

Composition and Structure of the Components of the Earth System

Central to the description of a thermodynamic system is its chemical composition and physical state. In the remainder of this chapter the composition, structure, and state of the atmosphere and ocean are described.

1.1 Composition of the Atmosphere

The Earth's atmosphere consists of a mixture of gases, water in the liquid and solid states, and other solid particles that are very small in size. The Earth's atmosphere up to about 110 km (the *homosphere*) is well mixed by turbulent air motions, and the composition and concentration of the passive constituent gases (*i.e.*, those that do not undergo phase changes or extensive chemical reactions) is fairly constant with height. Above the homosphere, the composition of the *heterosphere* is subject to diffusive stratification by the molecular weight of the gases and strong chemical and photochemical alterations. The focus here is on the composition of the homosphere.

The concentrations of the major gaseous constituents in the homosphere are shown in Table 1.1. It is seen that N_2 and O_2 comprise approximately 99% of the volume and mass of the homosphere. The concentrations of the gases in Table 1.1 are relatively constant throughout the homosphere, with the exception of water vapor. There are many other gases present in trace amounts in the homosphere (besides those shown in Table 1.1) that are of importance in atmospheric chemistry and radiative transfer (*e.g.*, ozone, methane, nitrous oxide, sulfur dioxide).

Water vapor comprises 0 to 4% of the atmospheric concentration of gases, the exact amount varying with time and location. Atmospheric water vapor has a maximum concentration near the surface of the Earth, indicating that the surface is the principal source of atmospheric water vapor. The water vapor concentration decreases with height above the surface, arising from condensation that occurs in clouds. Water vapor concentrations in the warm tropical atmosphere are much higher than in the cool polar regions. Water vapor is the most important gas in the atmosphere from a thermodynamical point of view because of its radiative properties as well as its ability to condense under atmospheric conditions. Water is the only substance in the atmosphere that occurs naturally in all three phases. Condensed water in the atmosphere consists of suspended cloud particles and hydrometeors. Cloud particles are either liquid (water droplets) or solid (ice crystals). *Hydrometeors* are bodies of liquid or solid water such as raindrops and snow that are falling through the air.

In addition to the gaseous constituents and condensed water particles, the atmospheric composition includes *aerosol* particles that are suspended in the air. Atmospheric aerosol particles are comprised of dust, sea-salt particles, soil particles, volcanic debris, pollen, by-products of combustion, and other small particles that arise from chemical reactions within the atmosphere. Concentrations of atmospheric aerosol particles range from values on the

order of 10^3 cm^{-3} over the oceans, to 10^4 cm^{-3} over rural land areas, to 10^5 cm^{-3} or higher in cities. Aerosol number density generally decreases with height above the Earth's surface, where most of the aerosol and gaseous precursors originate. Atmospheric aerosol particles commonly have sizes in the range between 0.1 and $10 \mu\text{m}$. Concentrations of aerosol fall off sharply with increasing size. Aerosol sizes are limited on the upper end by gravitational fallout and on the lower end by aggregation processes. Scavenging by precipitation accounts for about 80-90% of the mass of aerosol removed from the atmosphere. The primary importance of aerosols to atmospheric thermodynamics is that a select group of them are crucial for cloud formation. The atmospheric aerosol also influences radiative transfer within the atmosphere.

Table 1.1 Main gaseous constituents of air, relative to the percent composition of dry air.

Constituent	Formula	Molecular Weight	% by Volume	% by Mass
Nitrogen	N_2	28.016	78.08	75.51
Oxygen	O_2	31.999	20.95	23.14
Argon	Ar	39.948	0.93	1.28
Carbon Dioxide	CO_2	44.010	0.03	0.05
Water vapor	H_2O	18.005	0-4	

1.2 Composition of the Ocean

The principal characteristic that differentiates seawater from pure water is the presence of dissolved salts, or its *salinity*. For purposes here, a *salt* is defined as a substance that forms ions in a water solution. Dissolved salts comprise about 3.5% of seawater by weight. Table 1.2 lists the elements that comprise 99.9% of the dissolved constituents of seawater. Sodium and chloride make the largest contributions, accounting for approximately 90% of the ocean salinity. Although the total amount of dissolved salts may vary with time and location, the fractional contribution of the major ions to total salinity of the ocean remains approximately constant.

Salinity was originally conceived as a measure of the mass of dissolved salts in a mass of seawater. However, it is difficult to determine the salt content by drying seawater and weighing the remaining salts, since chemical changes occur at the heats necessary to accomplish the drying. A complete chemical analysis of seawater is too time consuming to be conducted routinely. A more practical method of estimating salinity is to infer the salinity from the electrical conductivity of seawater. Although pure water is a poor conductor of electricity, the presence of ions allows water to carry an electric current, and the conductivity of seawater is proportional to its salinity.

Table 1.2 Average concentrations of the principal ions in seawater (total 34.482‰)

Ion	Formula	‰ by weight
chloride	Cl ⁻	18.900
sodium	Na ⁺	10.556
sulfate	SO ₄ ⁻	2.649
magnesium	Mg ⁺⁺	1.272
calcium	Ca ⁺⁺	0.400
potassium	K ⁺	0.380
bicarbonate	HCO ₃ ⁻	0.140
bromide	Br ⁻	0.065
borate	H ₂ BO ₃ ⁻	0.026
strontium	Sr ⁺⁺	0.013
fluoride	F ⁻	0.001

By international convention, the practical salinity of a sample of seawater is defined in terms of the ratio of the conductivity of seawater to the conductivity of a standard KCl (potassium chloride) solution with concentration of 32.4356 g kg⁻¹ at 15°C and 1 atmosphere pressure. Conductivity depends not only on salinity, but also on temperature and pressure. Therefore conductivity cannot be interpreted unambiguously as the total dissolved salts in a seawater sample. The unit of salinity determined in this manner is the *practical salinity unit* (psu), which is nearly equivalent to the total mass of dissolved solids in parts per thousand (‰).

