Atmospheric Pollution

Lecture 4

Sahraei
Physics Department
Razi university

http://www.razi.ac.ir/sahraei

Equation of State

Boyle's Law $p \propto 1/V$

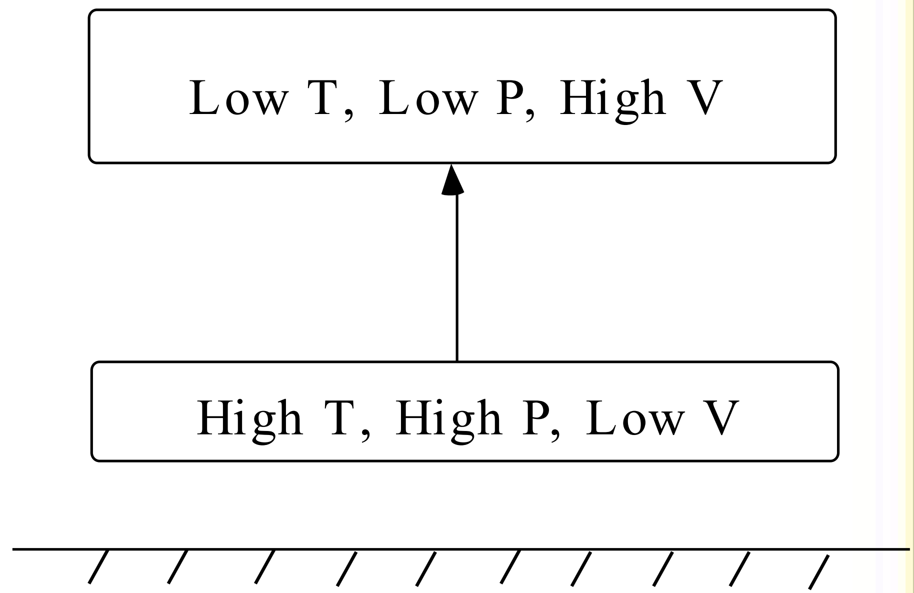
Charles' Law $V \propto T$

Avogadro's Law $V \propto n$

Ideal gas law
(simplified equation of state)

$$p = nR^*T/V = nA/V(R^*/A)T$$

Lifting of a parcel of air



Number concentration $N = nA/V$

Boltzmann's constant $k_B = R^*/A = 1.3807 \times 10^{-19}\ cm^3\ hPa\ K^{-1}$

$$P = Nk_BT$$

Charles Law and Hot Air Balloon

Montgolfier
Hot Air Balloon
June 4, 1783
www.aps.org

Charles's
Hydrogen Balloon
Aug. 27, 1783
www.aps.org

The country people who saw it fall were frightened and attacked it with stones and knives so that it was much mangled

Example

$p = Nk_BT$ $k_B = 1.3807 \times 10^{-19}$ cm^3 hPa K^{-1}

Earth's surface $p = 1013$ hPa $T = 288$ K

$N = 2.55 \times 10^{19}$ molecules cm^{-3}

48 km altitude $p = 1$ hPa $T = 270$ K

$N = 2.68 \times 10^{16}$ molecules cm^{-3}

Dalton's Law of Partial Pressure

Total air pressure equals sum of partial pressures of individual gases in the air.

Total atmospheric pressures $p_a = p_d + p_v$

Equation of state for dry air $p_d = N_d k_B T$

The number concentration of a gas (molecules per unit volume of air) is an absolute quantity.

The abundance of a gas may also be expressed in terms of a relative quantity,

volume mixing ratio

the number of gas molecules per molecule of dry air, and expressed for gas *q* as

$$\chi_q = \frac{N_q}{N_d} = \frac{p_q}{p_d}$$

(molecules of gas/molecule of dry air)

where N_q and p_q are the number concentration and partial pressure, respectively, of gas *q*.

volume mixing ratios may be multiplied by 100 and expressed as a percentage of dry air volume,

multiplied by 10^6 → parts per million volume (ppmv)

multiplied by 10^9 → parts per billion volume (ppbv)

multiplied by 10^{12} → parts per trillion volume (pptv)

$1\% = 0.01 = 10^4$ ppmv

1 ppmv = 0.000001 = 0.0001% = 1000 ppbv = 10^6 pptv

Example

Find the number concentration and partial pressure of ozone if its volume mixing ratio is 0.10 ppmv. Assume *T* = 288 K and p_d = 1013 mb

$$p_d = N_d k_B T \quad \rightarrow \quad N_d = 2.55 \times 10^{19} \text{ molecules cm}^{-3}$$

$$\chi_q = \frac{N_q}{N_d} = \frac{p_q}{p_d} \rightarrow N_q = 0.10\, ppmv \times 10^{-6} \times 2.55 \times 10^{19}\, molecules\ cm^{-3}$$

$$N_q = 2.55 \times 10^{12}\, molecules\ cm^{-3}$$

$$P_q = N_q k_B T = 0.000101\, mb$$

Composition of the Air
Well-Mixed Gases

Gas	Volume mixing ratio (percent)	(ppmv)
Nitrogen (N_2)	78.08	780,800
Oxygen (O_2)	20.95	209,500
Argon (Ar)	0.93	9,300
Neon (Ne)	0.0015	15
Helium (He)	0.0005	5
Krypton (Kr)	0.0001	1
Xenon (Xe)	0.000005	0.05

Variable Gases

		Volume Mixing Ratio (ppbv)		
Gas Name	**Chemical Formula**	**Clean Troposphere**	**Polluted Troposphere**	**Stratosphere**
Inorganic				
Water vapor	$H_2O(g)$	3000-4.0(+7)	5.0(+6)-4.0(+7)	3000-6000
Carbon dioxide	$CO_2(g)$	365,000	365,000	365,000
Carbon monoxide	$CO(g)$	40-200	2000-10,000	10-60
Ozone	$O_3(g)$	10-100	10-350	1000-12,000
Sulfur dioxide	$SO_2(g)$	0.02-1	1-30	0.01-1
Nitric oxide	$NO(g)$	0.005-0.1	0.05-300	0.005-10
Nitrogen dioxide	$NO_2(g)$	0.01-0.3	0.2-200	0.005-10
CFC-12	$CF_2Cl_2(g)$	0.55	0.55	0.22
Organic				
Methane	$CH_4(g)$	1800	1800-2500	150-1700
Ethane	$C_2H_6(g)$	0-2.5	1-50	---
Ethene	$C_2H_4(g)$	0-1	1-30	---
Formaldehyde	$HCHO(g)$	0.1-1	1-200	---
Toluene	$C_6C_5CH_3(g)$	---	1-30	---
Xylene	$C_6H_4(CH_3)_2(g)$	---	1-30	---
Methyl chloride	$CH_3Cl(g)$	0.61	0.61	0.36

CHARACTERISTICS OF SELECTED GASES AND AEROSOL PARTICLE COMPONENTS

gases and aerosol particle components relevant to each of five air pollution problems

Pollutants for Different Problems

each air pollution problem involves a different set of pollutants, although some pollutants are common to two or more problems.

a few gases and aerosol particle components are discussed in terms of their relevance, abundance, sources, sinks, and health effects.

Indoor air pollution

Gases: NO_2, CO, HCHO, SO_2, organic gases, radon

Particles: Black carbon, organic matter, sulfate, nitrate, ammonium, allergens, asbestos, fungal spores, pollen, tobacco smoke

Outdoor urban air pollution

Gases: O_3, NO, NO_2, CO, ethene, toluene, xylene, PAN

Particles: Black carbon, organic matter, sulfate, nitrate, ammonium, soil dust, sea spray, tire particles, lead

Acid deposition

Gases: SO_2, H_2SO_4, NO_2, HNO_3, HCl, CO_2

Particles: Sulfate, nitrate, chloride

Stratospheric ozone reduction

Gases: O_3, NO, HNO_3, HCl, $ClONO_2$, chlorofluorocarbons

Particles: chloride, sulfate, nitrate

Table 3.4

Global climate change

Gases: H_2O, CO_2, CH_4, N_2O, O_3, chlorofluorocarbons

Particles: black carbon, organic matter, sulfate, nitrate, ammonium, soil dust, sea spray

Table 3.4

Carbon Dioxide [$CO_2(g)$]

Colorless, odorless, greenhouse gas

Sources

Bacterial fermentation, respiration

Plant, animal, fungus, protozoa respiration

Evaporation from the oceans, chemical reaction

Volcanos; biomass, biofuel, fossil-fuel burning

Sinks

Photosynthesis

Autotrophic bacterial respiration

Dissolution into oceans, lakes; transfer to ice caps, soil

Chemical weathering, photolysis in upper atmosphere

Health effects

>15,000 ppmv affect respiration;

> 30,000 ppmv --> headaches, dizziness, nausea

Carbon Storage Reservoirs

Location	GT-C
Atmosphere	
Gas and particle	859
Surface oceans	
Live organic carbon	5
Dead organic carbon	30
Bicarbonate ion	500
Deep oceans	
Dead organic carbon	3000
Bicarbonate ion	40,000
Ocean sediments	
Dead organic carbon	10,000,000
Land/ocean sediments	
Carbonate rock	60,000,000
Land	
Live organic carbon	800
Dead organic carbon	2000

Carbon Dioxide Aqueous Chemistry

Dissolution/Dissociation

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$CO_2(g)$	$CO_2(aq)$
Gaseous carbon dioxide	Dissolve carbon dioxid

$$CO_2(aq) + H_2O(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

$CO_2(aq)$	$H_2O(aq)$	$H_2CO_3(aq)$	H^+	HCO_3^-	$2H^+$	CO_3^{2-}
Dissolved carbon dioxide	Liquid water	Dissolved carbonic acid	Hydrogen ion	Bicarbonate ion	Hydrogen ion	Carbonat ion

Formation of calcium carbonate

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s)$$

Ca^{2+}	CO_3^{2-}	$CaCO_3(s)$
Calcium ion	Carbonate ion	Calcium carbonate

Chemical Weathering

Breakdown and reformation of rocks and minerals at the atomic and molecular level by chemical reaction

