Ozone in the mesosphere and lower thermosphere

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Abstract. One-dimensional photochemical diffusive model has been used to obtain the altitude and temporal variation of O_3 in the range of 50 to 150 km height. More than 60 chemical reactions and photo-dissociations of oxygen-hydrogen atmosphere are incorporated. Their contribution in the formation or distribution directly or indirectly, is critically examined.

In the altitude profile of O_3 concentration, it is observed that there is slight increase in concentration around 85 km which is due to the increase in production rate at that height through the following reaction as: $O + O_2 + M \rightarrow O_3 + M$ (M = total atmospheric concentration) and the sharp decrease above 90 km is also through the same reaction. Two altitude profiles of ozone concentration, one from photochemical equilibrium and other from non-equilibrium model are obtained. It is seen that in the mesosphere these two profiles are comparable. Further it is also seen that the average night time concentration is more than that in the day. Results obtained are compared with experimental values.

Keywords. Ozone concentration; mesosphere; oxygen-hydrogen atmosphere; diffusion.

1. Introduction

Ozone in the atmosphere acts as a biological shield for the earth's biosphere because it absorbs almost all penetrating uv solar radiation harmful to lives on earth. Chapman (1930) suggested the existence of O_3 in the earth's atmosphere as a result of photodissociation of molecular oxygen and subsequent recombination of atomic and molecular oxygen in the presence of the third body. The O_3 in turn is destroyed by photodissociation and recombination with atomic oxygen.

The distribution of ozone in the middle atmosphere can be obtained from a static model as its chemical lifetime in this altitude range is smaller than that of the mixing time. Below 40 km equilibrium theory is not applicable because as the altitude decreases, the chemical lifetime of O_3 increases and the vertical as well as horizontal diffusion becomes important. However, other constituents involved in the production and loss mechanism of O_3 directly or indirectly have longer chemical lifetime than mixing time or diffusive time (*e.g.* O_2 , $O(^3P)$, H etc.). For them it is necessary to include the transport term in the model. Studies based on the dynamic model were started during the beginning of this decade (Shimazaki and Laird 1970, 1972; Hunt 1971, 1973; Thomas and Bowman 1972; Crutzen 1974; Shimazaki and Ogawa 1974; Fukuyama 1974). This paper presents more detailed aspect of chemical behaviour. One-dimensional photochemical diffusive model is developed and employed to study the chemical behaviour as well as altitude and temporal variation of O_3 in the mesosphere and lower thermosphere. Numerical technique used for the solution of the set of nonlinear differential equations is also presented.

2. Dynamic model

2.1 Theoretical formulation

Any molecule can in principle move from one point to another and while doing so, will carry with it its mass, velocity, and internal energy. This movement is mainly controlled by eddy diffusion, molecular diffusion, meridional circulation, planetary waves, solar radiation, and chemical sources and sinks. Therefore, concentration of any constituent in the atmosphere is controlled by the above parameters. Because of the strong meridional circulation and planetary waves in the lower atmosphere, horizontal gradient of the density of the minor constituent is strong and only three-dimensional (3-D) or to some extent two-dimensional (2-D) model can take care of this horizontal and vertical gradients. However, as altitude increases, the horizontal gradient decreases and above 50 km it is not comparable with the vertical gradient therefore, 1-D model governed by eddy, molecular diffusion as well as photochemical, chemical production and loss terms can give reasonable result in aeronomy with sufficient degree of accuracy. Accordingly we have designed the 1-D photochemical diffusion model for the present work in the region 50 to 150 km. The general form of the equations is as follows;

$$\begin{aligned} \frac{\partial Y_j(z, t)}{\partial t} = & P_j(z, t) - Q_j(z, t) \cdot Y_j(z, t) \\ & - \frac{\partial}{\partial z} \left\{ [Y_j] \left[\left(\frac{1}{[Y_j]} \cdot \frac{\partial Y_j}{\partial z} + \frac{1}{T} \cdot \frac{\partial T}{\partial z} \right) (K + E) \right. \right. \\ & \left. \left. + \left(\frac{K}{H_a} + \frac{E}{H_j} \right) \right] \right\}. \end{aligned} \quad (1)$$

