9

The Effect of the Greenhouse Gases

The Greenhouse Gases

Today, the Earth's atmosphere is primarily composed of nitrogen, oxygen, and argon, which constitute the primary gases of its atmosphere. Other gases present in the Earth's atmosphere are often referred to as trace gases, among which are the group of gases recognized as the *greenhouse gases.* At the Earth's surface, the atmosphere also includes a variety of trace amounts of human introduced chemical compounds. Also many substances of natural origin may be present in miniscule amounts, e.g., as aerosol in an unfiltered air sample, including dust of mineral and organic composition, pollen and spores, sea spray, and volcanic ash. In some industrial areas, various industrial pollutants also may be present as gases or aerosol, such as chlorine (elemental or in compounds), fluorine compounds and elemental mercury vapor. Sulfur compounds, e.g., hydrogen sulfide (H_2S), and sulfur dioxide (SO_2), which may be derived from natural or industrial sources.

The term *greenhouse gas*, GHG, used in this book, is defined as a gas in the Earth's atmosphere that absorbs and emits radiation within the thermal infrared range. This process of absorbing energy from the Sun is the fundamental effect of what is referred to as the *greenhouse effect*. The primary greenhouse gases in Earth's atmosphere are water vapor, carbon dioxide, methane, nitrous oxide, chlorofluorocarbons (CFCs) and hydrofluorocarbons (incl. HCFCs and HFCs). Some people also include ozone as a greenhouse gas; however, due to its significance, it has been separately discussed in Chapter 11.

The Classic *Greenhouse Effect*

The *greenhouse effect*, ΔT is the difference between an average planet's surface temperature, T_s, and its effective surface temperature, T_e, at which this planet can be seen from outer space:

$$\Delta T = T_s - T_e \qquad \text{(Eq. 9.1)}$$

As average surface temperature for Earth is approximately 288 K or +15 °C, and for Earth under the classical variant where the precession angle, $\psi = 0°$, $T_e = 255$ K or −18 °C, the greenhouse effect on Earth is currently recognized as 33 °C. However, in consideration of Earth's current precession angle, $\psi = 23.44°$ and $T_e = 263.5$ K (or −9.5 °C) the greenhouse effect is much lower, $-\Delta T = 24.5$ °C.

Figure 9.1 illustrates how energy from the Sun is reflected and/or absorbed and then radiated from the Earth's surface and atmosphere. The absorption of energy from the Sun's light waves by the greenhouse gas molecules, lengthens the light wave as the energy is absorbed by the gas, which is then emitted from the gas molecule with a longer wave length. In general, shorter electromagnetic waves carry more energy than longer ones. A portion of this energy is absorbed by the greenhouse gas molecules in the Earth's lower atmosphere, increasing the rate of vibration (temperature) of molecules. This process of the greenhouse molecules absorption of energy, increasing the vibration (temperature) of the molecules, is referred to as the *greenhouse effect*.

When the concentration and/or pressure of the greenhouse gases in the atmosphere change, the amount of energy that can be absorbed by the atmosphere also changes. However, changing the concentration of a gas in the atmosphere can also change the partial pressure of that gas component, which contributes to the total atmospheric pressure. Eq. 2.26 establishes that changes in pressure affect the absorption of energy by that

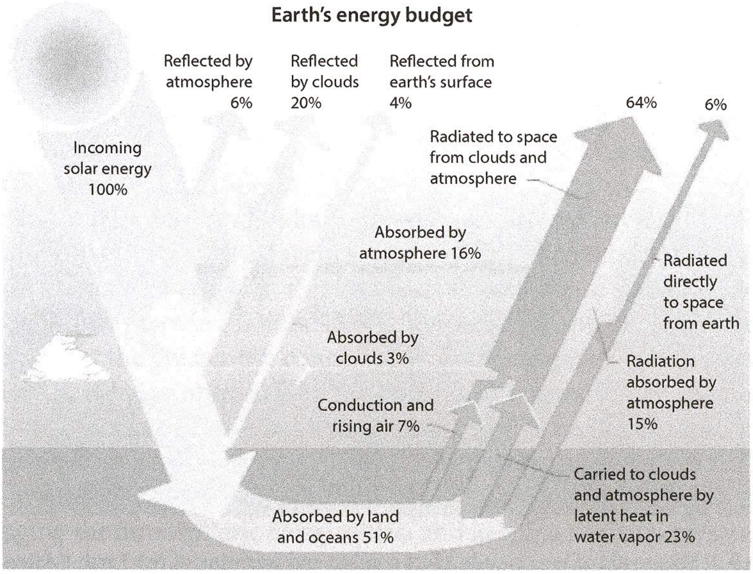

Figure 9.1 Schematic illustration showing the distribution of energy carrying light waves from the Sun to the Earth. (After Lightle, 2008.)

gas. In summary, increasing the gas concentration of carbon dioxide, can result in less absorption of energy if the atmospheric pressure remains the same. Figure 9.2 demonstrates how additional cloud cover can decrease the Earth's surface temperatures by reflecting more (albedo) energy carrying wave away from the Earth's surface. An excellent example of this albedo effect occurs as a result of volcanism where ash is injected into the atmosphere, reflecting more energy from the Earth, resulting in the cooling of the Earth.