The average salinity in the world ocean is 34.7 psu. Salinity in the open ocean ranges from about 33 to 38 psu. Higher values of salinity occur in regions of high evaporation such as the Mediterranean and Red Seas, where salinity values reach as high as 39 and 41 psu, respectively. Profiles of annual and zonal mean salinities are given in Figure 1.2. The salinity is large in the subtropical latitudes because evaporation exceeds precipitation and leaves the water enriched with salt. Salinities are low in the tropics and the mid-latitudes, where precipitation is high. The salinity of the North Atlantic Ocean averages 37.3 psu, compared with the North Pacific Ocean salinity of 35.5 psu.

In addition to dissolved salts, seawater also has dissolved gases (*e.g.*, oxygen, carbon dioxide, and sulphur dioxide) and a variety of suspended particles (*e.g.*, soil, atmospheric aerosol, and biogenic particulate matter).

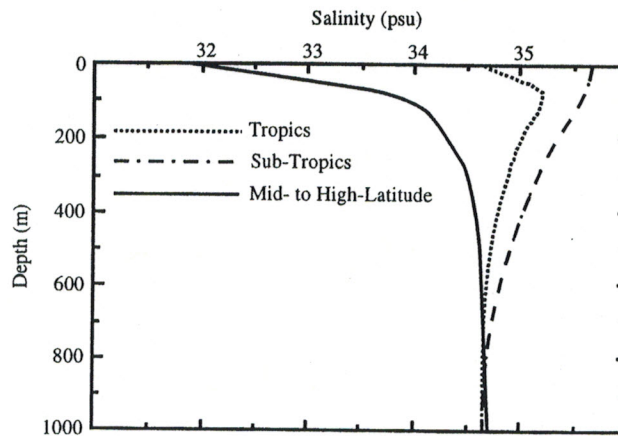


Figure 1.2 Profiles of annual mean ocean salinity in the upper ocean. High salinities near the surface are observed in subtropical latitudes because evaporation of fresh water from the ocean exceeds precipitation in these regions. In latitudes where precipitation exceeds evaporation, ~~and hence the flux of fresh water into the ocean is positive,~~ salinities are relatively low. In the deep ocean, salinity varies little with latitude, since evaporation and precipitation—the primary mechanisms influencing salinity—act at the surface. (Data from Levitus, 1982.)

1.3 Composition of the Solid Earth

The “bulk earth” composition is thought to be similar to the solar abundances, after subtracting out the light elements such as hydrogen and helium. The crust is depleted in iron and enriched in oxygen, silicon, aluminum, calcium, potassium, and sodium.

Table: Relative abundance by weight of elements in the whole Earth and the Earth’s crust

<u>Whole Earth</u>		<u>Earth’s crust</u>	
Iron	35%	Oxygen	46%
Oxygen	30%	Silicon	28%
Silicon	15%	Aluminum	8%
Magnesium	13%	Iron	6%
Nickel	2.4%	Magnesium	4%
Sulfur	1.9%	Calcium	2.4%
Calcium	1.1%	Potassium	2.3%
Aluminum	1.1%	Sodium	2.1%

1.4 Pressure

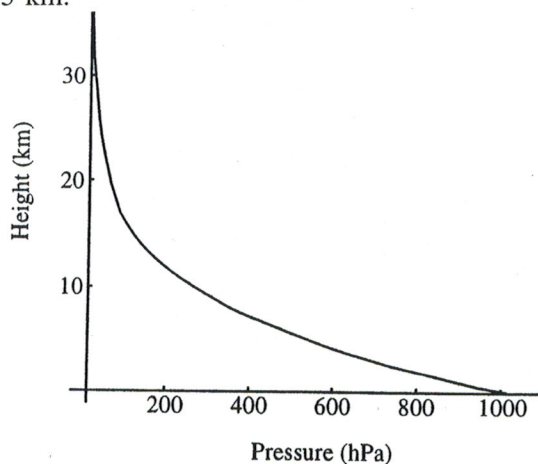
Pressure is defined as force per unit area, $p = F/A$. The pressure at any point in the atmosphere is the weight of air in a column above that point in a unit area. The pressure at any point in the ocean is the sum of the weight of the atmosphere plus the weight of the ocean in a column above the point per unit area. Since the mass of the world ocean is about 270 times the mass of the atmosphere, pressures in the ocean are substantially greater than those in the atmosphere.

In SI units, the Pascal (Pa) is the unit of pressure, where $1 \text{ Pa} = 1 \text{ N m}^{-2}$, and N is a Newton. Alternative units of pressure include:

Bar (bar):	$1 \text{ bar} = 10^5 \text{ Pa}$
Millibar (mb):	$1 \text{ mb} = 10^2 \text{ Pa}$
Torricelli (torr):	$1 \text{ torr} = 133.322 \text{ Pa}$
Atmosphere (atm):	$1 \text{ atm} = 1.01325 \text{ bar}$ $= 760 \text{ torr}$ $= 1.01325 \times 10^5 \text{ Pa}$

While Pa is the preferred unit of pressure, torr is a unit commonly used by atmospheric chemists and chemical oceanographers. The unit mb is frequently used by meteorologists, and oceanographers commonly use decibars (db). The preferred pressure unit for meteorology is hPa ($\equiv 10^2 \text{ Pa}$), which is equivalent to mb.

