
Chapter 3

Pressure, Temperature, Humidity, Visibility and Particulate

In order to do something interesting we first have to be familiar with some definitions.

The purpose of the lecture and practical this week is for you to become familiar with some terms that are important in the study of the atmosphere. We will address *atmospheric particulate*, which are also known as *aerosols*. Some of the *atmospheric particulate* is a form of pollution. You will become familiar with the science behind quantifying *visibility* and *particulate pollution*.

3.1 Pressure

An *equation of state* for any gas is the so called *ideal gas law*:

$$PV = nR_{gas}T \quad (3.1)$$

where P is pressure (units of pascals); V is the volume of the gas being considered (units of m^3); T is the temperature (units of kelvin), n is the number of moles of the gas and R_{gas} is the *universal gas constant*.

For air we can write the *ideal gas law* a different way if we define another constant, the *specific gas constant for air*, $R_a = \frac{R_{gas}}{M_a}$, where $M_a = 29 \text{ g mole}^{-1}$ is the *molecular weight of air*. Substituting this into Eq. 3.1 we get:

$$PV = nM_aR_aT \quad (3.2)$$

the molecular weight multiplied by the number of moles, nM_a , is just the total mass of air, M_{air} , and because the *density of a substance* is its mass divided by volume, the *density of air* is $\rho_a = \frac{M}{V}$. We can rewrite Eq. 3.2 as:

$$P = \rho_aR_aT \quad (3.3)$$

So the air *pressure* is proportional to the product of the *density of air* and its *temperature*.

In the atmosphere the pressure at any point is equal to the *weight of air above per unit area*. Therefore, since atmospheric pressure at the surface is measured to be $\sim 100,000 \text{ Pa}$, the weight of air pushing down on every square metre at the ground is $\sim 100,000 \text{ newtons}$ or $\sim 10,000 \text{ kg}$ (which is equivalent to 10 tonnes!).

3.2 Temperature

In the atmosphere the temperature of the air can be changed in many different ways:

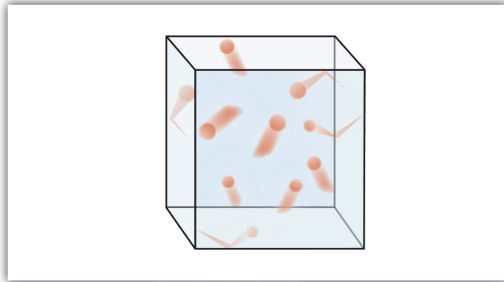


Figure 3.1: A gas is many molecules that move around in random motion. The higher the gas temperature the faster the molecules move. This imparts a pressure on the sides of a container. Taken from <http://www.peoi.org/Courses/Coursesch/chemintro/contents/frame6a.html>.

- Conduction of heat from the land to the air
- Convection can transport mass and heat
- Radiation can be absorbed by material in the atmosphere (gas, particulate).
- Chemical reactions and other transformations can occur, which release heat.

In addition the very act of moving air from an area of high pressure to low pressure causes the air temperature to change. The reason is that temperature and pressure of a gas are closely related. Temperature is related to *how fast the molecules of the gas are moving*. The faster they move, the hotter the gas is. For a given amount of gas the pressure is also increased by increasing the temperature and *vice-versa* (imagine a pressure cooker!). Consider a gas in a container: as for a pressure cooker, the molecules move around and collide with the sides of the container, which imparts a *steady pressure* on the container walls (see Fig. 3.1).

If the container is allowed to increase in size, the pressure will be reduced; the molecules of gas must *do work* against the container walls and therefore lose some of their energy. This reduces the pressure *and* the temperature.

3.3 Parcel lapse rate vs Environmental lapse rate

The rate that temperature reduces with height is known as the *lapse-rate*. We know that warm air will rise above cold air due to convection. The rate that the environment cools with height is crucial to whether the environment will be convective (unstable) or calm (stable). If an air parcel cools faster than the environment with height, as it ascends, the air will be stable and vice-versa.

