CHAPTER ONE

GENERAL CONCEPTS

The objective of atmospheric chemistry is to understand the factors that control the concentrations of chemical species in the atmosphere. In this chapter we will use three principal measures of atmospheric composition: *mixing ratio*, *number density*, and *partial pressure.*

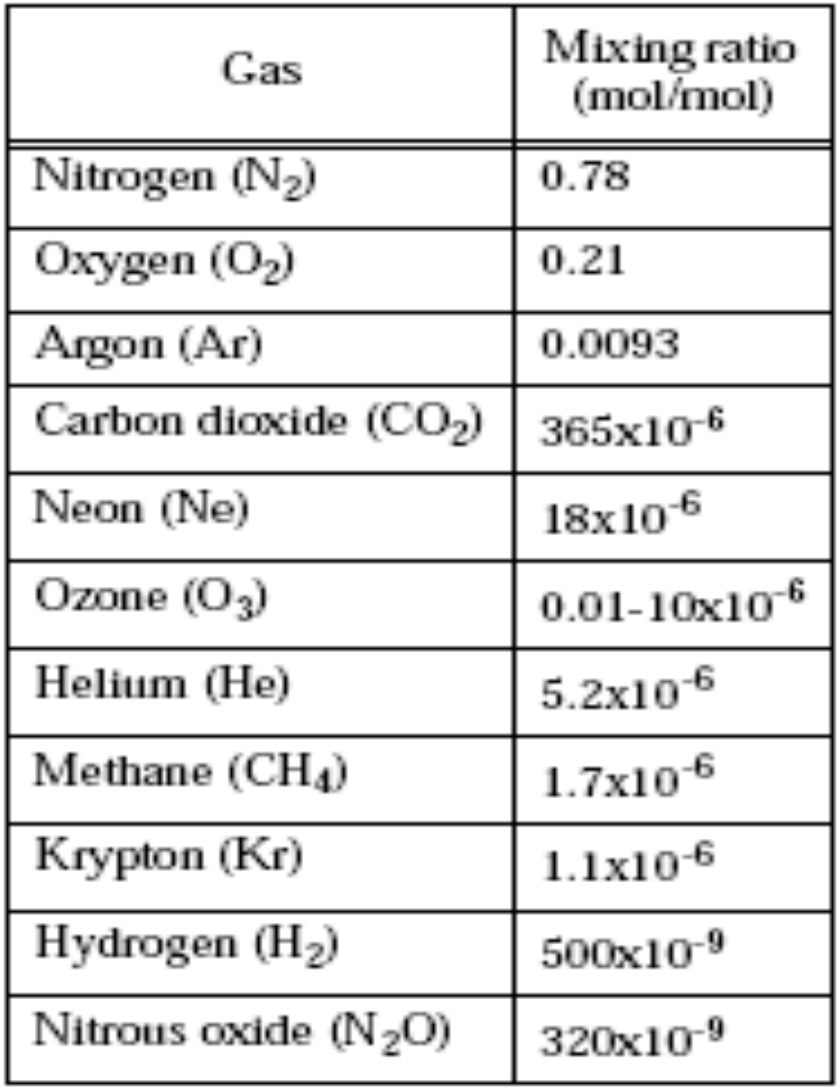
1.1 MIXING RATIO

The *mixing ratio* C_X of a gas X (equivalently called the *mole fraction)* is defined as the number of moles of X (such as gas) per mole of air. It is given in units of mol/mol (abbreviation for moles per mole), or equivalently in units of v/v (volume of gas per volume of air) since the volume occupied by an ideal gas is proportional to the number of molecules.

The mixing ratio of a gas has the virtue of remaining constant when the air density changes (as happens when the temperature or the pressure changes). Consider a balloon filled with room air and allowed to rise in the atmosphere. As the balloon rises it expands, so that the number of molecules per unit volume inside the balloon Decreases; however, the mixing ratios of the different gases in the balloon remain constant. The mixing ratio is therefore a robust measure of atmospheric composition.

Table 1-1 lists the mixing ratios of some major atmospheric gases. The most abundant is molecular nitrogen (N_2) with a mixing ratio $C_{N2} = 0.78$ mol/mol; N_2 accounts for 78% of all molecules in the atmosphere. Next in abundance are molecular oxygen (O_2) with C_{O2} = 0.21 mol/mol, and argon (Ar) with C_{Ar} = 0.0093 mol/mol. The mixing ratios in Table 1-1 are for dry air, excluding water vapor. Water vapor mixing ratios in the atmosphere are highly variable (10^{-6}-10^{-2} mol/mol). This variability in water vapor is part of our everyday experience as it affects the ability of sweat to evaporate and the drying rate of clothes on a line.

Gases other than N_2, O_2, Ar, and H_2O are present in the atmosphere at extremely low concentrations and are called *trace gases*. Despite their low concentrations, these trace gases can be of critical importance for the greenhouse effect, the ozone layer, smog, and other environmental issues. Mixing ratios of trace gases are commonly given in units of ***parts per million*** *volume (ppmv* or simply *ppm),* ***parts per billion volume*** *(ppbv* or *ppb),* or ***parts per trillion volume*** *(pptv* or *ppt);* 1 ppmv = 1×10^{-6} mol/mol, 1 ppbv = 1×10^{-9} mol/mol, and 1 pptv = 1×10^{-12} mol/mol. For example, the present-day CO_2 concentration is 365 ppmv (365×10^{-6} mol/mol).



Gas	Mixing ratio (mol/mol)
Nitrogen (N_2)	0.78
Oxygen (O_2)	0.21
Argon (Ar)	0.0093
Carbon dioxide (CO_2)	365×10^{-6}
Neon (Ne)	18×10^{-6}
Ozone (O_3)	$0.01\text{-}10 \times 10^{-6}$
Helium (He)	5.2×10^{-6}
Methane (CH_4)	1.7×10^{-6}
Krypton (Kr)	1.1×10^{-6}
Hydrogen (H_2)	500×10^{-9}
Nitrous oxide (N_2O)	320×10^{-9}

1.2 NUMBER DENSITY

The *number density* n_X of a gas X is defined ***as the number of molecules of X per unit volume of air***. It is expressed commonly in units of molecules cm^{-3} (number of molecules of X per cm^3 of air).

- ❖ Number densities are critical for calculating gas-phase reaction rates .
- ❖ Another important application of number densities is to measure the absorption or scattering of a light beam by an optically active gas. The degree of absorption or scattering depends on the number of molecules of gas along the path of the beam and therefore on the number density of the gas. Consider in Figure 1-1 the atmosphere as extending from the Earth's surface ($z = 0$) up to a certain top ($z = z_T$) above which number densities are assumed negligibly small. Consider in this atmosphere an optically active gas X. A slab of unit horizontal surface area and vertical thickness dz contains $n_X dz$ molecules of X. The integral over the depth of the atmosphere defines the *atmospheric column* of X as

$$column = \int_0^{z_T} n_x dz \text{ . … … … … … … … (1.2)}$$

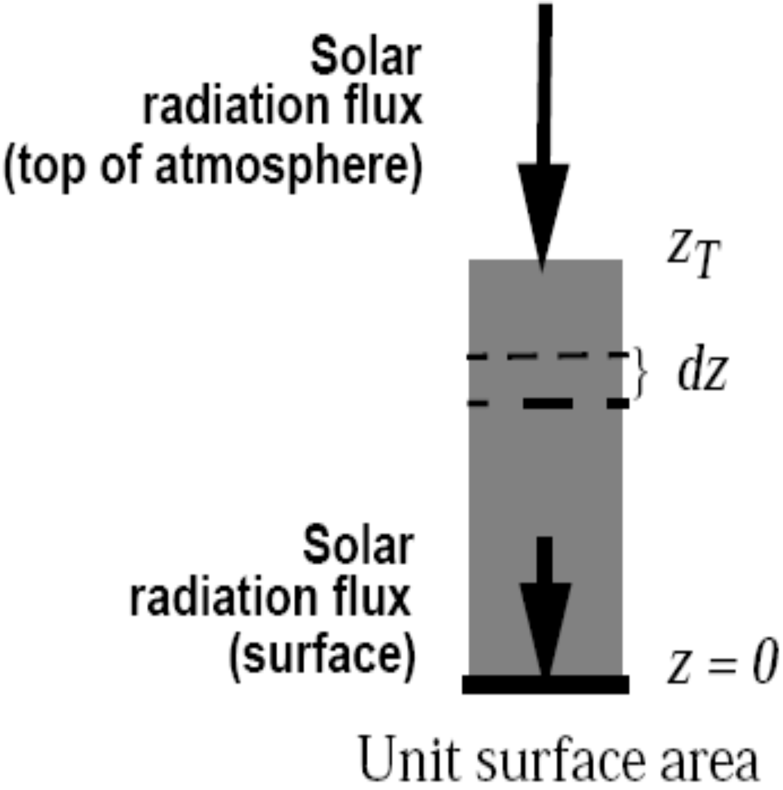


Figure 1-1 Absorption of radiation by an atmospheric column of gas.

This atmospheric column determines the total efficiency with which the gas absorbs or scatters light passing through the atmosphere. For example, the efficiency with which the ozone layer prevents harmful solar UV radiation from reaching the Earth's surface is determined by the atmospheric column of ozone.

The number density and the mixing ratio of a gas are related by the number density of air n_a (molecules of air per cm^3 of air):

$$n_X = C_X n_a \quad (1.3)$$

The number density of air is in turn related to the atmospheric pressure P by the ideal gas law. Consider a volume V of atmosphere at pressure P and temperature T containing N moles of air. The ideal gas law gives

$$PV = NRT \quad (1.4)$$

where R = 8.31 J mol^{-1} K^{-1} is the gas constant. The number density of air is related to N and V by

$$n_a = \frac{A_v N}{V} \qquad (1.5)$$

Where Av = 6.023x10^{23} molecules mol^{-1} is Avogadro's number. Substituting equation *(1.5)* into *(1.4)* we obtain:

$$n_a = \frac{A_v P}{RT} \qquad (1.6)$$

and hence

$$n_X = \frac{A_v P}{RT} C_X \qquad (1.7)$$

We see from *(1.7)* that n_X is not conserved when P or T changes. A related measure of concentration is the *mass concentration* ρ_X, representing the mass of X per unit volume of air (we will also use ρ_X to denote the *mass density* of a body, i.e., its mass per unit volume; the proper definition should be clear from the context). ρ_X and n_X are related by the molecular weight M_X (kg mol^{-1}) of the gas:

$$\rho_X = \frac{n_X M_X}{A_v} \qquad (1.8)$$

The mean molecular weight of air M_a is obtained by averaging the contributions from all its constituents i:

$$M_a = \sum_i C_i M_i \qquad (1.9)$$

and can be approximated (for dry air) from the molecular weights
of N_2, O_2, and Ar:

$$
\begin{aligned}
M_a &= C_{N2}M_{N2} + C_{O2}M_{O2} + C_{Ar}M_{Ar} \\
&= (0.78 \cdot 28\text{x}10^{-3}) + (0.21 \cdot 32\text{x}10^{-3}) + (0.01 \cdot 40\text{x}10^{-3}) \qquad (1.10) \\
&= 28.96\text{x}10^{-3} \text{ kg mol}^{-1}
\end{aligned}
$$

In addition to gases, the atmosphere also contains solid or liquid particles suspended in the gaseous medium. These particles represent the atmospheric *aerosol*; "aerosol" is a general term describing a dispersed condensed phase suspended in a gas. Atmospheric aerosol particles are typically between 0.01 and 10 mm in diameter (smaller particles grow rapidly by condensation while larger particles fall out rapidly under their own weight). General measures of aerosol abundances are the *number concentration* (number of particles per unit volume of air) and the *mass concentration* (mass of particles per unit volume of air).

Examples 1.1

Calculate the number densities of air and CO_2 at sea level for P=1013 hpa , T=0°C.

***Answer*:**

Apply *(1.6)* to obtain the number density of air n_a. Use International System (SI) units at all times in numerical calculations to ensure consistency:

$$n_a = \frac{A_v P}{RT} = \frac{(6.023x10^{23}) \cdot (1.013x10^{5})}{8.31 \cdot 273} = 2.69x10^{25} \text{ molecules m}^{-3}$$

After you obtain the result for n_a in SI units, you can convert it to the more commonly used unit of molecules cm^{-3}: $n_a = 2.69x10^{19}$ molecules cm^{-3}. The air density at sea level does not vary much around the world; the sea-level pressure varies by at most 5%, and the temperature rarely departs by more than 15% from 273 K, so that n_a remains within 25% of the value calculated here.

The number density of CO_2 is derived from the mixing ratio $C_{CO2} = 365$ ppmv:

$$n_{CO2} = C_{CO2} n_a = 365x10^{-6} x2.69x10^{25} = 9.8x10^{21} \text{ molecules m}^{-3}$$

Exercise (1-2)

In surface air over the tropical oceans the mixing ratio of water vapor can be as high as 0.03 mol/mol. What is the molecular weight of this moist air?

Answer:

The molecular weight M_a of moist air is given by

$$M_a = (1 - C_{H2O})M_{a,\,dry} + C_{H2O}M_{H2O}$$

Where $M_{a\,,dry}$ =28.96x10^{-3} kg mol^{-1} is the molecular weight of dry air derived in *(1.10)*, and M_{H2O} = 18x10^{-3} kg mol^{-1}. For C_{H2O} = 0.03 mol/mol we obtain M_a =28.63*10^{-3} kg/mol . A mole of moist air is lighter than a mole of dry air.

