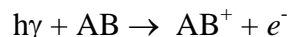# Structure and composition of the atmosphere
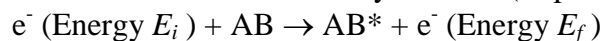
Basic features

The Earth's atmosphere is a gaseous envelope, retained by gravity, surrounding the Earth. The density falls rapidly with height. 90% of the mass of the atmosphere is contained within the first 20km; 99.9% within the first 50km. The atmosphere becomes increasingly tenuous with increasing height until at about 1000km (625 miles) it merges with interstellar space. Compare with the radius of the Earth (about 6400 km); 99.9% of the Earth's atmosphere is in a ring whose thickness is 0.8% of the radius of the Earth . This implies that almost every property of the atmosphere is strongly anisotropic. For example, the temperature decreases with height at a rate of 6K/km (up to about 15km), but the strongest horizontal temperature gradients (associated with warm or cold fronts) are about 0.05K/km. Away from the surface, the *isopleths* (lines or surfaces of equal quantity such as isobars (equal pressure) or isotherms (equal temperature)) are nearly horizontal and the atmosphere consists of horizontal layers. In particular, the atmosphere is divided into regions characterised by their temperature. Each layer is called a *sphere* and the boundary between layers is called a *pause*. The boundary is named from the lower layer.

- **Troposphere**. (0-10km) This is the lowest and contains 80% of the mass. Almost all the weather is confined to the troposphere; in particular, it contains the clouds. The temperature falls linearly with height until at the top of the troposphere the temperature is approximately -50^0C.
- **Stratosphere**. (10-50km) Above the *tropopause* the temperature begins to rise again. until at about 50km the temperature is about $+10^0$C. The upper part of the stratosphere contains *ozone* – an essential molecule for life on earth since it filters out (harmful) UV radiation
- **Mesosphere**. (50-85km) Above the *stratopause* the temperature falls rapidly to about -80^0C. This is the coldest region of the atmosphere
- **Ionosphere** (100-200km) This is an intensely ionised region of the atmosphere and the temperature rises rapidly. Solar UV ionises the molecules of the atmosphere
$$h\gamma + AB \rightarrow AB^+ + e^-$$
  The ionosphere reflects radio waves and is also the region of the *aurorae* seen in high latitudes in the northern (*aurora borealis*) and southern (*aurora australis*) hemispheres. Intense visible and UV lines caused by electron (or proton) collisions
$$e^- \text{ (Energy } E_i \text{)} + AB \rightarrow AB^* + e^- \text{ (Energy } E_f \text{)}$$
  where AB can be O_2, molecular oxygen, N_2. The energy $\Delta E = E_i - E_f$ given up by the electron excites the molecule to the AB* state. This then decays back to the ground state, releasing a photon of frequency $h\nu = \Delta E$
- **Thermosphere** (200-500km) Temperature rises rapidly and varies strongly with the time of day, degree of solar activity and latitude. Variation between 400^0C and 2000^0C possible. Minimum temperatures are at sunrise; maximum temperatures at about 1400. However, the pressures are very low (10^{-8}mb at 500km) and there is little heat transfer. The idea of a 'temperature' is becoming increasingly meaningless; better to think in terms of molecular speeds.

- **Exosphere** (500- about 1000km) Atoms and molecules are sparse and can escape into space
- **Magnetosphere** (Above 1000km) In this region the Earth's magnetic field interacts with the solar wind and traps charged particles (electrons and protons) in the *Van Allen belts*