Here, $Y_j(z, t)$ represents the concentration of the j th constituent at height z km above the ground and at time t . In our model j takes values from 1 to 13. T , D , E , H_j and H_a denote respectively the atmospheric temperature, molecular diffusion coefficient, eddy diffusion coefficient, scale heights of j th constituent and average scale height. It is not possible to list all the 13 constituents with their chemical and photochemical production P and destruction Q . However, as an example the production and destruction terms for atomic oxygen and atomic hydrogen are given as:

$$\begin{aligned} P_o(z, t) = & J_1[O_2] + 2J_2[O_2] + J_3[O_3] + J_4[O_3] K_{16}[OH][OH] \\ & + K_9[O_2][O, ^1D] + K_{48}[H][OH] + K_{42}[H][O_2] + \text{etc.}, \end{aligned} \quad (2)$$

$$\begin{aligned} Q_o(z, t) = & K_2[O_2][M] + K_3[O_3] + K_{21}[OH] + K_{22}[HO_2] \\ & + K_{33}[H_2O_2] + K_{35}[H_2] + \text{etc.}, \end{aligned} \quad (3)$$

$$\begin{aligned} P_H(z, t) = & K_{21}[O][OH] + J_5[H_2O] + K_{37}[H_2][OH] \\ & + K_{36}[H_2][O, ^1D] + K_{35}[H_2][O], \end{aligned} \quad (4)$$

$$\begin{aligned} Q_H(z, t) = & K_{20}[O_3] + K_{23}[O_2][M] + H_{29}[HO_2] \\ & + K_{30}[OH] + K_{34}[H_2O_2], \end{aligned} \quad (5)$$

where the rectangular bracket represents the concentration of the respective constituent, J_i are the photodissociation rate coefficients which are the functions of height

and time; and K_i the reaction rate coefficients. Equation (1) is a set of nonlinear, second order, couple partial differentials for 13 constituents and can be solved by a specially developed numerical scheme only.

Above 50 km altitude concentration of O_3 is obtained from its photochemical equilibrium model. However, as mentioned earlier ozone cannot be studied independently without considering other constituents which influence its distribution. We therefore, developed simultaneous partial differential equations for 13 constituents viz O_3 , O_2 , $O_2(^1\Delta_g)$, $O(^3P)$, $O(^1D)$, $O(^1S)$, H , OH , OH^* , H_2O , HO_2 , H_2O_2 , H_2 . Of these, constituents like O_2 , $O(^3P)$, H , H_2O , H_2O_2 , have longer chemical lifetime and hence only for these the transport term arising due to eddy or molecular diffusion is included. The chemical lifetime is obtained from:

$$\tau = [N_i]/[Q_i, N_i], \quad (6)$$

where Q_i is the rate of destruction, and N_i the density of the i th species.

2.2 Photodissociation

Photochemical and photolytic reactions are listed in table 1. The photodissociation rate coefficient is computed using the following formula:

$$J_i(z) = \sum Q_i(\lambda) \cdot \sigma(\lambda), L_T \exp \left[- \sum_{\lambda} \sigma(\lambda) \right] \\ \times [N_i(z)] \times [(1 + z/R)(1 + 2z/R - \cos^2 \phi)^{-1/2}], \quad (7)$$

where $\cos \phi = \cos \theta \cos \Lambda \cos \delta + \sin \Lambda \sin \delta$ and $J_i(z)$ is the photodissociation rate of i th constituent at height z ; $Q_i(\lambda)$ the quantum efficiency of i th constituent at wavelength λ ; $\sigma(\lambda)$ the absorption cross-section of i th constituent at wavelength λ ; L_T the solar photon flux (no. of photon/cm² at the top of the atmosphere); $N_i(z)$ the number density of i th constituent at height z ; R the radius of the earth; Λ the latitude of the earth; δ the solar declination angle; θ the zenith angle. Solar photon flux data and absorption cross-section data for O_3 and O_2 in the corresponding wavelength region have been taken mainly from Ackerman (1971) and Ackerman *et al* (1970).

2.3 Diffusion

In the mesosphere temperature decreases with altitude up to mesopause. Therefore the vertical convection should be greater than in the thermosphere where temperature increases with altitude. However, in the 85 to 110 km region, there is strong vertical shear in the horizontal wind induced by the upward propagating gravity waves and atmospheric tides and hence eddy diffusion increases up to the turbopause (at 110 km) above which molecular diffusion dominates the eddy diffusion. In fact there is no satisfactory way of determining accurately the eddy diffusion coefficient value. The eddy diffusion coefficient values adopted in our model are shown in figure 1. For molecular diffusion coefficient we have followed Colegrove *et al* (1965)

Table 1(a). Chemical reactions incorporated in the present model.