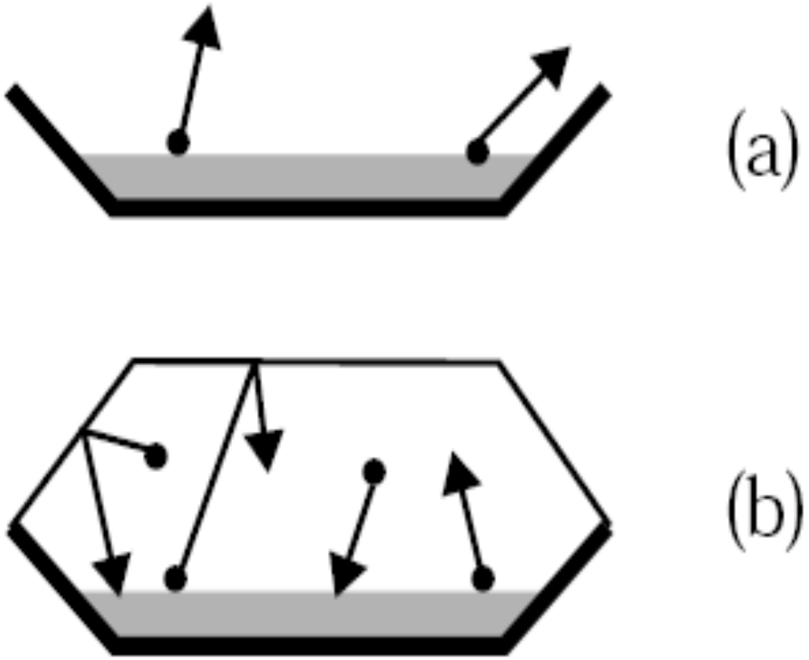
1.3 PARTIAL PRESSURE

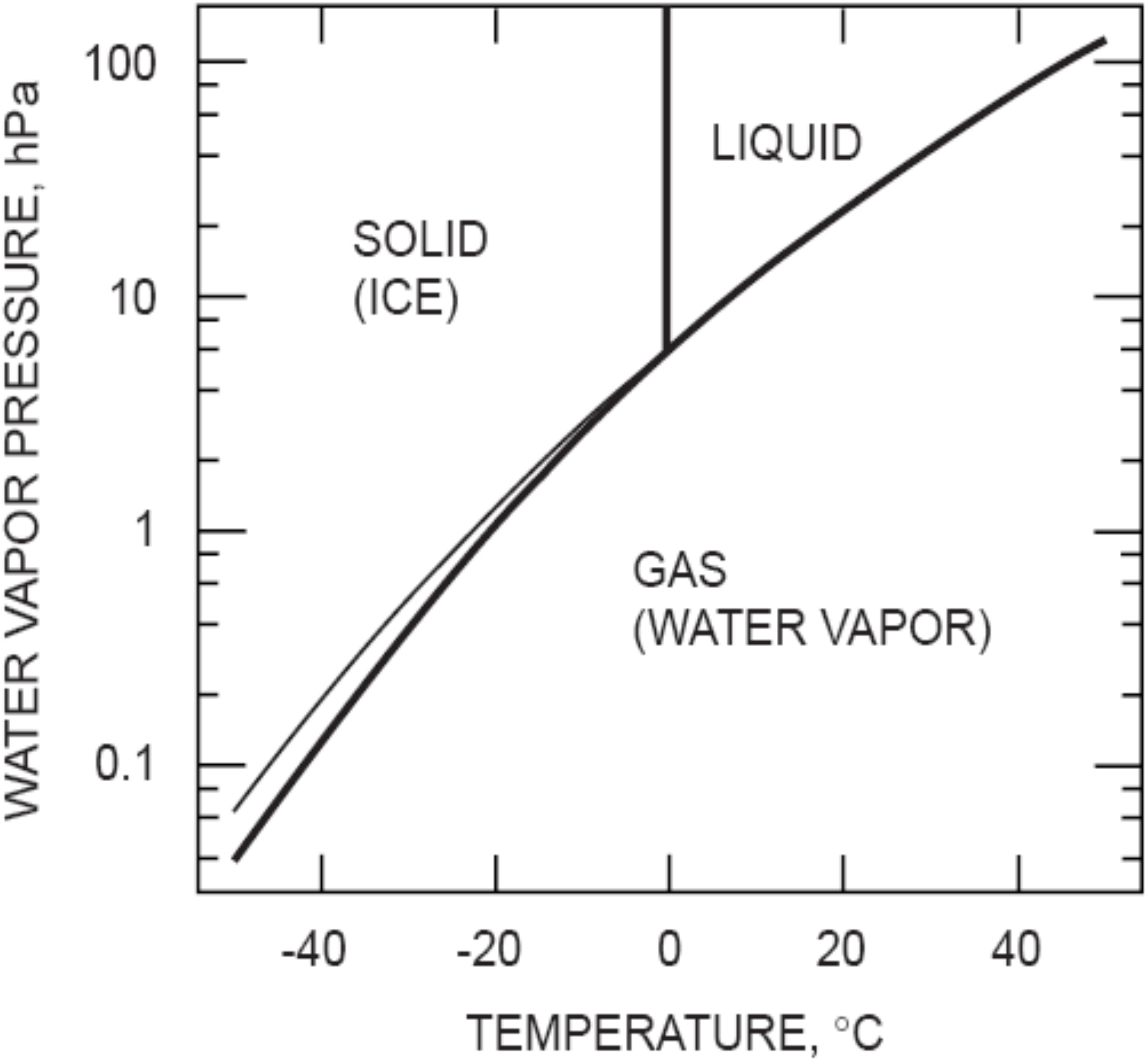
The partial pressure P_X of a gas X In a mixture of gases of total pressure *P* is defined as the pressure that would be exerted by the molecules of X if all the other gases were removed from the mixture. Dalton's law states that P_X is related to *P* by the mixing ratio C_X :

$$P_X = C_X\, P \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\,(1.11)$$

For our applications, *P* is the total atmospheric pressure. Similarly to *(1.6)*, we use the ideal gas law to relate P_X to n_X :

$$P_X = \frac{n_X}{A_v}\, R\, T \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1.12)$$


(a)
(b)


100
10
1
0.1
WATER VAPOR PRESSURE, hPa
LIQUID
SOLID
(ICE)
GAS
(WATER VAPOR)
-40
-20
0
20
40
TEMPERATURE, °C

CHAPTER TWO

GEOCHEMICAL CYCLES

2.1 GEOCHEMICAL CYCLING OF ELEMENTS

From an Earth system perspective, however, the composition of the atmosphere is ultimately controlled by the exchange of elements between the different reservoirs of the Earth. In the present chapter we examine atmospheric composition from this broader perspective, and focus more specifically on the biogeochemical factors that regulate the atmospheric abundances of N_2, O_2, and CO_2.

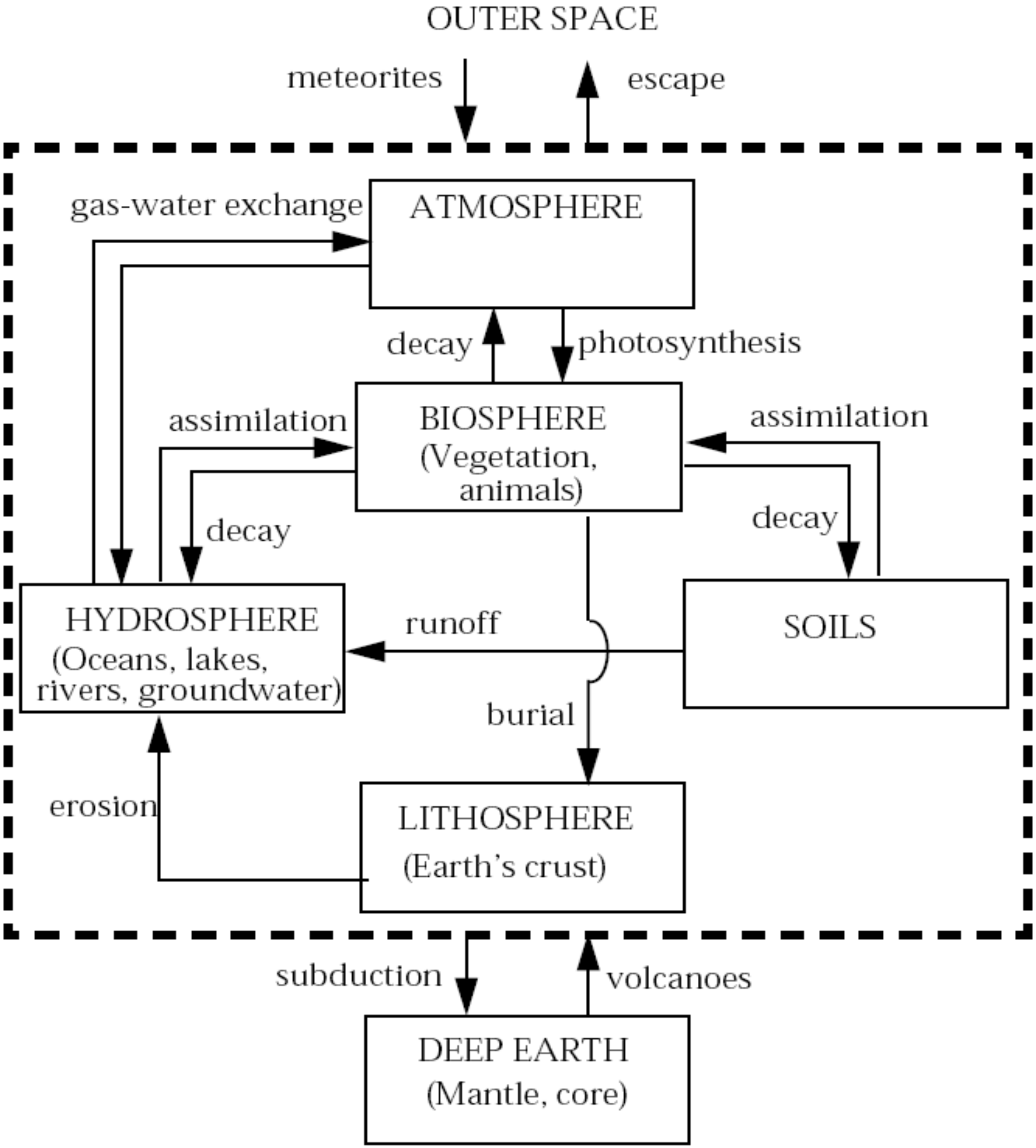
The Earth system (including the Earth and its atmosphere) is an assemblage of atoms of the 92 natural elements. Almost all of these atoms have been present in the Earth system since the formation of the Earth 4.5 billion years ago by gravitational accretion of a cloud of gases and dust. Subsequent inputs of material from extraterrestrial sources such as meteorites have been relatively unimportant. Escape of atoms to outer space is prevented by gravity except for the lightest atoms (H, He), and even for those it is extremely slow (home work). Thus the assemblage of atoms composing the Earth system has been roughly conserved since the origin of the Earth. The atoms, in the form of various molecules, migrate continually between the different reservoirs of the Earth system (Figure 2-1). *Geochemical cycling* refers to the flow of elements through the Earth's reservoirs; the term underlines the cyclical nature of the flow in a closed system.

The standard approach to describing the geochemical cycling of elements between the Earth's reservoirs is with the box models that we introduced in next chapters. The reservoirs may be those shown in Figure 2-1 or some other ensemble. Depending on the problem at hand, one may want a more detailed categorization (for example, separating the hydrosphere into oceans and freshwater), or a less detailed categorization (for example, combining the biosphere and soil reservoirs).

Most of the mass of the Earth system is present in the deep Earth, but this material is largely isolated from the *surface reservoirs*: atmosphere, hydrosphere, biosphere, soil, and lithosphere (Figure 2-1). Communication between the deep Earth and the surface reservoirs takes place by volcanism and by subduction of tectonic plates, processes that are extremely slow compared to those cycling elements between the surface reservoirs. The abundance of an element in the atmosphere can therefore be viewed as determined by two separable factors:

(a) the total abundance of the element in the ensemble of surface reservoirs.

(b) the partitioning of the element between the atmosphere and the other surface reservoirs.



OUTER SPACE

meteorites

escape

gas-water exchange

ATMOSPHERE

decay

photosynthesis

assimilation

BIOSPHERE
(Vegetation,
animals)

assimilation

decay

decay

HYDROSPHERE
(Oceans, lakes,
rivers, groundwater)

runoff

SOILS

burial

erosion

LITHOSPHERE
(Earth's crust)

subduction

volcanoes

DEEP EARTH
(Mantle, core)

HOME WORK

1- Helium (He, atomic weight 4 g mol^{-1}) and argon (Ar, atomic weight 40 g mol^{-1}) are both produced in the Earth's interior and exhaled to the atmosphere. Helium is produced by radioactive decay of uranium and thorium; argon is produced by radioactive decay of potassium-40 (^{40}K). Both helium and argon, being noble gases, are chemically and biologically inert and are negligibly soluble in the ocean. Present-day atmospheric mixing ratios of helium and argon are 5.2 ppmv and 9340 ppmv, respectively.

1. Atmospheric argon has no sink and has therefore gradually accumulated since Earth's formation 4.5x10^{9} years ago. In contrast, atmospheric helium has a sink. What is it?

