**Lecture 4**

## Composition and structure of planetary atmospheres.

## Basic properties of radiatively active species (gases, aerosols, and clouds).

***Objectives:***

1. Composition of the atmosphere:
   - Basic properties of atmospheric gases
   - Basic properties of aerosols
   - Basic properties of clouds
2. Structure of the atmosphere:
   - Vertical structure of the atmosphere
   - Hydrostatic law
3. Sun as an energy source. Solar spectrum and solar constant.

***Required reading***:

L80: 2.1-2.3; 3.1

***Additional/advanced reading***

Le93:15, 16/G&Y: 1.1-1.3

## 1. Composition of the atmosphere.

Atmosphere is composed of:

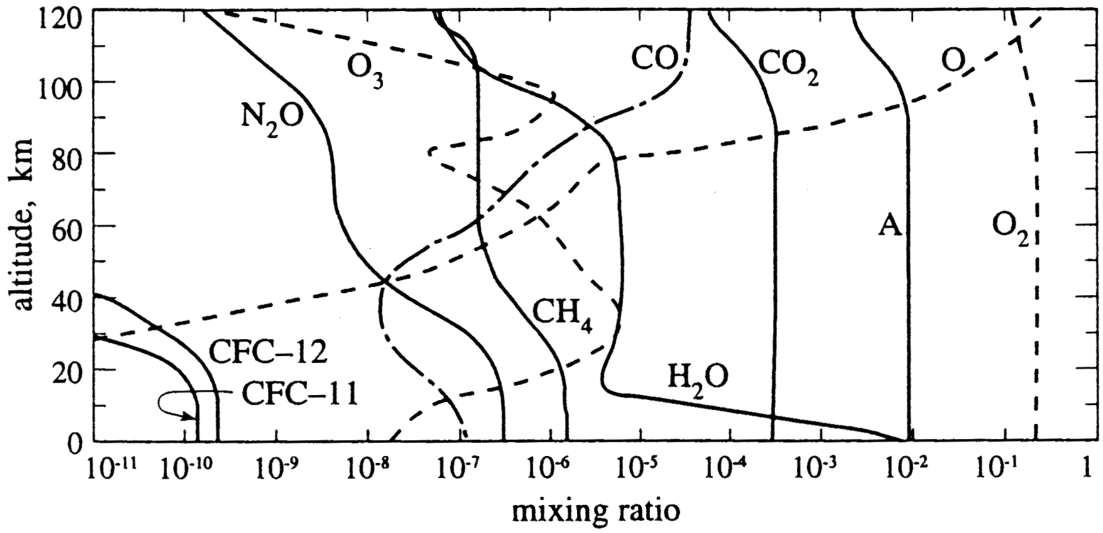
- Gases
- Aerosols
- Water and ice cloud droplets

## ➢ Atmospheric gases

Table 4.1 The gaseous composition of the atmosphere

| Gases | % by volume | Comments |
|---|---|---|
| | **Constant gases** | |
| Nitrogen, $N_2$ | 78.08% | Photochemical dissociation high in the ionosphere; mixed at lower levels |
| Oxygen, $O_2$ | 20.95% | Photochemical dissociation above 95 km; mixed at lower levels |
| Argon, Ar | 0.93% | Mixed up to 110 km |
| Neon, Ne | 0.0018% | Mixed in most of the middle atmosphere |
| Helium, He | 0.0005% | |
| Krypton, Kr | 0.00011% | |
| Xenon, Xe | 0.000009% | |
| | **Variable gases** | |
| Water vapor, $H_2O$ | 4.0% (maximum, in the tropics) 0.00001%(minimum, at the South Pole) | Highly variable; photodissociates above 80 km dissociation |
| Carbon dioxide, $CO_2$ | 0.0365% (increasing ~0.4% per year) | Slightly variable; mixed up to 100 km; photodissociates above |
| Methane, $CH_4$ | ~0.00018% (increases due to agriculture) | Mixed in troposphere; dissociates in mesosphere |
| Hydrogen, $H_2$ | ~0.00006% | Variable photochemical product; decreases slightly with height in the middle atmosphere |
| Nitrous oxide, $N_2O$ | ~0.00003% | Slightly variable at surface; dissociates in stratosphere and mesosphere |
| Carbon monoxide, CO | ~0.000009% | Variable |
| Ozone, $O_3$ | ~0.000001% - 0.0004% | Highly variable; photochemical origin |
| Fluorocarbon 12, $CF_2Cl_2$ | ~0.00000005% | Mixed in troposphere; dissociates in stratosphere |

