Atmospheric Physics

Lecture 9

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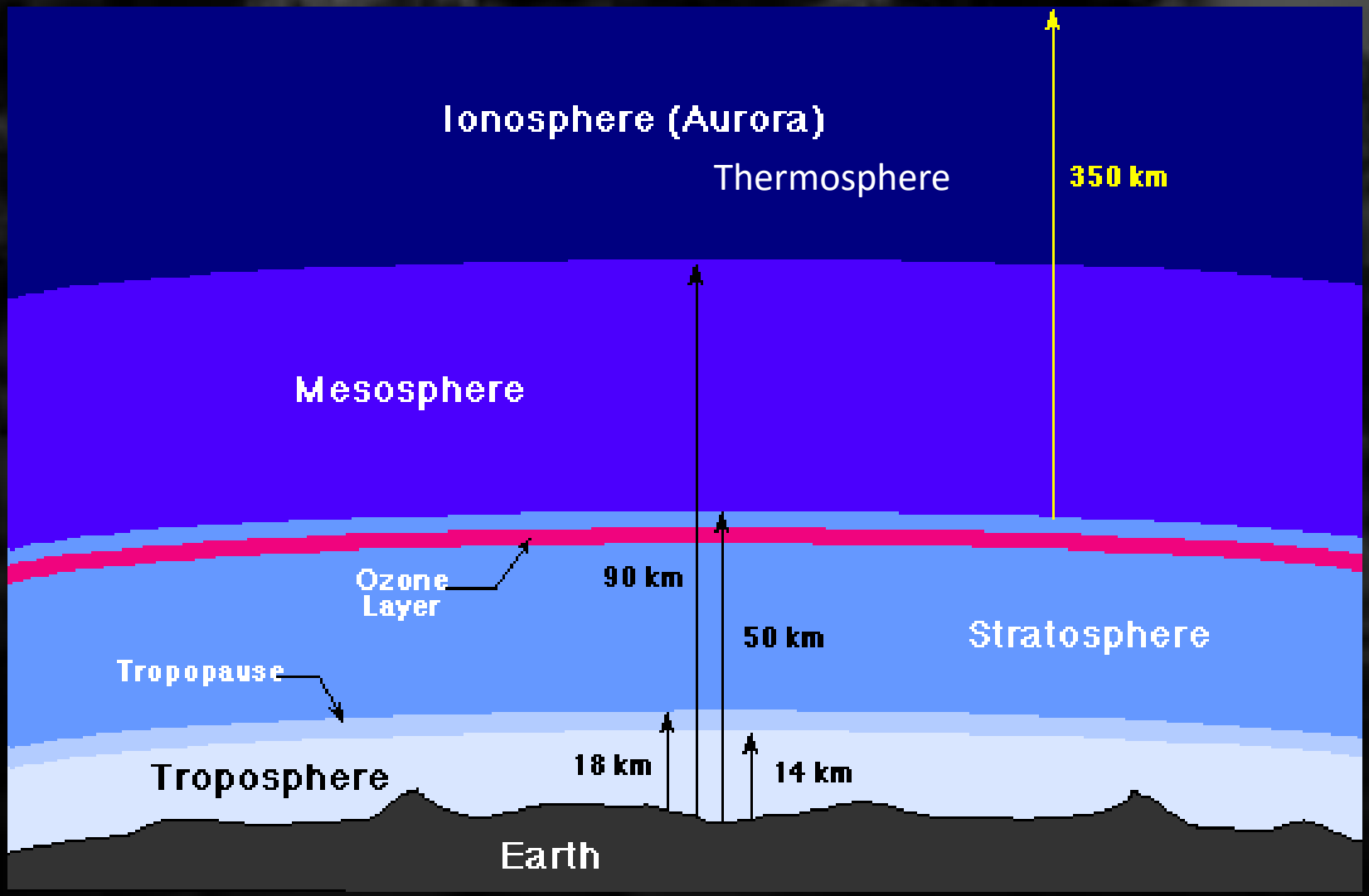
STRUCTURE OF THE ATMOSPHERE

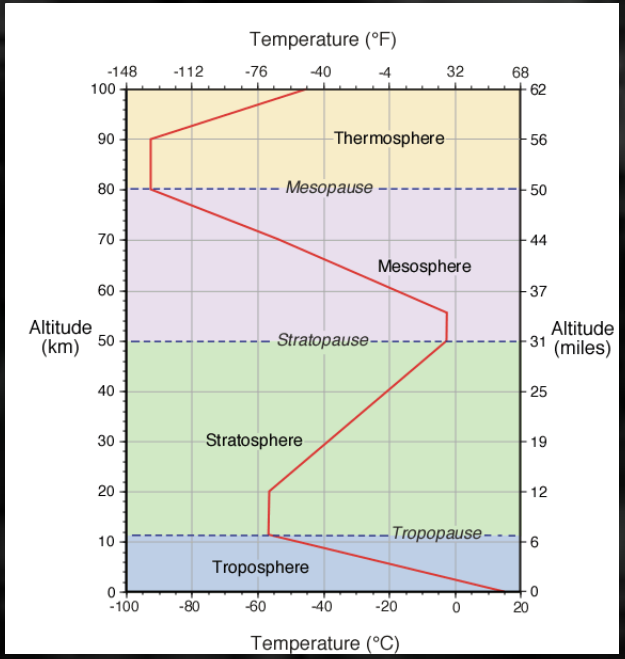


Layer Two (Stratosphere)

In the stratosphere (12 km - 50 km) the temperature increases with altitude from -55 °C to -2 °C.

Ozone layer found in the stratosphere

Ozone is a gas that absorbs harmful UV rays and protects us from too much solar radiation. Pollution has created a hole in the Ozone layer over the South Pole.



Ozone

Ozone is a natural gas that is found in two different layers of the atmosphere.

Ozone is very rare in our atmosphere

Ozone making up only one part in three million of all gases in the atmosphere.

In spite of this small amount, ozone plays a vital role in the atmosphere

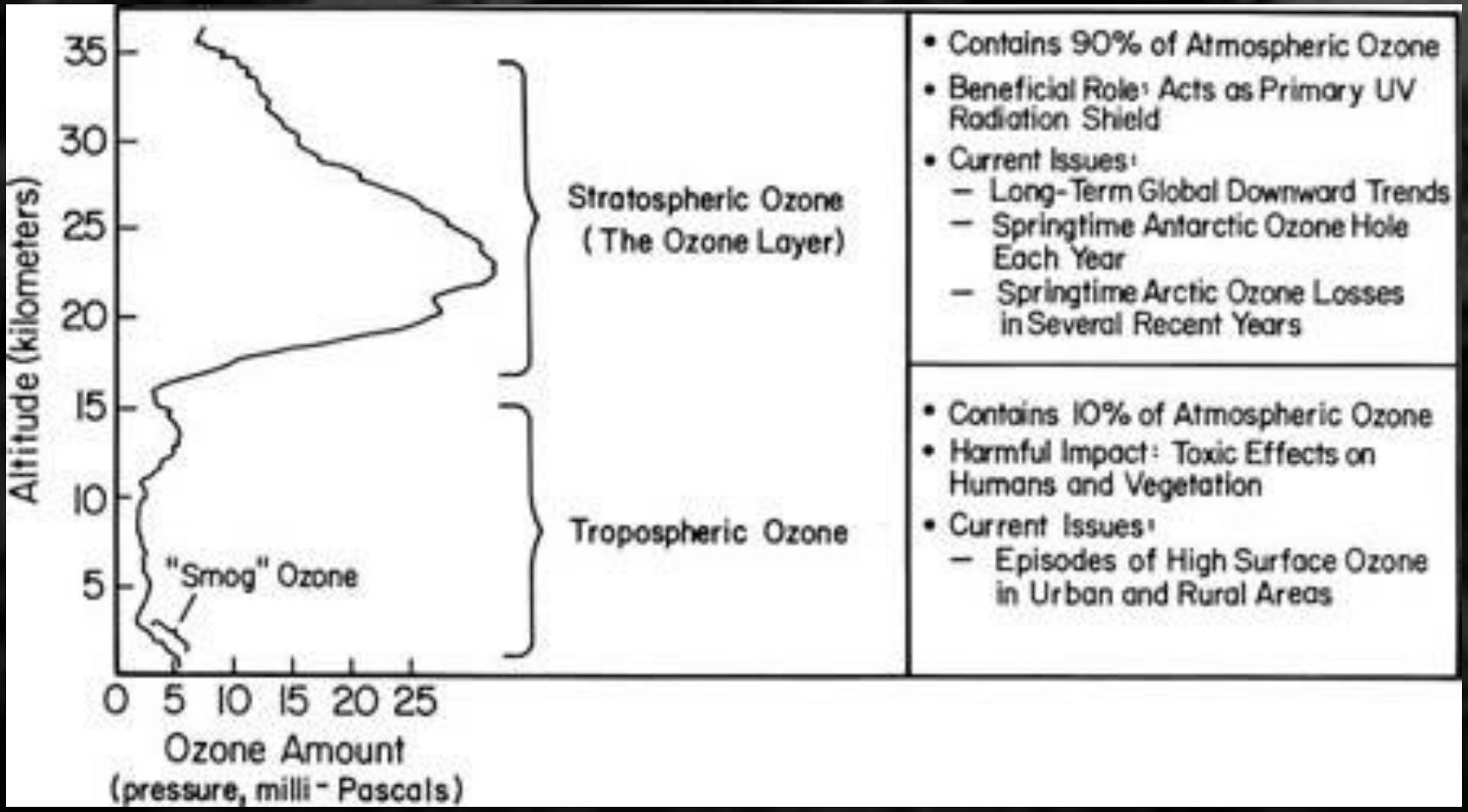
STRATOSPHERIC OZONE -- "Good"

Absorbs damaging solar UV radiation which is carcinogenic.

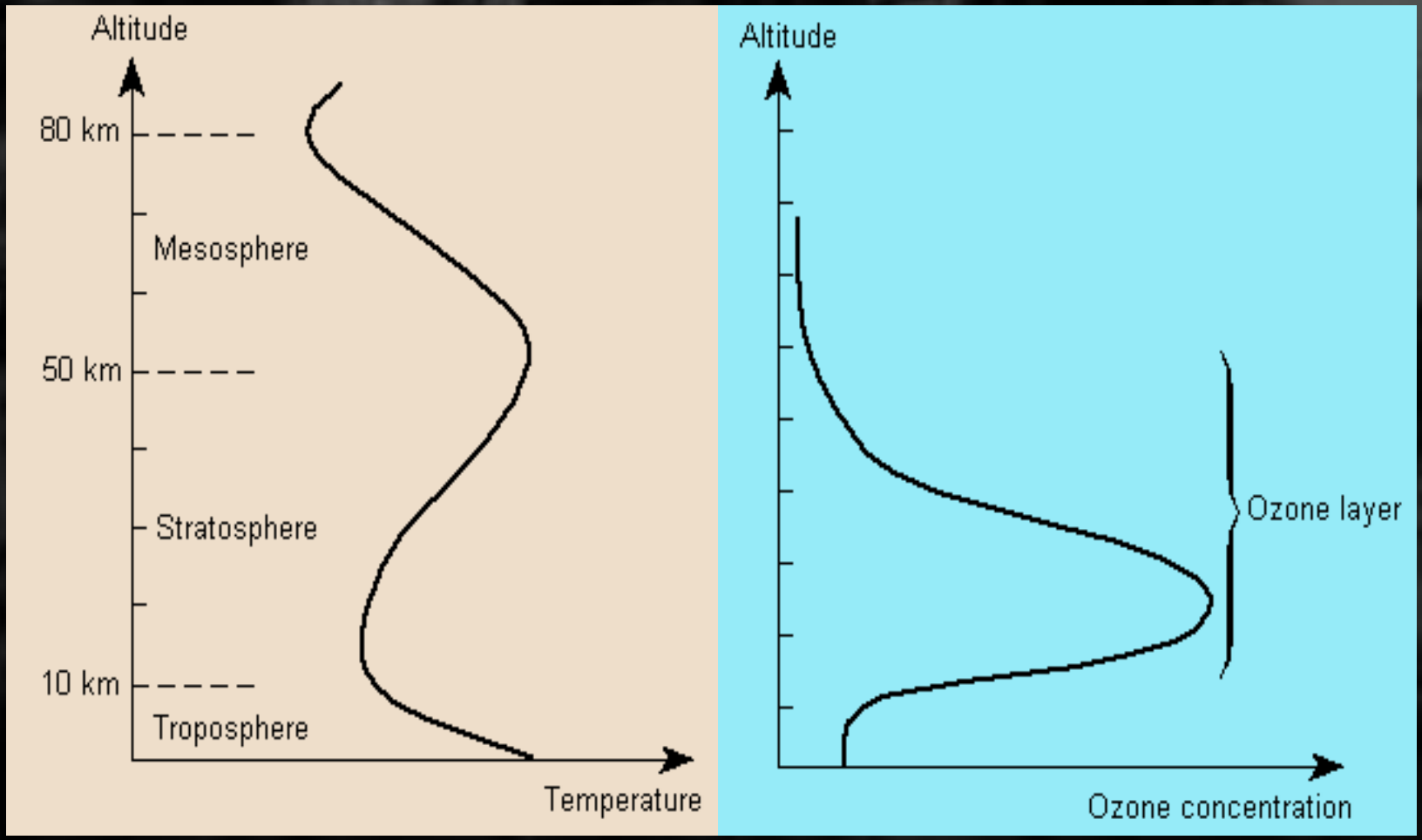
protective in the upper atmosphere O_3 is a filter for the most energetic and harmful UV radiation

Protects life on earth.

