Possible Feedback Processes of Gases in Atmospheric Chemical Transport Models (Physical Description)

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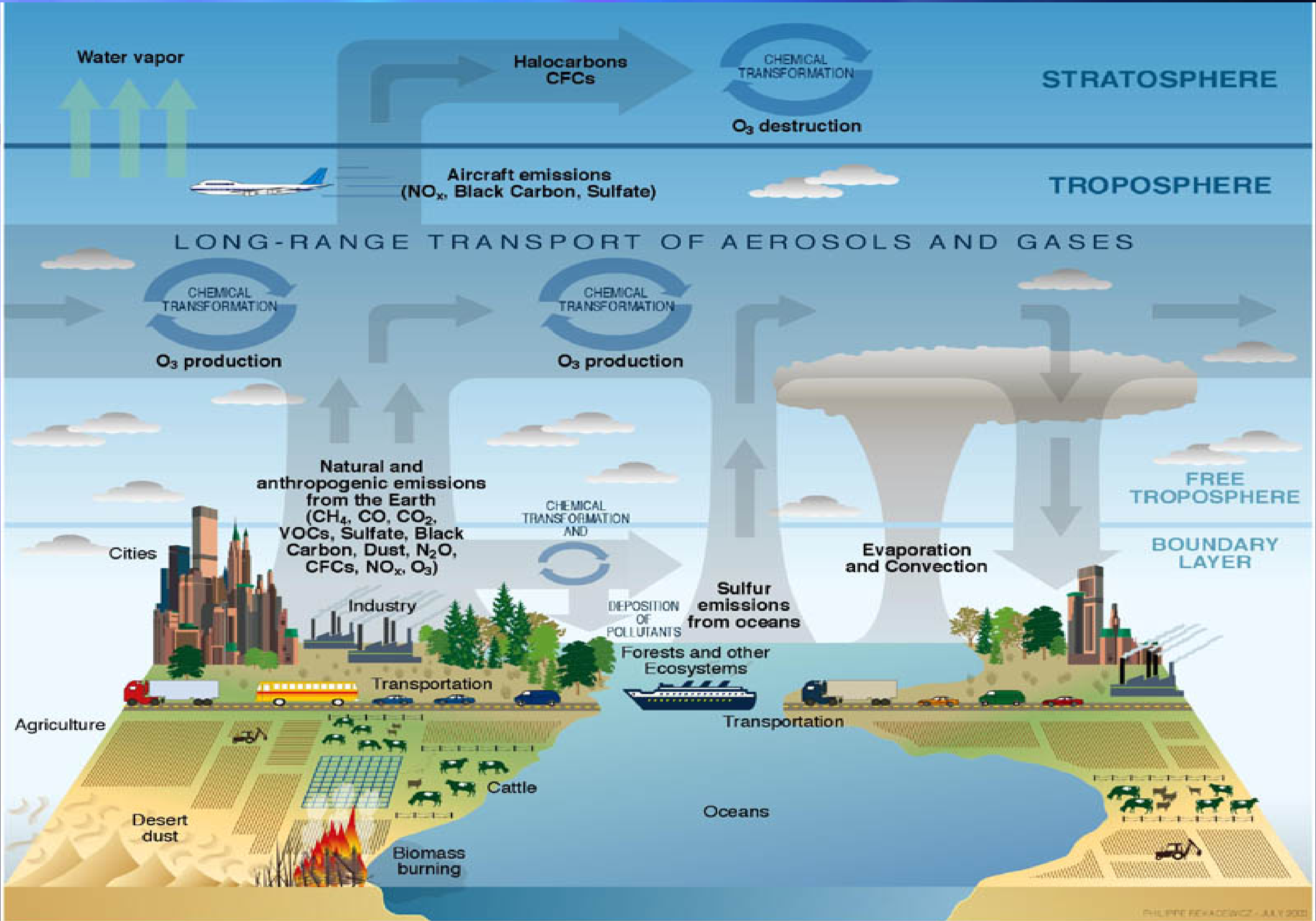
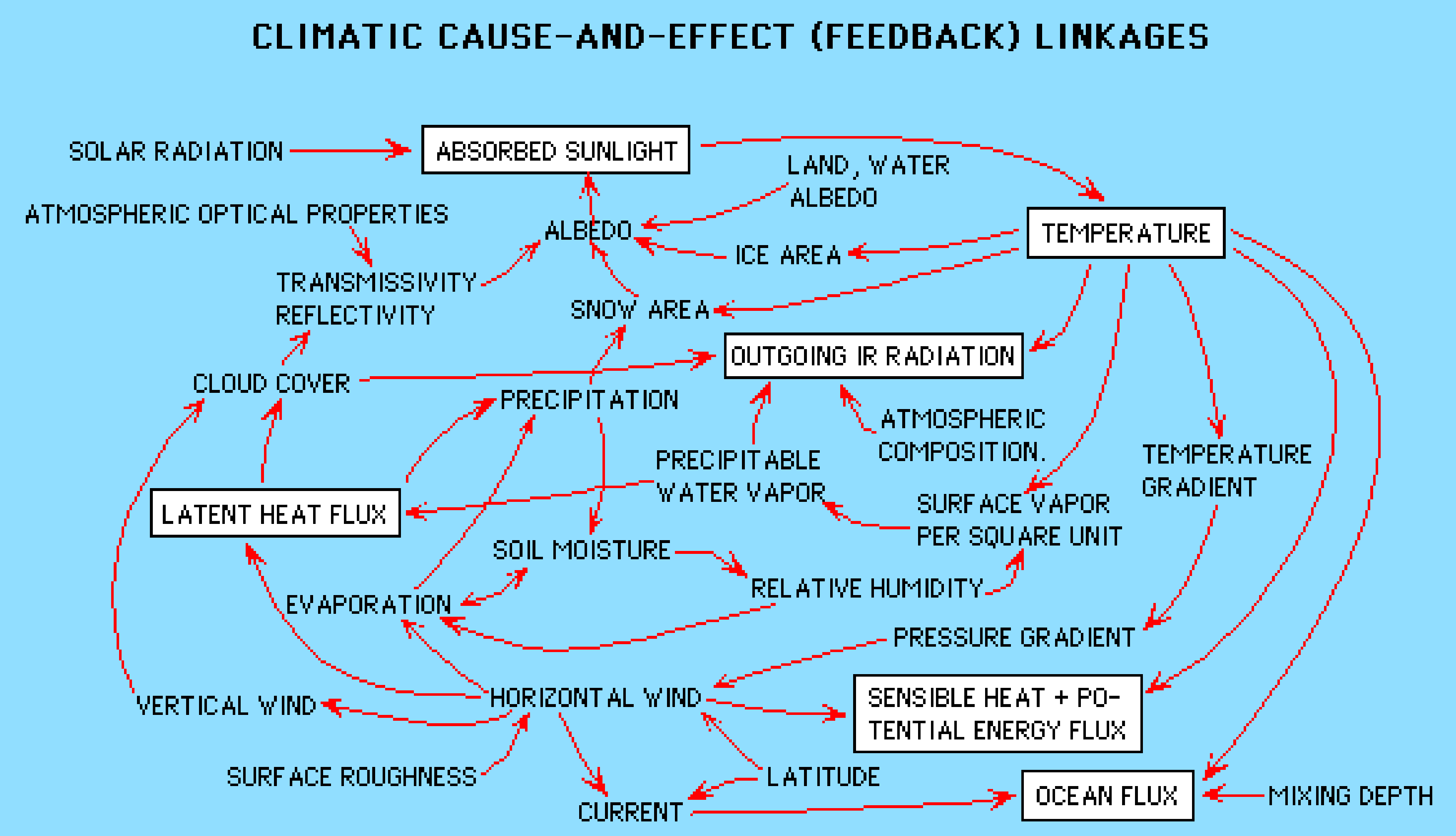
Atmospheric Gases



Feedbacks



A diagram by Sellers shows the many cause-and-effect linkages that must be accounted for in a comprehensive climate model.

Processes Affecting Temperature

Temperature
- Proportional to kinetic energy of an air molecule traveling at its average speed