**Figure 4.1** Vertical profiles of mixing ratios of some gases in the atmosphere.




## Some important properties of atmospheric gases:

➢ ***Obey the ideal gas laws:***

**Boyle's law:** V ~ 1/P (at constant T and the number of gas moles $\mu$)

**Charles's law:** V ~ T (at constant P and $\mu$)

**Avogadro's law**: V ~ number of gas molecules (at constant P and T)

**The equation of state:** says that the pressure exerted by a gas is proportional to its temperature and inversely proportional to its volume:

$$\mathbf{P\ V = \mu\ R\ T}$$

where **R** is the universal gas constant. If pressure **P** is in atmospheres (atm), volume **V** in liters (L) and temperature **T** in degrees Kelvin (K), thus **R** has value

**R = 0.08206 L atm K$^{-1}$ mol$^{-1}$**

- ***The distribution of velocities*** of ideal gas molecules (e.g., atmospheric gases) is described by the Maxwell-Boltzmann velocity distribution law:

$$f(v) = 4\pi \{m/ 2\pi \boldsymbol{k}_B T\}^{3/2} v^2 \boldsymbol{exp}( -mv^2/2\boldsymbol{k}_B T),$$

where v is velocity (m/s); m is mass of a gas molecule (kg), T is temperature (K), and $\boldsymbol{k}_B$ is Boltzmann's constant = $1.38066 \times 10^{-23}$ (J/K).

**NOTE: Most probable velocity** v (the velocity possessed by the greatest number of gas particles): $\mathbf{v = (2k_B T / m)^{1/2}}$ and the **mean velocity** of a gas molecule is

$$\mathbf{v = (8k_B T / p\, m)^{1/2}}$$

- ***The amount of the gas may be expressed in several ways:***

i) **Molecular number density = molecular number concentration = molecules per unit volume of air;**

ii) **Density = molecular mass concentration = mass of gas molecules per unit volume of air;**

iii) **Mixing ratios:**

**Volume mixing ratio** is the number of gas molecules in a given volume to the total number of all gases in that volume (when multiplied by $10^6$, in ppmv (parts per million by volume))

**Mass mixing ratio** is the mass of gas molecules in a given volume to the total mass of all gases in that volume (when multiplied by $10^6$, in ppmm (parts per million by mass))

**NOTE:** Commonly used mixing fraction: one part per million 1 **ppm** ($1 \times 10^{-6}$); one part per billion 1 **ppb** ($1 \times 10^{-9}$); one part per trillion 1 **ppt** ($1 \times 10^{-12}$).

iv) **Mole fraction** is the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.

**NOTE:** mole fraction is equivalent to the volume fraction.

**NOTE:** The equation of state can be written in several forms:

using molar concentration of a gas, $c = \mu/v$: $\mathbf{P = c\,T\,R}$

using number concentration of a gas, $N = c\,N_A$: $\mathbf{P = N\,T\,R/N_A}$ or $\mathbf{P = N\,T\,k_B}$

using mass concentration of a gas, $q = c\,m_g$: $\mathbf{P = q\,T\,R\,/m_g}$

## ➢ Atmospheric aerosols

***Atmospheric aerosols (or particulate matter)*** are solid or liquid particles or both suspended in air with diameters between about 0.002 μm to about 100 μm.

- Aerosol particles vary greatly in sources, production mechanisms, sizes, chemical composition, amount, distribution in space and time, and how long they survive in the atmosphere (i.e. lifetime).

**Important properties of atmospheric aerosols:**

1) **Primary and secondary aerosols.**

**Primary atmospheric aerosols** are particulates that emitted directly into the atmosphere (for instance, sea-salt, mineral aerosols (or dust), volcanic dust, smoke and soot, some organics).

**Secondary atmospheric aerosols** are particulates that formed in the atmosphere by gas-to-particles conversion processes (for instance, sulfates, nitrates, some organics).

