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Eugene F. Milone  
William J.F. Wilson

# Solar System Astrophysics

Planetary Atmospheres and the Outer  
Solar System

*Second Edition*



 Springer

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Planetary Atmospheres and the Outer  
Solar System

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# Preface

## Preface to the First Edition

This work is appearing in two parts because its mass is the result of combining detailed exposition and recent scholarship. Book I, dealing mainly with the inner solar system, and Book II, mainly on the outer solar system, represent the combined, annually updated, course notes of E. F. Milone and W. J. F. Wilson for the undergraduate course in solar system astrophysics that has been taught as part of the Astrophysics Program at the University of Calgary since the 1970s. The course, and so the book, assumes an initial course in astronomy and first-year courses in mathematics and physics. The relevant concepts of mathematics, geology, and chemistry that are required for the course are introduced within the text itself.

*Solar System Astrophysics* is intended for use by second- and third-year astrophysics majors, but other science students have also found the course notes rewarding. We therefore expect that students and instructors from other disciplines will also find the text a useful treatment. Finally, we think the work will be a suitable resource for amateurs with some background in science or mathematics. Most of the mathematical formulae presented in the text are derived in logical sequences. This makes for large numbers of equations, but it also makes for relatively clear derivations. The derivations are found mainly in Chaps. 2–6 in the first volume, *Background Science and the Inner Solar System*, and in Chaps. 10 and 11 in the second volume, *Planetary Atmospheres and the Outer Solar System*. Equations are found in the other chapters as well but these contain more expository material and recent scholarship than some of the earlier chapters. Thus, Chaps. 8 and 9, and 12–16 contain some useful derivations, but also much imagery and results of modern studies.

The first volume starts with a description of historical perceptions of the solar system and universe, in narrowing perspective over the centuries, reflecting the history (until the present century, when extra-solar planets again have begun to broaden our focus). The second chapter treats the basic concepts in the geometry of the circle and of the sphere, reviewing and extending material from introductory astronomy courses, such as spherical coordinate transformations. The third chapter

then reviews basic mechanics and two-body systems, orbital description, and the computations of ephemerides, then progresses to the restricted three-body and  $n$ -body cases, and concludes with a discussion of perturbations. The fourth chapter treats the core of the solar system, the Sun, and is not a bad introduction to solar or stellar astrophysics; the place of the Sun in the galaxy and in the context of other stars is described, and radiative transport, optical depth, and limb-darkening are introduced. In Chap. 5, the structure and composition of the Earth are discussed, the Adams–Williamson equation is derived, and its use for determining the march of pressure and density with radius described. In Chap. 6, the thermal structure and energy transport through the Earth are treated, and in this chapter the basic ideas of thermodynamics are put to use. Extending the discussion of the Earth’s interior, Chap. 7 describes the rocks and minerals in the Earth and their crystalline structure. Chapter 8 treats the Moon, its structures, and its origins, making use of the developments of the preceding chapters. In Chap. 9, the surfaces of the other terrestrial planets are described, beginning with Mercury. In each of the three sections of this chapter, a brief historical discussion is followed by descriptions of modern ground-based and space mission results, with some of the spectacular imagery of Venus and Mars. The chapter concludes with a description of the evidence for water and surface modification on Mars. This concludes the discussion of the inner solar system.

The second volume begins in Chap. 10 with an extensive treatment of the physics and chemistry of the atmosphere and ionosphere of the Earth and an introduction to meteorology, and this discussion is extended to the atmospheres of Venus and Mars. Chapter 11 treats the magnetospheres of these planets, after a brief exposition of electromagnetic theory. In Chap. 12, we begin to treat the outer solar system, beginning with the gas giants. The structure, composition, and particle environments around these planets are discussed, and this is continued in Chap. 13, where the natural satellites and rings of these objects are treated in detail, with abundant use made of the missions to the outer planets. In Chap. 14, we discuss comets, beginning with a historical introduction that highlights the importance of comet studies to the development of modern astronomy. It summarizes the ground- and space-based imagery and discoveries, but makes use of earlier derivations to discuss cometary orbits. This chapter ends with the demise of comets and the physics of meteors. Chapter 15 treats the study of meteorites and the remaining small bodies of the solar system, the asteroids (*aka* minor planets, planetoids), and the outer solar system “Kuiper Belt” objects, and the closely related objects known as centaurs, plutinos, cubewanos, and others, all of which are numbered as asteroids. The chapter ends with discussions of the origin of the solar system and of debris disks around other stars, which point to widespread evidence of the birth of other planetary systems. Finally, in Chap. 16, we discuss the methods and results of extra-solar planet searches, the distinctions among stars, brown dwarfs, and planets, and we explore the origins of planetary systems in this wider context.