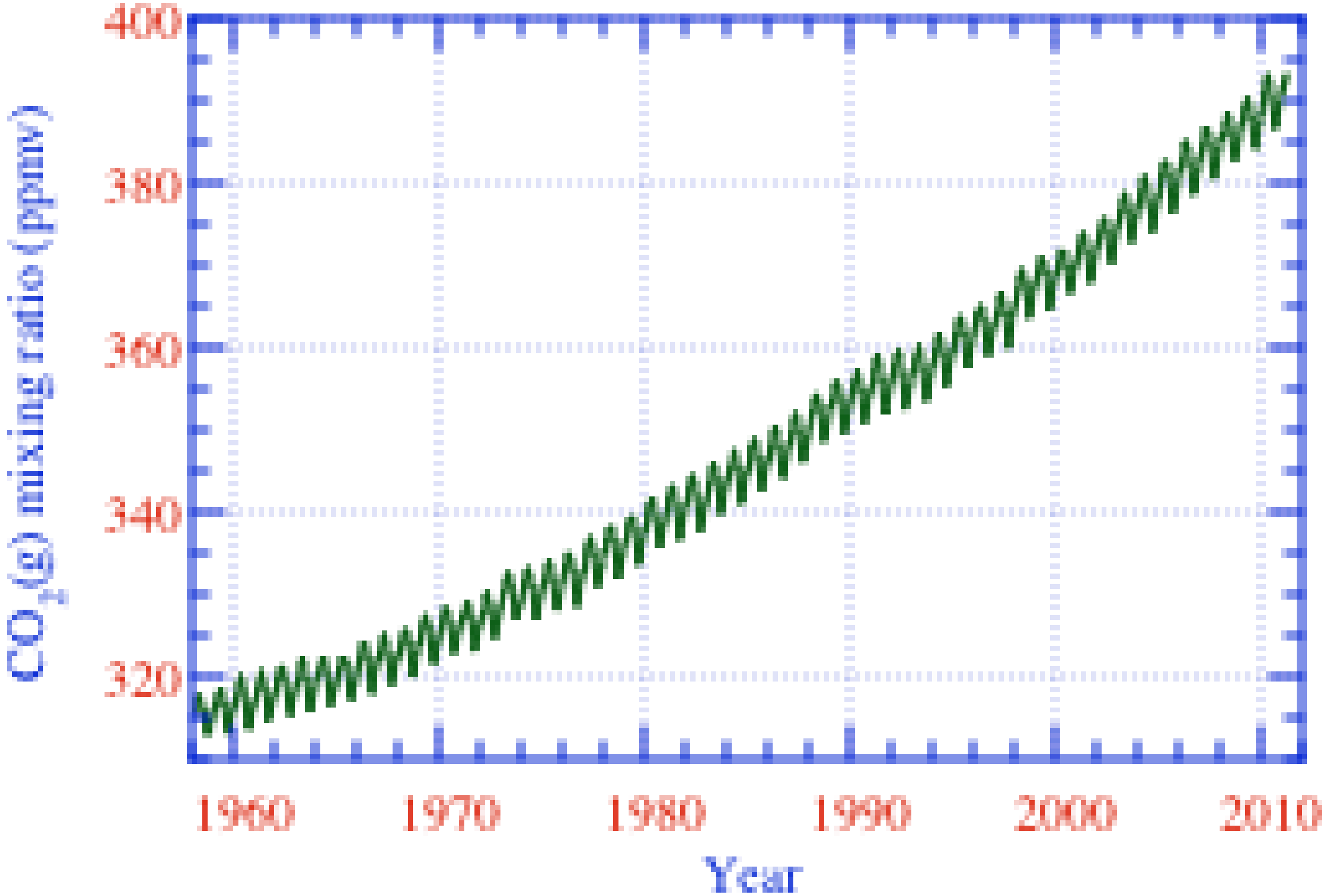
$$CaSiO_3(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + SiO_2(s)$$

$CaSiO_3(s)$	$CO_2(g)$	$CaCO_3(s)$	$SiO_2(s)$
Generic calcium silicate	Carbon dioxide	Calcium carbonate (calcite)	Silicon dioxid (quartz

$$CaCO_3(s) + CO_2(g) + H_2O(aq) \rightleftharpoons CaCO_3(s) + H_2CO_3(aq) \rightleftharpoons Ca^{2+} + 2\,HCO_3^-$$

$CaCO_3(s)$	$CO_2(g)$	$H_2O(aq)$	$CaCO_3(s)$	$H_2CO_3(aq)$	Ca^{2+}	$2\,HCO_3^-$
Calcium carbonate	Gaseous carbon dioxide	Liquid water	Calcium carbonate	Carbonic acid	Calcium ion	Bicarbonat ion

Carbon Dioxide Mixing Ratio



Los Angeles Smog

Los Angeles (July 23, 2000)

Photostationary State Ozone

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) \qquad (4.1)$$

Nitric oxide | Ozone | Nitrogen dioxide | Molecular oxygen

$$NO_2(g) + h\nu \longrightarrow NO(g) + O(g) \qquad \lambda < 420 \qquad (4.2)$$

Nitrogen dioxide | Nitric oxide | Atomic oxygen

$$O(g) + O_2(g) \xrightarrow{M} O_3(g) \qquad (4.3)$$

Ground-state atomic oxygen | Molecular oxygen | Ozone

Photostationary State Ozone

$\chi_{O_3} = (J/N_d k_1)(\chi_{NO_2(g)}/\chi_{NO(g)})$ (4.4)

Example 4.1.

Estimate ozone mixing ratio when

p_d	= 1013 mb	T	= 298 K
$\chi_{NO(g)}$	= 5 pptv	$\chi_{NO_2(g)}$	= 10 pptv
k_1	= 1.8×10^{-14} cm^3 molec.$^{-1}$ s^{-1}	J	= 0.01 s^{-1}

----> $N_{O_3(g)}$ = 1.1×10^{12} molec. cm^{-3}

----> N_d = 2.46×10^{19} molec. cm^{-3}

----> $\chi_{O_3(g)}$ = 44.7 ppbv

Daytime Nitrogen Oxide Removal

$$NO_2(g) + OH(g) \xrightarrow{M} HNO_3(g$$

Nitrogen dioxide · Hydroxyl radical · Nitric acid

(4.5)

Hydroxyl Radical Production

$O_3(g) + h\nu \longrightarrow O_2(g) + O(^1D)(g)$ $\lambda < 310$ (4.6)

Ozone — Molecular oxygen — Excited atomic oxygen

$O(^1D)(g) + H_2O(g) \longrightarrow 2\,OH(g)$ (4.7)

Excited atomic oxygen — Water vapor — Hydroxy radical

Nighttime Nitrogen Chemistry

$$NO_2(g) + O_3(g) \longrightarrow NO_3(g) + O_2(g) \qquad (4.8)$$

Nitrogen dioxide	Ozone	Nitrate radical	Molecula oxyger

$$NO_2(g) + NO_3(g) \overset{M}{\rightleftharpoons} N_2O_5(g) \qquad (4.9)$$

Nitrogen dioxide	Nitrate radical	Dinitrog pentoxi

$$N_2O_5(g) + H_2O(aq) \longrightarrow 2HNO_3(aq) \qquad (4.10)$$

Dinitrogen pentoxide	Liquid water	Dissolved nitric acid

Ozone Production From Carbon Monoxide

$$CO(g) + OH(g) \longrightarrow CO_2(g) + H(g) \qquad (4.11)$$

Carbon monoxide, Hydroxyl radical, Carbon dioxide, Atomic hydrog

$$H(g) + O_2(g) \xrightarrow{M} HO_2(g) \qquad (4.12)$$

Atomic hydrogen, Molecular oxygen, Hydropero radical

$$NO(g) + HO_2(g) \longrightarrow NO_2(g) + OH(g) \qquad (4.13)$$

Nitric oxide, Hydroperoxy radical, Nitrogen dioxide, Hydrox radical

$$NO_2(g) + h\nu \longrightarrow NO(g) + O(g) \qquad \lambda < 420 \ldots \qquad (4.14)$$

Nitrogen dioxide, Nitric oxide, Atomic oxygen

$$O(g) + O_2(g) \xrightarrow{M} O_3(g) \qquad (4.15)$$

Ground-state atomic oxygen, Molecular oxygen, Ozon

Ozone Production From Methane

$$CH_4(g) + OH(g) \longrightarrow CH_3(g) + H_2O(g) \quad (4.16)$$

Methane, Hydroxyl radical → Methyl radical, Water vapor

$$CH_3(g) + O_2(g) \xrightarrow{M} CH_3O_2(g) \quad (4.17)$$

Methyl radical, Molecular oxygen → Methylpero radical

$$NO(g) + CH_3O_2(g) \longrightarrow NO_2(g) + CH_3O(g) \quad (4.18)$$

Nitric oxide, Methylperoxy radical → Nitrogen dioxide, Methox radical

$$NO_2(g) + h\nu \longrightarrow NO(g) + O(g) \quad \lambda < 420 \quad (4.19)$$

Nitrogen dioxide → Nitric oxide, Atomic oxygen

$$O(g) + O_2(g) \xrightarrow{M} O_3(g) \quad (4.20)$$

Ground-state atomic oxygen, Molecular oxygen → Ozone

oxygen

Ozone Production From Ethane

$$C_2H_6(g) + OH(g) \longrightarrow C_2H_5(g) + H_2O(g) \qquad (4.26)$$

Ethane | Hydroxyl radical | Ethyl radical | Water vapo

$$C_2H_5(g) + O_2(g) \xrightarrow{M} C_2H_5O_2(g) \qquad (4.27)$$

Ethyl radical | Molecular oxygen | Ethylpero radical

$$NO(g) + C_2H_5O_2(g) \longrightarrow NO_2(g) + C_2H_5O(g) \qquad (4.28)$$

Nitric oxide | Ethylperoxy radical | Nitrogen dioxide | Ethox radical

$$NO_2(g) + h\nu \longrightarrow NO(g) + O(g) \qquad \lambda < 420 \qquad (4.29)$$

Nitrogen dioxide | Nitric oxide | Atomic oxygen

$$O(g) + O_2(g) \xrightarrow{M} O_3(g) \qquad (4.30)$$

Ground-state atomic oxygen | Molecular oxygen | Ozone

Production of Formaldehyde and Acetaldehyde

Formaldehyde (4.21)

$$CH_3O(g) + O_2(g) \longrightarrow HCHO(g) + HO_2(g)$$

Methoxy radical	Molecular oxygen	Formal-dehyde	Hydroperoxy radical

Acetaldehyde (4.22)

$$C_2H_5O(g) + O_2(g) \longrightarrow CH_3CH(=O) + H_2O(g)$$

Ethoxy radical	Molecular oxygen	Acetaldehyde	Hydroperoxy radical

Ozone From Formaldehyde

$$HCHO(g) + h\nu \rightarrow \begin{cases} HCO(g) + H(g) & \lambda < 334 \\ CO(g) + H_2(g) & \lambda < 370 \end{cases} \qquad (4.22)$$

HCHO(g): Formal-dehyde; HCO(g): Formyl radical; H(g): Atomic hydrogen; CO(g): Carbon monoxide; $H_2(g)$: Molecular hydrogen

$$HCHO(g) + OH(g) \rightarrow HCO(g) + H_2O(g) \qquad (4.23)$$

Formal-dehyde; Hydroxyl radical; Formyl radical; Water vapor

$$HCO(g) + O_2(g) \rightarrow CO(g) + HO_2(g) \qquad (4.24)$$

Formyl radical; Molecular oxygen; Carbon monoxide; Hydroperoxy radical

$$H(g) + O_2(g) \xrightarrow{M} HO_2(g) \qquad (4.25)$$

Atomic hydrogen; Molecular oxygen; Hydroperoxy radical

--> Form O_3 from both CO and HO_2

PAN Production From Acetaldehyde

$$CH_3CH(=O)(g) + OH(g) \longrightarrow CH_3C(=O)(g) + H_2O(g) \qquad (4.32)$$

Acetaldehyde, Hydroxyl radical, Acetyl radical, Water vapor

$$CH_3C(=O)(g) + O_2(g) \xrightarrow{M} CH_3C(=O)O_2(g) \qquad (4.33)$$

Acetyl radical, Molecular oxygen, Peroxyacetyl radical

$$CH_3C(=O)O_2(g) + NO_2(g) \underset{}{\overset{M}{\rightleftharpoons}} CH_3C(=O)O_2NO_2(g) \qquad (4.34)$$

Peroxyacetyl radical, Nitrogen dioxide, Peroxyacetyl nitrate (PAN)