2) **Location in the atmosphere**: **stratospheric and tropospheric** aerosols;

3) **Particle size: fine mode** ($d < 2.5$ μm) and **coarse mode** ($d > 2.5$ μm);

fine mode is divided on the **nuclei mode** (about $0.005$ μm $< d < 0.1$ μm) and **accumulation mode** ($0.1$μm $< d < 2.5$ μm).

NOTE: The distinction between fine and coarse particles is a fundamental because, in general, the fine and coarse particles mode originate separately, are transformed separately, are removed from the atmosphere by different mechanisms, have different chemical composition, have different optical properties, etc.

4) **Chemical composition**: **sulfate** ($SO_4^{2-}$), **nitrate** ($NO_3^-$), **soot** (elemental carbon), **sea-salt** (NaCl); **multi-component (MC)** aerosols, etc.;

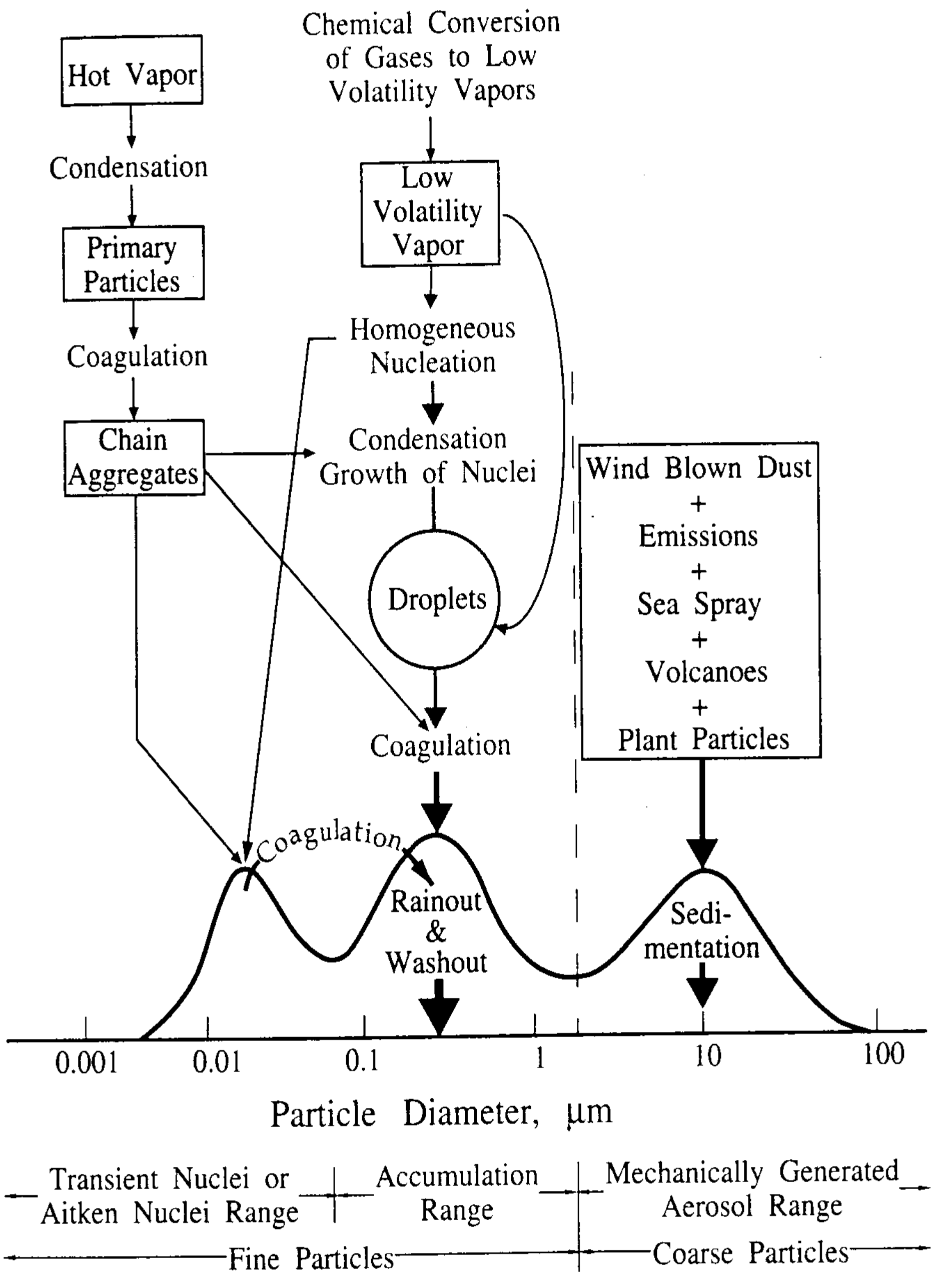
5) **Geographical location: marine, continental, rural, industrial, polar, desert** aerosols, etc.

