CHAPTER 4

The Atmosphere

4.1 INTRODUCTION

4.1.1 NATURE OF THE ATMOSPHERE

Many of the physical characteristics of the atmosphere, such as wind, temperature, cloud cover, humidity, and precipitation, are easily perceived. Sometimes, chemicals in the atmosphere also can be observed, as in smoke plumes and smog, and their physical transport tracked downwind just as downstream transport of substances in a river can be measured. Other atmospheric processes are less apparent to the unaided observer, however, occurring either on the microscopic scale of a chemical reaction, or on a global scale, or at high altitudes. Such processes may be detected only by instrumentation on satellites or some high-altitude aircraft.

Physical Attributes of the Atmosphere

The advent of aviation provided both the means and a greater incentive to investigate the atmosphere. Physical phenomena, such as winds, turbulence, atmospheric electricity, and the behavior of water (especially when it forms clouds or ice), were of great practical concern to early aviators (and atmospheric scientists). Although recent interest tends to focus on atmospheric chemicals, the physics of fluid behavior influence chemical transport and fate in the atmosphere no less profoundly than they do in surface waters and porous media; to understand atmospheric chemistry, a knowledge of atmospheric physics is essential. For the price of an airplane ticket, the modern student of the atmosphere can visit firsthand 75% (by mass) of Earth's atmosphere and directly observe processes that earlier generations of scientists had to infer from theory or indirect observation.

The initial part of an airplane flight is in the *troposphere*, the lowest layer of the atmosphere (Fig. 4-1). The word "troposphere" is based on the Greek word "tropos," meaning change. Immediately after takeoff, the turbulent nature of tropospheric airflow manifests itself; the ride is often bumpy as the plane passes through large eddies, sometimes called *air pockets*. These eddies may be due to wind flowing past irregularities on Earth's surface or due to *convective instability* (Section 4.2). Such eddy or turbulent diffusion causes significant Fickian transport and dominates the vertical mixing of atmospheric chemicals. Chemicals also are transported "via" or "by" advection by the wind. [Recall that eddy diffusion and advection are dominant transport processes in flowing surface waters (Section 2.2.1) as well.]

Clouds occur frequently in the troposphere, and from an airborne vantage point it is evident that clouds are not randomly scattered in the vertical direction. Usually, clouds have bases at relatively well-defined altitudes, because rising air containing water vapor (moisture) systematically becomes cooler with height, eventually reaching its *dew point*, the temperature at which water vapor condenses (Section 4.2.2). Water in both liquid and solid phases in the clouds facilitates a host of chemical reactions.

Climbing through the gray murk of a deep cloud layer, the plane emerges above into brilliant sunlight, which appears all the brighter because of reflection of light (*visible albedo*) from the clouds below. Light is a potent factor in chemical reactions in the atmosphere, and it is evident that clouds significantly influence the visible light flux.

Clouds reflect visible light and other portions of the incoming solar radiation, as well as absorb some fraction of all the incoming solar radiation. *Albedo* usually refers to the percentage of reflection of all incident solar radiation wavelengths, not just the percentage of reflection of the incident visible portion. (Albedo also can be expressed as a ratio of reflected radiation to incident radiation.) Reflection and absorption of solar radiation by clouds reduce the amount of solar radiation received at Earth's surface. Some clouds may reflect as much as 90% of incoming solar radiation, while others may absorb as much as 40% of incoming solar radiation (Rosenberg *et al.*, 1983). Clouds also radiate long-wave infrared energy (heat), both out toward space and toward Earth's surface.

