

Lecture 2

Factors that contribute to pollution buildup and dispersal

Objective – to describe the variation of pressure and temperature with altitude in the lower atmosphere

Reading – hydrostatic balance (Also, see “The Barometric Law” under “Additional Links” at the course web site)

Motivation – although the atmosphere rids itself of harmful pollutants by a series of reactions that eventually produce compounds that rain out or are deposited on surfaces, it does so on finite timescales. That is, the pollutants can spend long periods of time in the atmosphere, anywhere from hours to days or weeks, even years and centuries.

Question – what processes determine the rates at which pollutants are dispersed in the atmosphere?



Pollutants released at the ground or by elevated sources (smokestacks or aircraft) are transported by winds and gradually mixed with 'clean' air by processes such as turbulence and diffusion – the combination of which we refer to as *dispersion*.

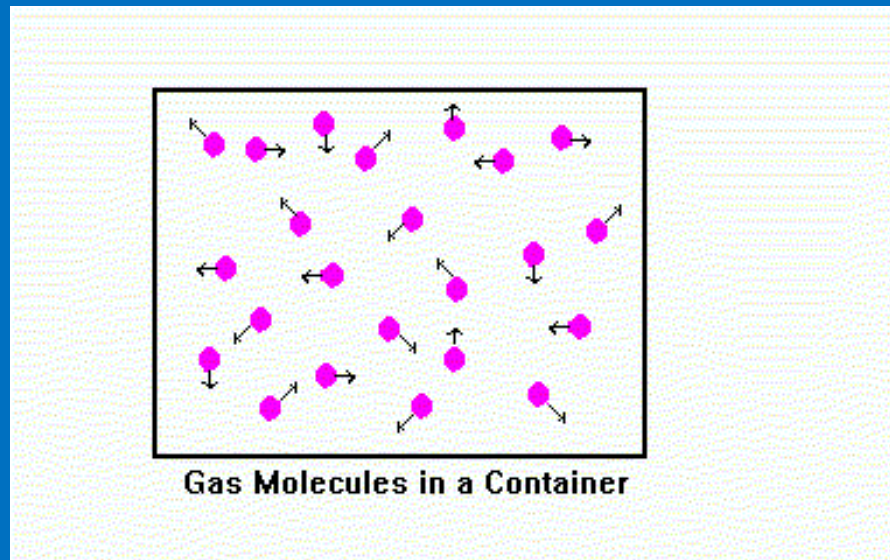
These processes are studied in the field called *fluid dynamics* (or *fluid mechanics*).



Ideal gas law

What, physically, is pressure? A measure of force exerted by a gas on its surroundings.

Through collisions with other molecules and with surfaces, individual gas molecules 'push' against each other. These collisions transfer momentum (in physics, this is referred to as " mv ", or "mass times velocity"). The faster the molecules are moving, the larger the momentum they transfer, so the larger the pressure they exert on a surface.



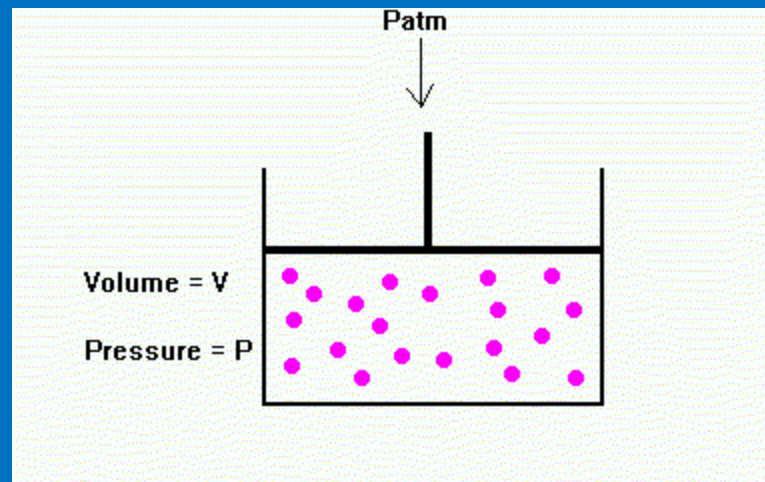
Pressure and temperature are two variables used to describe the "state" of a gas.

We have treated them as independent so far, but they are related.

Boyle's Law:

Established a relationship between pressure, P , and volume, V

Imagine a cylinder of gas with a piston on it (at constant T).