$$\frac{4}{\pi} k_B T = \frac{1}{2} \overline{M} \bar{v}_a^2$$

Conduction
- Transfer of energy from molecule to molecule

Convection
- Transfer of energy by vertical mass movement of a fluid

Advection
- Transfer of energy by horizontal movement of a fluid

Radiation
- Energy transferred in the form of electromagnetic waves

Emission Spectra of the Sun and Earth

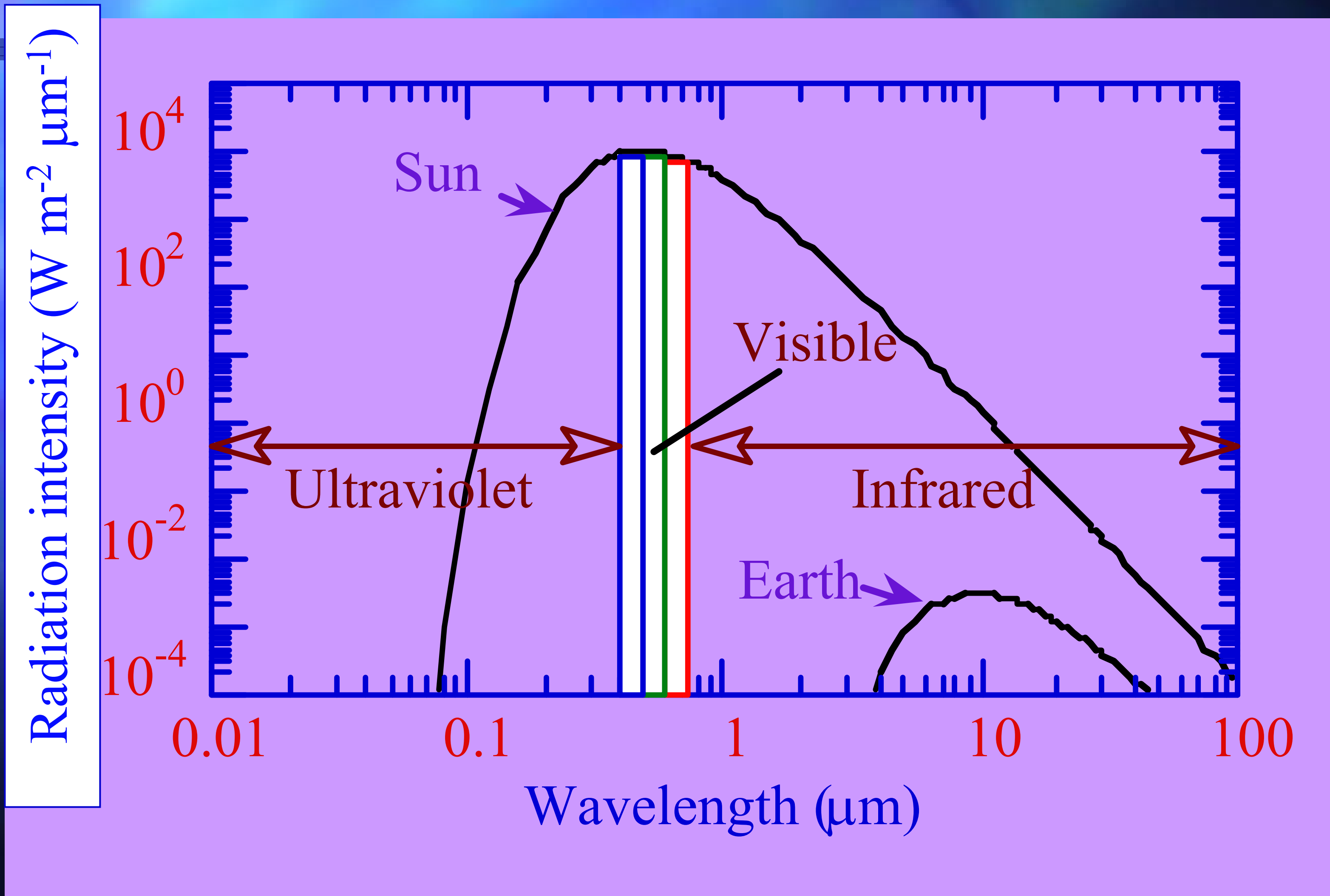


Figure 2.4

Gas Absorption

Conversion of radiative energy to internal energy by a gas molecule, increasing the temperature of the molecule

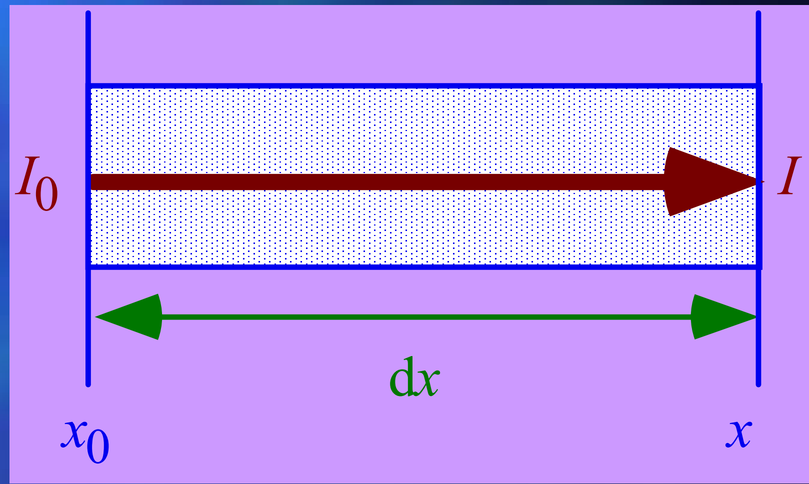
Attenuation of light intensity

- $I = I_0 e^{-\sigma_{a,g,q}(x-x_0)}$

Absorption extinction coefficient

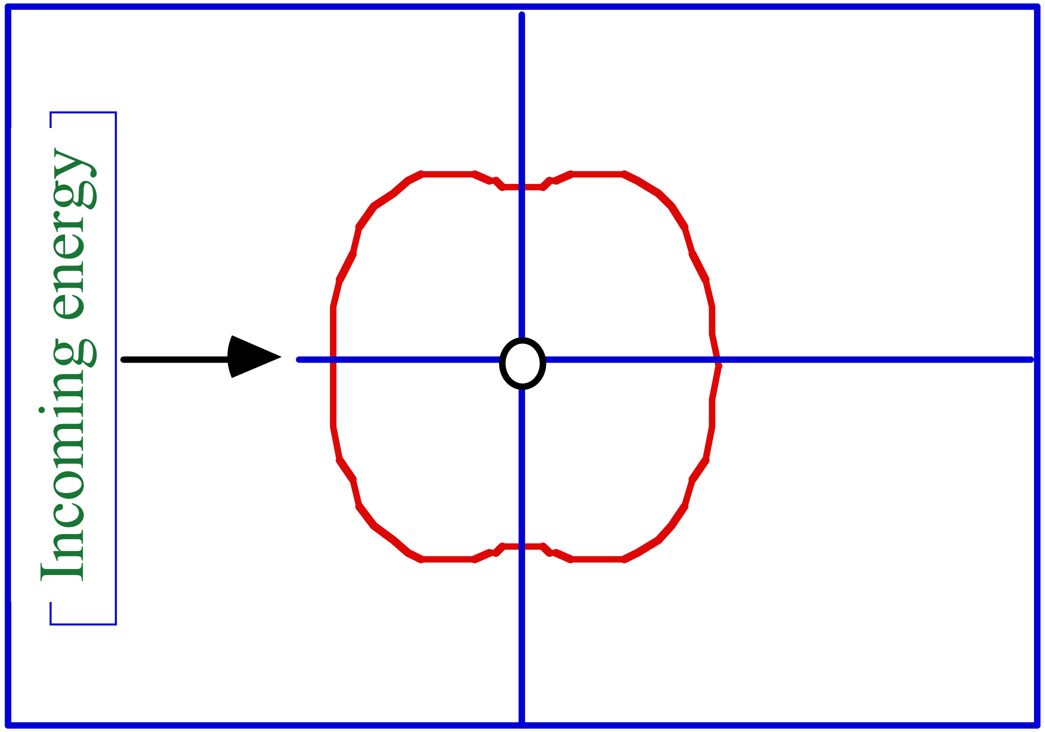
- $\sigma_{a,g,q} = N_q b_{a,g,q}$

- □ = gas absorption cross section
- N = gas concentration



Gas (Rayleigh) Scattering

Redirection of radiation by a gas molecule without a net transfer of energy to the molecule



