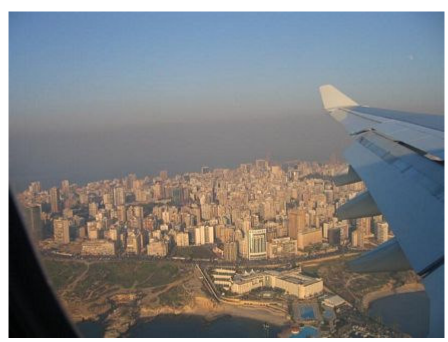
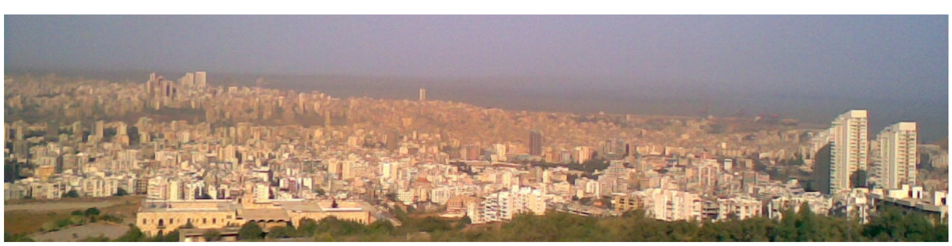
The Earth's Atmosphere

Environmental Chemistry, vanLoon & Duffy – Chapter 2

Houssam El-Rassy, PhD
Assistant Professor
Department of Chemistry, Room 520
Ext. 4051 , E-mail: Houssam.Rassy@aub.edu.lb



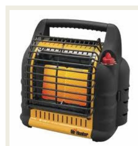


The atmosphere is the environmental compartment which is shared most obviously by mankind.

Air pollution doesn't stop at any border.

The individual *right to pollute* is not questioned in many places:

- our cars.
- our heaters.
- incinerators, power plants, industrial facilities.



The costs of air pollution are charged to the public.

AUB The Atmosphere - The Air We Breath

Mean composition of dry air in the troposphere	volume content in %	ppm (parts per million)
nitrogen	78.08	780 800
oxygen	20.95	209 500
argon	0.934	9 340
carbon dioxide	0.035	350
neon	0.0018	18
helium	0.0005	5
methane	0.00017	1.7
krypton	0.0001	1
xenon	0.000009	0.09
hydrogen	0.00005	0.5
dinitrogen monoxide	0.00003	0.3
carbon monoxide*	0.00002	0.2

* carbon monoxide shows periodic changes

AUB

The Nobel Prize in Chemistry - 1995

KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

Paul J. Cruzen

Mario J. Molina

F. Sherwood Rowland

Press Release

11 October 1995

The Royal Swedish Academy of Sciences has decided to award the 1995 Nobel Prize in Chemistry to
Professor Paul Crutzen, Max-Planck-Institute for Chemistry, Mainz, Germany (Dutch citizen),
Professor Mario Molina, Department of Earth, Atmospheric and Planetary Sciences and Department of Chemistry, MIT, Cambridge, MA, USA and
Professor F. Sherwood Rowland, Department of Chemistry, University of California, Irvine, CA, USA

for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone.

AUB

The Nobel Prize in Chemistry - 1995

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Press Release

"… *Paul Crutzen, Mario Molina* and *Sherwood Rowland* have all made pioneering contributions to explaining how ozone is formed and decomposes through chemical processes in the atmosphere. Most importantly, they have in this way showed how sensitive the ozone layer is to the influence of anthropo-genic emissions of certain compounds. The thin ozone layer has proved to be an *Achilles heel** that may be seriously injured by apparently moderate changes in the composition of the atmosphere.

… By explaining the chemical mechanisms that affect the thickness of the ozone layer, the three researchers have contributed to our salvation from a global environmental problem that could have catastrophic consequences."

* Achilles' heel: A seemingly small but mortal weakness. [From Achilles' being vulnerable only in the heel.]