No.	Reactions and references	Rate coefficient
R_1	$O + O + M \rightarrow O_2 + M$ Gattinger (1971)	$K_1 = (2.87 \pm 0.3) \times 10^{-34} \exp(710 \pm 175/T)$
R_2	$O + O_2 + M \rightarrow O_3 + M$ Hue <i>et al</i> (1972), NBSIR (1974).	$K_{2a} = 1.0 \times 10^{-34} \exp(104/RT)$ $K_{2b} = 1.1 \times 10^{-34} \exp(500/T)$ (for stratosphere)
R_3	$O + O_3 \rightarrow 2O_2$ Simonaitis and Heikoklen (1973)	$K_3 = 1.3 \times 10^{-11} \exp(-2200/T)$
R_4	$O + O + O \rightarrow O'S + O_2$ Felder and Young (1972)	$K_4 = 4.8 \times 10^{-33}$
R_5	$O(^1S) \rightarrow O^1D + h\nu$ Zipf (1969)	$K_5 = 1.4 \times 10^0$
R_6	$O(^1S) + O_2 \rightarrow O + O_2$ Atkinson and Welge (1972)	$K_6 = 4.9 \times 10^{-12} \exp(-850 \pm 100)$
R_7	$O(^1D) + M \rightarrow O + M$ Fukuyama (1974)	$K_7 = 5 \times 10^{-11}$
R_8	$O(^1D) \rightarrow O + h\nu$ Zipf (1969)	$K_8 = 1 \times 10^{-2}$
R_9	$O(^1D) + O_2 \rightarrow O_2 + O$ Zipf (1969)	$K_9 = 5 \times 10^{-11}$
R_{10}	$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$	$K_{10} = 2.5 \times 10^{-11}$
R_{11}	$O_2(^1\Delta_g) \rightarrow O_2 + h\nu$ Wallace and Hunten (1968)	$K_{11} = 8.5 \times 10^{-2}$
R_{12}	$O_2(^1\Delta_g) \rightarrow O_2 + h\nu$ Evans <i>et al</i> (1968)	$K_{12} = 2.8 \times 10^{-4}$
R_{13}	$(^1\Delta_g) + M \rightarrow O_2 + M$ Beaker (1971)	$K_{13} = 10^{-20}$
R_{14}	$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$ Findley and Snelling (1971)	$K_{14} = 3.2 \times 10^{-15}$
R_{15}	$O_2(^1D) + O \rightarrow O_2 + O$ Clark and Wayne (1969)	$K_{15} = 3 \times 10^{-11}$
R_{16}	$O(^1D) + H_2O \rightarrow 2OH$ Biedenkapp <i>et al</i> (1970)	$K_{16} = 3 \times 10^{-11}$
R_{17}	$O(^1S) + H_2O \rightarrow 2OH$ Filseth <i>et al</i> (1970).	$K_{17} = 7 \pm 3.5 \times 10^{-11}$
R_{18}	$O_2(^1\Delta_g) + O_2 \rightarrow 2O_2$ Findley and Snelling (1971)	$K_{18} = 2.2 \times 10^{-18}$
R_{19}	$O(^1S) + O(^3P) \rightarrow 2O$ Felder and Young (1972)	$K_{19} = 7.5 \times 10^{-12}$
R_{20}	$H + O_3 \rightarrow OH^* + O_2$ Koufman (1964), Nicolet (1971), Gattinger (1971).	$K_{20a} = 2.6 \times 10^{-11}$ $K_{20b} = 1.5 \times 10^{-12}$ $K_{20c} = 1.5 \times 10^{-11} \exp(-200/T)$
R_{21}	$OH + O \rightarrow H + O_2$ Koufman (1965) and Lloyd <i>et al</i> (1972).	$K_{21a} = 5.0 \times 10^{-11}$ $K_{21b} = 1.8 \times 10^{-12}$
R_{22}	$HO_2 + O \rightarrow OH + O_2$ Nicolet (1970)	$K_{22} = 3 \times 19^{-12} (T)^{1/2}$
R_{23}	$H + O_2 + M \rightarrow HO_2 + M$ Kurylo (1972)	$K_{23} = 1.9 \times 10^{-32} \exp(236/T)$
R_{24}	$OH + O_2 \rightarrow HO_2 + O_2$ Anderson and Koufman (1973)	$K_{24} = 1.3 \times 10^{-12} \exp(-950/T)$
R_{25}	$HO_2 + O_3 \rightarrow OH + 2O_2$ Simonaitis and Heicklen (1973)	$K_{25} = 3.3 \times 10^{-14} \exp(-1000/T)$
R_{26}	$OH + OH \rightarrow H_2O + O$ Whitten <i>et al</i> (1973)	$K_{26} = 1 \times 10^{-11} \exp(-550/T)$

