Part 1. The Earth's Atmosphere

Chapter 8.
The Chemistry of Global Climate

Chapter 8. Chemistry of Global Climates

8.1 Composition of the Earth's atmosphere

- Average composition of nine principal gases in the dry troposphere (Tab. 8.1)
- Water-most highly variable from day to day and place to place due to its relatively short residence time of 11 days, being much smaller than the time required for complete mixing of the troposphere. Maximum mixing ratio in the troposphere depends on temperature (Fig. 8.1)

Table 8.1 Average composition of the dry troposphere

Component	Mixing ratio
Nitrogen	78.08%
Oxygen	20.95%
Argon	0.93%
Carbon dioxide	365 ppmv
Neon	18 ppmv
Helium	5.2 ppmv
Methane	1.77 ppmv
Hydrogen	0.53 ppmv
Nitrous oxide	0.31 ppmv

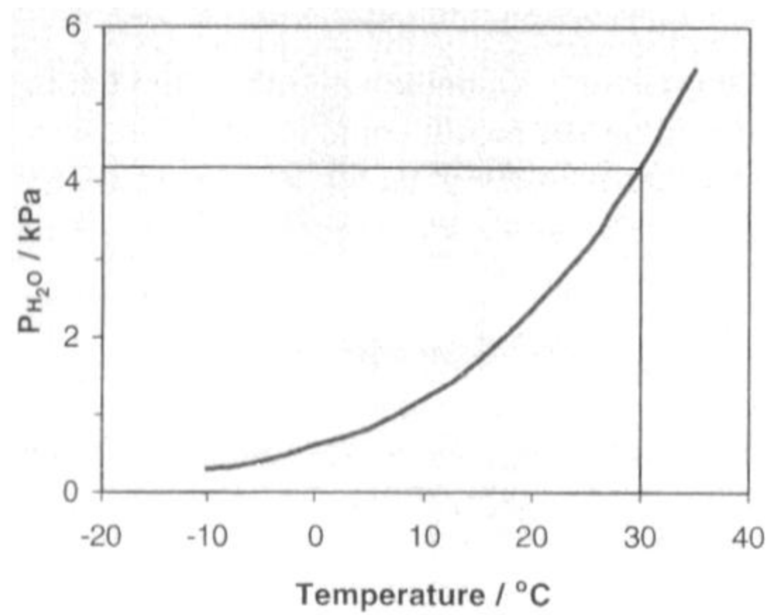

Fig. 8.1 The vapour pressure of water (P_{H_2O}) as a function of temperature. The value of (P_{H_2O}) at 30 °C is determined from the plot, or calculated to be 4.24 kPa.

Chapter 8. Chemistry of Global Climates

8.1 Composition of the Earth's atmosphere

- In the dry tropics, T=30 ^{0}C, RH=40% could be typical.

Then, P_{H2O} = 0.40 x 4.24 kPa = 1.7 kPa

Then, the mixing ratio of H_2O at P^0 is:

mixing ratio(%)=

Chapter 8. Chemistry of Global Climates

8.2 Energy balance

- Black body radiation

- Emissive energy per unit wavelength of any material with a finite T is given by,

$$M_{\lambda} = \frac{2\pi hc^2}{\lambda^5}\left(\frac{1}{e^{(hc/kT\lambda)} - 1}\right) \qquad (8.1)$$

where M_{λ}=the emissive energy Wm^{-3} (watts per square meter of surface per meter of wavelength), h = Planck's const. = 6.63 x 10^{-34} Js, c = velocity of light=3.0 x 10^{8} m/s; λ=wavelength/m; k=Boltzmann's const.=1.38 x 10^{-23} JK^{-1}, T=temperature/K