First we need to examine the forces that determine the vertical variation of pressure

Pressure is defined as *force (F) per unit area (A)*

$$P = F/A$$

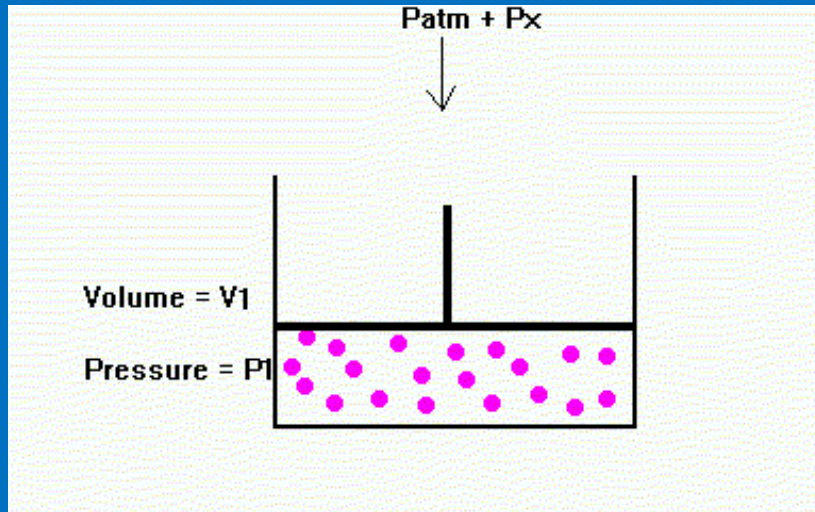
Force = mass X acceleration (that is, the famous expression “F=ma”)

The vertical force acting on air is gravity (g)

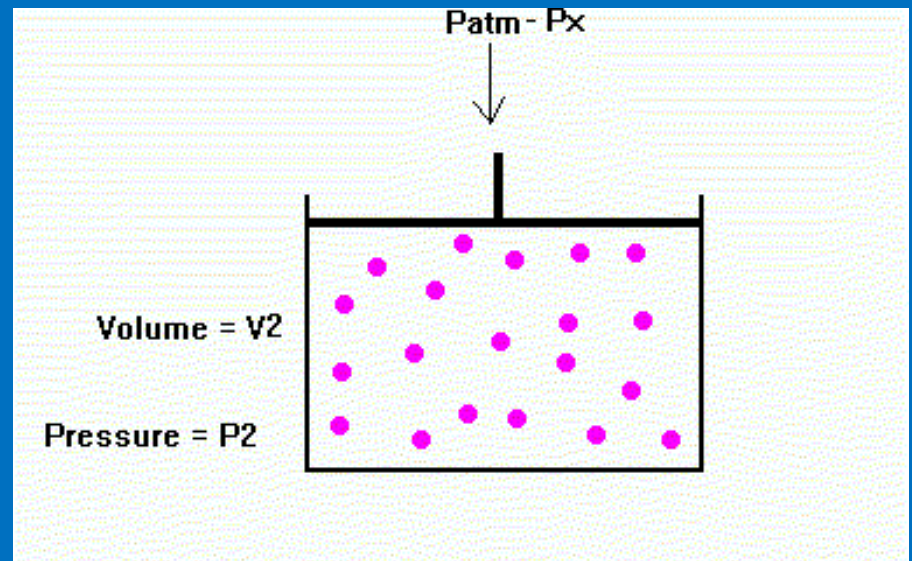
$$F = ma = mg$$

Where g = acceleration due to gravity = 9.8 m s^{-2}

If we apply an extra force to the piston, what happens?



Or, if we tug on the piston, what happens?



We find that the product of pressure and volume is a constant – that is, if pressure is increased, volume is decreased proportionally.

That is,

$$P \times V = \text{constant}$$

What about temperature? This takes a bit more thought, but it's still something we can reason:

Charles' Law: Volume and temperature of a gas are also related, such that V is proportional to T

A way to visualize this is to add hot water to an empty soft plastic bottle and swirl the water to heat up bottle. Then empty out the water and put the cap on. What happens as the air inside the bottle cools?

Charles also showed that pressure and temperature are related.

Digression on temperature: T turns out to be related to the velocity of molecules. It is a measure of the amount of internal energy of a system. Molecules are always in motion, thus always have energy of some type.

For thermal energy (energy that is related to the motions and collisions of molecules) there is a simple relationship between T and energy.

$$E = \frac{3}{2} k_B T = \frac{1}{2} m v^2$$

where k_B is the Boltzmann constant, 1.38×10^{-23} J/K

Short aside - This concept relates the motions of individual particles to the temperature of a bulk substance (statistical mechanics). In a real gas, there isn't just one velocity; rather there is a distribution (called the Maxwell distribution) of velocities. The "most probable" bears the closest relationship to a measurable temperature.