Table 1(a). (contd.)

No.	Reactions and references	Rate coefficient
R_{27}	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}$ Whitten <i>et al</i> (1973)	$K_{27} = \exp(-500/T)$
R_{28}	$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$ Trainor <i>et al</i> (1973)	$K_{28} = 2 \times 10^{-32} \times (273/T)^{0.81}$
R_{29a}	$\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$ Gattinger (1971)	$K_{29} = 1 \times 10^{-11}$
R_{29b}	$\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$ Whittens <i>et al</i> (1973)	$K_{29b} = 2.8 \times 10^{-10} \exp(1000/T)$
R_{30}	$\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$ Baulch <i>et al</i> (1972)	$K_{30} = 1.4 \times 10^{-14} \times T \exp(-3500/T)$
R_{31}	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$ Nicolet and Pettermans (1973)	$K_{31} = 4 \times 10^{-13} \exp(-600/T)$
R_{32}	$\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{H}_2\text{O} + \text{O}_2$ Gattinger (1971)	$K_{32} = 1.5 \times 10^{-13} \exp(-3000/T)$
R_{33}	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ Hochanadel <i>et al</i> (1972)	$K_{33} = 2 \times 10^{-10}$
R_{34}	$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{HO}_2$ Gattinger (1971)	$K_{34} = 1 \times 10^{-13}$
R_{35}	$\text{H} + \text{O} \rightarrow \text{H} + \text{OH}$ Scholfield (1967)	$K_{35} = 2.1 \times 10^{-11} \exp(-9400/RT)$
R_{36}	$\text{H}_2 + \text{O}(^1\text{D}) \rightarrow \text{H} + \text{OH}$ Donoven and Husain (1970)	$K_{36} = 1.9 \times 10^{-10}$
R_{37}	$\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$ Westenburg and De Haas (1973)	$K_{37} = 6.8 \times 10^{-14} \exp(-650/T) \text{ 150 T 300 K}$
R_{38}	$\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$ Wilson (1972)	$K_{38} = 3 \times 10^{-30}$
R_{39}	$\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$ Boulch <i>et al</i> (1972)	$K_{39} = 6.1 \times 10^{-26} T^{-2}$
R_{40}	$\text{OH}^* \rightarrow \text{OH} + h\nu$ Fukuyama (1974)	$K_{40} = 15.2$
R_{41}	$\text{OH}^* + \text{O}_2 \rightarrow \text{OH} + \text{O}_2$ Workley <i>et al</i> (1972)	$K_{41} = 1.0 \times 10^{-14}$
R_{42}	$\text{H} + \text{O}_2^* \rightarrow \text{OH}^* + \text{O}$ Komova (1973)	$K_{42} = 4.25 \times 10^{-12}$
R_{43}	$\text{OH}^* + \text{OH}^* \rightarrow \text{H}_2\text{O} + \text{O}$ Kaufman (1969)	$K_{43} = 3 \times 10^{-11}$
R_{44}	$\text{O}(^1\text{D}) + \text{O}_3 \rightarrow 2\text{O}_2$ Fitzsimmons and Bair (1964)	$K_{44} = 10^{-11}$
R_{45}	$\text{O}(^1\text{S}) + \text{O} \rightarrow \text{O} + \text{O}$ Felder and Young (1972)	$K_{45} = 7.5 \times 10^{-12}$
R_{46}	$\text{H} + \text{OH} + \text{M} \rightarrow \text{HO}_2 + \text{M}$ Thomas and Bowman (1972)	$K_{46} = 1.4 \times 10^{-31}$
R_{47}	$\text{H} + \text{O}^3\text{P} + \text{M} \rightarrow \text{OH} + \text{M}$ Bates and Nicolet (1950)	$K_{47} = 8 \times 10^{-33}$
R_{49}	$\text{OH}^* + \text{N}_2 \rightarrow \text{OH} + \text{N}_2$ Worley <i>et al</i> (1972)	$K_{49} = 3.6 \times 10^{-15}$
R_{50}	$\text{OH} + \text{O}(^1\text{S}) \rightarrow 2\text{OH}$ Filseth <i>et al</i> (1970)	$K_{50} = (71 \pm 3.5) \times 10^{-11}$