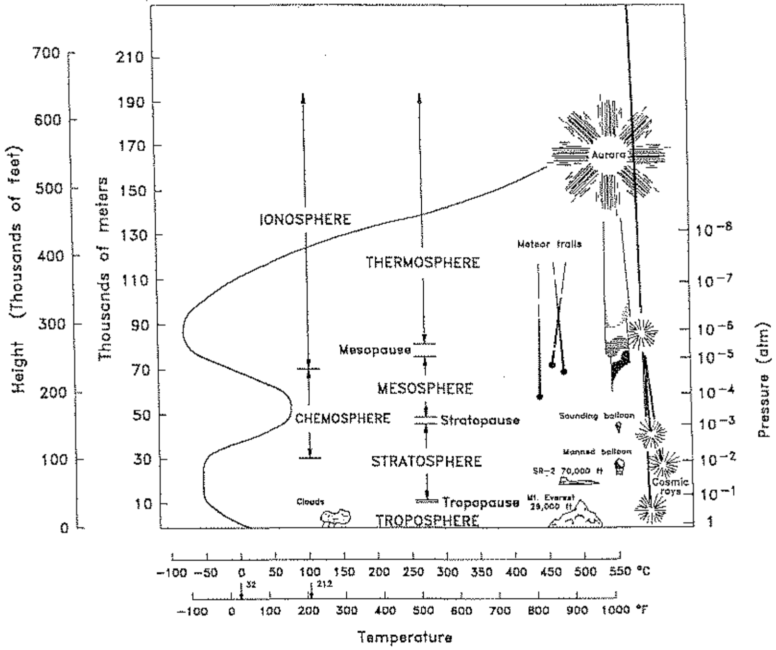


FIGURE 4-1 Vertical structure of the atmosphere. Weather phenomena are confined almost entirely to the troposphere, as are most air pollutants, which are removed by various processes before they can mix into the stratosphere. Certain long-lived pollutants, however, such as the chlorofluorocarbons (CFCs), do mix into the stratosphere, and other pollutants can be injected physically to stratospheric altitudes by processes such as volcanic eruptions or nuclear explosions. Note that more than one term may refer to a given layer of the atmosphere (adapted from *Introduction to Meteorology*, by F. W. Cole. Copyright © 1970, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.).

As the plane continues to climb, the ride becomes smooth. Coffee served in open cups does not spill, providing testimony that in the *tropopause* [at approximately 10,000 m (33,000 ft)] and the still higher *stratosphere* (Fig. 4-1), the size and energy of atmospheric eddies decrease. Weather phenomena are confined almost entirely to the troposphere. Being at the edge of the stratosphere is comparable to being in the thermocline of a stratified lake (Section 2.2.2); turbulent diffusion is suppressed, and vertical Fickian transport is slowed. Chemicals released into the air near Earth's surface may mix

EXAMPLE 4-1

A student pilot takes off from an airport at sea level, and flies to an airport that is 1000 ft above sea level. (a) As the pilot enters the traffic pattern 1000 ft above ground level at the destination airport, what would an air pressure gauge aboard the plane read? Assume an air temperature of 15°C and an atmospheric pressure of 1 atm at sea level. (b) The plane altimeter is a gauge that senses pressure and translates the pressure value to an altitude readout. Suppose that during the flight, the atmospheric pressure at sea level in the region increases to 1.02 atm. If the pilot does not correct for this, at what altitude will he or she enter the traffic pattern?

(a) The air pressure 2000 ft above sea level can be estimated by using Eqs. [4-5] and [4-6]. First, convert the altitude of 2000 ft to 610 m by using Table A-2 in the Appendix. Then combine Eqs. [4-5] and [4-6]:

$$P = 1\ \text{atm} \cdot e^{-(1.2\times10^{-6}/\text{cm})\cdot 61{,}000\,\text{cm}} = 0.93\ \text{atm}.$$

(For comparison, from Table 4-1, the pressure at 610 m in a Standard Atmosphere is 0.94 atm. This small difference is partly attributable to the assumption of a constant temperature of 15°C with no vertical temperature variations. The temperature in a Standard Atmosphere at 610 m is only 11°C.)

(b) The altimeter, if uncorrected for the change in air pressure at sea level, will read 2000 ft at the altitude where the pressure equals 0.93 atm, calculated in (a). However, due to the atmospheric pressure rise, the pilot will be flying at too high an elevation. This elevation can be estimated by again using Eqs. [4-5] and [4-6]:

$$0.93\ \text{atm} = 1.02\ \text{atm} \cdot e^{-(1.2\times10^{-6}/\text{cm})\cdot(h)}$$

$$-\ln\left(\frac{0.93\ \text{atm}}{1.02\ \text{atm}}\right) = (1.2 \times 10^{-6}/\text{cm}) \cdot (h)$$

$$h = 7.8 \times 10^{4}\ \text{cm or 2550 ft (1550 ft above ground level).}$$

Chemical Composition of the Atmosphere

Air is primarily composed of two chemicals: nitrogen, N_2, constituting approximately 78% of the molecules found in air and oxygen, O_2, constituting approximately 21% of the molecules. Such molar percentages are often called *mixing ratios*, but also can be thought of as volume percentages or as partial pressure percentages, because the pressure–volume product of a gas is very nearly a function of the number of molecules present in it (recall the ideal gas law in Section 1.8.1). As discussed in Chapter 2, oxygen is not only metabolically critical for most forms of life but also is an important oxidant in abiotic reactions. By comparison, nitrogen is much less chemically reactive, although small amounts of it, incorporated into organic forms, are essential to organisms. Most of the nitrogen required by organisms is *fixed* (converted from inorganic N_2 into a usable organic form) by specific bacteria and blue-green algae. Some N_2, however, is fixed in the atmosphere by a series of abiotic reactions initiated by electric discharges in lightning. These reactions fix N_2 as nitric acid, HNO_3.