- Approximate wavelength

$$\lambda_{max} = \frac{2.88 \times 10^{-3}}{T} \qquad (8.2)$$

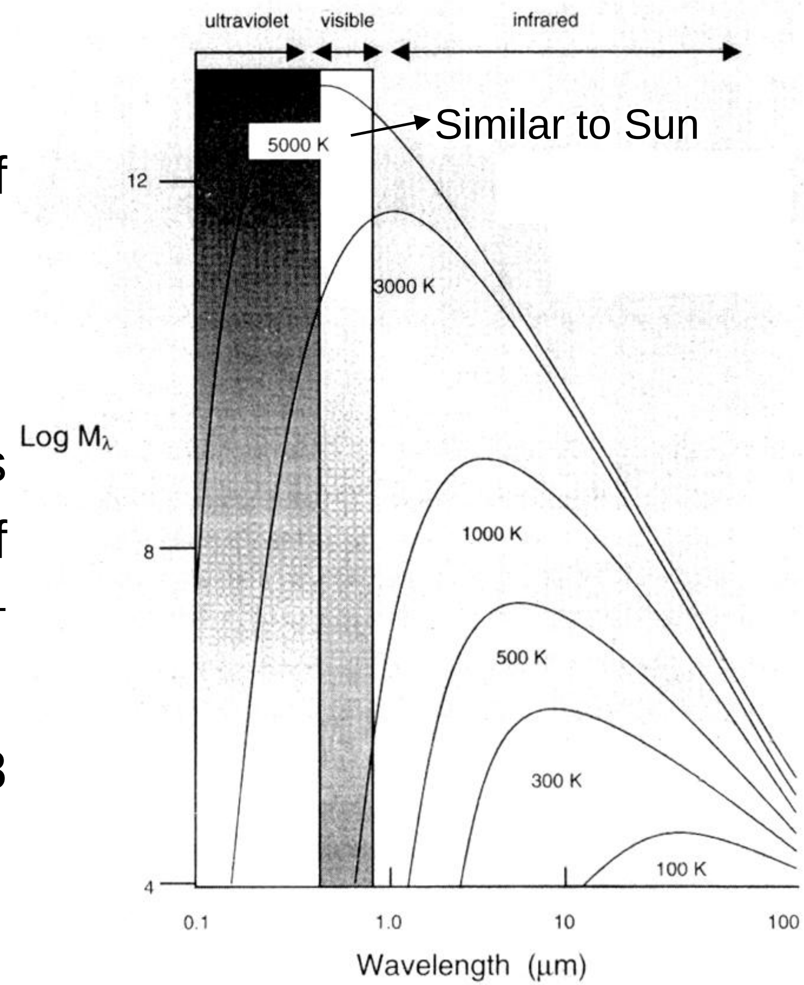

Fig. 8.2 Spectral distribution of a black-body emitter. Units of E_{λ} are W m^{-2} μm^{-1}. (Redrawn from Grum and Becherer, see Note 2.)

Chapter 8. Chemistry of Global Climates

8.2 Energy balance

- Black body radiation

  - Solar flux (F_s): the total energy reaching the part of space occupied by the Earth = avg. 1368 Wm-2, but only a portion of this E can actually be absorbed at the Earth's surface (see Fig. 8.3)

  - Earth's albedo: the total reflectivity of the Earth=

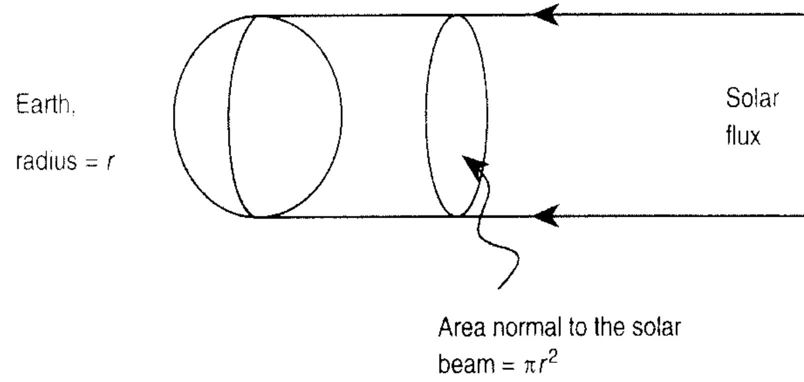

Fig. 8.4 Solar flux (F_s) and the Earth.

