12. Ozone photochemistry and surface destruction*

The ozone photochemical process in the stratosphere and the ozone destruction by heterogeneous chemical reactions in the planetary boundary layer are parameterized following Cunnold *et al.* (1975), and Schlesinger and Mintz (1979). (see also Schlesinger, 1976)

12.1 Photochemical reactions

The photochemical production and destruction of ozone in the stratosphere is comprised of both the Chapman reactions

$$O_2 + h\nu \xrightarrow{j_1} 2O \tag{12.1}$$

$$O + O_2 + M \xrightarrow{k_1} O_3 + M \tag{12.2}$$

$$O_3 + h\nu \xrightarrow{j_2} O_2 + O \tag{12.3}$$

$$O + O_3 \xrightarrow{k_2} 2O_2 \tag{12.4}$$

and the $NO-NO_2$ catalytic cycle

$$NO + O_3 \xrightarrow{k_3} NO_2 + O_2 \tag{12.5}$$

$$NO_2 + O \xrightarrow{k_4} NO + O_2 \tag{12.6}$$

$$NO_2 + h\nu \xrightarrow{j_3} NO + O \tag{12.7}$$

The chemical reaction rates k_i are

$$\begin{aligned} k_1 &= 1.1\times10^{-46}\exp(520/T) && m^6s^{-1}, \\ k_2 &= 1.9\times10^{-17}\exp(-2300/T) && m^3s^{-1}, \\ k_3 &= 2.1\times10^{-18}\exp(-1450/T) && m^3s^{-1}, \\ k_4 &= 9.1\times10^{-18} && m^3s^{-1}, \end{aligned} \tag{12.8}$$

and the photodissociation rate $j_n(p)$ of species n at pressure p is given by

$$j_n(p) = \int_0^\infty \alpha_n(\lambda)\, I_0(\lambda)\, \exp\left[-M_F \sum_{m=1}^{2} \alpha_m(\lambda)\, U_m(p)\right] d\lambda \tag{12.9}$$

Here $\alpha_n(\lambda)$ is the absorption cross section of species n (1 : O_2, 2 : O_3, 3 : NO_2) at wave length

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* This chapter is prepared by I. Yagai: Forecast Research Division

λ, $I_0(\lambda)$ is the extraterrestrial monochromatic photon flux per unit wave length. M_F is a magnification factor to account for the departure from the plane parallel atmosphere, which will be defined by (13.51) in Chapter 13, and U_m is the absorber amount of species m (1 : O_2, 2 : O_3) in a vertical column above pressure p, and the summation extends over all species m. To calculate photodissociation rates $j_n(p)$, the values of $\alpha_1(\lambda)$, $\alpha_2(\lambda)$ and $I_0(\lambda)$ are taken from Ackermann (1971), Kockarts (1971), and $\alpha_3(\lambda)$ from the data of The Natural Stratoshere of 1974, CIAP Monograph 1. Currently $j_n(p)$ is computed by a linear bivariate interpolation of precomputed values of $j_n(p)$ as a function of U_1 and U_2 to save CPU time.

12.2 Governing equations for the photochemical reactions

The equations governing the time change rates of the concentration of O, O_2, O_3, NO, and NO_2 given by reactions (12.1)—(12.7) are

$$\frac{\partial[O]}{\partial t}=2j_1[O_2]-k_1[O][O_2][M]+j_2[O_3]-k_2[O][O_3]-k_4[O][NO_2]+j_3[NO_2], \tag{12.10}$$

$$\frac{\partial[O_2]}{\partial t}=-j_1[O_2]-k_1[O][O_2][M]+j_2[O_3]+2k_2[O][O_3]+k_3[NO][O_3] +k_4[NO_2][O], \tag{12.11}$$

$$\frac{\partial[O_3]}{\partial t}= k_1[O][O_2][M]-j_2[O_3]-k_2[O][O_3]-k_3[NO][O_3], \tag{12.12}$$

$$\frac{\partial[NO]}{\partial t}=-k_3[NO][O_3]+k_4[NO_2][O]+j_3[NO_2], \tag{12.13}$$

$$\frac{\partial[NO_2]}{\partial t}=k_3[NO][O_3]-k_4[NO_2][O]-j_3[NO_2], \tag{12.14}$$

where [X] denotes the concentration of species X in molecules m^{-3} and M represents that of air.