6) **Anthropogenic (man-made) and natural aerosols:**
Anthropogenic sources: various (biomass burning, gas to particle conversion; industrial processes; agriculture's activities)
Natural sources: various (sea-salt, dust storm, biomass burning, volcanic debris, gas to particle conversion)

***Once in the atmosphere, aerosols evolve in time and space:***

- May be transported downwind from the source (by advection, turbulent mixing, etc.);
- May be removed from the atmosphere (by dry deposition, wet removal, and gravitational sedimentation);
- Can change their size and composition due to microphysical transformation processes (such as nucleation, coagulation, and condensation/evaporation);
- Can undergo chemical transformation (via aqueous or heterogeneous chemistry);
- Can undergo cloud processing.

**Figure 4.2** Idealized schematic of the distribution of particle surface area of an atmospheric aerosols (from Whitby and Cantrell, 1976).



- **The particle size distribution** of aerosols are often approximated by a sun of three log-normal functions as

$$N(r) = \sum_i \frac{N_i}{\sqrt{2p}\ \ \ln(s_i)\ \ r} \exp\left(-\frac{\ln(r / r_{0,i})^2}{2\ln(s_i)^2}\right)$$

where **N(r)** is the particle number concentration, $\mathbf{N_i}$ is the total particle number concentration of i-th size mode with its median radius $\mathbf{r_{0,i}}$ and geometric standard deviation $s_{\mathbf{i}}$.

Table 4.2 Representative parameters of model size distributions for major types of aerosols.

| **Mode I** | | | **Mode II** | | | **Mode III** | | |
|---|---|---|---|---|---|---|---|---|
| N(cm$^{-3}$) | D (μm) | log (σ) | N(cm$^{-3}$) | D (μm) | log (σ) | N(cm$^{-3}$) | D (μm) | log (σ) |
| **Urban aerosols** | | | | | | | | |
| 9.93x10$^{4}$ | 0.013 | 0.245 | 1.11x10$^{3}$ | 0.014 | 0.666 | 3.6x10$^{4}$ | 0.05 | 0.337 |
| **Marine aerosols** | | | | | | | | |
| 133 | 0.008 | 0.657 | 66.6 | 0.266 | 0.21 | 3.1 | 0.58 | 0.396 |
| **Rural aerosols** | | | | | | | | |
| 6650 | 0.015 | 0.225 | 147 | 0.054 | 0.557 | 1990 | 0.084 | 0.266 |
| **Remote continental aerosols** | | | | | | | | |
| 3200 | 0.02 | 0.161 | 2900 | 0.116 | 0.217 | 0.3 | 1.8 | 0.38 |
| **Polar aerosols** | | | | | | | | |
| 21.7 | 0.138 | 0.245 | 0.186 | 0.75 | 0.3 | 3.x10$^{-4}$ | 8.6 | 0.291 |
| **Mineral (soil-derived) aerosols** | | | | | | | | |
| 726 | 0.002 | 0.247 | 114 | 0.038 | 0.77 | 0.178 | 21.6 | 0.438 |
| **Free-troposphere aerosols** | | | | | | | | |
| 129 | 0.007 | 0.645 | 59.7 | 0.25 | 0.253 | 63.5 | 0.52 | 0.425 |

Table 4.3 Global emission estimates for major aerosol types (**estimated flux Tg yr$^{-1}$**)