Depletion of ozone is <u>not</u> the cause of global warming.


Altitude (kilometers)
35
30
25
20
15
10
5
"Smog" Ozone
Stratospheric Ozone
(The Ozone Layer)
Tropospheric Ozone
0 5 10 15 20 25
Ozone Amount
(pressure, milli - Pascals)
• Contains 90% of Atmospheric Ozone
• Beneficial Role: Acts as Primary UV Radiation Shield
• Current Issues:
– Long-Term Global Downward Trends
– Springtime Antarctic Ozone Hole Each Year
– Springtime Arctic Ozone Losses in Several Recent Years
• Contains 10% of Atmospheric Ozone
• Harmful Impact: Toxic Effects on Humans and Vegetation
• Current Issues:
– Episodes of High Surface Ozone in Urban and Rural Areas

The Stratospheric Ozone Layer



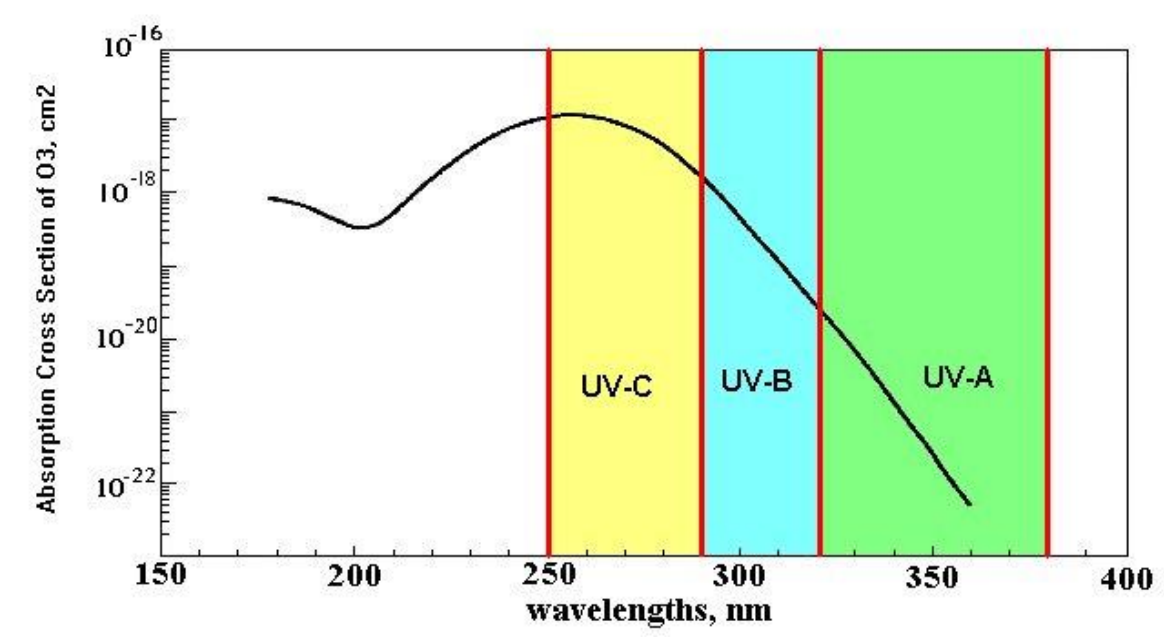
Most of the ozone is present in the stratosphere (maximum ozone concentration at an altitude of 25 km).

UV radiation regions

UV-A: 320 nm < λ< 380 nm

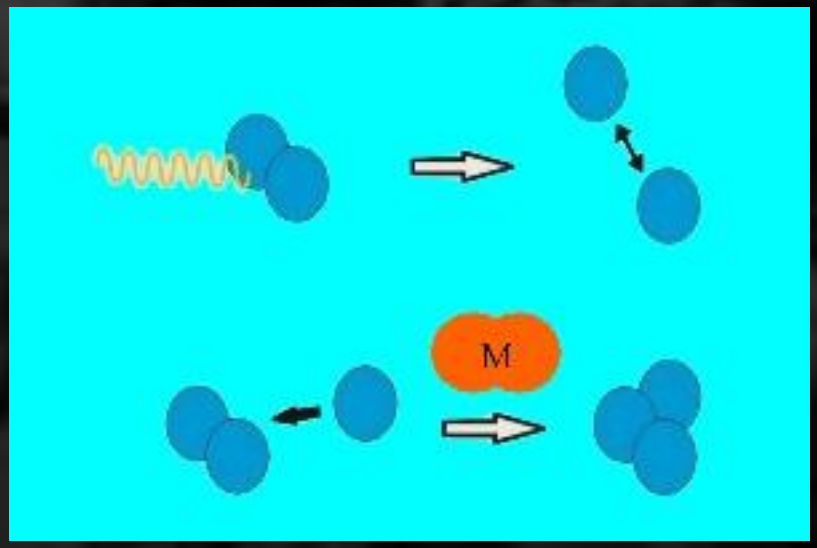
UV-B: 290 nm < λ < 320 nm

UV-C: 250 nm < λ < 290 nm



Ozone formation

The formation of ozone in the atmosphere depends on the presence of $O(g)$



$$O_2(g) + UV_C \rightarrow O(g) + O(g)$$

$$O(g) + O_2(g) \rightarrow O_3(g) + M^*(g) \text{ (heat released)}$$

Ozone absorbs photons with a B wavelength

$$O_3(g) + UV_B \rightarrow O_2(g) + O(g)$$

$$O(g) + O(g) + M^*(g) \rightarrow O_2(g) + M^*(g) \text{ (heat released)}$$

The oxygen atoms can collide with oxygen molecules to form ozone with excess energy, O_3^*:

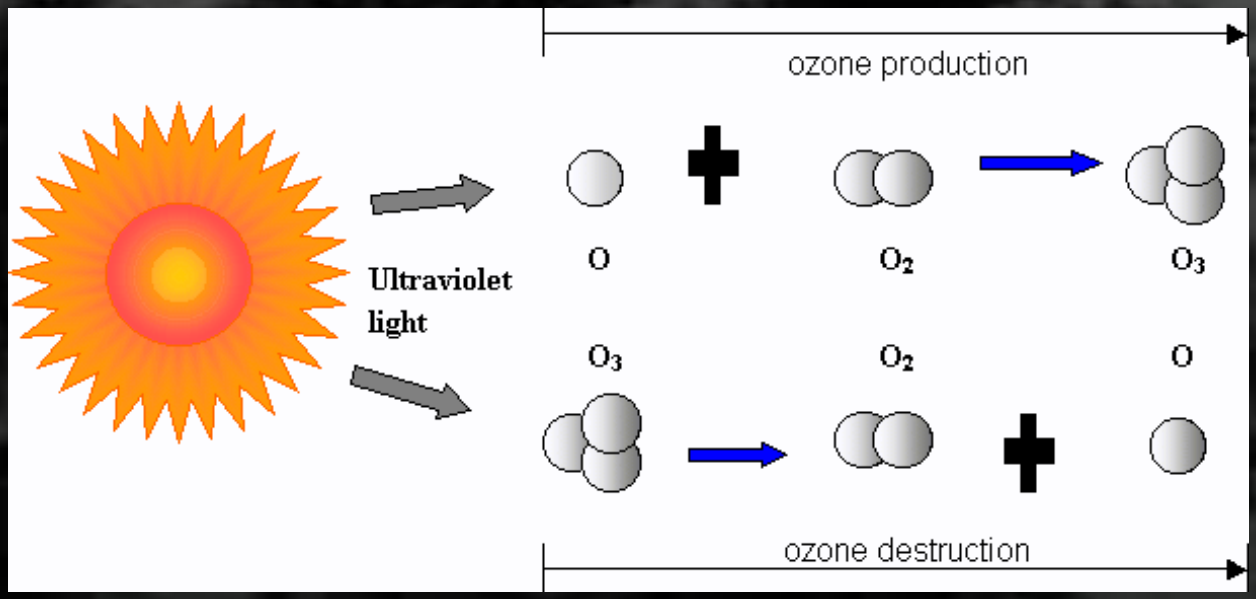
$$O(g) + O_2(g) \rightarrow O_3^*(g) \text{ (105kJ/mol)}$$

The excited ozone can loose energy by decomposing to oxygen atoms and oxygen molecules (the reverse reaction) or by transferring the energy to M (usually N_2 or O_2):

$$O_3^*(g) + M(g) \rightarrow O_3(g) + M^*(g)$$

Theory of stratospheric ozone production

Sidney Chapman developed a theory of stratospheric ozone production based upon an equilibrium model consisting of the photochemical dissociation and recombination of oxygen.



Production:

$O_2 + h\nu \longrightarrow O + O \quad (\lambda < 242\ nm)$

$O + O_2 + M \longrightarrow O_3 + M$

Destruction:

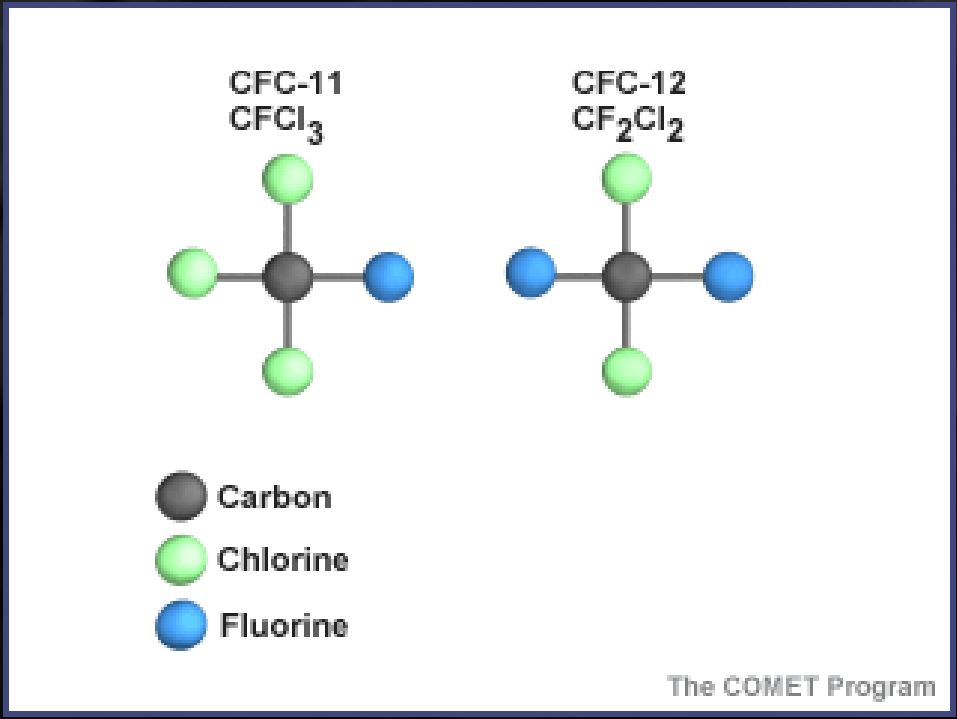
$O_3 + h\nu \longrightarrow O + O_2 \quad (\lambda < 320\ nm)$

$O + O_3 \longrightarrow 2\ O_2$

Depletion of the Ozone Layer

Ozone destroyed by Chlorine

The largest source is a class of chemical compounds known as chlorofluorocarbons (CFCs).