Ozone Production From Acetaldehyde

$$CH_3C(=O)O_2(g) + NO(g) \longrightarrow CH_3C(=O)O(g) + NO_2(g) \quad (4.35)$$

Peroxyacetyl radical; Nitric oxide; Acetyloxy radical; Nitrogen dioxide

$$CH_3CHO(g) + h\nu \longrightarrow CH_3(g) + HCO(g) \quad (4.36)$$

Acetaldehyde; Methyl radical; Formyl radical

--> Form O_3 from NO_2, CH_3, and HCO

Photochemical Smog Formation

$$NO(g) + RO_2(g) \longrightarrow NO_2(g) + RO(g) \qquad (4.37)$$

Nitric oxide; Organic peroxy radical; Nitrogen dioxide; Organic oxy radical

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) \qquad (4.38)$$

Nitric oxide; Ozone; Nitrogen dioxide; Molecular oxygen

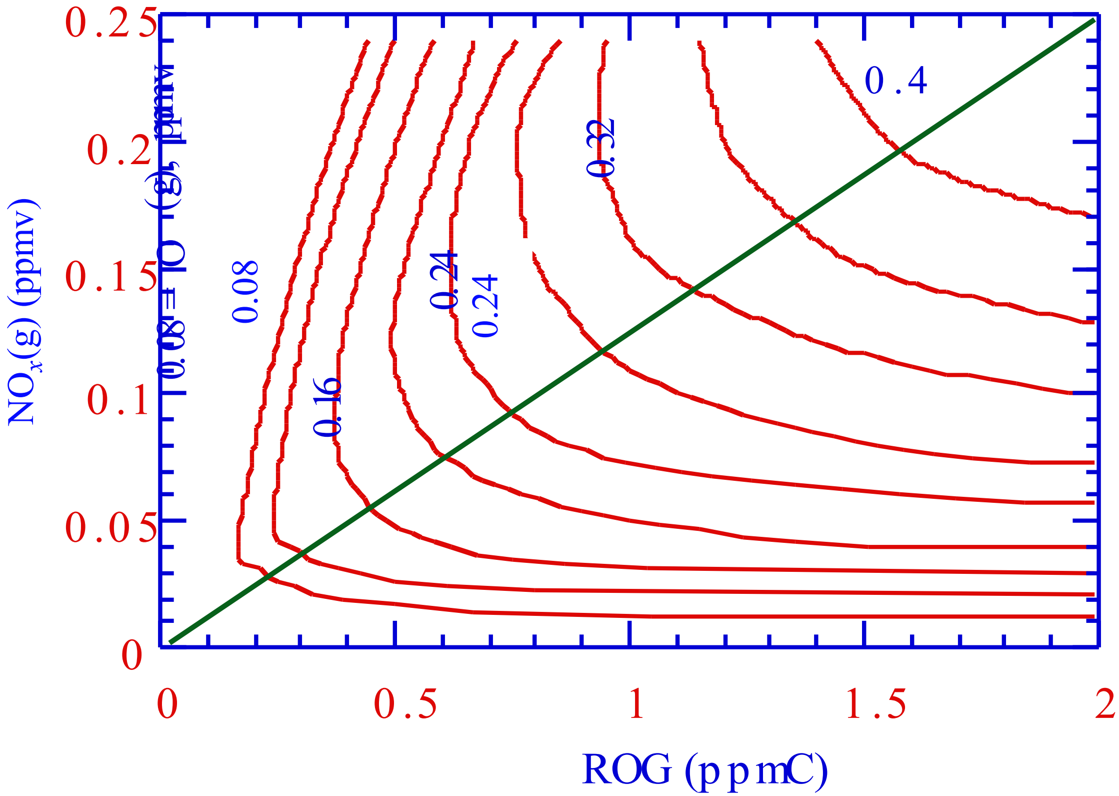
$$NO_2(g) + h\nu \longrightarrow NO(g) + O(g) \qquad \lambda < 420 \qquad (4.39)$$

Nitrogen dioxide; Nitric oxide; Atomic oxygen

$$O(g) + O_2(g) \xrightarrow{M} O_3(g) \qquad (4.40)$$

Ground-state atomic oxygen; Molecular oxygen; Ozone

Ozone Isopleth



Contours are ozone (ppmv)

Figure 4.9

Source/Receptor Regions in Los Angeles

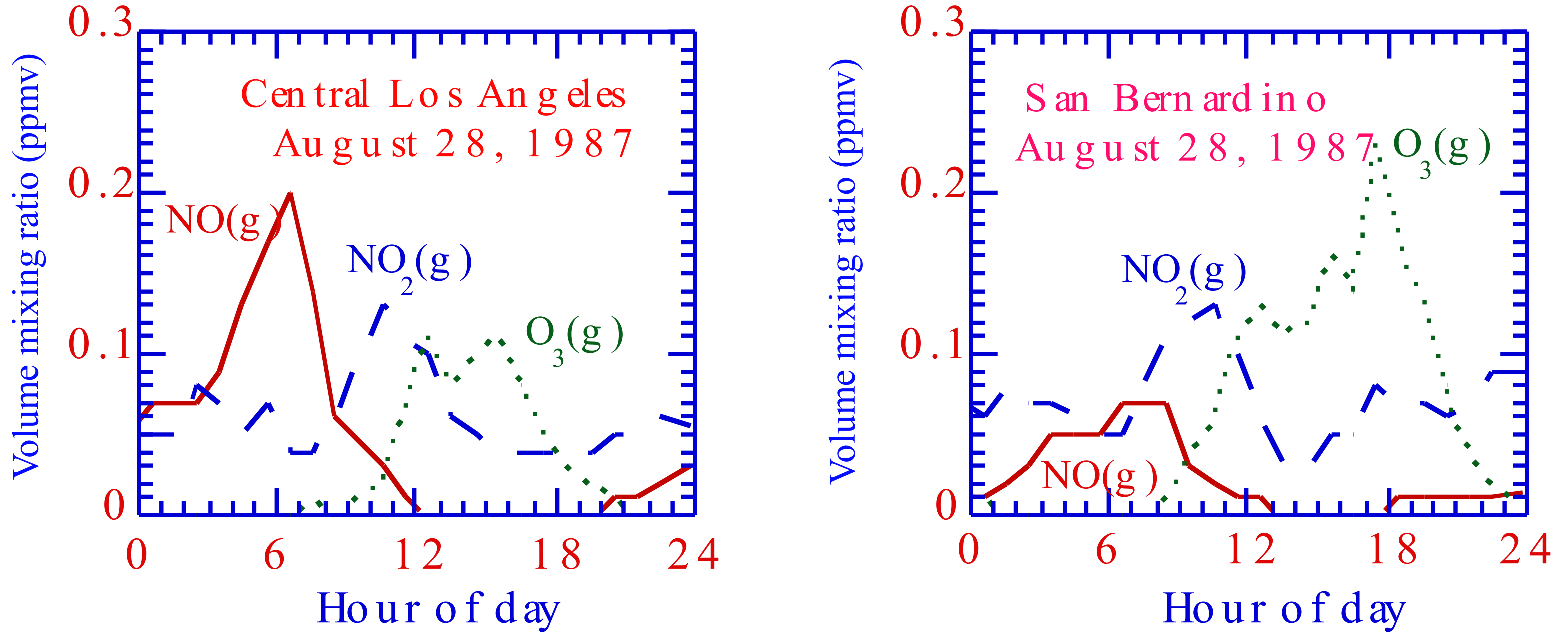


Figure 4.10

Daily Emissions in Los Angeles (1987)

Substance	Emissions (tons day^{-1})	Percent of total
Carbon monoxide [CO(g)]	**9796**	**69 3**
Nitric oxide [NO(g)]	754	
Nitrogen dioxide [NO_2(g)]	129	
Nitrous acid [HONO(g)]	6.5	
Total NO_x(g) + HONO(g)	**889.5**	**6.3**
Sulfur dioxide [SO_2(g)]	109	
Sulfur trioxide [SO_3(g)]	4.5	
Total SO_x(g)	**113.5**	**0.8**
Alkanes	1399	
Alkenes	313	
Aldehydes	108	
Ketones	29	
Alcohols	33	
Aromatics	500	
Hemiterpenes	47	
Total ROGs	**2429**	**17 2**
Methane [CH_4(g)]	**904**	**6.4**
Total Emissions	**14,132**	**100**

Table 4.1, Allen and Wagner, 1992

Percent Emission by Source

Source Category	CO(g)	NO_x(g)	SO_x(g)	ROG
Stationary	2	24	38	50
Mobile	98	76	62	50
Tota l	100	100	100	100

Table 4.2, Chang et al., 1991

Lifetimes of Organic Gases in Urban Air

ROG Species	Photolysis	[OH(g)] 5×	×	×	×	×
trans-*2*-Butene	---	52 m	4 y	6.3 d	4 m	17 m
Acetylene	---	3.0 d	---	2.5 y	---	200 d
Formaldehyde	7 h	6.0 h	1.8 h	2.5 y	2.0 d	3200 y
Acetone	23 d	9.6 d	---	---	---	---
Ethanol	---	19 h	---	---	---	---
Toluene	---	9.0 h	---	6 y	33 d	200 d
Isoprene	---	34 m	---	4 d	5 m	4.6 h

Table 4.3

Most Abundant Species in Terms of Abundance and Reactivity

1. *m*- and *p*-Xylene	6. *i*-Pentane
2. Ethene	7. Propene
3. Acetaldehyde	8. *o*-Xylene
4. Toluene	9. Butane
5. Formaldehyde	10. Methylcyclopentane

Table 4.4, Lurmann et al., 1992

Early Morning Source of OH in Polluted Air

$$HONO(g) + h\nu \longrightarrow OH(g) + NO(g) \quad \lambda < 400\ 1 \qquad (4.42)$$

Nitrous acid → Hydroxy radical + Nitric oxide

Mid-Morning Source of OH in Polluted Air

$$HCHO(g) + h\nu \longrightarrow HCO(g) + H(g) \qquad \lambda < 334 \qquad (4.43)$$

Formal-dehyde	Formyl radical	Atomic hydrogen

$$H(g) + O_2(g) \xrightarrow{M} HO_2(g) \qquad (4.44)$$

Atomic hydrogen	Molecular oxygen	Hydropero radical

$$HCO(g) + O_2(g) \longrightarrow CO(g) + HO_2(g) \qquad (4.45)$$

Formyl radical	Molecular oxygen	Carbon monoxide	Hydropero radical

$$NO(g) + HO_2(g) \longrightarrow NO_2(g) + OH(g) \qquad (4.46)$$

Nitric oxide	Hydroperoxy radical	Nitrogen dioxide	Hydrox radical

Afternoon Source of OH in Polluted Air

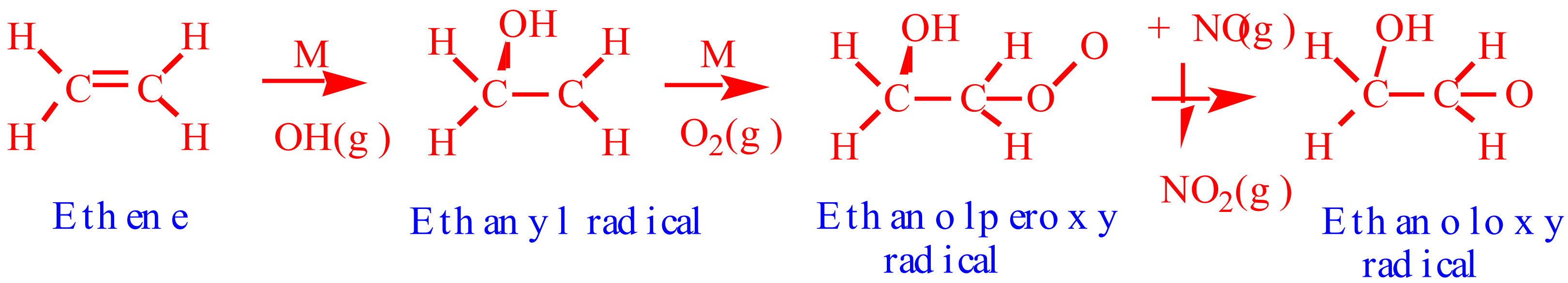
$$O_3(g) + h\nu \longrightarrow O_2(g) + O(^1D)(g) \qquad \lambda < 310 \qquad (4.47)$$