The vertical variation of pressure in the atmosphere is shown in Figure 1.3 to decrease almost exponentially with height, from a mean sea-level pressure of 1013.25 hPa. Approximately 90% of the weight of the atmosphere lies below 15 km.



The vertical variation of pressure with depth in the ocean is shown in Figure 1.4 to be approximately linear. In dealing with the pressure in the oceans, the atmospheric pressure is subtracted and the pressure at the sea surface is entered as zero. An increase of 10 m in depth in the ocean corresponds to an increase of 10^5 Pa , which is approximately 1 atm. Thus the pressure at a depth of 1 km in the ocean is equivalent to approximately 100 atm.

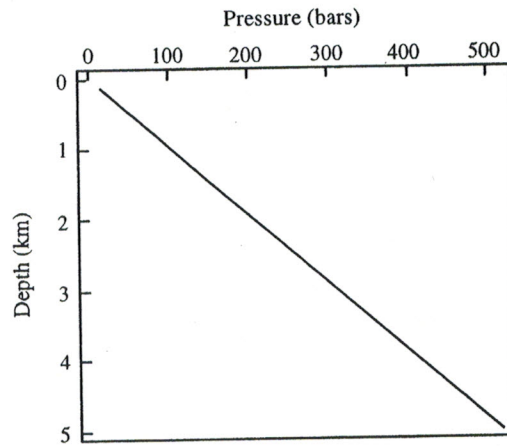
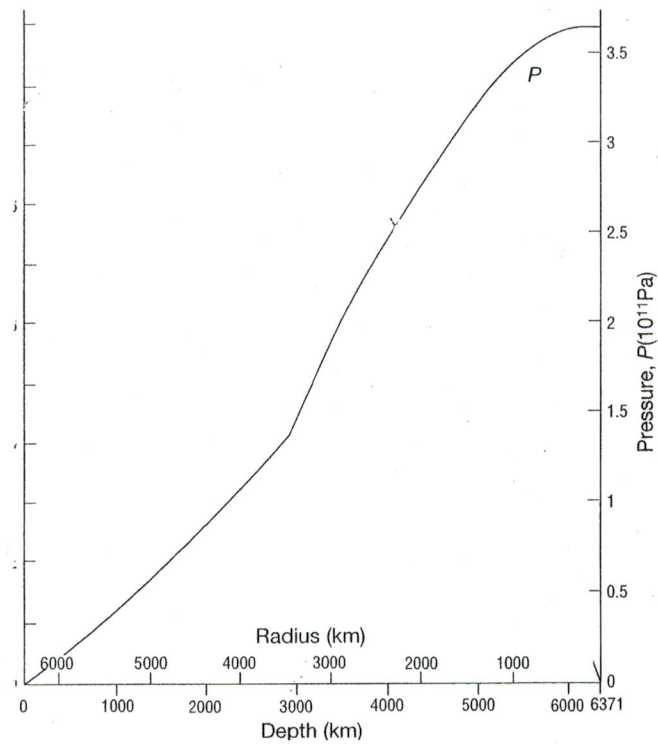


Figure 1.4 Vertical variation of pressure with depth in the ocean.

An estimate of the vertical distribution of pressure in the solid Earth is given below.



1.4 Density

Because of the large volumes characterizing the atmosphere, ocean and solid Earth, an intensive volume is desired. Such a volume, v , referred to as the *specific volume*, is given by $v = V/m$ so that the units of v are $\text{m}^3 \text{kg}^{-1}$. The specific volume is the inverse of the *density*, ρ , which has units of kg m^{-3} .

Figure 1.5 shows the vertical variation of density with height in the atmosphere. Density decreases with height nearly exponentially, which is related to the pressure decrease (Figure 1.3). A typical value of surface air density is 1.3 kg m^{-3} . The *mean free path* of molecules, which is determined by the frequency of intermolecular collisions, is inversely proportional to density. The mean free path increases exponentially from a value of about 10^{-7} m at the surface to the order of 1 m at 100 km .

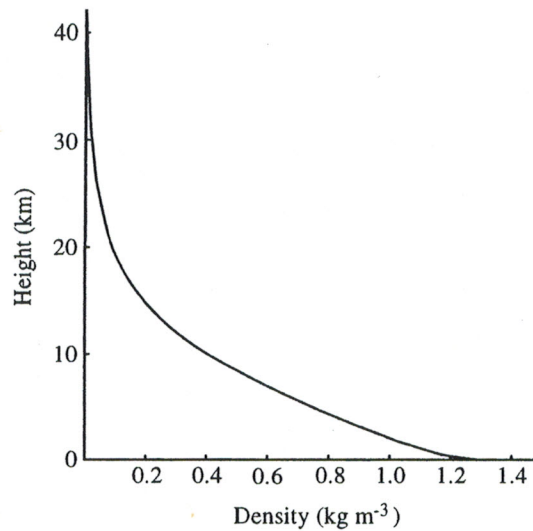


Figure 1.5 Vertical variation of density with height in the atmosphere. Density, like pressure, decreases nearly exponentially with height (U.S. Standard Atmosphere, 1976).