International Meetings

Stockholm Summit 1972

United Nations Summit on the Human Environment

United Nations Environment Programme

Programme des Nations Unies pour l'environnement

Rio Earth Summit 1992

Local, national and international action

New York 1997

World Summit on Sustainable Development Johannesburg 2002

COP15 COPENHAGEN

UN CLIMATE CHANGE CONFERENCE 2009

COP16 CMP6 Mexico2010

United Nations Climate Change Conference

COP 17-CMP 7 DURBAN 2011

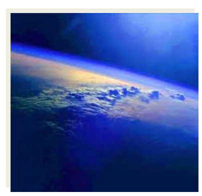
United Nations Conference on Climate Change

RIO+20

United Nations Conference on Sustainable Development

The Atmosphere

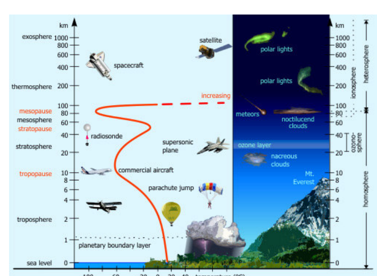
The atmosphere is a thin blanket of gas that envelops the earth.



The gases that make up the atmosphere are held close to the earth by the pull of gravity.

With increasing distance from the earth's surface, the temperature, density, and composition of the atmosphere gradually change.

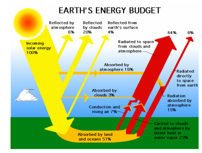
On the basis of air temperature, the atmosphere can be divided vertically into four major layers.



Functions of the Atmosphere

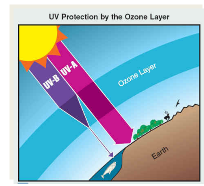
GLOBAL ENERGY BALANCE and ENERGY DISTRIBUTION

- Maintains global climate and weather



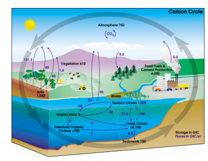
RADIATION SHIELD

- Filters UV radiation in the upper atmosphere ("ozone layer")



RESERVOIR in BIOGEOCHEMICAL CYCLES

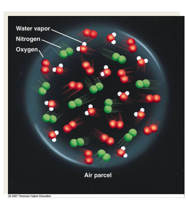
- Mobile reservoir for nitrogen, oxygen, carbon (as CO_2), sulphur, water

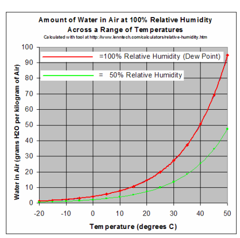


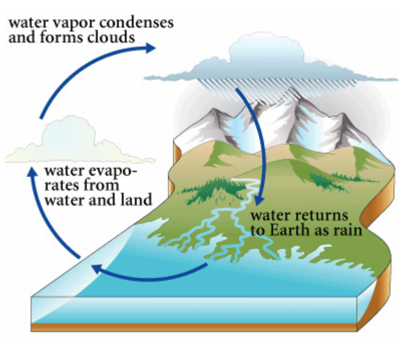
GEOLOGICAL WEATHERING of the EARTH'S SURFACE

- Drives the weathering/sedimentary cycle

Water vapor in the air

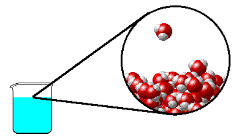






The % volume of Water vapor is variable, depending on temperature, precipitation, rate of evaporation and other factors at a particular location.

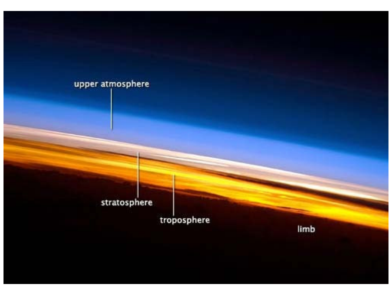
The percentage of water vapor ranges from 0.1-5%. Generally it is 1-3% (the 3rd most abundant constituents in the air). It might not exceed the vapor pressure of liquid water at temperature T

