

in or giving out heat, the temperature of the gas does not change. This statement, which is known as *Joule's law*, is strictly true only for an ideal gas.

Joule's law leads to an important conclusion concerning the internal energy of any ideal gas. If the gas neither does external work nor takes in or gives out heat, $dw = 0$ and $dq = 0$ in (2.37), so that $du = 0$. Also, according to Joule's law, under these conditions the temperature of the gas does not change, which implies that the kinetic energy of the molecules remains constant. Therefore, since the internal energy of the gas is also constant, that part of the internal energy due to the potential energy must also remain unchanged even though the volume of the gas changes. In other words, the internal energy of an ideal gas is independent of volume if the temperature is constant. This implies that the molecules of an ideal gas do not exert any attractive or repulsive forces on each other, so that the internal energy depends only upon the temperature.

2.3.2 Specific heats

Suppose a small quantity of heat dq is given to a unit mass of material and, as a consequence, its temperature increases from T to $T + dT$ without a phase change occurring. The ratio dq/dT is called the *specific heat* of the material. However, the specific heat defined in this way can have any number of values, depending on how the material changes as it receives the heat. If the volume of the material is kept constant, a *specific heat at constant volume* c_v is defined which is given by

$$c_v \equiv \left(\frac{dq}{dT} \right)_{\alpha \text{ const}} \quad (2.42)$$

But if the specific volume is constant (2.41) becomes $dq = du$; therefore,

$$c_v = \left(\frac{du}{dT} \right)_{\alpha \text{ const}}$$

But for an ideal gas Joule's law applies and therefore u depends upon temperature alone and we may write

$$c_v = \frac{du}{dT} \quad (2.43)$$

Therefore, from (2.41) and (2.43), the First Law of Thermodynamics for an ideal gas can be written in the form[†]

$$dq = c_v dT + p d\alpha \quad (2.44)$$

[†] The term dq is sometimes called the *diabatic* (or nonadiabatic) *heating* or *cooling*, where "diabatic" means involving the transfer of heat. The term "diabatic" would be redundant if "heating" and "cooling" were always taken to mean "the addition or removal of heat." However, "heating" and "cooling" are often used in the sense of "to raise or lower the temperature of," in which case it is meaningful to distinguish between that part of the temperature change dT due to diabatic effects (dq) and that part due to adiabatic effects ($p d\alpha$).

We may also define a *specific heat at constant pressure* c_p as

$$c_p \equiv \left(\frac{dq}{dT} \right)_{p \text{ const}} \quad (2.45)$$

where the material is allowed to expand as the heat is added and its temperature rises but its pressure is kept constant. In this case, a certain amount of the heat added will have to be expended to do work as the material expands against the constant pressure of the environment. Therefore, a larger quantity of heat must be added to the material to raise its temperature by a given amount than if the volume of the material were kept constant. This can be seen mathematically in the following way. Equation (2.44) can be rewritten in the form

$$dq = c_v dT + d(p\alpha) - \alpha dp \quad (2.46)$$

Making use of the ideal gas equation (2.3), this becomes

$$dq = (c_v + R) dT - \alpha dp \quad (2.47)$$

At constant pressure, the last term in (2.47) vanishes; therefore, from (2.45),

$$c_p = c_v + R \quad (2.48)$$

The specific heats at constant volume and at constant pressure for dry air are 717 and 1004 J deg⁻¹ kg⁻¹, respectively, and the difference between them is 287 J deg⁻¹ kg⁻¹, which is numerically equal to the gas constant for dry air. For an ideal monatomic gas $c_p : c_v : R = 5 : 3 : 2$ and for an ideal diatomic gas $c_p : c_v : R = 7 : 5 : 2$.[†]

By combining (2.47) and (2.48) we obtain an alternate form of the First Law of Thermodynamics:

$$dq = c_p dT - \alpha dp \quad (2.49)$$

2.3.3 Enthalpy

If heat is added to a material at constant pressure, so that the specific volume of the material increases from α_1 to α_2 , the work done by a unit mass of the material is $p(\alpha_2 - \alpha_1)$. Therefore, from (2.41), the heat dq added to a unit mass of the material at constant pressure is given by

$$dq = (u_2 - u_1) + p(\alpha_2 - \alpha_1) = (u_2 + p\alpha_2) - (u_1 + p\alpha_1)$$

where u_1 and u_2 are, respectively, the initial and final internal energies for unit mass. Therefore, at constant pressure,

$$dq = h_2 - h_1$$

[†] See, for example, F. W. Sears, "Thermodynamics, the Kinetic Theory of Gases and Statistical Mechanics," Addison-Wesley Publishing Co., 1953, p. 246-50.

where h is the *enthalpy* of a unit mass of material which is defined by

$$h \equiv u + p\alpha \quad (2.50)$$

Differentiating this expression, we obtain

$$dh = du + d(p\alpha)$$

Substituting for du from (2.43) and combining with (2.46), we obtain

$$dq = dh - \alpha dp \quad (2.51)$$

which is yet another form of the First Law of Thermodynamics.