So, then, how are P and T related? Quite simply, molecules that are at a higher temperature are moving faster, so will impact surfaces with more force. Thus, P is larger at higher pressure (so long as the number of molecules in the volume is the same).

Thus, P is proportional to T

Finally, there is Avogadro's Law: pressure depends on the number of gas molecules present. This one is pretty obvious. If there are no molecules, there are no collisions with walls, so no pressure! Similarly, it makes sense that if you double the number of molecules in a given volume (the “number density”), you double the number of collisions – so you double the pressure.

P is proportional to $N/V = n$ (number density)

This yields the “ideal gas law”

$$P = (\text{constant}) \times (N/V) \times T$$

We'll call the constant “ R ”, the gas constant

$$P = (N/V)RT$$

(where $R = 0.082 \text{ L atm mole}^{-1} \text{ K}^{-1}$)

There are many ways to write the ideal gas law. They are all equivalent. They just assume different units or dimensions.

For the atmosphere, where confined volumes are rare, we will use the density formulation. That is

$$P = [M] RT = \rho RT$$

[M] will be number density (in molecules cm^{-3})

ρ will be in g cm^{-3} or kg m^{-3}

To convert between these, we just need to express R in the proper units.

Pressure is expressed in a bewildering array!

Pressure = force per unit area

$$P = F/A = (\text{kg m s}^{-2}) / (\text{m}^2) = \text{kg m}^{-1} \text{ s}^{-2}$$

The SI unit of pressure is the Pascal (Pa): $1 \text{ Pa} = 1 \text{ N m}^{-2}$

$$1 \text{ atm} = 1 \text{ bar} = 1000 \text{ mbar} = 760 \text{ torr} = 760 \text{ mm Hg} \\ = 29.9 \text{ in Hg} = 14.7 \text{ psi}$$

More precisely,

$$1 \text{ atm} = 1013.25 \text{ mb} = 1.01325 \times 10^5 \text{ Pa}$$

Which units are used depends on field and country?

Meteorology: mbar (mb), hPa

Chemistry: torr or atm

TV weather: inches of Hg

A note on units for chemical species

Concentration: $[X]$, molecules cm^{-3}

(we reserve $[M]$ to be the concentration of air)

Mixing ratio (also called mixing fraction), $[X] / [M]$

Parts per million (ppm) = 1 in 10^6 (so multiply the mixing fraction by one million)

Parts per billion (ppb) = 1 in 10^9 (multiply by one billion)

Parts per trillion (ppt) = 1 in 10^{12} (multiply by one trillion).

For ppm, think of “parts of molecule X out of a million molecules of air”