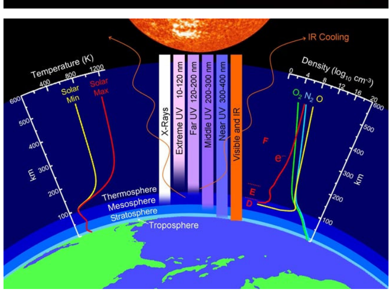


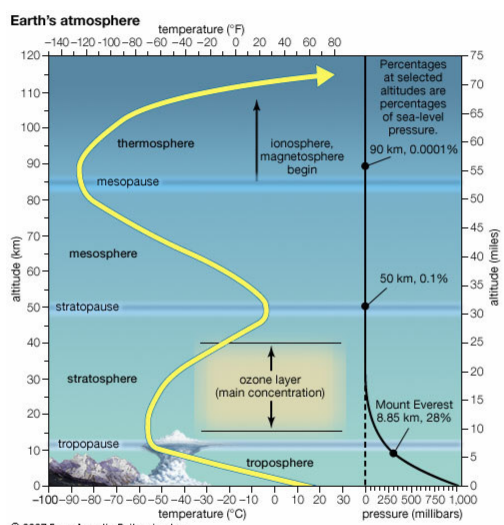
Typical mixing ratios for other gases of environmental importance

Carbon dioxide	355 ppm
Carbon monoxide	100 ppb to 20 ppm
Ozone	1 to 100 ppb
Methane	1.72 ppm
Nonmethane hydrocarbon	1 ppt to < 1 ppb
Nitric oxide (NO)	5 ppt to 1 ppb
Nitrogen dioxide (NO_2)	1 to 150 ppb
Nitrous oxide (N_2O)	310 ppb
Sulfur dioxide	1 t o 100 ppb
$CFCl_3$ (Freon 11)	200 ppt
CF_2Cl_2 (Freon 12)	350 ppt

Regions of the Atmosphere







Troposphere

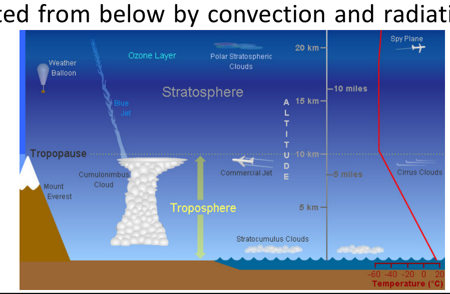
The troposphere is the layer from the earth's surface to the tropopause, which is at 10-15 km altitude depending on latitude and time of year (Mt. Everest 8.85km).

As altitude increases, air temperature decreases at a rate of about 3.5° per 1000 ft. The tropopause has a temperature of about –57°C.

The lower part of the troposphere interacts directly with the surface of the earth – this part of the troposphere is generally called "air".

The atmosphere in this layer is heated from below by convection and radiation from the earth's surface.

Most of our weather occurs in the troposphere.



Troposphere

Depending on the geographic situation the Troposphere is exposed to special conditions

Location	**Characteristics**
Oceans	Sea salt aerosol (Na^+, Ca^{++}, Mg^{++}, Cl^-, SO_4^{2-})
Dry Land	Airborne dust related to soil, plant pollen
Urban	smoke, dust, primary & secondary smog, chemicals
Arid tropics	Low humidity intense solar radiation
Humid tropics	High humidity, natural volatile compounds, intense solar radiation
Arctic	Sunlight period variable, *Arctic haze,* sulfate, aerosols, soot, metals

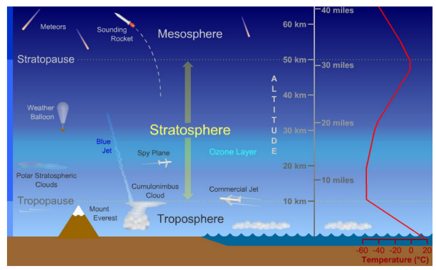
Stratosphere

The stratosphere is the layer above the troposphere and extends to about 50 km.

The temperature rises with increasing altitude, reaching a maximum of about –1°C at the stratopause.

The ozone layer is in the stratosphere. Ozone absorbs UV, causing the rising temperature with altitude in this layer.