By comparing (2.49) and (2.51) we note that

$$dh = c_p dT \quad (2.52)$$

or, in integrated form,

$$h = c_p T \quad (2.53)$$

where h is taken as zero when $T = 0$.

By combining (2.20), (2.51), and (2.53) we obtain

$$dq = d(h + \Phi) = d(c_p T + \Phi) \quad (2.54)$$

Hence, for an air parcel moving about in an hydrostatic atmosphere, the quantity $(h + \Phi)$ is constant if the gas under consideration neither gains nor loses heat (that is, $dq = 0$).[†]

2.4 LATENT HEATS

Under certain conditions heat may be supplied to a substance without its temperature changing. In this case the increase in internal energy is associated entirely with a change in molecular configurations produced by a change of phase. For example, if heat is supplied to ice at normal atmospheric pressure and 0°C, the temperature remains constant until all of the ice has melted. The *latent heat of melting* is defined as the heat required to convert a unit mass of a material from the solid to the liquid phase without a change in temperature. The temperature at which this phase change occurs is called the *melting point*. At normal atmospheric pressure and temperature the latent heat of melting of the water substance is $3.34 \times 10^5 \text{ J kg}^{-1}$; the *latent heat of fusion* has the same value. Similarly, the *latent heat of vaporization* is the heat required to convert a unit mass of material from the liquid to the vapor phase without a change in temperature. For the water substance at normal atmospheric pressure and 0°C, the latent heat of vaporization is $2.500 \times 10^6 \text{ J kg}^{-1}$; the *latent heat of condensation* has the same value.

[†] Strictly speaking, (2.54) holds only for an atmosphere in which there are no fluid motions. However, it is correct to within a few percent for the earth's atmosphere where the kinetic energy of fluid motions represents only a very small fraction of the total energy (see Problem 7.7). An exact relationship can be obtained by using Newton's Second Law of Motion and the continuity equation in place of (2.20) in the derivation. See E. Lorenz, "On the Nature and Theory of the General Circulation of the Atmosphere," Unipub, 1967, p. 15.

We will see in Section 2.8.2 that the melting and boiling points of a material depend on the pressure. Also, the latent heats of fusion and vaporization vary with temperature (see Problem 2.16).

2.5 ADIABATIC PROCESSES

If a material changes its physical state (that is, if its pressure, volume, or temperature change) without any heat being either added to it or withdrawn from it, the change is said to be *adiabatic*. Suppose that the initial state of a material is represented by the point A on the p - V diagram in Fig. 2.5 and that when it undergoes an isothermal transformation it moves along the line AB. If the same body underwent a similar change in volume but under adiabatic conditions, the transformation would be represented by a curve such as AC which is called an *adiabat*. The reason why the adiabat AC is steeper than the isotherm AB can be seen as follows: During the adiabatic compression the internal energy increases (since $dq = 0$ and $p d\alpha$ is negative in 2.41) and therefore the temperature of the material rises. However, for the isothermal compression, the temperature remains constant. Hence, $T_C > T_B$ and therefore $p_C > p_B$.

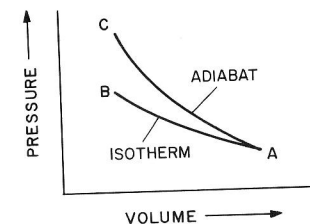


Fig. 2.5 Representation of an isothermal (AB) and an adiabatic (AC) transformation on a p - V diagram.

2.5.1 Concept of an air parcel

In many fluid mechanics problems, mixing is viewed as a result of the random motions of individual molecules. In the atmosphere molecular mixing is important only within a centimeter of the earth's surface and at levels above the turbopause ($\sim 105 \text{ km}$). At intermediate levels virtually all the vertical mixing is accomplished by the exchange of well-defined air parcels with horizontal dimensions ranging from a few centimeters to the scale of the earth itself.

In order to gain some insights into the nature of vertical mixing in the atmosphere it is useful to consider the behavior of an air parcel of infinitesimal dimensions that is assumed to be

- thermally insulated from its environment so that its temperature changes adiabatically as it rises or sinks,

- always at exactly the same pressure as the environmental air at the same level,[†] which is assumed to be in hydrostatic equilibrium, and
- moving slowly enough that its kinetic energy is a negligible fraction of its total energy.

Although in the case of real air parcels one or more of these assumptions is nearly always violated to some extent, this simple, idealized model is helpful in understanding some of the physical processes that influence the distribution of vertical motions and vertical mixing in the atmosphere.