At the end of nearly every chapter we have a series of challenges. Instructors may use these as homework assignments, each due 2 weeks after the material from that chapter were discussed in class; *we* did! The general reader may find them helpful as focusing aids.

## **Preface to the Second Edition**

As in the first edition, we maintain the two-volume bifurcation of the inner and outer regions of the solar system. In the first volume, we again begin with a historical overview but expand the horizon to include glimpses of extra-solar planetary systems. The basic mathematics, mechanics, geophysics, thermodynamics, chemistry, astrophysics, and mineralogical principles required for a sound introduction to space science have been revised with improved illustrations and examples drawn from wider sources. In Chap. 4, we have added descriptions of the features of the active Sun. Chapter 8, on the Moon, has been updated with results of probes of water at the poles and a fresh discussion of the Moon's origin. In Chap. 9, the Messenger mission has provided vital new details about Mercury, and the history of the study of Venus has been expanded. The Mars section includes results from the Curiosity mission and a description of current views of the search for life in the Viking mission. The crustal changes in Mars since its formation, and an enlarged discussion of climate changes, expand that section further. Similar expansions of the chapters of the second volume have vastly expanded the discussions of atmospheres, magnetospheres, the gas and ice giants of the outer solar system and their moons and ring systems. The discussion of meteors and meteorite impacts has been enlivened by recent events, and a deepening understanding of the role played by disks in the early history of planetary formation. The burgeoning field of extrasolar planets has been reflected in the vastly increased discussion in the last chapter, with the increasing knowledge of the properties of extrasolar planets and their more massive siblings, the brown dwarfs. The dynamical interactions being studied with increasingly sophisticated software simulations have greatly illuminated the likely dynamical development of the solar system. As in all such investigations, present questions have been and are being answered, but new puzzles arise, and it is the anticipation of the new adventures required to explain them that makes this field truly exciting.

Calgary, Alberta, Canada

Eugene F. Milone  
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In Chap. 3, the Bradstreet and Steelman software package *Binary Maker 3* was used to create an image to illustrate restricted three-body solutions.

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# Chapter 10

## Planetary Atmospheres

### 10.1 Atmospheric Constituents

The constituents of a planetary atmosphere are determined in a general way by the likelihood that a given constituent will be retained, rather than lost by evaporation into space over long periods of time. This likelihood is determined by three factors: (1) the equilibrium temperature of the planet, because the hotter the atmosphere, the larger the mean kinetic energy of its molecules,

$$E = \frac{3}{2} kT \tag{10.1}$$

where  $k = 1.3806488(13) \times 10^{-23}$  J/K is the Boltzmann constant,  $T$  is the equilibrium temperature in kelvin, and the number in parentheses is the uncertainty in the last two digits of the constant; (2) the molecular weight,  $m$ , of each atmospheric constituent, because equipartition of energy requires that more massive particles have smaller mean velocities,

$$E = \frac{1}{2} mv^2 \tag{10.2}$$

and (3) the planet's escape velocity,

$$v_{esc} = \sqrt{\frac{2GM}{R}} \tag{10.3}$$

where  $M$  and  $R$  are the planetary mass and radius, respectively. In a region of atmosphere in thermal equilibrium,<sup>1</sup> the distribution of the number of molecules

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<sup>1</sup>A system is in thermal equilibrium if its temperature is spatially uniform (the same temperature throughout the system) and is constant in time.

vs. the speed at which they are moving at any instant is said to be *Maxwellian* (See Schlosser et al. 1991/1994, Fig. 18.1).

The *molecular weight* of any species of molecule can be written

$$m = \mu m_u \quad (10.4)$$

where  $m_u = (1/12)[m(^{12}\text{C})] = 1.660538921(73) \times 10^{-27}$  kg is the unit atomic mass, and the dimensionless quantity  $\mu$  is expressed in units of  $m_u$ . It is not uncommon to refer to  $\mu$  as the *molecular weight*, the units of  $m_u$  being understood.