Liquid water is almost three orders of magnitude more dense than air. Hence, the interface between the atmosphere and ocean is very stable. Since liquid water is nearly incompressible, density changes in the ocean are relatively small. The density of seawater is a function not only of temperature and pressure, but also its salinity. Because of the small variations of density, we employ the notation σ_t as a shorthand way of expressing the density in terms of its departure from a reference value, ρ_0 :

$$\sigma_t = \rho - \rho_0 \quad (1.1)$$

The reference value is $\rho_0 = 1000 \text{ kg m}^{-3}$, which is the density of pure water at 4°C and 1 atm . A density value $\rho = 1025 \text{ kg m}^{-3}$ would thus correspond to $\sigma_t = 25 \text{ kg m}^{-3}$.

Depth profiles of σ_t for different latitudes are given in Figure 1.6. The shallow layer of near-constant density just below the ocean surface is called the *ocean mixed layer*. Regions in which density changes sharply with depth are known as *pycnoclines*.

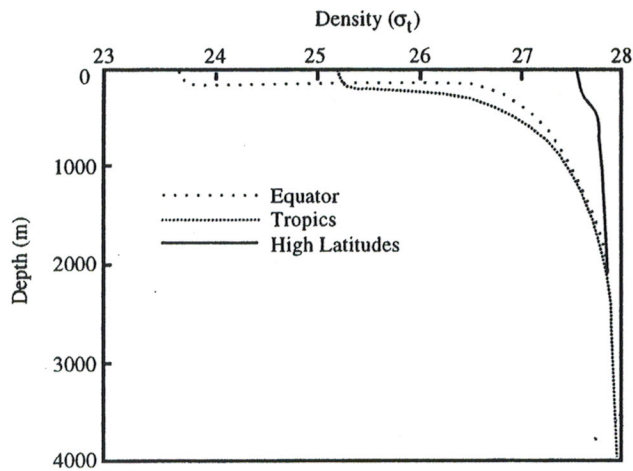
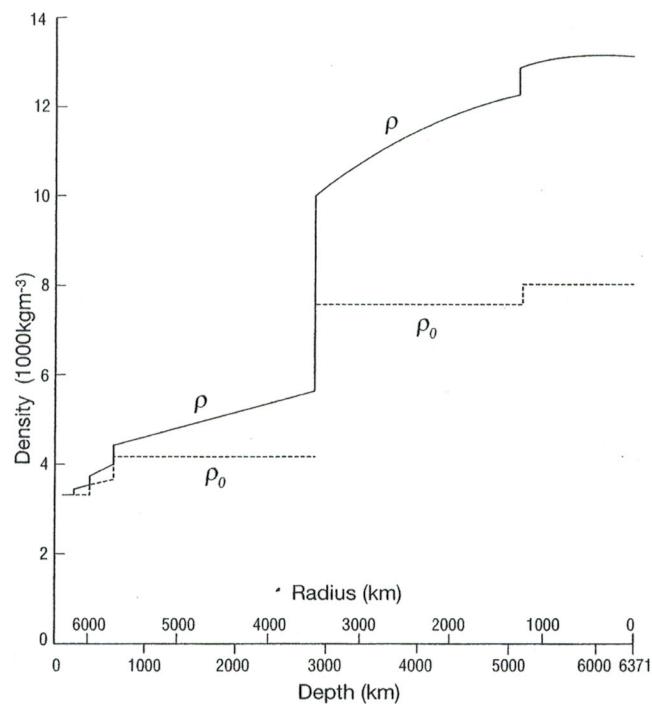


Figure 1.6 Density profiles in the ocean. Near the equator and throughout the tropics, the density increases rapidly with depth below a shallow surface layer of nearly constant density. This is due to the rapid cooling with depth in the ocean in these regions (see Figure 1.8).

The crust is the only part of the solid Earth that we have access to and is therefore the only part for which density can be measured directly. The value of the density of the upper mantle is close to 3300 kg m^{-3} . The figure below illustrates an modeled estimate of the vertical profile of density within the Earth's interior. The lower mantle is more dense than the upper mantle by about 700 kg m^{-3} . The jump in density is associated with phase transitions in silicates.



1.6 Temperature

An important property of *temperature* is that whenever two bodies are separately brought to be in equilibrium with a third body, these two bodies are then found to be in equilibrium with each other. This property is called the *zeroth law of thermodynamics*. The zeroth law tells us how to obtain a universal temperature scale: choose a particular system as a standard, select one of that system's possible temperatures and assign it a numerical value, and the same numerical value can be assigned to any other system in thermal equilibrium with the standard system.

A *thermometer* is an example of such a standard system. In order to assign a number to the temperature of a system, we need to define a temperature scale. This is done by choosing a thermometric substance and a thermometric property X of this substance which bears a one-to-one relation to its possible thermal states. The use of a thermometer allows us to specify temperature by using an arbitrary relation such as $T = aX + b$, which requires the choice of two well-defined thermal states as fixed points, to determine the constants a and b . The Celsius temperature scale assigns the fixed points so that 0°C is the temperature of melting ice and 100°C is the temperature of boiling water. An ideal gas thermometer can be used to determine an absolute temperature scale by making the temperature proportional to the pressure exerted by a sample of gas of low density held in a container at fixed volume. By defining the coldest possible temperature at zero, and using the unit of temperature in the ideal gas scale of temperature as equal in magnitude to the unit of the Celsius scale, the triple point of water is 273.15 . Thus the ideal gas temperature scale can be regarded as an absolute temperature scale, where temperatures cannot be negative.

