EPS 237 Lesson 4: Atmospheric Thermodynamics

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1 Thermodynamics fundamentals

The ideal gas law can be used in the vast majority of cases when studying atmospheres. It is

$$p = k_B n T \tag{1}$$

with p pressure, n number density, T temperature and k_B Boltzmann's constant. Now $n = \rho/\overline{m}$, where $\overline{m}$ is the mean molecular weight of the gas in kg and ρ is density in kg/m^3. Hence

$$p = (k_B/\overline{m})\rho T. \tag{2}$$

Defining the specific gas constant $R \equiv k_B/\overline{m}$ we have

$$p = \rho R T \tag{3}$$

This is the form most widely used in atmospheric physics. It is extremely important to remember that the value of R depends on the composition of the atmosphere! Note we could also write $R \equiv R^*/\tilde{m}$, where R^* is the universal gas constant and $\tilde{m}$ is the mean *molar* mass of the gas (in kg/mol provided you have R^* in units of J/mol/K).

The ideal gas law no longer holds when energy in interactions between molecules (v.s. mean kinetic energy) is no longer negligible. Theory gets more difficult rapidly, but one example is Van der Waals equation

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{4}$$

a measures attraction between particles, b measures volume excluded by one mole of particles, V is total volume. Further nonlinear equations are possible. But it's rarely a concern: only deep Venus and gas giant atmospheres go non-ideal, and they're also opaque down there at most wavelengths.

Some definitions

Molar mixing ratio

$$\tilde{f}_{1,2} = \frac{p_1}{p_2} \tag{5}$$

Molar concentration

$$f_i = \frac{p_i}{\sum_j p_j} \tag{6}$$

Not the same thing! But interchangeable for trace gases.

Mass mixing ratio is

$$\alpha_{1,2} = \frac{\rho_1}{\rho_2} = \frac{m_1}{m_2}\frac{p_1}{p_2}. \tag{7}$$

Mass concentration (sometimes called specific concentration)

$$q_i = \frac{\rho_i}{\sum_j \rho_j}. \tag{8}$$

Mass column / path of minor atmospheric species

For a pure atmosphere

$$u = \frac{p}{g} \tag{9}$$

in kg/m^2. Just remember $F = ma$ and $p = F/A$. However, for a component of a mixed atmosphere

$$u_i = q_i u = \frac{m_i p_i}{\overline{m} p}\frac{p}{g} = \frac{m_i}{\overline{m}}\frac{p_i}{g} \tag{10}$$

with $\overline{m}$ the mean molecular weight of the mixture. This is important to remember for things like calculations of the mass of CO_2 in Earth's atmosphere!

2 Hydrostatic equation

Consider a small parcel of air with density $\rho(z)$, height Δz and area A under gravity g. If the parcel has mass Δm, the gravitational force it experiences is

$$\Delta F_g = -\Delta m g = -\rho g A \Delta z. \tag{11}$$

because $\rho = \Delta m/V$ where volume $V = A\Delta z$. Now if the object is static, this gravitational force must be balanced by a pressure gradient.

Given a pressure that varies with height, that at the base of the object is $p(z)$ and that at the top is $p(z + \Delta z)$. Then by Taylor's theorem

$$\Delta p = p(z + \Delta z) - p(z) \approx \frac{\mathrm{d}p}{\mathrm{d}z}\Delta z \tag{12}$$

But pressure is force per unit area, so the net upwards force is simply

$$\Delta F_p = A\Delta p = A\frac{\mathrm{d}p}{\mathrm{d}z}\Delta z \tag{13}$$

Writing $\Delta F_g = \Delta F_p$ we get

$$\frac{\mathrm{d}p}{\mathrm{d}z} = -g\rho. \tag{14}$$

the *hydrostatic balance equation*. Hydrostatic balance holds pretty closely in almost all planetary atmospheres, except at the very top, or if we zoom in closely enough to resolve convective and turbulent processes. It is therefore key to understanding their bulk structure.