Equation of state

We can assume that the perfect gas law, applies to each of the gases in the atmosphere

$$PV = n_m RT \tag{1}$$

where n_m is the number of moles of the gas. (A mole is defined as Avogadro's number. The weight in *grams* of Avogadro's number of molecules is the *molecular weight*). The mass of the gas is $n_m M/1000$ kilograms where M is the molecular weight of the gas (quoted in grams by definition) and so the density of the gas, ρ, is $n_m M/1000V$. We can therefore write the equation of state as

$$P = [1000R/M]\rho T \tag{2}$$

However, the atmosphere is a mixture of gases. In this case, we can use *Dalton's Law of Partial Pressures*; the pressure of a mixture of gases in a container is the sum of the *partial pressure* of each gas; that is to say, the pressure that each gas would have if it were the only gas in the container. Thus,

$$P = \sum_i P_i = RT \sum_i 1000\rho_i / M_i$$

(3)

Since all the gases are in the same container, the total density is the sum of the partial densities, $\rho = \sum_i \rho_i$ where ρ is now the density of the atmosphere. Inserting this into the equation above, we obtain

$$P = 1000RT\rho \sum_i \frac{\rho_i}{\rho} \frac{1}{M_i} = 1000RT\rho \sum_i \frac{x_i}{M_i} \tag{4}$$

where we now have now defined the specific mass, $x_i = \rho_i / \rho$. We can return this to the form of the original equation of state if we define an effective mass (or mean molecular weight as it is often called) $\overline{M}$ for an 'atmosphere molecule' as

$$\frac{1}{\overline{M}} = \sum_i \frac{x_i}{M_i} \text{ giving } P = [1000R/\overline{M}]\rho T \tag{5}$$

The quantity $1000R/\overline{M}$ is often called the *specific gas constant* R_S

Note on units of pressure
The S.I. unit of pressure is the Pascal (N/m^2). However, a large number of other units are also in use.
1 atmosphere = 1.01325 x 10^5 Pa (about 0.1 MPa).
1 atmosphere = 760 mm of mercury (Hg) = 760 torr - definition of the torr
10^5 Pa = 1 bar (definition of the bar) in other words, one bar is about one atmosphere. Therefore 1mb (millibar) = 100Pa. This unit is standard for weather charts and we shall use it frequently.

The scale height

The pressure at the base of the atmosphere is due to the weight of the atmosphere on top. The density of air falls rapidly with height. Let us write this as ρ(z) where z is the height above sea level. Then, if the gravitational constant g does not change with height (it does of course, but not as rapidly as the density), then we can work out the pressure variation with height by the following argument. Consider a cylinder of atmosphere as shown in the diagram on the right. If the cylinder has unit cross-sectional area, then the mass of air in the cylinder is ρ(z) dz. Therefore, under gravity, the cylinder will experience a downward force

$$F = -g\rho(z) \, dz. \qquad (6)$$

If the cylinder of air is in static equilibrium with the rest of the atmosphere, (i.e. it does not move up or down) this force must be balanced by something. This comes from the pressure difference between the bottom of the cylinder and the top. Since the pressure at the bottom is greater, it tends to push the air upwards. In other words, there is an upwards force $(P + dP) - P = dP$. Since the cylinder is in mechanical equilibrium, the total force on the cylinder must be zero i.e. $dP + g\rho(z) \, dz = 0$.
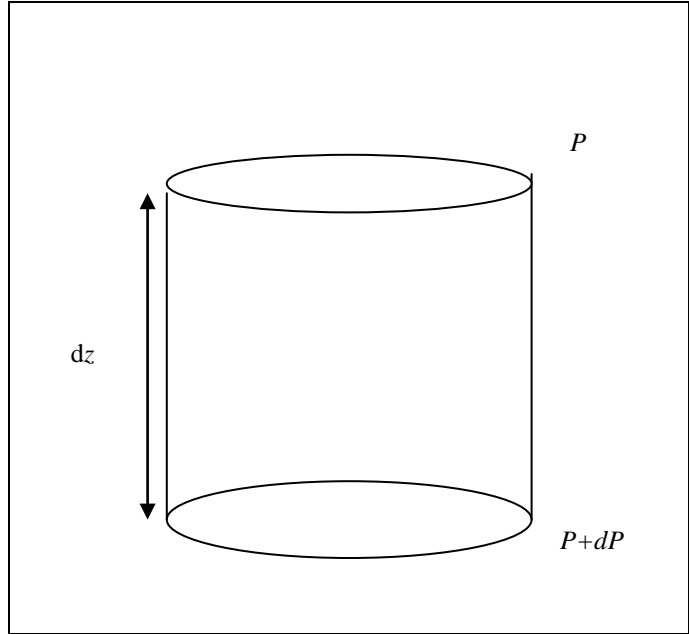
or