| ***Source*** | ***Low*** | ***High*** | ***Best*** |
|---|---|---|---|
| **NATURAL** | | | |
| **<u>Primary:</u>** | | | |
| **soil dust** | 1000 | 3000 | 1500 |
| **sea salt** | 1000 | 10000 | 1300 |
| **volcanic dust** | 4 | 10000 | 30 |
| **biological debris** | 26 | 80 | 50 |
| **<u>Secondary:</u>** | | | |
| **sulfates from biogenic gases** | 80 | 150 | 130 |
| **sulfates from volcanic SO2** | 5 | 60 | 20 |
| **organic matter from biogenic VOC** | 40 | 200 | 60 |
| **nitrates** | 15 | 50 | 30 |
| **<u>Total natural</u>** | 2200 | 23500 | 3100 |
| **ANTHROPOGENIC** | | | |
| **<u>Primary:</u>** | | | |
| **industrial particulates** | 40 | 130 | 100 |
| **dust** | 300 | 1000 | 600 |
| **soot** | 5 | 20 | 10 |
| **<u>Secondary:</u>** | | | |
| **sulfates from SO2** | 170 | 250 | 190 |
| **biomass burning** | 60 | 150 | 90 |
| **nitrates from NOx** | 25 | 65 | 50 |
| **organics from anthropogenic VOC** | 5 | 25 | 10 |
| **<u>Total anthropogenic</u>** | 600 | 1640 | 1050 |
| **Total** | 2800 | 26780 | 4150 |

**NOTE:** The optical and radiative properties of aerosols will be defined in Lecture 14.

## ➢ Cloud particles

**Major characteristics are *cloud type; cloud coverage; liquid water content of cloud; cloud droplet concentration; cloud droplet size.***

Important properties of clouds:

- Cloud droplet sizes vary from a few micrometers to 100 micrometers with average diameter in 10 to 20 μm range.
- Cloud droplet concentration varies from about 10 $cm^{-3}$ to 1000 $cm^{-3}$ with average droplet concentration of a few hundred $cm^{-3}$.
- The liquid water content of typical clouds, often abbreviated LWC, varies from approximately 0.05 to 3 g(water) $m^{-3}$, with most of the observed values in the 0.1 to 0.3 g(water) $m^{-3}$ region.

**NOTE:** Clouds cover approximately 60% of the Earth's surface. Average global coverage over the oceans is about 65% and over the land is about 52%.

Table 4.4 Types and properties of clouds.

| *Type* | *Height of base (km)* | *Freq. over oceans (%)* | *Coverage over oceans (%)* | *Freq. over land (%)* | *Coverage over land (%)* |
|---|---|---|---|---|---|
| **Low level:** | | | | | |
| **Stratocumulus(Sc)** | 0-2 | 45 | 34 | 27 | 18 |
| **Stratus (St)** | 0-2 | (Sc+St) | (Sc+St) | (Sc+St) | (Sc+St) |
| **Nimbostratus (Ns)** | 0-4 | 6 | 6 | 6 | 5 |
| **Mid level:** | | | | | |
| **Altocumulus (Ac)** | 2-7 | 46 | 22 | 35 | 21 |
| **Altostratus (As)** | 2-7 | (Ac+As) | (Ac+As) | (Ac+As) | (Ac+As) |
| **High level:** | | | | | |
| **Cirrus (Ci)** | 7-18 | 37 | 13 | 47 | 23 |
| **Cirrostratus (Cs)** | 7-18 | Ci+Cs+Cc | Ci+Cs+Cc | Ci+Cs+Cc | Ci+Cs+Cc |
| **Cirrocumulus (Cc)** | 7-18 | | | | |
| **Clouds with vertical development** | | | | | |
| **Cumulus (Cu)** | 0-3 | 33 | 12 | 14 | 5 |
| **Cumulonimbus (Cb)** | 0-3 | 10 | 6 | 7 | 4 |

- Cloud droplets size distribution is often approximated by a modified gamma distribution

$$N(r) = \frac{N_0}{\Gamma(a) r_n} \left( \frac{r}{r_n} \right)^{a-1} \exp(-r / r_n)$$

where $\mathbf{N_0}$ is the total number of droplets ($cm^{-3}$); $\mathbf{r_n}$ in the radius that characterizes the distribution ; a in the variance of the distribution, and G is the gamma function.

