Fundamentals of Atmospheric Physics

Lecture 2

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Atmospheric Thermodynamics

In this chapter we show how basic thermodynamic concepts can be applied to the atmosphere.

1) The atmosphere behaves as an ideal gas

2) Some basic information on the various gases comprising the atmosphere

- 3) The potential temperature
- 4) An air parcel concept

5) The thermodynamics of water vapour in the air

6) The tephigram

7) The formation of cloud droplets by condensation of water vapour

The ideal gas law

To a good approximation the atmosphere behaves as an ideal (or perfect) gas, with each mole of gas obeying the law

 $pV_m = RT, \qquad \rho = \frac{M_m}{V_m}$ $p = \frac{RT}{V_m} = \frac{R}{M_m}T\rho \qquad p = R_a T\rho \qquad R_a \equiv \frac{R}{M_m}$

Atmospheric composition

Consider a small sample of air

volume V,

temperature T

 G_i (i = 1,2,...)

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pressure p,

If there are n_i molecules of gas G_i in the sample, then the total number of molecules in the sample is

$$n = \sum n_i$$

 $m = \sum m_i n_i$

the total mass of the sample

We define the mass mixing ratio μ_i of gas G_i

 $\mu_i = \frac{m_i n_i}{m}$

We now introduce the ideal gas law in the form

 $pV = nk_{R}T$

for one mole, $n = N_A$, where N_A is Avogadro's number,

$$R = N_A k_B$$

The partial pressure p_i of gas G_i is the pressure that would be exerted by the molecules of G_i from the sample if they alone were to occupy volume V at temperature T

$$p_i = n_i \frac{k_B T}{V} \qquad \qquad V_i = n_i \frac{k_B T}{V}$$

 $p = \sum p_i$ Dalton's laws of partial pressures, $V = \sum V_i$ Dalton's laws of partial volumes,

we can relate the mass mixing ratio to the partial pressure as follows:

$$\mu_{i} = \frac{m_{i}n_{i}}{m} = \frac{nm_{i}p_{i}}{mp} = \frac{m_{i}p_{i}}{\overline{m}p} \qquad \overline{m} = \frac{m}{n} \text{ the mean molecular mass}$$
for the sample



Note that the two mixing ratios are related by $\mu_i = \frac{m_i}{\overline{m}} v_i$

Another measure of the concentration of an atmospheric gas is the number density (the number of molecules of the gas per unit volume),

 $\frac{n_i}{V}$

 $\begin{cases} m = \sum m_i n_i \\ \overline{m} = \frac{m}{n} \\ v_i = \frac{n_i}{n} = \frac{p_i}{p} \end{cases}$ $\Rightarrow \overline{m} = \frac{m}{n} = \sum m_i \frac{n_i}{n} = \sum m_i v_i$ the mean molecular mass of an air sample

Similarly, the mean molar mass

$$\bar{M} = \sum M_i v_i$$

Gas	Volume mixing ratio	Molar mass	Distribution
Nitrogen, N2	0.78	28.02	Well-mixed
Oxygen, O ₂	0.21	32.00	Well-mixed
Carbon dioxide, CO2	386 ppmv	44.01	Well-mixed
Water vapour, H ₂ O	$\lesssim 0.03$	18.02	Maximum in
Ozone, O ₃	$\lesssim 10 \mathrm{ppmv}$	48.00	troposphere Maximum in stratosphere
Argon, Ar	0.0093	39.95	Well-mixed

Using Table it can be verified that the mean molar mass of dry air is about 28.97.

Hydrostatic balance

For an atmosphere at rest, in static equilibrium, the net forces acting on any small portion of air must balance.

Consider for example a small cylinder of air, of height Δz and horizontal cross-sectional area ΔA ,

This is subject to a gravitational force $g \Delta m$ downwards,

its mass $\Delta m = \rho \Delta A \Delta z$

g is the gravitational acceleration

This force must be balanced by the difference between the upward pressure force $p(z)\Delta A$ on the bottom of the cylinder and the downward pressure force $p(z + \Delta z)\Delta A$ on the top.