2. Show that the average source of argon to the atmosphere over Earth's history is P_{Ar} = 1.5x10^{7} kg yr^{-1}.

3. Potassium-40 has no sources in the Earth's interior and decays radioactively with a rate constant k = 5.5x10^{-10} yr^{-1}. Hence the source of argon has decreased gradually since Earth's formation. Let $P_{Ar}(\Delta t)$ represent the present-day source of argon, where Δt = 4.5x10^{9} years is the age of the Earth. Show that

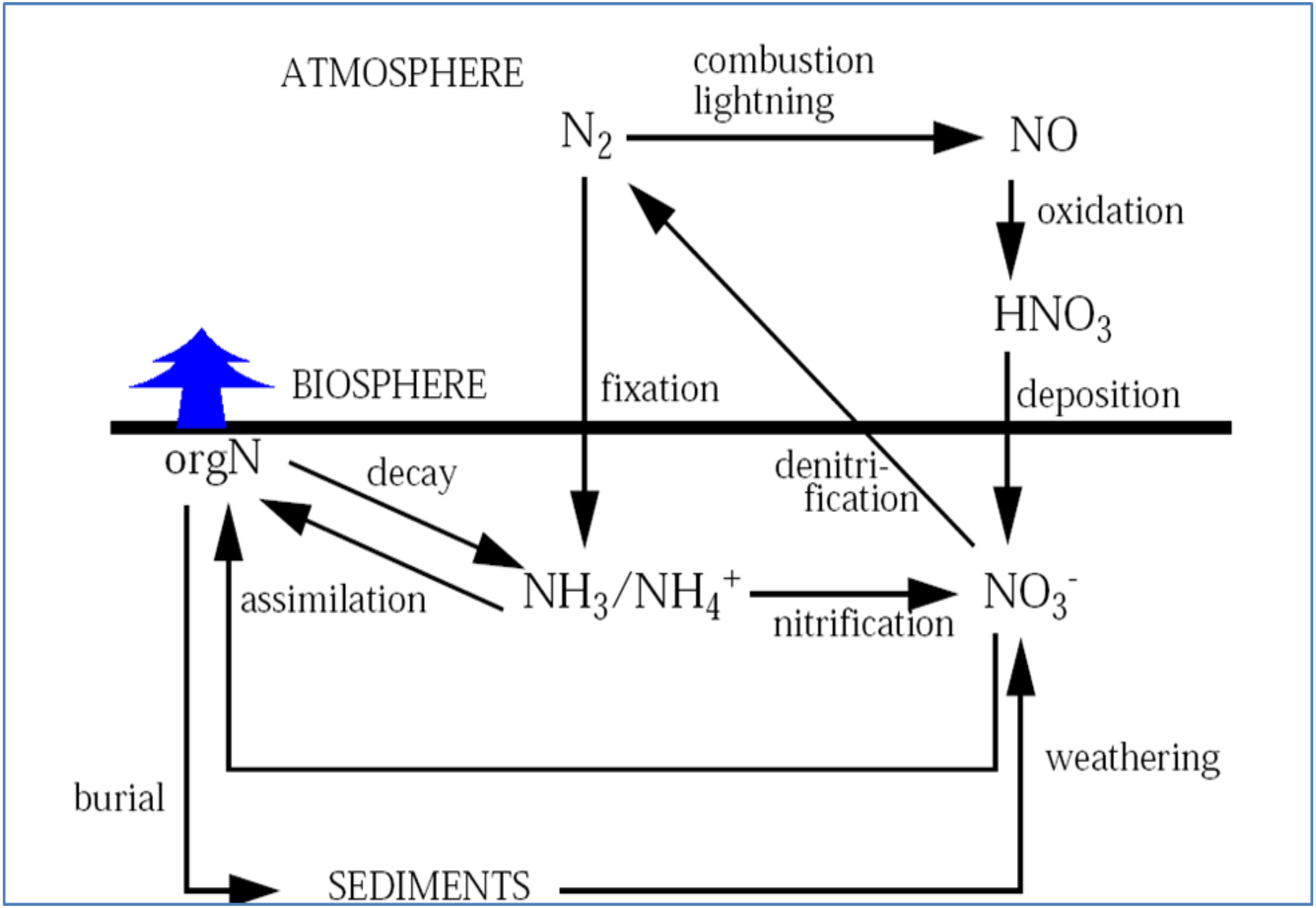
$$\frac{P_{Ar}(\Delta t)}{\bar{P}_{Ar}} = \frac{k\Delta t}{\exp(k\Delta t) - 1} = 0.23$$

4. Observations in geothermal and bedrock gases show that the present-day sources of atmospheric helium and argon (kg yr^{-1}) are of the same magnitude: $P_{Ar}(\Delta t) \approx P_{He}(\Delta t)$. Deduce the residence time of helium in the atmosphere.

2.2 The Nitrogen Cycle

Nitrogen (as N_2) accounts for 78% of air on a molar basis. Figure 2-1 presents a summary of major processes involved in the cycling of nitrogen between surface reservoirs. Nitrogen is an essential component of the biosphere (think of the **amino acids**) and the atmosphere is an obvious source for this nitrogen. Conversion of the highly stable N_2 molecule to biologically available nitrogen, a process called ***fixation***, is difficult. It is achieved in ecosystems by specialized symbiotic bacteria which can reduce atmospheric N_2 to ammonia (NH_3). The NH_3 is assimilated as organic nitrogen by the bacteria or by their host plants, which may in turn be consumed by animals. Eventually these organisms excrete the nitrogen or die; the organic nitrogen is eaten by bacteria and mineralized to ammonium (NH_4+), which may then be assimilated by other organisms.

Bacteria may also use NH^{4+} as a source of energy by oxidizing it to nitrite (NO_2^-) and on to nitrate (NO_3^-). This process is called ***nitrification*** and requires the presence of oxygen (aerobic conditions). Nitrate is highly mobile in soil and is readily assimilated by plant and bacteria, providing another route for formation of organic nitrogen.


ATMOSPHERE
combustion
lightning
N_2
NO
oxidation
HNO_3
BIOSPHERE
fixation
deposition
orgN
decay
denitri-
fication
assimilation
NH_3/NH_4^+
nitrification
NO_3^-
weathering
burial
SEDIMENTS

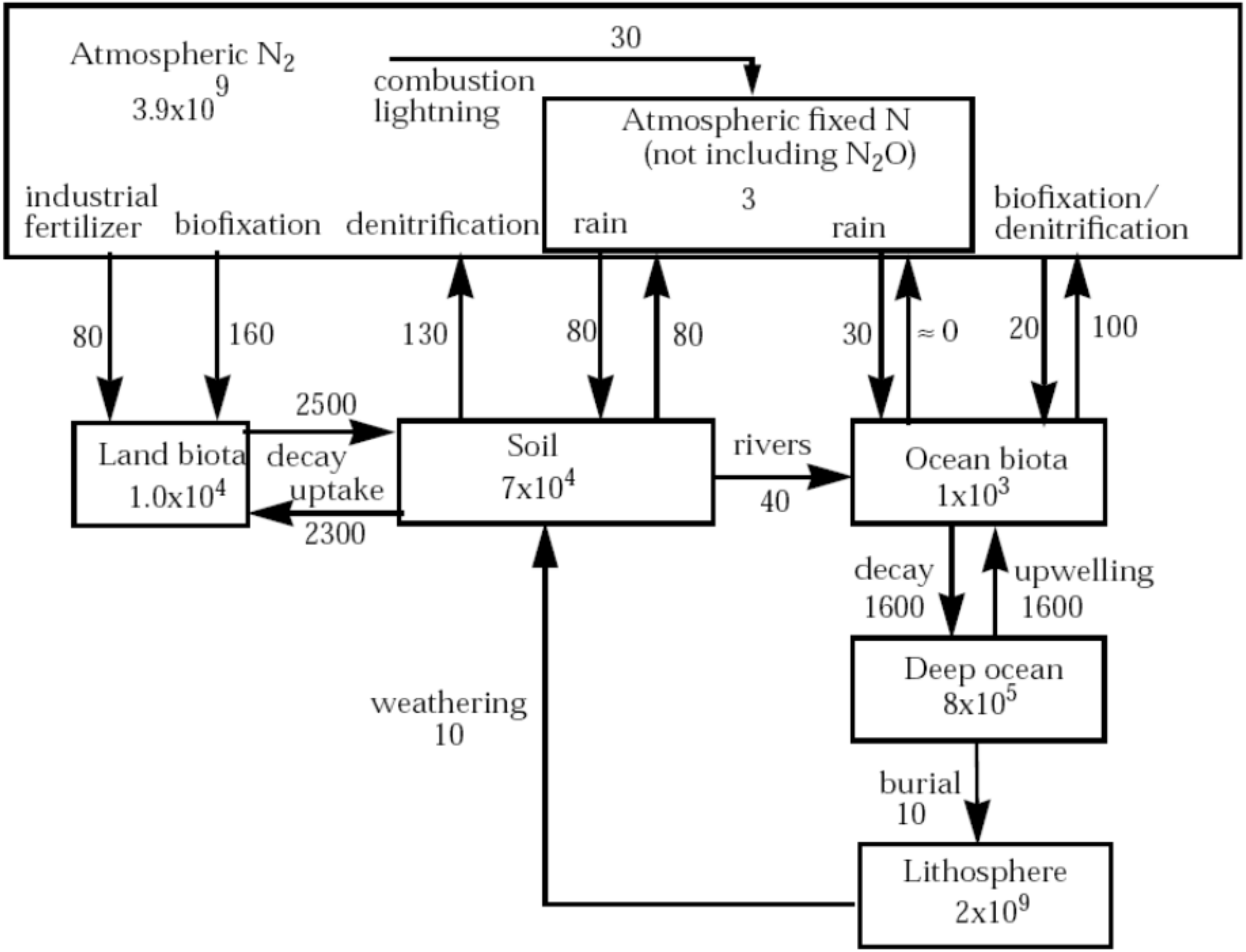
Under conditions when O_2 is depleted in water or soil (anaerobic conditions), bacteria may use NO_3^- as an alternate oxidant to convert organic carbon to CO_2. This process, called ***denitrification***, converts NO_3^- to N_2 and thus returns nitrogen from the biosphere to the atmosphere.

An additional pathway for fixing atmospheric N_2 is by high-temperature oxidation of N_2 to NO in the atmosphere during combustion or lightning, followed by atmospheric oxidation of NO to HNO_3 which is water-soluble and scavenged by rain. In industrial regions of the world, the fixation of N_2 in combustion engines provides a source of nitrogen to the biosphere that is much larger than natural N_2 fixation, resulting in an unintentional *fertilization* effect.

Transfer of nitrogen to the lithosphere takes place by burial of dead organisms (including their nitrogen) in the bottom of the ocean. These dead organisms are then incorporated into sedimentary rock.

Eventually the sedimentary rock is brought up to the surface of the continents and eroded, liberating the nitrogen and allowing its return to the biosphere. This process closes the nitrogen cycle in the surface reservoirs.

What about the possibility of depleting atmospheric N_2 by transferring the nitrogen to the other surface reservoirs? Imagine a scenario where denitrification were to shut off while N_2 fixation still operated. Under this scenario, atmospheric N_2 would be eventually depleted by uptake of nitrogen by the biosphere, transfer of this nitrogen to soils, and eventual runoff to the ocean where the nitrogen could accumulate as NO_3^-. The time scale over which such depletion could conceivably take place is defined by the lifetime of N_2 against fixation. With the numbers in Figure 6-3, we find a lifetime of $3.9x10^9/(80+160+30+20) = 13$ million years. In view of this long lifetime, we can safely conclude that human activity will never affect atmospheric N_2 levels significantly. On a geological time scale, however, we see that denitrification is critical for maintaining atmospheric N_2 even though it might seem a costly loss of an essential nutrient by the biosphere. If N_2 were depleted from the atmosphere, thus shutting off nitrogen fixation, life on Earth outside of the oceans would be greatly restricted.



Atmospheric N_2
3.9×10^9

combustion
lightning
30

Atmospheric fixed N
(not including N_2O)
3

industrial fertilizer 80

biofixation 160

denitrification 130

rain 80

80

rain 30

≈ 0

biofixation/
denitrification

20

100

Land biota
1.0×10^4

decay 2500

uptake 2300

Soil
7×10^4

rivers 40

Ocean biota
1×10^3

decay 1600

upwelling 1600

Deep ocean
8×10^5

burial 10

Lithosphere
2×10^9

weathering 10

2.2 THE OXYGEN CYCLE

Atmospheric oxygen is produced by photosynthesis, which we represent as:

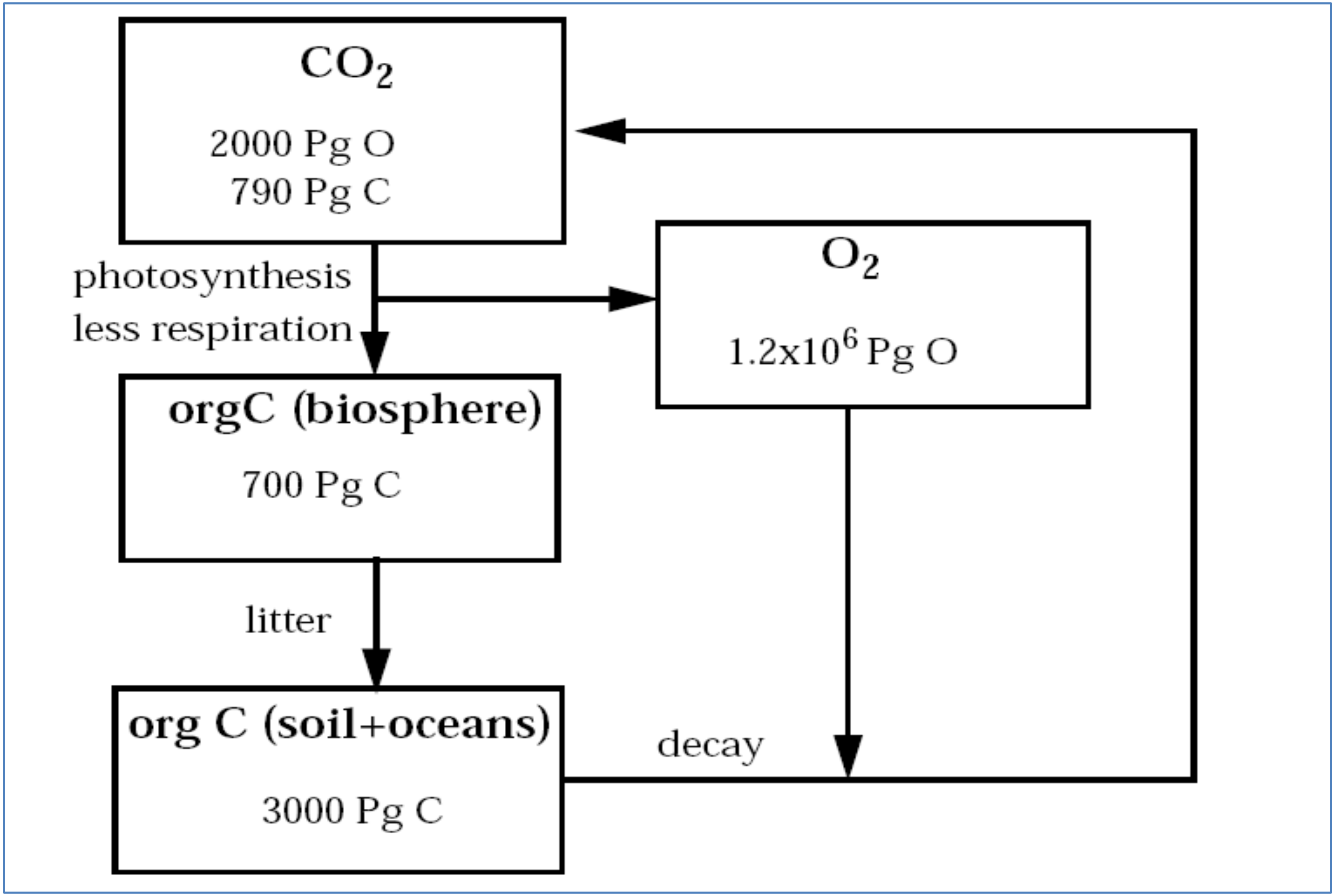
$$nCO_2 + nH_2O \rightarrow (CH_2O)_n + nO_2 \dots\dots\dots\dots\dots\dots\dots (2.1)$$

Where $(CH_2O)_n$ is a stoichiometric approximation for the composition of biomass material? This source of O_2 is balanced by loss of O_2 from the oxidation of biomass, including respiration by living biomass and microbial decay of dead biomass:

$$(CH_2O)_n + nO_2 \rightarrow nCO_2 + nH_2O \dots\dots\dots\dots\dots\dots\dots (2.2)$$

The cycling of oxygen by reactions *(2.1)* and *(2.2)* is coupled to that of carbon, as illustrated in Figure 2-2 .