From (10.1), (10.2) and (10.4), the root mean square speed of any constituent can be written in terms of  $\mu$  as

$$v = \sqrt{\frac{3kT}{m}} = 157.94 \sqrt{\frac{T}{\mu}} \text{ m/s} \quad (10.5)$$

A very massive planet will retain even the lightest gases over a wide range of temperatures. Quite generally, if  $v/v_{esc} = 1/3$ , the atmosphere can be expected to be lost in weeks; if  $v/v_{esc} = 1/4$ , 10,000 years; if  $v/v_{esc} = 1/5$ ,  $10^8$  years; and if  $v/v_{esc} = 1/6$ , it can be considered retained for eons, or billions of years (Gy), assuming no major departure from the assumed equilibrium planetary temperature over this interval of time.

From (10.3) and (10.5), the lower limit for the molecular weight of a molecule that can be *retained* is

$$\mu \geq \left( 157.94 \frac{\sqrt{T}}{(v_{esc}/6)} \right)^2 = 8.980 \times 10^5 \frac{T}{v_{esc}^2} \quad (10.6)$$

From (6.35) of Milone and Wilson (2014), the equilibrium temperature for an assumed black body, rapidly rotating planet is:

$$T = \{L_{\odot}(1 - A)/[16\pi\sigma r^2]\}^{\frac{1}{4}} = 1.078 \times 10^8 [(1 - A)/r^2]^{\frac{1}{4}} \text{ K}$$

where  $A$  is the bolometric albedo,  $\sigma = 5.671 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$  is the Stefan–Boltzmann constant,  $r$  is the distance from the sun in meters, and the solar luminosity is  $L_{\odot} = 3.845 \times 10^{26} \text{ W}$  (Cox 2000, p. 340).

For a particular molecule to be retained over a significant fraction of the solar system's lifetime (assuming the equilibrium temperature correctly indicates the effective mean temperature of the planet, and there is no significant change in this temperature over this interval),

$$\begin{aligned}\mu &\geq 8.980 \times 10^5 \times 1.078 \times 10^8 \frac{[(1-A)/r^2]^{1/4}}{2GM/R} \\ &= 7.254 \times 10^{23} \frac{R}{M} \left( \frac{1-A}{r^2} \right)^{1/4}\end{aligned}\quad (10.7)$$

where  $r$ ,  $R$ ,  $M$ , and  $G = 6.67428(67) \times 10^{-11} \text{ N m}^2/\text{kg}^2$  are in SI units. The corresponding numerical constant for a slowly rotating planet is greater by a factor  $2^{\frac{1}{2}} = 1.189$ . Finally, with  $R$  and  $M$  in units of the Earth's radius and mass ( $6.378 \times 10^6 \text{ m}$ ,  $5.972 \times 10^{24} \text{ kg}$ , respectively) and  $a$  in au,<sup>2</sup> (10.7) becomes

$$\mu \geq 2.002 \frac{R/R_{\oplus}}{M/M_{\oplus}} \left( \frac{1-A}{a^2} \right)^{1/4}\quad (10.8)$$

As an example, for the Earth,  $A \approx 0.307$ ,  $\mu > \sim 2 \times 0.91 = 1.82$ , provided  $T$  is correctly given by (10.7); i.e.,  $\langle T_{\oplus} \rangle = T_{\text{eq}} = 254 \text{ K}$ . In point of fact, the Earth is slightly warmer because of its atmosphere, so that  $\langle T_{\oplus} \rangle = 288 \text{ K}$ . Using this value directly in (10.6), one obtains,  $\mu = 2.07$ .

