Description of SOCRATES-
A Chemical Dynamical Radiative Two-Dimensional Model

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1. Overview

The NCAR interactive chemical dynamical radiative two-dimensional (2-D) model has undergone substantial changes since its description was last published (Brasseur et al 1990). This report presents the details of the most recent version SOCRATES (Simulation of Chemistry, Radiation, and Transport of Environmentally important Species). Major changes in SOCRATES from the previous version include:

- Model domain extended up to 120 km altitude to include mesospheric and thermospheric processes (molecular diffusion, simplified ionic productions, tidal wave forcing etc.).
- UV Radiative transfer that accounts for multiple scattering by air molecules, aerosols and clouds.
- Parameterization of aerosol and cloud radiative effects in the infrared.
- Non-LTE infrared radiation for the mesosphere.
- Planetary wave model to parameterize interactions between planetary wave and mean flow.
- Update of the gravity wave forcing parameterization.
- Option of imposing QBO forcing.
- Circulation boundary condition moved down to 2 km and determined from physical principles.
- Tropospheric winds and temperature calculated interactively with specified forcing.
- Semi-Lagrangian transport scheme used to solve for chemical transport.
- More detailed tropospheric hydrocarbon chemistry.
- Diurnal averaging scheme that allows for diurnal variation for chemical species.
- Parameterization of convective and frontal induced vertical transport in the troposphere.

The model domain extends from the surface to 120 km with a 1 km vertical resolution, and from -85° to 85° latitude with a 5° latitudinal resolution. Time step for the thermodynamic and the chemical transport equations can be varied, but for a general run, a time step of 1 day is being used. The radiative heating is calculated every 5 days. Different time steps can also be assigned for the time integration of the planetary wave model. Currently, a time step of 1 day for the wave model is used. In order to describe approximately the diurnal variation of chemical species, the chemical equation without the effect of transport is time integrated with 8 timesteps per day, with 4 timesteps per daytime, and 4 timesteps per nighttime.

SOCRATES has the capability of accounting for multiple-scattering of air molecules, aerosols and clouds in the calculation of the solar heating rate and photolysis rates. This is
performed by solving a multiple-scattering radiative transfer equation using the two-stream \( \delta \)-Eddington method. Absorption cross sections of chemical compounds have been updated to more recent data, and improved parameterization of the Schumann-Runge bands for \( O_2 \) photolysis rates and the \( \delta \) bands for \( NO \) photolysis rates were implemented.

In order to facilitate mesospheric studies of the model, a non-LTE \( CO_2 \) infrared radiative code of the mesosphere is incorporated in the model in place of the simple Newtonian cooling formulation. Solar heating from chemical recombination and solar energy loss to airglow process which are important in the mesosphere are taken into account. To consider the effect of molecular diffusion on the chemical species and heat budget, molecular diffusion and thermal conductivity are implemented in the chemical transport and the thermodynamic calculations.

New methods to estimate the dynamical forcing from planetary and gravity waves have been implemented. Planetary wave momentum forcing is calculated from a quasi-geostrophic wave model that takes into account dissipation caused by Newtonian cooling, Rayleigh friction, and wave breaking. For gravity wave forcing, the standard run utilizes the Lindzen (1981) formulation, although another option of a parameterization scheme that utilizes the observed energy spectral characteristic of gravity wave motions is available. Another update in the dynamic aspect of the model is the option of including a quasi-biennial oscillation (QBO) type forcing (deduced from observed zonal wind oscillation) in the temperature and circulation fields.

The lower boundary of the circulation and temperature has been moved from the tropopause level down to 2 km altitude. In addition, the lower boundary condition of the stream function at 2 km is interactive with the model-derived wave forcings. The temperature in the troposphere is explicitly calculated from thermodynamics consideration, through the specification of tropospheric wave momentum flux and latent heating according to climatology. This lessens the constraint of the lower stratospheric circulation to the lower boundary condition, and allows some degree of interaction between the troposphere and the stratosphere.

The most significant improvement made in the chemical module of the model is in treating explicitly the diurnal variation affecting chemical species. For this purpose, the timestep in the chemical equation has been shortened (8 timesteps per day). This eliminates the need to diurnally average the photolysis rates for the chemical time integration. In addition, the chemical family technique used in the previous version of the model has been replaced by a formulation in which each chemical compound is treated separately. Another improvement made is in the representation of tropospheric chemistry, in particular hydrocarbon chemistry. Chemical species and reactions important in the troposphere which may have non-negligible consequences in the stratosphere were added, including the chemistry of \( C_2H_6 \), \( C_3H_6 \), \( CH_2O \), PAN etc. In addition, a simple parameterization of vertical tropospheric tracer transport in convective and frontal regions is included in the model.
The logistical structure of SOCRATES (shown in Figure 1) is slightly modified from the previous version of the model in that solar heating rate is estimated along with the photolysis calculation instead of being separately calculated. The model starts off with using initial temperature and concentrations of chemical species to calculate the zonal wind (from geostrophic approximation), solar heating and infrared cooling rates. The planetary and gravity wave forcing, along with the eddy diffusivity, is then estimated according to the zonal wind profile. With this wave forcing and heating information, the circulation is derived. Subsequently, the model calculates the temperature for the next time step, according to thermodynamic principles from the circulation and heating rates. From here on, it calculates the photolysis rates, solar heating rate, and the concentration of the chemical species, and then continues on to the next time loop.
Figure 1. Numerical algorithm of the 2-D Model

The 2-D model extends vertically from the surface up to 120 km with a vertical resolution of 1 km, and latitudinally from -85 to 85 with a 5° resolution. Log-pressure height is used as the vertical coordinate. As in Garcia and Solomon (1983), the dynamical fields and temperature are governed by a set of zonally-averaged quasi-geostrophic equations of thermodynamics, momentum, and mass continuity, expressed in the transformed Eulerian mean (TEM) framework (symbol definition listed in Appendix A).

\[
\frac{\partial \tilde{\theta}}{\partial t} + \tilde{v}^* \frac{\partial \tilde{\theta}}{\partial y} + \tilde{w}^* \frac{\partial \tilde{\theta}}{\partial z} = Q_S + Q_{IR} + D_\theta
\]  

(1)

\[
\frac{\partial \tilde{u}}{\partial t} - \eta v^* + \frac{\partial \tilde{u}}{\partial z} = F_R + F_G + F_T
\]  