Probability distribution of where a gas molecule scatters incoming light

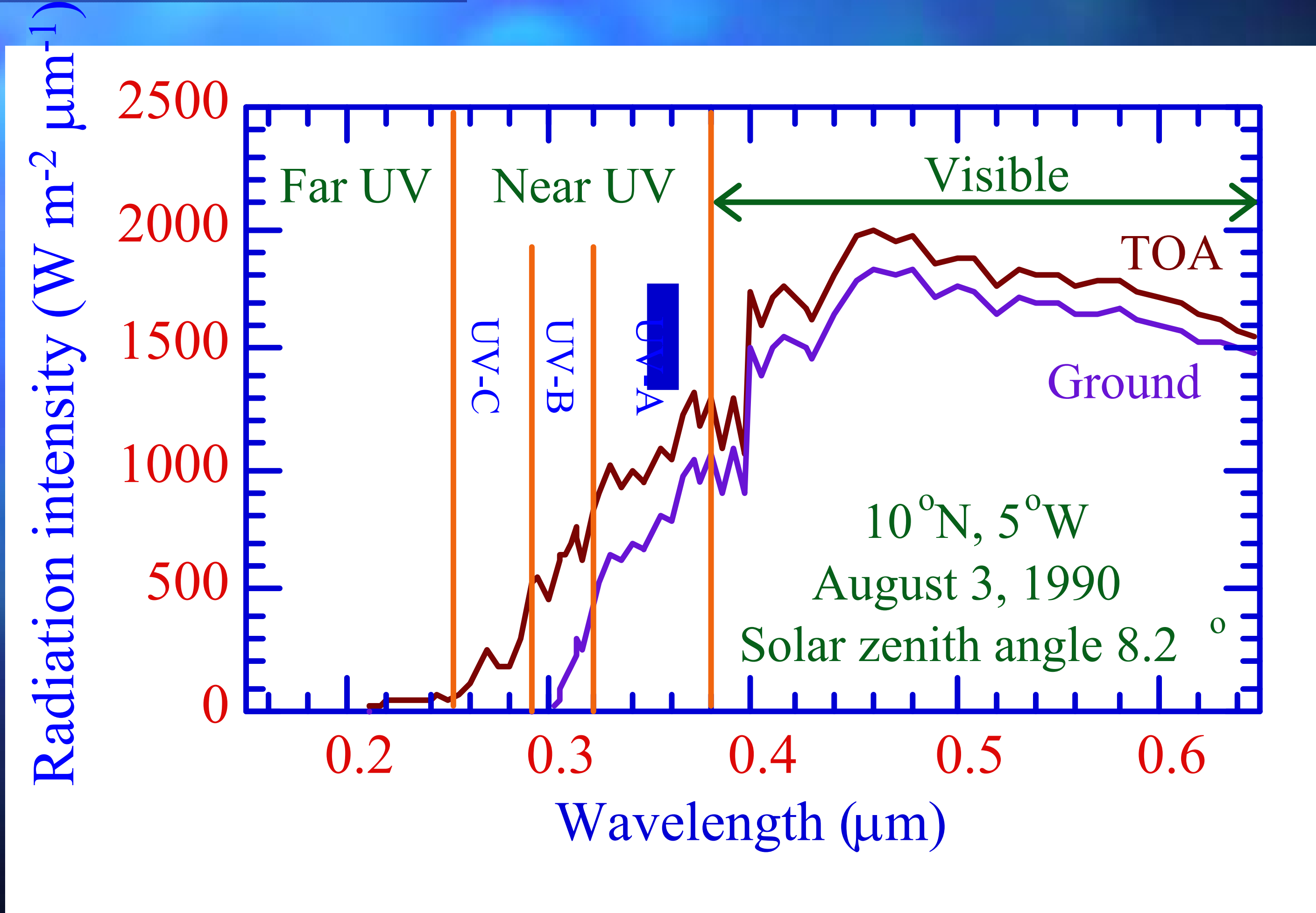
Potential Feedbacks

- Gases decrease net downward flux of solar radiation
  - Cooling in the underlying layer
- Gases absorb incoming radiation
  - Heating around gas location

Light-Absorbing Gases

Gas	Absorption wavelengths (μm)
Visible/Near-UV/Far-UV absorbers	
Ozone	< 0.35, 0.45-0.75
Nitrate radical	< 0.67
Nitrogen dioxide	< 0.71
Near-UV/Far-UV absorbers	
Formaldehyde	< 0.36
Nitric acid	< 0.33
Far-UV absorbers	
Molecular oxygen	< 0.245
Carbon dioxide	< 0.21
Water vapor	< 0.21
Molecular nitrogen	< 0.1

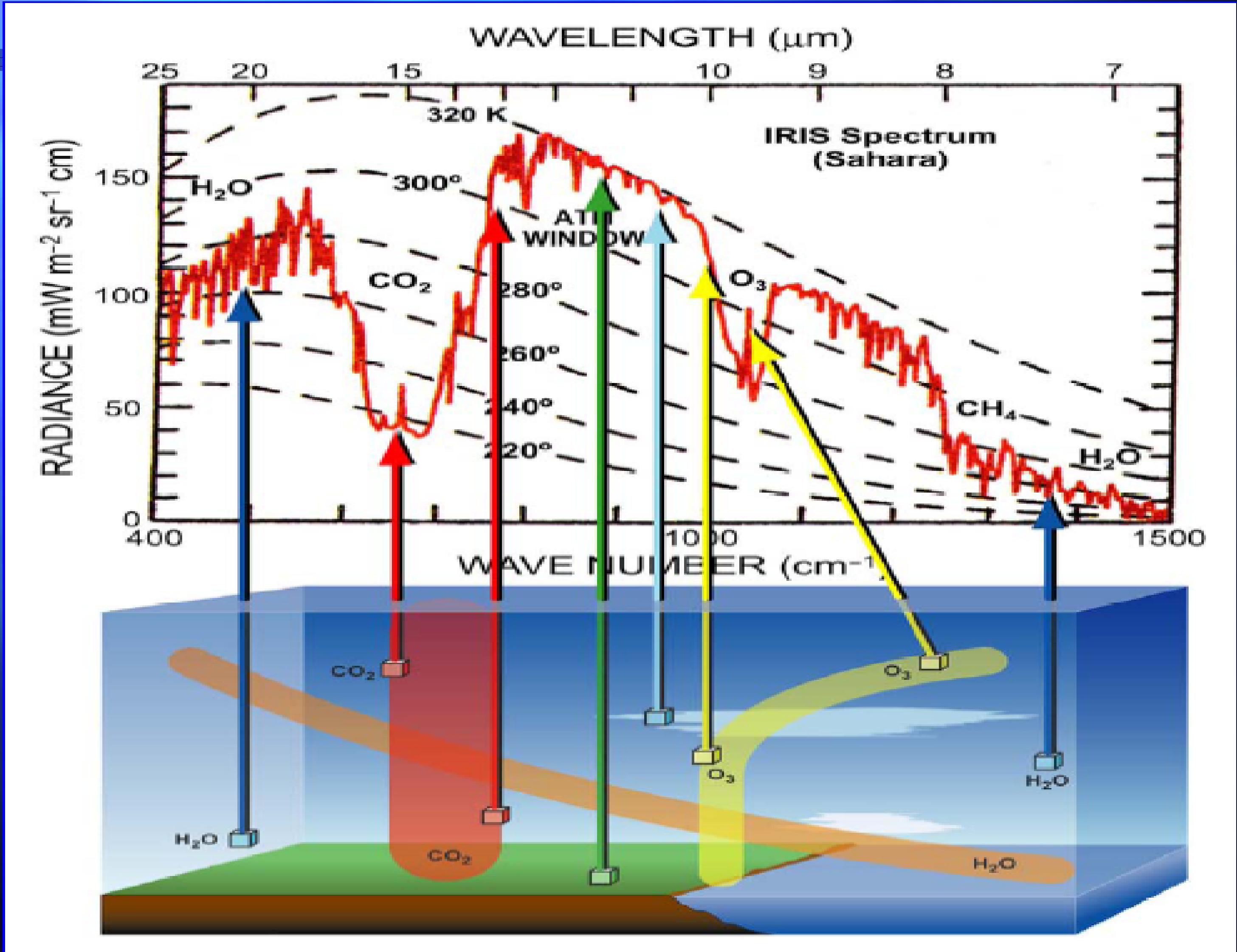
Downward Solar Radiation at Top of Atmosphere (TOA) and Ground



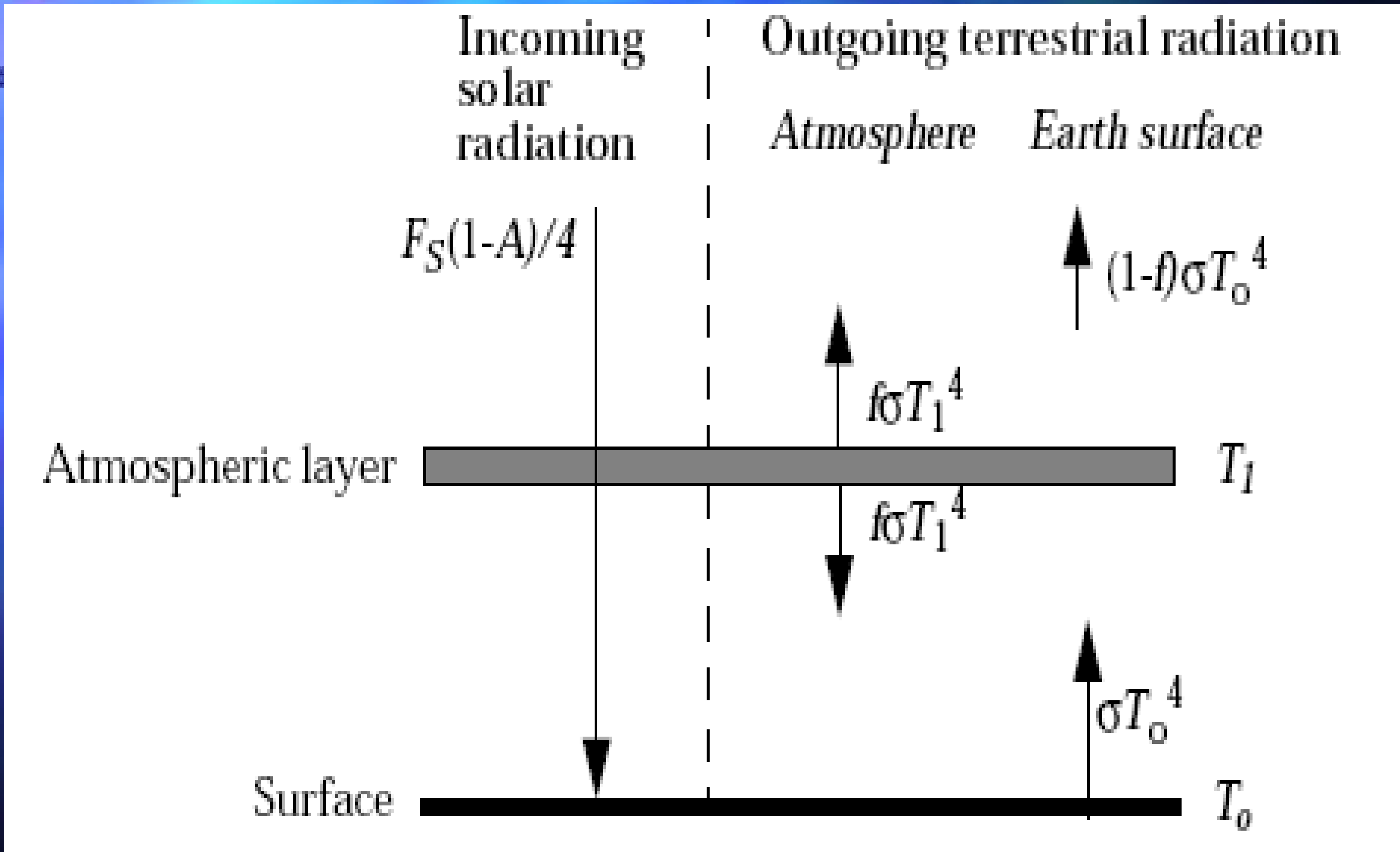
Major Absorbers of UV Radiation at Different Altitudes