To assess the potential for this cycle to regulate atmospheric O_2 levels, we need to determine inventories for the different reservoirs of Figure 2-4 : O_2, CO_2, and orgC. Applying equation *(2.1)* to O_2 and CO_2 with $C_{O2} = 0.21$ v/v and $C_{CO2} = 365 \times 10^{-6}$ v/v (See Mixing ratios of gases in dry air), we obtain $mO_2 = 1.2 \times 10^6$ Pg O and $mCO_2 =$ 2000 PgO = 790 PgC (*1 petagram (Pg) = 1×10^{15} g*).



CO_2

2000 Pg O
790 Pg C

photosynthesis
less respiration

O_2

$1.2x10^6$ Pg O

orgC (biosphere)

700 Pg C

litter

org C (soil+oceans)

3000 Pg C

decay

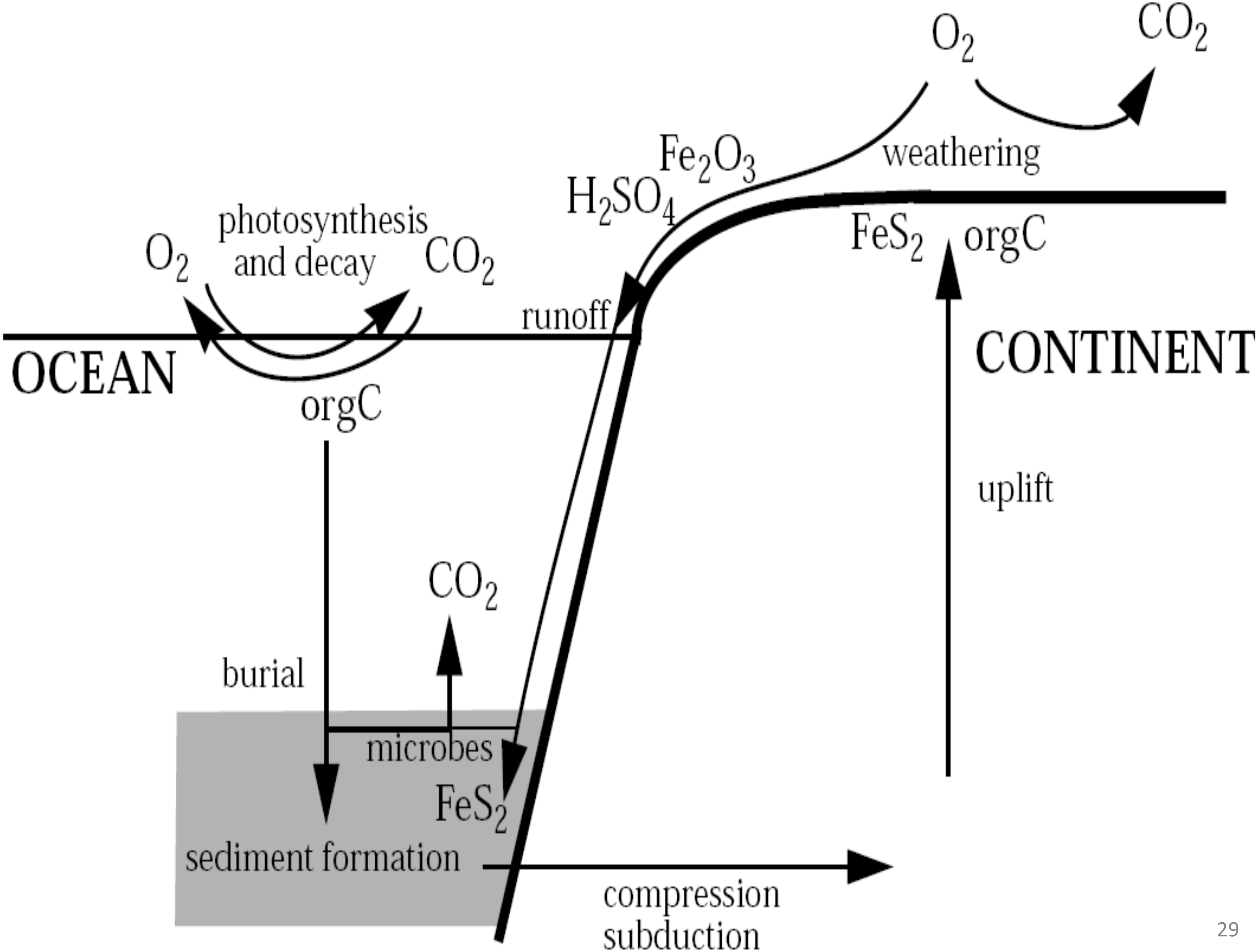
The total amount of organic carbon in the biosphere/soil/ocean system is estimated to be about 4000 PgC (700 Pg C in the terrestrial biosphere, 2000 Pg C in soil, and 1000 Pg C in the oceans).Simple comparison of these inventories tells us that cycling with the biosphere cannot control the abundance of O_2 in the atmosphere, because the inventory of O_2 is considerably larger than that of either CO_2 or organic carbon. If photosynthesis were for some reason to stop, oxidation of the entire organic carbon reservoir would consume less than 1% of O_2 presently in the atmosphere and there would be no further O_2 loss (since there would be no organic carbon left to be oxidized). Conversely, if respiration and decay were to stop, conversion of all atmospheric CO_2 to O_2 by photosynthesis would increase O_2 levels by only 0.2%.

What, then, controls atmospheric oxygen? The next place to look is the lithosphere. Rock material brought to the surface in a reduced state is weathered (oxidized) by atmospheric O_2. Of most importance is sedimentary organic carbon, which gets oxidized to CO_2, and FeS2 (pyrite), which gets oxidized to Fe_2O_3 and H_2SO_4. The total amounts of organic carbon and pyrite in sedimentary rocks are estimated to be $1.2x10^7$ Pg C and $5x10^6$ Pg S, respectively.

These amounts are sufficiently large that weathering of rocks would eventually deplete atmospheric O_2 if not compensated by an oxygen source. The turnover time of sedimentary rock, that is the time required for sedimentary rock formed at the bottom of the ocean to be brought up to the surface, is of the order of 100 million years. The corresponding weathering rates are 0.12 Pg C yr^{-1} for rock organic carbon and 0.05 Pg S yr^{-1} for pyrite. Each atom of carbon consumes one O_2 molecule, while each atom of sulfur as FeS_2 consumes 19/8 O_2 molecules. The resulting loss of O_2 is 0.4 Pg O yr^{-1}, which yields a lifetime for O_2 of 3 million years. On a time scale of several million years, changes in the rate of sediment uplift could conceivably alter the levels of O_2 in the atmosphere.

This cycling of O_2 with the lithosphere is illustrated in Figure 2-5. Atmospheric O_2 is produced during the formation of reduced sedimentary material, and the consumption of O_2 by weathering when this sediment is eventually brought up to the surface and oxidized balances the O_2 source from sediment formation.

Fossil records show that atmospheric O_2 levels have in fact not changed significantly over the past 400 million years, a time scale much longer than the lifetime of O_2 against loss by weathering. The constancy of atmospheric O_2 suggests that there must be stabilizing factors in the O_2-lithosphere cycle but these are still poorly understood. One stabilizing factor is the relative rate of oxidation vs. burial of organic carbon in the ocean. If sediment weathering were to increase for some reason, drawing down atmospheric O_2, then more of the marine organic carbon would be buried (because of slower oxidation), which would increase the source of O_2 and act as a negative feedback.


O_2
CO_2
weathering
Fe_2O_3
H_2SO_4
photosynthesis
and decay
O_2
CO_2
FeS_2
orgC
runoff
OCEAN
CONTINENT
orgC
uplift
CO_2
burial
microbes
FeS_2
sediment formation
compression
subduction

Exercise

The present-day sediments contain 1.2x10^7 *Pg C of organic carbon. How much* O_2 *was produced in the formation of these sediments? Compare to the amount of* O_2 *presently in the atmosphere. How do you explain the difference?*

Answer : One molecule of O_2 is produced for each organic C atom incorporated in the sediments. Therefore, formation of the present-day sediments was associated with the production of $(32/12)\text{x}1.2\text{x}10^7 = 3.2\text{x}10^7$ Pg O_2. That is 30 times more than the $1.2\text{x}10^6$ Pg O_2 presently in the atmosphere! Where did the rest of the oxygen go? Examination of Figure 2-3 indicates as possible reservoirs SO_4^{2-} and Fe_2O_3. Indeed, global inventories show that these reservoirs can account for the missing oxygen.

2.3 THE CARBON CYCLE

Ice core measurements show that atmospheric concentrations of CO_2 have increased from 280 ppmv in pre-industrial times to 365 ppmv today. Continuous atmospheric measurements made since 1958 at Mauna Loa Observatory in Hawaii demonstrate the secular increase of CO_2 (Figure 2-4). Superimposed on the secular trend is a seasonal oscillation (winter maximum, summer minimum) that reflects the uptake of CO_2 by vegetation during the growing season, balanced by the net release of CO_2 from the biosphere in fall due to microbial decay. The current global rate of increase of atmospheric CO_2 is 1.8 ppmv yr^{-1}, corresponding to 4.0 Pg C yr^{-1}. This increase is due mostly to fossil fuel combustion.

When fuel is burned, almost all of the carbon in the fuel is oxidized to CO_2 and emitted to the atmosphere. We can use worldwide fuel use statistics to estimate the corresponding CO_2 emission, presently 6.0±0.5 Pg C yr^{-1}. Another significant source of CO_2 is deforestation in the tropics; based on rates of agricultural encroachment documented by satellite observations, it is estimated that this source amounts to 1.6 ±1.0 Pg C yr^{-1}. Substituting the above numbers in a global mass balance equation for atmospheric CO_2,

$$\frac{dm_{CO2}}{dt} = \sum \text{sources} - \sum \text{sinks}$$

We find $\sum$ sinks = 6.0 + 1.6 - 4.0 = 3.6 Pg C yr^{-1}. Only half of the CO_2 emitted by fossil fuel combustion and deforestation actually accumulates in the atmosphere. The other half is transferred to other geochemical reservoirs (oceans, biosphere, and soils). We need to understand the factors controlling these sinks in order to predict future trends in atmospheric CO_2 and assess their implications for climate change. A sink to the biosphere would mean that fossil fuel CO_2 has a fertilizing effect, with possibly important ecological consequences.

Cycling of atmospheric CO_2 with the biosphere involves processes of photosynthesis, respiration, and microbial decay, as illustrated in Figure 2-2 . It is difficult to distinguish experimentally between photosynthesis and respiration by plants, nor is this distinction very useful for our purpose. Ecologists define the ***net primary productivity (NPP)*** as the yearly average rate of photosynthesis minus the rate of respiration by all plants in an ecosystem. The ***NPP*** can be determined experimentally either by long-term measurement of the CO_2 flux to the ecosystem from a tower or more crudely by monitoring the growth of vegetation in a selected plot. From these data, quantitative models can be developed that express the dependence of the ***NPP*** on environmental variables including ecosystem type, solar radiation, temperature, and water availability. Using such models one estimates a global terrestrial ***NPP*** of about 60 Pg C yr^{-1}.

The lifetime of CO_2 against net uptake by terrestrial plants is:

$$\tau_{CO2} = \frac{m_{CO2}}{NPP} = 9 \text{ years}$$

Which implies that atmospheric CO_2 responds quickly, on a time scale of a decade, to changes in ***NPP*** or in decay rates. It is now thought that increased ***NPP*** at middle and high latitudes of the northern hemisphere over the past century may be responsible for the 20% missing sink of CO_2 emitted by fossil fuel combustion (See Sinks of atmospheric CO_2 deduced from changes in atmospheric O_2). Part of this increase in ***NPP*** could be due to conversion of agricultural land to forest at northern midlatitudes, and part could be due to greater photosynthetic activity of boreal forests as a result of climate warming. The organic carbon added to the biosphere by the increased ***NPP*** would then accumulate in the soil. An unresolved issue is the degree to which fossil fuel CO_2 fertilizes the biosphere. Experiments done in chambers and outdoors under controlled conditions show that increasing CO_2 does stimulate plant growth. There are however other factors limiting ***NPP***, including solar radiation and the supply of water and nutrients, which prevent a first-order dependence of ***NPP*** on CO_2.