The modern absolute temperature scale, which is independent of the nature of the thermodynamic system used as a thermometer, is called *Kelvin* (K) and is defined by setting the temperature of the triple point of water at exactly 273.15 . This choice establishes the unit of temperature so that there are 100 units between the freezing point and the boiling point of water, consistent with the Celsius scale. An absolute temperature scale such as Kelvin is the appropriate temperature scale to use for thermodynamic calculations.¹ However, both the Celsius and Fahrenheit scales are commonly used to describe the weather, and the Celsius scale is widely used in oceanography. Scale conversions between the Kelvin, Celsius, and Fahrenheit temperature scales are:

$$\begin{aligned} \text{K} &= 273.15 + ^{\circ}\text{C} \\ ^{\circ}\text{C} &= 5/9 (^{\circ}\text{F} - 32^{\circ}) \\ ^{\circ}\text{F} &= (9/5^{\circ}\text{C}) + 32^{\circ} \end{aligned}$$

The vertical temperature structure of the atmosphere below 50 km is given in Figure 1.7. The average temperature of the earth's surface is 288 K. In the lower atmosphere, below approximately 10-15 km, temperature decreases with height except in the polar regions where surface temperatures are very

¹ This is easily illustrated by substituting a temperature such as -30°C into the ideal gas law; this would result in either a pressure or volume that is negative!

cold. At a height ranging from 8 km in the polar winter to 17 km in the tropics, an inflection point is seen in the temperature profile, called the *tropopause*. The atmosphere below the tropopause is called the *troposphere*. Above the troposphere (up to about 50 km) is the *stratosphere*.

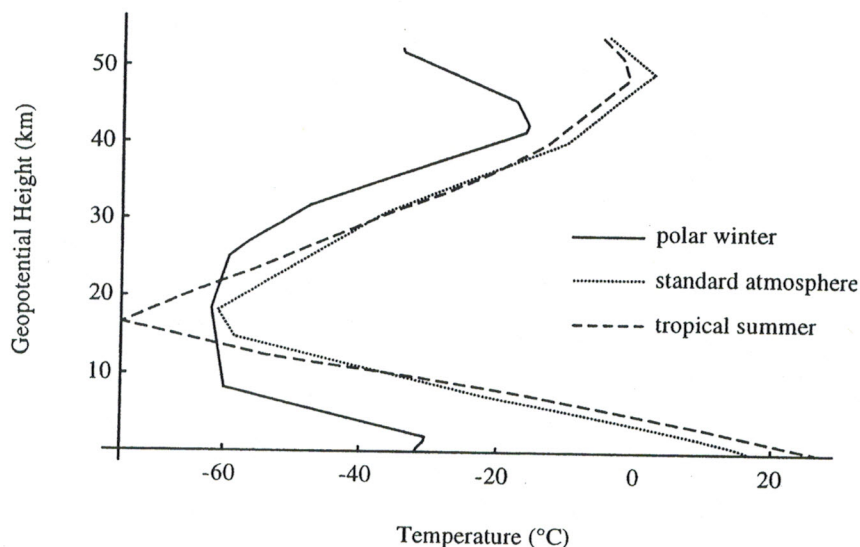


Figure 1.7 Vertical temperature structure in the atmosphere below about 50 km. Temperature decreases with height in the troposphere, except for the polar winter, where surface temperatures are very low, causing a temperature inversion near the surface (U.S. Standard Atmosphere, 1976).

The atmospheric temperature *lapse rate*, Γ , is defined to be minus the rate of temperature change with height:

$$\Gamma = - \frac{\partial T}{\partial z} \quad (1.2)$$

Note that $\Gamma > 0$ when temperature decreases with height. When a layer of the atmosphere has temperature that increases with height ($\Gamma < 0$), we call this layer a *temperature inversion*. If $\Gamma = 0$ (i.e., zero temperature change with height), the layer is called *isothermal*. Temperature inversions are seen in Figure 1.7 near the surface in the polar winter profile where the surface is very cold, and in the stratosphere, where ozone absorbs solar radiation. The average lapse rate in the troposphere is $\Gamma = 6.5 \text{ } ^\circ\text{C km}^{-1}$.

The distribution of temperature with depth in the ocean is shown in Figure 1.8. In sub-polar regions, large variations in temperature occur in the upper 100 m or so (the ocean mixed layer), due to fluctuations in forcing from the atmosphere. Between about 300 m and 1 km, the temperature decreases rapidly with depth. This region of steep temperature gradient is the permanent *thermocline*, beneath which there is virtually no seasonal variation, and the temperature decreases gradually to between 0 and 3°C. A seasonal thermocline often develops above the permanent thermocline. Strong latitudinal variations are seen particularly in the upper ocean. In the high latitudes there is no permanent thermocline because the temperature of the surface water is very cold, often covered by sea ice.