Note: (i) for three-body mechanism units are $\text{cm}^{-6} \text{sec}^{-1}$ and (ii) for two-body mechanism units are $\text{cm}^{-3} \text{sec}^{-1}$.

Table 1(b). Photodissociation processes.

$J_1 : \text{O}_2 + h\nu \rightarrow \text{O} (^1\text{D}) + \text{O} (^3\text{P})$
$(1351 < \lambda < 1754)$
$J_2 : \text{O}_2 + h\nu \rightarrow \text{O} (^3\text{P}) + \text{O} (^3\text{P})$
$(1750 < \lambda < 2431)$
$J_3 : \text{O}_3 + h\nu \rightarrow \text{O} (^1\text{D}) + \text{O}_2 (^1\Delta_g)$
$(1980 < \lambda < 2560)$
$J_4 : \text{O}_3 + h\nu \rightarrow \text{O} (^1\text{D}) + \text{O}_2 (^1\Delta_g)$
$(2560 < \lambda < 3125)$
$J_5 : \text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}$
$(\text{Lym} < \lambda < 2857)$
$J_6 : \text{H}_2\text{O}_2 + h\nu \rightarrow \text{OH} + \text{OH}$
$(1887 < \lambda < 2857)$
$J_7 : \text{HO}_2 + h\nu \rightarrow \text{OH} + \text{O} (^3\text{P})$
$(1887 < \lambda < 2857)$

Figure 1. Eddy diffusion coefficient cm^2/sec .

2.4 Computational technique

We aim to compute the diurnal variation of ozone concentration. This diurnal variation can be obtained only after an equilibrium or quasi equilibrium value (i.e. $dy/dt \rightarrow 0$) is obtained by fixing all parameters. In this study it was a most challenging and computer time consuming operation to obtain the condition $dy/dt \rightarrow 0$. In programme, we replace space derivatives by semi-implicit finite difference method, whereas time

derivatives are obtained by iteration method. This procedure involves two opposing constraints on the choice of the time step value: (i) To obtain the equilibrium value sufficiently rapidly, as well as to maintain stability and minimum expected accuracy time step should be as small as possible. (ii) To obtain the complete diurnal variation the time step should be as large as possible to economise on computer time. The following parametrization and mathematical technique is adopted to circumvent the above mentioned problems. Notations L_1 to L_6 and M_1 and M_2 are used to avoid complexity;

$$\left. \begin{aligned} L_1 &= E(z-1) + D_j(t, z-1); \quad L_2 = E(z) + D_j(t, z); \\ L_3 &= E(z+1) + D_j(t, z+1); \quad L_4 = \frac{E(z-1)}{H_a(z-1)} + \frac{D_j(t, z-1)}{H_j(z-1)}; \\ L_5 &= \frac{E(z)}{H_a(z)} + \frac{D_j(t, z)}{H_j(z)}; \quad L_6 = \frac{E(z+1)}{H_a(z+1)} + \frac{D_j(t, z+1)}{H_j(z+1)} \end{aligned} \right\} \quad (8a)$$

we further write,

$$\begin{aligned} M_1 &= \frac{(L_1 + L_2)}{4\Delta z} \left[\left(\frac{1}{Y_j(z-1, t)} + \frac{1}{Y_j(z, t)} \right) (Y_j(z, t) - Y_j(z-1, t)) \right. \\ &\quad \left. + \left(\frac{1}{T(z)} + \frac{1}{T(z-1)} \right) (T(z) - T(z-1)) \right] + \frac{1}{2} (L_4 + L_5), \end{aligned} \quad (8b)$$

$$\begin{aligned} M_2 &= \frac{(L_2 + L_3)}{4\Delta z} \left[\left(\frac{1}{Y_j(z, t)} + \frac{1}{Y_j(z+1, t)} \right) \right. \\ &\quad \times (Y_j(z+1, t) - Y_j(z, t)) + \left(\frac{1}{T(z+1)} + \frac{1}{T(z)} \right) \\ &\quad \left. \times (T(z+1) - T(z)) \right] + \frac{1}{2} (L_5 + L_6) \end{aligned} \quad (8c)$$