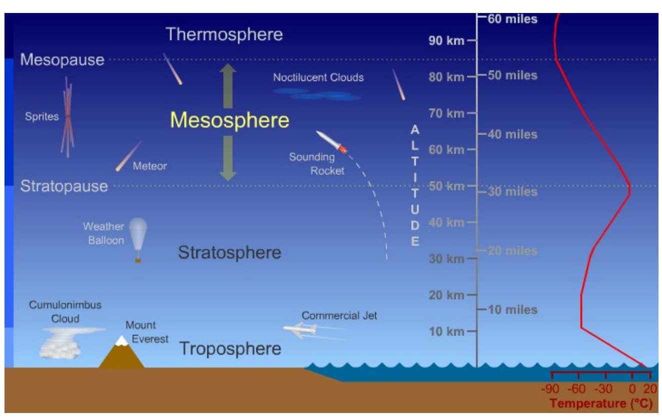
The temperature structure keeps the air calm in this layer. (That's why jet aircraft fly in the lower stratosphere!)



Mesosphere

The mesosphere extends from the top of stratopause to ~80 km.

In the mesosphere, the temperature decreases with altitude.



Thermosphere

The layer of air above mesosphere is called thermosphere.

In the thermosphere, temperature rises with altitude, caused by absorption of UV solar radiation by N_2 and O_2 gas.

This is an image of the space shuttle as it is orbiting around the Earth. The space shuttle orbits in the thermosphere of the Earth. (*Image from NASA)*

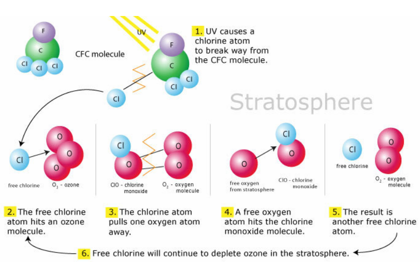
The Lower Atmosphere

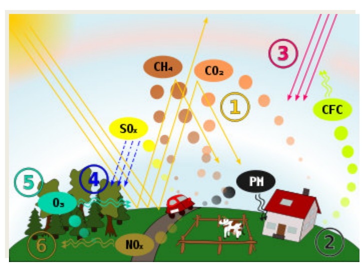
The ***troposphere*** and the ***stratosphere*** together are called the lower atmosphere.

The lower atmosphere account for *99.9%* of total atmospheric mass.

The lower atmosphere is the domain of main interest from an environmental perspective.

- Ozone depletion (stratosphere)
- Air pollution (troposphere)

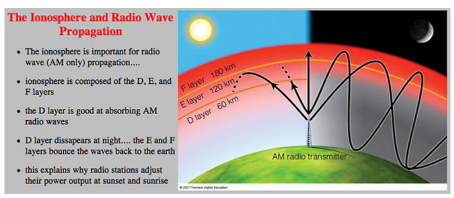


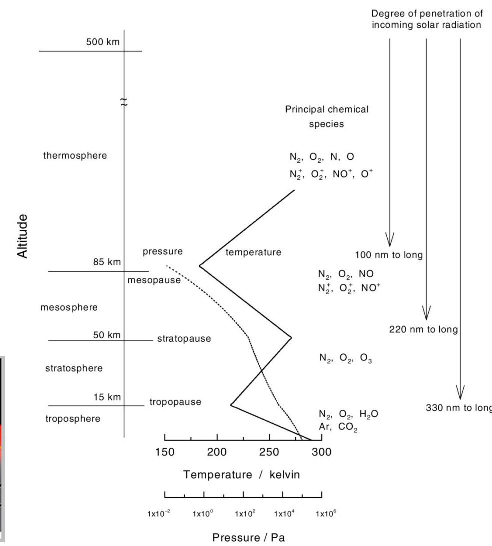


Ionosphere

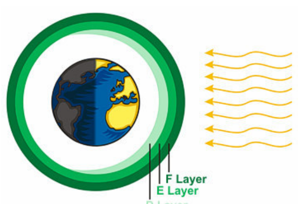
The ionosphere is a part of the upper atmosphere, comprising portions of the mesosphere, thermosphere and exosphere, distinguished because it is ionized by solar radiation.

Ionosphere is a region where ions and electrons are most abundant.