$$\frac{dP}{dz} = -\rho(z)g \qquad (7)$$

We have already seen how we can express the density in terms of other variables; we can write $\rho(z) = 1000 n_m(z)\overline{M}/V$ where now the number of moles of the gas must now depend on the height. Hence

$$P/RT = n_m/V = 1000\rho(z)/\overline{M} \qquad (8)$$

Substituting this into the equation we derived giving the pressure as a function of height, we get

$$\frac{dP}{dz} = -\frac{P\overline{M}g}{1000RT} \qquad (9)$$

which rearranges to give

$$\frac{dP}{Pdz} = \frac{d\ln P}{dz} = -\frac{\overline{M}g}{1000RT} \qquad (10)$$

which can readily be solved to give $P = P_0 \exp(-g\overline{M}z/1000RT)$ where we have assumed that the temperature T is constant. (This is not true, but is good enough for a rough estimate). We have also assumed $\overline{M}$ to be constant. If we are considering the atmosphere, $\overline{M}$ is the average molecular weight and might be expected to vary. Provided that the atmosphere is *well stirred* (i.e. the composition is constant because of

mixing) this is a good approximation. P_0 is the pressure when $z = 0$ in other words it is the atmospheric pressure at ground level. The quantity $H = 1000RT / g\overline{M}$ has the dimensions of a length and is called the *scale height*. We can make a rough estimate of this. We require the mean molecular weight of the gases in the atmosphere. The atmosphere consists of about 80% nitrogen and 20% oxygen by volume. The molecular weights of nitrogen and oxygen are 28 and 32 respectively. The specific masses of nitrogen and oxygen are therefore 0.755 and 0.231 respectively and the mean molecular weight of the atmosphere is 28.96. This is effectively constant for the troposphere and stratosphere. A reasonable estimate for the mean temperature of the atmosphere in the troposphere is 288K (15^0C). Hence H = 1000 * 8.31 * 288/9.81/28.96 which is approximately 8.4km (just over 5 miles, approximately the height of Mount Everest). The importance of this is that H defines the height at which the pressure has decreased to *1/e* (= 0.37) of its initial value. Our calculation shows that about 2/3 of the atmosphere lies below the top of Mt. Everest. Note the direct dependence on temperatures. When the weather is cold, the scale height is less i.e. the pressure of the atmosphere falls more rapidly with height. This has the effect that lines of constant pressure in the atmosphere slope downwards towards the poles, especially in winter.

It is interesting to compare this with the situation on other planets. The Table below gives the figures.

Planet	Main constituents of the atmosphere	$\overline{M}$ (gm)	g (N/m^2)	T (K)	H (km)
Earth	N_2, O_2	29	9.81	288	8.4
Mars	CO_2	44	3.73	210	10.6
Venus	CO_2	44	8.88	700	14.9
Jupiter	H_2 (some He)	2	26.20	160	25.3

The temperature in the lower atmosphere (temperature lapse rate)
From equation (7), we have a relation between the pressure and the height. We can rewrite this equation as

$$\frac{dP}{dz} = \frac{dP}{dT}\frac{dT}{dz} = -\frac{P\overline{M}g}{1000RT} \qquad (11)$$

To get any further, we require some thermodynamics. We need to consider a small volume of air (usually called an *air parcel*). As the parcel rises in the atmosphere, it expands and cools. Provided the vertical motion of the parcel is fast enough, and in the troposphere it almost always is, we can ignore outside effects such as the heating of the air parcel by the sun. We can therefore assume that the process is *adiabatic*; we assume that heat does not cross the boundaries of the parcel.