If we use the ideal gas law we can write

$$\frac{\mathrm{d}p}{\mathrm{d}z} = -\frac{pg}{RT} \tag{15}$$

$$\frac{\mathrm{d}\ln[p]}{\mathrm{d}z} = -\frac{g}{RT} \tag{16}$$

$$\ln[p] - \ln[p_0] = -\int_0^z \frac{g}{RT}\mathrm{d}z' \tag{17}$$

$$p(z) = p_0 e^{-\int_0^z \frac{g}{RT}\mathrm{d}z'}. \tag{18}$$

In the special case where T is a constant (isothermal atmosphere), we can write this as

$$p(z) = p_0 e^{-z/H}. \tag{19}$$

with *scale height* $H \equiv RT/g$. In general both g and T vary with z. In the simple limit of a thin isothermal atmosphere, however, H is exactly the height over which the pressure (or the density) of the atmosphere decays by e^{-1}. This is a reasonable first approximation for Earth and other rocky planets.

3 Tropospheric convection: the dry adiabat

Even though it is in hydrostatic balance on large scales, the lower atmosphere is extremely turbulent due to convection. To understand the temperature variation, we consider a fluid blob / gas parcel moving upwards. The first law of thermodynamics is

$$dU = \delta Q - \delta W \tag{20}$$

This states that the change in internal energy of system = heat gained minus work done by system. The internal energy is $\mathrm{d}U = C_v \mathrm{d}T$, where C_v is the heat capacity at constant volume. Furthermore, the work done is $\delta W = p\mathrm{d}V$, where p is pressure and V volume. Divide everything by the parcel mass to get

$$\frac{\delta Q}{M} = c_v \mathrm{d}T + p\mathrm{d}v. \tag{21}$$

Here $c_v = C_v/M$ and $v = V/M$ is specific volume $(1/\rho)$. The first term is the increase in *internal energy* of the system ($\delta U = c_v \mathrm{d}T$), the second term is work done by the system, and δQ is heat supplied to system. We apply the chain rule to get

$$\frac{\delta Q}{M} = c_v \mathrm{d}T + \mathrm{d}(p/\rho) - \frac{\mathrm{d}p}{\rho}. \tag{22}$$

Now use the ideal gas law, set $\delta Q = 0$ (adiabatic assumption) and note that the specific heat capacity at constant pressure $c_p = c_v + R$. Then

$$0 = c_p \mathrm{d}T - \frac{\mathrm{d}p}{\rho}. \tag{23}$$

Solving this we get

$$\mathrm{d}\ln T = \frac{R}{c_p}\mathrm{d}\ln p \tag{24}$$

$$T = T_0 \left(\frac{p}{p_0}\right)^{R/c_p}. \tag{25}$$

$R/c_p \sim 0.28$ for N_2. T vs. p is generally most useful for climate studies because p determines the atmospheric physics. The *atmospheric lapse rate* as a function of z is more useful for engineering and some science applications. To derive it, combine (23) with the hydrostatic balance relation (14) and get

$$\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{g}{c_p}. \tag{26}$$

4 Tropospheric convection: the moist adiabat

This derivation is almost the same as before but with a few new terms. Condensate is often H_2O but can really be anything (e.g. N_2 on Pluto, ammonia on Jupiter). First we have saturation vapour pressure, often approximated by the Clausius-Clayperon equation (which I'm not going to derive here).

$$p_{sat}(T) = p_{sat}(T_0)e^{-\frac{L}{R_v}\left(T^{-1}-T_0^{-1}\right)}. \tag{27}$$

p_0, T_0 can conveniently be defined as the triple point values (e.g. 611 Pa, 273.16 K for H_2O). These quantities and the latent heat L vary widely with compound, leading to wildly different regimes. C.f. Earth with active H_2O cycle and T_{surf} in the 260 to 310 K range, and Titan with T_{surf} of order 90 K but an active methane cycle.

For the moist adiabat, we start by writing the previous dry equation with subscripts and multiply by M_n

$$M_n\delta q = M_n c_{p,n}\mathrm{d}T - M_n\frac{\mathrm{d}p_n}{\rho_n} \tag{28}$$

n for non-condensable. M_n is mass of non-condensing part of fluid blob (e.g. N_2).