Ozone — Molecular oxygen — Excited atomic oxygen

$$O(^1D)(g) + H_2O(g) \longrightarrow 2\,OH(g) \qquad (4.48)$$

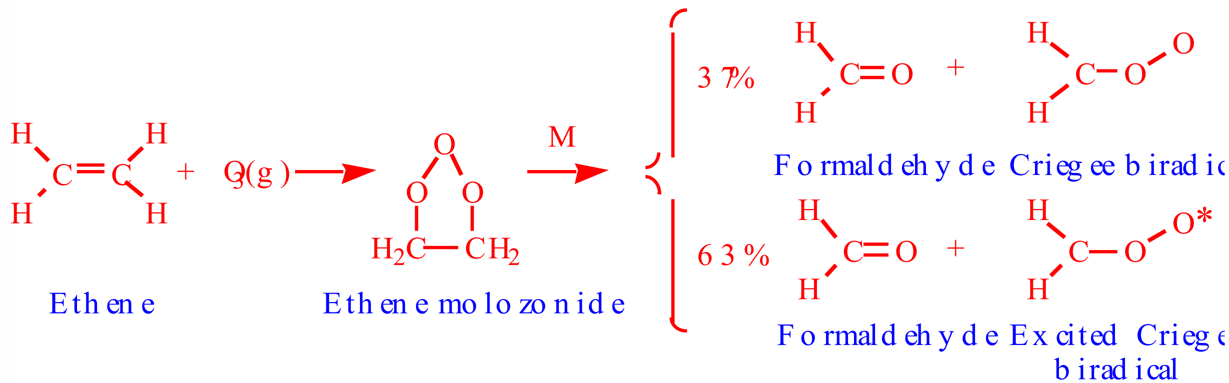
Excited atomic oxygen — Water vapor — Hydroxy radical

Alkene Reaction with OH



(4.49)

Alkene Reaction with Ozone

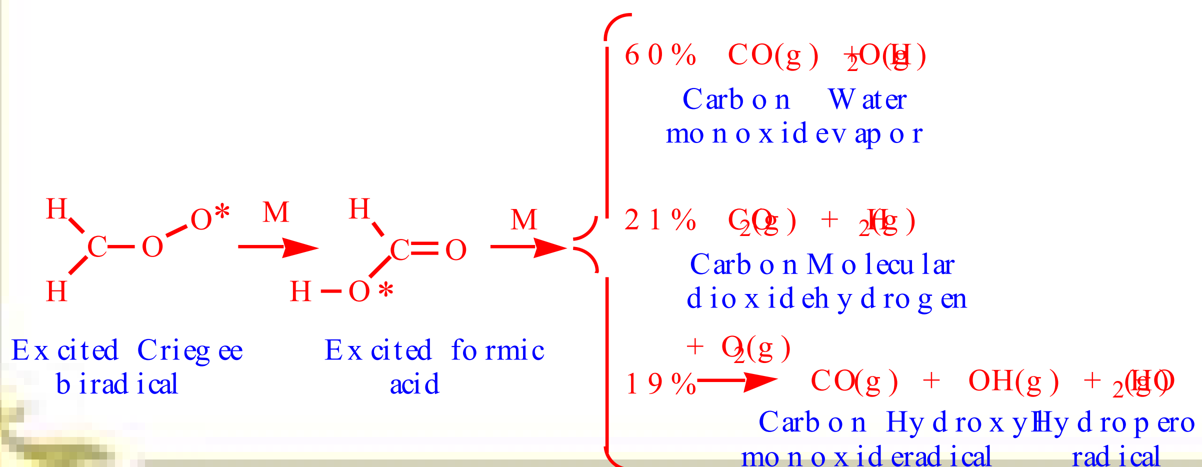


(4.50)

$$H_2COO(g) + NO(g) \longrightarrow HCHO(g) + NO_2(g)$$

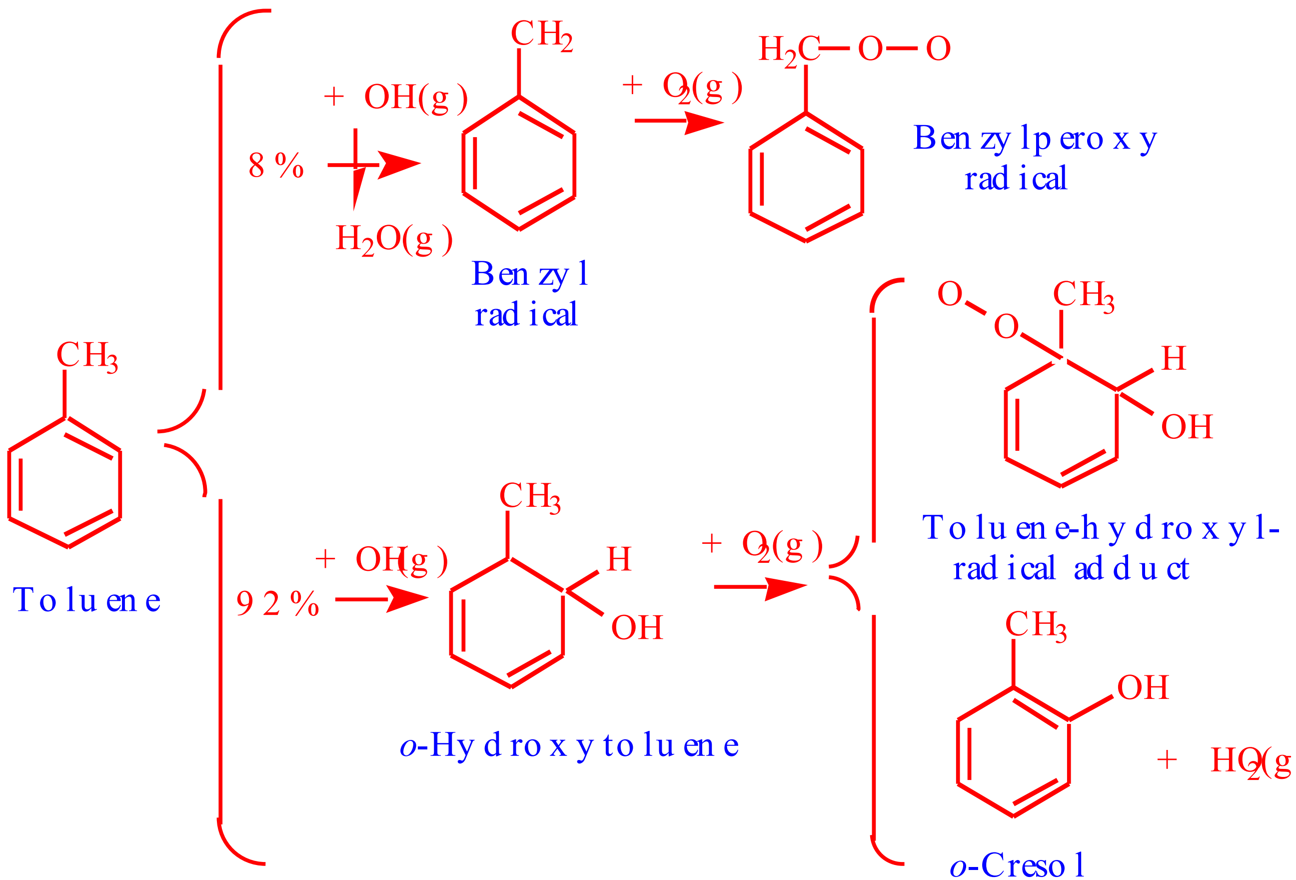
Criegee biradical; Nitric oxide; Formaldehyde; Nitrogen dioxide

(4.51)



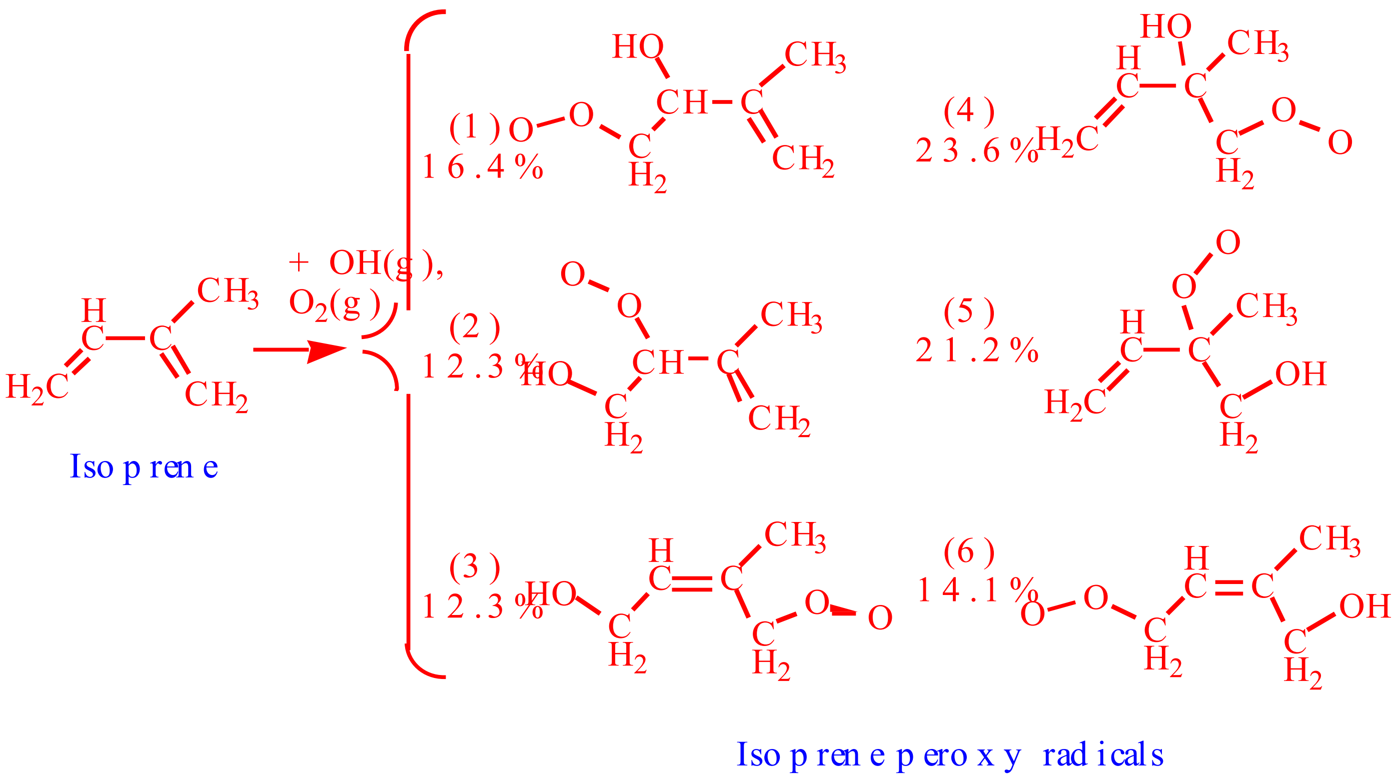
(4.52)