Spectrum	Wavelengths (μm)	Dominant Absorbers	Location of Absorption
Far-UV	0.01-0.25	N_2	Thermosphere
		O_2	Thermosphere
Near-UV			
UV-C	0.25-0.29	O_3	Stratosphere
UV-B	0.29-0.32	O_3	Stratosphere Troposphere
		Particles	Polluted troposphere
UV-A	0.32-0.38	NO_2	Polluted troposphere
		Particles	Polluted troposphere

TERRESTRIAL RADIATION



IR Radiation Transmission



Potential Feedbacks

- Gases trap outcoming IR radiation
- Gases reemit radiation corresponding their temperature (Kirchhoff's law)
  - Heating the underlying layer (Greenhouse effect)
  - Cooling the upper layer

Greenhouse Gases

- Atmospheric greenhouse gases play a critical role in shaping our global climate. Naturally-occurring trace gases in the atmosphere include water vapor, carbon dioxide, methane, nitrous oxide, and ozone;
- Human activities also impact the concentrations of these gases in the atmosphere.
- In addition, many commonly used industrial products, including solvents, adhesives, and pesticides, contain halocarbons which can also impact the climate.
- The full range of sources of greenhouses gases - both natural and anthropogenic - is not yet fully understood and continues to be the subject of both research and debate.

Water Vapor

- Water vapor is the most abundant of the greenhouse gases, and is the dominant contributor to the natural greenhouse effect. Human activity has little direct impact on the concentration of water vapor in the atmosphere; however, changes in its concentration cause an indirect result of climate feedbacks related to the warming of the atmosphere

Water Vapor Climate Feedback

- As temperatures rise, more water evaporates from ground sources - rivers, oceans, etc.
- Higher concentrations of water vapor are able to absorb more IR radiation from the Earth, further warming the atmosphere.
- The warmer atmosphere can then hold more water vapor, and the cycle continues.
- This is cycle is considered a *positive feedback loop*.
- However, uncertainty exists in both the extent and importance of this feedback loop. As water vapor increases in the atmosphere, more of it will also condense into clouds, which reflect incoming solar radiation away from the Earth's surface thereby becoming a cooling force

Carbon Dioxide

- Carbon dioxide is released into the atmosphere through both natural and human processes. Natural production and absorption of carbon dioxide is primarily through the biosphere and the oceans via the carbon cycle.
- Human activities such as fuel burning (coal, oil, natural gas, and wood), cement production, and changes in land use have altered the natural carbon cycle by increasing the concentration of carbon dioxide in the atmosphere

Methane

- Methane, which comes from both natural and human sources, is an extremely powerful warming agent - even more effective than carbon dioxide - and its lifetime in the atmosphere is about 12 years
- In nature, methane is released through biological processes in low oxygen environments, such as swamplands. Human activities, including growing rice, raising cattle, using natural gas and coal mining, are increasingly adding to the level of methane in the atmosphere.

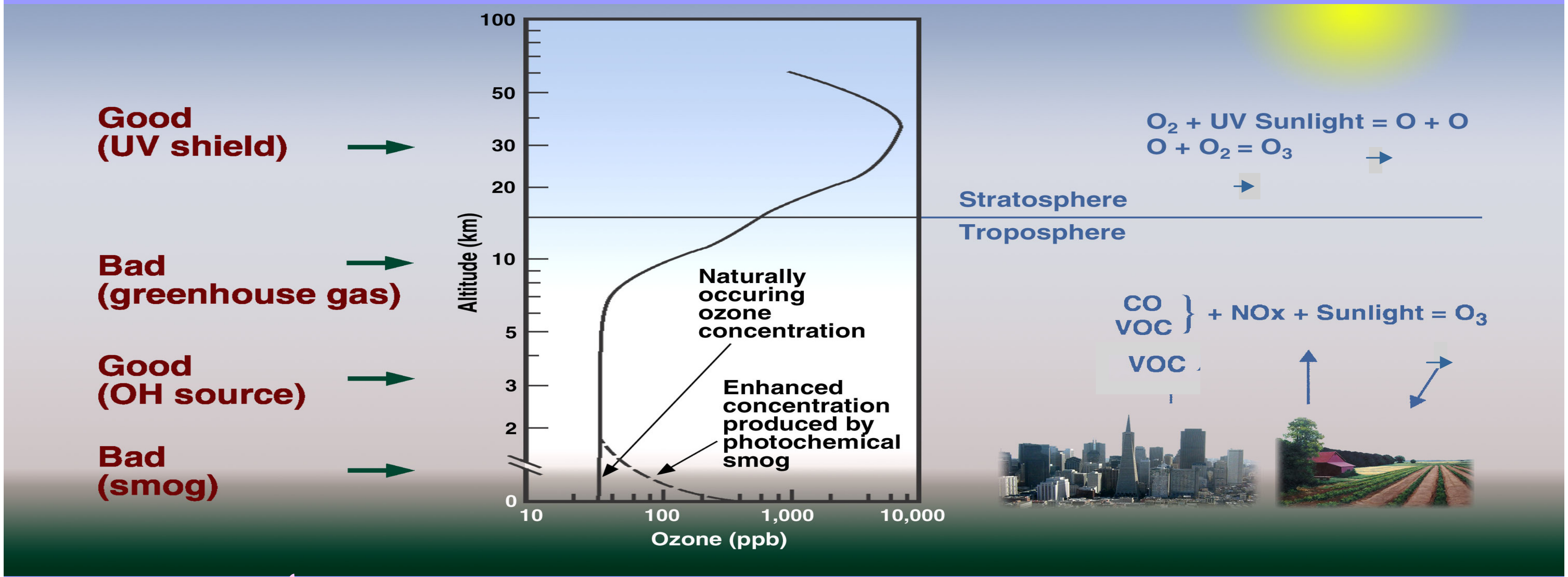
Nitrous Oxide

- Nitrous oxide is a long-lived warming gas, persisting in the atmosphere for approximately 120 years. It is produced naturally from a wide variety of biological sources in both soil and water, particularly microbial action in wet tropical forests.
- Human-related sources of nitrous oxide include agricultural soil management, animal manure management, sewage treatment, combustion of fossil fuel, and the production of a variety of acids

Ozone

- Ozone is a highly reactive molecule composed of three atoms of oxygen. Ozone concentrations vary by both geographic location and altitude. At lower levels in the trophosphere, ozone exerts a warming force upon the atmosphere, primarily due to human processes. Automobile emissions, industrial pollution, and the burning of vegetation increase the levels of carbon and nitrogen molecules which - when reacting to sunlight - produce ozone, an important contributor to photchemical smog.

OZONE: “GOOD UP HIGH, BAD NEARBY”



Tropospheric ozone precursors:

Nitrogen oxide radicals; $NO_x = NO + NO_2$

Sources: combustion, soils, lightning

Volatile organic compounds (VOCs)

- **Methane**

  Sources: wetlands, livestock, natural gas…

- **Non-methane VOCs (NMVOCs)**

  Sources: vegetation, combustion

Carbon monoxide (CO)