Thus, the Earth is marginally unable to retain hydrogen at present, but should have retained helium ( ${}^4\text{He}$ ,  $\mu \sim 4$ ). Nevertheless, the abundance of  ${}^4\text{He}$  in the Earth's atmosphere is much less than would be expected if all of its primordial helium were still present. In fact, the small amount present is equal to the amount being outgassed into the atmosphere every  $\sim 10^6$  years from  $\alpha$ -decay of uranium and thorium in the Earth's crust and mantle (Lie-Svendsen and Rees 1996). (An alpha particle is a  ${}^4\text{He}$  nucleus, and  $\alpha$ -decay involves the ejection of a  ${}^4\text{He}$  nucleus from an unstable atom.) This is a rapid rate of supply compared to the age of the Earth, so if there is not a comparable loss rate then there would be much more  ${}^4\text{He}$  in the atmosphere than we find. Thermal escape is insufficient, so other loss mechanisms are required. The two most promising are outflow of  $\text{He}^+$  along open magnetic field lines around the geomagnetic poles (planetary magnetospheres are discussed in Chap. 11) and exothermic charge exchange with atmospheric nitrogen,  $\text{He}^+ + \text{N}_2 \rightarrow \text{N}_2^+ + \text{He}$ . In the latter process, the He can gain enough kinetic energy to escape, and being neutral is not constrained by the magnetic field lines.

See Schlosser et al. (1991/1994, pp. 94–97) for further discussion of the species of molecules retainable in planetary atmospheres.

One of the more interesting concepts in planetary physics is the probability of escape of gases from the sub-solar region, where the instantaneous temperature is much higher than the global or even hemispherical average. How do we know if the evaporation from this location alone is the determining factor?

<sup>2</sup>for the astronomical unit, the semi-major axis of the Earth's orbit, defined by the IAU in 2012 formally as exactly equal to 149,597,870,700 m.

The answer probably lies in the *mean free path* of a molecule on the surface of a planet. The term refers to the average distance a molecule travels before colliding with another molecule. If a molecule receives sufficient energy for it to escape, how long does it take before it collides with another molecule? The problem and the solutions to it are described in, for example, Jeans' (1952) *Kinetic Theory of Gases*. The probability of collision depends strongly on the atmospheric density. In the hypothetical case where all molecules are stationary except one, it can be shown that the mean distance,  $d$ , which that one travels between collisions may be written

$$d = \frac{1}{\pi n R^2} \quad (10.9)$$

where  $n$  is the number density [the number of particles (in this case, molecules) per unit volume], and  $R$  is a characteristic distance about equal to the mean radius of a molecule. If, on the other hand, all molecules are moving and the gas is in thermal equilibrium then the molecular speeds correspond to a Maxwellian distribution.<sup>3</sup> In this case, the mean free path of a molecule depends on its speed; e.g., if the molecule is moving very quickly, then the other molecules are essentially at rest by comparison and  $d$  is given by (10.9). Averaged over molecules of all speeds in a Maxwellian distribution, the mean free path is

$$\frac{1}{\sqrt{2} \pi n R^2} \quad (10.10)$$

This number is about  $6 \times 10^{-8}$  m at sea level in the Earth's atmosphere, or about  $320R$  (Jeans 1952 pp. 44–49).

Thus, a great many collisions may occur prior to escape, the angle of alteration of direction in each collision being a further variable, and, at each collision, energy may be lost as well as gained; obviously, it will be easier to escape in a less dense environment.

Next we discuss the structure of atmospheres, and the behavior of pressure with height.

## 10.2 Atmospheric Structure

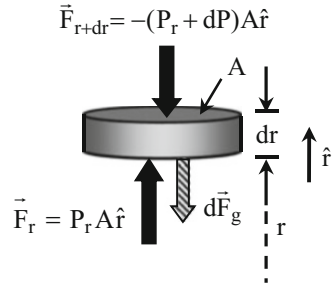
### 10.2.1 Pressure Variation with Height

For an atmosphere to be a reasonably permanent feature of a planet, the atmosphere must be in hydrostatic equilibrium, i.e., it should neither accelerate outward nor

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<sup>3</sup>A Maxwellian distribution gives the number of atoms or molecules vs. speed in a gas in thermal equilibrium.

**Fig. 10.1** Mechanical equilibrium of a parcel of air in a stationary atmosphere



collapse inward. Here, we will assume that the atmosphere can be approximated by spherical symmetry, e.g., only the radial components of force vectors are non-zero.

Figure 10.1 shows a free-body diagram for a small parcel of gas in such an atmosphere, in the form of a short cylinder of thickness  $dr$ , cross-section  $A$ , volume  $dV = Adr$ , density  $\rho$ , and mass  $dm = \rho dV$ , located at a distance  $r$  from the center of the planet. The unit vector,  $\hat{r}$ , signifies the positive radial direction; subscripts  $r$  or  $r + dr$  specify radial location.

