) moles cm\(^{-2}\), or \(3.6 \times 10^6\) g cm\(^{-2}\). Using the crustal density and FeO content from above, this requires oxidizing the topmost 140 km of the crust. That is difficult to do if the crust was solid, as it is on Earth today. The global rate of crustal generation at Earth’s mid-ocean ridges is \(\approx 21\) km\(^3\) yr\(^{-1}\). Earth’s surface area is \(\approx 5 \times 10^8\) km\(^2\), so the average rate of crust generation is \(\approx 4.2 \times 10^{-2}\) km yr\(^{-1}\). If Venus had the same crustal generation rate, and if all of this crust was oxidized, the time required to consume Venus’ leftover oxygen would be 3.3 by. Thus, this mechanism could conceivably have consumed a large amount of oxygen, but the time scale for doing so would probably have been quite long.

The oxygen loss problem largely goes away if the more recent climate models are correct. If Venus’ atmosphere remained in a runaway greenhouse state throughout the water loss process, its surface would have remained molten. Oxygen could thus have been directly taken up by the molten mantle, which would have outgassed much more quickly than Earth’s mantle does today (Hamano et al., 2013; Kurosawa, 2015). If so, then Venus-like planets around other stars might not show evidence of \(O_2\) buildup. So, observations of young exoplanets may eventually provide a test for this hypothesis.

### 13.5 Stability of Venus’ Present Atmosphere

Other researchers have proposed alternative explanations for how Venus’ atmosphere evolved. Bullock and Grinspoon (1996) suggested that the atmospheric pressure on present Venus is buffered by chemical interactions between the atmosphere and the planet’s surface. In their model, atmospheric \(CO_2\) was assumed to be in equilibrium with carbonate minerals in Venus’ crust. Specifically, they considered the following reaction.

\[
\text{CaSiO}_3 + \text{CO}_2 \leftrightarrow \text{CaCO}_3 + \text{SiO}_2
\]

(13.24)

Here, \(\text{CaSiO}_3\) is the mineral \textit{wollastonite}, \(\text{CaCO}_3\) is calcium carbonate (limestone), and \(\text{SiO}_2\) is silica, or quartz.

This reaction is called the \textit{wollastonite equilibrium}, or sometimes the \textit{Urey equilibrium}, as Harold Urey proposed this long ago as a buffer for atmospheric \(CO_2\) on Earth. According to Fogley (2012, 2014), the equilibrium \(CO_2\) partial pressure (in bar) for this reaction is given by

\[
\log_{10} p_{CO_2} = 7.97 - \frac{4456}{T}
\]

Equation (13.25) predicts that \(p_{CO_2} \approx 88\) bar at 740 K, which is close to the observed surface pressure. So, this does indeed suggest that the Urey equilibrium might apply. However, the consequences of adopting this assumption are probably unphysical, because the equilibrium defined by eqs. (13.24) and (13.25) is unstable: carbonates are favored at lower temperatures, whereas gaseous \(CO_2\) is favored at higher temperatures. Thus, the hotter the surface gets, the more \(CO_2\) goes into the atmosphere, and this makes the surface still hotter. Conversely, if the surface cools, atmospheric \(CO_2\) goes into the rocks, making the surface still colder.

This is a classic positive feedback loop, similar to the one involved in the runaway greenhouse. Hence, if this model were correct, Venus’ surface pressure would be poised precariously at an unstable equilibrium point. This seems unlikely, however, because the surface pressure ought to “run away” in one direction or the other. Furthermore, a simpler explanation is available: Chemical reaction rates between gases and dry rocks are exceedingly slow. (That is why the hydrated silicates predicted by John Lewis’ equilibrium condensation model should not have actually formed.) Such reactions can be further inhibited by the buildup of weathering products on the surfaces of mineral grains. Once a silicate grain becomes coated with calcium carbonate, no further reaction with atmospheric \(CO_2\) should occur. On Earth, the products of weathering are removed by liquid water, but on Venus this would not happen. So, it seems simpler to assume that surface interactions are indeed slow and that Venus’ atmosphere has served as a simple collector for \(CO_2\) that was released from its interior. If so, then the near coincidence between the surface pressure and the \(CO_2\) partial pressure predicted from the Urey equilibrium must be just that—a coincidence.