CFCs

Chlorofluorocarbons

example: CF_2Cl_2 (*di*chloro*di*fluromethane)

Developed by General Motors in 1928 to be used as non-toxic, non-flammable refrigerants

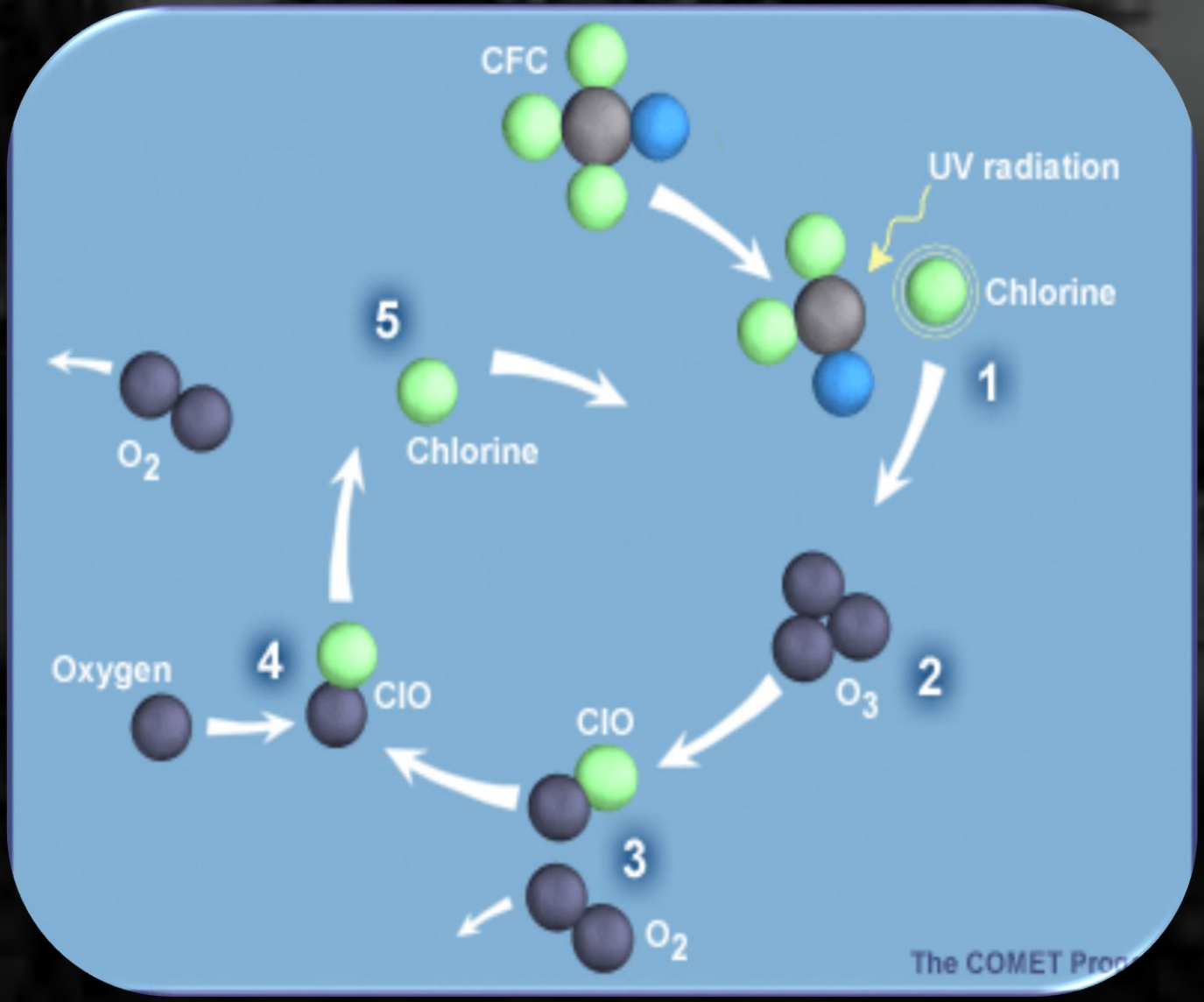
Previous refrigerants used

ammonia (NH_3) - TOXIC!

Butane (C_4H_{10}) - FLAMMABLE!

CFCs will not react in the Troposphere and will eventually reach the Stratosphere where they can react with high energy UV light

Gases such as CFCs that do not dissolve in water and that are relatively unreactive in the lower atmosphere are mixed relatively quickly and therefore reach the stratosphere regardless of their weight.


CFC
UV radiation
Chlorine
1
5
Chlorine
O_2
Oxygen
4
ClO
ClO
O_3
2
3
O_2
The COMET Prog

Reaction of CF_2Cl_2 in the stratosphere

1) UV radiation breaks off a chlorine atom from a CFC molecule.

$CF_2Cl_2 + UV \quad \text{-----} > \quad CF_2Cl + Cl$ (for $\lambda < 230$ nm)

2) The chlorine combines with an ozone molecule, destroys it, and forms chlorine monoxide and molecular oxygen.

$$Cl + O_3 \quad \text{-----} > \quad ClO + O_2$$

3)The chlorine monoxide combines with an atomic oxygen atom, releasing chlorine at the end of the process.

$$ClO + O \quad \text{-----} > \quad Cl + O_2$$

4) The chlorine atom is now free to attack and destroy another ozone molecule . One chlorine atom can repeat this destructive cycle thousands of times.

Cl speeds up (catalyzes) the conversion of O_3 to O_2

Net result: 100,000 O_3 destroyed by one Cl

$CFCl_3$ + UV Light ==> $CFCl_2$ + Cl (for $\lambda < 250$ nm)

$Cl + O_3 \Rightarrow ClO + O_2$

$ClO + O \Rightarrow Cl + O_2$

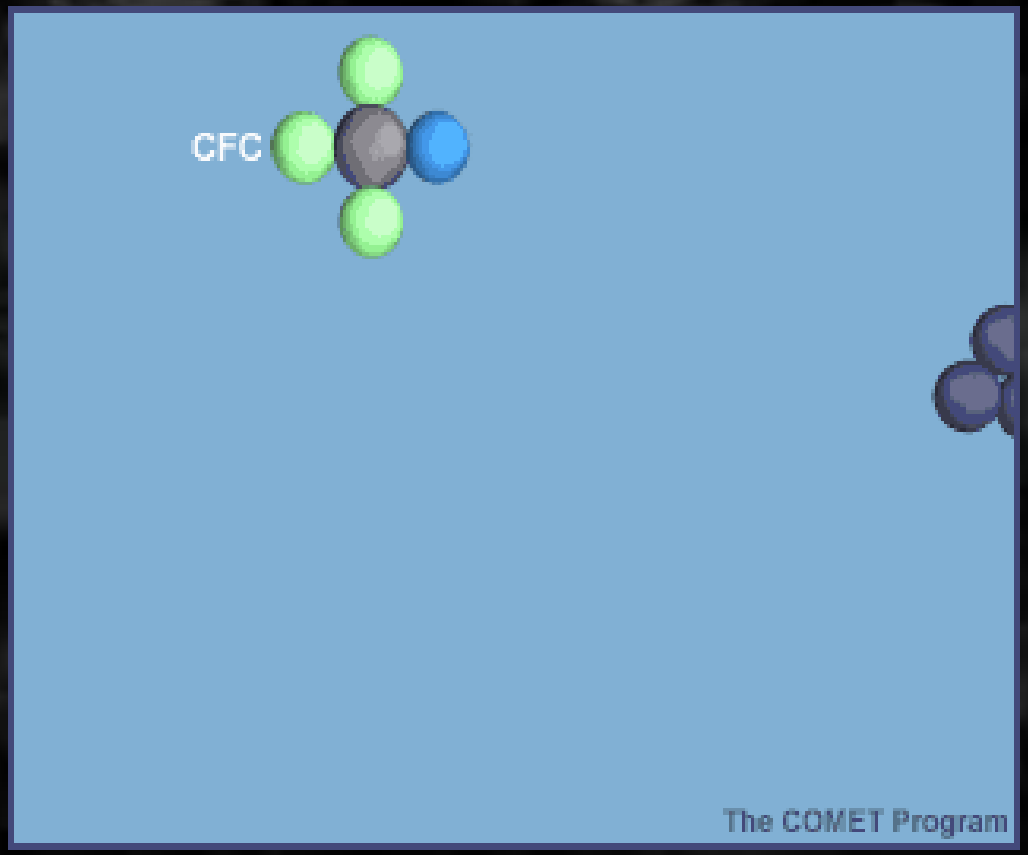
The free chlorine atom is then free to attack another ozone molecule

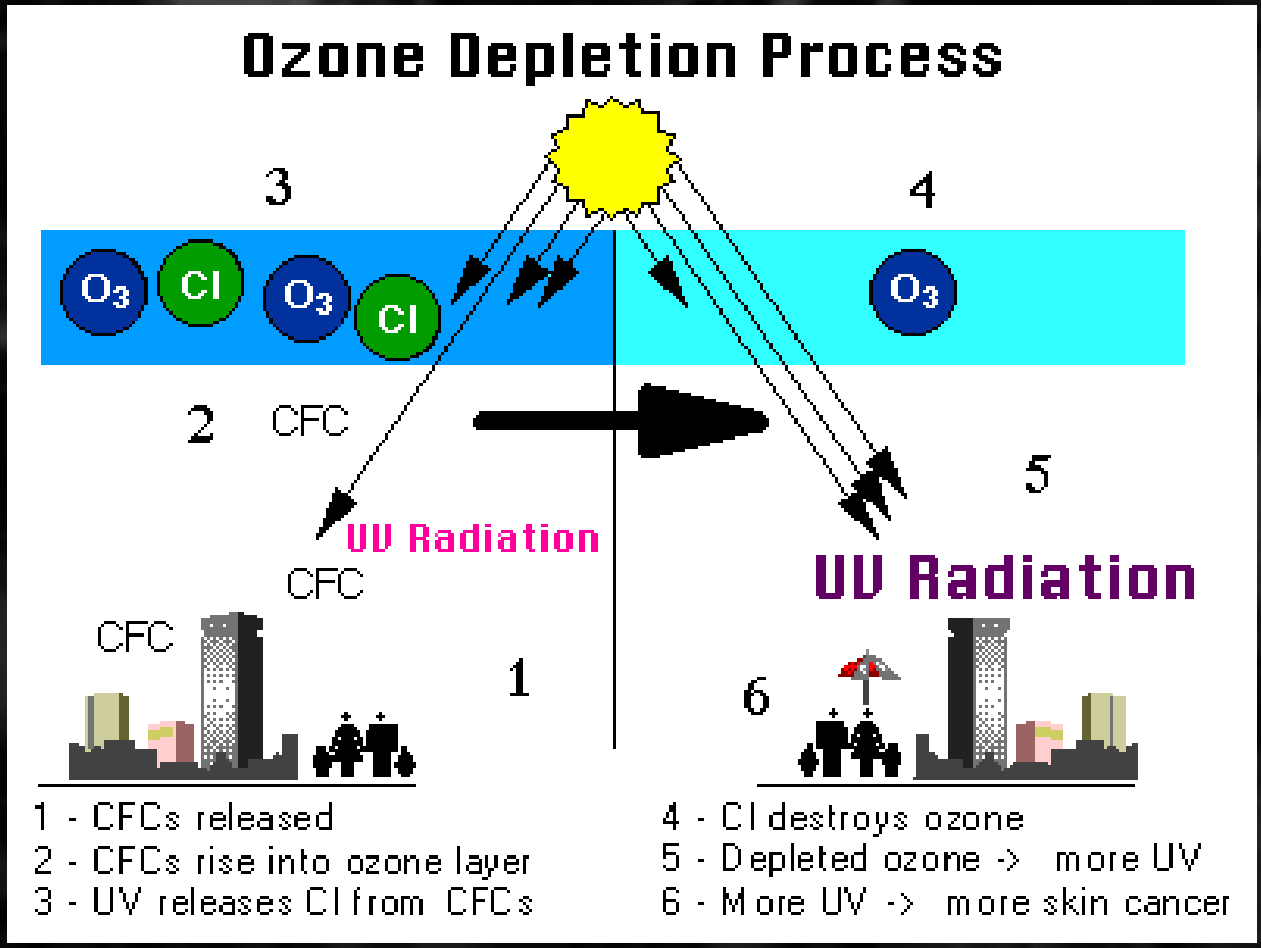
$Cl + O_3 \Rightarrow ClO + O_2$

$ClO + O \Rightarrow Cl + O2$

and again... for thousands of times.