The Earth's radiation budget is a concept that Lightle (2008) presented which helps us understand the quantity of energy that the Earth receives from the Sun, and how much of that energy the Earth absorbs and then radiates back to outer space (see Figure 9.1):

The Greenhouse Gases

The dominant atmospheric gases that absorb energy include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (NO_2), methane (CH_4), water vapor (H_2O), ozone (O_3) and any fluorocarbons. The details of what wavelengths each gas can absorb is shown in Figure 9.3. Also shown in this figure is the ability of the whole atmosphere (all gases) to absorb specific wave

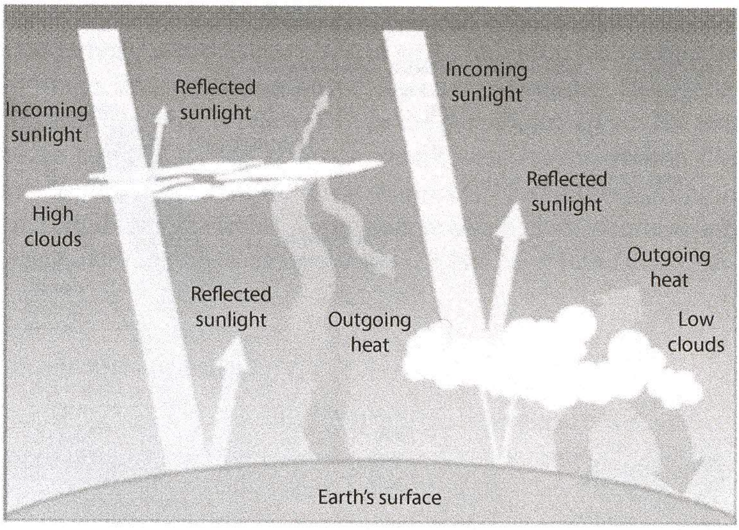

Figure 9.2 Schematic of how clouds affect cooling and warming of the Earth. (After NASA, 2017.)

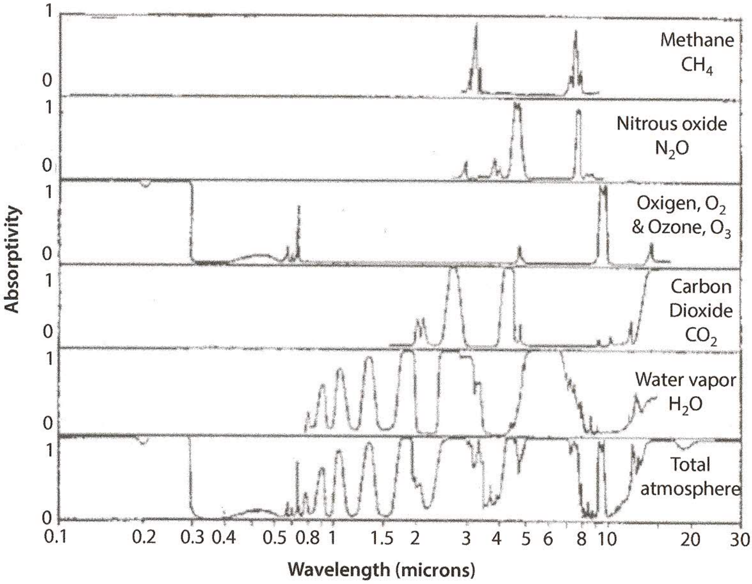

Figure 9.3 Wave length radiation absorptivity for various gases of the atmosphere. An absorptivity of zero means no absorption, while a value of one means complete absorption. The dominant gas absorbers for infrared radiation are water vapor and carbon dioxide, oxygen and ozone. (After J. N. Howard, 1959: Proc. I.R.E. 47, 1459; and R. M. Goody and G.D. Robinson, 1951: Quart. H. Roy. Meteorol. Soc. 77, (153); in: http://www.meteor.iastate.edu/gccourse/forcing/images.html.)

lengths. The dominant absorbers of infrared radiation are water-vapor, carbon dioxide, oxygen and ozone. These gases in the atmosphere are not pollutants as identified by some, but are natural and without them life on the Earth would not be possible.

Some of the radiated heat released by greenhouse gases reaches the Earth's surface, along with heat from the Sun that has penetrated the atmosphere. Both the solar and radiated energy are absorbed by the Earth's surface and its atmosphere and reemitted at longer wave lengths; some of this energy from waves reflected from the Earth's surface are again reabsorbed by greenhouse gases in the atmosphere, perpetuating the cycle. It is thought by some that the greater the concentration of these gases will always result in more heat being absorbed by the Earth and, consequently, the warmer the Earth's surface. Eq. 2.26 demonstrates that if the total atmospheric pressure increases, more heat will be absorbed by the atmosphere and, likewise, if the total atmospheric pressure decreases less heat will be absorbed. Changing the atmospheric composition and keeping the total pressure the same by the addition of a gas with a lower partial-pressure will lower the Earth's ability to absorb energy or its temperature.