(2)

\[
\frac{1}{\cos \phi} \frac{\partial (\tilde{v}^* \cos \phi)}{\partial y} + \frac{1}{\rho_0} \frac{\partial (\rho_0 \tilde{w}^*)}{\partial z} = 0
\]  

(3)

\[
(f + 2\tilde{u} \tan \phi) \frac{\partial \tilde{u}}{\partial z} = - \frac{g}{\theta} \frac{\partial \tilde{\theta}}{\partial y}
\]  

(4)

where

\[
\eta = f - \frac{1}{\cos \phi} \frac{\partial (\tilde{u} \cos \phi)}{\partial y}
\]  

(5)

Note that in these equations, \(z\) represents the log-pressure altitude defined as \(z = 7 \ln(p/p_0)\) (km), where \(p_0\) is the surface pressure. In Equation (1), thermodynamics is driven by solar heating \((Q_S)\), infrared heating \((Q_{IR})\), and small scale diffusive transport of heat \((D_\theta)\) by wave and molecular diffusion processes, given as:

\[
D_\theta = \frac{1}{\cos \phi} \frac{\partial}{\partial y} (K_{yy} \cos \phi \frac{\partial \tilde{\theta}}{\partial y}) + \frac{1}{\rho_0} \frac{\partial}{\partial z} (K_{zz} \rho_0 \frac{\partial \tilde{\theta}}{\partial z}) + \frac{1}{\rho_0} \frac{\partial}{\partial z} (K_T \rho_0 \frac{\partial \tilde{\theta}}{\partial z}).
\]

(6)

where \(K_{yy}\) is the meridional eddy diffusivity coefficient, \(K_{zz}\) the vertical diffusivity coefficient, and \(K_T\) is the molecular thermal conductivity coefficient. The temperature and wind fields are advected by the transformed Eulerian mean circulation \((\tilde{v}^*\) and \(\tilde{w}^*, \) also called residual circulation), a quantity that is more representative of the actual motions of air parcels in the meridional plane (see discussions in Andrews et al. 1987). The zonal momentum forcing (Equation (2)) is caused by planetary wave \((F_R)\), gravity \((F_G)\), and tidal wave \((F_T)\) dissipation and breaking.

The governing equations can be combined to form a diagnostic equation for the mean circulation, represented by the streamfunction \(\chi\) (Garcia and Solomon, 1983):

\[
C_{yy} \frac{\partial^2 \chi}{\partial y^2} + C_{yz} \frac{\partial^2 \chi}{\partial y \partial z} + C_{zz} \frac{\partial^2 \chi}{\partial z^2} + C_y \frac{\partial \chi}{\partial y} + C_z \frac{\partial \chi}{\partial z} = C_F \cos \phi
\]

(7)
where \( \chi \) is related to the residual velocities as:

\[
\begin{align*}
\bar{v}^* &= -\frac{1}{\rho_0 \cos \phi} \frac{\partial}{\partial z} (\rho_0 \chi) \quad (8a) \\
\bar{w}^* &= \frac{1}{\rho_0 \cos \phi} \frac{\partial}{\partial y} (\rho_0 \chi) \quad (8b)
\end{align*}
\]

The coefficients of the stream function equation (7) are functions of the mean zonal wind and temperature:

\[
\begin{align*}
C_{yy} &= N^2 \\
C_{yz} &= 2f \frac{\partial u}{\partial z} \\
C_{zz} &= f(f + \bar{u} \tan \phi - \frac{\partial \bar{u}}{\partial y}) \\
C_{y} &= N^2 \tan \phi \frac{f}{a} \frac{\partial \bar{u}}{\partial y} \\
C_{z} &= -\frac{f}{H} (f + \bar{u} \tan \phi - \frac{\partial \bar{u}}{\partial y}) + \frac{\partial \bar{u}}{\partial z} (2f \frac{\tan \phi}{a} + \frac{\partial f}{\partial y}).
\end{align*}
\]

The forcing term \( C_F \) on the right-hand side of Equation (7):

\[
C_F = \frac{R}{H} \frac{\partial}{\partial y} (Q_S + Q_{IR} + D_\theta) + f \frac{\partial}{\partial z} (F_R + F_G + F_T) \quad (10)
\]

Therefore, the circulation determined by Equation (7) is driven by the latitudinal gradient of the diabatic heating and the vertical gradient of the wave momentum forcing. Central to the improvements made in SOCRATES are the different ways in which these radiative and dynamic forcings are derived; these will be described in detail in the next section.
3. Radiation

3.1 Ultraviolet (UV) and visible radiative region (117 - 730 nm)

The 2-D model has a total of 170 wavelength bands: a resolution of 500 cm\(^{-1}\) wavenumber between 116.3 and 307.7 nm, a resolution of 5 nm in wavelength between 307.7 and 655 nm, and a resolution of 10 nm in wavelength between 655 and 735 nm (see Table 1). At each wavelength, the actinic flux is obtained by solving the equation of radiative transfer with the delta-Eddington method (Shettle and Wienman 1970, Joseph et al. 1976), which is a two-stream method (Meador and Weavor 1980; Toon et al., 1989).

The general equation for absorption and scattering of solar radiation in a plane-parallel atmosphere for each wavelength interval can be written as:

\[
\frac{dI(\tau, \mu)}{d\tau} = I(\tau, \mu) - \frac{\omega(\tau)}{2} \int_{-1}^{1} d\mu' p(\mu; \mu') I(\tau, \mu') - \frac{\omega(\tau) I^0}{4\pi} p(\mu; \mu_0) e^{-\tau/\mu_0}
\]

where \(I\) is the mean radiance, \(\tau\) is the optical depth, \(\omega\) is the single scattering albedo (ratio of scattering extinction and total extinction), \(p\) is the scattering phase function, \(\mu\) is the cosine of the zenith angle, \(\mu_0\) is the cosine of the zenith angle for the direct solar beam, and \(I^0\) is the mean radiance at the upper boundary of the model. The scattering phase function \(p\) is a non-dimensional quantity that describes the probability of angular distribution of the scattered energy. The first moment of the phase function is the asymmetry factor \(g\), which gives the overall directionality of the phase function. The first term in the right-hand side of Equation (11) represents attenuation by absorption, the second term represents the diffusive radiation increase by multiple scattering, and the last term is the contribution from single-scattering of the direct solar beam.