Toluene Reaction with OH



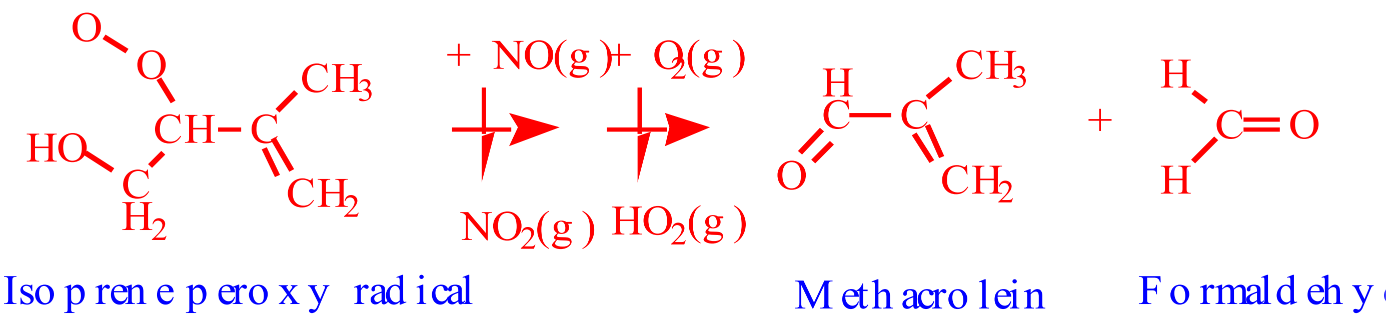
(4.53)

Isoprene Reaction with OH

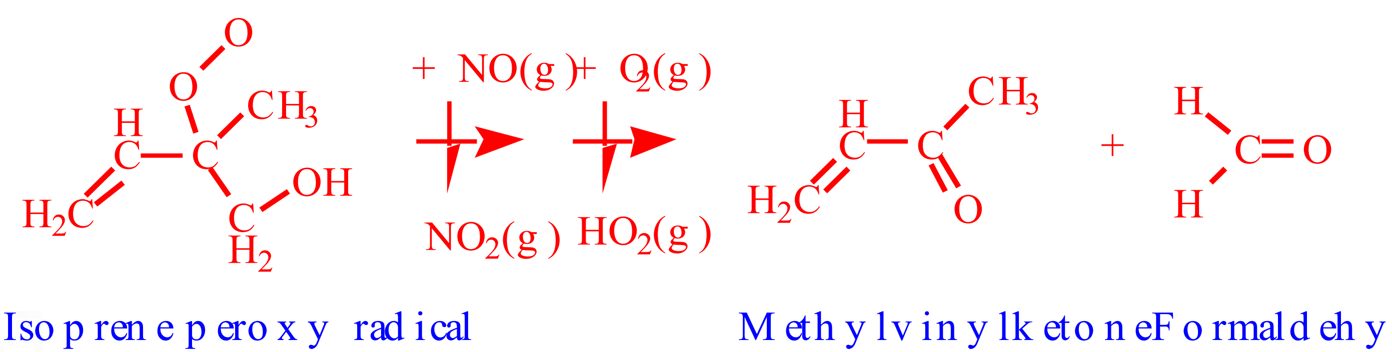


(4.54)

Methacrolein and Methyvinylketone Production



(4.55)



(4.56)

Alcohol Reactions with OH

$$CH_3OH(g) \xrightarrow[H_2O(g)]{+\ OH(g)} \begin{cases} 85\%\ CH_2OH(g) \xrightarrow[HO_2(g)]{+\ O_2(g)} HCHO(g) \\ 15\%\ CH_3O(g) \end{cases} \quad (4.57)$$

Methanol

85% $CH_2OH(g)$ → $HCHO(g)$ Formaldehy

15% $CH_3O(g)$ Methoxy radical

$$C_2H_5OH(g) \xrightarrow[H_2O(g)]{+\ OH(g)} \begin{cases} 5\%\ CH_2CH_2OH(g) \\ 90\%\ CH_3CHOH(g) \xrightarrow[HO_2(g)]{+\ O_2(g)} CH_3CHO(g) \\ 5\%\ CH_3CH_2O(g) \end{cases} \quad (4.58)$$

Ethanol

90% $CH_3CHOH(g)$ → $CH_3CHO(g)$ Acetaldehy

5% $CH_3CH_2O(g)$ Ethoxy radical

Chapter 2:

The Sun, the Earth, and the Evolution of the Earth's Atmosphere

Origin of the Sun

15 billion years ago (bya). Big bang. All mass in universe compressed to single point 10^9 kg m^{-3} density, T=10^{12} K

Aggregates of ejected material collapsed gravitationally to form earliest stars.

Temperatures in cores increased due to compressional heating

When temperatures reached 10 million K, nuclear fusion of H into He and other elements began, releasing energy to power the stars.

As early stars aged, they ultimately exploded, ejecting elements to the universe around

Cosmic Abundance of Hydrogen Relative to Other Elements

Element	Atomic Mass	Abundance of H Relative to Element
Hydrogen	1.01	1:1
Helium	4.00	14:1
Oxygen	16.0	1400:1
Carbon	12.0	2300:1
Nitrogen	14.0	11,000:1
Magnesium	24.3	24,000:1
Silicon	28.1	26,000:1
Iron	55.8	29,000:1
Aluminum	27.0	306,000:1
Sodium	23.0	433,000:1

Table 2.1

Origin of the Sun

4.6 bya interstellar material aggregated to form cloudy mass, the solar nebula

Sun formed from gravitational collapse of solar nebula

Today's Sun (90% H, 9.9% He)

- Core (8-15 million K)
- Intermediate interior (5-8 million K)
- Hydrogen convection zone (HCZ) (6400 K - 5 million K)
  - 10 million years for photon to travel from core to top of HCZ
- Photosphere (4000-6400 K, effective 5785 K)
- Chromosphere (4000 K - 1 million K. H energized and decays)
- Corona (1 - 2 million K. Consists of ionized gases)
- Solar wind --> Aurora Borealis and Aurora Australis on Earth
  - 300-1000 km/s, 200,000 K at Earth

Structure of the Sun

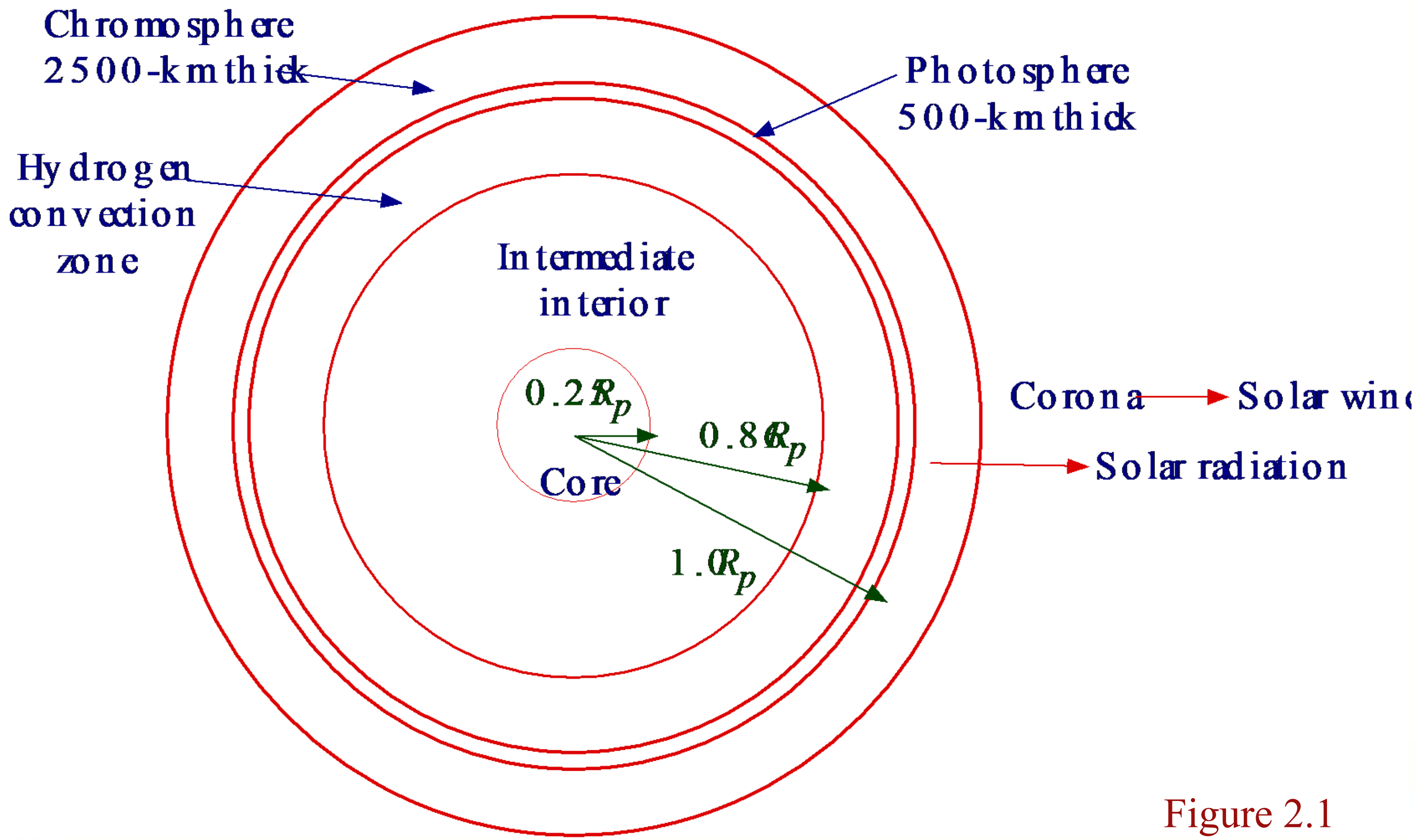


Figure 2.1

Aurora Australis

David Miller, National Geophysical Data Center, available from NOAA Central Library