This new notation can be combined so that,

$$\begin{aligned} Y_j(z, t) &= \frac{\sigma}{2\Delta z} \{ M_2 [Y_j(z, t) + Y_j(z+1, t)] - M_1 [Y_j(z, t) + Y_j(z-1, t)] \} \\ &\quad + P_j(z, t) + Q_j(z, t) \cdot Y_j(z, t) \end{aligned} \quad (8d)$$

(σ = filter for the constant error).

This time derivative is however considered by the predictor-corrector method by writing:

$$Y_j^*(z, t+1) = Y_j(z, t) + \Delta t \times \Delta Y_j(z, t), \quad (9)$$

where Y_j^* is a predicted value, which is further corrected as

$$Y_j(z, t+1) = Y_j^*(z, t+1) + (\Delta t/2) \{ \Delta Y_j(z, t) + Y_j^*(z, t+1) \}. \quad (10)$$

Equation (1) is therefore numerically solved (CDC 3600 and DEC 10 computer) using (8) to (10) for space and time parts respectively.

After considerable trial and errors, we could fix boundary conditions, initial values

and numerical smoothening coefficients used in (10) for obtaining stable and reasonable solutions. Initial conditions at $t = 0$ are defined as

$$Y_j(z, 0) = f_j(z) \text{ where } 50 < z < 150 \quad (11)$$

for all values of z . In this equation $f_j(z)$ are known functions. Next lower and upper boundaries are defined as

$$\begin{aligned} Y_j(z = 50, t) &= a_j(t) \\ Y_j(z = 150, t) &= b_j(t), \end{aligned} \quad t \geq 0 \quad (12)$$

where $a_j(t)$ and $b_j(t)$ are obtained from photochemical and diffusive equilibrium respectively. The coefficients $a_j(t)$ in (12) are fixed using photochemical equilibrium and mixing ratios of each constituents. As against this $b_j(t)$ are determined using conditions for diffusive equilibrium. The functions $f_j(z)$, which determine initial values at time $t = 0$, are computed by successive interactions between oxygen atmosphere and oxygen-hydrogen atmosphere. Moreover the numerical values of smoothening coefficients are selected after considerable trials for stability of solutions. Lastly, the stability considerations were mainly determined not from rigorous mathematical arguments but by appropriateness of physical situations. We could obtain solutions over the entire domain of z and t with steps as large as (10^5 cm) and 5 sec, whereas in initial trials we have started from steps as small as 0.01 km and 0.1 sec only.

In computer program check points have been put at many places to take care of mathematical errors which were never allowed to exceed the "change" which occurred due to physical and chemical processes during the flow pattern. Initially the solar zenith angle was fixed (*i.e.* overhead sun) and once the equilibrium or quasiequilibrium stage was obtained, solar zenith angle was allowed to vary to obtain temporal variation of neutral minor constituents.

3. Results and discussion

3.1 Photochemical model of O_3

Ozone is a highly chemically active species because of its lowest bond strength (1.04 eV). It readily undergoes reactions which are highly exothermic. This chemical energy appears in products like $O_2(^1\Delta_g)$, $OH^*(V \leq 9)$, $O(^1D)$, NaO^* etc., either as kinetic or as internal energy. Therefore, O_3 plays a crucial role in the photochemistry of the upper atmosphere. The equation for O_3 from table 1 can be written as:

$$\begin{aligned} \frac{d(O_3)}{dt} &= K_2 [O_2] [O] [M] - K_3 [O] [O_3] - K_{20} [H] [O_3] \\ &\quad - J_3 [O_3] - J_4 [O_3] - K_{24} [OH] [O_3] \\ &\quad - K_{25} [HO_2] [O_3], \end{aligned} \quad (13)$$

where the square bracket represents the concentration of the corresponding constituent.