The third main constituent of air is argon, a *noble* (chemically inert) *gas* with a mixing ratio of approximately 0.9%. Other gases with mixing ratios less than 1% are frequently called *trace gases*. These trace gases include, in order of decreasing concentration, four other noble gases at fairly constant mixing ratios: neon, helium, krypton, and xenon. Other trace gases are more variable in their concentrations because of their reactivity (i.e., they are not inert): carbon dioxide (CO_2), methane (CH_4), hydrogen (H_2), nitrous oxide (N_2O), and ozone (O_3). Several other chemicals are present in the atmosphere with highly variable mixing ratios. These include water, carbon monoxide (CO), nitrogen dioxide (NO_2), ammonia (NH_3), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S). The mixing ratios for all these atmospheric gases are provided in Table 4-2.

As shown in Table 4-2, the concentration of CO_2 in the atmosphere is approximately 356 ppm by volume (therefore, the current mixing ratio of CO_2 is approximately 0.0356%). Despite the relatively low abundance of CO_2, CO_2 is the source of carbon from which organic material is fashioned during photosynthesis. CO_2 is also a *radiatively active gas*. Radiatively active gases absorb long-wave infrared radiation emitted by Earth's surface, thereby trapping heat. Currently, the atmospheric mixing ratios are increasing for CO_2 and other radiatively active trace gases, such as CH_4, N_2O, and chlorofluorocarbons (CFCs). Therefore, these radiatively active gases are having an increased warming effect on the planet by enhancing the *greenhouse effect*, which is discussed in Section 4.7.

Table 4-2 also shows that water vapor is present in the atmosphere at mixing ratios ranging from a fraction of a percent to approximately 4%. (Recall that *vapor* refers to a gaseous chemical that also has a liquid phase at ordinary temperatures and pressures.) Atmospheric water is central to the global hydrologic cycle, and its phase transformations among vapor, liquid, and solid affect pollutant mixing and air movement. Water vapor also is a radiatively active gas that, globally, absorbs more long-wave infrared radiation than does CO_2. Water vapor concentration in a given parcel of air often is expressed by *relative humidity* (RH), which is the ratio of the actual partial pressure of water vapor in the atmosphere to the partial pressure of water vapor that would exist if the air were in equilibrium with liquid water at the

TABLE 4-2 Components of Atmospheric Air

Gas	Formula	Mixing ratio (percentage by volume)	Concentration [ppb by volume, ppb(v)]
		Major gases[a]	
Nitrogen	N_2	78.084	
Oxygen	O_2	20.946	
Argon	Ar	0.934	
		Inert trace gases[a]	
Neon	Ne		18,180
Helium	He		5240
Krypton	Kr		1140
Xenon	Xe		87
		Reactive trace gases[b]	
Carbon dioxide	CO_2		358,000
Methane	CH_4		1720
Hydrogen	H_2		500[a]
Nitrous oxide	N_2O		312
Ozone	O_3		10–50[c]
Water	H_2O	0.004–4[c]	
Carbon monoxide	CO		50–150[d]
Nitrogen dioxide	NO_2		0.1–5[c]
Ammonia	NH_3		0.1–10[c]
Sulfur dioxide	SO_2		0.03–30[c]
Hydrogen sulfide	H_2S		<0.006–0.6[c]

[a] Weast (1990).
[b] IPCC (1996), unless otherwise noted.
[c] Mészáros (1981).
[d] Prather *et al.* (1996).

same temperature (Table 4-3). For a parcel of air at a given temperature, as RH increases, the dew point also increases (i.e., as the concentration of water vapor increases, the air parcel does not have to be cooled as much for condensation to occur). In the limiting case of 100% RH, the dew point equals the temperature of the air parcel.

TABLE 4-3 Vapor Pressure of Water[a]

Temperature (°C)	V.P. (mm Hg)	Temperature (°C)	V.P. (mm Hg)
−5	3.16	16	13.63
−4	3.41	17	14.53
−3	3.67	18	15.48
−2	3.96	19	16.48
−1	4.26	20	17.54
0	4.58	21	18.65
1	4.93	22	19.83
2	5.29	23	21.07
3	5.68	24	22.38
4	6.10	25	23.76
5	6.54	26	25.21
6	7.01	27	26.74
7	7.51	28	28.35
8	8.04	29	30.04
9	8.61	30	31.82
10	9.21	31	33.70
11	9.84	32	35.66
12	10.52	33	37.73
13	11.23	34	39.90
14	11.99	35	42.18
15	12.79	36	44.56

[a] Weast (1990).