Radiation Spectra

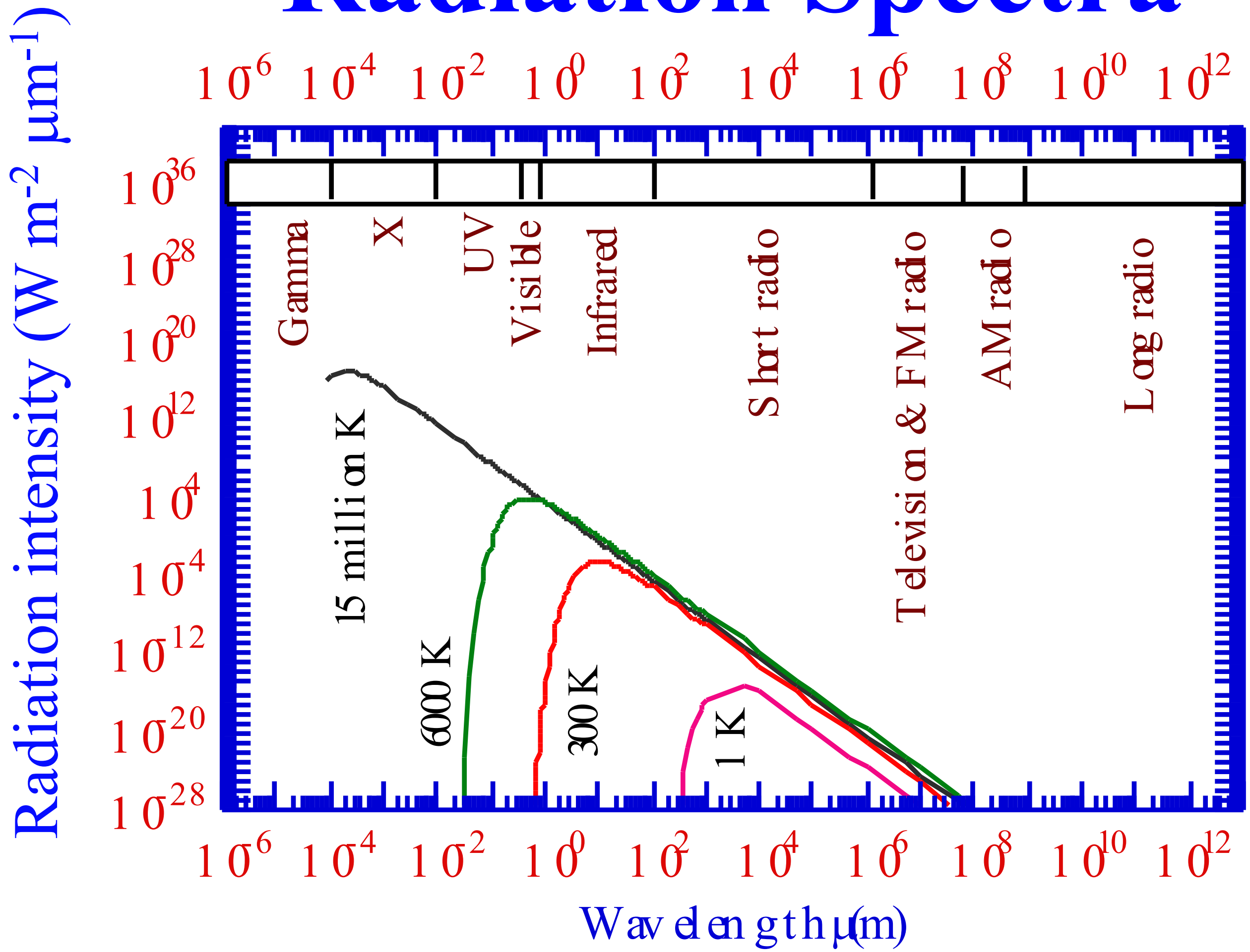


Figure 2.3

Wien's Law (2.1)

$\lambda_p(\mu m)=2897/T(K)$

Stefan-Boltzmann Law (2.2)

$F_b\,(W/m^2)=\varepsilon\sigma T(K)^4$

Emission Spectra of the Sun and Earth

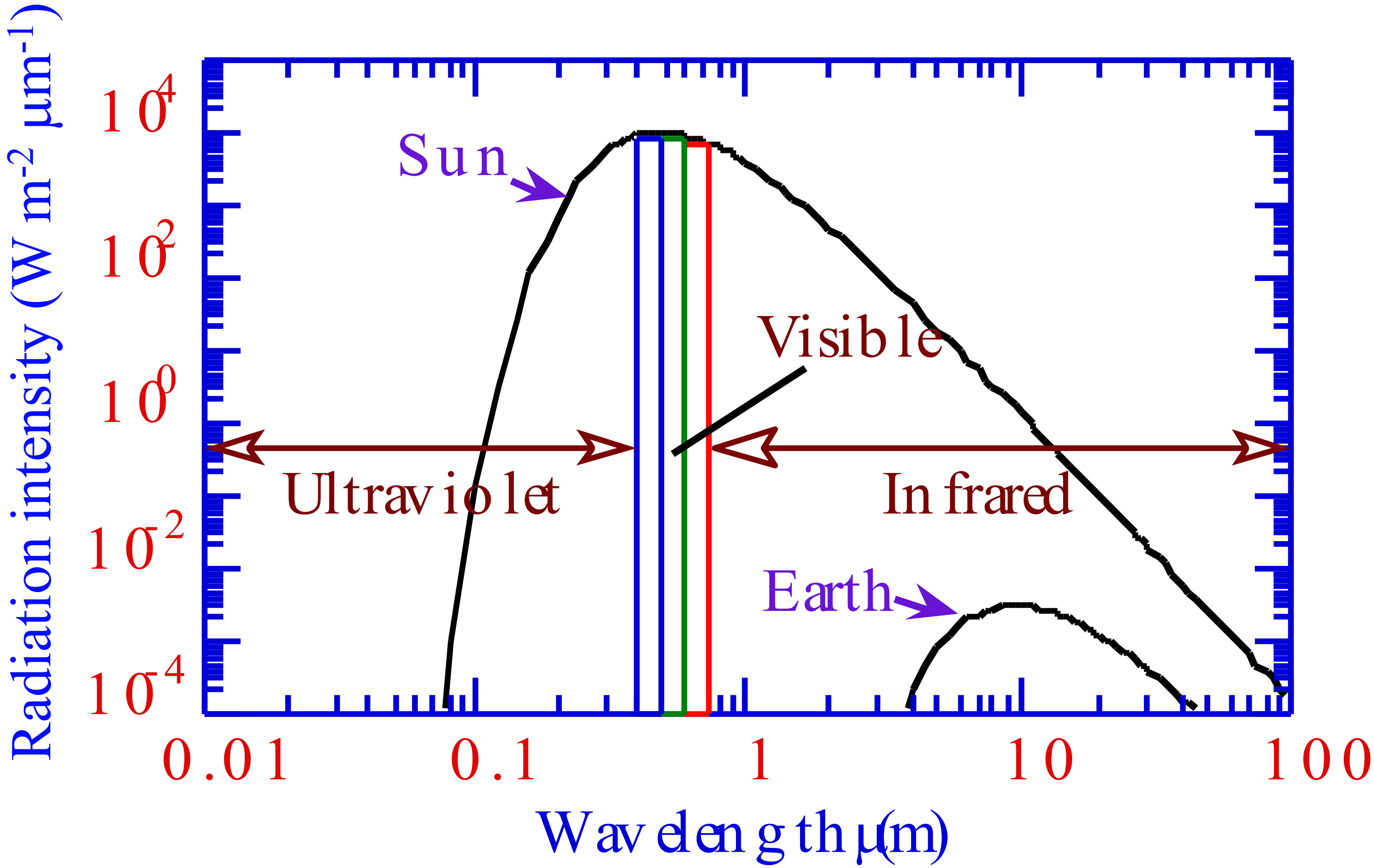


Figure 2.4

Ultraviolet and Visible Spectra of the Sun

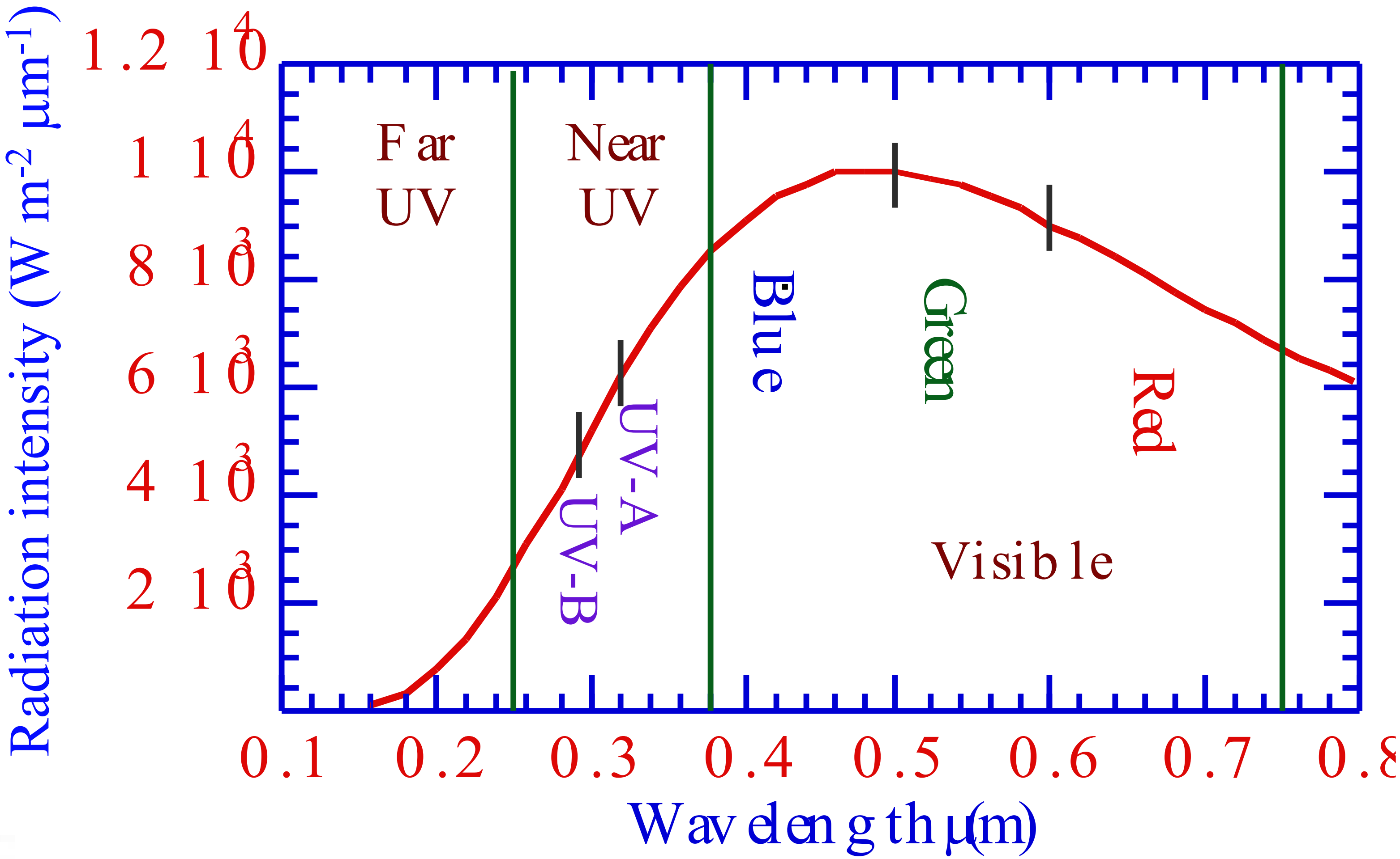


Figure 2.5

Origin of the Earth

4.6 bya, rock-forming elements, which were gases at high temperature in solar nebula, condensed into small solid grains as nebula cooled.

Grains accreted to planetesimals, such as asteroids and comets.

Asteroid: rocky body 1-1000 km in size that orbits sun.