Table 4.5 Characteristics of representative size distributions of some clouds

(for a =2)

| Cloud type | $N_o$ ($cm^{-3}$) | $r_m$ (mm) | $r_{max}$ (mm) | $r_e$ (mm) | $l$ ($g\ m^{-3}$) |
|---|---|---|---|---|---|
| **Stratus:** | | | | | |
| **over ocean** | **50** | **10** | **15** | **17** | **0.1-0.5** |
| **over land** | **300-400** | **6** | **15** | **10** | **0.1-0.5** |
| **Fair weather cumulus** | **300-400** | **4** | **15** | **6.7** | **0.3** |
| **Maritime cumulus** | **50** | **15** | **20** | **25** | **0.5** |
| **Cumulonimbus** | **70** | **20** | **100** | **33** | **2.5** |
| **Altostratus** | **200-400** | **5** | **15** | **8** | **0.6** |

Mean radius: $\mathbf{r_m = (a + 1)\, r_n}$

Effective radius: $\mathbf{r_e = (a + 3)\, r_n}$

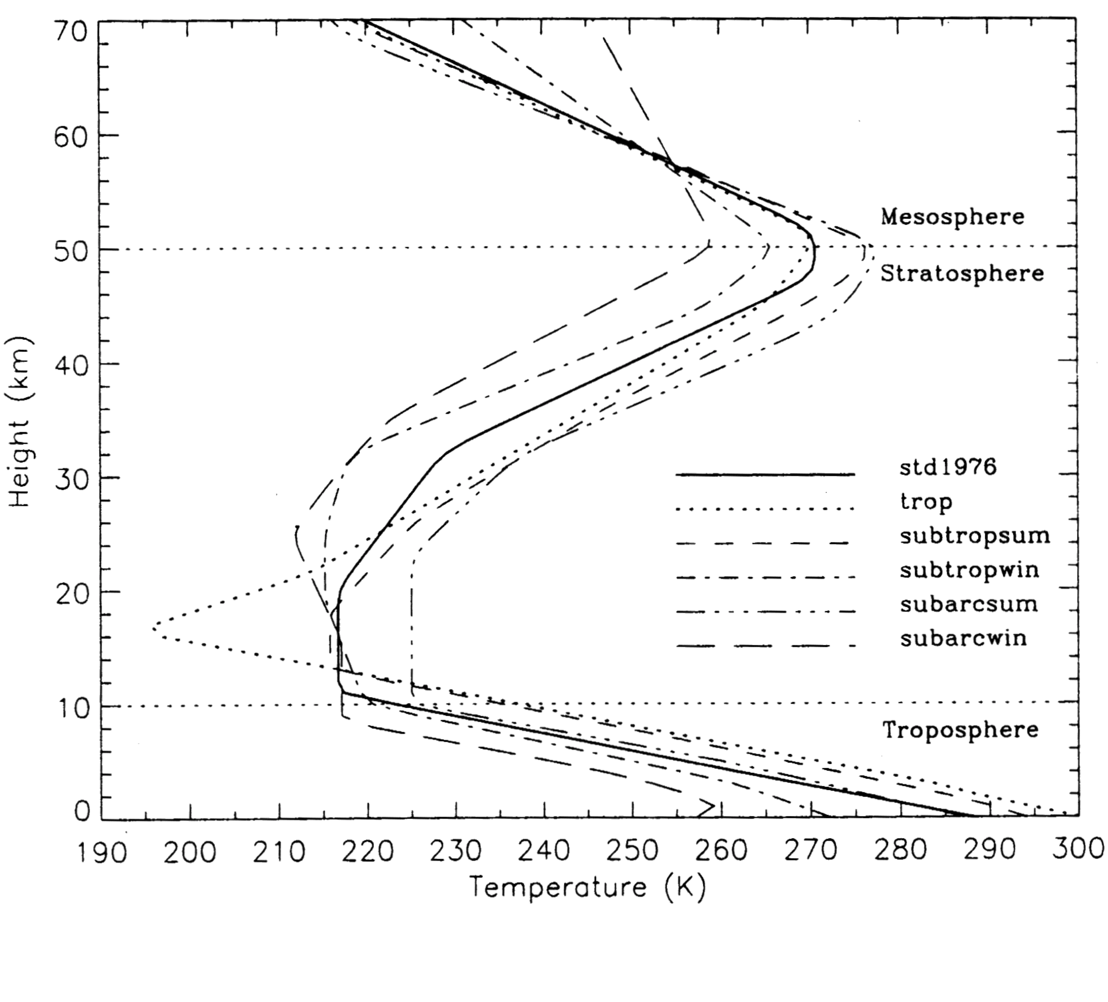
Cloud liquid water content: $l = r\ V = \frac{4}{3} r \int p r^3 N(r) dr$

**NOTE:** The optical and radiative properties of clouds will be discussed in Lecture 15.

## 2. Structure of the atmosphere.

- Variations of temperature, pressure and density are much larger in vertical directions than in horizontal. This strong vertical variations result in the atmosphere being **stratified** in layers that have small horizontal variability compare to the variations in the vertical.