Now we add a condensing component denoted by subscript v. On its own, such a gas would obey

$$M_v\delta q = M_v c_{p,v}\mathrm{d}T - M_v\frac{\mathrm{d}p_v}{\rho_v} + LdM_v. \tag{29}$$

But the 1st law of thermodynamics must be satisfied for the whole system, so we write

$$(M_v + M_n)\delta q = M_n c_{p,n}\mathrm{d}T - M_n\frac{\mathrm{d}p_n}{\rho_n} + M_v c_{p,v}\mathrm{d}T - M_v\frac{\mathrm{d}p_v}{\rho_v} + LdM_v \tag{30}$$

where LdM_v is the new latent heat term. Divide the whole thing by M_nT and define the condensable component mass mixing ratio

$$\alpha_v = \rho_v/\rho_n = M_v/M_n. \tag{31}$$

Then

$$(1+\alpha_v)\frac{\delta q}{T} = c_{p,n}dlnT - \frac{\mathrm{d}p_n}{T\rho_n} + \alpha_v[c_{p,v}dlnT - \frac{\mathrm{d}p_v}{T\rho_v}] + \frac{L}{T}d\alpha_v \tag{32}$$

Note that M_n is constant, so $dM_n = 0$. Then assume ideal gas law holds for both components ($p_v = \rho_v R_v T$, $p_n = \rho_n R_n T$)

$$(1+\alpha_v)\frac{\delta q}{T} = c_{p,n}dlnT - R_n dlnp_n + \alpha_v[c_{p,v}dlnT - R_v dlnp_v] + \frac{L}{T}d\alpha_v. \tag{33}$$

Note if there is no condensation, $d\alpha_v = 0$ and this is just the dry adiabat again, except now for two species. But now we make a key assumption of *saturation*: $p_v = p_{sat}$. Also adiabatic assumption so set $\delta q/T = ds = 0$ as before.

$$0 = c_{p,n} dlnT - R_n dlnp_n + \alpha_{sat}[c_{p,v} dlnT - R_v dlnp_{sat}(T)] + \frac{L}{T} d\alpha_{sat} \tag{34}$$

Our aim is to get $T(p)$, where $p = p_n + p_v$ is the total pressure. First collect terms:

$$0 = (c_{p,n} + \alpha_{sat} c_{p,v}) dlnT - R_n dlnp_n - \alpha_{sat} R_v dlnp_{sat}(T) + \frac{L}{T} d\alpha_{sat} \tag{35}$$

Note that if ideal gas law holds

$$d\alpha_v = d(\rho_v/\rho_n) = \frac{m_v}{m_n} d(p_v/p_n) = \frac{m_v}{m_n}\frac{p_v}{p_n}(dlnp_v - dlnp_n) = \alpha_v(dlnp_v - dlnp_n) \tag{36}$$

Hence

$$0 = (c_{p,n} + \alpha_{sat} c_{p,v}) dlnT - \left(R_n + \alpha_{sat}\frac{L}{T}\right) dlnp_n + \left(\frac{L}{T} - R_v\right) \alpha_{sat} dlnp_{sat}. \tag{37}$$

Now note that

$$dlnp_{sat} = \frac{L}{R_v T} dlnT \tag{38}$$

from the Clausius Clayperon equation. Hence

$$0 = \left[(c_{p,n} + \alpha_{sat} c_{p,v}) + \left(\frac{L}{T} - R_v\right) \alpha_{sat} \frac{L}{R_v T}\right] dlnT - \left(R_n + \alpha_{sat}\frac{L}{T}\right) dlnp_n \tag{39}$$

or

$$\frac{dlnT}{dlnp_n} = \frac{R_n}{c_{p,n}} \frac{1 + \frac{L}{R_n T}\alpha_{sat}}{1 + \left[\frac{c_{p,v}}{c_{p,n}} + \left(\frac{L}{T R_v} - 1\right)\frac{L}{c_{p,n} T}\right] \alpha_{sat}}. \tag{40}$$

Remember $\frac{R_n}{c_{p,n}} \sim 0.28$ for N_2. Take $\alpha_{sat} \to 0$ and we get the dry adiabat again.