For hydrostatic equilibrium, the forces acting on this pillbox-shaped parcel must add to zero:

$$\vec{F}_r + \vec{F}_{r+dr} + d\vec{F}_g = 0 \tag{10.11}$$

[N.B: The “+” symbols in (10.11) are addition operators, not signs of quantities. Vectors are defined by only two attributes: magnitude and direction.] From Fig. 10.1, and with  $M(r)$  being the total mass interior to radius  $r$ ,

$$d\vec{F}_g = -g dm \hat{r} = -g \rho dV \hat{r} = -g \rho A dr \hat{r} = -\frac{GM(r)}{r^2} \rho A dr \hat{r} \tag{10.12}$$

$$\vec{F}_r = P_r A \hat{r} \tag{10.13}$$

$$\vec{F}_{r+dr} = -P_{r+dr} A \hat{r} = -(P_r + dP) A \hat{r} \tag{10.14}$$

[For any two vectors,  $\vec{A}$  and  $\vec{B}$ , if  $\vec{B} = -\vec{A}$  then  $\vec{B}$  has the same magnitude as  $\vec{A}$  and the opposite direction. Thus, the “-” symbols in (10.12) and (10.14) and the implied “+” sign in (10.13) show how the three force vectors in (10.11) are directed relative to the chosen unit vector,  $\hat{r}$ .] Substituting (10.12)–(10.14) into (10.11) and taking vector components in the radial direction gives

$$P_r A - (P_r + dP) A - g \rho A dr = 0 \tag{10.15}$$



[Vector components are scalars with magnitude and sign, with the radial component being positive in the direction of  $\hat{r}$  (upward in Fig. 10.1) and negative in the direction opposite to  $\hat{r}$  (downward in Fig. 10.1). Because the individual quantities in (10.15) are magnitudes, the signs of the components appear explicitly in the equation.] Solving for  $dP$ ,

$$dP = -g\rho dr = -\frac{dF_g}{A} \quad (10.16)$$

The quantities  $g$  and  $\rho$  are positive, so  $dP$  is negative when  $dr$  is positive, i.e., pressure decreases outward in the atmosphere. The *pressure gradient* is the rate of change of pressure with distance, so

$$\frac{dP}{dr} = -g\rho \quad (10.17)$$

also known as the *equation of hydrostatic equilibrium*.

The pressure can also be expressed in terms of the *perfect gas law*, which provides an *equation of state*:

$$P = nkT \quad (10.18)$$

Here,  $n$  is again the number density, related to the density and the mean molecular weight,  $m$ , of the atmosphere through the relation

$$n = \rho/m \quad (10.19)$$

Then from (10.4),

$$P = \rho kT/m = \rho kT/\mu m_u \quad (10.20)$$

From (10.17), substituting for  $\rho$  from (10.20), we then get for the pressure gradient

$$\frac{dP}{dr} = -\frac{\mu m_u g P}{kT} \quad (10.21)$$

from which we obtain the differential equation

$$\frac{dP}{P} = -\frac{\mu m_u g}{kT} dr \quad (10.22)$$

The integrated solution to (10.22) is

$$\ln \frac{P}{P_0} = -\frac{\mu m_u g}{kT} (r - r_0) \quad (10.23)$$

or

$$\frac{P}{P_0} = \exp\left\{-\frac{\mu m_u g}{kT} (r - r_0)\right\} \quad (10.24)$$

where  $r_0$  is a reference height (e.g., the base of the atmosphere) and  $P_0$  is the pressure at  $r = r_0$ .

The *pressure scale height* is defined as

$$H = \frac{kT}{\mu m_u g} \quad (10.25)$$

Equation (10.25) can be expressed in terms of the universal gas constant,  $R = 8.3144621(75) \text{ J mol}^{-1} \text{ K}^{-1}$ , using the relationship  $R = kN_A$ . Here,  $N_A = 6.02214129(27) \times 10^{23} \text{ mol}^{-1}$  is Avogadro's number, the number of particles (e.g., atoms or molecules) in one mole.