Recall the first law of thermodynamics
$$dU = \delta Q + \delta W \qquad (12)$$
where dU is the change in internal energy of the system; δQ is the heat absorbed by the system and δW is the work done on the system by external forces. dU is a function of state, it depends only on the differences of values at the endpoints. $\delta Q, \ \delta W$ are functions

of path – they depend on which way you go. In this case, the work that matters is expansion and contraction of a gas, and so $\delta W = -PdV$. The parcel expands by a volume dV against the surrounding air at pressure P; thus the *parcel* is doing work against the external forces (which costs energy); hence the sign of δW is *negative.* It is convenient to define the thermodynamic potential $H = U + PV$. This is called the *enthalpy.* Hence

$$dH = dU + PdV + V\,dP = \delta Q + V\,dP. \tag{13}$$

Let us consider that the air parcel has unit mass. Then we can replace V in equation (13) by $(1/\rho)$. This is the usual way of writing these equations in meteorology. It makes more sense because we are not interested in the volume of one air parcel or another but rather in the constitutive behaviour of the atmosphere.

$$dH = dU + Pd(1/\rho) + (1/\rho)dP = \delta Q + (1/\rho)\,dP. \tag{14}$$

If C_P is the heat capacity of air at constant pressure (in Jkg^{-1}K^{-1}), then by definition of the specific heat, $[\delta Q]_P = C_P\,dT$. So when there is no change of state over the temperature interval, we have d$H = C_P$dT, and so,

$$\delta Q = C_P dT - (1/\rho)\,dP \tag{15}$$

For an adiabatic process, we know that $\delta Q = 0$ and therefore

$$C_P dT = (1/\rho)\,dP \tag{16}$$

We can use the equation of state $P = \rho T\left(1000R/\overline{M}\right)$ to substitute for ρ, to give

$$C_P dT = (1000RT/\overline{M})(dP/P) \tag{17}$$

This can readily be integrated to give

$$C_P \ln T = (1000R/\overline{M})\ln P + const$$

which can be rearranged to give the *Poisson equation*

$$TP^{-1000R/\overline{M}C_P} = const \tag{18}$$

Another important result can be obtained by using the pressure-height relation we derived earlier. For a unit mass of air, we can write the dependence of pressure on height as

$$\frac{dP}{dz} = \frac{dP}{dT}\frac{dT}{dz} = -\frac{P\overline{M}g}{1000RT} = -\rho g \tag{19}$$

Therefore, substituting for ρ_s using equation (16), we have

$$\frac{dP}{dT}\frac{dT}{dz} = -\rho g = -\frac{g}{C_P}\frac{dP}{dT}$$

which gives

$$\frac{dT}{dz} = -\frac{g}{C_P} \tag{20}$$

This is the *dry adiabatic lapse rate*. We can use this expression to estimate the temperature change from the ground to the top of the troposphere. $g = 9.81$N/m^2; $C_P = 1005$Jkg^{-1}K^{-1} and so dT / dz is about 0.01K/m. Thus if the height of the troposphere is about 10km, then the temperature of the top of the troposphere should be about 100K below the surface temperature; less than 200K. This temperature drop is about double the real value. The problem is that we have forgotten something; the air is never dry. As the parcel of air rises, the water condenses out into clouds and the latent heat of water is released. We shall consider this in more detail when we come to the hydrologic cycle.

The effect of the lapse rate has an interesting effect on the tropopause. The troposphere is deepest near the equator because the strong solar radiation flux maintains a deep and vigorous convection. The temperatures at the surface of the earth are among the warmest on the planet. However, the combination of the depth of the troposphere and the temperature lapse rate means that the temperature at the tropopause are lower than at any other latitude. At high altitudes, the air at the equator is *colder* than the air at the poles. This will have an effect on the pressure behaviour high in the atmosphere. Above, we argued that the lines of constant pressure (isobars) will slope downwards to the poles. From this argument, it is clear that at great heights they will slope the other way.