Before obtaining a solution of Equation (11) with a two-stream method, delta scaling of the optical parameters for cases of highly anisotropic phase functions is necessary to improve the accuracy of the solution, based on Joseph et al. (1976):

\[
g' = \frac{g}{1 + g}
\]

\[
\tau' = (1 - \omega \cdot g^2) \cdot \tau
\]

\[
\omega' = \frac{(1 - g^2) \cdot \omega}{1 - \omega \cdot g^2}.
\]

This is done to reduce the anisotropy caused by the strong forward-scattering peak characteristic of larger particles (aerosols and clouds).
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For the two-stream method, the diffuse radiance is divided into up-welling and down-welling components, $I^+$ and $I^-$, respectively. This produces a pair of integral radiance equations from Eq. (11) (for detail derivation, see Meador and Weaver 1980):

$$\frac{dI^+}{d\tau} = \gamma_1 I^+ - \gamma_2 I^- - I_0 \omega \gamma_3 e^{-\tau/\mu_0}$$  \hspace{1cm} (13a)

$$\frac{dI^-}{d\tau} = \gamma_2 I^+ - \gamma_1 I^- + I_0 \omega \gamma_4 e^{-\tau/\mu_0}$$  \hspace{1cm} (13b)

where coefficients $\gamma_i$'s are determined by the approximation used. For the Eddington approximation, $I^+$ and $I^-$ are assumed to have a simple angular distribution given as

$$I^\pm(\tau) = I_0(\tau) \pm \mu I_1(\tau).$$

This yields coefficients of the radiance equations as:

$$\gamma_1 = \frac{1}{4} [7 - \omega (4 + 3 g)]$$

$$\gamma_2 = -\frac{1}{4} [1 - \omega (4 + 3 g)]$$

$$\gamma_3 = \frac{1}{4} (2 - 3g\mu_0)$$

$$\gamma_4 = 1 - \gamma_3.$$  

The coefficients $I_0$ and $I_1$ are evaluated by solving the radiative equation for $I^+$ and $I^-$ subject to the boundary conditions that no diffuse radiation is incident at the top of the atmosphere, while at the bottom of the atmosphere (the Earth's surface), radiation is reflected isotropically with a known albedo. Vertical inhomogeneity of the atmosphere is parameterized by subdivision into 120 layers, each being then taken as internally homogeneous with specified vertical optical depth, single scattering albedo, and asymmetry factor. To solve for the set of two-stream equations in this multi-layer inhomogeneous atmosphere, the method described in Toon et al. (1989) is used. The tridiagonal matrix solution of their method provides improved computational speed necessary for the large number of vertical layers in our model.

The solar actinic flux at the top of the atmosphere ($q_0 = 4\pi f_0$) used in the model is shown in Table 1. The solar flux is in units of photons/cm$^2$/s, with the size of the wavelength bin taken into account ($q_0(\lambda)\Delta\lambda$). Between the wavelength of 120 to 417 nm, the solar flux is the average of the flux measured by UARS SOLSTICE from Jan 1st through March 31st, 1994 (representing long-term solar minimum condition) and from Jan 1st through March 29th, 1995 (representing solar maximum condition) (courtesy of G. Rottmann). Also listed in Table 1 is the fractional...
change of the solar flux from UARS day 169 to 1050 \([(\text{max-min})/(\text{min})]\) representing the long-term solar variability. For wavelength longer than 417 nm, the solar flux data are adapted from WMO (1986). To account for the ellipticity of the earth's orbit, the solar flux is adjusted with the annual variability: \([1.0-0.0342*cos(2\pi*\text{day}/365)]\), with maximum flux during the winter season and minimum flux during the summer season.

The altitude variation of the optical parameters: extinction optical depth (from absorption and scattering), single scattering albedo, and asymmetry factor, are needed to obtain the solution of the solar radiative flux. Optical depth \(\tau(z) = (1/\mu)\int_z \sigma[n]dz\) can be calculated knowing the absorption cross sections \(\sigma\) and number densities \([n]\) of absorbing particles. For a clear sky atmosphere, oxygen and ozone are the main absorbers of solar radiation in the middle atmosphere. Their wavelength dependent absorption cross sections are available from laboratory measurements, reported in DeMore et al. (1997) (Note: the particular case of the Schumann-Runge bands will be described later). For the Rayleigh scattering by air molecules, an empirical formula proposed by Nicolet (1984) is used for the cross section:

\[
\sigma_{\text{RAY}} = \frac{4.02 \times 10^{-28}}{\lambda^4 + x} \text{cm}^2
\]  

where \(x = 0.389\lambda + 0.09426/\lambda - 0.3228\) for \(0.2 \mu\text{m} < \lambda < 0.55\mu\text{m}\)

\(x = 0.4\) for \(0.55 \mu\text{m} < \lambda < 1\mu\text{m}\)

The single scattering albedo \(\omega\) is then calculated from \(\tau_{\text{scat}}/(\tau_{\text{scat}} + \tau_{\text{abs}})\). The asymmetry factor \(g\) for Rayleigh scattering is assumed to be zero (isotropic scattering).

To simulate aerosol scattering and absorption in the UV, some additional optical parameters are needed. Different approaches can be taken to obtain the optical parameters of scattering particles, depending on the conditions of interest. For background aerosol levels, Hitchman et al. (1994) compiled from SAGE and SAM measurements the climatology of aerosol extinction coefficient \(\text{ext}_{\text{aer}}\) at 1 \(\mu\text{m}\) over a period of roughly a decade. This aerosol extinction coefficient distribution can be used to calculate the extinction optical depth of aerosols by multiplying it with the thickness of the aerosol layer. To estimate its wavelength dependency, the simplest approach is to scale the extinction coefficient (for example, at 1 \(\mu\text{m}\)) by the inverse of wavelength, which is a fair assumption according to Mie scattering calculations (Pinnick et al. 1980). An alternative is to use a precalculated spectral distribution of the extinction coefficient for background aerosol levels to scale the satellite-measured extinction coefficient at a given wavelength (for example, calculations shown in Fenn et al. 1985). As for the scattering parameters, the sulfate aerosols are known to be very effective scatterers with a single scattering albedo value close to 1, and an asymmetry factor of 0.7, which are approximately independent of wavelength (Michelangeli et al. 1989).
Optical properties for water cloud absorption and scattering in the UV and visible are calculated by the parameterization scheme of Hu and Stamnes (1993) based on Mie theory. The input parameters needed to be specified for this scheme are the liquid water content, effective droplet radius, cloud location, and vertical thickness. Following Kylling (1992), a typical water cloud effective radius of 10 μm and a liquid water content of 0.15 g/m³ are used in the model.