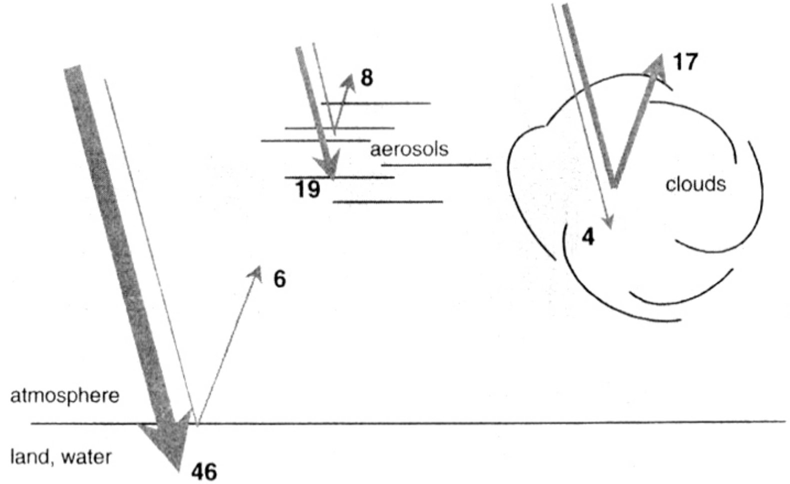

Fig. 8.3 Relative energy flows of solar radiation into the Earth's environment (based on 100 units). Arrows show solar energy that is absorbed or reflected by components of the Earth's environment.

Chapter 8. Chemistry of Global Climates

8.2 Energy balance

- T of the Earth's surface: on the assumption that the re-emitted E from Earth's surface) were completely lost in space,

- the total solar E absorbed by the Earth ($E_{s,}$ in Watt) is given by:

$$E_S = F_S(1-A)\pi r^2$$

- the total emitted energy from the Earth: $F_e = \sigma T_e^4$

(From Wien's law: $F = \sigma T^4$) Here, F_e=radiant flux from the Earth/Wm^{-2}

σ=the Stefan-Boltzmann constant

T_e=effective T of the Earth/K

$$\sigma = \frac{2\pi^5 k^4}{15h^3c^2}$$
$$= 5.67\times10^{-8} / Wm^{-2}K^{-4}$$

- the total radiative E, E_e(in Watt), emitted from the entire area of the Earth's surface is $E_e = 4\pi r^2 \sigma T_e^4$

In the steady state, total E absorbed from the sun (E_s) = total E emitted by the Earth (E_e), I.e.

Chapter 8. Chemistry of Global Climates

8.2 Energy balance

- T of the Earth's surface:

$$T_e = \left(\frac{(1-A)F_S}{4\sigma} \right)^{\frac{1}{4}}$$

$$T_e = \left(\frac{(1-0.31)\times 1368Wm^{-2}}{4\times 5.67\times 10^{-8}Wm^{-2}K^{-4}} \right)^{\frac{1}{4}}$$

$$= 254K$$

$$= -19℃$$

Predicted value

Table 8.2 Temperatures at the surface of three planets; $\Delta = T_{actual} - T_{calculated}$

	Calculated T/K	Actual T/K	Δ/K
Earth	254	290	+36
Mars	217	223	+6
Venus	227	732	+505

Chapter 8. Chemistry of Global Climates

8.3 The greenhouse gases and aerosols: water

- Water vapour:

  -the most important of all greenhouse gases

  -absorbs IR in the ranges 2.5 to 3.5 μm, 5-7 μm, >13 μm

  -portion in greenhouse warming: 110 Wm^{-2}

  -positive contribution:

  -negative contribution:

Chapter 8. Chemistry of Global Climates

8.3 The greenhouse gases and aerosols: CO_2 and CH_4

- CO_2:

-a major contributor to greenhouse warming

-absorbs IR in the ranges 4~4.5 and 14~19 μm, completely blocks b/w 15 and 16 μm

-portion in greenhouse warming: 50 Wm^{-2}

-

- CH_4:

-tropospheric life time = 7 yrs, conc. Is increasing at a rate of 0.5% per year

-absorbs IR in the ranges 3~4 and 7~8.5 μm

-sources:

: from organic matters subjected to an oxygen-depleted highly reducing aqueous or terrestrial environment.