We therefore have $g\rho \Delta A \Delta z = p(z) \Delta A - p(z + \Delta z) \Delta A$

by cancelling ΔA and using the Taylor expansion

$$p(z + \Delta z) \approx p(z) + \frac{dp}{dz} \Delta z,$$

we get the equation for hydrostatic balance,

$$\frac{dp}{dz} = -g\rho.$$

We can derive some basic properties of the atmosphere, given that it is an ideal gas and assuming that it is in hydrostatic balance.

$$p = R_a T \rho \rightarrow \rho$$
 $\frac{dp}{dz} = -\frac{gp}{R_a T}.$

If the temperature is a known function of height, T(z), we can in principle find the pressure and density as functions of height

$$\frac{d}{dz}(\ln p) = -\frac{g}{R_{\rm a}T}$$

$$\ln p - \ln p_0 = -\frac{g}{R_a} \int_0^z \frac{dz'}{T(z')}$$

$$p = p_0 \exp\left(-\frac{g}{R_a} \int_0^z \frac{dz'}{T(z')}\right)$$

The simplest case is that of an isothermal temperature profile, i.e. $T = T_0$ = constant, when the pressure decays exponentially with height:

$$p = p_0 \exp\left(-\frac{gz}{R_{\rm a}T_0}\right) = p_0 e^{-z/H},$$

$H = R_{\rm a}T_0/g$ the pressure scale height

The height over which the pressure falls by a factor of 1/e=0.368

Elevation	Density
0	ρο
н	(1/e)p _o = 0.368p _o
2H	(1/e ²)p ₀ = 0.135p ₀
зн	(1/e ³)p _o = 0.050p _o
4H	(1/e ⁴)p _o = 0.018p _o

In this isothermal case the density also falls exponentially with height in the same way:

 $\rho = \rho_0 \exp(-z/H)$

 P_0 being the density at the ground.

For an isothermal atmosphere with $T_0 = 260$ K, H is about 7.6 km

The lapse rate denotes the rate of decrease of temperature with height:

$$\Gamma(z) = -\frac{dT}{dz}$$

in general the temperature decreases with height ($\Gamma > 0$) in the troposphere and increases with height ($\Gamma < 0$) in the stratosphere; A layer in which the temperature increases with height ($\Gamma < 0$) is called an inversion layer.

If Γ is constant in the region between the ground and some height z_1 , say, then the temperature in that region decreases linearly with height and the integral in

$$p = p_0 \exp\left(-\frac{gz}{R_a T_0}\right) = p_0 e^{-z/H},$$

Another useful deduction from the hydrostatic equation in the form

$$\frac{dp}{dz} = -\frac{gp}{R_aT}.$$

is the 'thickness', or depth, of the layer between two given surfaces of constant pressure.

Suppose that the height of the pressure surface $p = p_1$ is z_1

and the height of the pressure surface $p = p_2$ is z_2

Then, if $p_1 > p_2$, we must have $z_1 < z_2$ since pressure decreases with height when hydrostatic balance applies

From
$$\frac{dp}{dz} = -\frac{gp}{R_aT}$$
. $g dz = -R_aT d(\ln p)$; integration gives

$$z_2 - z_1 = -\frac{R_a}{g} \int_{p_1}^{p_2} T \, d(\ln p)$$

The integral can in principle be evaluated if the temperature T is known as a function of pressure p: this may be provided for example by a weather balloon or a satellite-borne instrument.