The solar zenith angles chosen for the radiative transfer equation are a function of both latitude and time of the year. As will be mentioned in the description of chemistry, for daytime conditions, the chemical equation is integrated in time with a timestep equal to one quarter of the length of the daylight part of the day. Thus, 2 photolysis calculations are made per day for each molecule subject to photodissociation. The zenith angle Z is calculated from the formula

\[ \cos Z = \sin \phi \cdot \sin \delta + \cos \phi \cdot \cos \delta \cdot \cos(h_a) \]  

(16)

where \( \delta \) is the inclination angle which is a function of day of year only (the latitude at which the sun is directly over head with Z=0), and \( h_a \) is the hour angle (\( h_a=0 \) at noon). The value of the hour angle at sunrise or sunset \( h_{1/2\text{day}} \) as a function of day and latitude can be determined from Equation (16) by setting \( Z=90^\circ \). Once the hour angle at sunrise (or sunset) is determined, Z is estimated for two specific times: \( h_a=1/8h_{1/2\text{day}} \), and \( h_a=3/8h_{1/2\text{day}} \).

To account for the sphericity of the earth in spite of the plane-parallel approximation, the Chapman function replaces the secant of zenith angle in the calculation of the optical depth. The method described by Smith and Smith (1972) for zenith angle less than 90° is used to estimate the Chapman function \( (Ch(Z)) \):

\[ Ch(Z) = \sqrt{\frac{\pi x}{2}} \text{erfc}(\sqrt{\frac{x}{2}} \cos Z) \exp(\frac{x}{2} \cos^2 Z) \]  

(17)

where \( x=(a+z)/H \). For zenith angles equal to or larger then 90°, night conditions are assumed.

### 3.1.1. Photolysis rates

Once the solar flux at a given level is known from the solution of the radiative equation (Equation 11), the photodissociation coefficient for a given molecule can be calculated by:

\[ J_i(z;Z) = 4\pi \int \sigma_i(\lambda) \epsilon_i(\lambda) I(\lambda; z; Z) d\lambda \]  

(18)

This photolysis rate \( J \) (s⁻¹) for a given species \( i \) is proportional to the solar actinic flux \( 4\pi I \), the absorption cross section \( \sigma_i \) (cm²) and the quantum efficiency \( \epsilon_i \). The photodissociations considered in the model are listed in Table 2. The sources of reference for the absorption cross sections used in our model are listed in Table 3. Molecules cross section that exhibit temperature dependencies include: ozone in the 175.8 to 347.5 nm range, \( \text{N}_2\text{O}, \text{NO}_2, \text{HNO}_3, \text{CFC}_12, \text{CFC}-11, \text{CCl}_4 \) in the
200-250 nm range, ClONO$_2$, N$_2$O$_5$ in the 200-281.7 nm range, H$_2$O$_2$, H$_2$CO, PAN. For some source gases such as CH$_3$CCl$_3$, CH$_3$Cl, CFC-113, HCFC-22, Ha-1211, Ha-1301, CH$_3$Br, CFC-114, and CFC-115, temperature dependent cross section parameterizations are taken from Gillotay and Simon (1988) since data presented in DeMore et al. (1997) [JPL97] are for 298 K only. Cross checking of the cross sections from Gillotay and Simon (1988) and JPL97 showed that at 298 K, the values are close to identical. For OCIO, cross sections are spectrally interpolated directly from Wahner et al. (1987) instead of from JPL97 because its data are taken from band peak amplitude which tends to overestimate the cross sections. The quantum efficiency $\varepsilon$ is equal to unity in most cases, except for O$_3$, H$_2$CO, CF$_2$O, NO$_3$, ClONO$_2$, and HO$_2$NO$_2$. The sources of their $\varepsilon$ values are listed in Table 3.

The treatment of O$_2$ absorption in the Schumann-Runge bands (SRB: 175-205 nm) requires special attention because of the cross section's highly variable spectral structure in this wavelength region. The parameterization of the O$_2$ absorption developed by Kockarts (1994) is used in the model. The method uses recent spectroscopic data of O$_2$, and accounts for the temperature dependence of the O$_2$ cross sections. It remains valid even when the slant O$_2$ optical depth becomes very large. The photolysis rates for any molecule (M) other than O$_2$ in the SRB are computed by

$$J_{M(SRB)} = \sum_{iv(SRB)} q_0 \sigma_M \varepsilon_M R_{iv}(M) e^{-\tau_{iv}(O_3)}$$

(19)

where

$$R_{iv}(M) = a_{1(iv)} \exp(-a_{2(iv)}N) + a_{3(iv)} \exp(-a_{4(iv)}N) + a_{5(iv)} \exp(-a_{6(iv)}N) + a_{7(iv)} \exp(-a_{8(iv)}N) + a_{9(iv)} \exp(-a_{10(iv)}N) + a_{11(iv)} \exp(-a_{12(iv)}N)$$

and $N$ is the slant total O$_2$ overhead content ($N = \sec Z \int_0^\infty [O_2]dz$), and $q_0$ is the solar flux at the top of atmosphere. In the particular case of molecular oxygen (O$_2$), the photolysis frequency in the SRB is expressed by :

$$J_{O_2(SRB)} = \sum_{iv(SRB)} q_0 R_{iv}(O_2) e^{-\tau_{iv}(O_3)}$$

(20)

where

$$R_{iv}(O_2) = b_{1(iv)} \exp(-b_{2(iv)}N) + b_{3(iv)} \exp(-b_{4(iv)}N) + b_{5(iv)} \exp(-b_{6(iv)}N) + b_{7(iv)} \exp(-b_{8(iv)}N) + b_{9(iv)} \exp(-b_{10(iv)}N) + b_{11(iv)} \exp(-b_{12(iv)}N)$$

The SRB is divided into 17 ($iv$) wavelength subintervals, and each wavelength subinterval is assigned 12 coefficients ($a_1$-$a_{12}$, $b_1$-$b_{12}$) (Table 1 and 2 in Kockarts, 1994).
Table 2 Photodissociation process