**Figure 4.3** Temperature profiles of the standard atmospheric models often used in radiative transfer calculations. "Standard U.S. 1976 atmosphere" is representative of the global mean atmospheric conditions; "Tropical atmosphere" is for latitudes < $30^0$; "Subtropical atmosphere" is for latitudes between $30^0$ and $45^0$; "Subarctic atmosphere" is for latitudes between $45^0$ and $60^0$; and "Arctic atmosphere" is for latitudes > $60^0$.



- Except cases with temperature inversion, temperature always decreases in the lower troposphere.

**Temperature lapse rate** is the rate at which temperature decreases with increasing altitude.

$$G = -(T_2 - T_1) / (z_2 - z_1) = -DT/Dz$$

where T is temperature and the height z.

- Adiabatic process is of special significance in the atmosphere because many of the temperature changes that take place in the atmosphere can be approximated as adiabatic.

For a parcel of dry air under adiabatic conditions it can be shown that

$$dT/dz = -g/c_p$$

where $c_p$ is the heat capacity at constant pressure per unit mass of air and $c_p = c_v + R/m_a$ and $m_a$ is the molecular weight of dry air. The quantities $g/c_p$ is a constant for dry air equal to **9.76 C per km**. This constant is called **dry adiabatic lapse rate**.

- **The law of hydrostatic balance** states, that the pressure at any height in the atmosphere is equal to the total weight of the gas above that level.

**The hydrostatic equation:** $dP(z) / dz = - r(z)\, g$

where $r(z)$ is the mass density of air at height z, and $g$ = 8.31 m/s is the acceleration of gravity.

- Integrating the hydrostatic equation at constant temperature as a function of z gives

$$P = P_0 \exp(-z/H)$$

where $H$ is **the scale height:** $H = k_B T / mg$; and $m$ is the average mass of air molecule ($m$ = 4.8096x10$^{-26}$ kg/air molecule).

- **Air motion**

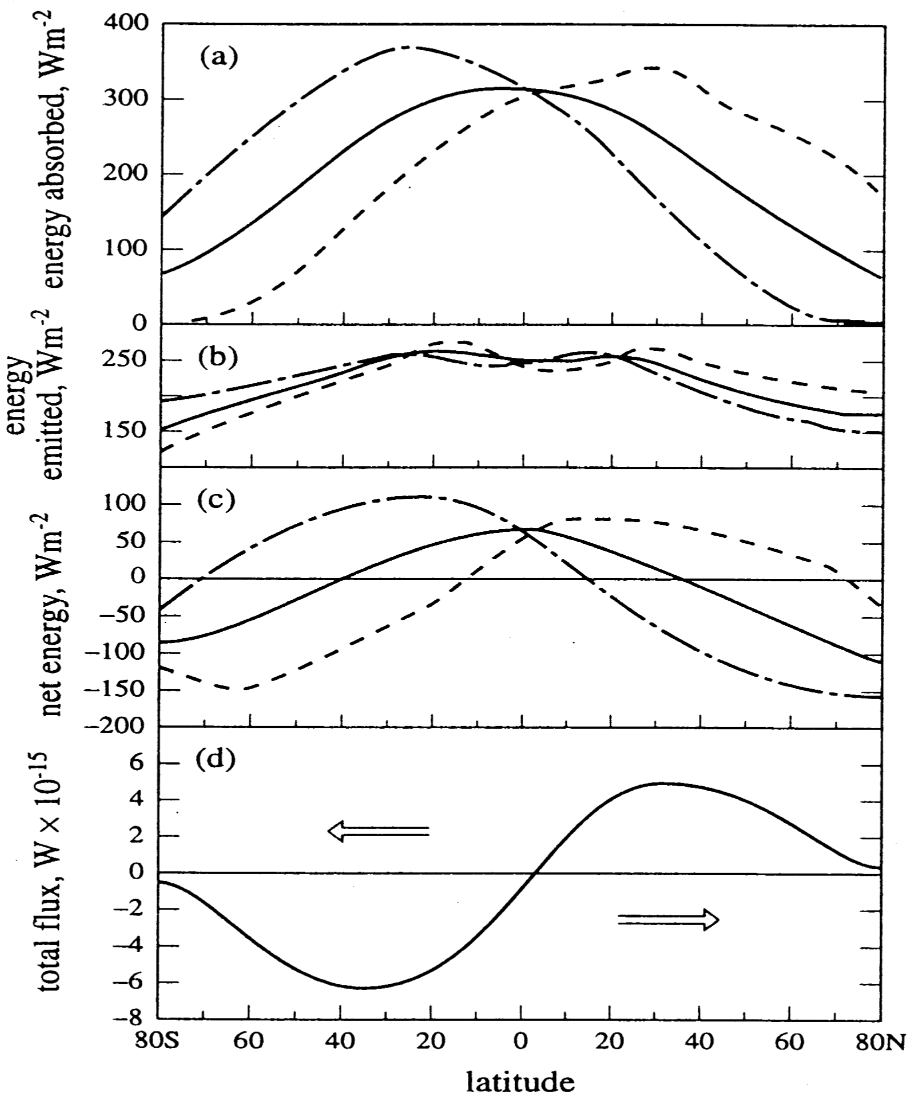
***The key energy sources driving the wind systems on our planet:***