CHAPTER THREE

CHEMICAL KINETICS

3.1 Rate Expressions for Gas-Phase Reactions

3.1.1 Bimolecular reactions

A *bimolecular* reaction involves the Collision of two reactants A and B to yield two products C and D. The collision produces an *activated complex* AB* which decomposes rapidly either to the original reactants A and B or to the products C and D. The reaction is written

$$A + B \rightarrow C + D \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(R1)$$

And its rate is calculated as

$$-\frac{d}{dt}[A] = -\frac{d}{dt}[B] = \frac{d}{dt}[C] = \frac{d}{dt}[D] = k[A][B] \ldots\ldots\ldots\ldots\ldots.(1)$$

Where k is the *rate constant* for the reaction. In this expression the concentrations [ ] are number densities so that the product [A] [B] is proportional to the frequency of collisions. The rate of the reaction depends on the frequency of collisions and on the fate of the activated complex. Typically k is given in units of cm^3 molecule^{-1}s^{-1}, in which case [A] and [B] must be in units of molecules cm^{-3}.

A special case of bimolecular reaction is the *self-reaction*:

$$A + A \rightarrow C + D \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (R2)$$

For which the rate expression is

$$-\frac{1}{2}\frac{d}{dt}\,[A] = \frac{d}{dt}\,[C\,] = \frac{d}{dt}[\,D] = k\,[A]^2 \ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

3.1.2 Three-body reactions:

A *three-body* reaction involves reaction of two species A and B to yield one single product species AB. This reaction requires a *third body* M to stabilize the excited product AB* by collision:

$$A + A \rightarrow AB^{*} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots . \dots . \dots \dots (R3)$$

$$AB^{*} \rightarrow A + B \dots \dots \dots \dots \dots \dots \dots \dots \dots . \dots . \dots \dots \dots (R4)$$

$$AB^{*} + M \rightarrow AB + M^{*} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots . (R5)$$

$$M^{*} \rightarrow M + Heat \dots \dots \dots \dots \dots \dots \dots \dots \dots . \dots \dots \dots . . (R6)$$

The third body M is any inert molecule (in the atmosphere, generally N_2 and O_2) that can remove the excess energy from AB* and eventually dissipate it as heat. Common practice is to write the overall reaction as

$$A + B + M \rightarrow AB + M \quad \dots \dots \dots \dots \dots \dots \dots \dots . . (R7)$$

To emphasize the need for a third body. The rate of a three-body reaction is defined as the formation rate of AB by reaction *(R5)*:

$$\frac{d\,[\,A\,B]}{dt} = k_5[\,A\,B^*]\,[M\,] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The excited complex AB* has a very short lifetime and reacts as soon as it is produced. We may therefore assume that it is in steady state at all times:

$$k_3\,[A\,][B\,] = k_4\,[A\,B^*\,] + k_5[\,A\,B^*\,][M\,] \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Rearranging and replacing into (3):

$$-\frac{d}{dt}\,[A] = -\frac{d}{dt}\,[B\,] = \frac{d[AB]}{dt} = \frac{k_3\,k_5\,[A][B][M]}{k_4 + k_5[M]} \ldots\ldots\ldots\ldots\ldots (5)$$

where the equality between production of AB on the one hand, and losses of A and B on the other hand, follows from the steady state assumption for AB*. In the atmosphere, [M] is simply the number density of air n_a.

Equation (5) is the general rate expression for a three-body reaction (a more detailed analysis would include a small correction factor). There are two interesting limits. In the low-density limit [M] << k_4/k_5 (called the *low-pressure limit), Equation* (5) simplifies to

$$-\frac{d}{dt}\,[A] = -\frac{d}{dt}\,[B\,] = \frac{d[AB]}{dt} = \frac{k3\;k5}{k_4}\,[A][B][M] \ldots\ldots\ldots\ldots(6)$$

So that the rate of the overall reaction depends linearly on [M]. One refers to $k_o = k_3k_5/k_4$ as the low-pressure limit rate constant. In the high-density limit [M] >> k_4/k_5 *(*called the *high-pressure limit)*, *(5)* simplifies to

$$-\frac{d}{dt}\,[A] = -\frac{d}{dt}\,[B\,] = \frac{d[AB]}{dt} = k_3[A][B] \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Which means that the rate of AB production is limited by production of AB* and is independent of [M]; M is sufficiently abundant to ensure that all AB* complexes produced stabilize to AB. The rate constant of a three-body reaction is sometimes given as one of the two limits; you can tell from the units of *k* (cm^6 molecule^{-2} s^{-1} for the low-pressure limit, cm^3 molecule^{-1} s^{-1} for the high-pressure limit) and you should then assume that the appropriate limit holds.

3.2 REVERSE REACTIONS AND CHEMICAL EQUILIBRIA

Reactions are reversible. If we can write

$$A + B \rightarrow C + D \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (R8)$$

Then simply from mass conservation we can also write

$$C + D \rightarrow A + B \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (R9)$$

The reverse reaction may however be extremely slow. If we wish to emphasize the reversible nature of a reaction then we need to write it as a two-way reaction,

$$A + B \leftrightarrow C + D \ldots\ldots\ldots\ldots\ldots\ldots\ldots (R10)$$

Eventually, steady state is reached between the forward and reverse reactions:

$$k_8\,[A][B] = k_9\,[C][D] \ldots\ldots\ldots\ldots\ldots\ldots\ldots. (9)$$

From which we define equilibrium constant K_{10} for the two-way reaction *(R_{10})*:

$$k_{10} = \frac{k_8}{k_9} = \frac{[C][D]}{[A][B]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

The equilibrium constant is a thermodynamic quantity and depends only on the free energies of molecules A, B, C, and D.

3.3 PHOTOLYSIS

A photolysis reaction involves the breaking of a chemical bond in a Molecule by an incident photon. The reaction is written:

$$X + hv \rightarrow Y + Z \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(R11)$$

And the rate of reaction is calculated as

$$-\frac{d}{dt}[X] = \frac{d}{dt}[Y\,] = \frac{d[Z]}{dt} = k\,[X] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(11)$$

Where k (units of s^{-1}) is a photolysis rate constant or photolysis frequency. Consider an elemental slab of air of vertical thickness *dz* and unit horizontal area. The slab contains [X]*dz molecules* of X (where [X] is a number density). A photon incident on a molecule of X has a probability σ_X/A of being absorbed, where *A* is the cross-sectional area of the molecule and σ_X is the absorption cross-section (units of cm^2 $molecule^{-1}$) which defines the absorption characteristics of X. The molecules of X in the elemental slab absorb a fraction $\sigma_X[X]dz$ of the incoming photons. We define the actinic flux I as the number of photons crossing the unit horizontal area per unit time from any direction (photons cm^{-2} s^{-1}) and the quantum yield q_X (units of molecules photon^{-1}) as the probability that absorption of a photon will cause photolysis of the molecule X. The number of molecules of X photolysis per unit time in the slab is $q_x\, \sigma_X [X] I dz$. To obtain the photolysis rate constant k, we divide by the number $[X]dz$ of molecules of X in the slab:

$$k = q_X\, \sigma_X\, I \quad \dots\dots\dots\dots\dots\dots\dots.\dots\dots.\dots\dots\dots (12)$$

Absorption cross-sections and quantum yields vary with wavelength. For polychromatic radiation, as in the atmosphere, equation (12) must be integrated over the wavelength spectrum:

$$k = \int_{\lambda} (\lambda) \sigma_X (\lambda) \quad I_\lambda d\lambda \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots.. (13)$$

Where I_λ is the actinic flux distribution function defined in the same way as the flux distribution function Φ_λ. The difference between the actinic flux I_λ and the radiation flux fl is that the former measures the number of photons crossing the unit horizontal surface from any direction, while the latter measures the photon energy flow perpendicular to the surface.

9.4 RADICAL-ASSISTED REACTION CHAINS:

Gases in the atmosphere are present at low concentrations - considerably lower than the concentrations generally used in laboratory experiments or in industrial processes. As a result, collisions between molecules are relatively infrequent. With few exceptions, the only reactions between molecules that proceed at appreciable rates in the atmosphere are those involving at least one *radical* species. Radicals are defined as chemical species with an unpaired electron in the outer (*valence*) shell. Because of this unpaired electron, radicals have high free energies and are much more reactive than non-radical species whose electrons are all paired up. You can electrons; an odd number identifies a radical and an even number a non-radical. For example NO is a radical (7+8 = 15 electrons), while HNO_3 is a non-radical (1+7+(3x)8 = 32 electrons). An important exception to this rule is atomic oxygen, which has 8 electrons but *two* unpaired valence shell electrons in its "triplet" O(3*P*) ground state ($2s^2 2p_x^2 2p_y^{\,1} 2p_z^{\,1}$) and is therefore a radical (or more exactly a *biradical*). Atomic oxygen with all electrons paired ($2s^2 2p_x^{\,2} 2p_y^2$) Is in a higher-energy "singlet" O(1*D*) state and is actually even more reactive than O(^3P).

Because radicals have high free energies, their formation from non-radical species is in general endothermic; an external source of energy is required. In the atmosphere, this source of energy is supplied by solar radiation:

$$nonradical + hv \ \rightarrow radical + radical \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (R12)$$

Generation of radicals by reaction *(R12)* provides the *initiation step* for radical reaction chains which are *propagated* by subsequent reactions of radicals with non-radical species:

$$radical + nonradical \ \rightarrow radical + nonradical \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(R13)$$

Note that reaction of a radical with a non-radical must always produce a radical in order to conserve the total odd number of electrons. The radical produced in *(R13)* goes on to react with another non-radical, propagating the chain, and in this manner a large number of non-radicals can be processed through the chain. During the propagation cycle, a non-radical species produced by a reaction of type *(R13)* may photolyze following *(R12)* to produce additional radicals; the photolysis is called a *branching reaction* as it accelerates (or "branches") the chain by augmenting the pool of radicals.

Termination of the chain requires reactions taking place between radicals:

$$radical + radical + M \rightarrow \ nonradical \ + \ M \ldots\ldots\ldots\ldots\ldots..R14$$
$$nonradical \ + \ hn \ \rightarrow \ radical \ + \ radical \ldots\ldots\ldots\ldots\ldots.\ldots..R15$$

Termination reactions are generally slower than propagation reactions because radicals are present at low concentrations and collisions between radicals are therefore relatively infrequent. In subsequent chapters we will encounter many types of radical-assisted chains following the general schematic *(R12)*-*(R15)*.

Due to the critical importance of solar radiation in initiating radical-assisted chain mechanisms in the atmosphere, these mechanisms are often referred to as *photochemical*.

CHAPTER FOUR
STRATOSPHERIC OZONE

The stratospheric ozone layer, centered at about 20 km above thesurface of the Earth (Figure 4-1), protects life on Earth byabsorbing UV radiation from the Sun. In this chapter we examinethe mechanisms controlling the abundance of ozone in thestratosphere and the effect of human influence.

4.1 CHAPMAN MECHANISM

The presence of a high-altitude ozone layer in the atmosphere was first determined in the 1920s from observations of the solar UV spectrum. A theory for the origin of this ozone layer was proposed in 1930 by a British scientist, Sydney Chapman, and is known as the ***Chapman mechanism***. It lays the foundation for current understanding of stratospheric ozone.

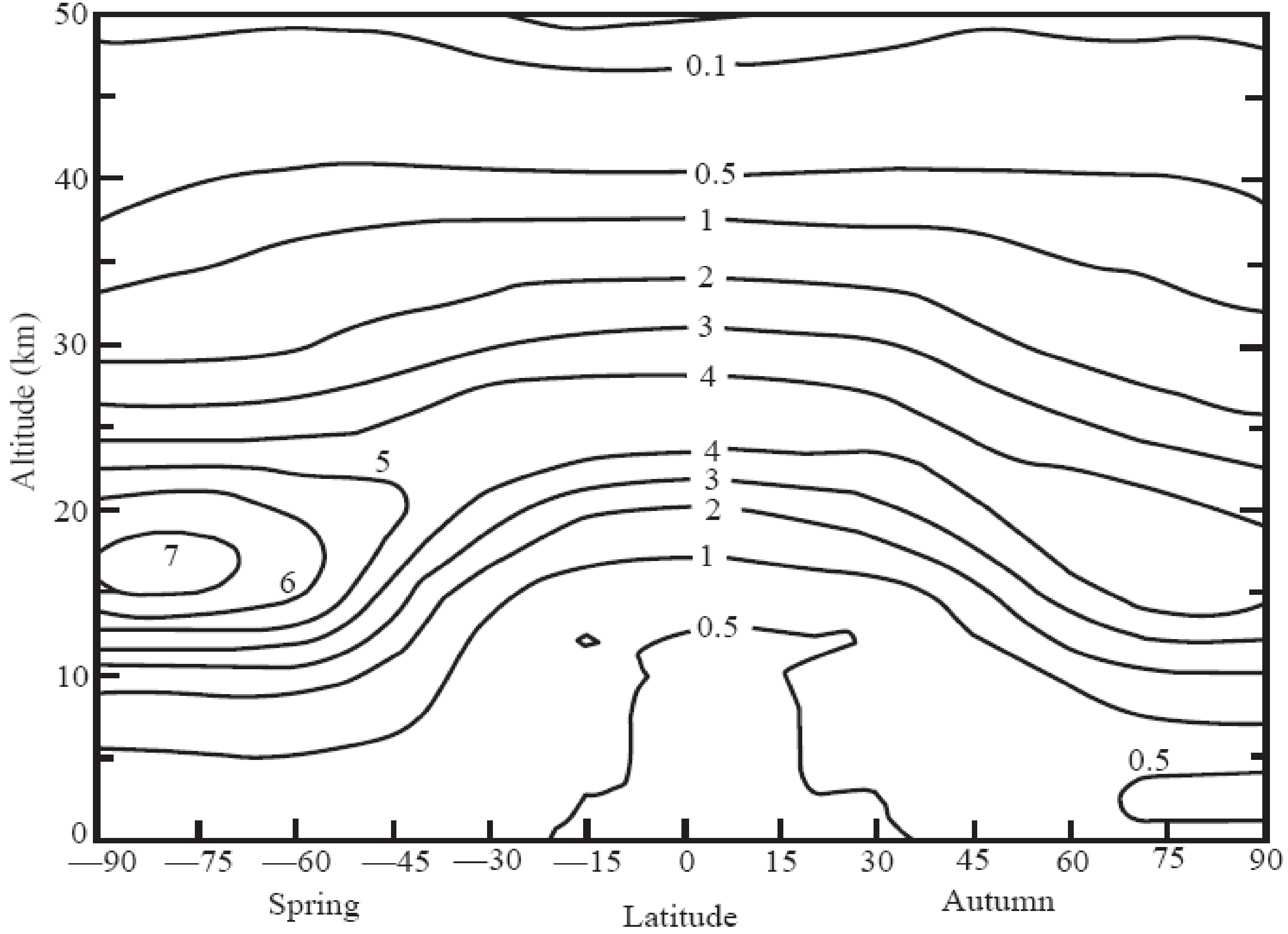


Figure 4-1 The natural ozone layer: vertical and latitudinal distribution of the ozone number density (10^{12} molecules cm^{-3}) at the equinox, based on measurements taken in the 1960s.