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<th>Products</th>
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<tr>
<td>$\text{O}_3 + \text{hv} \rightarrow \text{O}(3\text{P}) + \text{O}_2$</td>
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<td>$\text{N}_2\text{O} + \text{hv} \rightarrow \text{N}_2 + \text{O} + \text{O}(1\text{D})$</td>
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<tr>
<td>$\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}(3\text{P})$</td>
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<td>$\text{HNO}_3 + \text{hv} \rightarrow \text{OH} + \text{NO}_2$</td>
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<td>$\text{CFC}-12\ (\text{CCl}_2\text{F}_2) + \text{hv} \rightarrow \text{CCIF}_2 + \text{Cl}$</td>
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<td>$\text{HOCI} + \text{hv} \rightarrow \text{OH} + \text{Cl}$</td>
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<td>$\text{ClONO}_2 + \text{hv} \rightarrow \text{ClO} + \text{NO}_2$</td>
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<tr>
<td>$\text{N}_2\text{O}_5 + \text{hv} \rightarrow \text{NO}_2 + \text{NO}_3$</td>
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<tr>
<td>$\text{O}_3 + \text{hv} \rightarrow \text{O}(1\text{D}) + \text{O}_2$</td>
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</table>

$\text{BrONO}_2 + \text{hv} \rightarrow 0.71(\text{BrO} + \text{NO}_2) + 0.29(\text{Br} + \text{NO}_3)$

$\text{HOBr} + \text{hv} \rightarrow \text{OH} + \text{Br}$

$\text{CH}_3\text{Br} + \text{hv} \rightarrow \text{CH}_3\text{O}_2 + \text{Br}$

$\text{OClO} + \text{hv} \rightarrow \text{O} + \text{ClO}$

$\text{Cl}_2\text{O}_2 + \text{hv} \rightarrow \text{2Cl} + \text{O}_2$

$\text{Cl}_2 + \text{hv} \rightarrow \text{Cl} + \text{Cl}$

$\text{CCl}_2\text{O} + \text{hv} \rightarrow \text{products}$

$\text{CCl}_2\text{O} + \text{hv} \rightarrow \text{products}$

$\text{CF}_2\text{O} + \text{hv} \rightarrow \text{products}$

$\text{CFC}-114\ (\text{CCl}_2\text{CCIF}_2) + \text{hv} \rightarrow \text{products}$

$\text{CFC}-115\ (\text{CCIF}_2\text{CF}_3) + \text{hv} \rightarrow \text{products}$

$\text{HCl} + \text{hv} \rightarrow \text{H} + \text{Cl}$

$\text{CH}_2\text{O} + \text{hv} \rightarrow \text{CO} + \text{H}_2$

$\text{CH}_3\text{OOH} + \text{hv} \rightarrow \text{CH}_3\text{O} + \text{OH}$

$\text{CH}_3\text{CO}_3 + \text{hv} \rightarrow \text{products}$

$\text{PAN} (\text{CH}_3\text{C(O)OONO}_2) + \text{hv} \rightarrow 0.8 (\text{CH}_3\text{C(O)O}_2 + \text{NO}_2) + 0.2 (\text{CH}_3\text{C(O)O}_2 + \text{NO}_3)$

$\text{ClONO}_2 + \text{hv} \rightarrow \text{Cl} + \text{NO}_2$

$\text{NO}_3 + \text{hv} \rightarrow \text{NO}_2 + \text{O}$

$\text{NO} + \text{hv} \rightarrow \text{N} + \text{O}$

$\text{BrCl} + \text{hv} \rightarrow \text{Br} + \text{Cl}$

$\text{Br}_2 + \text{hv} \rightarrow \text{Br} + \text{Br}$

$\text{HO}_2\text{NO}_2 + \text{hv} \rightarrow \text{OH} + \text{NO}_3$

$\text{ClONO}_2 + \text{hv} \rightarrow \text{Cl} + \text{NO}_3$

$\text{NO}_3 + \text{hv} \rightarrow \text{NO} + \text{O}_2$

$\text{CHBr}_3 + \text{hv} \rightarrow \text{products}$

$\text{O}_2 + \text{hv} \rightarrow \text{O}(1\text{D}) + \text{O}(3\text{P})$
### Table 3 Cross section and quantum yield source references

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<th>Cross sections</th>
<th>Quantum yield</th>
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<tr>
<td>1. (\text{O}_2)</td>
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<tr>
<td>116.3-175.4 nm: Brasseur and Solomon (1986)</td>
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<td>2. (\text{O}_3 \rightarrow \text{O}(3P))</td>
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<td>347.5-735 nm: Brasseur and Solomon (1986)</td>
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<td>4. (\text{N}_2\text{O})</td>
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<td>5. (\text{CO}_2)</td>
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<td>8. (\text{HNO}_3)</td>
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<td>9. (\text{CFC-12})</td>
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<td>24. (\text{CH}_2\text{O} \rightarrow \text{H} + \text{HCO})</td>
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<td>32. (\text{CCIFO})</td>
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<td>33. (\text{CF}_2\text{O})</td>
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<td>34. (\text{CFC-114})</td>
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<td>36. (\text{HCl})</td>
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<td>38. (\text{CH}_3\text{OOH})</td>
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<td>39. (\text{CH}_3\text{CO}_3)</td>
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<td>40. (\text{PAN})</td>
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<td>41. (\text{ClNO}_2)</td>
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<td>42. (\text{NO}_3)</td>
<td>Magnotta and Johnston (1980)</td>
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<tr>
<td>43. (\text{NO})</td>
<td>Minschwaner and Siskind (1993)</td>
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15
<table>
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<th>Cross sections</th>
<th>quantum yield</th>
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<td>44........BrCl</td>
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<td>45........BrO</td>
<td>JPL97</td>
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<tr>
<td>46........HO₂NO₂ -&gt; NO₃</td>
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<tr>
<td>47........ClONO₂ -&gt; NO₃</td>
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<tr>
<td>48........NO₃</td>
<td>Magnotta and Johnston (1980)</td>
</tr>
<tr>
<td>49........CHBr₃</td>
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</table>
The photolysis of NO in the middle atmosphere occurs primarily in the $\delta(0-0)$ band (190.9 nm) and $\delta(1-0)$ band (182.7 nm). Since these bands coincide with the Schumann-Runge bands of oxygen, the determination of $J_{NO}$ requires a high spectral resolution treatment of the SRB absorption. Minschwaner and Siskind (1993) use the method of opacity distribution function to parameterize $J_{NO}$ with the latest spectroscopic information of both $O_2$ and NO. Their scheme is used in SOCRATES to estimate the photolysis rates of NO. The photolysis frequency of NO coincident with a given SR band of $O_2$ [(5-0), (9-0) and (10-0)] is determined by

$$J_{NO}(z) = q_0 e^{-\tau(O_3)} P(z) \sum_{i=1}^{6} \{ \exp[-\sigma_{O_2}^{i} N_{O_2}(z)] \}^{2} \sum_{j=1}^{2} W_{NO}^{i,j} \sigma_{NO}^{i,j} \exp[-\sigma_{NO}^{i,j} N_{NO}(z)]$$

(21)

where $P(z) = 1$ for the $\delta(1-0)$ band, and $P(z)=1.65e9/(5.1e7+1.65e9+1.5e-9[N_2(z)])$ for $\delta(0-0)$. One given SR band is subdivided into six wavelength regions ($i=1,6$) and inside each of these six regions by two values ($j=1, 2$) of NO cross section and weighting factor ($W_{NO}$). The values of these coefficients are listed in Table 1 of Minschwaner and Siskind (1993).