Sources: combustion, VOC oxidation

Percent Absorption of Infrared Radiation by Greenhouse Gases

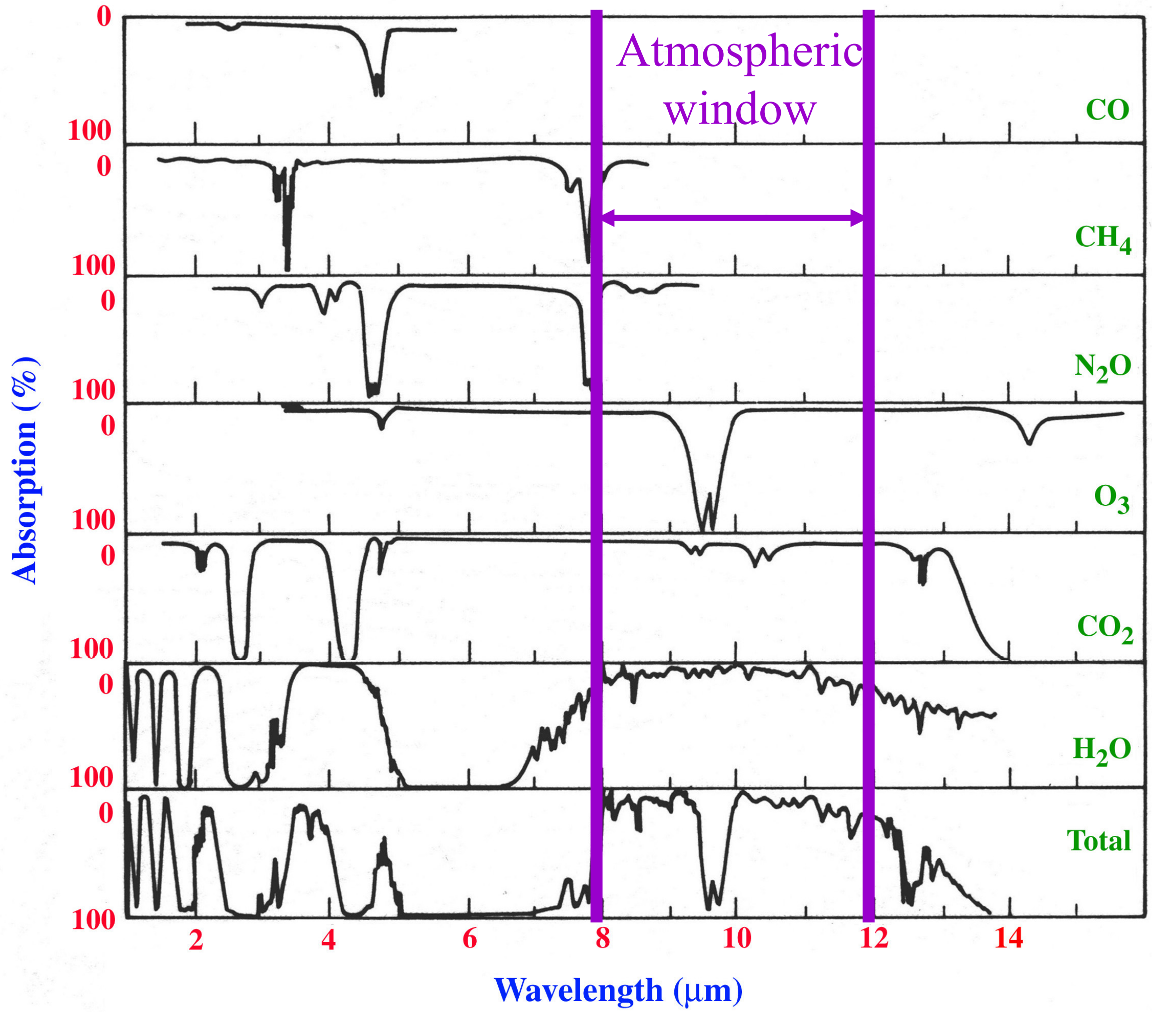


Figure 12.4

Estimated Global Warming Due to Different Gases and Particles

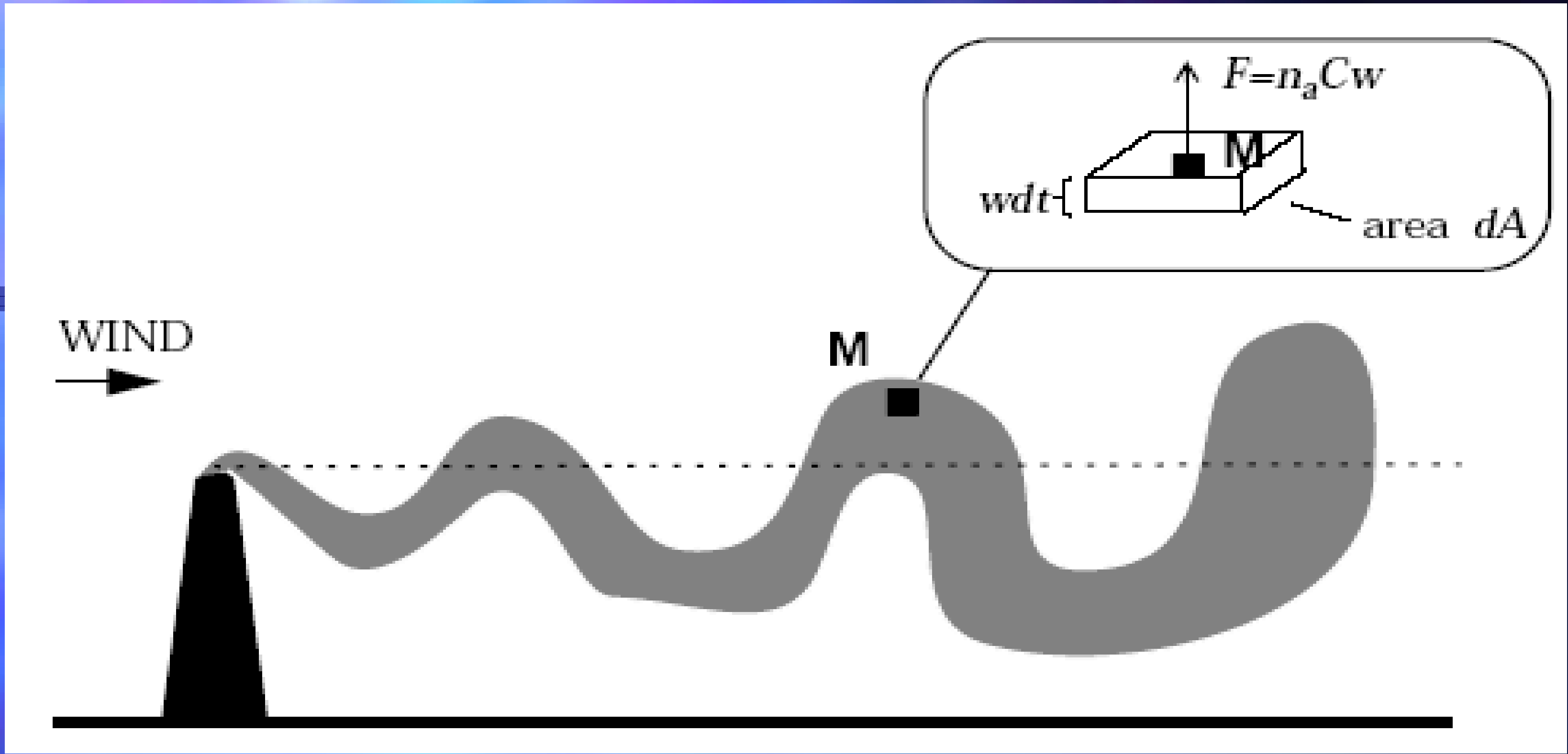
Chemical	Percent Natural Greenhouse Effect Due to Chemical	Percent Global Warming Due to Chemical
$H_2O(g)$	88.9	0
CO_2 (g)	7.5	46.6
C(s)	0.2	16.4
$CH_4(g)$	0.5	14.0
$O_3(g)$	1.1	11.9
$N_2O(g)$	1.5	4.2
$CH_3Cl(g)$	0.3	0.
$CFCL_3(g)$	0	1.8
$CF_2Cl_2(g)$	0	4.2
$CF_2ClH(g)$	0	0.6
$CCl_4(g)$	0	0.3

Feedback from gases to advection

- Net heating govern atmospheric circulation (thermal wind)
- Circulation transport gases to other locations, that lead to
- Changes in net heating

Turbulence Effect

- There are two limiting regimes for fluid flow: *laminar* and *turbulent*.
- Laminar flow is smooth and steady; turbulent flow is irregular and fluctuating.
- Flows in the atmosphere are generally turbulent



- Air parcels moving upward through *M* contain higher pollutant concentrations than air parcels moving downward; therefore, even with zero mean vertical motion of *air*, there is a net upward flux of pollutants.

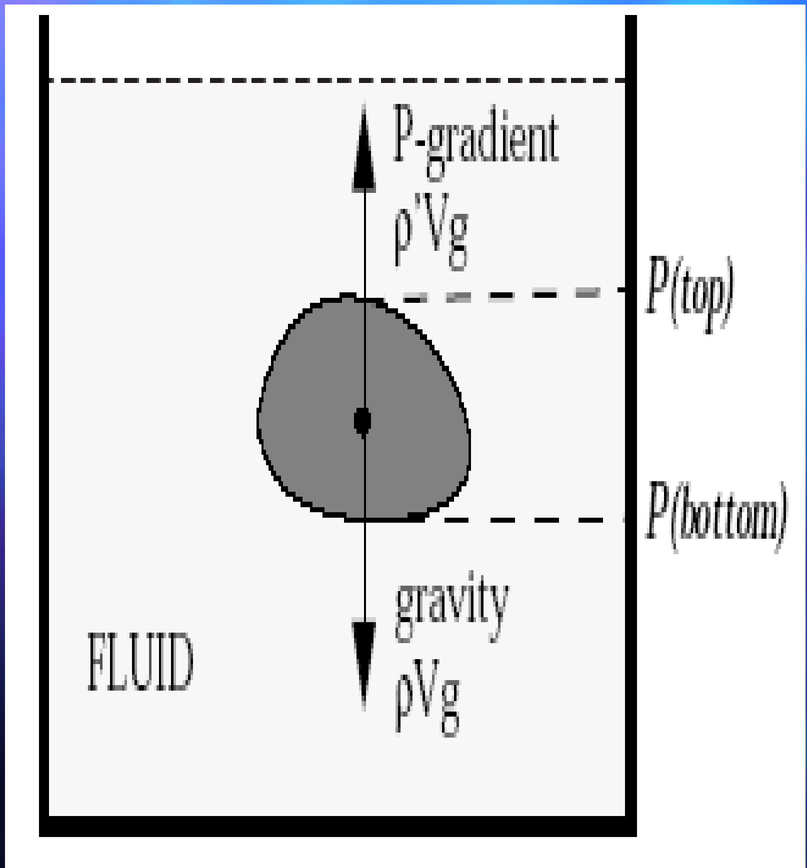
Feedback from gases to turbulence

- In practice, one finds that eddy flux can be expressed with some reliability in the lower troposphere as a function of
- (a) the wind speed and surface roughness (which determine the mechanical turbulence arising from the collision of the flow with obstacles),
- (b) the heating of the surface (which determines the buoyant turbulence), and
- (c) the altitude (which determines the size of the turbulent eddies).

