Atmospheric Sciences 501. Course Notes Autumn 1998.

1. Ideal Gas Law and Hydrostatics.

1.1 Ideal Gas Law.

Basic thermodynamic variables are:

Pressure, p (N m^{-2}; 1 N m^{-2} = 1 pascal (Pa) = 0.01 millibar (mb) = 0.01hectoPascals (hPa).

Density, ρ (kgm^{-3})

Temperature, T (K) .

If the energy due to intermolecular forces is small relative to molecular kinetic energy, the ideal gas law is an excellent approximation to the equation of state relating these variables:

$$\boxed{p = R\rho T} \tag{1.1}$$

where $R = \frac{R^*}{M}$ = gas constant; R^* = universal gas constant = 8314J $kmol^{-1}$ K^{-1}; M = molar weight (kg/kg-mole) and R = specific gas constant for dry air = 287 J kg^{-1} K^{-1}.

1.2 Molecules and the ideal gas law, Maxwell's kinetic interpretation.

Note that

$$\rho = \rlap{n}\surd\rlap{m}\surd \tag{1.2}$$

where $\rlap{n}\surd$ = number density (number of molecules per unit volume m^{-3}), and

$\rlap{m}\surd$ = molecular mass (kg).

Also

$$M = \rlap{m}\surd A \tag{1.3}$$

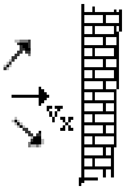
where A = Avogadro's Number = 6.022×10^{26} molecules per mole; note that, since SI units are used, moles here are kilogram-moles, not gram-moles.

Substituting (1.2) and (1.3) into (1.1):

$$\boxed{p = \left(\frac{R^*}{A}\right) n T = k n T} \qquad (1.4)$$

where $k = \left(\frac{R^*}{A}\right) = 1.381 \mathrm{x} 10^{-23}$ J K^{-1} is Boltzmann's Constant.

Now consider the pressure exerted by molecules of gas on a surface perpendicular to the x-axis in a Cartesian reference frame. This is the force per unit area and is equivalent to the average flux in the x-direction of molecules with x-momentum $m v_x$, $\left(\overline{m v_x \cdot n v_x}\right)$



where $\left(\bar{\ }\right)$ represents averaging over molecular velocities. Since this momentum flux per unit area is equal to the pressure,

$$p = n\overline{m v_x^2} \quad .$$

But $\overline{m v_x^2} = \frac{1}{3} m\left(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\right) = \frac{2}{3}\overline{KE}$ where $\overline{KE}$ is mean kinetic energy per molecule.

From thermodynamics and the definition of Boltzmann's Constant,

$$\overline{KE} = \frac{3}{2} kT, \qquad (1.5)$$

so $n\overline{m v_x^2} = nkT = p$. Hence, if the only momentum flux is due to mean molecular kinetic energy, the ideal gas law applies. It is an excellent approximation for the atmosphere and is used in meteorology almost without exception.

1.3 Dalton's Law.

Under conditions where the ideal gas law applies, individual molecules in a gas exert independent partial pressures

$$\boxed{p_i = n_i kT \ , \quad p = \sum_i p_i \ , \quad n = \sum_i n_i} \qquad (1.6)$$

where $(\ )_i$ corresponds to species i whose partial pressure is p_i . We can use Dalton's Law to determine the molar weight of a mixture of gases:

$$p = \left(\sum_i \tilde{n}_i\right)\cdot kT \quad , \qquad \rho = \sum_i \tilde{n}_i \tilde{m}_i \tag{1.7}$$

so

$$p = \left(\frac{\sum_i \tilde{n}_i}{\sum_i \tilde{m}_i \tilde{n}_i}\right)\cdot k\rho T = \left(\frac{k}{\overline{\tilde{m}}}\right)\rho T = \left(\frac{R^*}{A\overline{\tilde{m}}}\right)\rho T = R\rho T \tag{1.8}$$

where

$$\overline{\tilde{m}} = \frac{\sum_i \tilde{m}_i \tilde{n}_i}{\sum_i \tilde{n}_i} \quad , \qquad R = \frac{R^*}{\overline{M}}$$

, and $\overline{M}$ is the mean molar weight,

$$\boxed{\overline{M} = \frac{\sum_i \tilde{n}_i M_i}{\sum_i \tilde{n}_i} = \frac{\sum_i n_i M_i}{n}} \tag{1.9}$$

expressed in terms of both partial number density $\tilde{n}_i$ and partial and total number of moles (n_i, n). For dry air its value is 28.97.

The ideal gas law and mean molar weight can also be expressed in terms of moles, n, and total volume V (as in MS, eqn. 1.1):

$$n = \left(\frac{\tilde{n}V}{A}\right) \quad . \tag{1.10}$$

Also, since m = total mass = $n\overline{M}$,

$$\boxed{pV = nR^*T = \frac{m}{\overline{M}}R^*T = mRT} \quad . \tag{1.11}$$

1.4 Composition of air.

The mole fraction of gas species i is given by

$$N_i = \frac{n_i}{n} = \frac{\tilde{n}_i}{\overline{\tilde{n}}}. \tag{1.12}$$

Volume mixing ratio and mass mixing ratio are given respectively by

$$\mu_i = \frac{n_i}{n_d} = \frac{\check{n}_i}{\check{n}_d} \tag{1.13}$$

and

$$q_i = \frac{m_i}{m_d} = \frac{\check{m}_i \check{n}_i}{\check{m}_d \check{n}_d} = \frac{M_i n_i}{M_d n_d} = \varepsilon_i \mu_i \tag{1.14}$$

in which $\varepsilon_i \equiv \frac{M_i}{M_d}$ is the molar weight ratio for dry air and q_i is the mass mixing ratio of gas species i.

