M.Sc. in Meteorology

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Part 2

Atmospheric Thermodynamics

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Thermodynamics plays an important role in our quantitative understanding of atmospheric phenomena, ranging from the smallest cloud microphysical processes to the general circulation of the atmosphere.

The purpose of this section of the course is to introduce some fundamental ideas and relationships in thermodynamics and to apply them to a number of simple, but important, atmospheric situations.

The course is based closely on the text of <u>Wallace & Hobbs</u>

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- 7 The Second Law of Thermodynamics

The Kinetic Theory of Gases

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To begin to understand atmospheric dynamics, we must first understand the way in which a gas behaves, especially when heat is added are removed. Thus, we begin by studying thermodynamics and its application in simple atmospheric contexts.

The Kinetic Theory of Gases

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Fundamentally, a gas is an agglomeration of molecules. We might consider the dynamics of each molecule, and the interactions between the molecules, and deduce the properties of the gas from direct dynamical analysis. However, considering the enormous number of molecules in, say, a kilogram of gas, and the complexity of the inter-molecular interactions, such an analysis is utterly impractical. We resort therefore to a statistical approach, and consider the average behaviour of the gas. This is the approach called the <u>kinetic theory of gases</u>. The laws governing the bulk behaviour are at the heart of thermodynamics. We will not consider the kinetic theory explicitly, but will take the thermodynamic principles as our starting point.

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The ideal gas equation may be written

pV = mRT

Where the variables have the following meanings:

p = pressure (Pa) $V = \text{volume (m^3)}$ m = mass (kg) T = temperature (K) $R = \text{gas constant (J K^{-1} kg^{-1})}$

Again, the gas law is:

$$pV = mRT$$

The value of R depends on the particular gas. For dry air, its value is $R = 287 \, \text{J} \, \text{K}^{-1} \, \text{kg}^{-1}$. Again, the gas law is:

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Exercise: Check the dimensions of R.

Since the density is $\rho = m/V$, we may write

 $p = R\rho T$.

Defining the *specific volume*, the volume of a unit mass of gas, as $\alpha = 1/\rho$, we can write

 $p\alpha = RT$.

Special Cases

Boyle's Law: We may write

$$V = \frac{mRT}{p}$$

For a fixed mass of gas at *constant temperature*, mRT is constant, so volume is *inversely proportional* to pressure:

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Charles Law: We may write

$$V = \left(\frac{mR}{p}\right)T.$$

For a fixed mass of gas at constant pressure, mR/p is constant, so volume is directly proportional to temperature: $V \propto T$.

Avogadro's Hypothesis

One *mole* (mol) of a gas is the molecular weight in grams. One *kilomole* (kmol) of a gas is the molecular weight in kilograms. For example, the molecular weight of nitrogen N_2 is 28 (we ignore the effects of isotopic variations). So:

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According to *Avogadro's Hypothesis*, equal volumes of different gases at a given temperature and pressure have the same number of molecules; or, put another way, gases with the same number of molecules occupy the same volume at a given temperature and pressure. The number of *molecules* in a *mole* of any gas is a universal constant, called *Avogadro's Number*, N_A . The value of N_A is 6.022×10^{23} . So:

28 g of nitrogen contains N_A molecules of N_2

28 kg contains $10^3 \times N_A$ molecules.

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For a gas of molecular weight M, with mass m (in kilograms) the number n of kilomoles is

$$n = \frac{m}{M}$$

So, we use m = nM in the gas law to write it

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By Avogadro's hypothesis, equal volumes of different gases at a given temperature and pressure have the same number of molecules. Therefore, the value of MR is the same for any gas. It is called the *universal gas constant*, denoted:

 $R^* = MR = 8.3145 \,\mathrm{J} \,\mathrm{K}^{-1} \,\mathrm{mol}^{-1} = 8314.5 \,\mathrm{J} \,\mathrm{K}^{-1} \,\mathrm{kmol}^{-1}$.

Then the gas law may be written in the form normally found in texts on chemistry:

$$pV = nR^*T$$
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with *n* the number of moles of gas and $R^* = 8.3145 \, \mathrm{J} \, \mathrm{K}^{-1} \, \mathrm{mol}^{-1}$.

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The gas constant for <u>a single molecule</u> of a gas is also a universal constant, called Boltzmann's constant, k. Since the gas constant R^* is for N_A molecules (the number in a kilomole), we get

$$k = \frac{R^*}{N_A}$$

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Now, for a gas containing n_0 molecules per unit volume, the equation of state is

$$p = n_0 kT$$
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Thus, the mean molecular weight, M_m , of *moist air*, which is a a mixture of dry air and water vapour, is <u>less than</u> that, M_d , of dry air and <u>more than</u> that of water vapour:

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The gas constant for water vapour is larger than that for dry air:

$$R_d = \frac{R^*}{M_d}$$
, and $R_v = \frac{R^*}{M_v}$

so that

$$M_v < M_d \implies R_v > R_d.$$

The numerical values of R_d and R_v are as follows:

$$R_d = \frac{R^*}{M_d} = 287 \,\mathbf{J} \,\mathbf{K}^{-1} \mathbf{k} \mathbf{g}^{-1} \,, \qquad R_v = \frac{R^*}{M_v} = 461 \,\mathbf{J} \,\mathbf{K}^{-1} \mathbf{k} \mathbf{g}^{-1} \,.$$

We define the ratio of these as:

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It is inconvenient to use a gas 'constant' which varies in this way. It is simpler to retain the constant $R = R_d$ for dry air, and to use a *modified temperature*, T_v , in the ideal gas equation. We call this the *virtual temperature*.