2.5.2 The adiabatic lapse rate

We will now derive an expression for the rate of change of temperature with height of a parcel of dry air which moves about in the earth's atmosphere while always satisfying the conditions listed above. Since the air parcel undergoes only adiabatic transformations ($dq = 0$), and the atmosphere is in hydrostatic equilibrium, for a unit mass of air in the parcel we have, from (2.54),

$$d(c_p T + \Phi) = 0 \quad (2.55)$$

Dividing through by dz and making use of (2.20) we obtain

$$-\left(\frac{dT}{dz}\right)_{\text{dry parcel}} = \frac{g}{c_p} \equiv \Gamma_d \quad (2.56)$$

where Γ_d is called the *dry adiabatic lapse rate*. Since an air parcel expands as it rises in the atmosphere, its temperature will decrease with height so that Γ_d as defined by (2.56) is a positive quantity. Substituting $g = 9.81 \text{ m s}^{-2}$ and $c_p = 1004 \text{ J kg}^{-1} \text{ deg}^{-1}$ into (2.56) gives $\Gamma_d = 0.0098 \text{ deg m}^{-1}$ or 9.8 deg km^{-1} .

It should be emphasized again that Γ_d is the rate of change of temperature following a parcel of dry air which is being raised or lowered adiabatically. The actual lapse rate of temperature (which we will indicate by Γ) in the atmosphere, as measured by a radiosonde, averages $6\text{--}7 \text{ deg km}^{-1}$ in the troposphere but it takes on a wide range of values at individual locations.

2.5.3 Potential temperature

The *potential temperature* θ of an air parcel is defined as the temperature which the parcel of air would have if it were expanded or compressed adiabatically from its existing pressure and temperature to a standard pressure p_0 (generally taken as 1000 mb).

We can derive an expression for the potential temperature of air in terms of its pressure p , temperature T , and the standard pressure p_0 as follows. For an

[†] Any pressure differences between the parcel and its environment give rise to sound waves which produce a rapid adjustment. Temperature differences, on the other hand, are eliminated by much slower processes.

adiabatic transformation ($dq = 0$), (2.49) becomes

$$c_p dT - \alpha dp = 0$$

Combining this with (2.3) and rearranging terms yields

$$\frac{c_p}{R} \frac{dT}{T} - \frac{dp}{p} = 0$$

Integrating upward from p_0 (where $T = \theta$) to p , we obtain

$$\frac{c_p}{R} \int_{\theta}^T \frac{dT}{T} = \int_{p_0}^p \frac{dp}{p}$$

or

$$\frac{c_p}{R} \ln \frac{T}{\theta} = \ln \frac{p}{p_0}$$

Taking the antilog of both sides,

$$\left(\frac{T}{\theta}\right)^{c_p/R} = \frac{p}{p_0}$$

or

$$\theta = T \left(\frac{p_0}{p}\right)^{R/c_p} \quad (2.57)$$

Equation (2.57) is called *Poisson's[†] equation*. For dry air, $R = R_d = 287 \text{ J deg}^{-1} \text{ kg}^{-1}$ and $c_p = 1004 \text{ J deg}^{-1} \text{ kg}^{-1}$; therefore, $R/c_p = 0.286$.

If an air parcel is subjected to only adiabatic transformations as it moves through the atmosphere, its potential temperature remains constant. Parameters which remain constant during certain transformations are said to be *conserved*. Thus, potential temperature is a conservative quantity for adiabatic transformations. Potential temperature is an extremely useful parameter in atmospheric thermodynamics, since atmospheric processes are often close to adiabatic, and therefore θ remains essentially constant (see Sections 8.1.2 and 8.7.1).

2.5.4 The pseudoadiabatic chart

Poisson's equation may be conveniently solved in graphical form. If pressure is plotted on a distorted scale, in which the distance from the origin is proportional to p^{R_d/c_p} or $p^{0.286}$, (2.57) becomes

$$T = (\text{const})\theta p^{0.286} \quad (2.58)$$

Each value of θ represents a dry adiabat which is defined by a straight line with a particular slope which passes through the point $p = 0$, $T = 0$. If the pressure

[†] **Simeon Denis Poisson** (1781–1840) French mathematician. Studied medicine but turned to applied mathematics and became the first professor of mechanics at the Sorbonne.

scale is inverted so that p increases downward, the relation takes the form shown in Fig. 2.6, which is the basis for the *pseudoadiabatic chart* frequently used in meteorological computations. The region of the chart of greatest interest in the atmosphere is the portion shown within the dotted lines in Fig. 2.6, and this is generally the only portion printed. A copy of the normally printed pseudoadiabatic chart (but extending only to 100 mb) is shown on the back endpapers of this book. The sloping heavy black lines are the *dry adiabats* (that is, lines of constant potential temperature), some of which have the potential temperatures (in degrees Kelvin) printed over them. It should be noted that, as required by the definition of potential temperature, the actual temperature of the air (given on the abscissa) at 1000 mb is equal to its potential temperature. Several other sets of lines are printed on the pseudoadiabatic chart, some of which will be discussed later in this chapter.