According to many scientists, without the greenhouse effect, which smooths out the atmospheric temperature extremes, the Earth's surface temperature would be 5 °F rather than 59 °F. The greenhouse effect has been going on, throughout the Earth's history for the past 4.5 BY. The French mathematician, Joseph Fourier, first recognized the greenhouse effect in 1824 (Mester, 1996). At the end of the nineteenth century, Arrhenius (1896) presented a hypothesis on heating of the atmosphere by increasing the content of carbon dioxide, ignoring the effect it would have on the total atmospheric pressure. Even though it is incorrect, for a long time his hypothesis has been accepted as factual. Unfortunately, it has been incorrectly used to predict disastrous effects by increasing the absorption of heat in the atmosphere, e.g., carbon dioxide. This never verified concept is still believed by many today, even though it has been shown to be wrong (Greenhouse Effect, 1989; Green Peace Report, 1993; Budyco, 1997).

Along the same line, some environmentalists have erroneously predicted that increasing the concentration of greenhouse gases will accelerate climatic change, earthquakes, heavier storms, etc., and that the global surface temperature could rise from 1 to 4.5 °F over the next 50 years, and 2.2 to10 °F in 100 years, e.g., Kyoto Protocol (1997), without any creditable scientific proof. They predict that this proposed rise in temperature would increase evaporation, which, in turn, will increase the global precipitation and more intense rainstorms around the world would occur. These proposed elevated global temperatures would increase melting of Arctic and

Antarctic ice, resulting in a rise of the Earth's sea levels over 0.6 m, flooding the coastal areas over the next 50 years. All these disastrous climatic changes have been attributed to increasing the greenhouse gas concentration in the atmosphere without scientific support or understanding of thermodynamics. Therefore, over the past 50 years, their dire climatic predictions have never happened. Yet today we see many individuals making similar unfounded claims, blaming any recent climatic problems on the increase of anthropogenic carbon dioxide emissions without verification. Serious analyses and critique of these fallacious environmental predictions have been made, based upon geologic history and scientific analysis, by Robinson *et al.* (1998), Sorokhtin (2001a, b), and Khilyuk and Chilingar (2003, 2004, 2006).

An examination of many of these theories shows a lack of understanding of thermodynamics. Some of these numerical calculations and several climatic predictions have often been based on intuitive models, using poorly defined parameters (Greenhouse Effect, 1989). Examination of these environmental models reveals inherent uncertainties in the model parameters (several models contained at least 30 such parameters) making the numerical solution of the problem itself questionable.

Our investigation of the greenhouse effect is based on the scientific relationships of the physical parameters, including the description of the mass and heat transfer within the atmosphere, i.e., synergetic approach (Haken, 1980, 1983; Prigozhin and Stengers, 2003). Many of these future predictions of the Earth's temperature, ignoring the thermodynamics of the atmosphere over the past 40 years, have proven to be incorrect. Today, globally there are polar ice caps and shrinking and growing glaciers, even though several of these earlier predictions forecast that they all would be melted by today.

Understanding the Greenhouse Effect

The Earth's atmosphere is an example of an open dissipative system, which can be described by nonlinear equations of mathematical physics. This permits one to assume that the organization of physical fields and the formation of stable thermodynamic structures can be defined for the Earth's atmosphere, considering the time-space scale as determined by the parameters of the phenomenon. One may use significant and reliable parameters of the atmosphere and the primary characteristics of the processes driving the Earth's climate to construct a climatic model, e.g., one may use such general parameters as the total mass of atmosphere, its thermal capacity, and the averaged energy of solar irradiation. In addition, one must take into consideration, the existence of a strong negative feedback between the spherical *albedo* (albedo: the fraction of solar radiation that is reflected into space) of Earth and its averaged surface temperature. In such an approach, however, the localized details in the description of the greenhouse effect are lost, because the constructed model becomes one-dimensional and averaged over the entire Earth.

In many cases, however, this general approach possesses definite advantages, as one obtains an analytical and unambiguous solution of global problems of the entire planet, e.g., the influence of the composition of atmosphere on the total magnitude of the greenhouse effect. In addition, a constructed general model can be specified, by adding additional parameters and local variables. In the general model, one can incorporate the crucial factors that can further improve the model, e.g., (1) the latitude of a certain locality; (2) inclination of the axis of Earth's rotation to the ecliptic plane; (3) the precession of Earth's and Sun's axis; (4) inflow of additional heat with the air flows (cyclones); (5) the reflection capacity of snow cover, and (6) etc. In such a way, one can construct a three-dimensional or even four-dimensional model (the fourth dimension is the time) of the greenhouse effect. The major factor determining the climate of the Earth is the quantity of solar radiation absorbed by Earth's atmosphere. Also to be considered is the Earth's atmosphere, composition, pressure, and thermal capacity (Sorokhtin, 1990, 2001a, b; Sorokhtin and Ushakov, 2002).