Mixing Ratio

Let's consider a fixed volume V of moist air at temperature T and pressure p which contains a mass m_d of dry air and a mass m_v of water vapour. The total mass is $m = m_d + m_v$. The mixing ratio is defined by

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In middle latitudes, w is typically a few grams per kilogram. In the tropics it can be greater than 20 g kg^{-1} . If there is no evapouration or condensation, the mixing ratio is a *conserved quantity*.

Mixing Ratio and Vapour Pressure

By the ideal gas law, the partial pressure pressure exerted by a constituent of a mixture of gases is proportional to the number of kilomoles of the constituent in the mixture. Thus:

> $p_d = n_d R^* T$ dry air $e = n_v R^* T$ water vapour $p = n R^* T$ moist air

where p_d is the pressure due to dry air, e the pressure due to water vapour and p the total pressure.

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Therefore,

$$\frac{e}{p} = \frac{n_v}{n} = \frac{n_v}{n_v + n_d} = \frac{m_v/M_v}{m_v/M_v + m_d/M_d}$$

Dividing by M_v/m_d , this gives

$$\frac{e}{p} = \frac{w}{w + \varepsilon}$$

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$$e = \left(\frac{w}{w+\varepsilon}\right)p \approx \frac{w}{\varepsilon}p$$

where $\varepsilon = 0.622$. Substituting $w = 5.5 \text{ g kg}^{-1} = 0.0055 \text{ g g}^{-1}$, we find that e = 9 hPa.

The density of the mixture of air and water vapour is

$$\rho = \frac{m_d + m_v}{V} = \rho_d + \rho_v$$

where ρ_d is the value the density would have if *only* the mass m_d of dry air were present and ρ_v is the value the density would have if *only* the mass m_v of water vapour were present.

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We apply the ideal gas law to each component:

$$p_d = R_d \rho_d T$$
$$e = R_v \rho_v T$$

where p_d and e are the *partial pressures* exerted by the dry air and water vapour respectively.

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Combining the above results,

$$\begin{split} \rho &= \rho_d + \rho_v = \frac{p_d}{R_d T} + \frac{e}{R_v T} \\ &= \frac{p - e}{R_d T} + \frac{R_d}{R_v} \frac{e}{R_d T} \\ &= \frac{p}{R_d T} - \frac{e}{R_d T} + \varepsilon \frac{e}{R_d T} \\ &= \frac{p}{R_d T} \left[1 - \frac{e}{p} (1 - \varepsilon) \right] \end{split}$$

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$$= \frac{p}{R_d T} \left[1 - \frac{e}{p} (1 - \varepsilon) \right]$$

We may write this equation as

$$p = R_d \rho T_v$$

where the *virtual temperature* T_v is defined by

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The virtual temperature is the temperature that dry air must have in order to to have the same density as the moist air at the same pressure. Note that the virtual temperature is *always greater* than the actual tempeature:

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.

Typically, the virtual temperature exceeds the actual temperature by only a few degrees.

Approximate Expressions for T_v

We can assume that $e \ll p$ and also that w is small. By the binomial theorem,

$$\frac{1}{1 - (e/p)(1 - \varepsilon)} \approx 1 + (e/p)(1 - \varepsilon)$$

and the virtual temperature is

$$T_v \approx T \left[1 + \frac{e}{p} (1 - \varepsilon) \right] \,.$$

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Now substituting for e/p, we get

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But we assume that $w \ll \varepsilon$, so we get

$$\left[1 + \frac{w}{w + \varepsilon}(1 - \varepsilon)\right] \approx \left[1 + \frac{1 - \varepsilon}{\varepsilon}w\right]$$

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Since $\varepsilon = 0.622$ we have $(1 - \varepsilon)/\varepsilon = 0.608$. Thus, $T_v \approx T [1 + 0.608w]$.

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Problem: Calculate the virtual temperature of moist air at 30° C having a mixing ratio of 20 g kg^{-1} .

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 $T_v \approx T \left[1 + 0.608 w \right] \,.$

Problem: Calculate the virtual temperature of moist air at 30° C having a mixing ratio of 20 g kg^{-1} .

Solution: First, T = 30 + 273 = 303 K and w = 20 g kg⁻¹ = 0.02 g g⁻¹. Then

 $T_v \approx 303 \left[1 + 0.608 \times 0.02\right] = 306.68 \,\mathrm{K}$

So, the virtual temperature is $(306.68 - 273) = 33.68^{\circ}$ C, an elevation of 3.68° C above the actual temperature.

End of §2.1