Convection Feedback

- Horizontal convergence and divergence of air in the circulation induce vertical motions but the associated vertical wind speeds are only in the range 0.001-0.01 m/s (compare to 1-10 m/s for typical horizontal wind speeds)
- The resulting time scale for vertical transport from the surface to the tropopause is about 3 months
- Faster vertical transport can take place by locally driven ***buoyancy***

Buoyancy



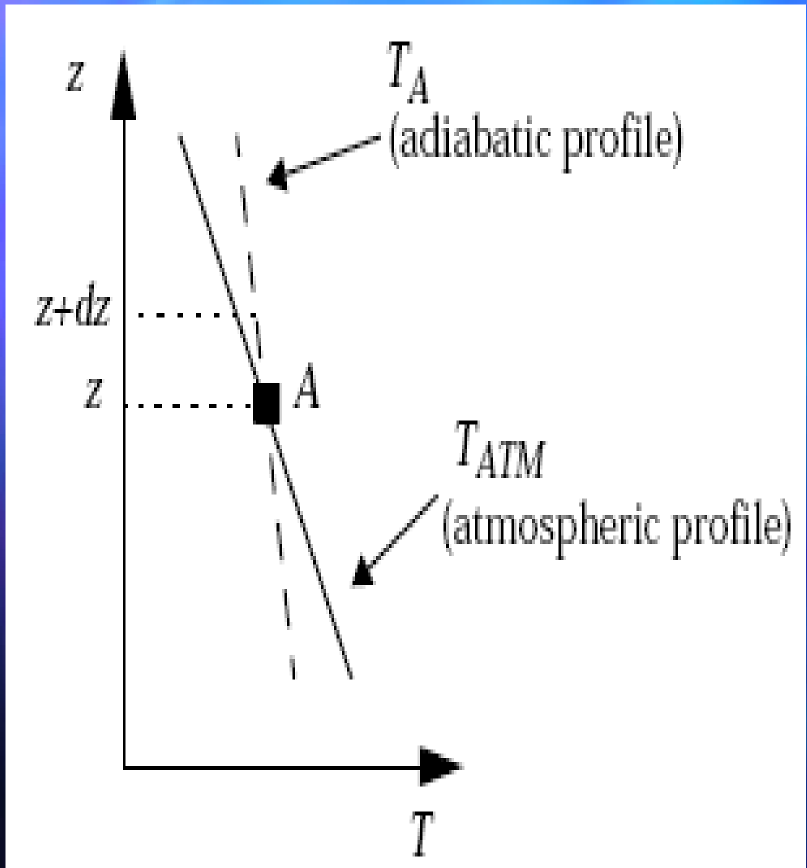
- The fluid pressure exerted on the top of the object is less than that exerted on the bottom;
- The resulting pressure-gradient force pushes the object upward, counteracting the downward force ρVg exerted on the object by gravity;
- The net force exerted on the object, representing the difference between the pressure-gradient force and gravity, is called the *buoyancy*.

The buoyant acceleration

$$\gamma_b = \frac{\rho' - \rho}{\rho} g ,$$

- If the object is lighter than the fluid in which it is immersed, it is accelerated upward; if it is heavier it is accelerated downward.

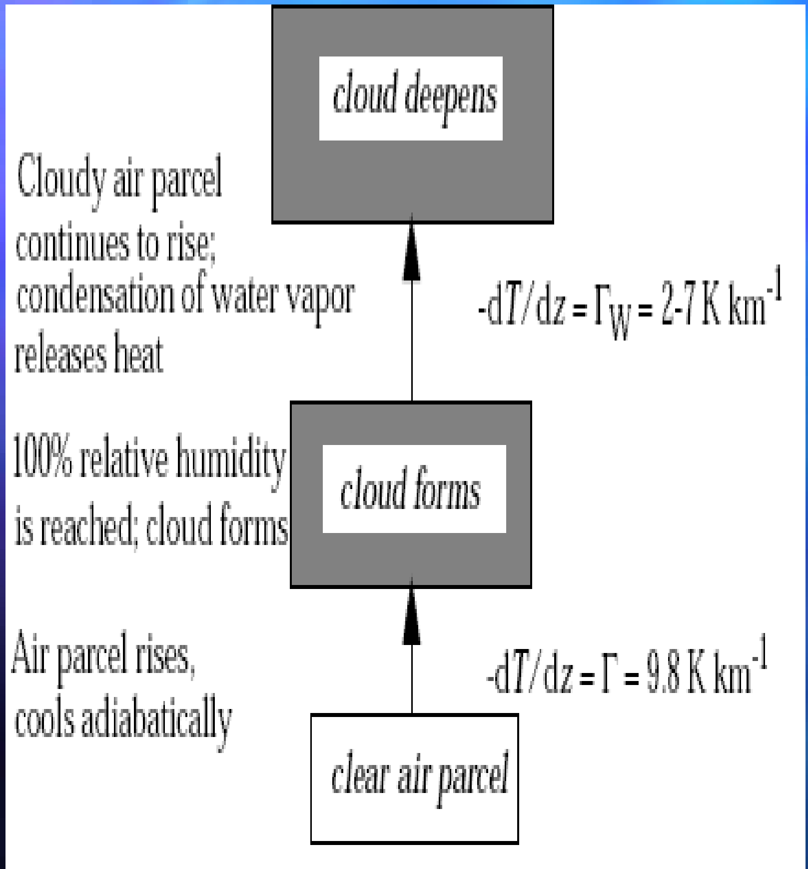
Atmospheric stability



- If $T_A(z+dz) > T_{ATM}(z+dz)$, as the rising air parcel at altitude $z+dz$ is warmer than the surrounding atmosphere at the same altitude;
- As a result, its density ρ is less than that of the surrounding atmosphere and the air parcel is accelerated upward by buoyancy.
- The atmosphere is *unstable* with respect to vertical motion, because any initial push upward or downward on the air parcel will be amplified by buoyancy.

- On the contrary, if $T_A(z+dz) < T_{ATM}(z+dz)$, then the rising air parcel is colder and heavier than the surrounding environment and sinks back to its position of origin; vertical motion is suppressed and the atmosphere is *stable*.
- Note that stability is a *local* property of the atmosphere defined by the local value of the atmospheric lapse rate; an atmosphere may be stable at some altitudes and unstable at others;
- Also note that stability refers to both upward and downward motions; if an atmosphere is unstable with respect to rising motions it is equivalently unstable with respect to sinking motions.
- Instability thus causes rapid vertical mixing rather than unidirectional transport.

Wet Convection

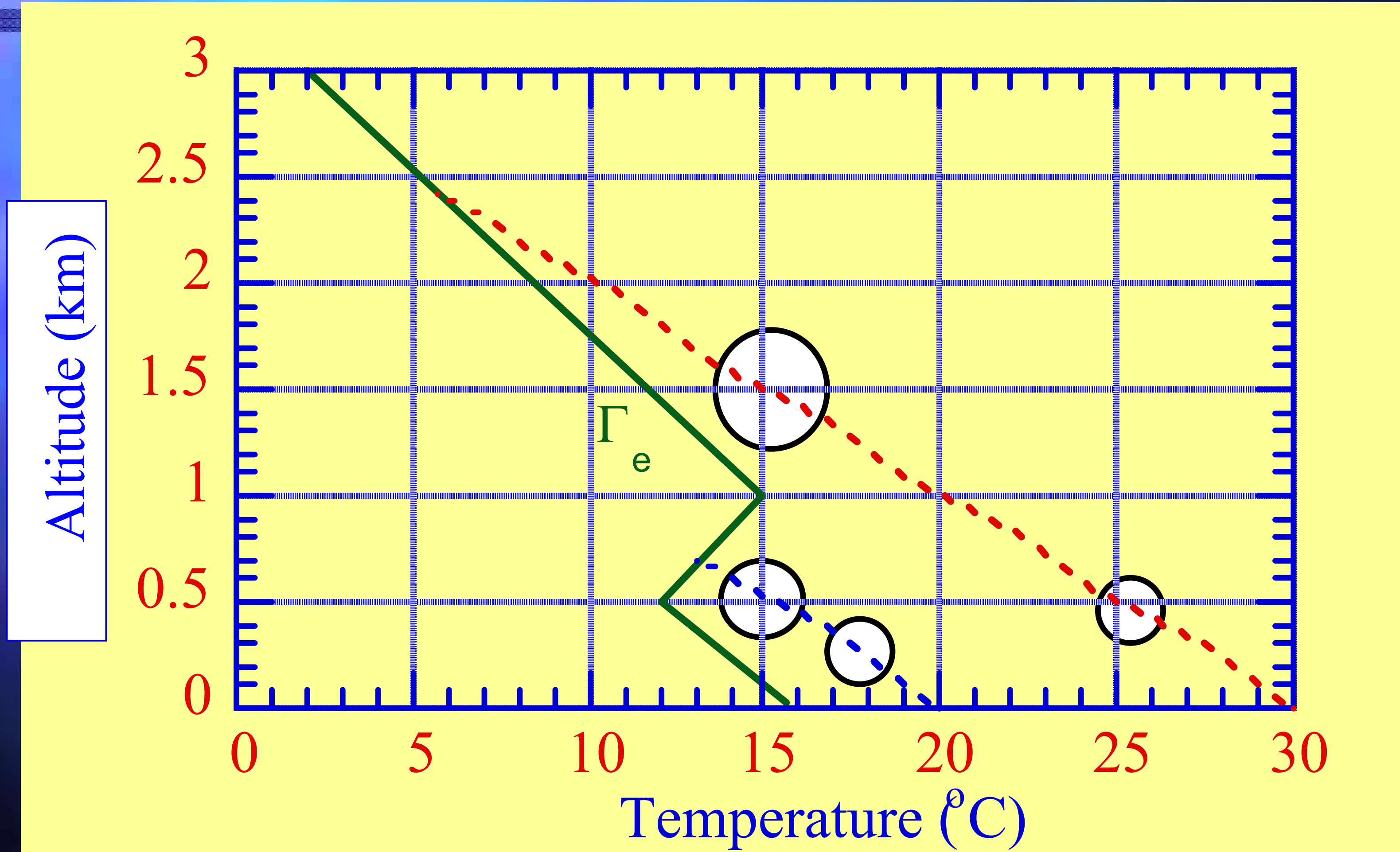


- Condensation of water vapor is an *exothermic* process, meaning that it releases heat *(latent heat release)*.
- Cloud formation in a rising air parcel provides an internal source of heat that partly compensates for the cooling due to expansion of the air parcel and therefore increases its buoyancy.