The Greenhouse Effect

The average surface temperature for Earth is ≈288 °K or 15 °C, and its effective radiation temperature is determined by the classic Stefan-Boltzmann law:

$$T_c^4 = \frac{(1-A)S}{4\sigma}, \qquad \text{(Eq, 9.2)}$$

where $\sigma = 5.67 \times 10^{-5}$ erg/cm$^2 \cdot$ s $\cdot$ °C^4 is the Stefan-Boltzmann constant; S, is the solar constant at the distance of the Earth from the Sun ($S = 1.367 \times 10^6$ erg/cm$^2 \cdot$ s); A is the albedo, which is mostly due to Earth's cloud cover ($A \approx 0.3$). According to Eq. 9.2, the effective temperature, T_e, is equal to 255 K (or 18 °C). Therefore, the present-day greenhouse effect for the Earth would be equal to 33 °C.

Applying the Stefan-Boltzmann law to evaluate the heat transfer in the atmosphere: (1) the heat transfer by radiation dominates only in the upper diffuse layers of the atmosphere, e.g., stratosphere, mesosphere, and thermosphere; (2) the heat transfer in the troposphere, the lowest and denser layer, occurs mostly by convection (Sorokhtin, 2001a, b). In the Earth's atmosphere, where the air pressure exceeds 0.2 atm, the heat transfer by convection is dominant. When the temperature of a given mass of air increases, its volume also increases proportionally. This is the model of a system that defines the Earth's climatic atmospheric system, but it is also one that recognizes cooling and heating by convection in the troposphere, rather than a model dependent upon radiation.

A significant conclusion from this observation is that the temperature distribution in the Earth's troposphere must be close to adiabatic, as when the air mass warms and compresses while moving down and cools while expanding and rising. This does not necessarily imply that at any instant, distribution of temperature must be totally adiabatic. There are several processes of heat transfer occurring in the Earth's atmosphere: radiation, convection and conduction.

The adiabatic temperature distribution is determined by the atmospheric pressure, *p*, and by the effective thermal capacity of atmosphere:

$$\frac{pV}{T} = \text{constant (ideal gas law)}, \qquad \text{(Eq. 9.3)}$$

as the volume never changes. The thermal capacity considers its additional heating capability as a result of the absorption of infrared radiation of the Earth's surface by the greenhouse gases and heat of condensation of water vapor in the troposphere. For an adiabatic process, the temperature of gas is a function of pressure that can be presented in the following form (Landau and Lifshits, 1979):

$$T = Cp^{\alpha}, \qquad \text{(Eq. 9.4)}$$

where C is a constant, which can be estimated using the experimental data, $\alpha = (\gamma - 1)/\gamma$; $\gamma = c_p/c_v$ and c_p and c_v are the specific heats of gas at constant pressure and constant volume, respectively. For triatomic gases, CO_2 and H_2O, $\gamma = 1.3$ and $a = 0.2308$, whereas for the diatomic gases, N_2 and $O_{2,}$ $\gamma = 1.4$ and $a = 0.2857$. Because of condensation of water vapor m troposphere, which process emits heat, the adiabatic exponent, a, decreases, e.g., the average value of this parameter for the humid and heat-absorbing troposphere, $a = 0.1905$, whereas for the dry air, $a = 0.2846$ (Sorokhtin and Ushakov, 1999).

Condensation of water vapor in the troposphere creates cloudiness, which is the primary factor that determines the Earth's albedo, *A*. This process gives rise to a strong negative feedback between the near-surface and radiation temperatures for the Earth, stabilizing the temperature regime of the troposphere. A rising surface temperature increases the water evaporation and the resulting cloudiness in the troposphere, which increases the albedo of planet and the reflection capacity of Earth's atmosphere. The portion of solar radiation reflected to space increases, decreasing the heat (energy) supplied to the Earth. As a result, the average temperature of Earth's surface decreases.

In any system, a negative feedback leads to a linear dependence of the system's output on the system's input. This is a universal property of systems with negative feedbacks. This property manifests itself in various systems, e.g., the centrifugal regulator of James Watt in a steam engine or the thermal (self-organizing) system of atmosphere.