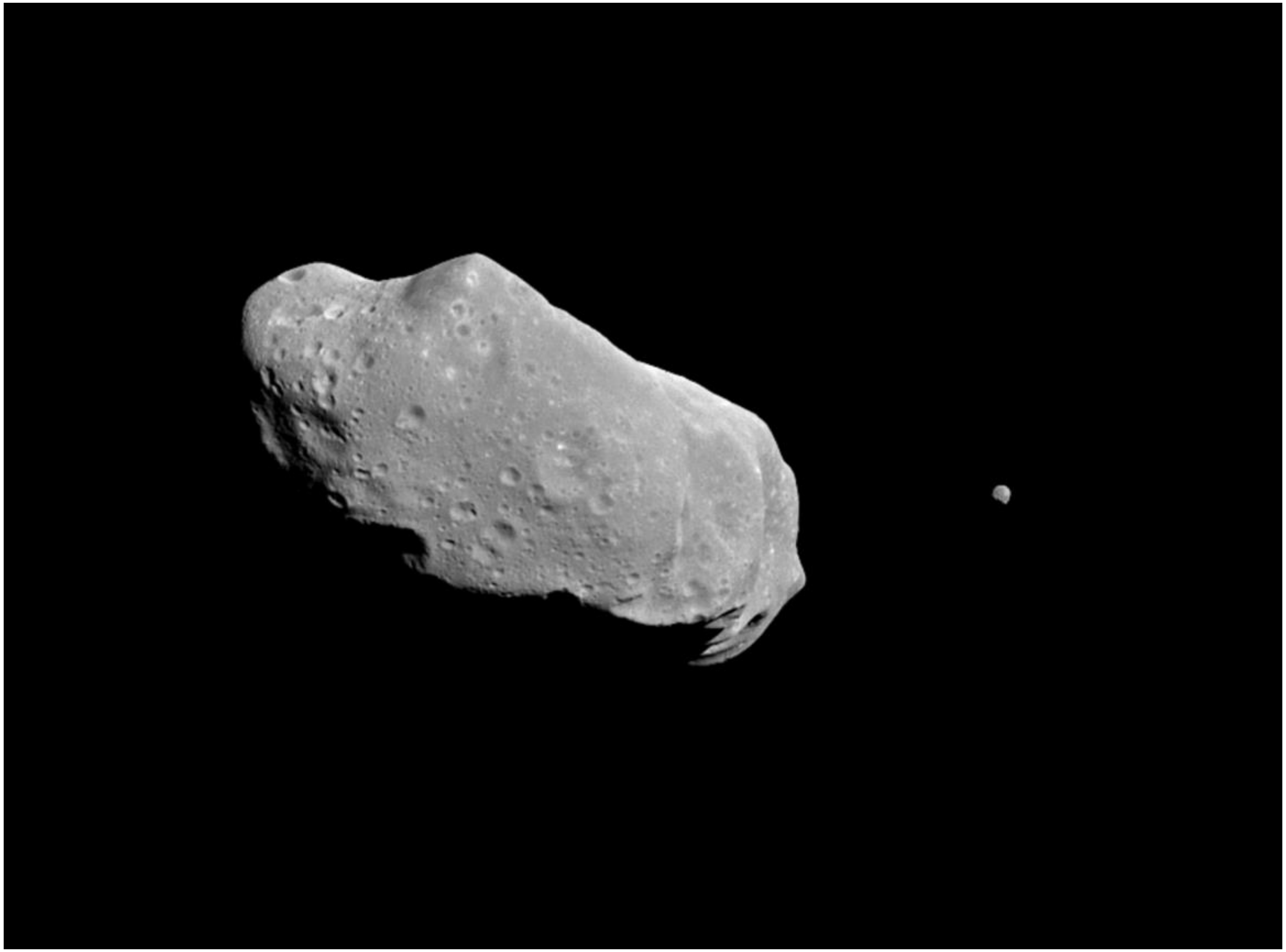
Comet: a small frozen mass that orbits sun

Planetesimals accreted to form the Earth

Meteorite bombardment over 500 million years aided Earth’s growth.

Meteorite: Solid mineral or rock that reaches a planet’s surface without vaporizing.

Asteroid Ida and its Moon, Dactyl



Meteorite Impacts

Meteorites contained rock-forming elements (Mg, Si, Fe, Al, Ca, Na, Ni) that condensed in solar nebula and noncondensable elements (H, He, O, C, Ne, N, S, Ar, P).

How did noncondensable elements enter meteorites?

They chemically reacted as gases to form high molecular-weight compounds that condensed.

Upon impact with Earth, some noncondensable elements (volatiles) evaporated (volatilized) on impact. Others have volatilized over time and have been outgassed through volcanos, fumaroles, steam wells, geysers.

Composition of Stony Meteorites, Total Earth, and Earth's Crust

	<---- Mass percent of element in			--->
Element	Stony Meteorites	Total Earth	Soil Crust	Ocean Crust
Oxygen	33.24	29.50	46.6	45.4
Iron	27.24	34.60	5.0	6.4
Silicon	17.10	15.20	27.2	22.8
Magnesium	14.29	12.70	2.1	4.1
Sulfur	1.93	1.93	0.026	0.026
Nickel	1.64	2.39	0.075	0.075
Calcium	1.27	1.13	3.6	8.8
Aluminum	1.22	1.09	8.1	8.7
Sodium	0.64	0.57	2.8	1.9

Table 2.2

Formation of the Earth's Crust

4.5-4 bya, Earth's core hotter than today. Only mechanism of energy escape was conduction (transfer of energy molecule to molecule).

Because conduction is slow, internal energy could not dissipate, so entire Earth became molten and surface was magma ocean.

At that point, energy could be transferred to the surface by convection, the mass movement of molecules.

Convection allowed energy release and cooling at the surface, forming the Earth's crust 4.3-3.8 bya.

Dense elements (Fe, Ni) settled to core. Light ones (Si, Al, Na, Ca) rose to surface. Certain Mg, Fe silicates settled to mantle.

Today, land crust granite (quartz, potassium feldspar). Ocean crust basalt (plagioclase feldspar, pyroxene). Outer core liquid Fe, Ni; inner core solid Fe, Ni

The Earth's Interior

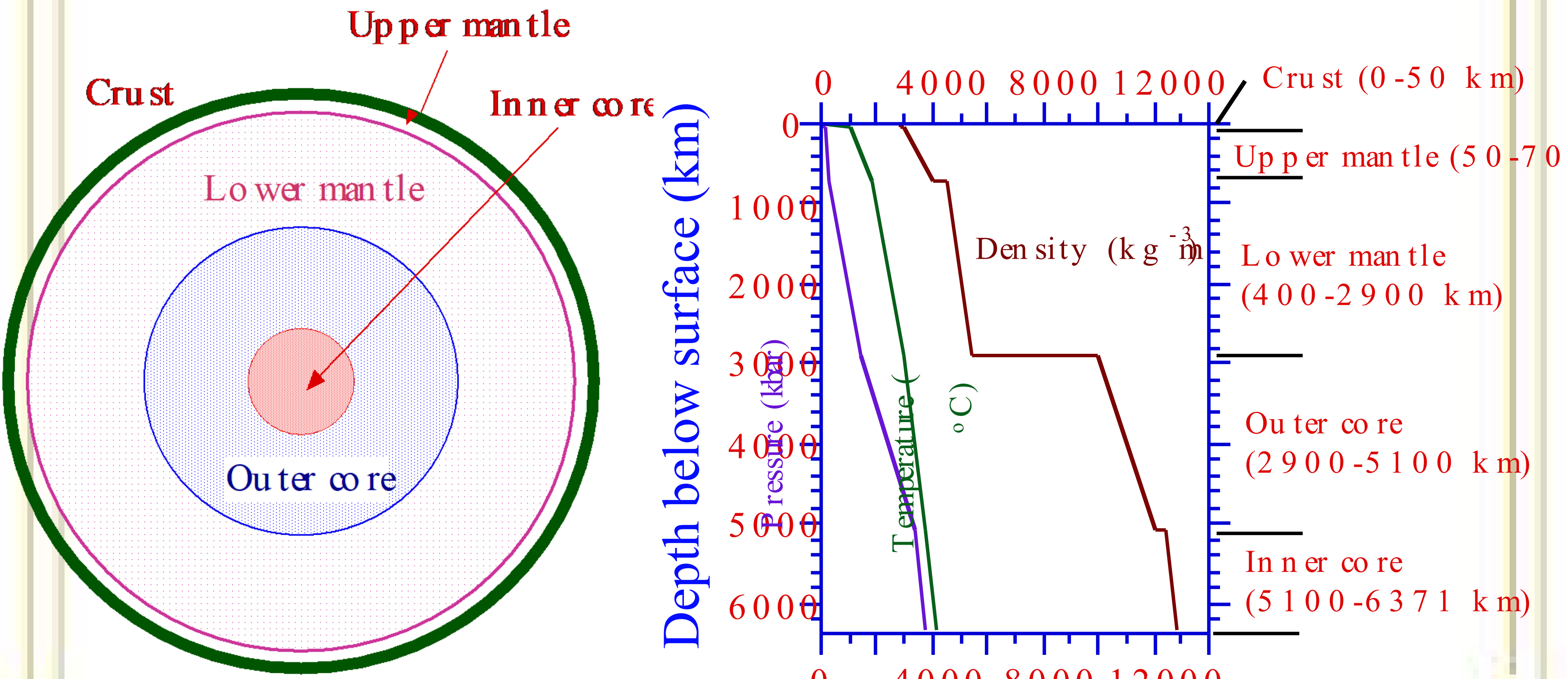


Figure 2.7

Earth's First Atmosphere

Consisted mostly of H, He

During birth of the Sun, nuclear reactions are enhanced, increasing solar wind speeds and densities (T-Tauri stage of solar evolution).

Enhanced solar wind stripped off most H, He from the Earth.

Additional H, He lost by escape from Earth's gravitational field.

Earth's Second Atmosphere

Initially due to outgassing by volcanos, fumaroles, steam wells, geysers.

Hydroxyl molecules (OH) bound in crustal minerals, became detached and converted reduced gases to oxidized gases:

$H_2(g)$ + OH --> … --> $H_2O(g)$

$CH_4(g)$ + OH --> …. --> $CO_2(g)$

$NH_3(g)$ + OH -->…--> NO(g), $NO_2(g)$

$N_2(g)$ + OH -->…--> NO(g), $NO_2(g)$

$H_2S(g)$ + OH -->…--> $SO_2(g)$

Second atmosphere dominated initially by $CO_2(g)$, $H_2(g)$

Outgassed water vapor condensed to form the oceans.

Timeline of Earth's Evolution

4.6 bya	Formation of the Earth
3.5 bya	Abiotic synthesis, 1953 Miller and Urey

$H_2(g)+H_2O(g)+CH_4(g)+NH_3(g)+H_2O(aq)+$ electricity or UV --> complex organics, amino acids

--> first prokaryotes

single strand of DNA but no nucleus

conventional heterotrophs

Classification of Organisms

Energy Source	
Sunlight	Phototroph
Oxidation of inorganic material	Lithotroph
Oxidation of organic material	Conventional heterotroph
Carbon source	
Carbon dioxide	Autotroph
Organic material	Heterotroph

*Conventional heterotrophs obtain
Energy and carbon from organic material

Table 2.3

Classification of Organisms

Photoautotrophs

- Green plants, most algae, cyanobacteria, some purple and green bacteria

Photoheterotrophs

- Some algae, most purple and green bacteria, some cyanobacteria

Lithotrophic autotrophs

- Hydrogen bacteria, colorless sulfur bacteria, methanogenic bacteria, nitrifying bacteria, iron bacteria

Lithotrophic heterotrophs

- Some colorless sulfur bacteria

Conventional heterotrophs

- Animals, fungi, protozoa, most bacteria

Table 2.4

Hot Sulfur Springs in Lassen National Park

Lithotrophic autotrophs oxidize H_2S(aq) to H_2SO_4(aq), which dissolves minerals into a “mud pot.” Alfred Spormann, Stanford University

CO_2(g) and CH_4(g) From Bacteria

Anaerobic respiration: production of energy from food where electron acceptor is not oxygen.