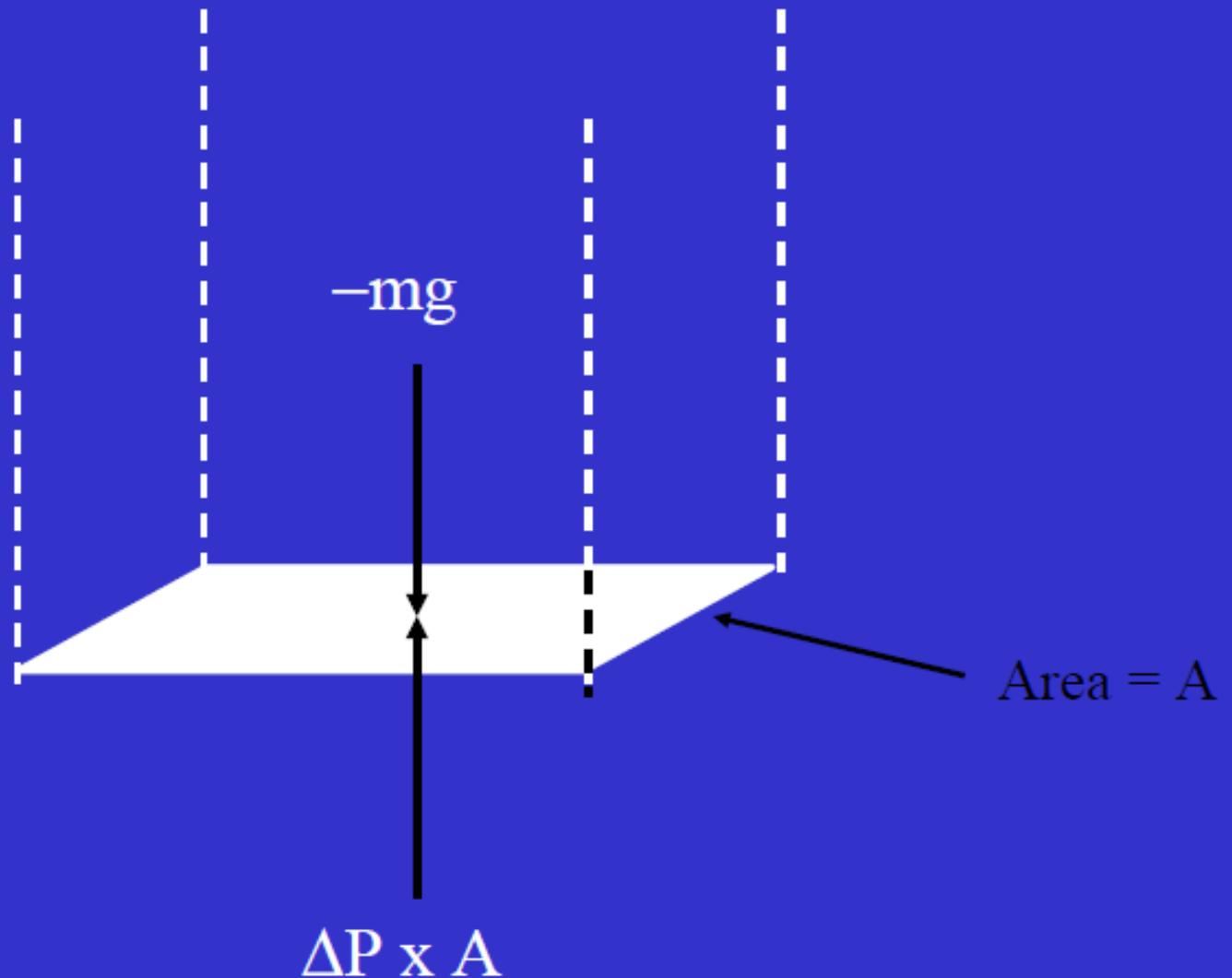
We often write “ppmv” to express the fraction by number. This is because the volume of a gas and number density are related to each other by the ideal gas law.

To determine mixing ratio “by mass” (e.g., ppbm), we divide the mass of X by the total mass of air (m_X/m_{tot}). This isn’t used as often (although it’s popular for water vapor). This is because the rates of chemical reactions depend on number densities, and there aren’t that many properties of air that depend on mass (although our next problem will!).

The barometric law (hydrostatic balance, etc. etc.)

Why we care – in order to calculate the rates of chemical reactions, we will need the concentration of reactants, and usually, these are expressed in mixing ratio, which is dimensionless. We need to multiply by the number density of air, $[M]$, in order to calculate the concentration of the molecules of interest. From Homework problem 1, we note that in order to do this, we need temperature and pressure. Pressure decreases with altitude, so we need to find a quick way to estimate the pressure at any altitude. This will be the ‘hydrostatic equation’ which is used often in atmospheric sciences.

Hydrostatic balance – balance downward force due to weight of air ($F = mg$) with the upward force due to pressure gradient force, $\Delta P \times \text{Area}$



Assume a thin layer of gas. The pressure change across this layer is:

$$A \Delta P = -mg = -\rho g (A \Delta z)$$

Change finite difference (Δ) to infinitesimal (d) (i.e. 'calculus')

$$dP = -g\rho \, dz$$

Remember that density (ρ) is related to pressure by the ideal gas law

$$P = \rho RT$$

Substituting the ideal gas law into the hydrostatic balance equation:

$$\begin{aligned} dP &= -g(P/RT) \, dz \\ dP/P &= -g(1/RT) \, dz \end{aligned}$$

Assuming that g and T are approximately constant with altitude (a good assumption for g , but a slight bit of a stretch for T , which varies by ~30% with altitude, as we have seen in class)

$$P/P_o = \exp [-gz/RT]$$

Where $z = 0$ at sea level

The exponent is typically simplified by substituting $H = RT/g$, which is known as the "scale height", yielding the barometric law:

$$P = P_o \exp[-z/H]$$

The value of H is about 7 km in the troposphere and stratosphere.