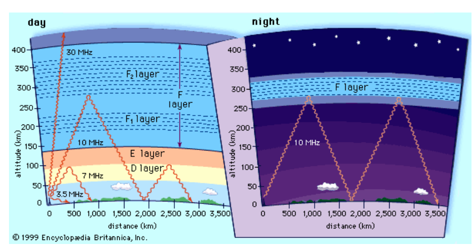


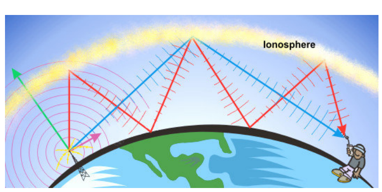


Ionosphere



The Ionosphere acts as a conducting layer in the upper atmosphere that would allow a transmitted electromagnetic signal to be reflected back toward the Earth.





Aurora Borealis above Bear Lake - Alaska

Layers of the Atmosphere

The importance of the Atmosphere as a protective shield of the global ecosystem is fully appreciated today.

The *Nobel-Prize Committee* awarded this most recognized prize to *Paul Crutzen, Mario Molina* and *Sherwood Rowland for their contribution to Ozone-Chemistry.*

The atmosphere shows a discrete vertical zones. The layers are separated by 'pauses', zones where the temperature changes remarkably.

The so called lower Atmosphere, i.e. the Troposphere & the Stratosphere contains about 99.9% of the atmospheric gases.

Expressing the amount of substances in the atmosphere

Concentration

- the amount (mass, moles, molecules, etc) of a substance in a given volume divided by that volume.
- The example concentration units are mg/m^3, mol/m^3, molecules/cc, etc...

Mixing ratio

- the ratio of the amount of the substance in a given volume to the total amount of all constituents in that volume.

Mixing Ratio

$$\zeta_i = \frac{n_i}{n_{total}}$$

n_i is the molar concentration of *i*

n_{total} is the total molar concentration of all constituents

parts per million (ppm) 10^{-6} µmol mol^{-1}

parts per billion (ppb) 10^{-9} nmol mol^{-1}

parts per trillion (ppt) 10^{-12} pmol mol^{-1}

$$\zeta_i(ppm) = 10^6 \cdot \frac{n_i}{n_{total}}$$

Conversion between ppm(v) and µg/m³

$$n_i = \frac{10^{-6} m_i}{M_i}$$

$$n_{total} = \frac{N}{V} = \frac{P}{RT}$$

$$\text{mixing ratio in ppm} = 10^6 \frac{n_i}{n_{total}} = 10^6 \frac{10^{-6}\frac{m_i}{M_i}}{\frac{P}{RT}} = \frac{RT}{PM_i} m_i$$

$$= \frac{RT}{PM_i} \cdot \text{Conc. in µg/m}^3$$

Definitions:

n_i: mol/m³

m_i: µg/m³

M_i: g/mol

P= 1.01325×10^5 Pascal

R= 8.314 J/K.mol for P in Pa and volume in m³

Conversion between ppm(v) and µg/m³

Example:

The Hong Kong Air Quality Objective for ozone is 240 µg/m³. The U.S. National Ambient Air Quality Standard for ozone is 120 ppb. Which standard is stricter at the same temperature (25°C) and the pressure (1atm)?

$$\text{mixing ratio in ppm} = 10^6 \frac{n_i}{n_{total}} \qquad = \frac{RT}{PM_i} \cdot \text{Conc. in } \mu\text{g/m}^3$$

Use the figures from the example:

$$= \frac{8.314 \cdot 298}{1.01325 \cdot 10^5 \cdot 48} \cdot 240\ \mu g/m^3 = 0.122\, ppm = 122\, ppb$$

ppm in solution vs. ppm as mixing ratio for airborne substances

Air:

$$\zeta_i = \frac{\text{mole of species i}}{\text{mole of air molecules}}$$

Solution:

$$C_i(ppm) = \frac{\text{weight of species i}}{\text{weight of solution}} \cdot 10^6$$

The density of dilute aqueous solutions is nearly the density of water, so we can apply weight of solution or volume of solution
1 kg dilute aqueous solution = 1000 mL
thus 1mg of substance per liter = 1 ppm