4.1.1 THE MECHANISM

Chapman proposed that the ozone layer originates from the photolysis of atmospheric O_2. The bond energy of the O_2 molecule (498 kJ mol^{-1}) corresponds to the energy of a 240 nm UV photon;only photons of wavelengths less than 240 nm can photolysis the O_2molecule. Such high-energy photons are present in the solarspectrum at high altitude (Figure 4-2). Photolysis of O_2 yields twoO atoms:

$$O_2 + hv \rightarrow O + O \qquad (\lambda < 240\,nm) \ldots\ldots\ldots\ldots\ldots\ldots..(R1)$$

Where the O atoms are in the ground-level triplet state $O(^3P)$ and are highly reactive due to their two unpaired electrons. They combine rapidly with O_2 to form ozone:

$$O + O_2 + M \rightarrow O_3 + M \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(R2)$$

Where M is a third body,theO_3 molecules produced in reaction *(R2)* go on to photolysis.Because the bonds in theO_3molecule are weaker than those in the

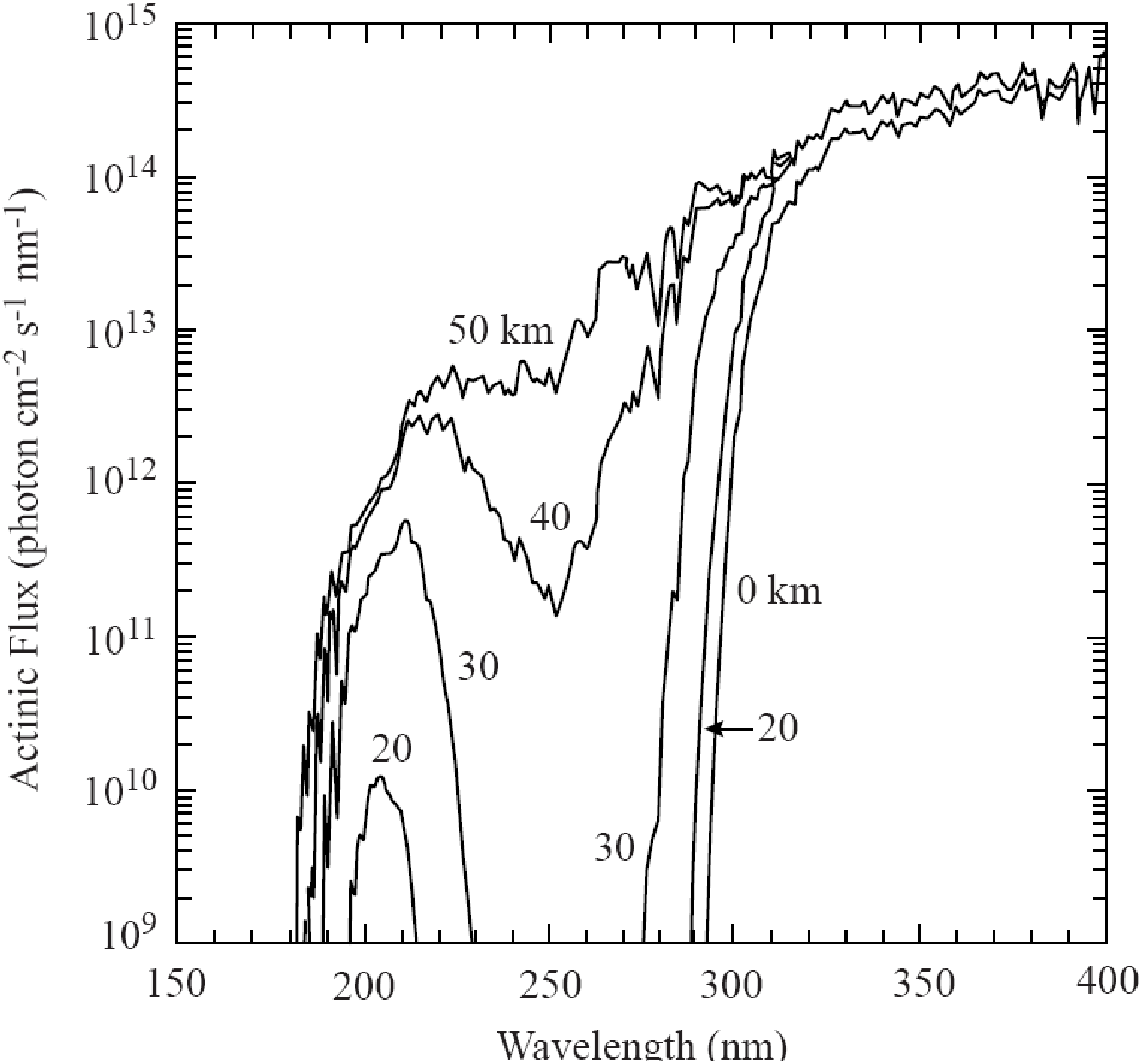


Figure 4-2 Solar actinic flux at different altitudes, for typical atmospheric Conditions and a 30^o solar zenith angle.

O_2 molecule, photolysis is achieved with lower-energy photons:

$$O_3 + hv \rightarrow O_2 + O\left({}^1D\right)(l < 320\,nm)$$
$$O({}^1D) + M \rightarrow O + M$$
$$Net: \quad O_3 + hv \rightarrow O_2 + O \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (R3)$$

Where $O(^1D)$ is the O atom in an excited singlet state and is rapidly stabilized to $O(^3P)$ by collision with N_2 or O_2. Note that *(R3)* is not a terminal sink for O_3 since the O atom product may recombine with O_2 by *(R2)* to regenerate O_3. For O_3 to actually be lost the O atom must undergo another reaction, which in the Chapman mechanism is

$$O_3 + O \rightarrow 2O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . R4$$

4.1.2 STEADY-STATE SOLUTION:

A schematic for the Chapman mechanism is shown in Figure 4-3.Rate constants for reactions *(R1)*-*(R4)* have been measured in thelaboratory. Reactions *(R2)* and *(R3)* are found to be much fasterthan reactions *(R1)* and *(R4)*, as might be expected from ourdiscussion above. We thus have a rapid cycle between O and O_3 byreactions *(R2)* and *(R3)*, and a slower cycle between O_2 and ($O+O_3$)by *(R1)* and *(R4)*. Because of the rapid cycling between O and O_3 itis convenient to refer to the sum of the two as a *chemical family*, oddoxygen ($O_x \equiv O_3 + O$), which is produced by *(R_1)* and consumed by*(R4)*.

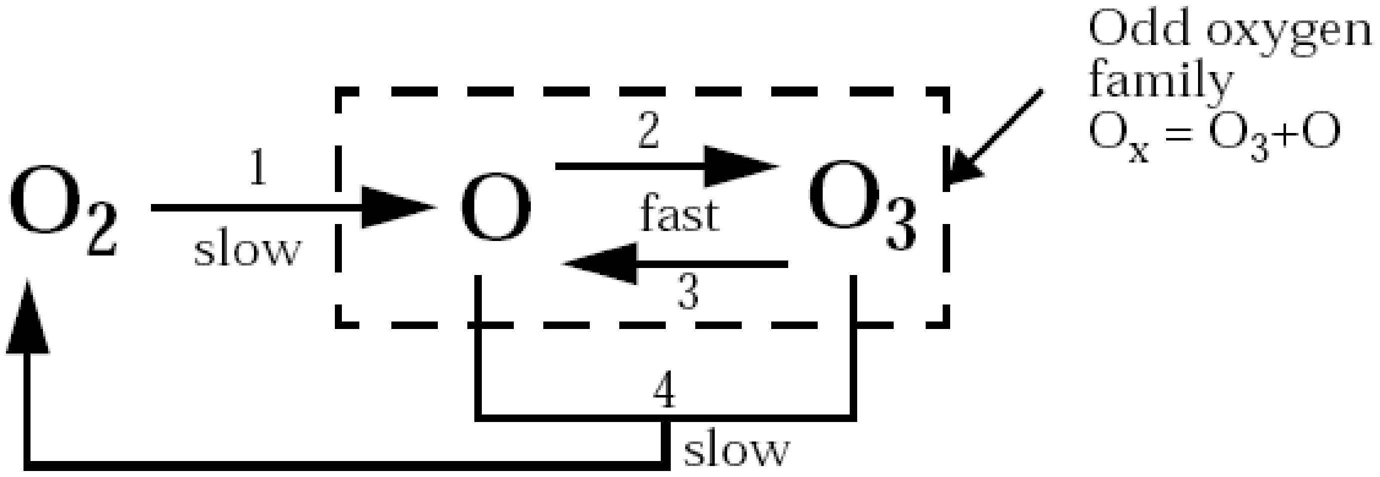


Figure 4-3 The Chapman mechanism

Simple relationships between O_2, O, and O_3 concentrations can bederived from a chemical steady-state analysis of the Chapmanmechanism. As we saw in previews sections chemical steady state canbe assumed for a species if its production and loss rates remainroughly constant over its lifetime. We **first** examine if

chemicalsteady state is applicable to the shortest-lived species in Figure4-3, the O atom. The lifetime τ_0 of the O atom against conversionto O_3 by *(R2)* is

$$\tau_0 = \frac{[O]}{k_2[O][O_2][\,M]} = \frac{1}{k_2[O_2][\,M]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(4.1)$$

Wherewe have used the low-pressure limit in the rate expressionfor *(R2)*, as is appropriate for atmospheric conditions. In equation*(4.1)*, [M] is the air number density n_a, and $[O_2] = C_{O2}.na$ where C_{O2}= 0.21 mol/mol is the mixing ratio of O_2. Thus:

$$\tau_O = \frac{1}{k_2 C_{O2} n_a} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4.2)$$

All terms on the right-hand side of *(4.2)* are known. Substitutingnumerical values one finds that τ_o in the stratosphere is of theorder of seconds or less. Production and loss ratesofthe O atom depend on the meteorological environment(pressure, temperature, and radiation) and on the O_3 abundance,neither of which vary significantly over a time scale of seconds. Wecan therefore assume chemical steady state for O atoms betweenproduction by *(R3)* and loss by *(R2)*, neglecting reactions *(R1)* and*(R4)* which are much slower:

$$k_2[O][O_2][M] = k_3[O_3] \dots\dots\dots\dots\dots\dots\dots\dots\dots.. (4.3)$$

Rearrangement of *(4.3)* yields

$$\frac{[O]}{[O_3]} = \frac{k_3}{k_2 C_{O2} {n_a}^2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. (4.4)$$

Substituting numerical values one finds $[O]/[O_3] << 1$ throughoutthe stratosphere . Observed concentrations (Figure4.4)obey closely this steady state.An important result of our steady-state analysis for the O atom isthat O_3 is the main component of the O_x family: $[O_x] = [O_3] + [O] \approx [O_3]$. This result has two implications:

The concentration of O_3 is controlled by the slow production and loss of O_x from reactions *(R1)* and *(R4)* rather than by the fast production and loss of O_3 from reactions *(R2)* and *(R3)*.

The effective lifetime of O_3 against chemical loss is defined by the lifetime of Ox.