### 3.1.2. UV Solar heating

The thermal effect of the solar radiation can be calculated from the radiative transfer equation (11) for the mean radiance $I$. Solar photon absorption by $O_2$ and $O_3$ are the major sources of heat in the stratosphere and mesosphere. Heating in the UV by $O_2$ and $O_3$ knowing $I$ (J/s/cm$^2$) and the absorption cross section $\sigma$ of $O_2$ and $O_3$ (expressed in cm$^2$) can be determined by

$$Q_S(z;Z) = 4\pi \frac{6 \times 10^{23}}{c_p m_{\text{air}}[M]} \left\{ [O_2] \int_{\lambda} \frac{hc}{\lambda} \sigma_{O_2}(\lambda; z, Z) d\lambda \right\} + [O_3] \int_{\lambda} \frac{hc}{\lambda} \sigma_{O_3}(\lambda) I(\lambda; z, Z) d\lambda$$

(22)

where $m_{\text{air}}$ is the molecular weight of air (28.8 g/mole), $[M]$ is the air number density (in cm$^{-3}$), $[O_2]$ is the $O_2$ number density (cm$^{-3}$), and $[O_3]$ the ozone number density (cm$^{-3}$). When the effect of aerosol and cloud scattering is considered in the radiative transfer equation, solar heating due to aerosol ($\text{aer}$) and cloud ($\text{wc}$) heating is determined by:

$$Q_{S(\text{aer,wc})}(z;Z) = 4\pi \int_{\lambda} \frac{hc}{\lambda} I(\lambda; z, Z) \text{ext}_{\text{aer,wc}}(\lambda) [1 - \omega_{\text{aer,wc}}(\lambda)] d\lambda \frac{6 \times 10^{23}}{c_p m_{\text{air}}[M]}$$

(23)

in units of (K/s).

In Equation (22), it is assumed that the products of $O_2$ and $O_3$ photolysis recombine instantly as the solar energy is absorbed, so that the heat release is equal to the solar energy
absorbed. Although this is generally valid for altitudes below 80 km, the recombination may not be instantaneous at altitudes above 80 km where the atmospheric density is low. Instead, at these higher altitudes, chemical combination may occur only after some time span comparable to the transport time scale. Under this circumstance, the solar energy absorbed less the dissociation energy of photolyzed molecules shall be called 'residual heating' \( (Q_R) \), and the heat released as a result of chemical recombination called 'chemical heating' \( (Q_C) \). Thus, the residual heating is calculated by:

\[
Q_R(z; Z) = 4\pi \frac{6 \times 10^{23}}{c_p m_{\text{air}}[M]} \left\{ \int_{\lambda}^{\infty} \left( \frac{h\nu}{\lambda} - \zeta_{O_2} \right) \sigma_{O_2}(\lambda) I(\lambda; z; Z) d\lambda \right\} + \left\{ \int_{\lambda}^{\infty} \left( \frac{h\nu}{\lambda} - \zeta_{O_3} \right) \sigma_{O_3}(\lambda) I(\lambda; z; Z) d\lambda \right\}
\]

where \( \zeta \) is the energy required to break the \( O_2 \) and \( O_3 \) bonds. To estimate heating from exothermic chemical reactions, the recombination of odd oxygen species and odd hydrogen species are considered, following Brasseur and Offermann (1986):

\[
\begin{align*}
O+O+M & \rightarrow O_2+M \quad k_1, e_1 \\
O+O_2+M & \rightarrow O_3+M \quad k_2, e_2 \\
O+O_3 & \rightarrow 2O_2 \quad k_3, e_3 \\
H+O_3 & \rightarrow OH+O_2 \quad k_4, e_4 \\
OH+O & \rightarrow H+O_2 \quad k_5, e_5 \\
HO_2+O & \rightarrow OH+O_2 \quad k_6, e_6 \\
H+O_2+M & \rightarrow HO_2+M \quad k_7, e_7
\end{align*}
\]

\( k \) and \( e \) are the reaction rate and the bond breaking energy, respectively. The rate of energy released by these chemical reactions is given by:

\[
Q_C = e_1 k_1 [M][O]^2 + e_2 k_2 [M][O][O_2][O] + e_3 k_3 [O_3][O] + \kappa e_4 k_4 [H][O_3] + e_5 k_5 [OH][O] + e_6 k_6 [HO_2][O] + e_7 k_7 [M][H][O_2]
\]

For reaction \( k_4 \), the heating term is multiplied by \( \kappa \), a solar energy efficiency factor, whose value is given below. The unit of \( Q_C \) is converted from \( J/s/cm^2 \) to \( K/s \), by multiplying \( Q_C \) by \( N_A/(\left[ M \right] m_{\text{air}} c_p) \), where \( N_A \) is Avogadro's number, \( m_{\text{air}} \) is the air molecular mass and \( c_p \) is the specific heat at constant pressure.

In and above the mesosphere, solar energy absorbed by molecules in the form of chemical potential energy may be lost by airglow from excited photolysis products or by chemiluminescent emission from product species of exothermic chemical reactions before the energy is able to be...
converted to thermal energy. Mlynczak and Solomon (1993) evaluated the reduction of the solar heating efficiency by airglow processes for different absorption bands of $O_2$ and $O_3$, and by chemiluminescent loss for exothermic chemical reactions. They showed the heating efficiencies ($\eta$) to be less than one in the $O_3$ Hartley band, the $O_2$ Schumann-Runge continuum, the $O_2$ Lyman alpha line, and in the case of $H+O_3$ chemical reaction. These efficiencies are expressed by the following expressions:

- **$O_3$ Hartley band (200 - 310 nm)**
  \[ \eta_{O_3} = c_0 + c_1 x + c_2 x^2 + c_3 x^3 \]
  where \[ x = \log_{10} p + 3 \] for $10^{-4} \leq p (mb) \leq 10^{-2}$, \[ x = \log_{10} p + 1 \] for $10^{-2} \leq p (mb) \leq 10^0$.
  For $10^{-4} \leq p (mb) \leq 10^{-2}$, $c_0 = 0.66965$, $c_1 = -0.009682$, $c_2 = 0.033093$, and $c_3 = -0.017938$.
  For $10^{-2} \leq p (mb) \leq 10^0$, $c_0 = 0.92621$, $c_1 = -0.133960$, $c_2 = -0.076863$, and $c_3 = -0.006897$.