In the Earth's atmospheric thermal system, the input is the temperature T_{gb}, which is determined by solar radiation (for the distance of Earth from the Sun) whereas the output is the average surface temperature, T_s; for the Earth, the temperature $T_{gb} = 288.2$ K or 15 °C. Thus, the average surface temperature, T_s; is a linear function of T_{gb}, which characterizes the solar radiation at the distance from Earth to Sun. This enables one to determine the average temperature, T, at any point in the troposphere with pressure, p:

$$T = T_{gb}\left(\frac{p}{p_o}\right)^{\alpha}. \qquad \text{(Eq. 9.5)}$$

In Eq. 9.4, C and α are defined for the temperature $T_{gb} = 288.2$ K and the atmospheric pressure at sea level, one can rewrite Eq. 9.5 in the following form:

$$T_{gb} = Cp_o^{\alpha}. \qquad \text{(Eq. 9.6)}$$

In Eq. 9.6, the constant C is equal to 288.2. One can then define the average temperature at any elevation in the troposphere by the following exponential function at $p > 0.2$ atm:

$$T = 288.2\left(\frac{p}{p_o}\right)^{\alpha}. \qquad \text{(Eq. 9.7)}$$

It is noteworthy that in the formula,

$$T_{bg} = \left(\frac{S}{4\sigma}\right)^{\frac{1}{4}} \qquad \text{(Eq. 9.8)}$$

for computing the temperature of an *absolutely black-body*, the solar constant S is divided by 4, because the area of Earth's disk insolation is four times lower than the total illuminated area of the Earth. Eq. 9.8 is valid only if the axis of rotation of the planet is strictly perpendicular to the ecliptic plane and the angle of precession, ψ, is equal to zero.

Effect of the Precession Angle

In our solar system, the angle of inclination of the equatorial plane to the ecliptic plane is not equal to zero for either the Sun or the Earth and it changes seasonally with time. Therefore, each of the Earth's polar regions is insolated for half a year. The other half of a year, it is deprived of the influx of solar energy. When one of the polar regions is insolated, the other lies in the shadow of the Earth's body and cannot receive solar energy. The remainder of the Earth's surface receives its portion of solar energy on a regular basis and, consequently, Eq. 9.8 is valid for the calculation of temperature. Therefore, in computing the average temperature of an *inclined* planet at high latitudes (polar regions) one needs to divide the solar constant by 2 (not by 4). In addition, one must take into consideration the spherical shape of polar region. As a result, the solar constant, S, in Eq. 9.8 must be divided by a number, N, which lies between 2 and 4. Considering all the above and that the precession angle is relatively small, one can develop the following equation (see Chapter 2 for derivation)) for the distribution of average temperature in the troposphere,

$$T = \left[\frac{S}{\frac{4\sigma\left(\left(\frac{\pi}{2}\right)-\psi\right)}{\left(\frac{\pi}{2}\right)} + 2\psi\left(\frac{\pi}{2}\right)\left(\frac{2}{(1+\cos\psi)}\right)} \right]^{\frac{1}{4}} \left(\frac{p}{p_o}\right)^{\alpha} \qquad \text{(Eq. 2.25)}$$

where ψ is the Earth's precession angle; p is the atmospheric pressure at a given altitude, e.g., 0.2 atm $< p < P_o$), $P_o = 1$ atm, and $\alpha = (c_p/c_o)$ where c_p and c_o are the specific heats of atmosphere at constant pressure and constant volume, respectively

Today, the Earth's precession angle is $\psi = 23.44°$ *and* the Earth's average surface temperature is $T_s \approx 288.2$ K at sea level. This implies, that the average surface temperature of Earth, considering the Earth's precession, is equal to the efficient temperature of an effectively *gray-body* at the average distance of the Earth to the Sun, ($T_s = T_{gb}$). Thus, the average temperature of contemporary troposphere at any altitude, where $p > 0.2$ atm, is equal to:

$$T = T_{gb}\left(\frac{p}{p_o}\right)^{\alpha} = 288.2\left(\frac{p}{p_o}\right)^{\alpha} \qquad \text{(Eq. 9.9)}$$

If the axis of the Earth's rotation were perpendicular to the ecliptic plane, then, at $p = 1$ atm, the average surface temperature would be equal to 278.6 °K, the temperature of *absolutely black-body* at the distance from Earth to Sun. This difference in temperature for $y \approx 23.44°$ and $\psi = 0°$ approaches 9.6 to 10 °C. Consequently, the present-day radiation temperature, considering the precession angle, for the distance from the Earth to the Sun is equal to 263.6 K and not 255 K. Under the classical concept, the precession angle, $\Psi = 0$. The Earth's effective temperature, T_e, is 255 °K or −18 °C. The greenhouse effect for the Earth is currently accepted at +33 °C and a precession angle value of $\Psi = 23.44°$. Correcting the precession angle to $\psi = 0$, the effective temperature would be $T_e = 263.5$ °K or −9.5 °C. This gives a corrected greenhouse effect for the Earth that is much lower, $\Delta T = 24$ °C.

The greenhouse effect is a real phenomenon, although the term itself is unfortunate, misunderstood, and often physically wrong. Common belief is that the Earth's atmosphere, containing the so-called greenhouse gases, weakly absorbs energy from the short-wave solar radiation from the Sun, of which ≈51% (see Figure 9.2) reaches the Earth's surface, but impedes the long-wave (thermal) radiation that is reflected from the Earth's surface, thereby significantly decreasing the Earth's energy loss into the outer space. This has been often accepted as the main cause of atmospheric temperature increase. Thus, it is often felt, the higher the concentration of greenhouse gases in the atmosphere, those gases that absorb the thermal radiation, the greater the heating of the atmosphere. The effect of atmospheric heating under the influence of absorption of energy by the greenhouse gases of heat radiation coming from the Earth's surface was called the greenhouse effect.