4.1.2 SOURCES OF POLLUTANT CHEMICALS TO THE ATMOSPHERE

Human activities contribute large fluxes of gases and particles to the atmosphere. Many of these fluxes are associated with combustion; such fluxes date back to prehistory, when humans first built fires. Historical records of air pollution from fossil fuel combustion appear in the late 13th century, when King Edward I banned coal burning in kilns in London and Southwark due to the detrimental impact of coal combustion on air quality (Wilson and Spengler, 1996). Although King Edward I ordered that kilns be heated by brushwood or charcoal, the combustion of virtually any fuel produces a range of pollutants: CO_2, pollutants derived from impurities and additives (e.g., sulfur dioxide from sulfur impurities), oxides of nitrogen, and products of incomplete combustion (PICs) such as carbon monoxide, soot particles, and hydrocarbons. PIC production is greatly influenced by the conditions of combustion (e.g., the air to fuel ratio). Besides combustion, sources of pollutant gases and particles include evaporation of volatile chemicals; vapor emissions from metallurgical operations; and mechanical activities, such as grinding, sandblasting, and chipping, which produce coarse particles.

Gases and Vapors

Foremost among the many gases emitted by human activities is carbon dioxide. At natural levels, CO_2 is not an air pollutant, but an atmospheric comp[illegible]t essential to the functioning of ecosystems. Anthropogenic emissions of CO_2 primarily originate from fossil fuel combustion in industries and vehicles and from the effects of *deforestation.* Deforestation refers to the large-scale removal of trees in a region by cutting or burning, and is followed by the oxidation of soil organic material. Both the oxidation of soil organic material and the burning of organic carbon release large amounts of CO_2 to the atmosphere. Furthermore, the destruction of trees removes their photosynthetic ability to serve as a sink for atmosphere CO_2. CO_2 fluxes to the atmosphere from deforestation and fossil fuel combustion are now a significant fraction of the natural production of CO_2 and may be threatening the stability of Earth's climate.

In many industrial areas, emissions of gaseous oxides of sulfur (SO_x), especially sulfur dioxide (SO_2), also rival natural sulfur gas emissions from volcanoes, wetlands, and oceans. SO_x are produced from the oxidation of sulfur in fuels, especially coals and residual oils, and are responsible in large part for acid rain (Section 4.6.3). In fuels, sulfur typically occurs either in organic compounds (organic S) or as pyrite (FeS_2). SO_x also are formed from the refining of the ores of the many metals that occur in the form of metal sulfides [e.g., copper (Cu), lead (Pb), and nickel (Ni)].

Oxides of nitrogen (NO_x) occur naturally as a result of bacterial activity, wildfires, and lightning, but their atmospheric loading is greatly enhanced by industrial combustion processes. Both organic nitrogen impurities in fuel and nitrogen from the air (N_2) can be oxidized during combustion to form nitric oxide (NO), nitrous oxide (N_2O), and nitrogen dioxide (NO_2). Oxidation of atmospheric N_2 is most pronounced during high-temperature combustion. Because high temperatures are desirable from the standpoint of power plant thermal efficiency, there is a tradeoff between higher efficiency and lower NO_x emissions in many combustion systems. Emissions of NO_x not only contribute to acid deposition (Section 4.6.3), but also contribute to ozone depletion and the greenhouse effect (Section 4.7).

Carbon monoxide (CO), a toxic gas, is produced during combustion, both in wildfires and in fuel-burning devices; CO also can be produced and consumed by bacterial activity. The presence of CO may indirectly increase the atmospheric mixing ratios of other gases by competing for oxidant species (such as the hydroxyl radical, OH·), thereby decreasing the oxidation rates of the other gases. This competition for oxidant species is believed to be one reason for the current increase in atmospheric methane, whose major atmospheric sink is reaction with the hydroxyl radical.