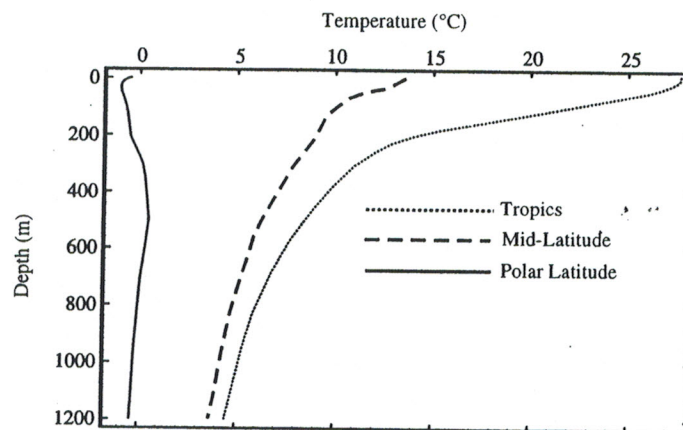
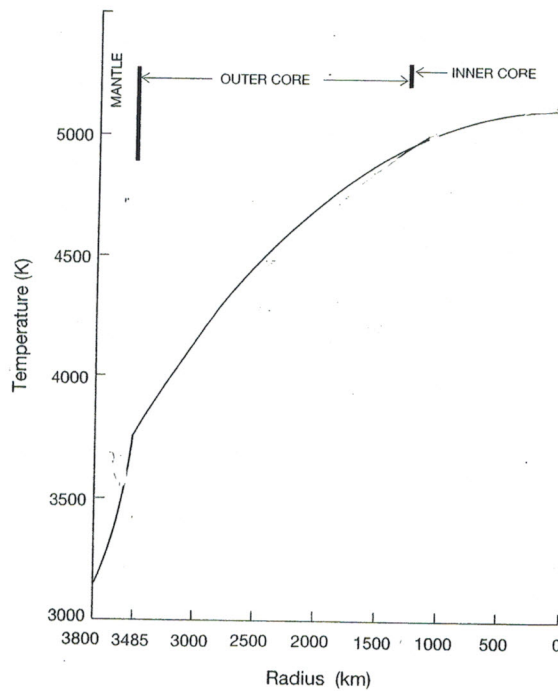
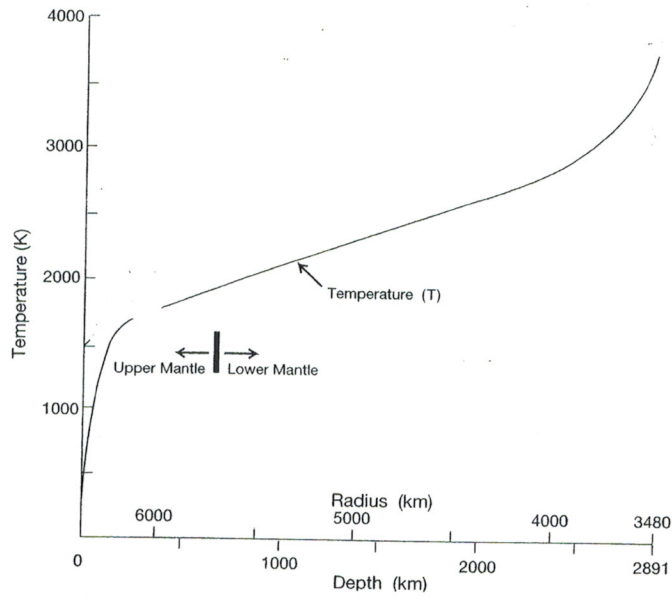


Figure 1.8 Variation of temperature with depth in the upper ocean. The vertical temperature gradient in the upper ocean is largest in the tropics, where surface water is warm. The latitudinal variation of temperature with depth is large in the upper ocean, where surface effects are important. (Data from Levitus, 1982.)

heating and cooling

In the Earth's mantle, there is a strong temperature gradient in the upper part of the mantle, where the Earth's temperature increases to over 1500K in the upper 200 km. In the Earth's core, the temperature increases to what has been estimated to be 4423 K.



1.7 Equation of State for Air

Except when water vapor is near condensation, air is observed to obey the ideal gas law. The ideal gas law (1.9) is written in extensive form, since the volume V , and number of moles n , are extensive variables. When applying the ideal gas law to the atmosphere, it is convenient to write the equation in terms of intensive variables. This is accomplished by dividing both sides of (1.9) by mass, m , yielding

$$p \frac{V}{m} = \frac{n}{m} R^* T \quad (1.10)$$

Using the definition of *molecular weight*, $M = m/n$, and the definition of specific volume, (1.10) can be written as

$$p v = \frac{R^*}{M} T \quad (1.11)$$

A *specific gas constant*, R , may be defined as $R = R^*/M$, so that (1.11) becomes

$$p v = R T \quad (1.12)$$

Strictly speaking, air does not have a molecular weight, since it is a mixture of gases and there is no such thing as an "air molecule." However, it is possible to assign an apparent molecular weight to air, since air as a mixture is observed to behave like an ideal gas. To apply the ideal gas law to the mixture of atmospheric gases, consider first the mixture of "dry-air" gases, excluding for now the variable constituent water vapor. To understand the behavior of a mixture of gases, we employ *Dalton's law of partial pressures*. Dalton's law states that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures that would be exerted by each constituent alone if it filled the entire volume at the temperature of the mixture. That is,

$$p = \sum_j p_j \quad (1.13)$$

where p is the total pressure and the p_j are the partial pressures.

Dalton's law implies that each gas individually obeys the ideal gas law and that the ideal gas law (1.12) for a mixture of gases can be written using (1.13) as

$$V \sum_j p_j = T \sum_j m_j R_j$$

1.7 Equation of State for Air

where we have used $v = V/m$. We can now define a mean specific gas constant as

$$\bar{R} = \frac{\sum_j m_j R_j}{m} \quad (1.14)$$

The equation of state for the mixture of dry-air gases can therefore be written in intensive form as

$$p v = \bar{R} T \quad (1.15)$$

where R_d is the specific gas constant for dry air. Using Table 1.1 and (1.14), a value for R_d is determined to be $287.104 \text{ J K}^{-1} \text{ kg}^{-1}$. The mean molecular weight of the mixture is

$$\bar{M} = \frac{\sum_i n_i M_i}{n} = \frac{m}{n} \quad (1.16)$$

The mean molecular weight for dry-air gases, M_d , is determined to be $28.96 \text{ g mole}^{-1}$.