Both the isotherms and isobars slope downwards from the equator to the pole. However the isotherms tilt much more. Thus the isobars and isotherms will intersect. This happens at the middle latitudes, which are therefore referred to as *baroclinic* whereas the tropics, where the isobars and isotherms are (more or less) parallel are *barotropic*. This is responsible for the fundamentally different kinds of weather that is observed in these regions. This will be taken up in more detail later.

The parcel view and the environmental view
We have considered the temperature lapse rate with the model of a parcel of air moving through the atmosphere and have obtained equation (20). However, if we simply measured the temperature lapse rate as a function of height (for example by sending a thermometer up in a balloon), it is not obvious that we would get the same answer. What this experiment would give is $\dfrac{\partial T}{\partial z}$. The point is that in the first case we are moving up with a particular parcel of air. In the second, we are simply constructing the temperature profile for the whole atmosphere at once. The first approach is the *parcel view*, the second is the *environmental view*. However they are closely connected with each other. The ability of a parcel of air to rise depends how dense it is compared to the surrounding air and that depends on the temperature (through the gas law); the hotter the parcel, the less dense it is. Thus, if $\dfrac{\partial T}{\partial z} > \dfrac{dT}{dz}$, as the parcel moves up, it gets warmer faster than the surrounding air, thus it gets less dense than the surrounding air and moves up even faster. The situation is *superadiabatic* and is unstable. Similarly, if the parcel starts moving down, it is accelerated downwards. If $\dfrac{\partial T}{\partial z} < \dfrac{dT}{dz}$ on the other hand, the parcel is stable; if it tries to move up or down, it gets warmer (or colder) slower than the surrounding air and moves back. This situation is *subadiabatic.* The situation of *neutral stability* $\dfrac{\partial T}{\partial z} = \dfrac{dT}{dz}$ means that the parcel is stable wherever it is moved to (and that the parcel and environmental viewpoint give the same answer). The reason why this is commonly found to be the case takes us far beyond this course. It is essentially due to the effects of convection (brought about by the first case we have considered) and the mixing of the air parcels that move up and down in the atmosphere. This tends to move the environmental lapse rate towards the adiabatic lapse rate predicted by the parcel model.

The composition of the Earth's atmosphere

In the troposphere, stratosphere and mesosphere, mixing mechanisms ensure that there is essentially a constant chemical composition with an N_2/O_2 ratio of (about) 4:1. This uniform composition gives these three regions the collective name of the *homosphere*. Above 100km (the *mesopause*) the ratio changes as a function of height. This (upper) region is called the *heterosphere*.

The atmosphere contains a number of trace gases whose concentration does change with height. The most important cases are

1. *Ozone* - concentrated in the stratosphere (sometimes called the ozonosphere) at a height of 20-30km
2. *Water* – very variable concentration throughout the homosphere
3. *Carbon dioxide* – important greenhouse gas in the upper troposphere [0.03% of the atmosphere]

Escape velocity and the composition of the atmosphere

The Earth's atmosphere is retained by gravity. We recall the idea of an escape velocity. Consider a rocket of mass m launched from the surface of the Earth at a velocity fast enough so that it just escapes from the gravitational influence of the earth. Then

*Work done = m * Potential difference between the surface of the earth and infinity*

$$= m \, (GM_E / R_E) \qquad\qquad (21)$$

where G is the gravitational constant and $M_E \, R_E$ are the mass and radius of the Earth. But this work must come from the kinetic energy of the rocket. So if the initial velocity of the rocket is v, then

$$\frac{1}{2} mv^2 = \frac{GmM_E}{R_E} \qquad\qquad (22)$$

The starting velocity (which is the escape velocity) $v = \sqrt{2GM_E / R_E}$ We know that $g = GM_E / R_E^2$, and so we can write $v = \sqrt{2gR_E}$. Putting in values appropriate for Earth ($g = 9.81\text{N/m}^2$; $R_E = 6400$km), we get $v = 11{,}200$ m/sec.

