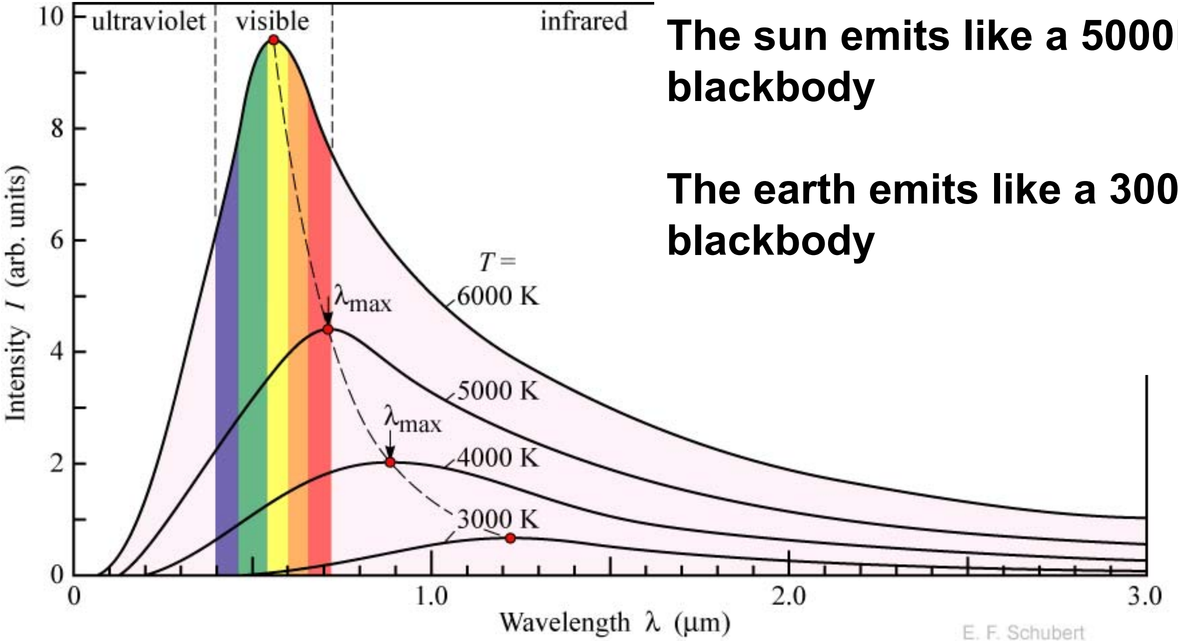
Actinic flux is the flux of photons entering a spherical volume element of air. The sun's radiation to a good approximation emits radiation as a blackbody A blackbody emits radiation with a spectrum depends on its temperature, T. The hotter the temperature, the more radiation emitted, and the quantity emitted follows an expression of ~ T^4 and the hotter the temperature the shorter the wavelength (greater the frequency) of the peak, Figure 2.