The equation of state for air is complicated by the presence of water vapor, which has a variable amount in the atmosphere (Table 1.1). Assuming that the water vapor is not near condensation, the ideal gas law may be used and we have

$$e = \rho_v R_v T \quad (1.17)$$

where the notation e is commonly used to denote the partial pressure of water vapor and the subscript v denotes the vapor. The specific gas constant for water vapor is $R_v = R^*/M_v = 461.51 \text{ J K}^{-1} \text{ kg}^{-1}$. In a mixture of dry air and water vapor (*moist air*), the equation of state is

$$p = p_d + e = (\rho_d R_d + \rho_v R_v) T \quad (1.18)$$

The subscript d denotes the dry-air value, and the absence of a subscript denotes the value for the mixture of dry air plus water vapor.

The specific gas constant for moist air is determined from (1.14) to be

$$R = \frac{m_d R_d + m_v R_v}{m_d + m_v} \quad (1.19)$$

where m_d and m_v are the mass of dry air and water vapor, respectively, and $m = m_d + m_v$.

An intensive variable, the *specific humidity*, q_v , is defined as

$$q_v = \frac{m_v}{m_v + m_d} \quad (1.20)$$

so that the specific gas constant for moist air can be written as

$$R = (1 - q_v) R_d + q_v R_v \quad (1.21)$$

Using the definition of the specific gas constant, the specific gas constant for water vapor, R_v , may be written in terms of R_d

$$R_v = \frac{M_d}{M_v} R_d = \varepsilon^{-1} R_d \quad (1.22)$$

where $\varepsilon = M_v/M_d = 18/29 = 0.622$. The specific gas constant for moist air may then be written as

$$R = R_d \left[1 + q_v \left(\frac{1}{\varepsilon} - 1 \right) \right] = R_d (1 + 0.608 q_v) \quad (1.23)$$

Incorporating (1.23) into (1.18), the equation of state for moist air becomes

$$p v = R_d (1 + 0.608 q_v) T \quad (1.24)$$

It is awkward to have a variable gas constant, so it is the convention among meteorologists to make the humidity adjustment to the temperature rather than to the gas constant. Thus we define a *virtual temperature*, T_v

$$T_v = (1 + 0.608 q_v) T \quad (1.25)$$

so that the ideal gas law for moist air becomes

$$p v = R_d T_v \quad (1.26)$$

The virtual temperature may be interpreted as the temperature of dry air having the same values of p and v as the moist air under consideration. Since q_v seldom exceeds 0.02, the virtual temperature correction rarely exceeds more than 2 or 3°C; however, it is shown in Chapter 7 that the small virtual temperature correction has an important effect on buoyancy and hence vertical motions in the atmosphere.

1.8 Equation of State for Seawater

For a one-component fluid such as pure water, density is a function only of temperature and pressure. Since seawater is a multi-component fluid owing to its dissolved salts, its density is a function of temperature, pressure, and salinity: $\rho = \rho(T, p, s)$. Seawater density is observed to increase with increasing pressure and salinity, but decrease with increasing temperature.

An accepted theory for the density of pure water, analogous to the kinetic theory of ideal gases, does not exist. Therefore, an empirically-determined equation of state is used for seawater. An internationally agreed-upon equation of state (UNESCO, 1981) fits the available ocean density measurements to high accuracy. This equation has the form

$$\rho = \rho(T, p, s) = \frac{\rho(T, 0, s)}{1 - K_T(T, s, p)} \quad (1.27)$$

where $K_T(T, s, p)$ is the *mean bulk modulus*, which is inversely proportional to the compressibility (see Section 1.9). Each quantity on the right-hand side of (1.27), except pressure, is expressed as a polynomial series in s and T , expanded about values for zero salinity and a pressure of 1 bar. The density at the surface pressure ($p = 0$) is given by the polynomial form

$$\rho(T, 0, s) = A + B s + C s^{3/2} + D s^2 \quad (1.28)$$

The mean bulk modulus is given by

$$K_T(T, s, p) = E + F s + G s^{3/2} + (H + I s + J s^{3/2}) p + (M + N s) p^2 \quad (1.29)$$

The coefficients A, B, \dots, N in (1.28) and (1.29) are polynomials up to fifth degree in temperature (Table 1.3). In Table 1.3 and (1.27)–(1.29), the temperature is specified in °C, the pressure in bars, the salinity in psu, and density is $\text{m}^3 \text{kg}^{-1}$. This equation of state is accurate to within a standard error of approximately 0.009 kg m^{-3} over the entire oceanic pressure range.

For seawater at standard atmospheric pressure, a contour plot of ρ is given in Figure 1.10 as a function of temperature and salinity. Values of constant density are called *isopycnals*. Near the freezing point, the density of seawater is relatively insensitive to temperature variations and small salinity differences can play a major role in density variations.

An expression for the temperature of maximum density of seawater, T_p , can be obtained by differentiating with respect to temperature the equation of state for seawater.