: during extraction and inefficient combustion of fossil fuels

: from the digestive tract of ruminants (cattle, sheep, goats) and termites.

- portion in greenhouse warming: 1.7 Wm^{-2}

Chapter 8. Chemistry of Global Climates

8.3 The greenhouse gases and aerosols: O_3 and N_2O

- O_3:

-absorbs IR in the ranges 9~10 and hence highly effective greenhouse gas

-portion in greenhouse warming: 1.3 Wm^{-2}

- N_2O:

-absorbs IR in the ranges 3~5 and 7.5~9 μm

-sources:

: from industrial processes such as the production of adipic acid and nitric acid

: from microbial denitrification, conversion of nitrate to nitrous oxide, in soils, lakes, and oceans (major source)

: from urban waste landfill sites

-tropospheric residence time = 120 yrs

-portion in greenhouse warming: ca. 1.3 Wm^{-2}

Chapter 8. Chemistry of Global Climates

8.3 The greenhouse gases and aerosols: CFCs and Aerosols

- CFCs and other chlorinated gases:

  -absorbs IR in the ranges 8~12 μm

- Aerosols:

  -clouds have cooling effects on warm days, warming effects on cool nights

  -sulfate aerosols:

  : backscatter incoming short-wave solar radiation,

  : affect the processes of cloud formation

  -biomass aerosols from combustion

  -aerosols of industrial origin

  -These are all readily washed out with precipitation, having small atmospheric residence time, of the order of a few days, so their contribution to greenhouse warming is local and short lived

Chapter 8. Chemistry of Global Climates

8.3 The greenhouse gases and aerosols: summary

Table 8.3 Relative contributions to global warming

Gas	Residence time/y[a]	Relative instantaneous radiative forcing (RIRF)	Global warming potential[c] (GWP)
CO_2	50–200[b]	1	1
CH_4	12	43	21[d]
N_2O	120	250	310[d]
CFC-11	60	15000	3400[e]
CFC-12	195	19000	7100[e]
HCFC-22	12	13000	1600[e]

[a] Most of the atmospheric lifetime values are taken from ref. 1.
[b] Reported residence time values for carbon dioxide are highly variable. Differences are associated with the way in which oceanic uptake is measured, particularly whether the surface layer or the entire ocean is considered in the calculation.
[c] GWP values are obtained by integration over a 100 year period.
[d] GWP values from *CO_2/Climate Report*, Issue 97-1, Environment Canada, Spring 1997.
[e] GWP values from *CO_2/Climate Report*, Special Issue, Environment Canada, 1993. These values relate to direct effects; interactions of CFCs with ozone in the lower stratosphere may reduce the amount of radiation into the lower atmosphere, contributing to a cooling effect. The GWP values would be correspondingly reduced.

$$GWP = \frac{\int_0^t a_i(t)C_i(t)dt}{\int_0^t a_C(t)C_i(t)dt}$$

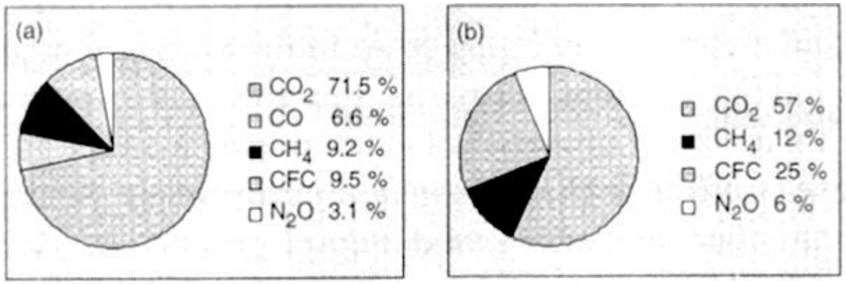

Fig. 8.10 Relative contributions of gases to global warming potential (a) in 1985, and (b) throughout the 1980s. (Reference in Note 5. Reprinted with permission.)