The equilibrium concentrations of atomic oxygen O and nitric monooxide NO are calculated by (12.10) and (12.13),

$$[O]_e = \frac{2j_1[O_2]+j_2[O_3]+j_3[NO_2]}{k_1[O_2][M]+k_2[O_3]+k_4[NO_2]}, \tag{12.15}$$

$$[NO]_e = \frac{k_4[NO_2][O]+j_3[NO_2]}{k_3[O_3]}, \tag{12.16}$$

the relaxation times are approximately given by $\tau_O \approx (k_1[O_2][M])^{-1}$ and $\tau_{NO} \approx (k_3[O_3])^{-1}$; their representative values are order 1 minute and 10 minutes, respectively. Then, it can be assumed that O and NO are in equilibrium with other constituents, and we can approximate $[O]_e$ and $[NO]_e$ instead of $[O]$ and $[NO]$.

Substituting (12.15) and (12.16) into (12.12) gives

$$\frac{\partial [O_3]}{\partial t} = A - B[O_3] - C[O_3]^2 \tag{12.17}$$

where

$$A = 2\frac{k_1 j_1 [O_2]^2[M] - k_4 j_1 [O_2][NO_2] - k_4 j_3 [NO_2]^2}{k_1[O_2][M] + k_2[O_3] + k_4[NO_2]}$$

$$B = 2\frac{k_2 j_1 [O_2] + (k_2 j_3 + k_4 j_2)[NO_2]}{k_1[O_2][M] + k_2[O_3] + k_4[NO_2]}$$

$$C = 2\frac{k_2 j_2}{k_1[O_2][M] + k_2[O_3] + k_4[NO_2]}$$

$[O_2]$ can be given as $[O_2] = 0.21[M]$, and $[NO_2]$ is prescribed to vary only in the vertical with the relation

$$[NO_2](z) = \beta [NO_2]_{McElroy}(z) \tag{12.18}$$

where $[NO_2]_{McElroy}(z)$ is the one-dimensional profile calculated by McElroy *et al.* (1974), and β is an empirical constant to adjust the simulated O_3 mixing ratio to the observed value at 10 mb in the tropics. Currently β is set to 1.62.

12.3 Vertical distribution of absorber amounts

The integrated absorber amount of species m in a vertical column above pressure p is defined by

$$U_m(p) = \frac{1}{g}\int_0^p [\ \ ]_m(p) \frac{dp}{\rho} \tag{12.19}$$

where $[\ \ ]_m$ is the concentration of species m in molecules m^{-3}. We assume that molecular oxygen is well-mixed throughout the atmosphere, $[O_2] = 0.21[M]$; then for molecular oxygen

$$U_1(p) = \frac{0.21\, a\, p}{g\, m} \tag{12.20}$$

where a is Avogadro's number, and m is the molecular weight of air. For ozone, it is assumed that the number density $[O_3(z)]$ above the midlevel of layer 1 decays exponentially with altitude following Krueger (1973). Thus

$$[O_3(z)] = [O_3(z_1)] \exp\left(-\frac{z-z_1}{H}\right) \qquad z \geq z_1 \tag{12.21}$$

where $[O_3(z_1)]$ is the GCM predicted ozone number density for layer 1, and H is the scale height for ozone (=4.45km). Then (12.19) can be written as

$$U_2(p) = \int_{Z_1}^{\infty} [O_3(z)]\,dz + \frac{a}{g m_{O3}} \int_{P_1}^{P} q_{O3}\,(p)\,dp \tag{12.22}$$

where m_{O3} is the molecular weight of ozone.

12.4 Ozone destruction at the earth's surface

Ozone is destroyed at the earth's surface by heterogeneous chemical reactions. The rate of destruction D_{O3} may be expressed as

$$D_{O3} = \rho K\,(q_{O3})_s \tag{12.23}$$

where ρ is the air density, K the reaction rate constant, $(q_{O3})_s$ the surface ozone mixing ratio. We assume that the destruction D_{O3} is approximately compensated by the downward ozone flux at the top of the planetary boundary layer (PBL), $(F_{O3})_B$ which may be approximated as

$$(F_{O3})_B = \rho D \frac{\partial q_{O3}}{\partial Z} \fallingdotseq \rho D \frac{(q_{O3})_{LM} - (q_{O3})_S}{Z_{LM} - Z_S} \tag{12.24}$$

where D is the eddy diffusivity at the top of the PBL, Z the altitude, and subscript LM denotes the midlevel of the lowest layer. $(q_{O3})_s$ is determined by equating (12.23) with (12.24) as

$$(q_{O3})_S = \frac{D}{D + K(Z_{LM} - Z_S)} (q_{O3})_{LM} \tag{12.25}$$

The constants K and D are currently assigned to 0.0008 m sec^{-1} and 10 $m^2 sec^{-1}$ after Cunnold *et al.* (1975).