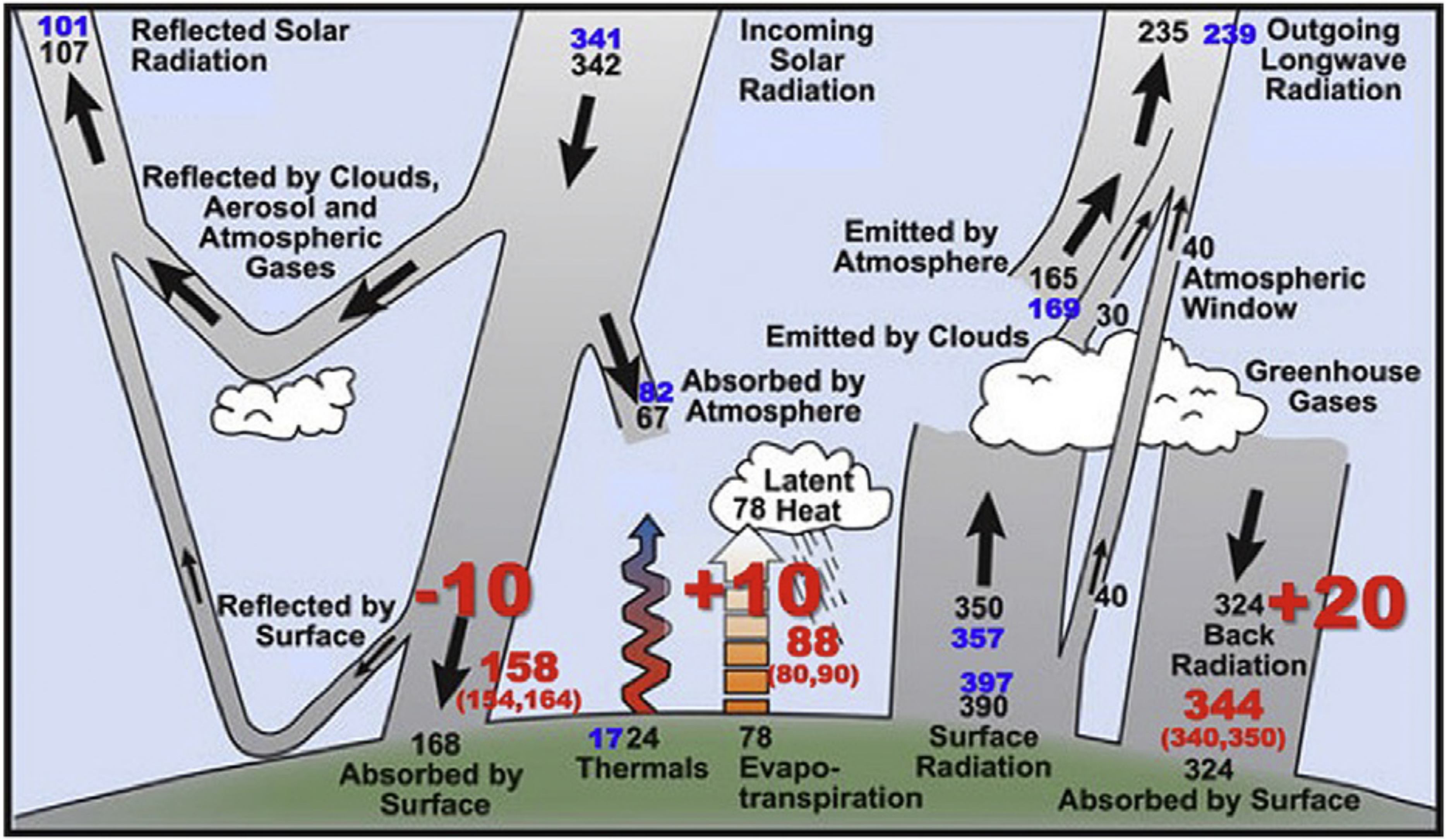
The sun emits like a 5000K blackbody

The earth emits like a 300 K blackbody



E. F. Schubert
Light-Emitting Diodes (Cambridge Univ. Press)
www.LightEmittingDiodes.org

Revisions to the 15 yr old picture (1)



From Wild (2012) (A **facelift** for the picture of the global energy balance)

Lazaros Oreopoulos, NASA Goddard, Climate and Radiation Lab (613)

Beltsville PBL Air Quality Modeling – Atmospheric Chemistry
Application Box Models Impact Climate Change Air Quality
(William Stockwell/Rosa Fitzgerald)

Objective: 1) To examine how the radiation balance between the solar extraterrestrial flux and radiation affects the Earth's temperature. 2) To apply your box model to investigate the effects of temperature changes on the formation of ozone and other air pollutants.

Radiation Balances and the Earth's Temperature

In the unit on solar actinic flux measurements, photolysis, simulation and impact on air quality the blackbody emission of solar radiation was mentioned. Here that discussion is extended and first you will calculate the Earth's temperature ignoring its atmosphere.

Consider the integrated solar extraterrestrial flux reaching the Earth's surface. We denote this flux by the symbol Ω. The photons comprising the integrated solar extraterrestrial flux may be considered to be passing through a disk perpendicular to the Earth and Sun. Assume that for a solar distance of $1.50 \times 10^{+8}$ km that the integrated solar extraterrestrial flux $\Omega = 1.372$ W m^{-2}.

What is the average flux reaching the Earth's surface? The area of a circle is πr^2 and the area of a sphere is $4\pi r^2$. If a flux, Ω, coming over an area of a circle, is mapped onto the area of sphere, the flux becomes $\Omega/4$. Note this results in a flux to the Earth's surface that is averaged over all latitudes, longitudes and between day and night and $\Omega/4 = 0.343$ W m^{-2}.

A key assumption is based on the observation that the Earth is not melting. Therefore, we can assume that the energy flux from the sun is in balance with the energy flux emitted by the Earth. The Earth reflects about 30% of the radiation from the sun and absorbs abut 70%. The reflectivity of the Earth called albedo and it has an average value of 0.30. Below the albedo will be represented as the symbol, a.

Assume that the Earth is a blackbody radiator as discussed in the unit on solar actinic flux measurements. A blackbody radiator emits radiation according to the Stefan-Boltzmann Law where ϕ is radiant energy, σ is the Stefan-Boltzmann constant equal to 5.67×10^{-8} W m^{-2} K^{-4}.

$$\phi = \sigma T^4$$

Collecting the radiation flux coming from the Sun, ϕ_{in}, and the radiation flux of the Earth, ϕ_{out}, the following equations result.

$$\phi_{in} = \frac{\Omega}{4}$$

$$\phi_{out} = \frac{a\Omega}{4} + \sigma T_{Earth}^4$$

Following the assumption that the outgoing flux equals the incoming flux the following equations result.

$$\phi_{in} = \phi_{out}$$

$$\frac{\Omega}{4} = \frac{a\Omega}{4} + \sigma T_{Earth}^4$$

Assignment

1) Solve this equation to calculate T_{Earth}.