Chapter 8. Chemistry of Global Climates

8.4 Energy resources

Table 8.4 Sources of usable energy

Primary sources	
Solar energy	Used directly or converted into electricity *via* photoelectric cells. Also is the driving force for the water cycle, the ultimate energy source creating fossil fuels, and (through differential heating) causing wind and wave action
Lunar energy	The cause of tides which may be converted to electricity
Geo energy, nuclear energy, geothermal energy	Includes nuclear and geothermal energy. May be used as a source of heat which, in turn, is converted to mechanical or electrical energy
Derived sources	
Fossil fuels	Includes coal, petroleum and natural gas from various sources. These are primary combustion sources used as fuel for engines or to generate heat which is often converted to electricity
Biomass	Includes wood, straw, animal dung, sugar cane, corn, waste paper products, etc. Used as fuels, or converted to other fuels or to electricity
Hydro energy, wind energy, wave energy	Through the Sun's heating action on land and water these forms of energy are developed and the power can be used directly, but is most often converted to electricity
Tidal energy	May be used to generate electricity
Electricity	Always a derived form of energy based on primary sources (solar, nuclear) or on other derived sources (fossils fuels, hydro power, etc.)

Chapter 8. Chemistry of Global Climates

8.4 Energy resources

Table 8.5 Units of energy and equivalents in joules

Energy source	Unit	Abbreviation	Equivalent in joules
Natural gas	Cubic metre	m^3	3.7×10^7
	Cubic foot	ft^3	1×10^6
Petroleum	Barrel	bbl	5.8×10^9
	Tonne	t	3.9×10^{10}
Tar sand oil	Barrel	bbl	6.1×10^9
Shale oil	Tonne	t	4.1×10^{10}
Coal			
Anthracite	Tonne	t or TCE	3.0×10^{10}
Bituminous	Tonne	t or TCE	3.0×10^{10}
Sub-bituminous	Tonne	t or TCE	2.0×10^{10}
Lignite	Tonne	t or TCE	1.5×10^{10}
Charcoal	Tonne	t or TCE	2.8×10^{10}
Biomass (all on a dry weight basis)			
General	Tonne	t	1.5×10^{10}
Miscellaneous farm wastes	Tonne	t	1.4×10^{10}
Animal dung	Tonne	t	1.7×10^{10}
Assorted garbage	Tonne	t	1.2×10^{10}
Wood	Tonne	t	1.5×10^{10}
	Cubic metre	m^3	5×10^9
	Cord	128 ft^3	2×10^{10}

Energy source	Unit	Abbreviation	Equivalent in joules
Fission			
Natural	Tonne	t	8×10^{16}
Complete mass → energy conversion, $E = mc$	Tonne	t	9×10^{19}
Electricity	Kilowatt hour	kwh	3.6×10^6
	Terawatt year	Twy	3.2×10^{19}
General units	Erg	erg	1×10^{-7}
	Calorie	cal	4.18
	British thermal unit	BTU	1.05×10^3
	(10 BTU)	therm	1.05×10^8
	(10 BTU)	quad	1.05×10^{16}
	(10 BTU)	Q	1.05×10^{21}
	Horsepower hour	hp h	2.7×10^6

The data for individual commodities are obtained from several sources and many are estimates. Values for particular materials vary, especially for highly heterogeneous substances and substances with variable moisture content, such as different forms of biomass.

Chapter 8. Chemistry of Global Climates

8.4 Energy resources

Table 8.6 Annual commercial energy consumption in the regions of the world

Region	Energy consumption		Population (millions)	Annual commercial energy consumption per capita
	$EJ\ y^{-1}$	of total		$GJ\ pc\ y^{-1}$
Africa	9.8	3	731	13
Asia Pacific	89	27	3300	27
Mid-East	13	4	160	81
USSR (f)	36	11	293	122
Europe	70	21	507	138
Latin America	13	4	488	27
North America	96	29	295	325
World	327	100	4500	67

1996 energy consumption data from *BP Statistical Review of World Energy*, 1997. The British Petroleum Company p.l.c.; 1997.
USSR (f) refers to the countries that made up the former Soviet Union.