Since this is independent of the mass of the object; this analysis is equally appropriate for a molecule . The distribution of speeds of a molecule in the atmosphere is given by the Maxwell speed distribution. The most probable speed (top of the distribution) is given by $v_p = \sqrt{2k_B T / m}$ where k_B is Boltzmann's constant. At 288K, $v_p\,(O_2) = 387$m/sec and $v_p\,(N_2) = 414$m/sec. These will both be retained. But $v_p(\text{He}) = 1094$ m/sec and $v_p(H_2) = 1550$ m/sec. This is

Number [N]

cold

hot

V_C

V_H

velocity
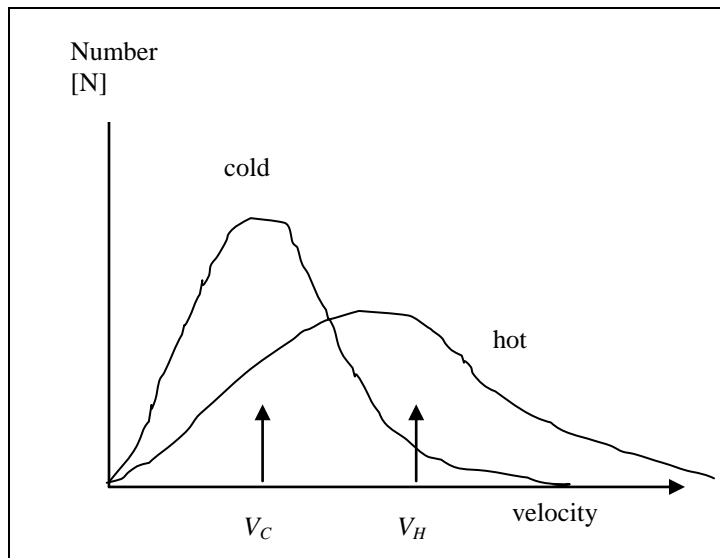
much faster. Moreover, at the top of the atmosphere the temperature is much higher. These gases can leak away. Over 10^9 years, He and H_2 have been lost to space.

Residence times (rate of turnover)
The *residence time,* τ is the mean lifetime of a molecule of gas in the atmosphere. This is as important as the concentration. Indeed, when considering pollutants, it is the most important parameter. It is given by $\tau = <M> / <F>$ where $<M>$ is the total average mass of the gas in the atmosphere and $<F>$ is the total average influx (or outflux) . $1 / \tau$ is therefore the *rate of turnover* of the gas. If τ is small, then the molecule (or atom) is in the atmosphere for only a short time. For example, it may be reactive and so will not be homogeneous throughout the atmosphere, but will be localised in particular areas. (Acid rain is an example). Another possibility is that the compounds may be part of a *cycle*. (Water is an example; the *hydrologic cycle* circulates water from sea to clouds to rain to sea again with a residence time of about 10 days). Using the residence time as a measure, we can divide the constituents of the atmosphere into three categories
1. *Permanent* - τ is very long (order of a few million years) e.g N_2, O_2, rare gases (CO_2 but see also later)
2. *Semi-permanent* - τ is of order months to years e.g. CH_4, N_2O, CO, CFCs
3. *Variable* - τ is of order days to weeks e.g. ozone O_3 [cycle in the stratosphere], H_2O [cycle in the troposphere], SO_2 and H_2S (acid rain), NO_2, NH_3 [car exhausts] but also part of the nitrogen cycle.