Control of atmospheric \(SO_2\) by surface–atmosphere interactions is much more plausible, as \(SO_2\) is present in much lower concentrations (\(\approx 150\) ppm), and so less surface rock would be needed to control its concentration. Subsequently, Bullock and Grinspoon (2001) suggested that \(SO_2\) in Venus’ atmosphere is buffered by the following equilibrium reaction.
\[ \text{SO}_2 + \text{CaCO}_3 \rightarrow \text{CaSO}_4 + \text{CO} \]  
(13.26)

Here, CaSO\textsubscript{4} is the mineral \textit{anhydrite}. This reaction could proceed both ways (as implied by thermodynamic equilibrium) if both calcite and anhydrite were present on Venus’ surface. The equilibrium SO\textsubscript{2} concentration predicted from this reaction, though, is only about 1\% of the observed SO\textsubscript{2} concentration in the atmosphere (Hashimoto and Abe, 2005), and the predicted lifetime of SO\textsubscript{2} with respect to this reaction is relatively short, only 20 million years. Hence, if this reaction occurs, it probably goes only in one direction, from left to right, and continued volcanic outgassing of SO\textsubscript{2} right up to the present day would be needed to maintain its atmospheric concentration.

Alternatively, Hashimoto and Abe (2005) proposed that Venus’ SO\textsubscript{2} is buffered by reaction with pyrite, FeS\textsubscript{2}. The reaction in this case is as follows.

\[ 3\text{FeS}_2 + 16\text{CO}_2 \rightarrow \text{Fe}_2\text{O}_4 + 6\text{SO}_2 + 16\text{CO} \]  
(13.27)

Fe\textsubscript{2}O\textsubscript{4} is the mineral \textit{magnetite}. As discussed in Sec. 10.3, pyrite is one of the reduced minerals whose presence (in detrital form) is considered to be an indicator of low O\textsubscript{2} levels on the early Earth. Although we do not know the exact O\textsubscript{2} concentration in Venus’ lower atmosphere, it is thought to be well below the upper limit of 0.3 ppm that is present above the cloud tops (Mills and Allen, 2007; Trauger and Lunine, 1983). So, this reaction is plausible, and it predicts an equilibrium atmospheric SO\textsubscript{2} concentration close to the various observations discussed in Sec. 13.1.1. Pyrite might also account for the anomalously high radar reflectivity of high-altitude regions of Venus’ surface (Klose \textit{et al.}, 1992). So, it may be that the SO\textsubscript{2} in Venus’ atmosphere is actively controlled by surface interactions, even if CO\textsubscript{2} is not.

### 13.6 Implications for Earth and Earth-Like Planets

Although Venus is an interesting planet in its own right, more interesting to us is what we can learn from Venus about the limits of climatic stability on Earth and on other Earth-like planets that may exist elsewhere in the galaxy. The latter topic will be discussed at some length in Ch. 15. Below, we look at how the runaway/moist greenhouse theory might apply to our own planet Earth.

#### 13.6.1 Can CO\textsubscript{2} Cause a Runaway Greenhouse on Earth?

A question that has arisen more than once in the context of the modern global warming problem is whether or not CO\textsubscript{2} increases could create a runaway greenhouse on present Earth. Kasting and Ackerman (1986) concluded that the answer was “no.” These older calculations are shown by the solid curves in Fig. 13.16. In the Kasting and Ackerman model, Earth’s albedo increases rapidly as CO\textsubscript{2} is added to the atmosphere because of the high Rayleigh scattering cross section of CO\textsubscript{2} (about 2.5 times that of air) (Fig. 13.16(a)). Consequently, the calculated surface temperature never exceeds the critical temperature for water, 647 K, and so the ocean never boils (Fig. 13.16 (b)). People often mistakenly assume that the oceans would boil at 373 K, or 100 °C, as this is the normal boiling point for water. But the boiling temperature is a function of the overlying atmospheric pressure: water boils at 100 °C today because the corresponding saturation vapor pressure is just over 1 bar. But if the entire planetary surface was at 100 °C, the atmospheric pressure would be 2 bar (1 bar N\textsubscript{2}/O\textsubscript{2} plus 1 bar H\textsubscript{2}O), and the ocean would not boil.
This problem has been revisited because of the newer HITTEMP absorption database for H₂O mentioned earlier in the chapter. Stronger absorption of incoming solar radiation in the visible causes a warm Earth to have a lower albedo, thereby making the climate more susceptible to runaway (Goldblatt et al., 2013). These authors argue that a CO₂ increase up to 100 PAL might trigger a runaway. But Ramirez et al. (2014b) have challenged their conclusion with results shown in Fig. 13.16 (dashed curves). In these 1-D calculations, surface temperature increases sharply to over 500 K at a CO₂ pressure of 6×10⁻⁶ bar, or ~12 PAL. This sharp uptick in surface temperature is caused by an assumed relative humidity feedback that was present in the original Kasting and Ackerman (1986) model, as well. Its effects are magnified in the new model, however, because of the stronger absorption of sunlight by H₂O. A second reason why Ramirez et al. find higher surface temperatures is that their model also predicts an increase in surface relative humidity as the climate warms (Fig. 13.17). By contrast, Kasting and Ackerman assumed a fixed surface relative humidity of 0.8. Actual surface relative humidity must increase at high surface temperatures in order to balance the surface energy budget. (If the surface relative humidity is too low, evaporation will remove energy from the surface ocean faster than solar heating can provide it (Ramirez et al., 2014b).)