The following animation shows the destruction of an ozone molecule by a chlorine atom.




Ozone Depletion Process
3
4
O3
Cl
O3
Cl
O3
2
CFC
5
UV Radiation
CFC
UV Radiation
CFC
1
6
1 - CFCs released
2 - CFCs rise into ozone layer
3 - UV releases Cl from CFCs
4 - Cl destroys ozone
5 - Depleted ozone -> more UV
6 - More UV -> more skin cancer

Important Points

Stable CFCs reach stratosphere

CFCs react with UV light to release Cl atoms in stratosphere

one Cl atoms react with thousands of O_3 molecules

CATALYTIC DESTRUCION OF OZONE

more CFCs $\rightarrow$ more Cl $\rightarrow$ less O_3

less O_3 $\rightarrow$ less UV absorbed in stratosphere

more UV reaches the troposphere

Fact: CFCs are DENSER than air

How do they get to the stratosphere?

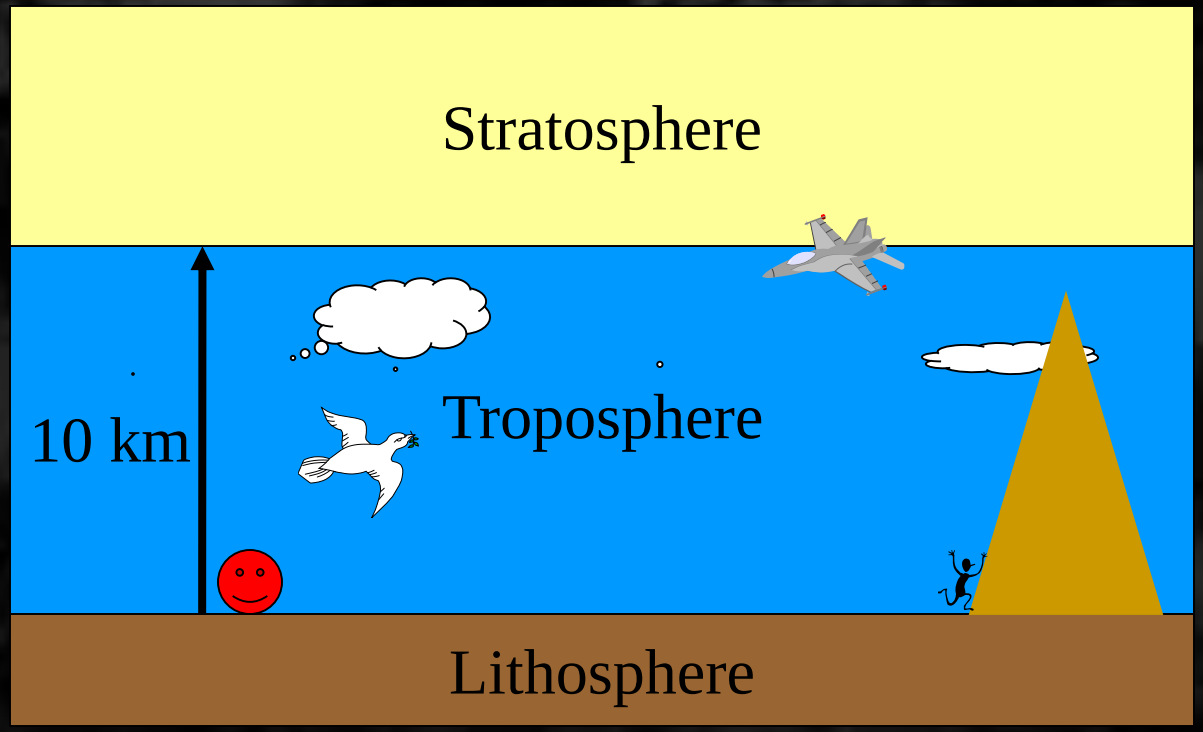
Wind, collective mixing

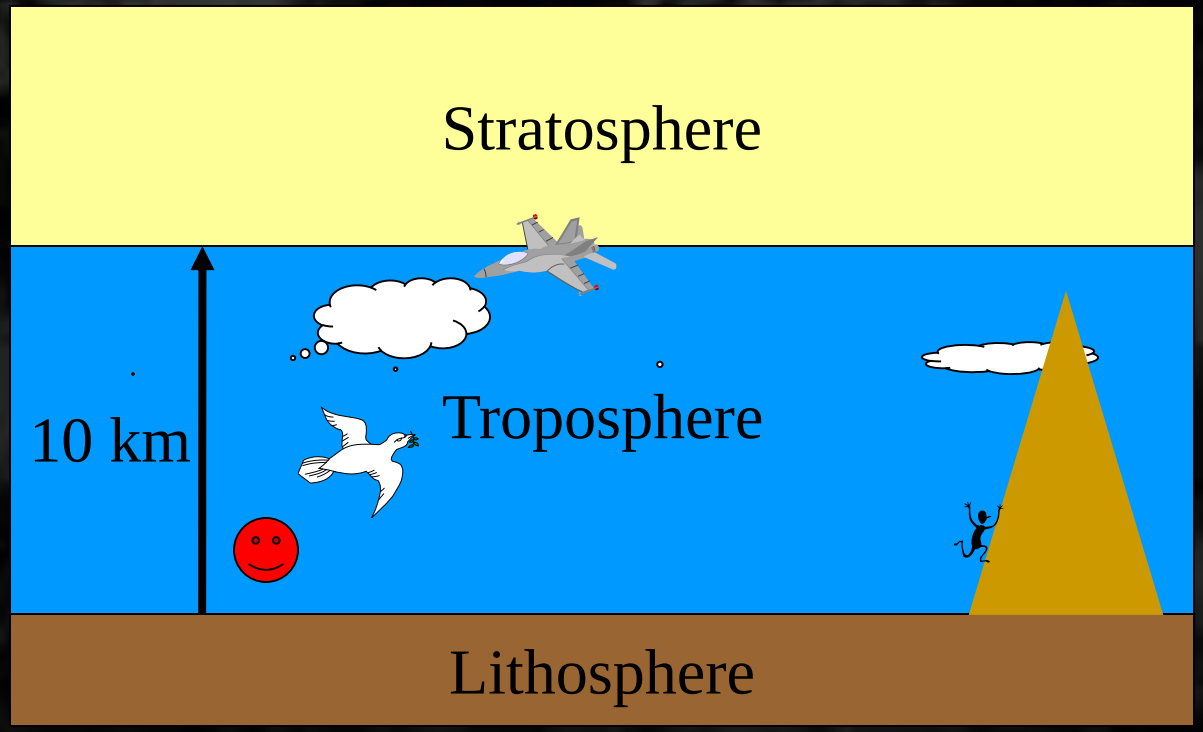
CFCs reach the stratosphere because the Earth's atmosphere is always in motion and mixes the chemicals added into it.

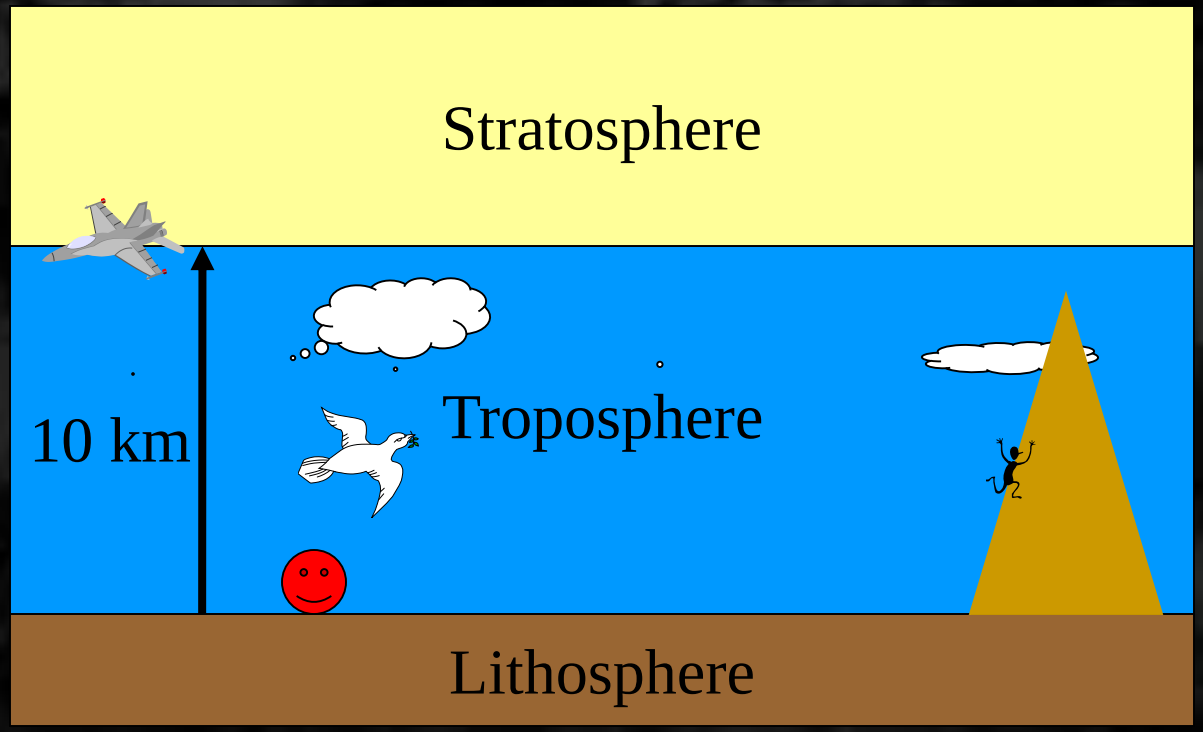
CFC molecules are indeed several times heavier than air.

This is because winds and other air motions mix the atmosphere to altitudes far above the top of the stratosphere much faster than molecules can settle according to their weight.