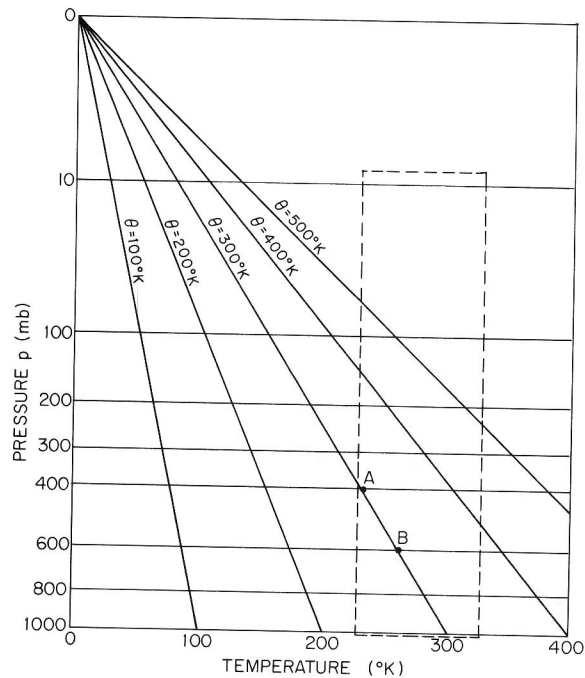


Fig. 2.6 The pseudoadiabatic chart. The region of the chart which is generally printed and used in meteorological computations is enclosed by the dotted lines. A portion of this chart is shown on the back endpapers of this book.

Problem 2.6 A parcel of air has a temperature of 230°K at the 400-mb level. What is its potential temperature? What temperature will the parcel have if it descends adiabatically to the 600-mb level?

Solution This problem is solved with reference to Fig. 2.6 but the student should follow the same steps on the pseudoadiabatic chart (back endpapers).

The original state of the air parcel is indicated by point A on Fig. 2.6 where its pressure is 400 mb and temperature (on the abscissa) 230°K or -43°C . The value of the dry adiabat which passes through point A is 300°K , which is therefore the potential temperature of the air. If an adiabatic transformation occurs to a pressure of 600 mb, the air along the dry adiabat with potential temperature 300°K descends to point B on Fig. 2.6 where the pressure is 600 mb and its new temperature (read off the abscissa) is -13°C or 260°K .

2.6 WATER VAPOR IN THE AIR

So far we have indicated the presence of water vapor in the air through the vapor pressure e which it exerts and we have allowed for its effect on the density of air by introducing the concept of a virtual temperature. However, the amount of water vapor present in a certain quantity of air may be expressed in many different ways; some of the more important of these are considered below.

2.6.1 Moisture parameters

Mixing ratio

The amount of water vapor in a certain volume of air may be defined as the ratio of the mass m_v of water vapor to the mass m_d of dry air; this is called the *mixing ratio* w . That is,

$$w \equiv \frac{m_v}{m_d} \quad (2.59)$$

The mixing ratio is generally expressed in grams of water vapor per kilogram of air. In the atmosphere the magnitude of w is typically a few grams per kilogram in middle latitudes but in the tropics it can reach values of 20 g kg^{-1} . It should be noted that if neither condensation nor evaporation take place, the mixing ratio of an air parcel is a conservative quantity.

Problem 2.7 If air contains water vapor with a mixing ratio of 5.5 g kg^{-1} and the total pressure is 1026.8 mb, calculate the vapor pressure e .

Solution The partial pressure exerted by any constituent in a mixture of gases is proportional to the number of kilomoles of the constituent in the mixture. Therefore, the pressure e due to water vapor in the air is given by

$$e = \frac{m_v/M_w}{m_d/M_d + m_v/M_w} p \quad (2.60)$$

where m_v and m_d are the masses of water vapor and dry air in the mixture, M_w the molecular weight of water, M_d the apparent molecular weight of dry air, and p the total pressure of the moist air. From (2.59) and (2.60) we obtain

$$e = \frac{w}{w + \varepsilon} p \quad (2.61)$$

where $\varepsilon = 0.622$ as defined in (2.14). Substituting $p = 1026.8 \text{ mb}$ and $w = 5.5 \times 10^{-3} \text{ kg kg}^{-1}$ into (2.61), we obtain $e = 9 \text{ mb}$.