Then

$$H = \frac{RT}{\mu m_u N_A g} = (10^3 \text{ mol kg}^{-1}) \frac{RT}{\mu g} \quad (10.25a)$$

The factor in parentheses in (10.25a) may be combined with  $R$  to obtain a new constant (commonly and somewhat confusingly also written  $R$ ; check its units if in doubt!),  $R = 8314.4621(75) \text{ J kg}^{-1} \text{ K}^{-1}$ ; then

$$H = \frac{RT}{\mu g} \quad (10.26)$$

Then, letting  $h = r - r_0$ , we get the *pressure scale height equation*,

$$P = P_0 e^{-h/H} \quad (10.27)$$

Equation (10.27) has been used to compute the mean molecular weight for outer planet atmospheres. In particular, the occultation of a star by Jupiter or another planet provides such an opportunity. The geometry, technique, and many results are reviewed by Elliott and Olkin (1996). A similar opportunity is provided by the occultation of an orbiting spacecraft passing behind the planet's atmosphere, as seen from Earth. Radio waves in the GHz range interact differently with the neutral and ionized components of the atmosphere, allowing the effects of ionization to be subtracted out and thus providing information about the neutral components (and

vice versa); see, e.g., Jenkins et al. (1994). As the planet progressively covers the star, astronomers at various sites on the Earth measure the optical depth along the line traversed by the starlight through the planet's atmosphere as a function of time. The *optical depth* is a measure of the absorptive/scattering properties of an atmosphere; an optical depth of one corresponds to the distance required for the transmitted light to decrease in intensity by a factor  $e$ . The curve of optical depth vs. time can be converted to a curve of refractive index vs. depth vertically into the atmosphere. Refractive index in turn depends on the number density of absorbers,  $n$ , as does the atmospheric pressure by (10.18),  $P = nkT$ , so that the index of refraction demonstrates similar behavior to pressure as the occultation proceeds. The refractivity scale height allows a determination of the pressure scale height, and from that the mean molecular weight of the atmosphere. In practice, the temperature and therefore pressure scale height vary with height through the atmosphere, and this variation is not generally known, so the profiles are compared to those predicted from atmospheric models with a number of parameters that are adjusted to achieve best fits. An example of the usefulness of an occultation for determining an atmosphere's mean molecular weight is given in Sect. 12.1.1.

## 10.2.2 Temperature Variation with Height

The temperature structure of a planetary atmosphere, as for the interior, is reached through a consideration of the heat flow.

We consider an atmosphere in which heat flow is dominated by *adiabatic convection*, i.e., parcels of air convect without exchanging heat with their surroundings.

The adiabatic relation between pressure and density in an ideal gas is

$$P = \text{const } \rho^\gamma \quad \text{or} \quad PV^\gamma = \text{const} \quad (10.28)$$

where  $\gamma = c_p/c_v$  is a quantity known as the *ratio of specific heats* (discussed below). Writing  $n = N/V$ , where  $N$  is the number of particles in volume  $V$ , we may solve the perfect gas law (10.18) for  $V$  to obtain

$$V = \frac{NkT}{P} \quad (10.29)$$

Then from (10.28) and (10.29),

$$P \left( \frac{NkT}{P} \right)^\gamma = \text{const} \quad (10.30)$$

or

$$(Nk)^{\gamma} T^{\gamma} P^{1-\gamma} = \text{const} \quad (10.31)$$

Finally,

$$T = \text{const}' P^{(\gamma-1)/\gamma} \quad (10.32)$$

We have shown that  $P$  depends on the altitude above the ground; we can now expect  $T$  to have such a dependence also.

The *heat capacity*,  $C$ , of a system is the heat input per unit temperature increase, i.e., the heat required to raise the temperature of the system by  $1^{\circ}$ :

$$C \equiv \frac{dQ}{dT} \quad (10.33)$$

Two types of heat capacity are particularly useful:

1. Heat capacity at constant pressure,  $P$ ,

$$C_P \equiv \left( \frac{dQ}{dT} \right)_{P = \text{const}}$$

2. Heat capacity at constant volume,  $V$ ,

$$C_V \equiv \left( \frac{dQ}{dT} \right)_{V = \text{const}}$$

If heat is added to a gas, the change shows up as an increase in internal energy and as work done,

$$dQ = dU + P dV \quad (10.34)$$

In (10.34), known as the differential form of the *first law of thermodynamics*,  $dQ$  is the heat entering the system,  $dU$  is the change in the internal energy of the gas, and  $P dV$  is the work done by the gas on its surroundings.