In particular, if T is constant,

$$z_2 - z_1 = \frac{R_{\rm a}T}{g} \, \ln\!\left(\frac{p_1}{p_2}\right)$$

If T is not constant, we can still write

$$z_2 - z_1 = \frac{R_{\rm a}\overline{T}}{g}\ln\left(\frac{p_1}{p_2}\right)$$

provided that we define T as a suitably weighted mean temperature within the layer:

$$\overline{T} = \frac{\int_{p_2}^{p_1} T \, d(\ln p)}{\int_{p_2}^{p_1} d(\ln p)},$$

Thus the thickness of the layer between two pressure surfaces is proportional to the mean temperature of that layer.

Entropy and potential temperature

The First Law of Thermodynamics, applied to a small change to a closed system, such as a mass of air contained in a cylinder with a movable piston at one end can be written

$$\delta U = \delta Q + \delta W$$

$$\delta U = T \,\delta S - p \delta V$$



where S is the entropy of the system

An alternative form

$$\delta H = T\,\delta S + V\,\delta p$$

 $H = U + pV \qquad \qquad \text{the enthalpy} \qquad \qquad$

These equations apply both for reversible and for irreversible changes. However, we shall mostly restrict our attention to reversible changes, for which the equations

$$\delta Q = T \,\delta S, \qquad \qquad \delta W = -p \,\delta V$$

For unit mass of ideal gas, for which $V = 1/\rho$, it can be shown that

$$U = c_v T$$
,

where $c_{\rm v}$ is the specific heat capacity at constant volume and is independent of T.

Therefore the ideal gas law, equation $p = R_a T \rho$ implies that, for unit mass of air

$$H = c_v T + R_a T = c_p T$$

$$c_p = c_v + R_a$$

the specific heat capacity of air at constant pressure On substituting the expression

$$H = c_v T + R_{\rm a} T = c_p T,$$

and $V = 1/\rho = R_a T/p$ into equation

$$\delta H = T\,\delta S + V\,\delta p,$$

we get

$$T\,\delta S = c_p\,\delta T - \frac{R_{\rm a}T}{p}\,\delta p$$

Division by T gives

$$\delta S = c_p \, \frac{\delta T}{T} - R_{\rm a} \, \frac{\delta p}{p} = c_p \, \delta(\ln T) - R_{\rm a} \, \delta(\ln p),$$

and integration gives the entropy per unit mass

$$S = c_p \ln T - R_a \ln p + \text{constant} = c_p \ln(Tp^{-\kappa}) + S_0,$$

 $\kappa = R_{\rm a}/c_p$, which is approximately 2/7 for a diatomic gas, and S₀ is a constan

An adiathermal process is one in which heat is neither gained nor lost, so that δQ = 0

An adiabatic process is one that is both adiathermal and reversible;

from equation

$$\delta Q = T \, \delta S,$$

δS = 0

Imagine a cylinder of air, originally at temperature T and pressure p, that is compressed adiabatically until its pressure equals p_0 .

We can find its resulting temperature, θ say, using equation

 $\delta S = c_p \,\delta(\ln T) - R_{\rm a} \,\delta(\ln p)$

with the fact that $\delta S = 0$, For an adiabatic process, so that



Integrating and using the end conditions $T = \theta$ and $p = p_0$ then gives

$$c_p \ln\left(\frac{\theta}{T}\right) = R_a \ln\left(\frac{p_0}{p}\right)$$
 $\kappa = R_a/c_p,$

$$\theta = T \left(\frac{p_0}{p}\right)^{\kappa}$$

The quantity θ is called the potential temperature of a mass of air at temperature T and pressure p. The value of p_0 is usually taken to be 1000 hPa.

Using equation

$$S \equiv c_p \ln(Tp^{-\kappa}) + S_0,$$

it follows that the potential temperature is related to the specific entropy S by

$$S = c_p \ln \theta + S_1, \qquad \mathbf{w}$$

where S_1 is another constant

By definition, the potential temperature of a mass of air is constant when the mass is subject to an adiabatic change;

conversely, the potential temperature will change when the mass is subject to a non-adiabatic (or diabatic) change.

As we shall see, the potential temperature is often a very useful concept in atmospheric thermodynamics and dynamics.