- **$O_2$ SR continuum (137-183 nm)**
  \[ \eta_{O_2} = c_0 + c_1 x + c_2 x^2 + c_3 x^3 \]
  where \[ x = \log_{10} p + 3 \] for $p$ in (mb).
  \[ c_0 = 0.75349, c_1 = 0.0036, c_2 = 0.059468, \text{ and } c_3 = -0.022795. \]

- **$O_2$ Lyman-$\alpha$ line (121.6 nm)**
  \[ \eta_{O_2} = 0.95 \]

- **$H+O_3 \rightarrow OH+O_2$**
  \[ \kappa = 0.6 \]

$\eta = 1$ for all other wavelengths. To obtain the residual solar heating rate, Equation (24) is multiplied by $\eta$ at each wavelength region mentioned above. Thus,

\[
Q_R(z;Z) = 4\pi \int \eta_{O_2}(\lambda) \left( \frac{hc}{\lambda} - \zeta_{O_2} \right) \sigma_{O_2}(\lambda) I(\lambda; z; Z) d\lambda \\
+ \int \eta_{O_3}(\lambda) \sigma_{O_3}(\lambda) I(\lambda; z; Z) d\lambda \tag{26}
\]

### 3.2 Infrared (IR) radiative regime \((\lambda > 3 \mu m)\)

#### 3.2.1. Troposphere and stratosphere

The infrared radiative transfer routine used in SOCRATES for altitudes between 0 to 50 km is the long wave band model described in Briegleb (1992). Briegleb's model computes broadband absorptivity and emissivity with a modified Malkmus random band model, corrected for over absorption of the traditional Malkmus band transmission. The model covers a spectral region of 0 to 3000 cm$^{-1}$ with a spectral width of 100 cm$^{-1}$. With this wide spectral region and a relatively high spectral resolution, minor bands of CO$_2$ and O$_3$, and several other radiatively active trace gases can
be included in the calculation. In SOCRATES, radiative contributions from CO₂, H₂O, O₃, CH₄, N₂O, CFC11, CFC12, and aerosols are included.

The optical depths for all gases are computed first, then the broadband transmission is calculated as an exponential of the summed optical depths of all gases. The optical depth for CO₂, O₃, CH₄ and N₂O for each 100 cm⁻¹ band takes the form

\[
\tau = \frac{1}{2} \frac{S_d \bar{p}^*}{s_p} \left[ \left( 1 + 8 \frac{S_p \beta \bar{u}_a}{\bar{p}} \right)^{1/2} - 1 \right]
\]  

(27)

where \( \bar{u}_a \) is the column absorber amount (g/cm²), \( S_p \) and \( S_d \) are band parameters [see Appendix of Brigleb (1992)] calculated as a function of line strength and half-line width taken from the HITRAN database (Rothman et. al 1987), \( \beta \) is the band dependent diffusivity factor to take into account the effect of solid angle integration, \( \alpha \) is a band dependent parameter which can be estimated from reference calculations, and \( \bar{p}^* = \bar{p} + \delta \), where \( \delta \) is an asymptotic pressure required to simulate Voigt line effects. For H₂O, a different transmission function is given due to the more gradual variation of absorption strength with wavenumber and its wide wavelength absorption span:

\[
\tau = \frac{1}{2} \frac{S_d \bar{p}^*}{s_p} \left[ \left( 1 + 4 \frac{S_p \beta \bar{u}_a}{\bar{p}} \right)^{1/2} - 1 \right].
\]

(28)

CFC11 and CFC12 weakly absorb in the H₂O window region between 800 to 1200 cm⁻¹, and their optical depths are given as

\[
\tau = \beta(\tau) \sigma \bar{u}_a
\]

(29)

where \( \sigma \) is the absorption cross section in units of cm²/g, and \( \beta(\tau) \) the diffusivity factor. The data for the absorption cross sections of the CFCs are from Massie et al. (1991). The diffusivity factor for the CFCs is taken from Ramanathan et al. (1985) as:

\[
\beta(\tau) = 1.5 + \frac{0.5}{1 + 4 \tau + 10 \tau^2}
\]

(30)

where \( \tau \) is the total optical depth of all absorbing species. Similarly, the aerosol optical depth is calculated by multiplying its spectral extinction coefficient (provided either through observation or through theoretical calculations) by the aerosol column depth.

Knowing the transmission \( (I = e^{-\tau}) \), the absorptivity \( (A) \) and emissivity \( (E) \) of the infrared radiative transfer equation is calculated by:

\[
A(p, p') = \frac{1}{dB(T')/dT} \int (1 - \Gamma(p, p')) \frac{dB(T)}{d\lambda} d\lambda
\]

(31a)
\[ E(p, p_t) = \frac{1}{B(T_t)} \int (1 - \Gamma(p, p_t)) B(T_t) d\lambda \]

(31b)

\( B(T) \) is the spectrally integrated Planck function, and \( \Gamma \) is the transmission for all gases absorbing between pressure \( p \) and \( p' \) for \( \text{abs} \), and \( p \) and \( p_t \) (top boundary pressure) for \( \text{ems} \), respectively. The longwave fluxes (upward + and downward -) at pressure \( p \) are calculated from the transfer equation by the formulation:

\[ F^-(p) = B(T_t) E(p, p_t) + \int_{p_t}^{p} A(p, p') \frac{d B(T)}{dp'} dp' \]

(32a)

\[ F^+(p) = e B(T_g) + (1-e) F^-(p_s) \\
+ \{B(T_s) - [e B(T_g) + (1-e) F^-(p_s)]\} A(p, p_s) m \\
- \int_{p}^{p_s} A(p, p') \frac{d B(T)}{dp'} dp' \]