We now apply (10.34) to three different processes in a planetary atmosphere.

First, in an *adiabatic* process, such as occurs during adiabatic convection, no heat enters or leaves a parcel of gas as it convects, i.e.,  $dQ = 0$ . Equation (10.34) then shows that, in an adiabatic process, any work done by expansion of the gas is carried out at the expense of internal energy:

$$P dV = -dU \quad (10.35)$$

Second, if a process occurs at constant volume (referred to as an *isochoric* process), then no work is done and (10.34) gives

$$dQ = dU \quad (10.36)$$

that is, the heat goes into raising the internal energy because no expansion is permitted. The definition of  $C_V$  then gives

$$C_V = \left( \frac{dQ}{dT} \right)_{V=\text{const}} = \frac{dU}{dT} \quad (10.37)$$

for a process at constant volume.

Third, in an *isobaric* process, when the pressure is constant and the volume is allowed to change, (10.34) gives

$$C_P = \left( \frac{dQ}{dT} \right)_{P=\text{const}} = \frac{dU}{dT} + P \frac{dV}{dT} \quad (10.38)$$

Now noting from (10.37) that  $dU/dT$  equals  $C_V$ , we arrive at

$$C_P = C_V + P \frac{dV}{dT} \quad (10.39)$$

We now write the equation of state, (10.18),  $P = nkT$ , as

$$PV = NRT \quad (10.40)$$

where now  $N$  is the number of mol<sup>4</sup> and  $R$  is the *molar gas constant*,<sup>5</sup> which has the value

$$\begin{aligned} 8.3144621(75) \text{ J mol}^{-1} \text{ K}^{-1} &\cong 1.987 \text{ kcal kmol}^{-1} \text{ K}^{-1} \\ &\cong 0.08208 \text{ L atm mol}^{-1} \text{ K}^{-1} \end{aligned}$$

We can differentiate (10.40) to get

$$P \frac{dV}{dT} + V \frac{dP}{dT} = NR \quad (10.41)$$

---

<sup>4</sup>Or *moles*, gram-molecular weights or the mass equivalent of Avogadro's number ( $6.02214129(27) \times 10^{23}$ ) of molecules of this species. The latest values for physical constants, generally accepted worldwide, may be found on the National Institute for Standards and Technology (NIST) Website, <http://physics.nist.gov/cuu/Constants/>. At current writing (May 2013), these are the 2010 CODATA recommended values, where CODATA is the Committee on Data for Science and Technology.

<sup>5</sup>Or *universal gas constant*. See also Sect. 10.2.1.

Then for a process at constant pressure,

$$P \frac{dV}{dT} = NR \quad (10.42)$$

and (10.39) becomes

$$C_P = C_V + NR \quad (10.43)$$

We now define the *specific heat capacity*, also called the *specific heat*,  $c$ , by either

$$c \equiv \frac{C}{N} = \frac{1}{N} \frac{dQ}{dT} \quad \text{molar specific heat}$$

or

$$c \equiv \frac{C}{m} = \frac{1}{m} \frac{dQ}{dT} \quad \text{specific heat per unit mass}$$

depending on context. Equation (10.43) then shows that the molar specific heats are related by

$$c_P = c_V + R \quad (10.44)$$

The specific heat of an ideal gas depends on the number of degrees of freedom,  $g$ , of its particles (N.B.: this  $g$  is **not** gravitational acceleration). In general, the molar specific heats are given by

$$c_V = (g/2)R, \quad c_P = [(g/2) + 1]R$$

so the ratio of specific heats is

$$\gamma \equiv \frac{c_P}{c_V} = \frac{\left(\frac{g}{2} + 1\right)R}{\left(\frac{g}{2}\right)R} = \frac{g + 2}{g} \quad (10.45)$$

In an ideal, monatomic gas the particles have only the three translational degrees of freedom in the  $x$ ,  $y$ , and  $z$  directions, so  $g = 3$  and

$$c_V = (3/2)R, \quad c_P = (5/2)R$$

For the light diatomic gases  $H_2$ ,  $N_2$ ,  $CO$  and  $O_2$ , the molecules have at least five degrees of freedom: three translational and two rotational (about the two axes perpendicular to the long axis of the molecule). If temperatures are high enough, vibration adds a sixth. Thus at the lower temperatures,