Mole fractions of nitrogen, oxygen, argon, and other noble gases are constant in space up to an altitude of about 100km and constant in time for periods of order 10^7yr or more. These are permanent gases. Other gaseous constituents of the atmosphere are variable either in time, or space, or both (variable gases). By far the most abundant of the variable species is water vapor (number density and volume mixing ratio n_w and μ_w). Its molecular weight ratio ε_w is $\varepsilon_w = \frac{18.00}{28.97} = 0.621$. Values of μ_w can range up to as much as 0.03, so that mole fraction and volume mixing ratio of water vapor can differ by up to 3%. The mole fractions of other variable constituents of the atmosphere (gases other than argon, nitrogen, and oxygen) are always much less than μ_w and the difference between mole fraction and volume mixing ratio can usually be neglected for these gases. Thus, for water vapor,

$$N_w = \mu_w (1 + \mu_w)^{-1} \quad , \tag{1.15}$$

while for other variable gases, mole fractions and volume mixing ratios are related by

$$N_i \approx \mu_i (1 + \mu_w)^{-1}.$$

Atmospheric composition and some factors controlling it are summarized in the following table.

Table 1. Composition, sources, sinks, and mean residence times of the atmospheric gases

Molecule	Molar weight	Mole fraction	Major Source	Major Sink	Mean residence time	Greenhouse gas?
Permanent Gases:						
Nitrogen (N2)	28	78.08	Bacterial denitrification	Bacterial nitrogen fixation	2E06yr	No
Oxygen (O2)	32	20.95	Photosynthesis	Respiration, Decay	4000yr	No
Argon (A)	40	0.94	Radioactive decay of ^{40}K	None	4E09yr	No
Neon (Ne)	20	2E-03	None	None	4E09 yr	No
Helium (He)	4	5E-04	Radioactive decay of ^{235}U	Escape to space	4E04 yr	No
Krypton (Kr)	84	1E-04	None	None	4E09 yr	No
Xenon (Xe)	131	9E-06	None	None	4E09 yr	No
Variable Gases:						
Water Vapor	18	up to 0.03	Evaporation	Condensation	1wk	yes#
Carbon dioxide (CO2)	44	3.5E-04	Respiration; decay, exchange with sea	Photosynthesis	6yr	Yes#
Methane (CH4)	16	2E-04	Anaerobic decay of organic matter	Reaction with OH*	10 yr	Yes#
Nitrous oxide (N_2O)	44	3E-05	Bacterial denitrification	Dissociation in the upper atmosphere	5 yr	Yes#
Ozone (O3)	48	3E-08 to E-05**	O2 Photo-dissociation	Catalytic recombination	10 yr	Yes#
Nitrogen dioxide (NO2)	46	1E-07	Combustion	Conversion to nitrates, rainout	0.2 days	Yes
CFCs (various, compounds of C, Cl,F)	--	3E-09	Industrial products	Slow conversion to HCl followed by rainout	50-150 yr	Yes#
Non-methane hydrocarbons	--	E-08 less	Industry,cars, emissions from Vegetation	Reaction with OH*, rainout	hrs to days	Yes
Sulfur dioxide(SO2)	64	E-08	Combustion##	Reaction with OH	hrs to days	No

Notes on Table 1. (1) Sources and sinks. For most of the gases in the atmosphere, the concentration is maintained by an approximate balance between sources and sinks. The dominant sources and sinks are indicated. (2) Mean Residence Time. This is the ratio of the total amount of a gas in the atmosphere to its rate of loss (the destruction rate or strength of the sink). If the mean residence time is short, the concentration tends to be highly variable in space with the gas concentrated near the source. If the mean residence time is long, the concentration is nearly uniform. If the mean residence time is long compared with about a year, roughly the time to mix from pole to pole in the lowest 10km of the atmosphere, the concentration in that region tends toward uniformity. (3) Greenhouse gas. These gases absorb and reemit thermal infrared radiation emitted from the surface, and thereby tend to warm the surface. The most important greenhouse gases are marked with (#).

*Several of the gases in Table 1 are removed from the atmosphere by reaction with the hydroxyl radical (OH). It is a fragment produced by dissociation of water vapor that is so reactive it acts as a kind of "atmospheric vacuum cleaner". It is produced in the lower atmosphere when ozone, water vapor, and sunlight are all available. It is also produced by photochemical breakdown of water vapor in the upper atmosphere.

** The smaller value of ozone concentration corresponds to typical surface air; the larger value corresponds to the region of maximum mole fraction near 25 km altitude.

##The major source of atmospheric sulfur dioxide is industrial combustion of fossil fuels, notably coal. This source is larger than the largest non-anthropogenic source, emission of reduced sulfur gases by marine microorganisms followed by release to the atmosphere and oxidation to SO_2.

Note that almost all atmospheric gases have biological sources or sinks (including human activities)!