TABLE A.3.2 Accuracy of measurement of salinity, temperature and pressure and related accuracies of density and specific volume

Accuracy of measurement	Related accuracies of	
	Density (kg m ⁻³)	Specific volume (m ³ kg ⁻¹)
$\Delta S = \pm 0.003$	$\Delta \rho = \Delta \sigma_t = \pm 0.002$	$\Delta \alpha = \Delta(\alpha_{s,t}) = \mp 0.2 \times 10^{-8}$
$\Delta T = \pm 0.02^\circ\text{C}$	$\Delta \rho = \Delta \sigma_t \mp 0.002$ ($T = 2^\circ\text{C}$, $S = 35$)	$\Delta \alpha = \Delta(\alpha_{s,t}) = \pm 0.3 \times 10^{-8}$
	to ∓ 0.006 ($T = 25^\circ\text{C}$, $S = 35$)	
$\Delta p = \pm 50 \text{ kPa}$	$\Delta \rho = \pm 0.24^*$	$\Delta \alpha = \mp 2.2 \times 10^{-8}$
($\equiv \Delta z = \pm 5 \text{ m}$ for upper 1000 m)		
For sea water of: $S = 35.00$ then $\rho = 1026.95 \text{ kg m}^{-3}$		
$T = 10.00^\circ\text{C}$ $\sigma_t = 26.95 \text{ kg m}^{-3}$		
$p = 0$ $\alpha = 0.97376 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$		
$\Delta_{s,t} = 109.7 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$		

* The uncertainty due to pressure differences may be greater in deep water because of greater uncertainty in pressure measurement.

A.3.2 International Equation of State of Sea Water, 1980

The new equation of state is presented by Millero and Poisson (1981) and also given in Unesco Technical Paper in Marine Science Number 36 (Unesco, 1981). The density of sea water as a function of practical salinity (S), temperature ($T^\circ\text{C}$) and sea pressure (p bars) is given by

$$\rho(s, t, p) = \rho(s, t, 0) [1 - p/K(s, t, p)]$$

where $K(s, t, p)$ is the secant bulk modulus (see Section A.1.11). The specific volume is given by

$$\alpha(s, t, p) = \alpha(s, t, 0) [1 - p/K(s, t, p)].$$

The polynomial expressions for $\rho(s, t, 0)$ and $K(s, t, p)$ are given below.

For the IES 80, the density of sea water at one standard atmosphere pressure ($p = 0$) is given by:

$$\begin{aligned} \rho(s, t, 0) = & +999.842\,594 & +6.793\,952 \times 10^{-2} \times T \\ & -9.095\,290 \times 10^{-3} \times T^2 & +1.001\,685 \times 10^{-4} \times T^3 \\ & -1.120\,083 \times 10^{-6} \times T^4 & +6.536\,332 \times 10^{-9} \times T^5 \\ & +8.244\,93 \times 10^{-1} \times S & -4.089\,9 \times 10^{-3} \times T \times S \\ & +7.643\,8 \times 10^{-5} \times T^2 \times S & -8.246\,7 \times 10^{-7} \times T^3 \times S \\ & +5.387\,5 \times 10^{-9} \times T^4 \times S & -5.724\,66 \times 10^{-3} \times S^{3/2} \\ & +1.022\,7 \times 10^{-4} \times T \times S^{3/2} & -1.654\,6 \times 10^{-6} \times T^2 \times S^{3/2} \\ & +4.831\,4 \times 10^{-4} \times S^2. \end{aligned}$$

For the IES 80, the secant bulk modulus is given by:

$$\begin{aligned} K(s, t, p) = & +19\,652.21 & -2.327\,105 & \times T^2 \\ & +148.420\,6 & \times T & -5.155\,288 \times 10^{-5} \times T^4 \\ & +1.360\,477 \times 10^{-2} \times T^3 & +1.437\,13 \times 10^{-3} \times T \times p \\ & +3.239\,908 & \times p & -5.779\,05 \times 10^{-7} \times T^3 \times p \\ & +1.160\,92 \times 10^{-4} \times T^2 \times p & -6.122\,93 \times 10^{-6} \times T \times p^2 \\ & +8.509\,35 \times 10^{-5} \times p^2 & & \\ & +5.278\,7 \times 10^{-8} \times T^2 \times p^2 & & \\ & +54.674\,6 & \times S & -0.603\,459 \times T \times S \\ & +1.099\,87 \times 10^{-2} \times T^2 & \times S & -6.167\,0 \times 10^{-5} \times T^3 \times S \\ & +7.944 \times 10^{-2} & \times S^{3/2} & +1.648\,3 \times 10^{-2} \times T \times S^{3/2} \\ & -5.300\,9 \times 10^{-4} \times T^2 & \times S^{3/2} & +2.283\,8 \times 10^{-3} \times p \times S \\ & -1.098\,1 \times 10^{-5} \times T \times p & \times S & -1.607\,8 \times 10^{-6} \times T^2 \times p \times S \\ & +1.910\,75 \times 10^{-4} & \times p \times S^{3/2} & -9.934\,8 \times 10^{-7} \times p^2 \times S \\ & +2.081\,6 \times 10^{-8} \times T \times p^2 \times S & +9.169\,7 \times 10^{-10} \times T^2 \times p^2 \times S \end{aligned}$$

The above polynomials are taken from Unesco Technical Papers in Marine Science No. 36, 1981.

The following values may be used for checking the correct use of the IES 80, ρ being in kg m⁻³ and K in bars:

S	$T^\circ\text{C}$	p bars	$\rho(s, t, p)$	$K(s, t, p)$
0	5	0	999.966 75	20 337.803 75
		1000	1044.128 02	23 643.525 99
	25	0	997.047 96	22 100.721 06
		1000	1037.902 04	25 405.097 17
35	5	0	1027.675 47	22 185.933 58
		1000	1069.489 14	25 577.498 19
	25	0	1023.343 06	23 726.349 49
		1000	1062.538 17	27 108.945 04

In the above polynomials, the pure-water terms are those not containing salinity (S). Procedures for converting salinities estimated by earlier methods to the Practical Salinity Scale, 1978, for use with the above polynomials are given by Lewis and Perkin (1981).

Tables of sea-water properties derived from the International Equation of State 1980 are promised as future volumes of the International Oceanographic Tables (Unesco, 1981).