Problem: An airplane typically flies at 10 km (33,000 ft) altitude. What is the approximate pressure there?

$$P = P_0 \exp(-z/H) = 1013 \text{ mb} \bullet \exp(-10/7) = 240 \text{ mb}$$

Note – this is about $\frac{1}{4}$ the pressure at sea level

On your own – repeat the calculation for the summit of Mt. Everest, which is at 29,000 feet. Why do you suppose most climbers use bottles of pure O₂?

Aside – what is a good value for H in the atmosphere?

Depends on where you are (since H depends on T).

$$H = RT/g$$

For an average temperature of about 250 K (we'll see where this number comes from next week)

$$H = (0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (250 \text{ K}) / (9.8 \text{ m s}^{-2})$$

To simplify this, we note the following:

Air weighs $28.9 \text{ g mol}^{-1} = 0.0289 \text{ kg mol}^{-1}$

$1 \text{ L} = 1000 \text{ cm}^3$

$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 101325 \text{ kg m}^{-1} \text{ s}^{-2}$

$$H = (0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (1000 \text{ cm}^3 \text{ L}^{-1}) \times (1/0.0289 \text{ mol kg}^{-1}) \\ \times (101325 \text{ kg m}^{-1} \text{ s}^{-2}) \times (10^{-6} \text{ m}^3 \text{ cm}^{-3}) \times (250 \text{ K}) / (9.8 \text{ m s}^{-2})$$

$$= 7.33 \times 10^3 \text{ m} \sim 7 \text{ km}$$

Sample Problem: The mixing ratio of water vapor in the stratosphere is about 5 ppmv. If the ambient temperature is 210 K and the pressure is 100 mbar, what is the concentration of water?

The mixing ratio of water is defined as $[H_2O]/[M]$. The mixing ratio is 5 ppmv $= 5 / (1 \times 10^6) = 5 \times 10^{-6}$

We must calculate $[M]$ first. ($[M] = P/RT$)

From Homework 1, $[M] = (7.26 \times 10^{18}) \times (100 \text{ mbar}) / (210 \text{ K})$
 $= 3.46 \times 10^{18} \text{ molec cm}^{-3}$

So $[H_2O] = (5 \times 10^{-6}) \times [M] = (5 \times 10^{-6}) \times (3.49 \times 10^{18}) \text{ molec cm}^{-3}$
 $= 1.75 \times 10^{13} \text{ molec cm}^{-3}$

How temperature varies with altitude

In the troposphere, the average temperature structure is determined by ideal gas behavior

($p = \rho RT$). But in the atmosphere, density and pressure both decrease with altitude, so we need a more sophisticated picture to calculate magnitude of change.

Consider a thermodynamic situation called *adiabatic*, meaning that when a process occurs there is no gain or loss of heat (expressed in thermodynamics as the identity $dQ = 0$) .

Temperature, T , is related to heat energy, but does that mean for an adiabatic process where there is no change in T ?

⇒ If volume stays constant, YES! That is, if you don't put in any heat or take any out, there will be no change in temperature – pretty logical. But when air moves up or down in the atmosphere, pressure changes.

Imagine a balloon filled with air in Boulder and released. As the balloon rises, what happens?

The balloon expands and the air inside it cools.

If the balloon were filled on the top of Long's Peak and forced down to Boulder, what would happen?

The balloon is compressed and the air inside warms.

In both cases, the volume changes, so WORK is done.

Pressure-volume work: $dW = -PdV$

“PV work” – work due to a change in volume.

As volume grows for an air parcel that rises, the molecules inside the parcel do work – specifically, they push external molecules away. They are able to do this by using some of their internal energy, and so their temperature drops, and the parcel gets colder.

Alternatively, if the volume of an air parcel decreases, work is done on the parcel by external molecules, so the parcel gets warmer.

Real world examples (other than the atmosphere itself)

Expansion: A can of “Dust-off” Compression: Filling a bike tire

Thus, in the troposphere, temperature decreases with increasing altitude due to expansion, so long as that process occurs on relatively short (e.g. hours-days) time scales, which are typical of most convective situations.

Back to temperature change in the troposphere (This is the part that is important to know!)

The change in temperature (dT) with altitude (dz) is called the “lapse rate”, which we label with the Greek letter “Gamma” (Γ)

That is, $-(dT/dz) = \Gamma$

The convention is to call the lapse rate the negative of dT/dz because temperature most often decreases with increasing altitude, so when we say “10 degrees per km” we mean that it gets colder as one goes up in altitude.