a) **Solar radiation** (energy emitted by Sun)

b) Latent heat

c) Thermal radiation (energy emitted by the surface of the Earth and the atmosphere

Figure 4.4 Latitudinal distributions of radiative fluxes at TOA, except (d) which gives the horizontal flux that must be carried across latitudes. Solid curves are annual averages; dash-dot and dashed curves are averages over NH winter and summer months, respectively (from Goody, 1995).



**NOTE**:

- The uneven distribution of solar energy results from latitudinal variations in solar insolation (more in tropics, less at poles), and from differences in absorptivity of the Earth's surface. It creates the large-scale air motion to transport energy from the tropics toward the polar regions.
- This energy transport is affected by the rotation of Earth (the Coriolis effect). Thus, the general pattern of global air circulation is chiefly due to both solar radiation and Earth rotation.

**NOTE**: Atmospheric radiation and climate will be discussed in Lectures 24-25

## 3. Sun as an energy source. Solar spectrum and solar constant.

- Solar flux reaching the earth is a function of time determined by 1) the orbital characteristics of the earth and the sun (i.e., eccentricity; obliquity, and periodic precession) and 2) the sun properties (e.g., solar surface activity).

**NOTE:**

a) Sun is a gaseous sphere consisting of hydrogen, helium, iron, silicon, etc.

b) Sunspots are cooler regions of the sun (with T = 4000K). Period between sunspot maxima is about 11 years (called **11-year-cycle**).

c) Solar energy: nuclear fusion (conversion of four hydrogen atoms to one helium atom)

**Solar constant** is defined as total flux of solar energy, reaching the top of the atmosphere, per unit surface normal to the solar beam at the mean distance between the sun and the earth: mean measured value $\mathbf{F_0 = 1366}$ W $m^{-2}$ with the measurement uncertainty +/ 3 W $m^{-2}$.

**Actual solar total flux at the top of the atmosphere** at a given time is

$$F_s = \left( \frac{d_{es}}{d_{es}*} \right)^2 F_0$$

where $\boldsymbol{d_{es}}^*$ is the mean distance from the center of the sun to the earth ($1.5 \times 10^{11}$ m) and $\boldsymbol{d_{es}}$ is the actual distance on a given day

$$\left( \frac{d_{es}}{d_{es}*} \right)^2 \approx 1.00011 + 0.034221 \cos(\theta_j) + 0.00128 \sin(\theta_j) +$$
$$+ 0.00719 \cos(2\theta_j) + 0.000077 \sin(2\theta_j)$$

here $\theta_j = 2\pi D_j/D_y$, where $D_y$ is the number of days in a year (365 or 366) and $D_j$ is the Julian day of the year.

**Solar zenith angle cos ($\theta_0$):**

$$\cos\theta_s = \sin(\varphi)\sin(\delta) + \cos(\varphi)\cos(\delta)\cos(h)$$

where $\phi$ is the latitude; $\delta$ is the solar inclination angle, and $\boldsymbol{h}$ is the local hour angle of the sun.