The Life of a CFC molecule




Stratosphere
10 km
Troposphere
Lithosphere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10 km
Troposphere
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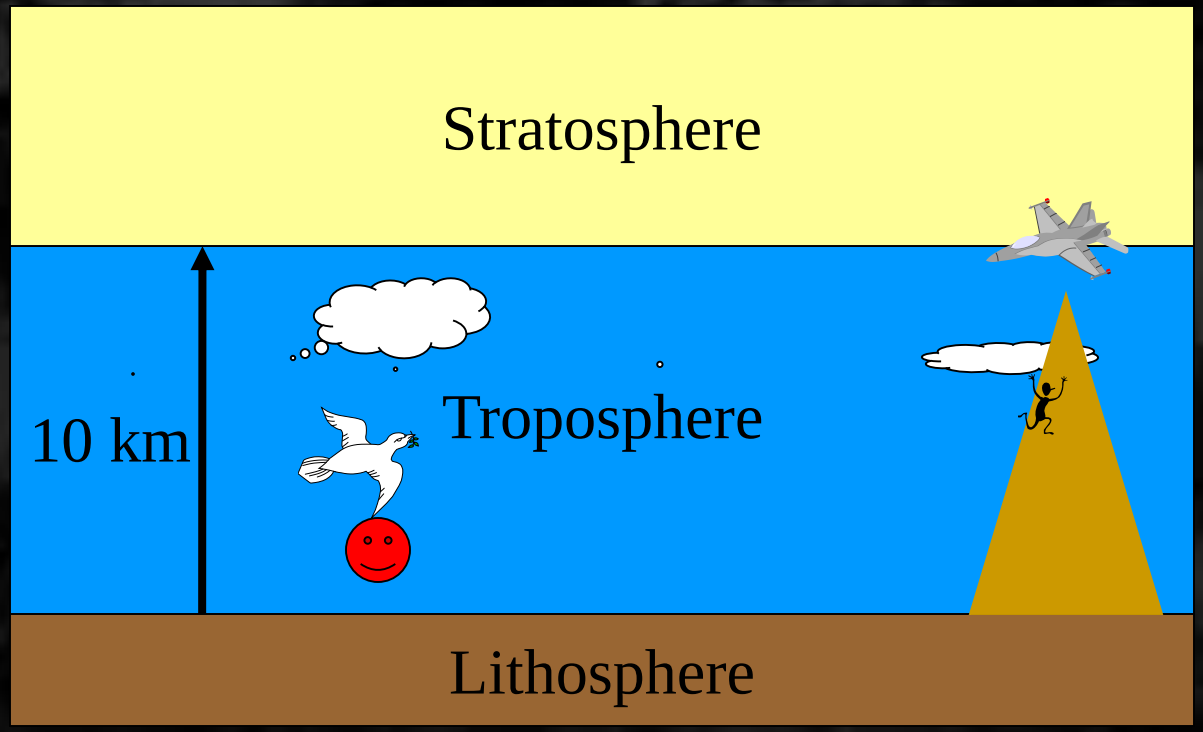
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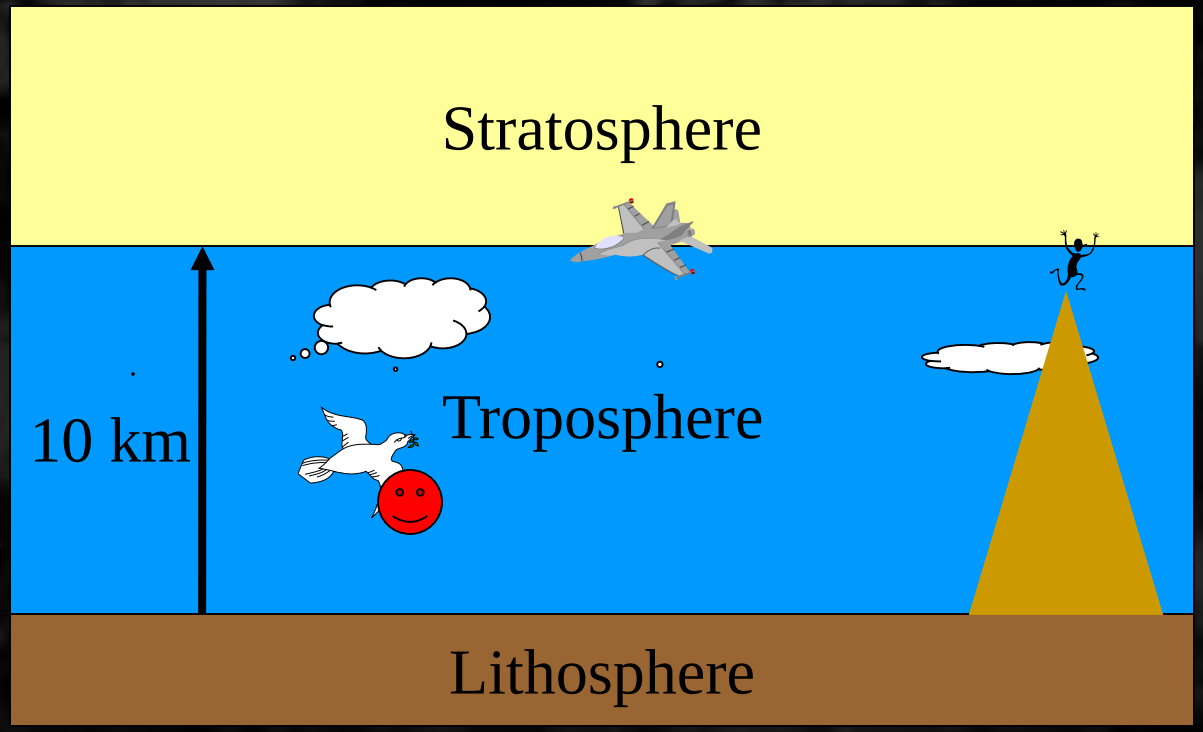
10 km
Troposphere
Lithosphere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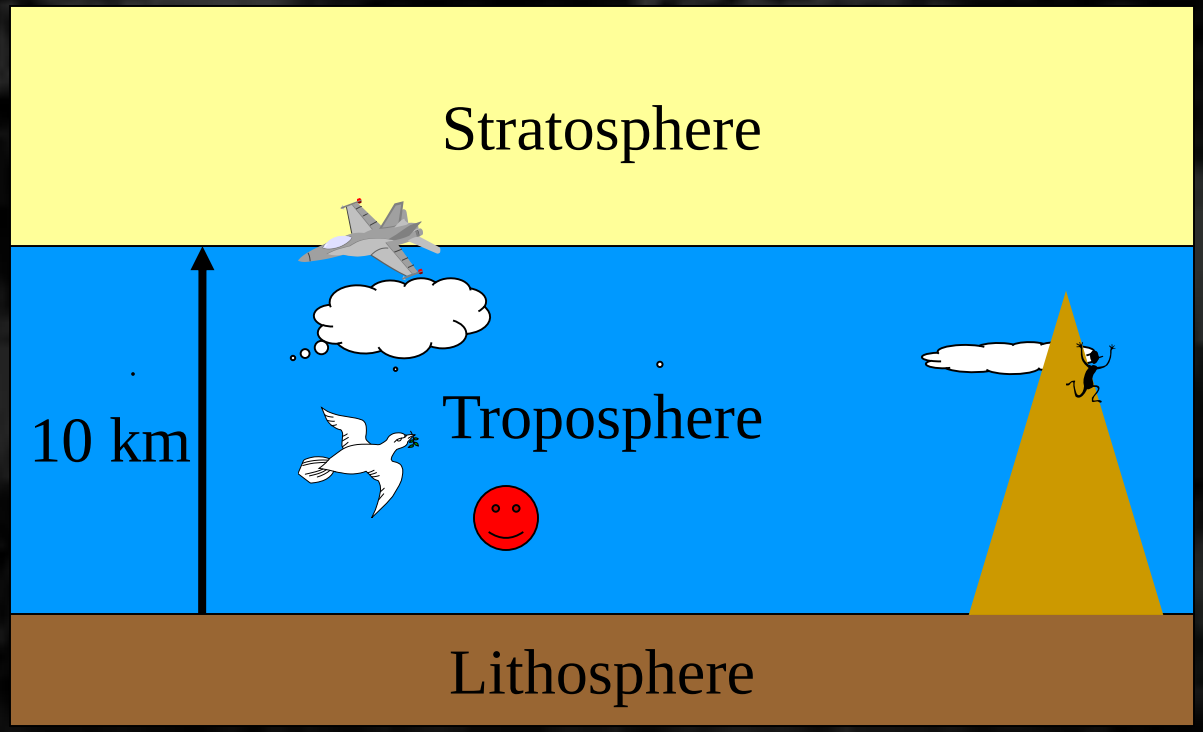
Troposphere
Lithosphere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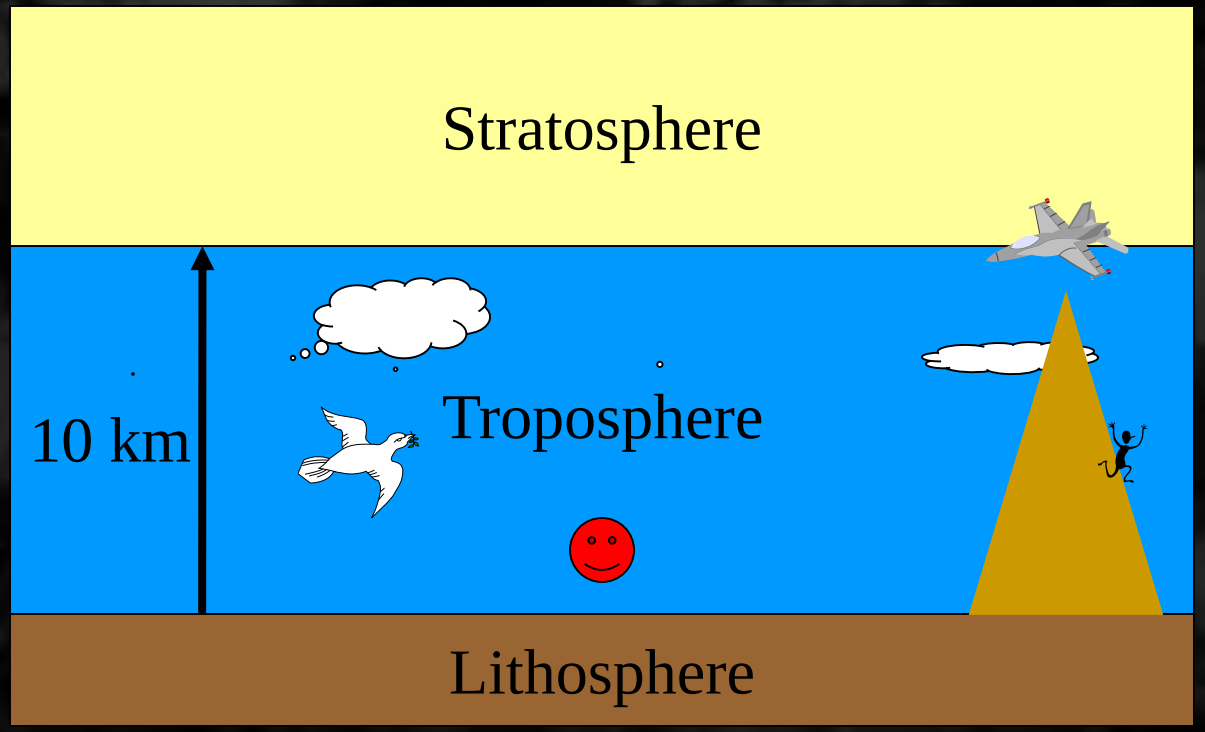
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Troposphere
