Problem 1.

A 1 m$^3$ volume of dry air contains a concentration $C$ of CO$_2$. For simplicity, let's express the volume as $V$. The photons from below are emitted from a source characterized by a brightness temperature $T_b$ that is in general a function of wavenumber $\nu$. The photons from above are characterized by a brightness temperature $T_a$ at wavenumber $\nu$. The absorption cross section per molecule for CO$_2$ is given as a function of wavenumber by the symbol $\sigma(\nu)$. Let's characterize the incoming photons as irradiance given as a function of wavenumber as

$$F(T, \nu) = \frac{\pi \nu^3 2hc^2}{\exp\left(\frac{hc\nu}{kT}\right) - 1}.$$ 

You can just use the symbol $F(T)$ below when you need to refer to blackbody radiation having brightness temperature $T$.

**HINT:** 1. Helpful notes are at http://www.paternott.com/atms749/pdf/WimpAbsorptionByYourHead.pdf
OBTAIN EXPRESSIONS FOR THE FOLLOWING:
A. How many CO$_2$ molecules are in the V as a function of P, T, and C?

B. What is the average distance between CO$_2$ molecules as a function of P and T? It may be helpful to think of the molecules filling a cubic lattice.

C. Assume for the moment that the volume has no molecules in it that absorb photons at wavenumber $\nu$. How many photons of wavenumber $\nu$, and energy $E=hc \nu$, in the wavenumber range from $\nu$ to $\nu + d\nu$ are in the volume at any time that come in from the outside? (Hint: look at the first hint above, and carefully work out the units of the Planck blackbody function expressed in terms of wavenumber).

D. Now let's put the absorbing gas back into the volume. How many photons of wavenumber $\nu$, and energy $E=hc \nu$, in the wavenumber range from $\nu$ to $\nu + d\nu$ are created per second by emission by the CO$_2$?

E. How many outside photons of wavenumber $\nu$, and energy $E=hc \nu$, in the wavenumber range from $\nu$ to $\nu + d\nu$ are destroyed per second by absorption by the CO$_2$?

Now for the remainder of the problem, let's consider specific units and number. Let's consider a temperature of 296 K, and 1013 mb pressure. Let's consider only photons associated with a single strong spectral line having absorption cross section per molecule $
 = 1.28 \times 10^{-18}$ cm$^2$ / molecule at the wavenumber $\nu = 667.661347$ cm$^{-1}$. Let's consider the spectral interval to be twice the pressure broadened half width of the line, so that $d\nu = 0.128$ cm$^{-1}$. Since we are considering such a strong spectral line, let's also consider the brightness temperature associated with photons coming from above and below to be the air temperature, 296 K. Let’s use a concentration C=385 ppm for CO$_2$.

In parts F-J of this question, calculate numbers for parts A-E above.
2. This problem analyzes how much black carbon aerosol must be present in the atmosphere so that the amount of solar radiation absorbed by it will be comparable to the amount of solar radiation absorbed at the surface of the Earth. This problem was motivated by measurements of aerosol light absorption in Mexico City where, on some days, light absorption values were quite large, though other large cities like Las Vegas Nevada may also behave in a similar way. This issue is related to the development of the mixed layer during daylight hours.

A. Consider a layer of atmosphere of thickness $dz$. Show that the heating rate for this layer can be calculated from the relationship

$$\frac{dT}{dt} = \frac{1}{\rho c_p} \frac{dF_{\text{net}}}{dz}$$

where $\rho$ is the layer density, $c_p$ is the layer heat capacity per unit mass, and $F_{\text{net}}$ is the net irradiance. It is helpful to draw a layer with irradiance coming and going from both the layer bottom and top, and to carefully define the net irradiance. This is a very simple equation that could also be used to calculate the time rate of change of the temperature of a cup of tea subjected to heat absorbed per unit volume per unit time.

B. For now, let’s consider the surface albedo to be zero so that all light arriving at the surface is absorbed. The spectral net irradiance as a function of height in the atmosphere is given by the down welling solar irradiance

$$F(\lambda, z) = F_0(\lambda) \exp\left[-\tau_{\text{abs}}(\lambda, z)\right]$$

where $F_0(\lambda)$ is the solar irradiance at the top of the atmosphere as a function of wavelength $\lambda$, and $\tau_{\text{abs}}(\lambda, z)$ is the absorption optical depth. The absorption optical depth can also be given by

$$\tau_{\text{abs}}(\lambda, z) = \int_{z'}^{H} \beta_{\text{abs}}(\lambda, z') dz'$$

which is the total absorption optical depth of the atmosphere above the layer $dz$ where $\beta_{\text{abs}}(\lambda, z)$ is the absorption coefficient that we measure with our photoacoustic instruments. Dig out the fundamental theorem of calculus from your calculus book, along with the chain rule for differentiation, and see if you agree with me that the heating rate can be expressed as
\[
\frac{dT}{dt} = \frac{1}{\rho c_p} \int_0^\infty \beta_{abs}(\lambda, z) F_0(\lambda) \exp\left[-\tau_{abs}(\lambda, z)\right] d\lambda.
\]

Why do we have to integrate this equation over wavelength? We are faced with the need to specify the wavelength dependence of the absorption coefficient.