Methane (CH_4), a key greenhouse gas, has many natural sources, including wetlands and termites. Methane is also released by the petroleum industry, landfills, cattle, rice cultivation, and wastewater treatment plants. (Wastewater treatment plants often burn off CH_4 at the top of a tall stack in a process

termed *flaring.*) Collectively, these sources are significant to the global budget (see Table 4-17 later). Many other *nonmethane hydrocarbons* (chemicals composed of carbon and hydrogen) are emitted in large amounts by industrial processes and as by-products of combustion. Hydrocarbon fuels and solvents escape by spillage, or are deliberately released into the atmosphere by usage or disposal; for example, the release of solvent from drying paint represents a purposeful use of the atmosphere as the primary sink for an anthropogenic chemical. Natural releases of certain hydrocarbon molecules, such as terpenes $(C_{10}H_{16})_n$ from pine trees and other vegetation, and ethylene from ripening fruits, also occur. Anthropogenic releases of hydrocarbon fuels and solvents, however, usually overwhelm natural sources in industrialized areas.

Halogenated solvents are an example of a class of chemicals that with a few exceptions (such as methyl chloride, CH_3Cl, produced by some marine algae) are not naturally present in the atmosphere. Currently, such solvents are released in large amounts (Table 4-4). Many are degraded in the lower atmosphere (Section 4.6). Some, however, such as the CFCs, pose a unique set of problems because their low reactivity allows them to escape destruction in the troposphere; therefore, they can enter the stratosphere, where they take part in a catalytic cycle that destroys beneficial high-altitude ozone (Sectior 4.6.4).

4.2 Atmospheric Stability

In any discussion of air movement in the atmosphere, the issue of atmospheric stability must be considered. The role of stability in lakes was discussed in Section 2.2.2; recall that in a lake, the occurrence of higher temperatures near the lake surface greatly inhibits vertical mixing. Similarly, the vertical temperature profile of the atmosphere can either enhance or suppress vertical mixing of air and the chemicals contained in it. In a lake, the essentially incompressible water column is in a condition of neutral stability when water is at a *constant temperature* throughout; in contrast, in the atmosphere, due to the compressibility of air, neutral stability occurs when the *actual* vertical temperature gradient (the *actual lapse rate*) is equal to the *adiabatic lapse rate*. The adiabatic lapse rate is the rate at which the temperature of an air parcel changes in response to the compression or expansion associated with elevation change, under the assumption that the process is *adiabatic;* that is, no heat exchange occurs between the given air parcel and its surroundings. (This is the same phenomenon that is responsible for the warmth of a tire pump after it has been used to pump up a tire; the pump barrel becomes warmest at the air outlet where the highest compression occurs. Friction, which also causes heat, is more evenly distributed along the barrel.)

4.2.1 THE DRY ADIABATIC LAPSE RATE

The adiabatic lapse rate for a *dry atmosphere*, which may contain water vapor but which has no liquid moisture present in the form of fog, droplets, or

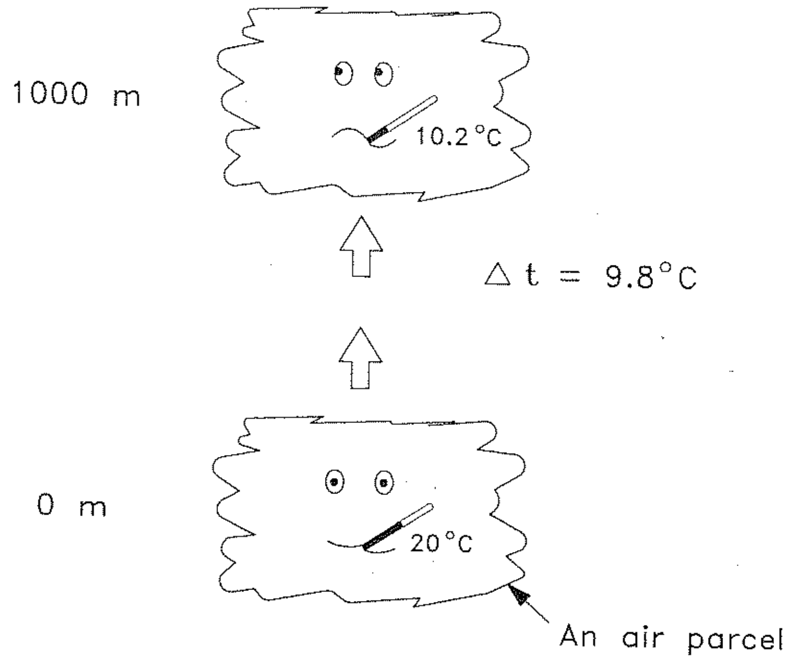


FIGURE 4-5 Illustration of the adiabatic lapse rate. As this air parcel is raised in altitude by 1000 m, the air pressure decreases and the parcel expands and cools by 9.8°C (5.4°F for an altitude increase of 1000 ft). Assuming no heat is lost or gained by the parcel (i.e., the process is *adiabatic*), its temperature will increase to its original value on being lowered to its original height.

clouds, is approximately 9.8°C/1000 m (5.4°F/1000 ft). A hypothetical parcel of air placed in an insulated but expandable container and raised in height by 1000 m would become 9.8°C cooler than its initial temperature (Fig. 4-5). This value, borne out by experiment, is predictable on the basis of the atmospheric pressure profile and thermodynamic principles.