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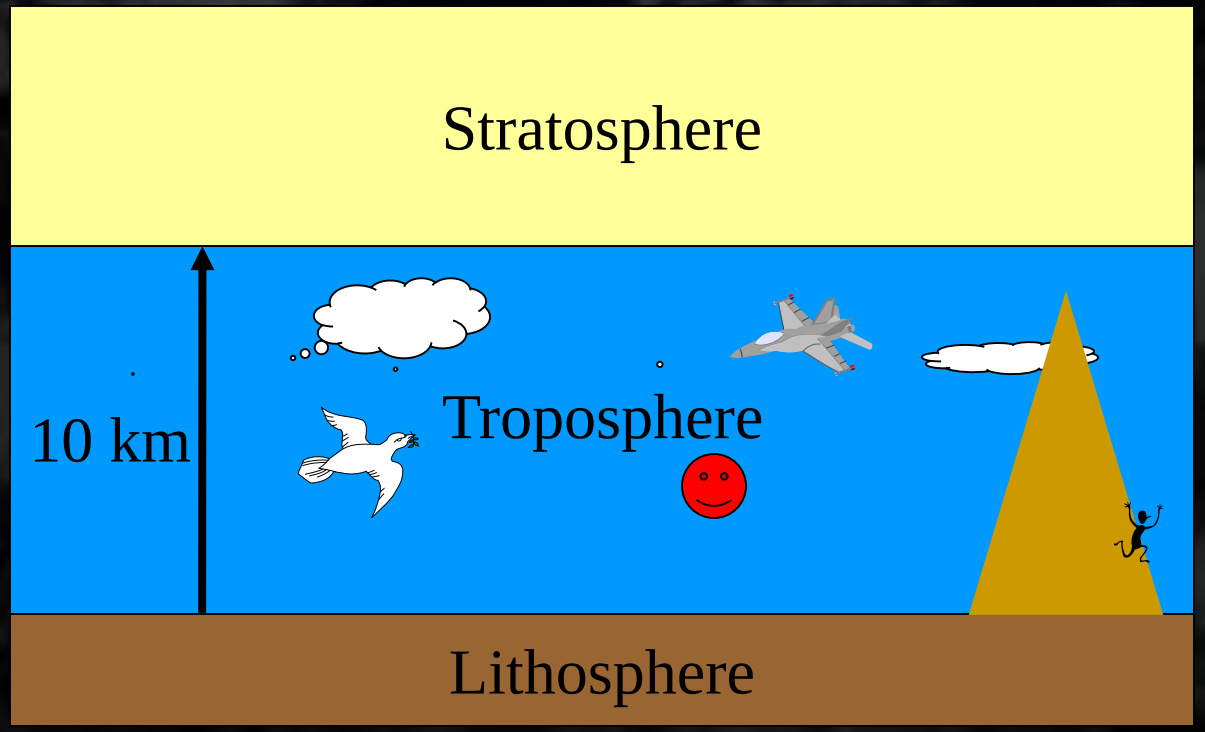
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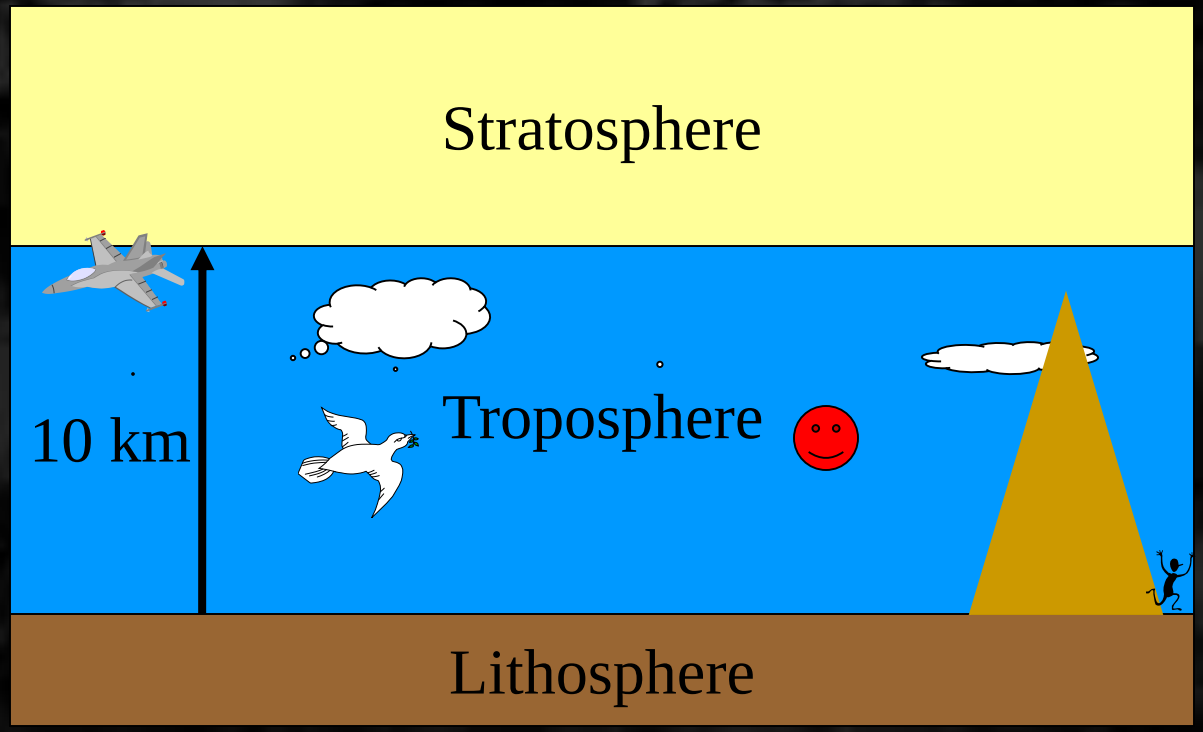
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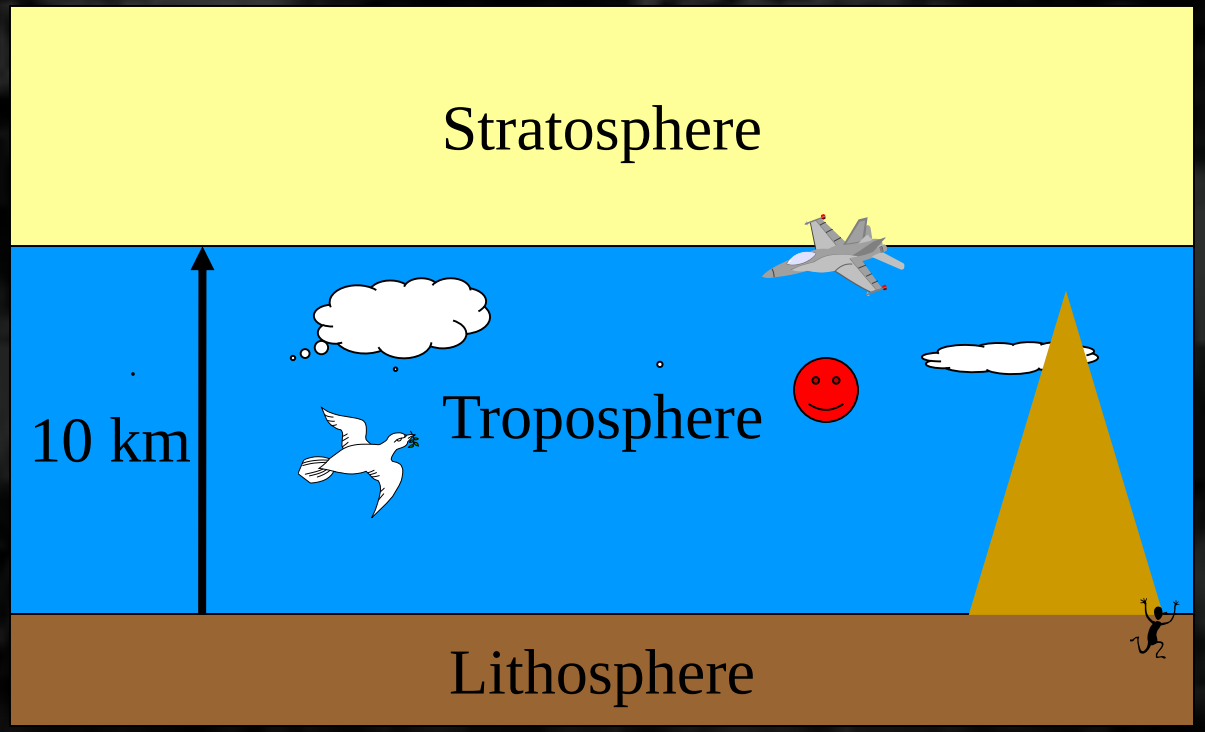
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Troposphere
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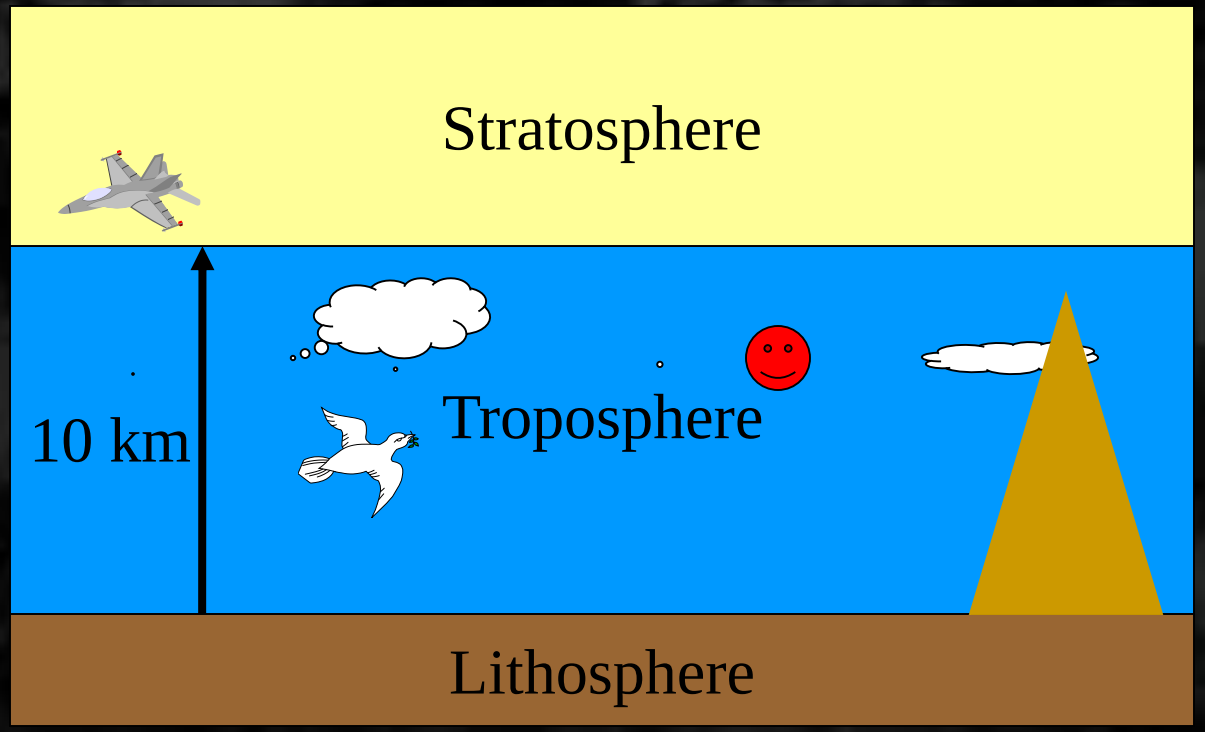
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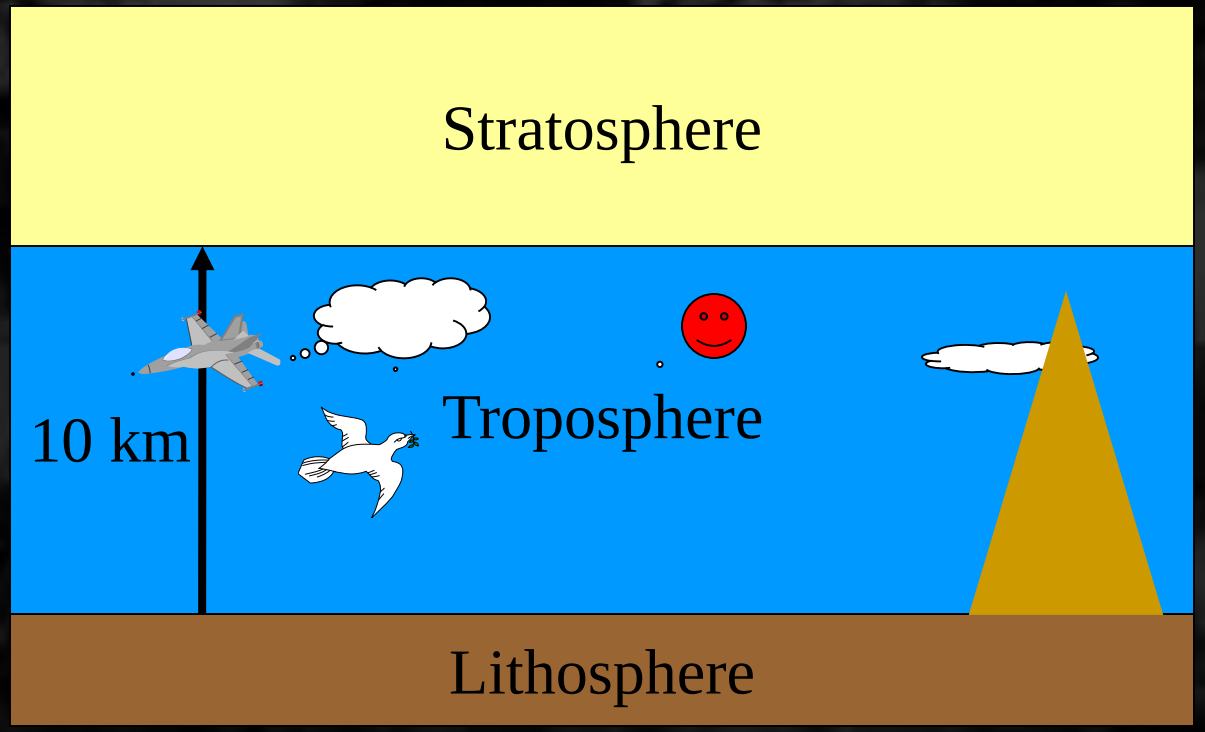
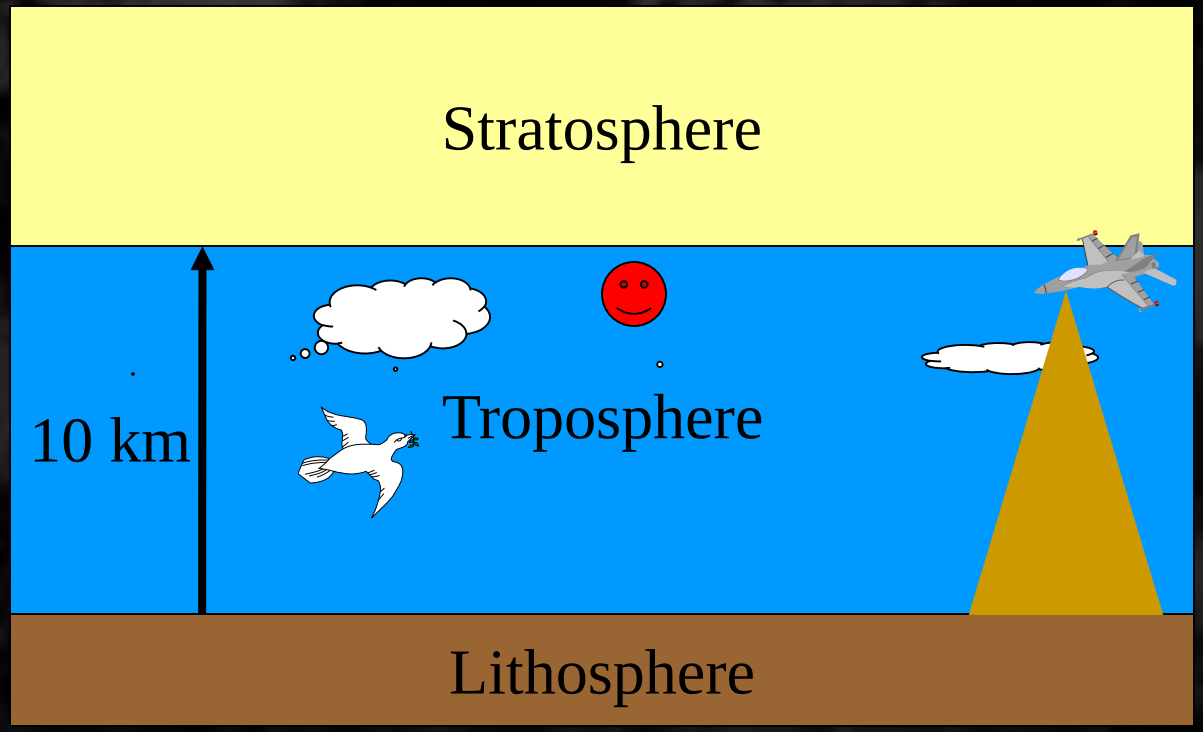
10 km
Troposphere
Lithosphere