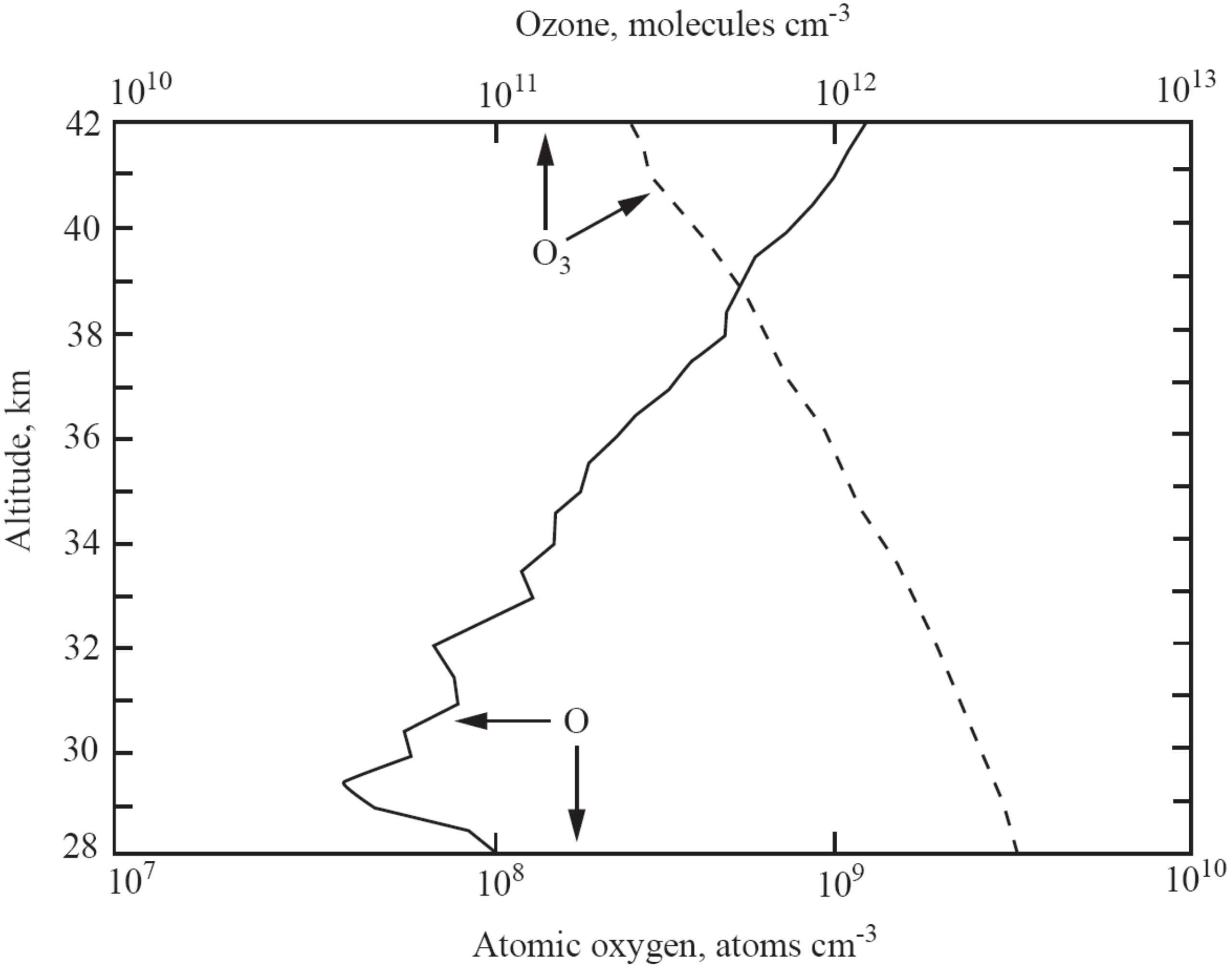
The lifetime of Ox is given by:

$$\tau_{O_x} = \frac{[O_x]}{2k_4[O][O_3]} \approx \frac{1}{2k_4[O]} \dots\dots\dots\dots\dots\dots\dots\dots (4.5)$$

Where we have included a factor of 2 in the denominator because*(R4)* consumes two Ox (one O_3 and one O). The factor of 2 can bederived formally from a mass balance equation for Ox as the sum ofthe mass balance equations for O_3 and O:

$$\begin{aligned}\frac{d}{dt}[O] = \frac{d}{dt}([O_3] + [O]) &= [\,rate\ (2) - rate\ (3) - rate\ (4)] \\ &+ [2x\,rate\ (1) + rate\ (3) - rate\ (2) - rate\ (4)] \\ &= 2x\,rate(1) - 2x\ \ rate(4) \quad \dots\dots\dots\dots\dots\dots\dots\dots (4.6)\end{aligned}$$

Values of τ_{Ox} computed from *(4.5)* range from less than a day inthe upper stratosphere to several years in the lower stratosphere,reflecting the abundance of O atoms (Figure 4-4)*.In the upper stratosphere at least, the lifetime of Ox is sufficientlyshort that chemical steady state can be assumed to hold. Thissteady state is defined by:


Ozone, molecules cm-3
10^10
10^11
10^12
10^13
42
40
38
36
34
32
30
28
Altitude, km
O3
O
10^7
10^8
10^9
10^10
Atomic oxygen, atoms cm-3

4.2 CATALYTIC LOSS CYCLES

4.2.1 Hydrogen oxide radicals (HOx)

In the late 1950s it was discovered that catalytic cycles initiated byoxidation of water vapor could represent a significant sink for O_3 inthe stratosphere. Water vapor is supplied to the stratosphere bytransport from the troposphere, and is also produced within thestratosphere by oxidation of CH_4. Water vapor mixing ratios in thestratosphere are relatively uniform, in the range 3-5 ppmv. In thestratosphere, water vapor is oxidized by $O(^1D)$ produced from*(R3)*:

$$H_2O + O(\,^1D) \rightarrow 2OH \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (R5)$$

The high-energy $O(^1D)$ atoms are necessary to overcome thestability of the H_2O molecule.The hydroxyl radical OH produced by *(R5)* can react with O_3,producing the hydroperoxy radical HO_2 which in turn reacts withO_3:

$$OH \ + \ O_3 \ \rightarrow \ HO_2 \ + \ O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (R6)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (R7)$$

$$Net: 2O3 \rightarrow 3O_2$$

We refer to the ensemble of OH and HO_2 as the HOx chemicalfamily. The sequence of reactions *(R6)* and *(R7)* consumes O_3 whileconserving HOx. Therefore HOx acts as a *catalyst* for O_3 loss;production of one HOx molecule by *(R5)* can result in the loss of alarge number of O_3 molecules by cycling of HOx through *(R6)* and*(R7)*. Termination of the catalytic cycle requires loss of HOx by a reaction such as :

$$OH + HO_2 \rightarrow H_2O + O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (R8)$$

The sequence *(R5)*-*(R8)* is a ***chain reaction***for O_3 loss in which *(R5)* isthe ***initiation step****, (R6)-(R7)* are the ***propagation steps***, and *(R8)* is the***termination step***. There are several variants to the HOx-catalyzedmechanism, involving reactions other than *(R6)*-*(R8)**.

From knowledge of stratospheric water vapor concentrationsand rate constants for *(R5)*-*(R8)*, and assuming chemical steadystate for the HOx radicals (a safe assumption in view of their shortlifetimes), one can calculate the O_3 loss rate. Such calculationsconducted in the 1950s and 1960s found that HOx catalysis was asignificant O_3 sink but not sufficient to reconcile the chemicalbudget of O_3. Nevertheless, the discovery of HOx catalysisintroduced the important new idea that species present at tracelevels in the stratosphere could trigger chain reactions destroyingO_3. This concept was to find its crowning application in subsequentwork, as described below. Another key advance was theidentification of *(R5)* as a source for the OH radical, a strongoxidant. As we will see in next chapters, oxidation by OH providesthe principal sink for a large number of species emitted in theatmosphere. Finally, recent work has shown that theHOx-catalyzed mechanism represents in fact the dominant sink of O_3 in the lowest part of the stratosphere.

4.2.2 Nitrogen oxide radicals (NOx)

The next breakthrough in our understanding of stratospheric O_3came about in the late 1960s when the United States and othercountries considered the launch of a supersonic aircraft fleet flyingin the stratosphere. Atmospheric chemists were called upon toassess the effects of such a fleet on the O_3 layer. An importantcomponent of aircraft exhaust is nitric oxide (NO) formed byoxidation of atmospheric N_2 at the high temperatures of the aircraftengine. In the stratosphere NO reacts rapidly with O_3 to produceNO_2, which then photolysis:

$$NO + O_3 \rightarrow NO_2 + O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (R9)$$

$$NO_2 + hv \rightarrow NO + O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (R10)$$

$$O + O_2 + M \rightarrow O_3 + M \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (R11)$$

This cycling between NO and NO_2 takes place on a time scale ofabout one minute during daytime. It has no net effect on O_3 and iscalled a *null cycle*.

It causes, however, rapid exchange between NOand NO_2. We refer to the ensemble of NO and NO_2 as a newchemical family, NOx.Further investigation of NOx chemistry in the stratosphere showedthat a fraction of the NO_2 molecules produced by *(R9)* reacts withoxygen atoms produced by *(R3)*:

$$NO_2 + O \rightarrow \ NO + O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (R12)$$

The sequence of reactions *(R9)* and *(R11)* represents a catalytic cyclefor O_3 loss with a net effect identical to *(R4)*:

$$NO \ + \ O_3 \ \rightarrow \ NO_2 \ + \ O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (R9)$$
$$NO_2 + \ O \ \rightarrow NO + \ O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (R11)$$
$$net\text{: } O_3 \ + \ O \ \rightarrow \ 2O_2$$

Each cycle consumes two Ox molecules, which is equivalent to twoO_3molecules . The rate-limiting step in the cycleis *(R11)* because NO_2 has the option of either photolyzing (nullcycle) or reacting with O (O_3 loss cycle). The O_3 loss rate istherefore given by:

$$-\frac{d[O]}{dt} \approx -\frac{d[O_X]}{dt} = 2\, k_{11}[NO_2][O] \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (4.12)$$

Termination of the catalytic cycle involves loss of NOx radicals. In the daytime, NOx is oxidized to HNO_3 by the strong radical oxidant OH (section 4.2.1):

$$NO_2 + OH + M \rightarrow HNO_3 + M \dots \dots \dots \dots \dots \dots \dots \dots (R12)$$

At night OH is absent, because there is no $O(^1D)$ to oxidize H_2O by*(R5)*. Loss of NOx at night takes place through the oxidation ofNO_2 by O_3 and subsequent conversion of the NO_3 radical to N_2O_5:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (R13)$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \dots \dots \dots \dots \dots \dots \dots \dots (R14)$$

This formation of N_2O_5 can take place only at night, because duringdaytime NO_3 is photolyzed back to NO_2 on a time scale of a fewseconds:

$$NO_3 + hv \rightarrow NO_2 + O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (R15)$$

The products of NOx oxidation, HNO_3 and N_2O_5, are non-radicalspecies and have therefore relatively long lifetimes againstchemical loss (weeks for HNO_3, hours to days for N_2O_5). They areeventually converted back to NOx:

$$HNO_3 + hv \rightarrow NO_2 + OH \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (R16)$$

$$HNO_3 + OH \rightarrow NO_3 + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (R17)$$

$$NO_3 + hv \rightarrow NO_2 + O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (R15)$$

$$N_2O_5 + hv \rightarrow NO_3 + NO_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (R18)$$

And serve therefore as *reservoirs* for NOx. We refer to the ensembleof NOx and its reservoirs as yet another chemical family, NOy.Ultimate removal of NOy is by transport to the troposphere whereHNO_3 is rapidly removed by deposition.A diagram of the ensemble of processes is shown in Figure 4-6.

The loss rate of O_3 can be calculated from knowledge of the aircrafte mission rate of NO, the chemical cycling within the NO_y family,and the residence time of air (and therefore NO_y) in thestratosphere. Model calculations conducted in the 1970s found thatan aircraft fleet in the stratosphere would represent a serious threatto the O_3 layer.

This environmental concern, combined witheconomic considerations, led to scrapping of the supersonic aircraftplan in the United States (the Europeans still built the Concorde).

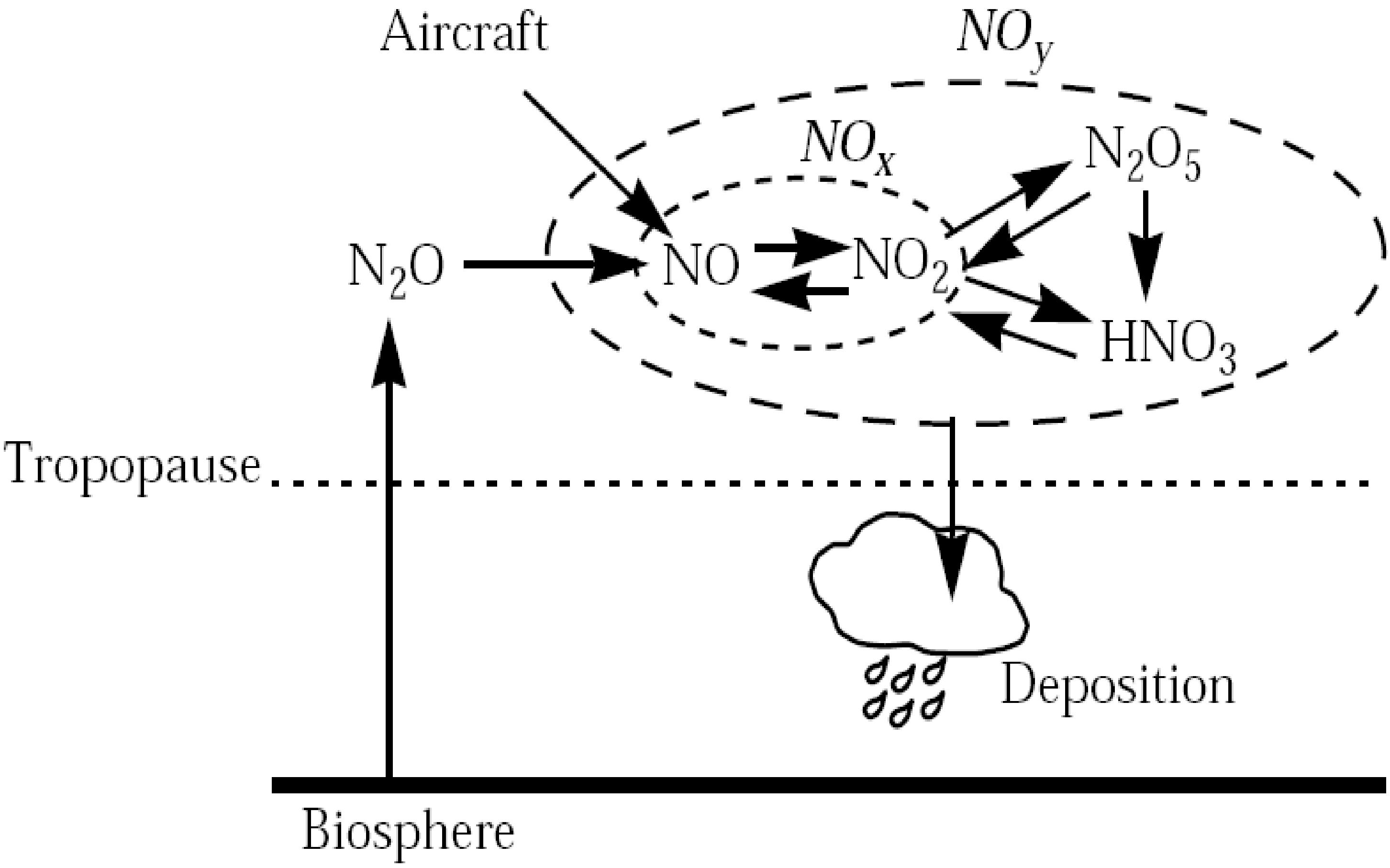


Figure 4-6 Sources and sinks of stratospheric NOx and NOy. The direct conversion of N_2O_5 *to* HNO_3 *takes place in aerosols and will be discussed insection 4.4.*

The identification of a NOx-catalyzed mechanism for O3 loss turnedout to be a critical lead towards identifying the missing O3 sink inthe Chapman mechanism. Beyond the source from supersonicaircraft, could there be a natural source of NOx to the stratosphere?Further work in the early 1970s showed that N2O, a low-yield product of nitrification and denitrification processes in thebiosphere (section 6.3), provides such a source. N_2O is a verystable molecule which has no significant sinks in the troposphere.It is therefore transported to the stratosphere where it encountershigh concentrations of $O(^1D)$, allowing oxidation to NO by

$$N_2O + O(^1D) \rightarrow 2NO \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(R19)$$

Reaction *(R19)* actually accounts for only about 5% of loss of N_2O inthe stratosphere; the remaining 95% are converted to N_2 byphotolysis and oxidation by $O(^1D)$ via an alternate branch. Theconversion to N_2 is however of no interest for driving stratosphericchemistry.On the basis of Figure 4-6, we see that the loss rate of O_3 by theNO_x-catalyzed mechanism can be calculated from knowledge ofthe production and loss rates of NO_y, and of the chemical cyclingwithin the NO_y family.