2) Wien's displacement law gives the wavelength of a blackbody, λ, were it emits with the highest radiation intensity. Note that this wavelength depends only on temperature, T. In the equation below d represents Wien's displacement law constant and it is equal to 2.8978×10^{-3} m K

$$\lambda = \frac{d}{T}$$

Use Wien's displacement law to calculate λ for T_{Earth}. What region of the electromagnetic spectrum is T_{Earth}?

3) Discuss why this temperature is much lower that the measured average surface temperature of the Earth. You answer may depend on T_{Earth} and its corresponding λ.

Relationship Between Vapor Pressure and Temperature

Emissions of volatile organic compounds (VOC), such as gasoline component compounds, increase due to their increased vapor pressure at higher temperatures. Increases in VOC emissions caused by evaporation on high temperature days increase ozone production leading to poor air quality days. Here we examine the effect of temperature on vapor pressure.

The Clausius–Clapeyron equation describes the relationship between vapor pressure and temperature. The Antoine equation is an empirical equation that may be derived from the Clausius–Clapeyron equation. One form is given below.

$$log_{10}P = A - \frac{B}{C + T}$$

The P is the vapor pressure, the coefficients A, B and C are obtained from the curve fitting of experimental data and T is the temperature. The Antoine equation may be rearranged to give the following equation.

$$P = 10^{\left(A - \frac{B}{C+T}\right)}$$

For ethanol (CH_3OH) in the temperature range between 216 K (− 57 °C) and 353 K (80 °C) the coefficients are:

A = 8.20417
B = 1642.89
C = 230.300

Using these coefficients with T in °C provides the vapor pressure in Torr (mmHg). Note that atmospheric pressure is 760 Torr and this is equal to 1013.25 mbar.

Assignment

1) Plot the vapor pressure of ethanol for a temperature range between 0 °C and 50 °C. What is the ratio of the vapor pressure of ethanol at 40 °C and 20 °C.

2) Using the Antoine equation and the coefficients estimate the boiling point of ethanol.

Temperature Effects on Chemical Reaction Rates

Episodes with high ozone concentrations are associated with clear days and high temperatures. Photolysis rates will be higher for clear days and as shown above evaporative emissions increase with temperature. These two factors are likely to be among the most significant for increasing ozone production. In addition, increases due to the effect of temperature on the rates of ozone producing reactions should not be ignored.

As discussed in a previous unit, reaction rate coefficients that follow the Arrhenius equation increase with increasing temperature if the activation energy is positive. In the Arrhenius equation given below A is the pre-exponential factor, E_a is the activation energy per mole, R is the ideal gas constant and T is the temperature.

$$k_{AB} = A \times \exp\left(\frac{-E_a}{RT}\right)$$

Figure 1 shows simulated maximum diurnal ozone concentrations for a polluted urban case (Stockwell, 2012). The simulations were made for temperatures of 296, 298 and 300 K. For these three simulations the response of the maximum O_3 to temperature was very linear (R = 0.999). The slope of the best-fit line for this case was 4.3 ppb O_3 K^{-1}. The conclusion is that temperature increases due to climate change will make it more difficult to reduce ozone concentrations in polluted urban areas.

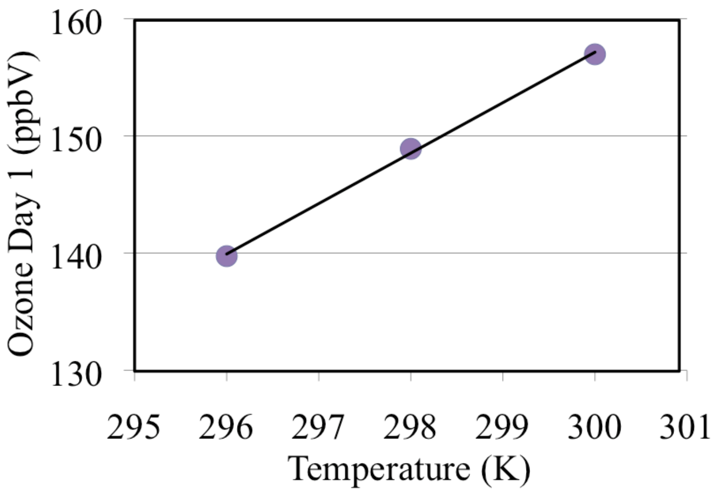


Figure 1. Simulated diurnal maximum O_3 mixing ratios as a function of temperature for a polluted urban atmosphere case (Stockwell, 2012).

Assignment

1. Use your box model without boundary layer effects to model a series of temperatures using the initial conditions given in previous unit on box modeling.

2. Speculate on how a warmer surface would affect the boundary layer evolution and how that effect your chemical results.

References

Stockwell, W.R., C.V. Lawson, E. Saunders and W.S. Goliff, A Review of Tropospheric Atmospheric Chemistry and Gas-Phase Chemical Mechanisms for Air Quality Modeling, *Atmosphere*, *3*, 1–32, 2012. doi:10.3390/atmos30100012011 available at https://www.mdpi.com/2073-4433/3/1/1