It turns out that, *because pressure decreases with altitude*, for dry air parcels rising in earth's atmosphere the temperature decreases at approximately 10 K km^{-1} .

When the air is *moist* (i.e. it contains water vapour) a point will be reached where the air parcel cools enough to *condense liquid water* onto small particles known as *aerosols*. When this happens *haze* can form and with more cooling a fog or cloud can form.

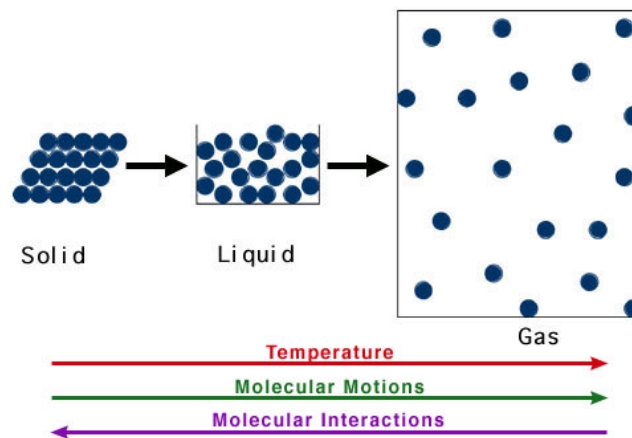


Figure 3.2: Molecules must lose energy to transition from gas to liquid to solid. Taken from <http://www.chemistry.wustl.edu/~edudev/LabTutorials/Thermochem/Fridge.html>

- Haze and fog affects visibility.
- Haze can affect air quality depending on its thickness.

When water is condenses out of the air the fast moving water vapour molecules must slow down dramatically so that they can form a liquid (see Fig. 3.2). They get rid of this excess of energy by releasing heat in the form of latent heat. For every kilogram of water that condenses out of the air 2.5×10^6 joules is liberated in the form of latent heat. The quantity $L_v = 2.5 \times 10^6 \text{ J kg}^{-1}$ is called the *latent heat of vapourisation*. The result is that when a cloud forms the air cools at $\sim 6 \text{ K km}^{-1}$

3.4 Humidity, partial pressure and mass-mixing ratio

The atmosphere is not composed of one gas, but many. However, an important gas is water vapour. The *total pressure* of all of the gases is the force that *all* of the gases together impart on a unit area.

We define *partial pressure* as the pressure that is imparted by just one gas component. For example, in the atmosphere, CO_2 has a *partial pressure*, as does oxygen, and nitrogen.

Water vapour also has a partial pressure, e , (units of pascals) and its partial pressure depends on how much of it there is in the air.

The partial pressure of all gases in the atmosphere can be described by an *ideal gas law* see Eq. 3.3, and for water vapour this is:

$$e = \rho_v R_v T \quad (3.4)$$

where ρ_v is the mass of water vapour per unit volume (variable in the atmosphere). Sources and sinks of water vapour range from:

- evaporation

- burning of fuels and other chemical reactions (see last week).
- Condensation and precipitation, etc.

Warm air can hold more water vapour than cold air: this is why dew droplets on a car window evaporate off when you turn on the heater.

The point where air can hold no more water vapour is a *saturation point*. If the air were cooled any further then water vapour would start to condense out of the air. We can therefore define the *saturation vapour pressure*, e_s (units of pascals), as the partial pressure of water vapour at this *saturation point*.

This *saturation point* depends only on temperature: the colder it is the lower the *saturation vapour pressure* will be:

$$e_s(T) = 610.7 \exp \left[\frac{L_v}{R_v} \left(\frac{1}{273.15} - \frac{1}{T} \right) \right] \quad (3.5)$$

this is known as the *Clausius-Clapeyron* relation.