4.2.3 Chlorine radicals (ClOx)

In 1974, Mario Molina and Sherwood Rowland pointed out the potential for O3 loss associated with rising atmospheric concentrations of chlorofluorocarbons (CFCs). CFCs are not found in nature; they were first manufactured for industrial purposes in the 1930s and their use increased rapidly in the following decades. During the 1970s and 1980s, atmospheric concentrations of CFCs rose by 2-4% yr-1 .CFC molecules are inert in the troposphere; they are therefore transported to the stratosphere, where they photolyze to release Cl atoms. For example, in the case of CF2Cl2 (known by the trade name CFC-12):

$$CF_2Cl_2 + hn \rightarrow CF_2Cl + Cl \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (R20)$$

The Cl atoms then trigger a catalytic loss mechanism for O_3 involving cycling between Cl and ClO (the ClOx family). The sequence is similar to that of the NOx-catalyzed mechanism:

$$Cl + O_3 \rightarrow ClO + O_2 \text{..............................} (R21)$$
$$ClO + O \rightarrow Cl + O_2 \text{..................................} (R22)$$
$$net: O_3 + O \rightarrow 2O_2$$

The rate-limiting step for O3 loss in this cycle is *(R22)** ,so that the O_3 loss rate is:

$$d[O_3]dt = -d[O_x]dx = 2k_{22}[CLO][O] \text{........................} (4.13)$$

The catalytic cycle is terminated by conversion of ClOx to non-radical chlorine reservoirs, HCl and $ClNO_3$:

$$Cl + CH_4 \rightarrow HCl + CH_3 \text{..............................} (R23)$$
$$ClO + NO_2 + M \rightarrow ClNO_3 + M \text{ ....} (R24)$$

The lifetime of HCl is typically a few weeks and the lifetime of $ClNO_3$ is of the order of a day. Eventually these reservoirs return ClOx:

$HCl + OH \rightarrow Cl + H_2O$……………………………$(R25)$
$ClNO_3 + hv \rightarrow Cl + NO_3$………………………..$(R26)$

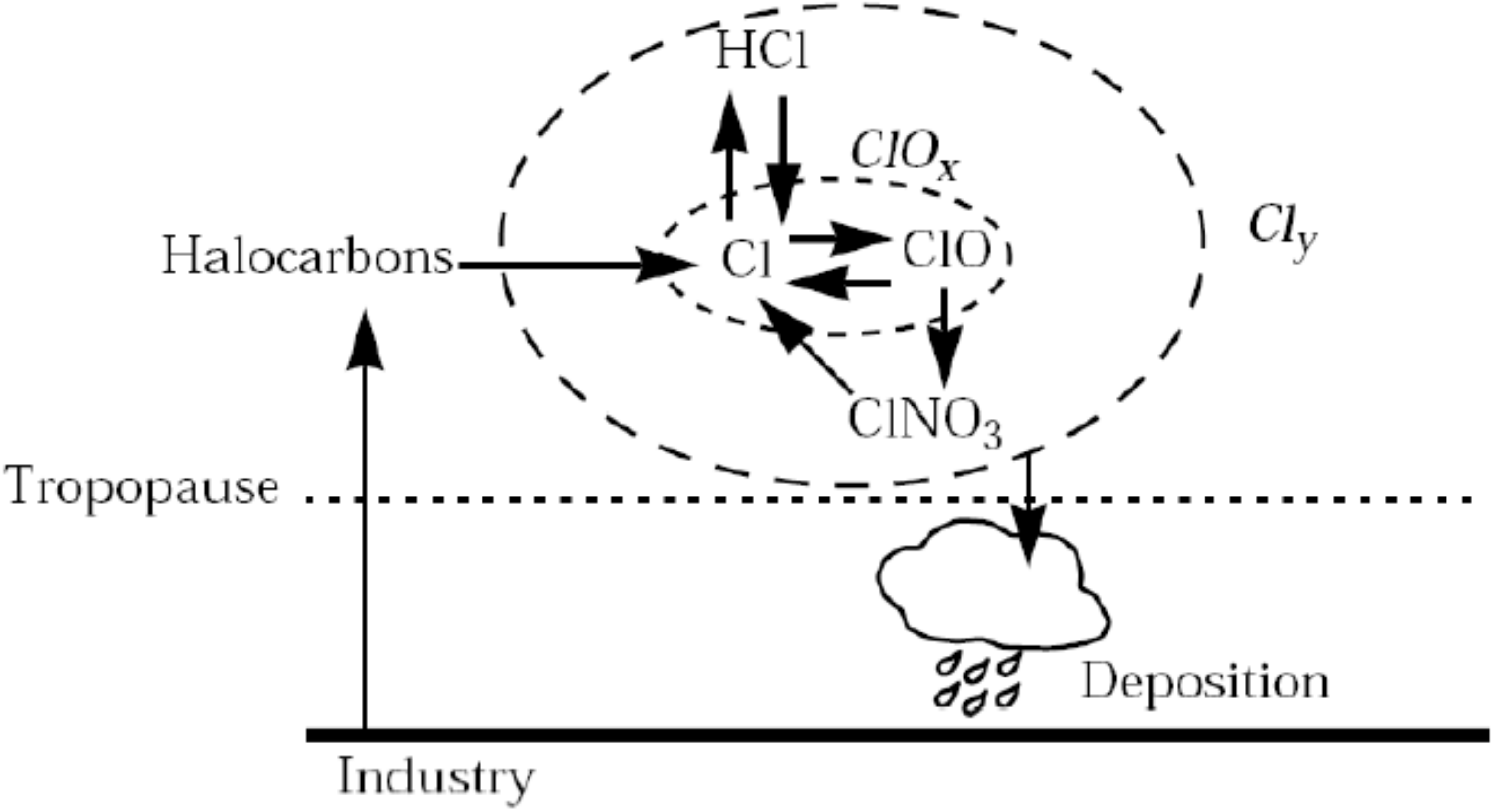


Figure 4-8 Sources and sinks of stratospheric ClOx and Cly

We thus define a chemical family Cl_y as the sum of ClO_x and its reservoirs. A diagram of the ensemble of processes is shown in Figure 4-8. Note the similarity to Figure 4-6. Similarly to the NO_x-catalyzed mechanism, the rate of O_3 loss by the ClO_x-catalyzed mechanism can be calculated from knowledge of the concentrations of CFCs and other halocarbons in the stratosphere, the residence time of air in the stratosphere, and the ClO_x/Cl_y chemical partitioning. Molina and Rowland warned that ClO_x-catalyzed O_3 loss would become a significant threat to the O_3 layer as CFC concentrations continued to increase. Their warning, backed up over the next two decades by increasing experimental evidence and compounded by the discovery of the antarctic ozone hole, led to a series of international agreements (beginning with the Montreal protocol in 1987) which eventually resulted in a total ban on CFC production as of 1996. For this work they shared the 1995 Nobel Prize in Chemistry with Paul Crutzen.

4.3 POLAR OZONE LOSS

In 1985, a team of scientists from the British Antarctic Survey reported that springtime stratospheric O_3 columns over their station at Halley Bay had decreased precipitously since the 1970s . The depletion was confined to the spring months (September-November); no depletion was observed in other seasons. Global satellite data soon confirmed the Halley Bay observations and showed that the depletion of stratospheric O_3 extended over the totality of the antarctic vortex, a large circumpolar region including most of the southern polar latitudes.

Circumpolar region including most of the southern polar latitudes. The depletion of O_3 has worsened since 1985, and springtime O_3 columns over Antarctica today are less than half of what they were in the 1960s. Measured vertical profiles show that the depletion of O_3 is essentially total in the lowest region of the stratosphere between 10 and 20 km (Figure 4-3), which normally would contain most of the total O_3 column in polar spring.

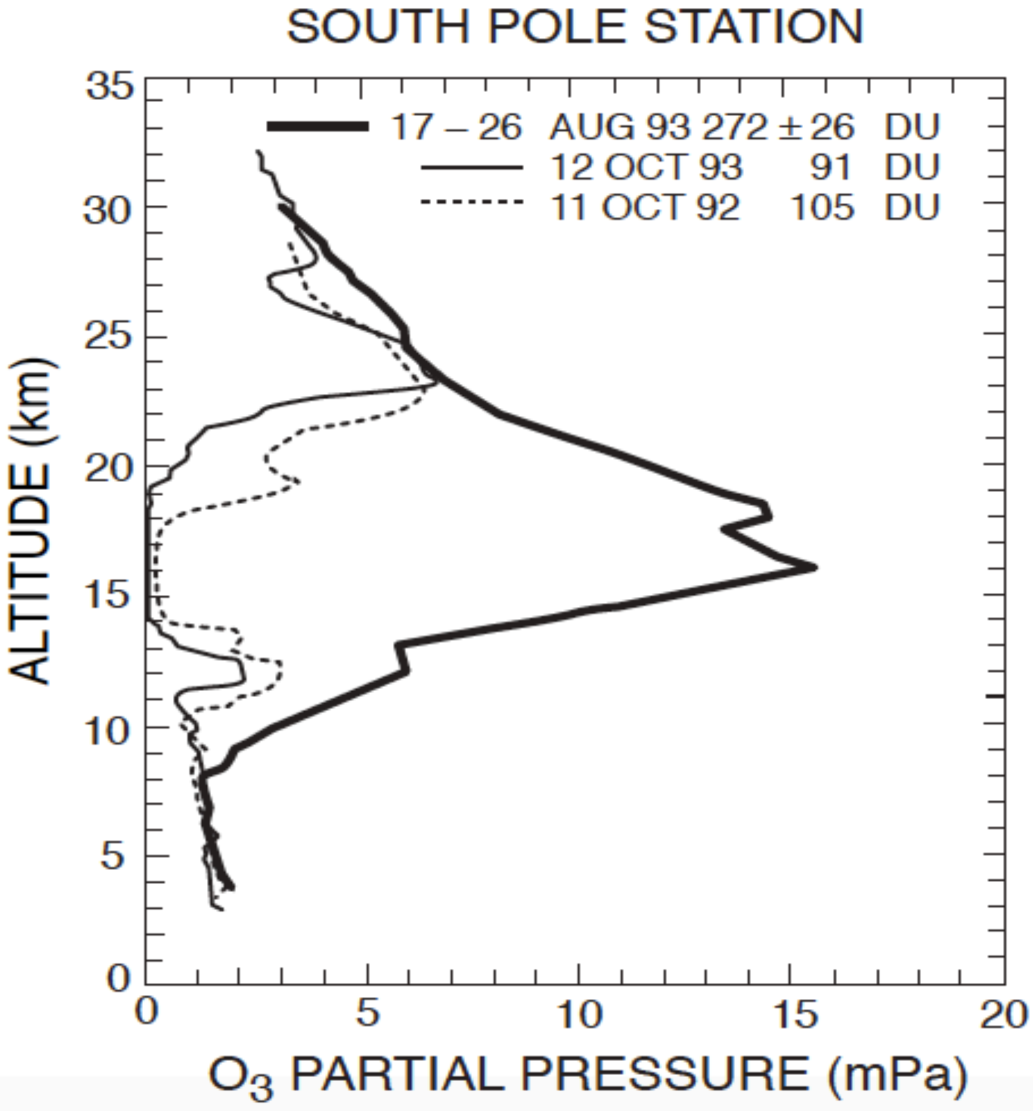


Figure 4-3 Vertical profiles of ozone over Antarctica measured by chemical sondes. In August the ozone hole has not developed yet, while in October it is fullydeveloped. From Harris, N.R.P., et al., Ozone measurements, in WMO, op. cit..

Discovery of this “antarctic ozone hole” (as it was named in the popular press) was a shock to atmospheric chemists, who thought by then that the factors controlling stratospheric O_3 were relatively well understood. The established mechanisms could not explain the O_3 depletion observed over Antarctica. Under the low light conditions in that region, concentrations of O atoms are very low. This severe failure of theory sent atmospheric chemists scrambling to understand what processes were missing from their understanding of stratospheric chemistry, and whether the appearance of the antarctic O_3 hole could be a bellwether of future catastrophic changes in stratospheric O_3 levels over other regions of the world.