We call the actual temperature change with altitude (that is, the value that is observed) the “environmental lapse rate (Γ_e)”

The idealized change in temperature with altitude will be called the “adiabatic lapse rate”, because this is the change in temperature with altitude that a parcel of air would achieve if there were no heat going into or coming out of the parcel of air as it rises upward.

This is the rigorous part (read if you are interested, but you don't need to reproduce this for this class!)

We can appeal to thermodynamics to determine how the temperature of an ideal gas will vary if the pressure on that gas changes. We need a few definitions first.

$$\begin{aligned} \text{(Change in internal energy)} = & \text{(Heat added to system)} \\ & + \text{(Work done on system)} \end{aligned}$$

Or:
$$dU = dQ + dW$$

The next definition we need is a bit strange – it's simply a mathematical construct – something we call in thermodynamics “a state function” – like the ideal gas law, but in this case, a function that serves to tell us how much internal energy (that is, temperature) and potential energy are in a system. We define “enthalpy” as $H = U + PV$, so that a change in enthalpy can be written as:

$$\begin{aligned} dH &= dU + d(PV) = dU + PdV + VdP \\ &= dQ + dW + PdV + VdP \end{aligned}$$

Note that the enthalpy of a system can change for three reasons: (1) if heat is added or removed from the system; (2) the air does work on the surroundings (or vice versa), or (3) the air experiences a change in pressure or volume. From here, we need to know a few more things from thermodynamics. One can consider them definitions, but they are a bit more than that – they are relationships that describe the behavior of an ideal gas, and they are a bit beyond the scope of this class. In any case, consider them definitions, which we will substitute back into the equation for enthalpy.

Work done by an ideal gas: $dW = -VdP$

Change in enthalpy of an ideal gas: $dH = m \times C_p(dT)$

So, our equation becomes:

$$m \times C_p(dT) = dQ - VdP + PdV + VdP = dQ + VdP$$

M is the mass of the air, C_p is called the ‘heat capacity’ of air, dT and dP represent changes in temperature and pressure, respectively.

We define an adiabatic process for which $dQ = 0$ (no heat into or out of the parcel of air from the surroundings).

$$m \times C_p(dT) = VdP$$

All we need to know to simplify this equation is how dP changes with altitude, since we ultimately want to derive dT/dz , the change in temperature with change in height. This is where we need the hydrostatic balance relationship,

$$dP = -\rho g(dz)$$

Substituting, we have our final equation:

$$m \times C_p(dT) = -g \times V \times \rho(dz)$$

We can simplify this if we recall that $\rho = m/V$.

$$m \times C_p(dT) = -g \times m \times (dz)$$

$$dT/dz = -g/C_p$$

This is a remarkably simple relationship!

For $g = 9.8 \text{ m s}^{-2}$ and $C_p = 1004 \text{ J kg}^{-1} \text{ K}^{-1}$ we get the result that

$$dT/dz = - 9.8 \text{ }^\circ\text{K km}^{-1}$$

That is, for a parcel of air that has no exchange of heat with the surroundings ($dQ = 0$), the temperature will drop about ten degrees K per km of altitude increase. This is a very easy number to remember.

There is one ‘catch’ here. $dQ = 0$ as long as there is no water condensing (or evaporating) in the air. When water condenses, it releases latent heat (heat that was put into the air to evaporate that water in the first place). Conversely, if water evaporates, it will cool the air. So we call this value of $9.8 \text{ }^\circ\text{K km}^{-1}$ the “dry adiabatic lapse rate” to distinguish it from a value that is somewhat smaller (between about 5 and $8 \text{ }^\circ\text{K km}^{-1}$, if water is condensing or evaporating) – a value that we call the “wet adiabatic lapse rate.”

The dry adiabatic lapse rate is very important in the atmosphere, so we give it the Greek name “Gamma”, or Γ_d . Next Tuesday we will examine the importance of this quantity for atmospheric stability and dispersal of pollutants.

What about other regions of the atmosphere? We cannot always assume adiabatic conditions.

In the stratosphere, ozone absorbs sunlight, breaks apart and releases energy to the surroundings, heating them. Thus, as one moves upward in the stratosphere into regions with more UV light, the temperature gets warmer. This is a situation called an “inversion” – rather than a decrease in temperature with altitude, there is an increase.

Why is an inversion important? Air below is trapped – it can't rise because if it were to rise, it would cool because of expansion into a region of lower pressure, but we know that cold air is more dense than the warmer surrounding air, so the cooler air would sink...i.e. it can't rise because it isn't buoyant!

The same thing happens near the ground when the surface cools at night due to radiation (especially true where the climate is very dry, like a desert).