C. For air, show that \( \rho c_p = \frac{7}{2} \frac{P}{T} \) where T and P are the local temperature and pressure. You will have to dig out your atmospheric thermodynamics books or notes on that one. Let's proceed by making the standard soot assumption that aerosol light absorption varies inversely with wavelength,

\[
\beta_{abs}(\lambda, z) = \beta_{abs}(\lambda_0, z) \frac{\lambda_0}{\lambda}
\]

where \( \beta_{abs}(\lambda_0, z) \) is the measured aerosol light absorption coefficient at wavelength \( \lambda_0 \), such as 532 nm, the wavelength we used in Mexico City. Let's make the approximation that the solar irradiance in the integral in part B can be taken as

\[
F_0(\lambda) \exp\left[-\tau_{abs}(\lambda, z)\right] = \left(\frac{r_s}{r_{se}}\right)^2 \frac{2\pi h c^2}{\lambda^5 \left(\exp\left[\frac{h c}{\lambda k T_{sun}}\right] - 1\right)} \cos(\theta_t)
\]

where \( r_s \) is the radius of the sun, \( r_{se} \) is the sun to earth distance, \( T_{sun} \) is the sun temperature, and \( \cos(\theta_t) \) is the cosine of the solar zenith angle relative to a surface normal from the earth. Let \( x = \frac{h c}{\lambda k T_{sun}} \). Hold on tight, you are going to calculate something akin to the Stefan Boltzmann 'radiation law'. Show that the heating rate goes as

\[
\frac{dT}{dt} = (1 + A) \frac{14.2 \pi T}{P} \lambda_0 \beta_{abs}(\lambda_0, z) \left(\frac{k T_{sun}}{h^4 c^3}\right)^{\frac{5}{2}} \left(\frac{r_s}{r_{se}}\right)^2 \cos(\theta_t)
\]

where the surface albedo is A, and the factor \( (1+A) \) models a two way path through the atmosphere (solar radiation causes heating when it first passes through the atmosphere to the surface, and when it is reflected from the surface back towards space. We just stick this factor in near the end of the problem, for convenience.) Hint: You may need the integral relationship

\[
\int_0^\infty \frac{x^4}{e^x - 1} dx = 24.89, \quad \text{and if you can check this by digging out an integral table, that would be very helpful. Notice that the heating rate goes as the 5th power of the sun's temperature, whereas the total emission from the sun as a black body emitter goes as the 4th power of the sun's temperature.}
\]
D. The Stefan Boltzmann constant is $\sigma = \frac{2\pi^7 k^4}{15h^3 c^2}$. The solar irradiance at the top of the atmosphere is approximately $F_0 = \sigma T_{sun}^4 \left( \frac{r_s}{r_{sc}} \right)^2$. Use these two items to rewrite the heating rate in part C as

$$\frac{dT}{dt} = \left(1 + A\right) \frac{106.5}{\pi} \frac{T}{P} \frac{\lambda_0 \beta_{abs} (\lambda_0, z) kT_{sun}}{hc} F_0 \cos(\theta_t).$$

Now that you have come all this way, interpret this equation in words.

E. You can do this part even if you cannot do any other part of this problem. It involves some estimation perhaps, and some looking up of parameters. Being careful with units, put in numbers for the various constants and parameters, and evaluate the heating rate due to black carbon. Note: the highest value obtained for the absorption coefficient in Mexico City was 180 Mm$^{-1}$ at 532 nm where 1 Mm=10$^6$ meters. The elevation of Mexico City is around 7,300 feet, and this corresponds to an air pressure of around 773 mb. The air temperature can be taken as 300 K.

F. Discuss at least 3 criticisms of the results given in part D. **BONUS:** When sunlight is absorbed at the surface, heat travels initially by conduction into the air, into the ground, and into liberating water vapor molecules (latent heat.) The wind and convection can take away the heat and vapor that goes into the air. See if you can calculate a heating rate for the air at the surface that you can compare with the heating rate caused directly by black carbon. See the boundary layer chapter in the new Wallace and Hobbs book.
3. Prepare a model to explain the observation described in Figure 4.5 of Stamnes and Thomas, reproduced here.

**Figure 4.5** Dots: Ultra-high-resolution measurement of an individual molecular absorption line of CO$_2$ in the 936-cm$^{-1}$ region from solar spectra obtained from Denver, Colorado during sunset on January 12, 1989, with a BOMEM model DA3.002 interferometer (see Endnote 9). Solid curve: theoretical line profile (see Eq. 10.50).