In Section 4.1.1, Eqs. [4-1] and [4-2] were used to estimate the relationship between air pressure and altitude, assuming temperature to be constant with height. When combined with a third equation, Eqs. [4-1] and [4-2] also can be used to calculate the dry adiabatic lapse rate. The third equation, presented as the following Eq. [4-7], is based on an adiabatic process for air that rises and expands due to a decrease in pressure. By definition for an adiabatic process, heat flow into the rising air is assumed to be zero. Therefore, conservation of energy requires that the mechanical (pressure–volume) work performed by the air as it expands equal the decrease in the internal energy of the air. The change in the internal energy of the air is given by its heat capacity, C_v (energy per unit mass per degree), multiplied by the change in temperature,

$$P \cdot \frac{\partial}{\partial h}\left(\frac{1}{\rho}\right) = -C_v \cdot \frac{\partial T}{\partial h}, \qquad [4\text{-}7]$$

where P is pressure [M/LT^2], h is height [L], ρ is density [M/L^3], C_v is heat capacity [L^2/T$^2 \cdot$ K], and T is absolute temperature [K]. (Note that $1/\rho$ is volume per unit mass.)

Equation [4-2], which is derived from the ideal gas law, can be rearranged as

$$T = \frac{\text{MW}}{R} \cdot \frac{P}{\rho}, \qquad [4\text{-}8]$$

where MW is the molecular weight and R is the gas constant. (Note that V/n equals MW/ρ.) By differentiating Eq. [4-8]:

$$\frac{\partial T}{\partial h} = \frac{\text{MW}}{R} \cdot \left(P \cdot \frac{\partial}{\partial h}\left(\frac{1}{\rho}\right) + \frac{1}{\rho} \cdot \frac{\partial P}{\partial h}\right). \qquad [4\text{-}9]$$

From Eqs. [4-2] and [4-3]:

$$\frac{\partial P}{\partial h} = -\rho \cdot g. \qquad [4\text{-}10]$$

Substituting Eqs. [4-7] and [4-10] into Eq. [4-9] gives:

$$\frac{\partial T}{\partial h} = \frac{\text{MW}}{R} \cdot \left(-C_v \cdot \frac{\partial T}{\partial h} + \frac{1}{\rho} \cdot (-\rho \cdot g)\right). \qquad [4\text{-}11]$$

Eq. [4-11] can be rearranged:

$$\frac{\partial T}{\partial h} = \frac{-g \cdot \text{MW}}{R + C_v \cdot \text{MW}}. \qquad [4\text{-}12]$$

The quantity ($C_v \cdot$ MW) is the heat capacity expressed in units of energy *per mole* per degree, and equals 5/2 · R for diatomic gases. Thus,

$$\frac{\partial T}{\partial h} = \frac{-g \cdot \text{MW}}{R + 5/2 \cdot R} = \frac{(981 \text{ cm/sec}^2) \cdot (28.96 \text{ g/mol})}{(7/2) \cdot (8.31 \times 10^7 \text{ erg/mol} \cdot \text{K})} = 9.8 \text{ K/km}.$$

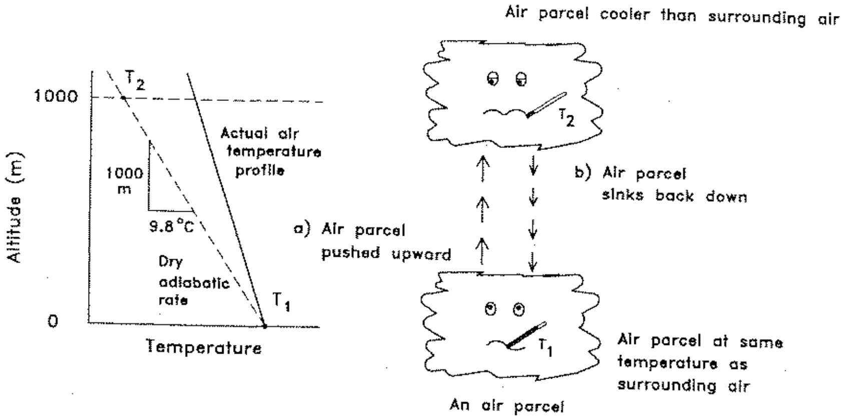


FIGURE 4-6a A *stable* atmosphere. The actual, measured temperature profile of the atmosphere decreases at a rate *less* than the adiabatic rate. Thus, when this air parcel is pushed upward, perhaps by an eddy in a turbulent atmosphere, it finds itself in warmer, and hence less dense, surroundings; being cooler and denser it sinks back down. This stable situation tends to suppress vertical mixing.