You'll often hear an atmospheric scientist talk about a quantity known as *relative humidity*, RH . *Relative humidity* defines how much water vapour is in the air, but in a way that is *relative to the saturation point*. It is defined (approximately) as the ratio of the *partial pressure of water vapour* to the *saturation vapour pressure*:

$$RH = \frac{e}{e_s(T)} \quad (3.6)$$

Basically when RH is equal to 1 (or 100%), and the air is cooling, a cloud has formed or is about to form. In the atmosphere RH can take on any value between 0 and about 1 (100%). In some instances it can take on values a bit above 1 but this is rare.

In addition to *relative humidity* atmospheric scientists will also talk about the *mass-mixing ratio* of water vapour, r_w . This is the *mass of water vapour per unit mass of air*. We can derive this from the ideal gas law for water vapour and air (Eqs. 3.3 and 3.4).

First rearrange Eq. 3.4 for the density of water vapour:

$$\rho_v = \frac{e}{R_v T} \quad (3.7)$$

this tells us how much water vapour mass there is per unit volume.

Second rearrange Eq. 3.3 for the density of air:

$$\rho_a = \frac{P}{R_a T} \quad (3.8)$$

this tells us the mass of air per unit volume.

Then take the ratio of Eqs. 3.7 and 3.8:

$$\frac{\rho_v}{\rho_a} = r_w = \frac{\frac{e}{R_v T}}{\frac{P}{R_a T}} \quad (3.9)$$

$$r_w = \frac{R_a e}{R_v P} \quad (3.10)$$

i.e. dividing the partial pressure of water vapour by the total pressure and multiplying by the ratio of specific gas constants gives the mass of water vapour in the air per unit mass of air.

3.5 Particles in the atmosphere

Most *aerosols* in the atmosphere are made of soluble substances, a common one being *ammonium sulphate*: $(NH_4)_2SO_4$.

For reasons that we will not go into, these particles swell and get larger as the *relative humidity* increases. The increasing partial pressure of water vapour pushes water vapour molecules towards the aerosols and they condense onto the aerosols. The theory describing how this happens is called Köhler theory and is shown below:

$$RH = \frac{n_w}{n_w + \nu n_s} \exp\left(\frac{4M_w\sigma}{R_{gas}T\rho_w D}\right) \quad (3.11)$$

where n_w is the number of moles of water; n_s is the number of moles of solute; M_w is the molecular weight of water (18 g mole⁻¹); σ is the surface tension of water (0.075 newtons per metre); ρ_w is the density of liquid water (1000 kg m⁻³) and D is the aerosol particles diameter. ν is the number of ions that the substance dissociates into (between 2 and 3 in the case of ammonium sulphate).

Eq. 3.11 states that the relative humidity over an aerosol particle depends on its physical diameter, D and the number of moles of water in the drop to the number of moles of everything else.

We should note that the size of an aerosol particle and the number of moles of water and solute in it are related by the following:

$$\frac{\pi}{6}D^3\rho_{sol} = n_wM_w + n_sM_s \quad (3.12)$$

where M_s is the molecular weight of the solute (132 g mole⁻¹ for ammonium sulphate) and ρ_{sol} is the density of the water / solute mixture.

The density of the solution and can be determined from:

$$\frac{n_w \times M_w + n_s \times M_s}{\rho_{sol}} = \frac{n_w \times M_w}{\rho_w} + \frac{n_s \times M_s}{\rho_s} \quad (3.13)$$

where ρ_s is the density of the solute alone (1770 kg m⁻³ for ammonium sulphate). Eq. 3.13 is derived by considering that the volume of the aerosol particle is equal to mass divided by density and the total volume is conserved.

Below about 100% *RH*, the above 3 equations describe how the size of a particle depends on its *RH*. However, for some applications we may ignore the exponential factor in Eq. 3.11 (it is close to zero). This is shown in question 6 on the Köhler equations.