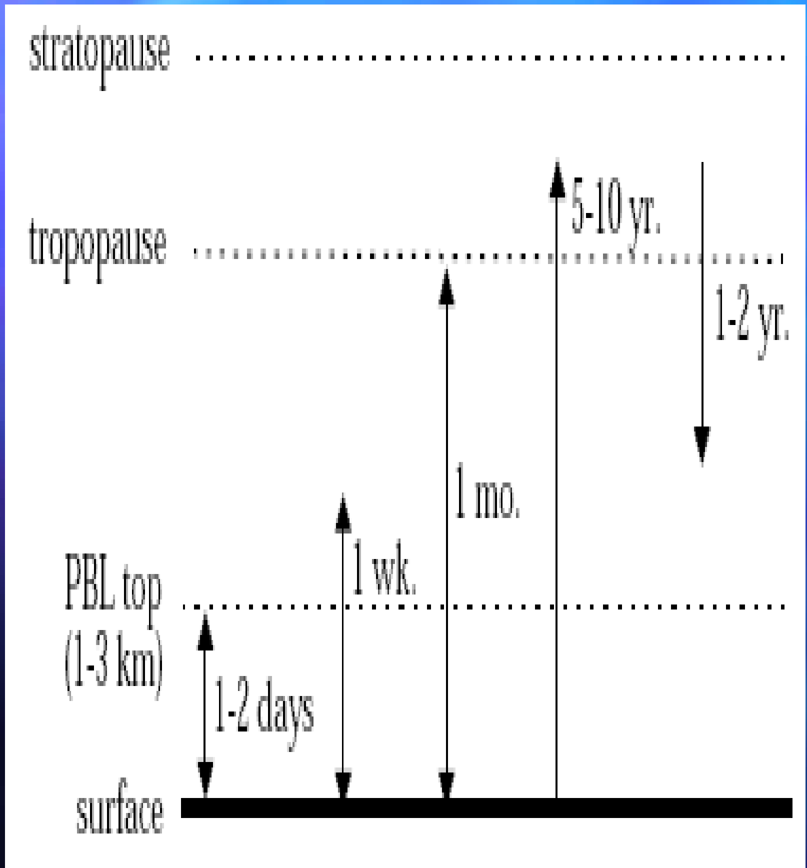
Feedback

- Convention may pump gases from Earth surface to the upper troposphere
- Their lifetime in the upper troposphere is normally longer that near the surface
- They can longer act as a radiation absorber, or heater, or cooler or chemical agent in the upper troposphere

Trapping Pollutants Under an Inversion



Time scales for vertical transport



- Age of air
- Exchange of air between the troposphere and the stratosphere is considerably slower than mixing of the troposphere because of the temperature inversion in the stratosphere

Chemical Reaction Feedback

$$k = A\exp(-E/RT)$$

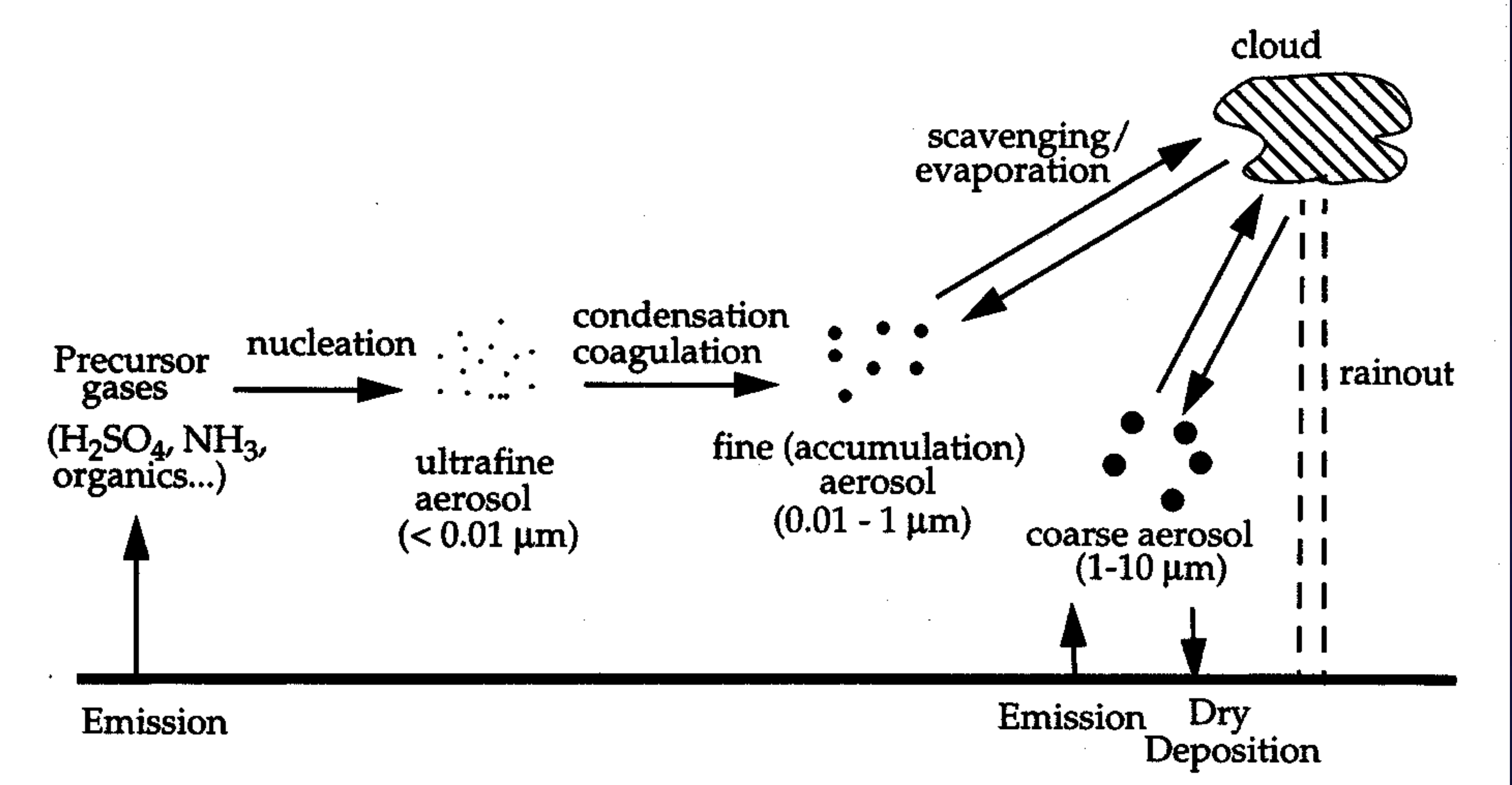
- Rates of chemical reactions depend on temperature
- Heating or cooling leads to repartioning of chemical species, and to
- Changes in net heating

Photolysis Feedback

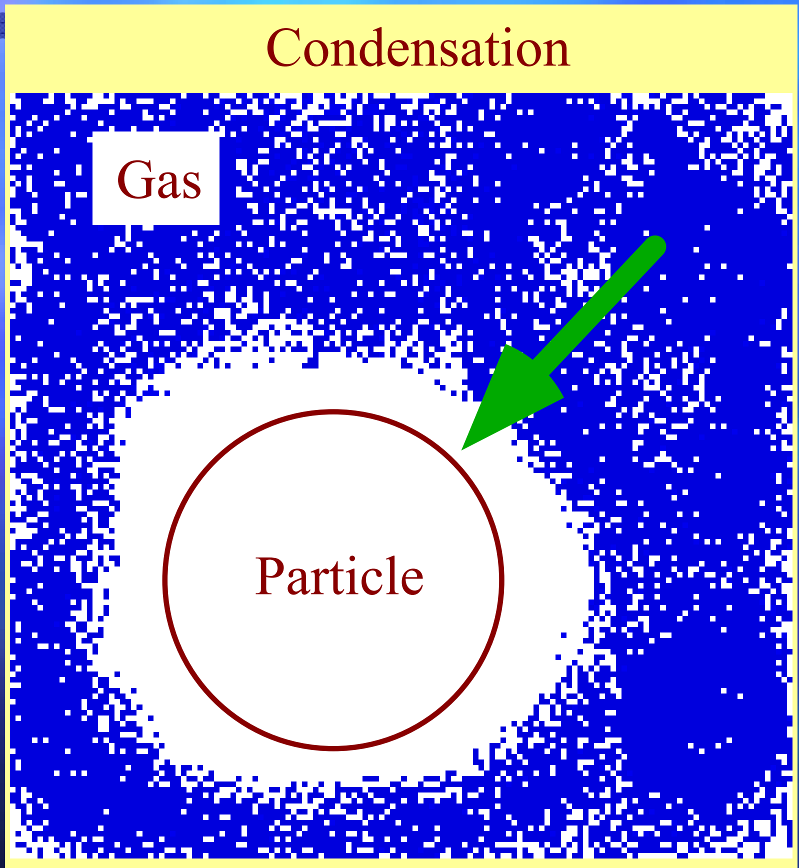
$$k = \int_{\lambda} q_X(\lambda)\sigma_X(\lambda) I_{\lambda}\, d\lambda$$