Photochemical pollution: This is an example of transitory processes and 'local' concentrations of 'trace species'. Photochemical smog is induced by sunlight which powers the following series of reactions
1. NO_2 + radiation ($\lambda < 385$nm) $\rightarrow$ NO + O
2. $O + O_2 +$ (molecule) $\rightarrow O_3 +$ (molecule) ;
3. $O_3 + NO \rightarrow O_2 + NO_2$
 The molecule in step 2 can be any species; it is needed to take the reaction energy away from the system. There is no overall change in the concentration of the reactants; the effect of the set of reactions is simply to convert the energy of the radiation into the kinetic energy of molecules. However, in the steady state, there will be finite concentrations of the intermediate species. In particular, the concentration of ozone is in the range 0.005-0.05ppm. This ozone near the surface is poisonous in itself and also reacts with olefins (carbon compounds with carbon-carbon double bonds. They are present in car exhausts) such as ethylene ($H_2C=CH_2$) and propylene ($H_2C=CH-CH_3$) to give products such as formaldehyde ($H_2C=O$), acrolein ($H_2C=CH-CH=O$) and (with NO_2) peroxy-acetylnitrate ($H_3C-(C=O)-O-O-NO_2$). These irritate the eyes and nose.

Sources and sinks of atmospheric compounds
Sources of trace species are often labelled 'natural' (such as O_3 in the stratosphere by UV light) or 'man-made' (such as CFCs). This crude separation encounters the obvious problem of what counts as 'natural' and further, one species may have more than one source (O_3 near the surface is 'man-made'). Biological processes produce the bulk of the CH_4, N_2O, H_2, NH_3, H_2S and NO_2 in the atmosphere. Even today, most CO_2 is generated (and cycled through photosynthesis) by biological processes rather than through burning

fossil fuels. However, it is true that 'man-made' combustion is responsible for most SO_2, NO, NO_2, NO_3^- [acid rain] and also for the rising CO_2 (greenhouse effect) levels.

A note on photosynthesis

Vegetation is an essential part of the biosphere. In 1772 Joseph Priestley demonstrated the importance of plants in atmosphere by enclosing a mouse and a living mint plant in a glass jar; a mouse on its own a second jar and a mint plant on its own in a third. Only in the first case did either survive and then both did. The mouse had *respiration* (absorbing O_2, producing CO_2); the plant *photosynthesis* (absorbing CO_2, producing O_2). In the plant there are cells containing *chloroplasts* within which the absorbed CO_2 and water react to form a carbohydrate (mostly glucose) and oxygen in the presence of chlorophyll. The reaction is endothermic; it requires solar energy to drive it to the right. Formally, the reaction can be written as

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$
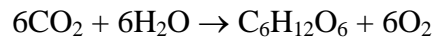
but this gives no idea of the complexity of the mechanism involved. The carbohydrates formed are then available for metabolism. If we write a carbohydrate using the general formula $[CH_2O]$, the general equation of metabolism is

$$[CH_2O] + O_2 \rightarrow CO_2 + H_2O + heat$$

Photosynthesis involves two stages. *Light reactions* involve the photolysis of water by sunlight and the evolution of oxygen. Light is absorbed by molecules of chlorophyll A. The energy is stored in the ATP (adenosine triphosphate) molecule. *Dark reactions* involve the fixation of CO_2, reducing it to carbohydrate.

Not all solar wavelengths are used in photosynthesis. Some are reflected (giving rise to green leaves).Others are absorbed but simply raise the temperature of the leaf. Red light is the most effective, although blue, orange and yellow also work.

Cycles and budgets of the major elements
Chemicals in the atmosphere can be conveniently grouped by composition; in particular as containing the elements *sulphur, carbon and nitrogen.* These can be discussed as a *cycle* of the form
SOURCES $\rightarrow$ CHEMICAL TRANSFORMATIONS $\rightarrow$ SINKS
1. *Nitrogen cycles:* Most nitrogen in the atmosphere is in the form of gaseous N_2. This is largely inert (an uncertain amount of N_2 is converted into nitrogen oxides by lightning). However, nitrogen in the form of NH_3 (ammonia) or NO_x (nitrogen oxides- including the nitrate ion) does cycle.
   1.1.   *Ammonia cycle* The source is the biological decay of material. NH_3 is linked to the water cycle since it is soluble in water (giving ammonium hydroxide). The estimated production rate is of the order 113-244Tg/yr. The main sinks are wet deposition (dissolved in rain) as NH_4^+ (72-151Tg/yr) and dry deposition (as ammonia (38-75Tg/yr).