It is important not to confuse this dry adiabatic lapse rate with the rate of change in temperature with height in a Standard Atmosphere. The latter represents average conditions in Earth's atmosphere, where heating, mixing, and wet adiabatic processes also are occurring.

Actual temperature profiles are measured routinely by *sondes,* which are devices that measure temperature, pressure, and often water vapor content of the air. Sondes are either carried by weather balloons or dropped from airplanes and transmit their data to ground stations as they travel vertically through the atmosphere. If the actual measured lapse rate of the atmosphere is less than 9.8°C/1000 m, a parcel of air initially at a temperature equal to that of the surrounding air becomes warmer than the surrounding air on being pushed downward (Fig. 4-6a). By being warmer and therefore less dense than its surroundings, it experiences an upward force tending to restore it to its original height. (Forces that arise from density differences in a fluid are called *buoyancy* forces.) Likewise, if the parcel of air is pushed upward, its temperature increases with height more slowly than that of the surrounding air, so that it experiences a downward buoyant force, again tending to restore it to its original height. The net result is that vertical air movements, such as those associated with eddies, are suppressed by buoyant forces; the atmosphere is *stable,* and vertical transport of chemicals is suppressed.

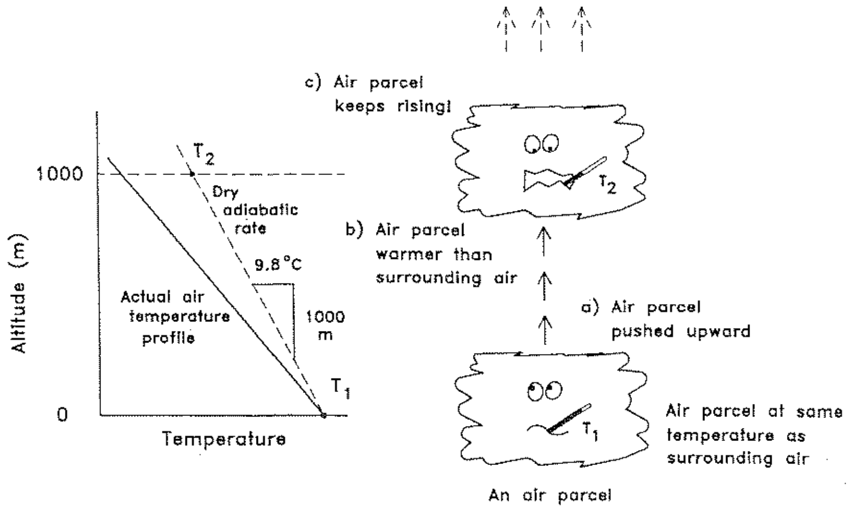


FIGURE 4-6b An *unstable* atmosphere. The same air parcel pictured in Fig. 4-6a is again pushed upward. This time, the temperature of the surrounding atmosphere decreases more rapidly with altitude than the adiabatic rate that the air parcel follows. As it rises, the air parcel finds itself in air that is increasingly cooler and denser than itself and consequently it is pushed up further by buoyancy. Vertical mixing is enhanced by unstable conditions such as these; the mixing, however, tends to reduce the magnitude of the instability, unless an external influence, such as heating by a warm surface, maintains the unstable temperature gradient.

Conversely, if the actual measured lapse rate is greater than 9.8°C/1000 m, a parcel of air displaced upward from its initial height becomes warmer than its surroundings and therefore tends to rise (Fig. 4-6b). If pushed downward, the parcel becomes colder than its surroundings and therefore tends to keep sinking. In this case, buoyant forces amplify any initial upward or downward movement of the air parcel, thus creating an *unstable* atmosphere.