By analogy for greenhouses covered with glass, the glass allows the visible light of the electromagnetic spectrum to pass through the glass carrying energy; however, when some of the energy of the light ray is absorbed by the surface that it falls on, the ray is then emitted (radiated) as IR radiation which now has a longer wave length (due to loss of energy) and can no longer pass back through the glass, entrapping the energy within the greenhouse. However, the consequence of the greenhouse effect in the Earth's atmosphere is different. The difference is that in the case of the greenhouse, the air is isolated from the air outside the greenhouse which prevents a convective mixing with the outside air. As a result, as soon as greenhouse windows are opened and the connection to the air outside space is restored, air convection immediately cools the inside of the greenhouse and any greenhouse effect vanishes from the greenhouse.

Convective Heat Transfer in Troposphere

The domination of the convective component in the heat loss by the troposphere has a natural explanation. Upon absorption of energy by the greenhouse gases, the light wave itself vanishes as its energy passes to the oscillatory motions of gas molecules, i.e., to heating of the irradiated gas volume. The heated gas expands and becomes less dense, the air mass then rises toward the stratospheric strata (by buoyancy) where the energy (heat) is dispersed through convection. Upon cooling, this gas in the atmosphere then descends, restoring the air to the previous or even a lower temperature. An analogous situation occurs with heating air containing moisture which condenses within it. The rate of convection (removal of heat from air) is always many orders of magnitude greater than the diffusion rate of heat transfer.

Effect of Water Vapor on Heat Transfer

Water vapor is a greenhouse gas that plays an important part in the temperature distribution within a cloudy troposphere. The temperature distribution, below the cloud cover (see Figure 9.2) may be defined by the humid-air adiabatic curve, and above it, by a dry-air adiabatic curve. The temperature distribution within the cloud cover depends upon the energy released during the moisture condensation process. The average mass of water vapor in the atmosphere, m_u, may be determined from the average atmospheric moisture heat absorbing capacity of the condensation process, $C_W = 0.0791$ cal/g · K. The heat absorbing capacity of 1 gram of water vapor is equal to 0.47 cal/K. The moisture content above 1 cm^2 area of the Earth's surface:

$$m_w \approx \frac{0.49}{0.0791} \approx 6.2 \text{ g/cm}^2 . \qquad \text{(Eq. 9.10)}$$

The moisture content, (H_2O), within the atmosphere, near the Earth's surface is ≈0.62%. The heat absorbing capacity of humid and heat-absorbing air is:

$$\begin{aligned} \sum C_c &= (c_p + C_w + C_r) = 0.2394 + 0.0791 + 0.0412 \\ &= 0.3597 \text{ cal/g} \cdot \text{K}, \qquad \text{(Eq. 9.11)} \end{aligned}$$

whereas total heat absorbing capacity of dry and IR radiation absorbing air is:

$$\sum C_r = (c_p + C)_r = 0.2394 + 0.0412 = 0.2806 \text{ cal/g} \cdot \text{K}. \qquad \text{(Eq. 9.12)}$$

If the cloud cover extends from one to 2.5 km altitude, then the specific air mass within this cloud cover is approximately equal to the difference of pressures at its boundaries:

$$m_{cl} = \Delta p = 887 - 737.1 = 149.9 \text{ g/cm}^2, \qquad \text{(Eq. 9.13)}$$

and the moisture mass within the cloud stratum is equal,

$$m_{w_{cl}} = 149.9\left(\frac{0.0062}{2}\right) \approx 0.465 \text{ g/cm}^2. \qquad \text{(Eq. 9.14)}$$

The moisture condensation internal heat, $q = 595.8$ cal/g, the average air heating in the cloud stratum is:

$$\Delta T = \frac{q m_{w_{cl}}}{m_{cl}(C_w)_s} \approx 5.14°\text{C}. \qquad \text{(Eq. 9.15)}$$

The temperature distribution within the troposphere with a cloud cover is illustrated by Figure 9.2. In the case of cloud cover, it is likely air temperature inversions may emerge even without a horizontal transfer of air mass.

Effect of Carbon Dioxide on Temperature Distribution

Looking at the carbon dioxide effect on temperature distribution in the planetary troposphere, the air pressure distribution in the troposphere is defined by the following exponential equation:

$$p = p_o e^{-h\frac{g\mu}{RT}} \qquad \text{(Eq. 9.16)}$$

Then, at $p_0 = 1$ atm:

$$h = \frac{-RT}{g\mu} \ln p \qquad \text{(Eq. 9.17)}$$

where R = 1.987 cal/deg · mol is the gas constant; g = 981 cm/s^2 is the gravity acceleration; μ is molecular weight of the air gas mixture in degrees Kelvin, *K*, at the elevation *h*.