Stratosphere
10 km
Troposphere
Lithosphere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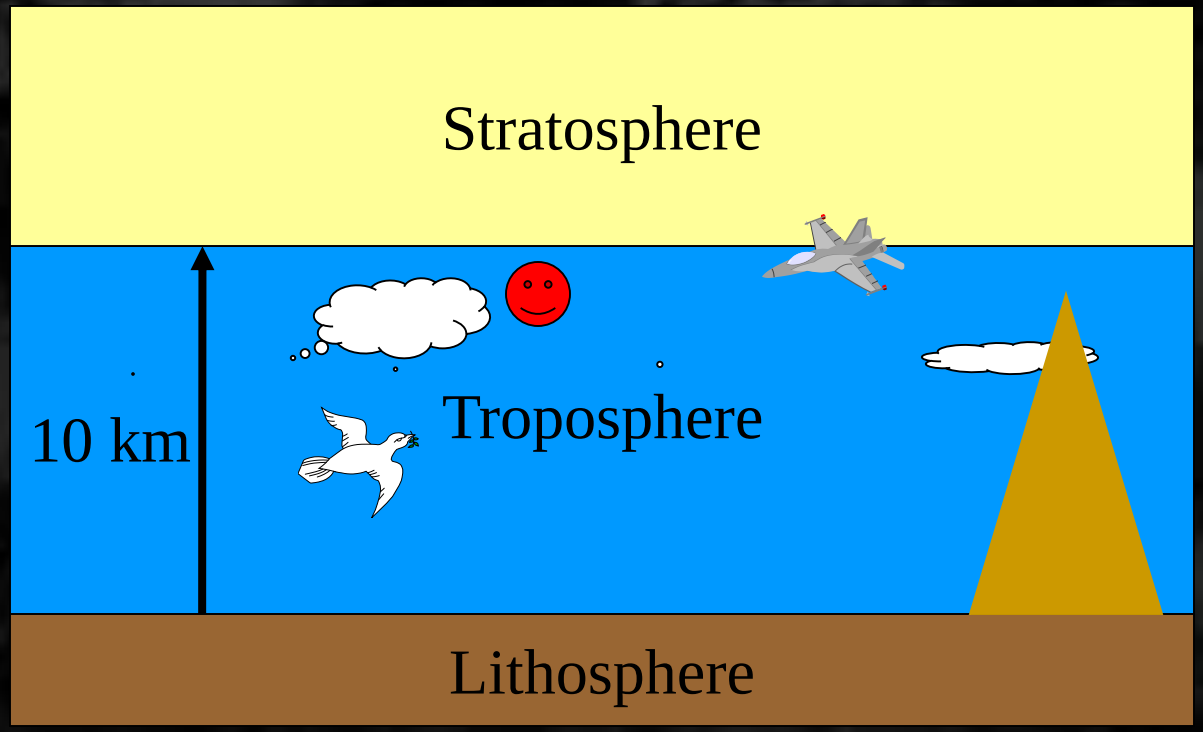
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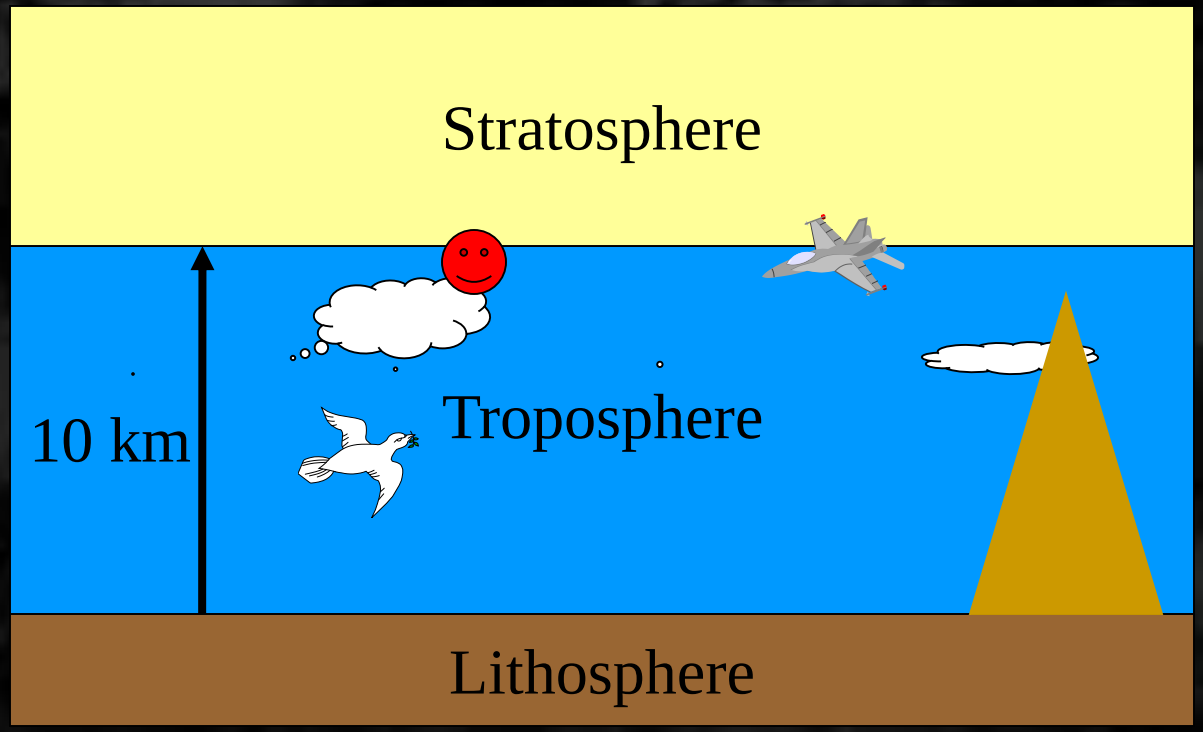
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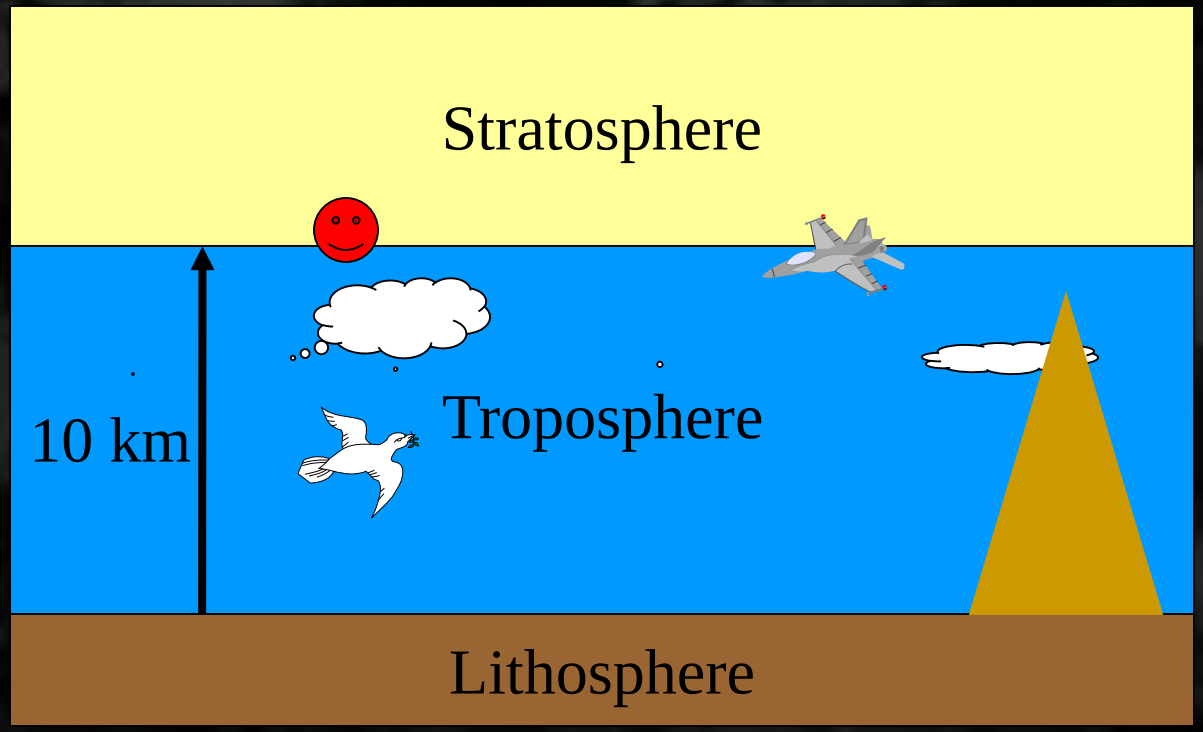
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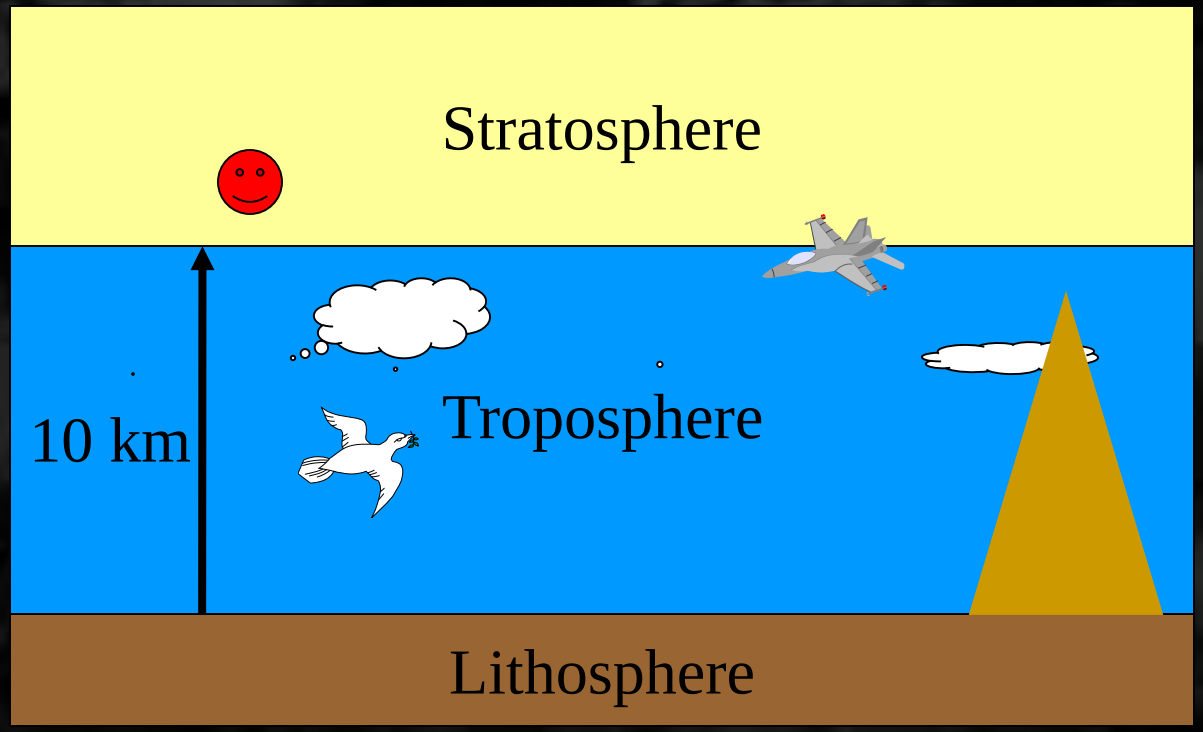
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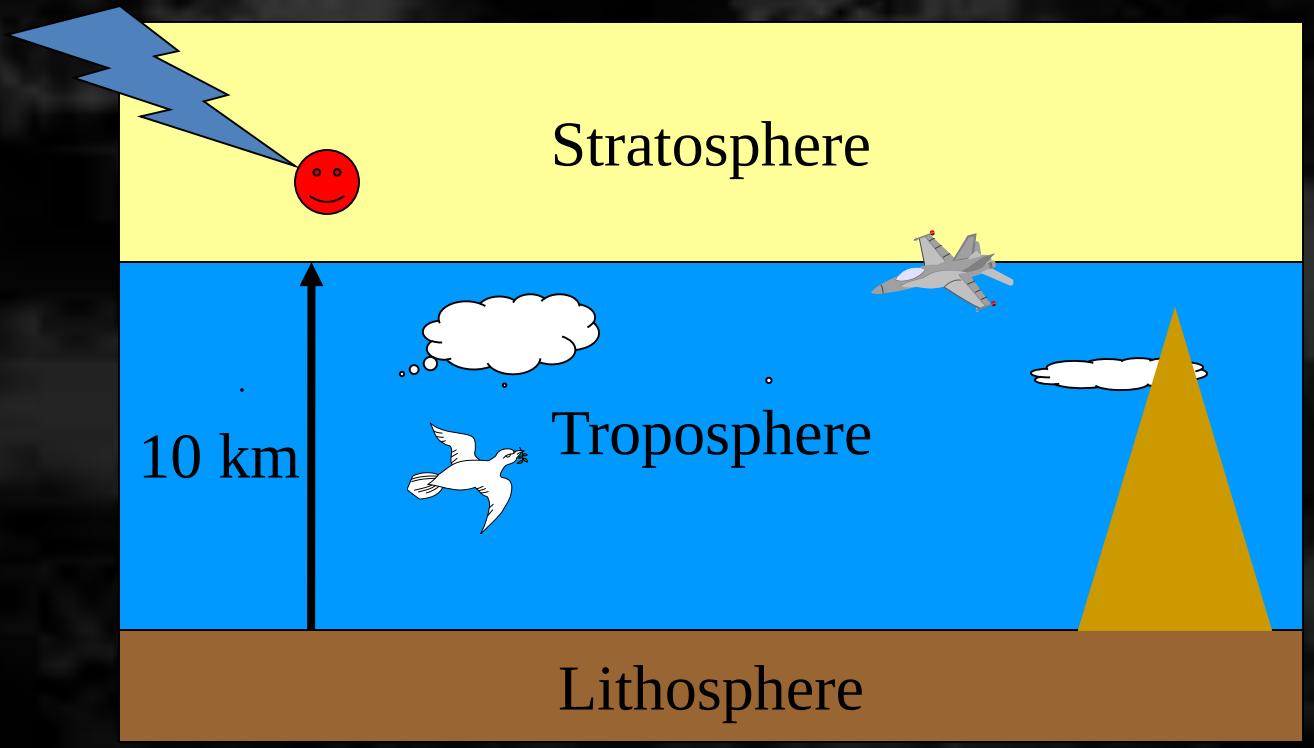
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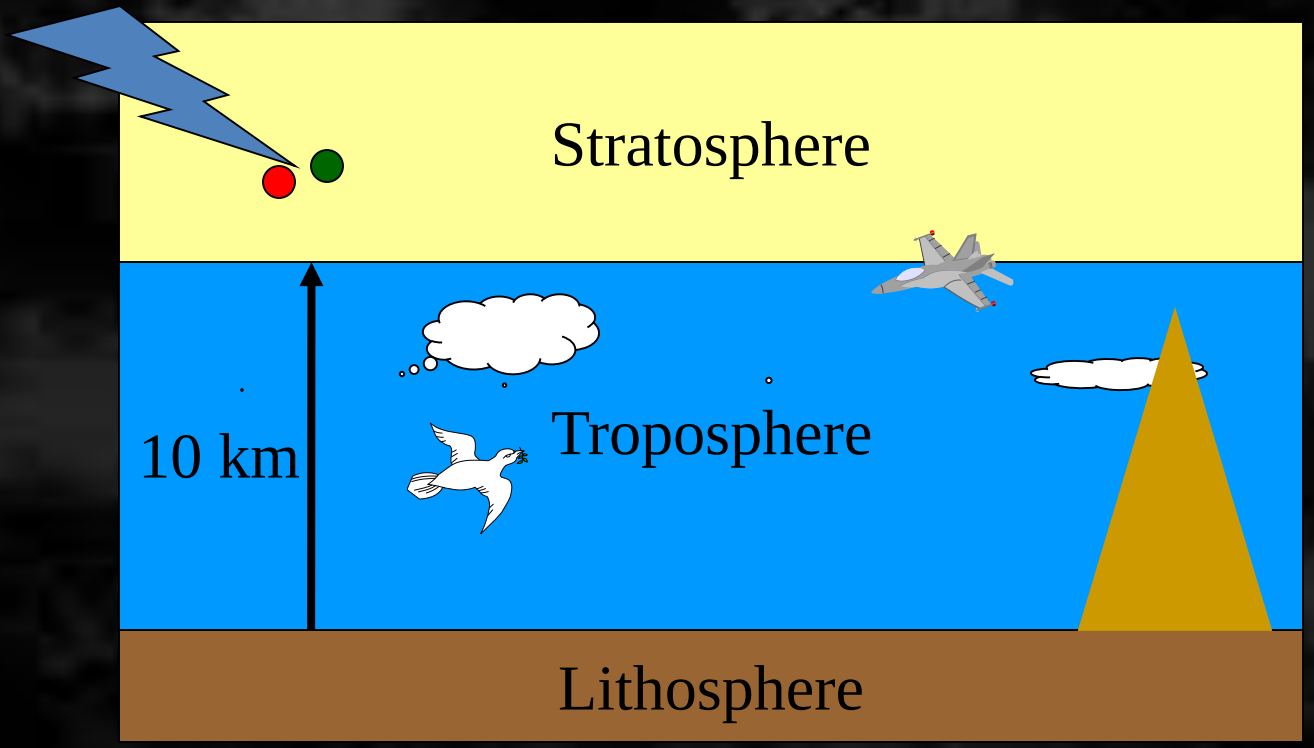
Stratosphere
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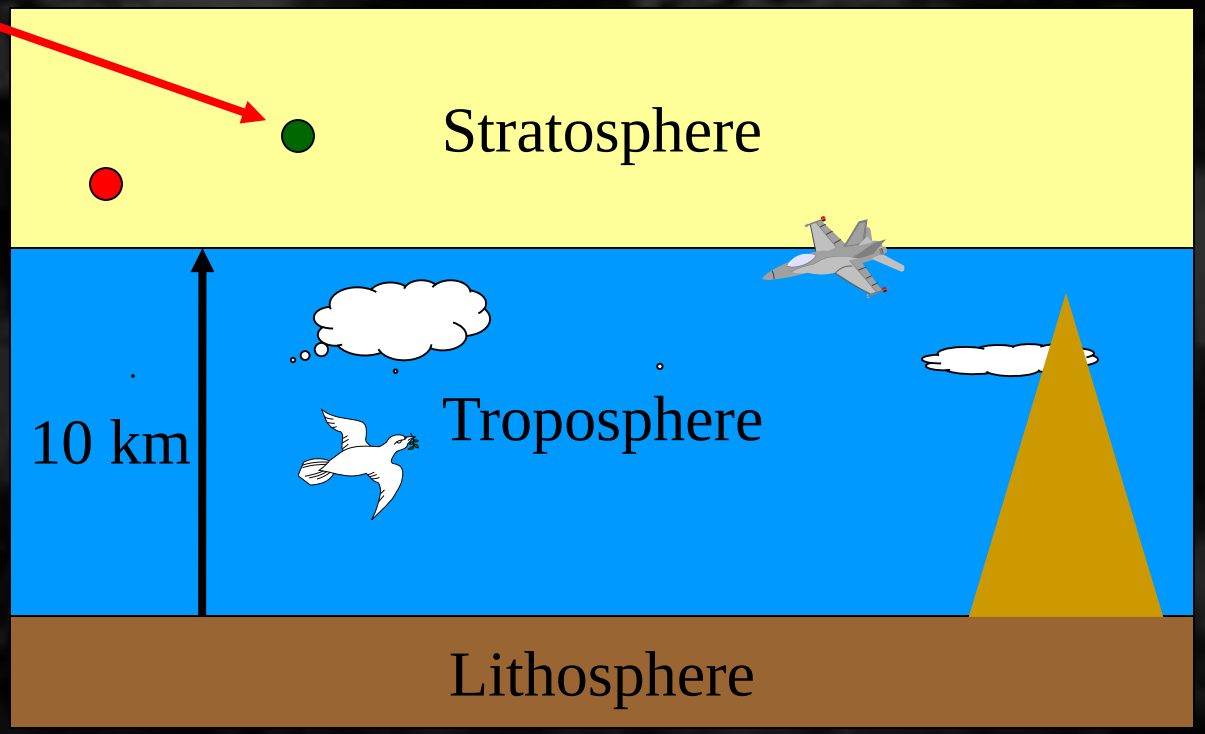
Nasty Chlorine