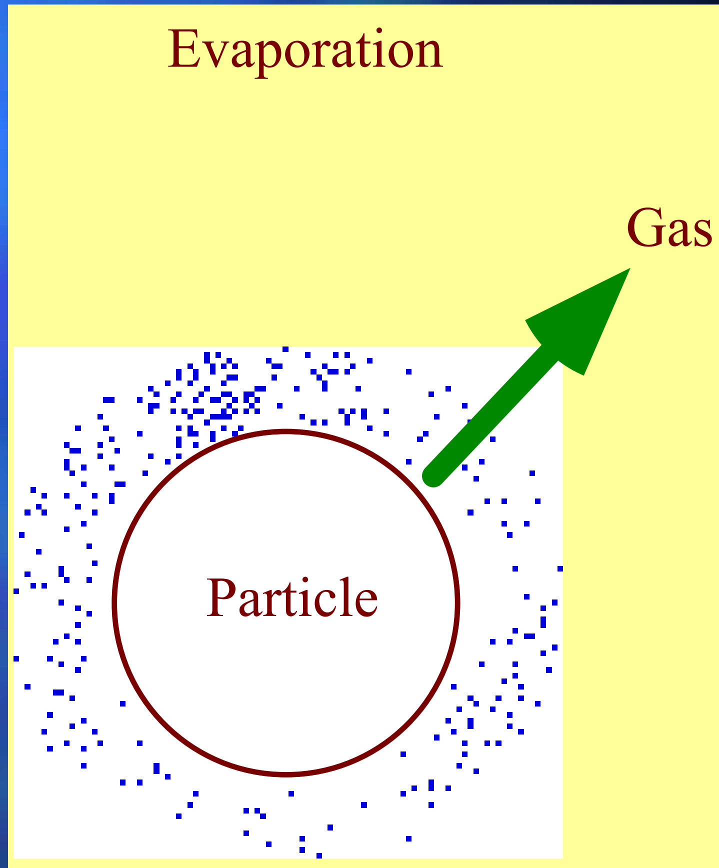
- Gas cross sections depend on temperature
- Radiation flux depends on absorption and scattering

Feedbacks of Gases and Aerosol



Condensation/Evaporation





Condensing Gases

Condensation occurs primarily on accumulation mode since it contains the largest surface area concentration of all modes.

Water vapor

- Condenses on accumulation and coarse-mode particles to form cloud drops

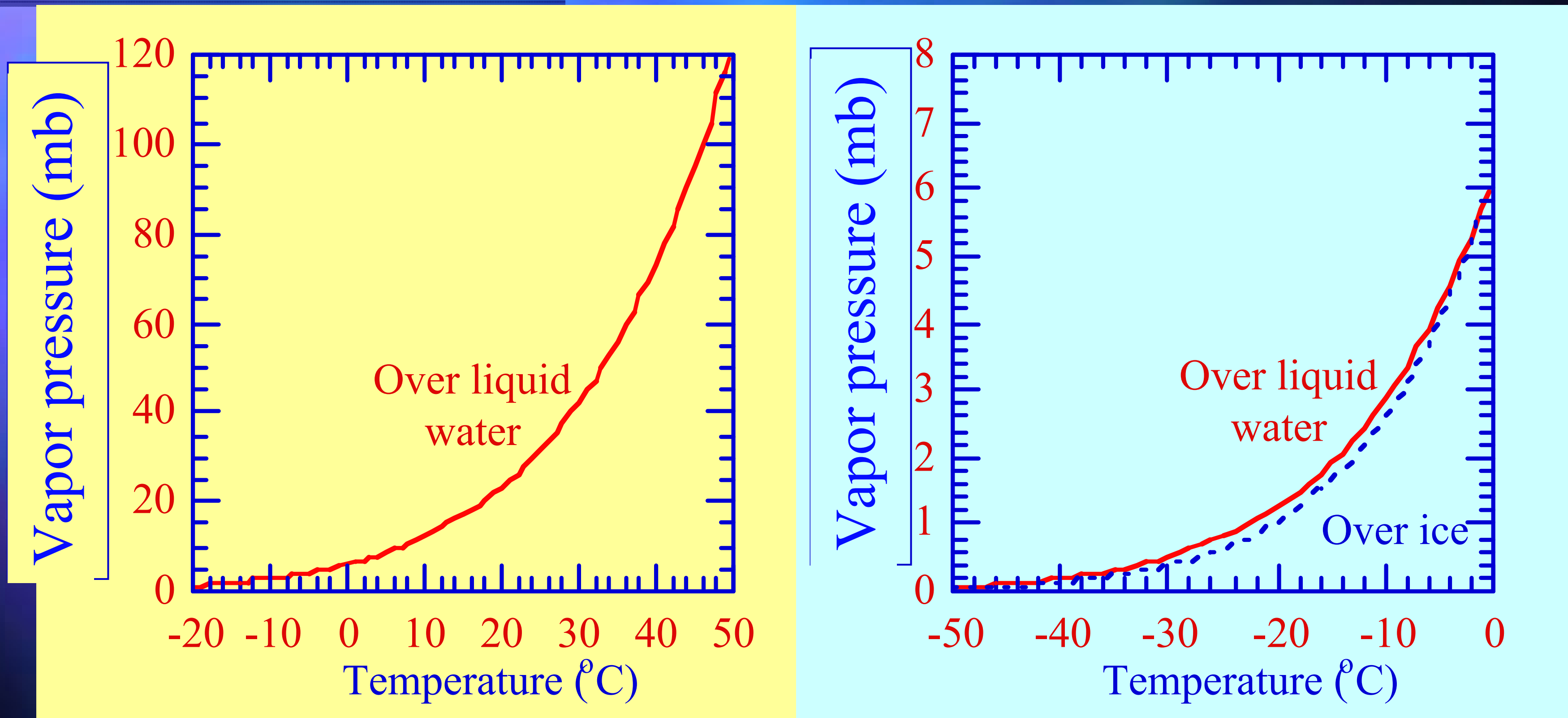
Sulfuric acid

- Condensation onto accumulation mode affects visibility

High-molecular weight organic gases

- Products of toluene, xylene, alkylbenzene, alkane, alkene, biogenic hydrocarbon oxidation condense onto accumulation mode primarily.

Saturation Vapor Pressure feedback to temperature



Dissolution

Dissolution

Process by which a gas diffuses to and dissolves in a liquid on a particle surface.

Solvent

A liquid in which a gas dissolves

Solute

Gas, liquid, or solid that dissolves in a solvent

Solution

One or more solutes plus the solvent.

Solubility

Maximum gas that can dissolve in a quantity of solvent

Common dissolving gases

$HCl(g)$, $HNO_3(g)$, NH_3 (g), $SO_2(g)$

Heterogeneous Reactions

$$ClONO_2(g) + H_2O(s) \rightarrow HOCl(g) + HNO_3(a)$$

Chlorine nitrate	Water-ice	Hypochlorous acid	Adsorbed nitric acid

$$ClONO_2(g) + HCl(a) \rightarrow Cl_2(g) + HNO_3(a)$$

Chlorine nitrate	Adsorbed hydrochloric acid	Molecular chlorine	Adsorbed nitric acid

$$N_2O_5(g) + H_2O(s) \rightarrow 2HNO_3(a)$$

Dinitrogen pentoxide	Water-ice	Adsorbed nitric acid

$$N_2O_5(g) + HCl(a) \rightarrow ClNO_2(g) + HNO_3(a)$$

Dinitrogen pentoxide	Adsorbed hydrochloric acid	Chlorine nitrite	Adsorbed nitric acid

$$HOCl(g) + HCl(a) \rightarrow Cl_2(g) + H_2O(s)$$

Hypochlorous acid	Adsorbed hydrochloric acid	Molecular chlorine	Water-ice

Additional Feedbacks of Gases

Positive

- Water-vapor-temperature-rise feedback
- Snow-albedo feedback
- Water-vapor-high-cloud feedback
- Solubility-carbon dioxide feedback
- Saturation-vapor-pressure-water-vapor feedback
- Microbe-carbon-dioxide feedback
- Permafrost-methane feedback

Negative

- Water-vapor-low-cloud feedback
- Plant-carbon-dioxide feedback

Effects of Meteorology and Climate on Gases

- Changes in temperature, humidity, and precipitation directly affect species conc.
- The cooling of the stratosphere due to the accumulation of GHGs affects lifetimes
- Changes in tropospheric vertical temperature structure affect transport of species
- Changes in vegetation alter dry deposition and emission rates of biogenic species
- Climate changes alter biological sources and sinks of radiatively active species