There exists only a single important production mechanism:

Because of its chemical activity ozone interacts with several species and hence there are several sink terms appearing in this model. We have therefore, examined the respective contribution of each reaction and selected only a few important ones for simplicity. There are thus four principal loss mechanisms besides photodissociation *viz* R_3 , R_{20} , R_{24} and R_{25} (figure 2).

Hunt (1971, 1973) and Battaner (1975) neglected the reactions R_{24} and R_{25} . However, we have found that these are of considerable significance below 80 km during night time. This may be because atomic oxygen and atomic hydrogen decrease sharply below 80 km as shown in figures 3a, b.

Figure 2. Reaction rate (mol/cm³/sec).

Figure 3. a. Ground state atomic oxygen concentration. b. Concentration of atomic hydrogen: Curve I is for day-time concentration and curve II is for night-time concentration.

3.2 *Altitude and temporal variation*

Figure 4 shows altitude profiles of O_3 during night and day. It shows a smaller peak at about 85 km. Ozone plays a central role in the airglow emission of the O_2 (${}^1\Delta_g$), OH^* and Na (2P). It is well established both theoretically and experimentally that peak emission of the above constituents appear around 85 km. Above 90 km concentration of O_3 decreases rapidly. This can be interpreted as the total concentration (M) and the concentration of O_2 are not sufficient to maintain the fast rate of three body mechanism R_2 . It also appears that the concentration of ozone is greater during night than during day around 85 km. This may be because during night atomic oxygen get transformed in to O_3 through reaction R_2 .

Further as mentioned earlier during night and below 80 km reactions R_{24} and R_{25} are important among loss reactions. These reactions need not be included during day time computation. We get reasonable accurate values of O_3 concentrations within the range of 55 to 80 km, from its photochemical equilibrium model as given below:

$$(O_3)_{\text{day}} = \frac{K_2 [O] [O_2] [M]}{J_3 + J_4 + K_3 [O] + K_{20} [H]}, \quad (15)$$

$$\text{and } (O_3)_{\text{night}} = \frac{K_2 [O] [O_2] [M]}{K_3 [O] + K_{20} [H] + K_{24} [OH] + K_{25} [HO_2]}. \quad (16)$$

The results based on (15), (16) and (3) are given in table 2 to illustrate this point. In figure

Figure 4. Daytime and nighttime concentration of ozone.

Table 2. Comparison of the results obtained from equilibrium and nonequilibrium model.

Altitude (km)	$(O_3)_{\text{night}} \text{ (cm}^{-3}\text{)}$		$(O_3)_{\text{day}} \text{ (cm}^{-3}\text{)}$	
	Equilibrium	Nonequilibrium	Equilibrium	Nonequilibrium
55	1.3×10^{10}	1.8×10^{10}	1.8×10^{10}	1.2×10^{10}
60	7.7×10^9	7.5×10^9	8.5×10^9	1×10^{10}
65	1.5×10^9	1.1×10^9	1.9×10^9	3×10^9
70	6×10^8	8.1×10^8	9.7×10^8	1.2×10^9
75	5.3×10^8	3.1×10^8	3.8×10^8	2×10^8

5 we compare our results with earlier experimental and theoretical results. Weeks *et al* (1972) measured the O_3 value up to 80 km where they reported a steady decrease. In this region our results are closer to their results. Recently Llewellyn and Witt (1977) also measured O_3 concentration during twilight using a combined technique of solar occultation and 1.27μ oxygen emissions. Our results agree qualitatively up to 95 km. However, quantitative difference exists possibly due to difference in latitude and time of measurement.

Figure 6 presents the temporal variation of O_3 for 24 hr at heights 70, 75, 80, 85, 95 and 100 km. From this figure we see that above 90 km there is no significant variation in the O_3 concentration, below these altitudes the temporal variation increases with decrease in height. Further during sunset and sunrise, concentration decreases suddenly and again recovers within a period of 10–20 min. At this time (sunset/sunrise); photodissociation processes of O_3 and O_2 stop/start due to which a sharp decrease of O_3 concentration takes place.

Figure 5. Comparison of O_3 concentration profiles.

Figure 6. Diurnal variation of O_3 (curve I is the integrated diurnal variation of O_3).

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