Chapter 8. Chemistry of Global Climates

8.5 Greenhouse gases associated with use of C-based fuel: coal

- Structure and ranks

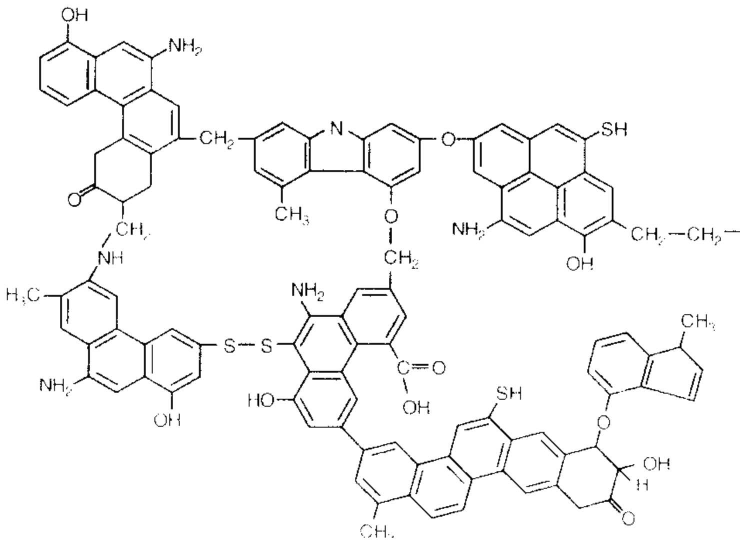

Fig. 8.11 A hypothetical structure of coal. Note the similarities and differences between this structure and that of a hypothetical humate molecule as shown in Fig. 12.3.

Table 8.7 Chemical properties of representative coal types

Coal rank	Lignite	Sub-bituminous	Bituminous	Anthracite
Location	McLean, North Dakota	Sheridan, Wyoming	Muhlenberg, Kentucky	Lackawanna, Pennsylvania
Moisture/%	37	22	9	4
Carbon/%	41	54	65	80
Ash/%	6	4	11	10
Sulfur/%	0.9	0.5	2.8	0.8

US Department of Energy, *Coal Data: Cost and Quality of Fuels*; 1979.
The ranking, from left to right, represents increasing coalification. Ash and sulfur concentrations are independent of the coalification processes.

coal $\mathrm{C+O_2 \rightarrow CO_2} \quad \Delta H = -393.5kJ$

Natural gas $\mathrm{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O} \quad \Delta H = -890.3kJ$

Heavy oil $\mathrm{C_{20}H_{42} + 30\tfrac{1}{2}O_2 \rightarrow 20CO_2 + 21H_2O} \quad \Delta H = -13315.2kJ$

Chapter 8. Chemistry of Global Climates

8.5 Greenhouse gases associated with use of C-based fuel: coal

- coal gasification to enhance efficiency of coal combustion

Table 8.8 Reaction sequences used in coal gasification processs

Process	Reactions used	
Partial gasification	Coal $\xrightarrow{500-700\,^{\circ}C}$ $C + CH_4 + H_2$	Produces a relatively small amount of high energy content gases
Carbon–oxide	$C + O_2 \rightarrow CO_2$ $2C + O_2 \rightarrow 2CO$	The carbon monoxide is a combustible product
Steam–carbon	$C + H_2O \xrightarrow{heat, air} CO + H_2$	The two product gases are both combustible, but are diluted by nitrogen, giving a low energy content fuel
Catalytic methanation	$3H_2O + CO \rightarrow CH_4 + H_2O$	Catalysts such as nickel oxide can enhance conversion of carbon monoxide into ethane, which has a higher energy content

Chapter 8. Chemistry of Global Climates

8.5 Greenhouse gases associated with use of C-based fuel: natural gas

Table 8.9 The principal components of natural gas

Methane (75 to 100%)	Used as an industrial and domestic fuel
Ethane (6 to 10%)	Used as a fuel or as a feedstock for petrochemical plants manufacturing ethylene
Propane and butane (5 to 8%)	Liquefied petroleum gases (LPGs)—used as fuels or as petrochemical feedstocks
Pentane and heavier hydrocarbons (1 to 4%)	Condensate, used as petrochemical feedstock
Nitrogen, carbon dioxide, hydrogen sulfide, helium (variable)	Components other than hydrocarbons