So what is the problem with CFCs?

THEY ARE TOO STABLE!

Why has caused the depletion Stratospheric Ozone over some regions of the Earth?

Why does a "Ozone Hole" form over the Antarctic?

Reservoir Molecules

One Cl atom can catalyze the destruction of about 100000 ozone molecules

Some Cl atoms can be temporarily trapped in "reservoir molecules" by reacting with methane (CH_4) or nitrogen dioxide (NO_2)

$$Cl + CH_4 \rightarrow \mathbf{HCl} + CH_3$$

$$ClO + NO_2 \rightarrow \mathbf{ClONO_2}$$

HCl and $ClONO_2$ are "reservoir" molecules as the serve as a "reservoir" of Cl atoms (for future use!)

Why does a "Ozone Hole" form over the Antarctic?

Polar vortex creates a region of very cold isolated air and "polar stratospheric clouds"

Frozen particles in these clouds allow "chlorine reservoir" molecules to react to form Cl_2

$$ClONO_2 + HCl \rightarrow \mathbf{Cl_2} + HNO_3$$

Cl_2 accumulates during winter

When the first light of spring arrives Cl_2 is cleaved into Cl atoms

$$Cl_2 + light \rightarrow Cl + Cl$$

This sudden release of large amounts of Cl atoms results in a rapid decrease in ozone levels

Environmental Consequences of Stratospheric Ozone Depletion

Less "shielding" of high energy UV radiation

UV radiation is harmful to biological organisms

breaking of chemical bonds

DNA damage

mutations, cancer

impairs immune system

Loss of plant life

loss of food crops

Deleterious impact on ocean ecosystems

phytoplankton and zooplankton zooplankton

Thanks for your attention