Physics of Atmospheres and Oceans: Class Question Sheets

OZONE

*Indicates optional question

O.1 (i) Write down an expression for the heating rate of the atmosphere h (i.e. dT/dt in units of K s^{-1}) at height z due to absorption of solar spectral irradiance $E_{\tilde{\nu}s}\Delta\tilde{\nu}$ (integrated over the absorption band) by an absorber of density $\rho_a(z)$ with constant absorption coefficient k when the sun is overhead.

(ii) A simple model of radiative heating by solar radiation in the upper stratosphere and lower mesosphere assumes that ozone has a mass mixing ratio

$$x(p) = ap^{1/2}$$

where a is a constant and p is pressure. Show that the heating rate h due to ozone is proportional to

$$p^{1/2}\exp\left(-\frac{2ak}{3g}p^{3/2}\right)$$

where k is the absorption coefficient of ozone for solar radiation. Sketch this function against height or $\ln(p)$, and show that the pressure $p_{\rm m}$ at which h is a maximum is close to that of the stratopause, and evaluate $h(p_{\rm m})$ in K day^{-1}.

[Take $k = 1.5\times10^4\,{\rm m^2\,kg^{-1}}$ in a spectral region where the solar flux is 7 W m^{-2}, $a = 3\times10^{-7}$ Pa$^{-1/2}$, and the specific heat capacity of air, $c_{\rm p} = 1000$ J kg^{-1} K^{-1}.]

(iii) In a simple model of radiative cooling due to thermal emission by CO_2 ('cooling to space'), the cooling rate C is given by

$$C = -\frac{g}{c_{\rm p}}\left(\frac{d\tau}{dp}\right)\pi B(T)\Delta\tilde{\nu}$$

where τ is the transmittance from pressure level p to space. The spectrally integrated Planck function $B(T)\Delta\tilde{\nu}$ can be approximated in the CO_2 band by

$$B(T)\Delta\tilde{\nu} = 15(T/300)^{3.8}\quad {\rm W\,m^{-2}\,ster^{-1}}$$

and τ can be taken to have the form

$$\tau = \exp(-\beta p)$$

where $\beta = 3.6\times10^{-4}$ Pa^{-1}. Estimate the temperature needed at $p_{\rm m}$ for the atmosphere to be in radiative equilibrium. Diurnal variations of heating can be roughly accounted for by dividing $h(p_m)$ by 2 (why?).

O.2 By analogy with the Planck function, write down an expression for the spectral flux of photons (photons per unit area per unit time per unit wavenumber) emitted by a black body. Assuming that the sun is a black body at 5800 K, and that the solar flux E_s at the top of the atmosphere is $1370\,\mathrm{W\,m^{-2}}$, estimate the flux of solar photons P_s incident on the atmosphere.

Calculate the fraction of the total photon flux that lies in each of the wavelength ranges (i) $\lambda < 1180$ nm (dissociation of O_3), (ii) $240 < \lambda < 280$ nm (Hartley band), (iii) $\lambda < 240$ nm (dissociation of O_2).

[Use the following data: given $f(y) = \int_y^\infty x^2/(e^x - 1)\,dx$, then $f(0) = 2.40$, $f(2.09) = 1.37$, $f(8.81) = 1.44 \times 10^{-2}$ and $f(10.28) = 4.32 \times 10^{-3}$. Also $\int_0^\infty x^3/(e^x - 1)\,dx = \pi^4/15$ and Stefan's constant $\sigma = 5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$.]

O.3 The Chapman scheme for ozone has two time constants for the return to equilibrium, fast and slow. The slow time constant is given by (see lecture notes):

$$\tau_{\mathrm{SLOW}} = \frac{1}{2k_3\bar{n}_1}\,.$$

Obtain the alternative forms:

$$\tau_{\mathrm{SLOW}} = \frac{k_1 n_2 n_m}{2k_3 J_3} \cdot \frac{1}{\bar{n}_3} = \frac{1}{2}\left(\frac{k_1 n_m}{J_2 J_3 k_3}\right)^{\frac{1}{2}} = \frac{\bar{n}_3}{2J_2 n_2}\,.$$

Show that the fast time constant is given by:

$$\tau_{\mathrm{FAST}} \simeq \frac{1}{k_1 n_2 n_m}\,.$$

[Hint: ignore the slow reactions.] Estimate both time constants at 25mb, 10 mb and 1 mb.

[Rate constants etc. can be found in the lecture notes.]

O.4 Add the catalytic reactions

$$\mathrm{X} + \mathrm{O_3} \rightarrow \mathrm{XO} + \mathrm{O_2}$$
$$\mathrm{XO} + \mathrm{O} \rightarrow \mathrm{X} + \mathrm{O_2}$$

with rates k_{X} and k_{XO} to the Chapman scheme and explain how this modifies the algebra for the Chapman scheme. Assuming that the extra reactions are much slower than the fast equilibrium between O_3 and O_2+O, show that the vertical distribution of ozone is given by

$$\frac{n_3}{n_2} \approx \left(\frac{J_2 k_1 n_M}{J_3 k_3}\right)^{1/2} - \left(\frac{k_1 k_X n_M n_X}{2J_3 k_3}\right)\,.$$

[Hint: obtain and solve a quadratic equation for n_3/n_2; then make a suitable approximation.]

What mixing ratios (i.e. n_X/n_M and n_{XO}/n_M) would be required to make a significant difference to ozone at 1 mb, for the case X=Cl?

O.5 What happens to O and O_3 according to the Chapman scheme when solar radiation switches off at sunset? How quickly does it happen? If catalysts are present, what happens to X and XO? How quickly does it happen in the case X = Cl? [Assume that $k_1 n_2 n_M + k_3 n_3 \geq 10^{-1}\,\mathrm{s}^{-1}$ throughout the stratosphere.]

*O.6 Measurements are made of solar ultraviolet radiation at the surface, at a single wavelength and two solar zenith angles θ_1 and θ_2. The solar radiance at the top of the atmosphere is not known. How would you determine the total column amount of ozone assuming that the absorption is entirely due to atmospheric ozone, with known absorption coefficient k?

If there is another absorber present (e.g. aerosol) with an absorption coefficient which is independent of wavelength, and if measurements are also made at two wavelengths λ_1 and λ_2 where the ozone absorption with known absorption coefficients are k_1 and k_2 respectively, how would you derive the total ozone column?

Can you still obtain total ozone if the instrument's gain (i.e. its radiometric calibration) is unknown?

[10.05]