Eq. 9.7 determines the temperature distribution in the Earth's troposphere for air mixtures of various molar weights. Figure 9.8 is a comparison of the temperature distribution for a normal Earth type nitrogen-oxygen atmosphere with (1) the molar weight, $\mu = 29.89$; (2) an adiabatic exponent, $a = 0.1905$; (3) a hypothetical carbon dioxide atmosphere with the molar weight $\mu = 44$; (5) a pressure, $p = 1$ atm; and (6) a a exponent determined from Eqs. 2.14 and 2.15. At $a = 0.1428$, the, coefficient, $b^{\alpha} = 1.597^{0.1428} = 1.069$, and the near-surface temperature of this hypothetical carbon dioxide atmosphere is 281.6 K, which is 6.4 °C lower than for the nitrogen-oxygen atmosphere.

Figure 4.6 shows that the temperature distribution curve for a carbon dioxide atmosphere is always below that of the nitrogen-oxygen atmosphere curve. The near-Earth surface temperature for the carbon-dioxide atmosphere *curve 2* turns is lower than the nitrogen/oxygen *curve 1* by ≈6.4 °C than the nitrogen-oxygen atmosphere and not substantially higher as it is assumed by orthodox ecologists. Thus, substantial amounts of carbon dioxide in atmosphere will only cause cooling of the Earth, whereas relatively minuscule changes in the CO_2 partial pressure (by hundreds ppm) have had practically no effect on the temperature of the tropospheric and Earth's surface as seen in measurements over the past 20 years.

Similarly hypothesizing the imaginary replacement of the carbon dioxide Venus atmosphere with a nitrogen-oxygen one at the same pressure of 90.9 atm, the surface temperature would rise from 735 to 796 K (462 to 523 °C). This demonstrates that the atmosphere saturation with carbon dioxide, with all other conditions equal (atmospheric pressure), would always result in a decrease of the greenhouse effect and average temperature within the troposphere. The reason for this is simple; the carbon dioxide molar weight is 1.5 times greater and its heat-absorbing capacity is about 1.2 times lower than for Earth's atmospheric air. As a result, as it follows from Eq. 2.15, the adiabatic exponent for the Venus carbon dioxide atmosphere, with all other conditions equal, is lower, $a_{(CO2)} = 0.1786$ (approximately by a factor 1.067), than for the nitrogen-oxygen composition air, $a_{(N2+O2)} = 0.1905$. The increase in the heat absorption by carbon dioxide will result in an increase of the correction factor C_r and resulting in an additional decline of the adiabatic exponent, $a_{(CO2)}$. This, will cause an additional temperature decline. As noted in the imaginary experiment with Earth's atmosphere, equal pressures as defined by Eq. 9.7, for a carbon dioxide and nitrogen-oxygen atmospheres, are positioned at different elevations. Because a carbon dioxide atmosphere's molar weight is heavier, its equal pressure level is always lower than that for a nitrogen-oxygen atmosphere. This results in a higher temperature distribution for a Venus nitrogen-oxygen troposphere.

The Effect of Carbon Dioxide Anthropogenic Emissions

Various estimates of CO_2 anthropogenic emissions resulting from burning hydrocarbon fuels (2005 data) produce 5 to 7 billion tons of carbon dioxide or 1.4 to 1.9 billion tons of pure carbon to the atmosphere. It has been thought by some that the amount of carbon entering the atmosphere in recent years may have even reached 20 to 35 billion tons. Some people believe that this colossal amount of carbon entering the atmosphere can not only alter the composition of its gas mixture and decline in its heat absorbing capacity, but also increase the total atmospheric pressure.

These two factors operate in opposite directions. As a result, in theory, the average Earth's surface temperature will almost remain unchanged. The Earth's temperature will not change, even if carbon dioxide concentration in the atmosphere doubles, which is currently anticipated by some in 2100. One should also consider that the major portion of carbon dioxide entering the atmosphere, under Henry's law, dissolves in the oceanic water and in hydration of Earth's crust carbon dioxide is bonded in carbonates. Thus, along with carbon, part of the atmospheric oxygen passes into carbonate rocks. Therefore, rather than a slight increase in the atmospheric pressure, we are likely to see a slight decrease, and therefore a slight climate cooling.

The carbon dioxide partial pressure in the atmosphere is regulated by the ocean water temperature. Carbon dioxide solubility in water is controlled by Henry's law:

$$C_{(\mathrm{CO_2})} = p_{\mathrm{CO_2}}\left(H \cdot e^{-\frac{-\Delta H}{\mathrm{R}T}}\right), \tag{Eq. 9.18}$$

where p_{CO2} is the atmospheric carbon dioxide partial pressure; $\mathrm{C}_{(\mathrm{CO2})} = 0.1544 \cdot 10.^{3}$ is the carbon dioxide concentration in oceanic water (HCO_3^{1-} plus CO_3^{2-}) (Kokin *et al.*, 1990); H is the Henry coefficient; ΔH is the enthalpy of carbon dioxide dissolution in the water process; $\mathrm{R} = 1.987$ cal/mole $\cdot$ K is the gas constant; and T is upper oceanic water-layer temperature, deg. K. Eq. 9.18 states that the CO_2 partial pressure in the atmosphere will increase when water is heating and decrease when cooling (this is well known to many as the Champaign effect). Figure 9.4 demonstrates the solubility of carbon dioxide gas in water.