Köhler theory is a key theory used in *atmospheric models* and *air quality models* to predict *visibility* and *air quality*.

The table below shows parameters for different compounds. These are common compounds that aerosols consist of. NaCl is especially prevalent in the marine environment.

Compound	NaCl	H ₂ SO ₄	organic acid	NH ₄ NO ₃
Dissociation factor, ν	2	2.5	1	2
Density of solute, ρ_s (kg m ⁻³)	2160	1840	1500	1725
Molecular weight, M_s (kg mole ⁻¹)	58.44×10^{-3}	$98. \times 10^{-3}$	$200. \times 10^{-3}$	$80. \times 10^{-3}$

3.6 Visibility

Obviously visibility gets lower the more particles there are in the air. Visibility is related to how much light is attenuated as it passes through the atmosphere. Particles get in the way of light travelling from a source.

The important quantity is the *total projected area of the particles* per unit volume. This is called *extinction*.

$$\beta = \frac{2\pi D^2}{4} \times N_p \quad (3.14)$$

where N_p has units of m⁻³ (i.e. number of particles per unit volume) and $\frac{\pi D^2}{4}$ is the projected area of a single particle in units of m².

Visual range is the distance that can be seen through the atmosphere. It is related to β by:

$$\beta = \frac{K}{\text{visual range}} \quad (3.15)$$

K is called the Koschmieder constant and is equal to approx. 1.9.

3.7 Particulate matter

Particulate matter is harmful to human health. It is usually expressed in units of $\mu\text{g m}^{-3}$ of air.

We quantify / measure: total particulate matter, that is particulate mass of all sizes; PM10, that is particulate mass of diameters less than 10 μm ; PM2.5, mass of particulate with diameters less than 2.5 μm and PM1.0, diameters less than 1 μm .

As particulate in the atmosphere has different sizes we have to add up the mass of all the particles to get the total. However, in this short course we will assume they are all the same size.

3.8 Questions to go through

3.8.1 Pressure

1. Calculate how many moles of air there are in a container of 2 m^3 at $P = 1000 \text{ hPa}$ and $T = 290 \text{ K}$.
2. How many molecules is that? (Avogadro's number $N_A = 6.02 \times 10^{23}$)
3. What is the density of air at $P = 1000 \text{ hPa}$ and $T = 280 \text{ K}$?
4. What is the density of air at $P = 100 \text{ hPa}$ and $T = 210 \text{ K}$?

3.8.2 Lapse rate

1. A dry thermal starts at the ground with initial temperature, $T = 290 \text{ K}$ and rises a distance of 3000 m through the atmosphere. What will its temperature be? (assume no mixing)
2. A moist thermal starts at 1000 m and is saturated with respect to water vapour with initial temperature, $T = 280 \text{ K}$ and rises a distance of 200 m through the atmosphere. What will its temperature be? (assume no mixing).
3. A thermal with temperature 300 K that contains water vapour starts at the ground and rises a distance 800 m where it saturates. It then rises a further 300 m . What is its temperature at the end? (assume no mixing)

3.8.3 Humidity, partial pressure and mass-mixing ratio

1. An air mass contains 3 g of water vapour per cubic metre of air at a temperature of 280 K . What is the partial pressure of this water vapour?
2. For the same mass of air in 1 calculate the saturation vapour pressure and, therefore, the relative humidity. Is the air saturated?
3. The total pressure of the air mass in 1 is 800 hPa , what is the mass-mixing ratio of water vapour in the air?
4. What is the density of the air?

3.8.4 Köhler equation

The density of ammonium sulphate, ρ_s , is 1770 kg m^{-3}

1. A spherical ammonium sulphate particle has a dry diameter (i.e. without any water condensed onto it) of $D = 150 \text{ nm}$. How many moles is that?
2. If the same aerosol particle above has 10 times as many moles of water what will its density be? (use Eq. 3.13)
3. What will the wet diameter of the particle be? (use Eq. 3.12)
4. If the temperature is 290 K , at what humidity will this particle exist with this amount of water? (use $\nu = 2$ and Eq. 3.11)
5. What is the water vapour pressure at this humidity and temperature? (use definitions for RH and saturation vapour pressure).