This problem is admittedly not well handled by 1-D climate models. Such models can be used to estimate surface relative humidity, as discussed above, but they cannot calculate vertical relative humidity distributions self-consistently. A recent 3-D simulation of CO₂ increases up to 256 PAL by Russell et al. (2013) is also shown in Fig. 13.16(b). Their results agree more closely with the old Kasting and Ackerman (1986) calculations. These authors make no mention of HITTEMP, however, and so they presumably used older absorption coefficients for H₂O. Finally, Popp et al. (2016) find that CO₂ can drive the planet into a moist greenhouse even with the old HITRAN coefficients, likely because of positive cloud feedback in their GCM.

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3 One has to be careful when measuring atmospheric gas inventories in terms of pressure because, contrary to what one would expect based on Dalton’s Law, the partial pressure of a gas in a planetary atmosphere does depend on the other gases that are present. If a light gas is added to a heavier one, for example, it mixes with the heavier gas, increasing the pressure scale height (eq. (1.12), \(H = \frac{kT}{m g}\), where \(m\) is lower), causing the heavier gas to spread away from the planet’s surface, thereby lowering its partial pressure. The pressure depicted on the horizontal axis of Fig. 13.16 is the pressure that CO₂ would exert if it was present by itself.
weathering will win out, and atmospheric CO$_2$ should begin to decrease.

The future evolution of the Earth system has been simulated by several groups using coupled climate/geochemical cycling models (Caldeira and Kasting, 1992a; Franck et al., 1999; Lovelock and Whitfield, 1982; Ramirez et al., 2014b; Von Bloh et al., 2003). In the earliest model, atmospheric CO$_2$ was predicted to fall below 150 ppm about 100 million years from now. A CO$_2$ concentration of 150 ppm represents a critical level, called the CO$_2$ compensation point, below which C$_3$ plants cannot live, because they respire faster than they photosynthesize. (The name C$_3$ refers to the length of the carbon chain that is created during the initial step of photosynthesis.) C$_3$ plants account for about 95% of all plants on Earth, including trees and most agricultural crops. Hence, Lovelock and Whitfield concluded that Earth might be able to support an active biosphere for only another 100 million years.

Caldeira and Kasting (1992a) revisited this calculation by using an improved climate model and a different set of assumptions about how weathering rates vary with temperature. The results are shown in Fig. 13.18(b). Their model was based on older absorption coefficients for H$_2$O and CO$_2$, but the results are not greatly affected compared to using newer coefficients, because surface temperatures remain relatively low during the next billion years. The model included the so-called terrestrial biological pump, which enhances pCO$_2$ in soils through root respiration and decay of organic matter. In the calculation shown, C$_4$ plants like corn and sugar cane are assumed to dominate productivity once atmospheric CO$_2$ concentrations decline below 10 ppm. These plants go extinct about 900 million years from now in the simulation. And even C$_3$ plants last for 500 million years — five times longer than predicted by Lovelock and Whitfield. Of course, photosynthetic life could even last longer if it evolves more efficient ways of fixing carbon, which has a precedent in the evolution of C$_4$ plants.

In the Caldeira and Kasting (1992a) model, once atmospheric CO$_2$ declines below 10 ppm, its greenhouse effect is greatly diminished, its stabilizing effect on climate vanishes, and the surface temperature climbs rapidly over the next few hundred million years (Fig. 13.18(b)). Unlike the CO$_2$-induced greenhouse described earlier, water should be rapidly lost during this process because the stratosphere will become water-dominated and the warming will be permanent. It might take a few hundred million years to lose the oceans, but the Earth will eventually be left completely dry, as Venus is today, unless descendants of humans (if they exist) somehow intervene. Indeed, this should be the fate of any Earth-like planet that absorbs a stellar flux more than about 10% higher than Earth does today.

To sum up, Venus today is hot and inhospitable to life. The planet may well have had surface liquid water early in its history, but it lost that water through a runaway or moist greenhouse. Whether a terrestrial planet evolves more like Venus or more like Earth depends primarily on the amount of energy it absorbs from its parent star, and to a lesser extent on how much CO$_2$ its atmosphere contains. These inferences will be used in Ch. 15 to help delineate the region around a star in which Earth-like planets can exist. Indeed, it seems reasonable to predict that that one day astronomers will observe an early Venus-like exoplanet shedding its water under the intense glow of extreme ultraviolet light from its young parent star. Studying such a phenomenon would help confirm the theory of atmospheric evolution presented in this chapter.