It might be inferred from the preceding discussion that, based on its average lapse rate, the Standard Atmosphere is stable with little vertical mixing; yet, on average, the troposphere is reasonably well mixed. Tropospheric mixing occurs in part because of atmospheric variability; although widespread areas of stable air exist, there are also areas where, even in a "dry" atmosphere, the actual lapse rate exceeds the adiabatic lapse rate. As described in the following section, moisture also contributes to tropospheric mixing. In clouds, the adiabatic lapse rate can be as small as 3.6°C/1000 m (2°F/1000 ft). When this occurs, an actual lapse rate of, for example, 7.2°C/1000 m (4°F/1000 ft),

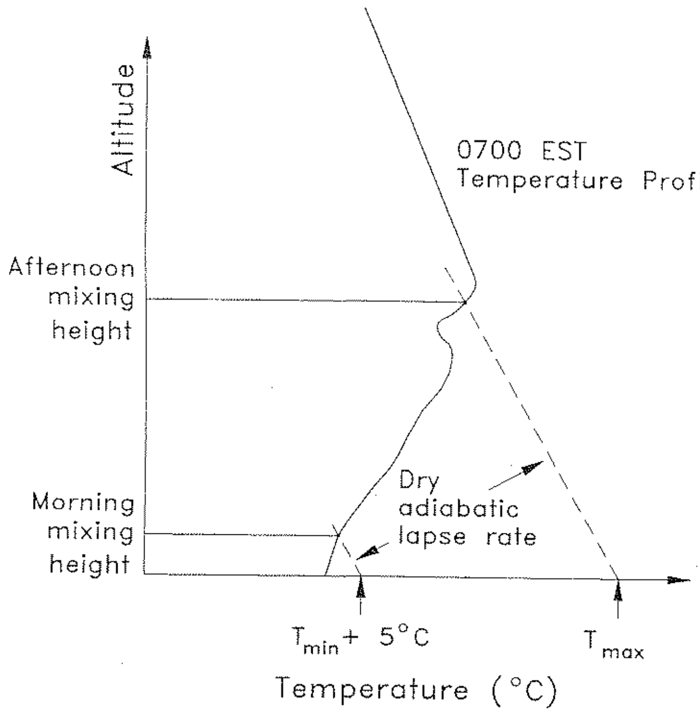
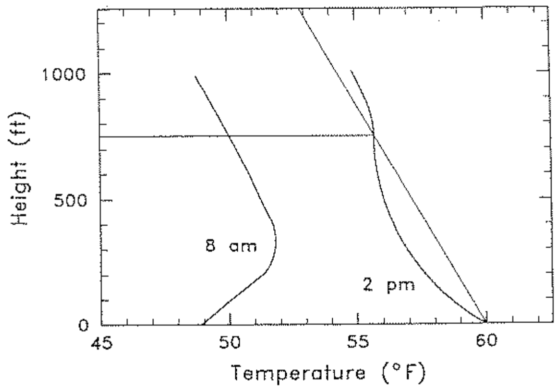


FIGURE 4-9 Mixing height is usually estimated by drawing a line originating at the surface temperature and having a slope equal to the applicable adiabatic lapse rate; the intersection of the line with the actual temperature profile approximates the mixing height. In this figure, which shows a set of approximations commonly used in urban air quality work, only one measured temperature profile from a rural area is available; it is assumed that the upper portions of this 1200 GMT (700 EST) profile are applicable for both the A.M. and P.M. mixing height estimates. An estimated correction for urban surface temperature is made by offsetting the rural surface temperature by 5°C in the graphic construction, giving a somewhat higher A.M. mixing height than if the directly measured surface temperature were used. The afternoon maximum surface temperature (T_{max}) in the urban area is used to estimate the maximum daytime mixing height.

At night, cooling of the land surface lowers the temperature of the air close to the ground and decreases the actual lapse rate, in many cases creating an *inversion,* which is a layer of atmosphere in which the actual lapse rate is negative; air becomes warmer with increased altitude. Nighttime inversion development is favored by clear nighttime skies that radiate little long-wave radiation downward to offset the loss of heat through long-wave radiation upward from the ground surface. This represents an exceptionally stable situation. Nighttime inversions trap pollutant chemicals in a relatively thin layer of atmosphere and lead to lowered air quality near the ground surface. As examples of the role of atmospheric stability in influencing pollutant dispersal, diagrams showing stability effects on the plume of emissions from a smokestack are presented in Fig. 4-10.

EXAMPLE 4-3

What is the mixing height associated with the temperature profile of the following figure at 2:00 P.M.? At 8:00 A.M.? Assume the air is "dry," as defined in Section 4.2.1.



To determine the mixing height, draw a line with a slope equal to the dry adiabatic lapse rate beginning at the temperature and elevation of the ground surface. The height where the line intersects the 2 P.M. temperature profile is the mixing height, at approximately 750 ft. Pollutants released at the surface in the afternoon will not mix readily beyond this height. The mixing height at 8:00 A.M. is zero; inversion conditions prevail.