6. For some applications we can ignore the exponential factor in Eq. 3.11 as it is close to unity. Calculate the factor $\frac{n_w}{n_w + \nu n_s}$ for this particle and show it is close to the relative humidity (use $\nu = 2$ and your values for n_w and n_s from previous questions).

3.8.5 Visibility

1. A haze in the atmosphere contains aerosols that all have a wet diameter of $1 \mu\text{m}$ and have a total concentration of $1000 \times 10^6 \text{ m}^{-3}$. What is the extinction coefficient, β ?
2. What would be the visible range for such a haze?
3. What would be the effect of increasing the humidity of the visibility? Explain your answer referencing the appropriate equations.

3.8.6 Particulate matter

1. A haze in the atmosphere contains aerosols that all have a wet diameter of $1 \mu\text{m}$, a density of 1003 kg m^{-3} , and have a total concentration of $1000 \times 10^6 \text{ m}^{-3}$. What is the total particulate matter loading in $\mu\text{g m}^{-3}$?
2. A haze in the atmosphere contains two populations of aerosols. One that all have a wet diameter of $5 \mu\text{m}$, a density of 1001 kg m^{-3} , and have a total concentration of $100 \times 10^6 \text{ m}^{-3}$ and the other that all have a wet diameter of $1 \mu\text{m}$, a density of 1003 kg m^{-3} , and have a total concentration of $800 \times 10^6 \text{ m}^{-3}$. What are the total, PM10 and PM2.5 particulate matter loading (in units of $\mu\text{g m}^{-3}$)?

3.9 Answers to questions

3.9.1 Pressure

- Use the ideal gas law: $PV = nRT$, $n = \frac{PV}{RT}$
Therefore, $n = \frac{1000 \times 10^2 \times 2}{8.314 \times 290} = 82.95$
- To get the number of molecules multiply the number of moles by Avogadro's number: $82.95 \times 6.02 \times 10^{23} \cong 5 \times 10^{25}$
- Use the second form of the ideal gas law: $P = \rho R_a T$ or $\rho = \frac{P}{R_a T}$.
Therefore, $\rho = \frac{1000 \times 10^2}{287 \times 280} \cong 1.24 \text{ kg m}^{-3}$.
- Similar to above:
Therefore, $\rho = \frac{100 \times 10^2}{287 \times 210} \cong 0.17 \text{ kg m}^{-3}$.

3.9.2 Lapse rate

- If the thermal is dry the temperature will reduce by 10 degrees for every kilometre of ascent.
Therefore: $T_{final} = 290 - 10 \times \frac{3000}{1000} = 260 \text{ K}$.
- If the thermal is moist and saturated the temperature will reduce by ~ 6 degrees for every kilometre of ascent.
Therefore: $T_{final} \cong 280 - 6 \times \frac{200}{1000} = 278.8 \text{ K}$.
- As the thermal rises the temperature decreases by 10 degrees per kilometre until it saturates, after which the temperature decreases by 6 degrees per kilometre.
Therefore: $T_{final} \cong 300 - 10 \times \frac{800}{1000} - 6 \times \frac{300}{1000} = 290.2 \text{ K}$.