1.2.   *NO_x cycle*. The major source of oxides in the atmosphere is the bacteriological decomposition of nitrates (21-89Tg/yr), but also a significant contribution from industry (19Tg/yr). Main sinks are wet deposition (NO_3^- dissolved in rain) 18-46Tg per year, dry deposition (NO, NO_2) 25-70Tg/yr. An important flow of nitrogen in the environment is run-off from fields into rivers and the sea (5-11Tg/yr). The total budget of the cycle is thus about 100Tg/yr

2. *Sulphur cycle:* The main sources of sulphur are H_2S (from the decay of organic matter (32Tg/yr) and also from volcanoes (1-2Tg/yr)), SO_2 and SO_4^{2-} from industry (mainly- 65Tg/yr)), from seaspray (44Tg/yr) and a little from volcanoes and erosion. The sinks are dry deposition as SO_2 (38Tg/yr) and wet deposition (acid rain) 106Tg/yr giving a total budget of about 144Tg/yr.

3. *Carbon cycle.* here there are three cycles based on CH_4 (methane), CO (carbon monoxide) and CO_2 (carbon dioxide). The first two have mainly biological sources. The third is a combination of natural and man-made. Both CH_4 and CO_2 are greenhouse gases. Let us consider the CO_2 cycle briefly:
The sources of CO_2 are combustion (natural and man-made), breathing and organic decay. The sinks are photosynthesis (plants using light to make sugars and oxygen out of CO_2 and water. The oceans (and sedimentary rocks – chalk, limestones) are sinks of carbon (present as the carbonate ion, CO_3^-). It is notorious that the combination of industry and forest reduction is causing a large increase in the amount of CO_2 in the atmosphere. We will discuss this in more detail later.

The atmospheric aerosol

An aerosol contains solid or liquid particles in suspension (e.g. dust particles). In the atmospheric aerosol, particles arise from
1. Combustion – forest fires or industry (soot)
2. Gas phase reactions (particles of sulphates or nitrates)
3. Dispersion of solids (wind and water erosion of rocks)
4. Dispersion of salts from the sea (sea-spray)
5. Volcanoes

Typical concentrations are 10^3 particles cm^{-3} (over the ocean); 10^4 particles cm^{-3} (over the country); 10^5 particles cm^{-3} (over cities). The size ranges from aggregates of a few hundred molecules (diameter about 1nm) to the largest particles (about 10 microns). The removal of the aerosol from the atmosphere depends on the size of the particles
1. *Aitken nuclei* have diameters less than a 0.1μm. They make up the majority of particles able to nucleate cloud droplets in a cloud chamber (a fact originally used to count them). Once away from where they are produced, the numbers are rapidly reduced by collision (due to Brownian motion) and coagulation to give larger particles. These nuclei make up about 20% of the aerosol mass
2. *Large nuclei* (diameters 0.1-1μm). Although much less numerous than Aitken nuclei they make up about 50% of the aerosol mass. Fall speeds are still much lower than the ability of up-draughts to maintain them in the atmosphere, but the concentration above the cloud base is greatly reduced because they are excellent nuclei for cloud droplets
3. *Giant nuclei* (diameters greater than 1μm). Although the number density is low, they comprise at least 30% of the aerosol mass. They are mainly produced by fine dust

lifted by the wind off arid surfaces. As with large nuclei, they are very effective nuclei for droplets. Also, they are efficiently swept out of the atmosphere by falling rain (the pressure wave around a falling drop is not strong enough to push them away). Also, their falling speed is now great enough for gravitational settling (sedimentation) to be important when the updraughts are low.