CO_2(g) by fermentation (2.3)

$$C_6H_{12}O_6(aq) \longrightarrow 2\,C_2H_5OH(aq) + 2\,CO_2(g)$$

Glucose — Ethanol — Carbon dioxide

CH_4(g) by methanogenesis (lithotrophic autotrophs) (2.4)

$$4\,H_2(g) + CO_2(g) \longrightarrow CH_4(g) + 2H_2O(aq)$$

Molecular hydrogen — Carbon dioxide — Methane — Liquid water

Evolution of Molecular Nitrogen

4.6 bya — $N_2(g)$ by ammonia photolysis — (2.5-2.6)

$$NH_3(g) + h\nu \longrightarrow N(g) + 3H$$

Ammonia → Atomic nitrogen + Atomic hydrog

$$N(g) + N(g) \xrightarrow{M} N_2(g)$$

Atomic nitrogen → Molecula nitrogen

Evolution of Molecular Nitrogen

3.2 bya Denitrification: 2-step process

N_2(g) by anaerobic respiration (2.7-2.8)

(conventional heterotrophs)

$$\text{Organic compound} + NO_3^- \rightarrow CO_2(g) + NO_2^- +$$

Nitrate ion → Carbon dioxide, Nitrite ion

$$\text{Organic compound} + NO_2^- \rightarrow CO_2(g) + N_2(g) +$$

Nitrite ion → Carbon dioxide, Molecular nitrogen

Photosynthesis

Anoxygenic photosynthesis (photoautotrophs) (2.9)

$$CO_2(g) + 2H_2S(g) + h\nu \longrightarrow CH_2O(aq) + H_2O(aq) + 2S($$

Carbon dioxide, Hydrogen sulfide → Carbo-hydrate, Liquid water, Atomic sulfur

2.3 bya Oxygenic photosynthesis (cyanobacteria) (2.10)

1.4 bya Oxygen levels still 1% of today

0.395-0.43 bya Green plant photosynthesis

$$6CO_2(g) + 6H_2O(aq) + h\nu \longrightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

Carbon dioxide, Liquid water → Glucose, Molecul oxygen

Photsynthesis in chlorophylls *a*,*b* :pigments that absorb visible

Chlorophyll *a*. Absorbs red more efficiently

Chlorophyll *b*. Absorbs blue more efficiently

Hot Spring in Yellowstone National Park

Different colored photosynthetic cyanobacteria grow at in hot spring due to different temperatures. Alfred Spormann, Stanford University

Aerobic Respiration

$O_2(g)$ reacts with organic cell material to produce energy during cellular respiration, which is oxidation of organics in living cells.

$$C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(aq) \quad (2.12)$$

Glucose — Molecular oxygen — Carbon dioxide — Liquid water

Aerobic respiration developed first in prokaryotes (bacteria, blue-green algae), but spread with the advent of eukaryotes.

Eukaryote. Cell containing DNA surrounded by a true membrane-enclosed nucleus. Cells of higher organisms all eukaryotic.

Eukaryotic cells usually switch from fermentation to aerobic respiration when oxygen reaches 1% of present levels --> Eukaryotes developed about 1.4 bya, after oxygen rose to 1%

Timeline of Earth's Evolution

4.6 bya	Formation of the Earth
3.5 bya	Abiotic synthesis,
3.2 bya	Denitrification
2.3 bya	Oxygen-producing photosynthesis by cyanobacteria
	Start of ozone formation
1.8 bya	Nitrification (aerobic)
1.5 bya	Nitrogen fixation (aerobic)
1.4 bya	Earliest eukaryotes
0.57 bya	First shelled invertebrates
0.43-0.5 bya	Primitive fish
0.395-0.43 bya	First land plants -- oxygen and ozone increase

Figure 2.8

The Nitrogen Cycle

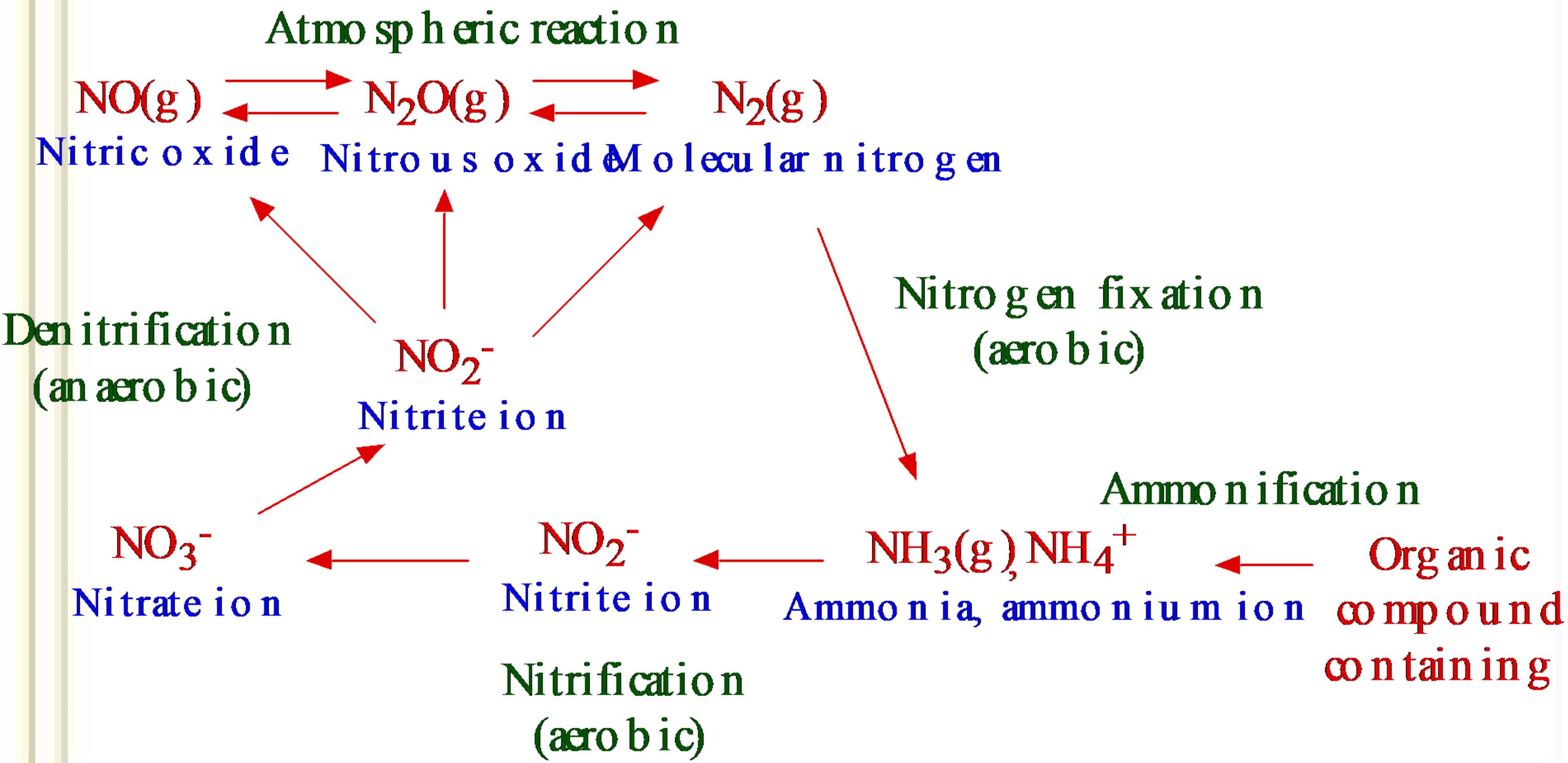


Figure 2.11

Evolution of the Earth's Second Atmosphere

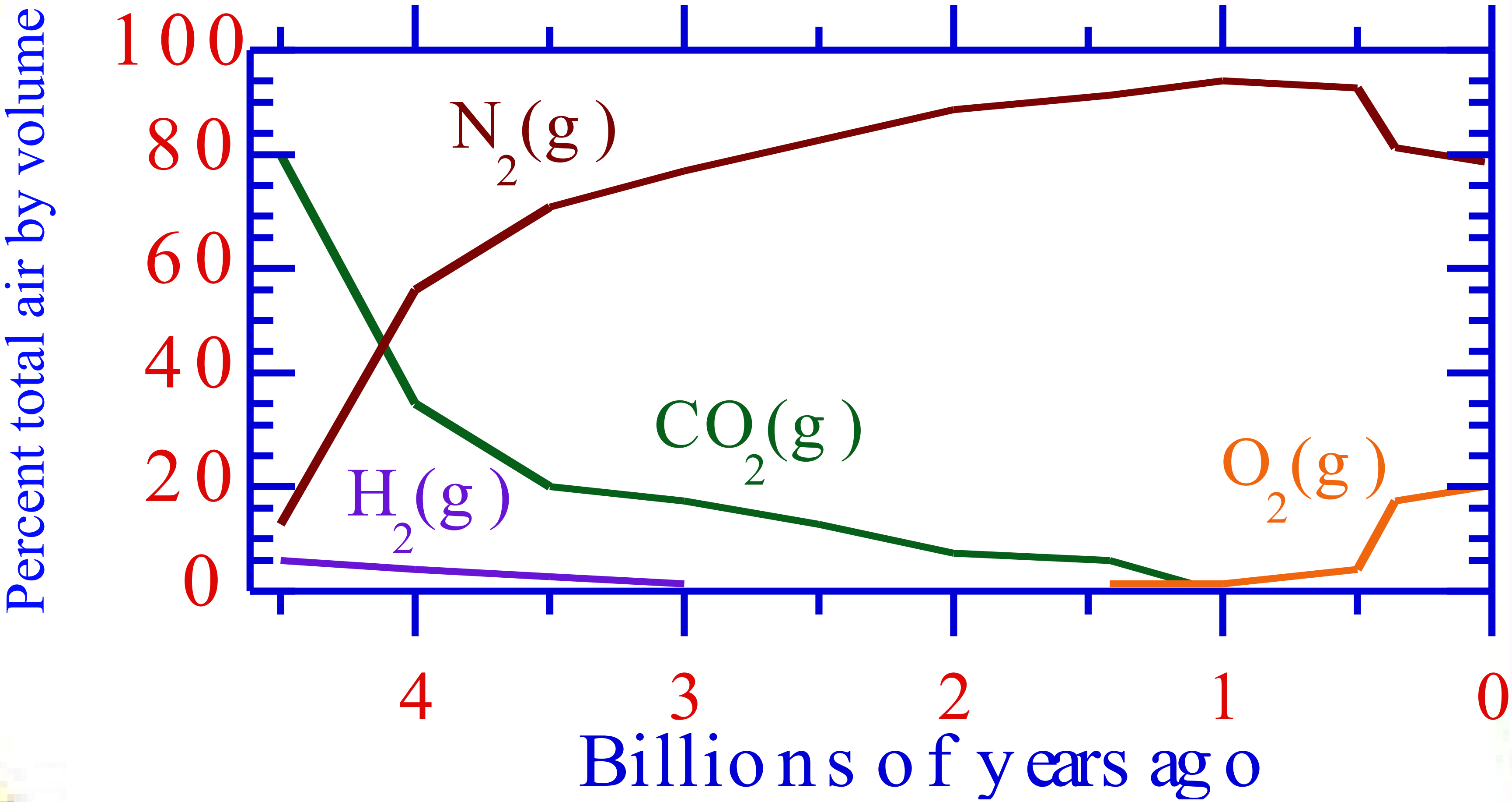


Figure 2.12