3.9.3 Humidity, partial pressure and mass-mixing ratio

- Use the ideal gas law for water vapour: $e = \rho_v R_v T$.
Therefore: $e = 3 \times 10^{-3} \times 461 \times 280 = 387.24 \text{ Pa}$.
- Use the Clausius-Clapeyron equation: $e_s(T) = 610.7 \exp \left[\frac{2.5 \times 10^6}{461} \left(\frac{1}{273.15} - \frac{1}{280} \right) \right]$
Therefore, $e_s = 992.6 \text{ Pa}$. Thus the $RH = \frac{387.24}{992.6} \cong 0.39$.
- Use equation for mass-mixing ratio: $r_l = \frac{287 \times 387.24}{461 \times 800 \times 10^2} \cong 0.003$ or 3.0135 g kg^{-1}
- Density of the air: $\rho = \frac{P}{R_a T}$
Therefore: $\rho = \frac{800 \times 10^2}{287 \times 280} \cong 1.0 \text{ kg m}^{-3}$.

3.9.4 Köhler equation

- Molecular weight of ammonium sulphate: 132 g mole^{-1} .
Mass of ammonium sulphate particle: $\frac{\pi}{6} \times 1770 \times d_{dry}^3 \cong \frac{\pi}{6} \times 1770 \times (150 \times 10^{-9})^3 \cong 3.13 \times 10^{-18} \text{ kg}$.
Number of moles: $\frac{mass}{molecularweight} \cong \frac{3.13 \times 10^{-18}}{132 \times 10^{-3}} \cong 2.37 \times 10^{-17} \text{ moles}$.
- Use the equation for density (i.e. conservation of volume).
Therefore: $\frac{n_w \times M_w + n_s \times M_s}{\rho_{sol}} = \frac{n_w \times M_w}{\rho_w} + \frac{n_s \times M_s}{\rho_s}$.
and solve for ρ_{sol} . It works out to be: 1226 kg m^{-3} .

3. Use the equation for the mass: $\frac{\pi}{6}D^3\rho_{sol} = n_wM_w + n_sM_s$
and solve for D , using ρ_{sol} from above. It works out to be: $D = 2.259 \times 10^{-7}$ m.
4. Use the Köhler equation substituting D , n_w and n_s in. The answer is $RH = 0.84$ or 84%
5. Multiply the RH by the saturation vapour pressure.
Answer is ~ 1600 Pa.
6. Calculate $\frac{2.37 \times 10^{-16}}{2.37 \times 10^{-16} + 2 \times 2.37 \times 10^{-17}}$. The answer should approximately equal the relative humidity $\cong 0.84$.

3.9.5 Visibility

1. $\beta = \frac{2\pi D^2}{4} \times N_p$
Therefore, $\beta = \frac{2\pi(1 \times 10^{-6})^2}{4} \times 1000 \times 10^6 \cong 1.6 \times 10^{-3} \text{ m}^{-1}$
2. $\beta = \frac{1.9}{\text{visual range}}$
Therefore, $\text{visual range} = \frac{1.9}{1.6 \times 10^{-3}} \cong 1200$ m.
3. Increasing humidity would increase the amount of water on the particles and hence their size (Köhler equation). This would increase the extinction coefficient, β and thus reduce visual range.

3.9.6 Particulate matter

1. Calculate the total mass:
 $\frac{\pi}{6}1003 \times (1 \times 10^{-6})^3 \times 1000 \times 10^6 \cong 5.25 \times 10^{-7} \text{ kg m}^{-3}$
or $525 \mu\text{g m}^{-3}$.
2. First, calculate the mass of diameters less than $2.5 \mu\text{m}$:
 $\frac{\pi}{6}1003 \times (1 \times 10^{-6})^3 \times 800 \times 10^6 \cong 4.20 \times 10^{-7} \text{ kg m}^{-3}$
or $420 \mu\text{g m}^{-3}$. This is the PM2.5
Next, calculate the mass of particles with diameter equal to 5 microns μm :
 $\frac{\pi}{6}1001 \times (5 \times 10^{-6})^3 \times 100 \times 10^6 \cong 6.565 \times 10^{-6} \text{ kg m}^{-3}$
or $6565 \mu\text{g m}^{-3}$.
add both together to get the PM10 and total PM: $6985 \mu\text{g m}^{-3}$.