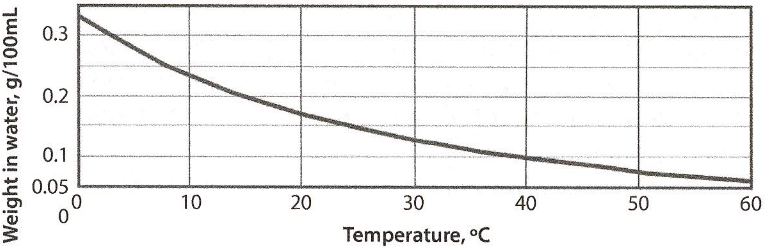

Figure 9.4 Relationship between the temperature and the solubility of CO_2 dissolved in water. (After Wallace, 2009.)

The enthalpy of carbon dioxide's dissolution in water is controlled by the difference between the enthalpy of carbon dioxide solution in water and the enthalpy of CO_2 gas phase: $\Delta H = -98.9 - (-94.05) = 4.85$ kcal/mole (Naumov *et al.*, 1971). Eq.9.8 may be solved for an earlier time period by assuming a preindustrial value for the CO_2 partial pressure and temperature, e.g., a preindustrial time like 1880: $p_{(CO2)} = 2.9 \times 10^{-4}$ bar and $T = 287.2$ K. In this case $H = 10^{-4}$ 1/bar. Currently carbon dioxide amount dissolved in oceanic water is approximately 60 to 90 times its amount in the atmosphere. For calculations it may be assumed $C_{(CO2)} \approx$ const. Even a slight increase in the average temperature of oceanic water results in a notable increase in the atmospheric carbon dioxide partial pressure. A significant increase in $p_{(CO2)}$ was observed due to the anthropogenic influence (on the order of $\Delta p = 60$ ppm). A more modest contribution was introduced by the increase in Earth's surface temperature from 287.2 K to 288 K, $Dp = 6.9$ ppm. A natural warming during the recent 120 years by 0.8 °C would result in an increase in carbon dioxide partial pressure by $\Delta p = 6.9$ ppm. Anthropogenic emissions added 53 ppm more, although this addition likely had nothing to do with the observed climate warming as this warming was associated with a change in the Sun's activity. It has been noted that atmospheric carbon dioxide concentration fluctuations in the Pleistocene occurred at changes of glaciation epochs, by glaciation interstadials, and they exceeded 150 ppm, naturally, without any anthropogenic intervention.

Similar conclusions to those above have been arrived at by many scientists studying climate change. Robinson *et al.* (1998) and others have reported no climate warming at all. Seitz has written: "Experimental data of climate change do not show any harmful effect from the anthropogenic use of hydrocarbons. Contrary to that, there is evidence that increases in carbon dioxide content in atmosphere may be beneficial". F. Seitz prepared a petition by scientists to the U.S. government with an appeal to reject the international agreement on the global climate warming concluded in Kyoto (Japan) in December of 1997 and other similar agreements. The petition stated: “There are no convincing scientific evidences that the anthropogenic emissions of carbon dioxide, methane and other greenhouse gases are incurring or may in the foreseeable future cause a catastrophic warming of Earth atmosphere and destruction of its climate. Besides, substantial scientific evidences are available, which indicate that an increase of carbon dioxide concentration in the atmosphere renders positive effect on the natural growth of plants and animals in Earth's ambient medium”. By 2005, almost 17,000 U.S. scientists and engineers had signed this petition.

The conventional concept of climate warming due to the accumulation, in the troposphere, of anthropogenic CO_2 and other greenhouse gases is a myth and has no scientific support. The accumulation of CO_2 in the atmosphere has historically shown no noticeable effect on the temperature regime of Earth's climate. Temperature changes are the result of primary causes, whereas carbon dioxide concentration variations (except for the anthropogenic influence) are secondary causes and are the consequence and not the cause of temperature changes. Peaks in the Sun's irradiation preceed the peaks in CO_2 concentration in the atmosphere.

Greenhouse gas, especially carbon dioxide and water vapor, accumulation in the troposphere can increase somewhat the convective air mass heat exchange in the troposphere. This, in turn, may cause intensification of the synoptic processes and storm activity within the troposphere. Strengthening of hurricanes and tornados, in recent years, incurring substantial damages in the southern portion of the United States, should only be associated with fluctuations in the solar activity. Maximum solar activity (sunspots) were observed in 2000–2002; however, due to a high heat absorbing capacity of water in the surface oceanic stratum, the climatic reaction to a change in solar activity was delayed by a few years, relative to its 11-year cycle. That may be the reason why maximum activity of the synoptic processes moved to the initial years of the twenty-first century.