(32b)

where subscript \( g \) denotes surface ground, subscript \( s \) denotes surface air, \( e \) is the broadband isotropic surface emissivity, and \( m \) is an empirical constant which partially corrects a bias in the surface atmosphere exchange. The upward and downward fluxes are differenced across layers to produce the longwave heating rates

\[ Q_{IR} = \frac{e}{c_p} \frac{F^-(p_{k+1}) - F^+(p_{k+1}) - F^-(p_k) + F^+(p_k)}{p_{k+1} - p_k} \]

(33)

**3.2.2. Mesosphere and lower thermosphere (CO\(_2\) 15 \( \mu \)m)**

The infrared radiative heating above the stratosphere is dominated by the CO\(_2\) 15 \( \mu \)m bands, while contributions from other trace gases are negligible (Kuhn and London, 1969). Above 60 km, where the local thermodynamic equilibrium (LTE) does not necessarily apply due to low air density, a different method for the longwave radiation is required for the CO\(_2\) 15 \( \mu \)m band. Under non-LTE conditions, the populations of the excited vibrational levels are no longer controlled by collisional processes and the source function of CO\(_2\) is no longer equal to the Planck function. For this purpose, Formichev et al. (1993) developed a parameterization scheme for the 15 \( \mu \)m CO\(_2\) band radiative heating rate for the middle atmosphere, which is incorporated in SOCRATES to estimate the infrared radiative heating rate above 60 km.

The parameterization scheme of Formichev et al. (1993) for altitudes 15 to 85 km is largely based on the work of Akmaev and Shved (1982), but accounts for the line overlapping in the CO\(_2\) band and for the non-LTE effects, in order for the parameterization scheme to be applicable to a
wide altitude range, including a non-LTE layer (70-85 km). The cooling rate is calculated by the following formula:

\[ Q_{IR}(x_0) = \frac{1}{c_p} (1 - 3 \phi_0 \sum_{j=-8}^{5} [a_j(x_0) + \phi_0 b_j(x_0) + \phi_0^2 c_j(x_0)] \phi_j ) \quad (K/s) \]  

(34)

where \( j \) is altitude index set from -8 to 5, \( x = \ln(1000/p(mb)) \) is the dimensionless height, and \( \phi_j = \exp(-960.24 / T_j) \). The cooling rate accounts for the radiative exchange between a given level \( x_0 \) and the other layers of the atmosphere denoted with subscript \( j \). The coefficients \( a_j, b_j, \) and \( c_j \) in Equation (34) are listed in Tables A, B, and C of Formichev et al. (1993).

For the non-LTE layer between 85 to 115 km, the cooling rate calculation is based on the recurrence formula of Kutepov and Fomichev (1993), which is expressed by

\[ Q_{IR}(x_j) = \frac{1}{c_p} 8.6301 \times 10^9 X_{CO_2,j} (1 - \lambda_j) \tilde{\varepsilon}(x_j) \quad (K/s) \]  

(35)

where \( X_{CO_2,j} \) is the mixing ratio of CO\(_2\) at level \( j \). The quantum probability \( \lambda_j \) is calculated by

\[ \lambda_j = \frac{1.5638}{1.5638 + \exp(-x_j) [X_{N_2,j}(2.9T_j^2 - 1060T_j + 145000) + X_{O_2,j}(4.23T_j^2 - 1490T_j + 180000) + X_O,jk_0]] \]  

(36)

where \( X_{N_2,j}, X_{O_2,j}, \) and \( X_O,j \) are the mixing ratios of N\(_2\), O\(_2\), and O, respectively, at level \( j \), and \( k_0 \) is the collisional deactivation rate between O and CO\(_2\), which is not known with certainty. Currently, \( k_0 \) is set at \( 5 \times 10^7 \) s\(^{-1}\)atm\(^{-1}\). The value of \( \tilde{\varepsilon}(x_j) \) is determined by the recurrence formula

\[ A_j \tilde{\varepsilon}(x_j) = A_{j-1} \tilde{\varepsilon}(x_{j-1}) + D_{j-1} \phi_{j-1} - D_j \phi_j \]  

(37)

where \( A_j, \) and \( D_j \) are calculated from

\[ A_j = 1 - \lambda_j (1 - \frac{3}{4} d_{j-1} - \frac{3}{4} d_j); \quad A_{j-1} = 1 - \lambda_{j-1} (1 - \frac{3}{4} d_{j-1} - \frac{1}{4} d_j); \]  

\[ D_j = \frac{1}{4} (d_{j-1} + 3d_j); \quad D_{j-1} = \frac{1}{4} (3d_{j-1} + d_j) \]  

(38)

The parameters \( d_j \) are listed in Table D in Formichev et al. (1993).
4. Dynamics

The dynamical wave forcing and associated diffusion in SOCRATES are estimated as a function of the zonal wind and derived according to linear wave theories. Although it is still necessary to parameterize wave processes, the wave components are able to respond to and interact with the mean field. Three types of waves are included in the model: planetary, gravity and tidal waves. Transience, dissipation, and breaking of these waves produces convergence of the wave fluxes and deposit momentum on the zonal wind field, which is reflected in the governing equations (Eq. 2). Wave diffusive mixing is also generated in the process and principally affects the temperature distribution (Eq. 1) and chemical transport (Eq. 79). Details of how the wave forcing and diffusion are derived is described next.

4.1 Planetary waves

Following Smith and Avery (1987), the vorticity and thermodynamic equations for the planetary wave take the forms:

\[
\frac{\partial}{\partial t} + \frac{\bar{u}}{a \cos \phi} \frac{\partial}{\partial \lambda} q' + v' \frac{\partial q}{\partial \phi} - \frac{f e z}{a} (e^{-z} w') = -(\beta + \delta) q' \tag{39}
\]

\[
\frac{\partial}{\partial t} + \frac{\bar{u}}{a \cos \phi} \frac{\partial}{\partial \lambda} T' + v' \frac{\partial T}{\partial \phi} + w' \frac{N^2 H}{R} = - (\alpha + \delta) T \tag{40}
\]

The potential vorticity \( q \) is:

\[
q = f + \frac{1}{a \cos \phi} \frac{\partial v}{\partial \lambda} - \frac{1}{a \cos \phi} \frac{\partial}{\partial \phi} (u \cos \phi) \tag{41}
\]

and the wave component of the meridional wind \( v' \) is:

\[
v' = \frac{1}{f \cos \phi} \frac{\partial \Phi'}{\partial \lambda} - \frac{1}{f^2 a^2} \frac{\bar{u}}{a \cos \phi} \frac{\partial^2 \Phi'}{\partial \lambda \partial \phi} \tag{42}
\]

where \( \Phi' \) is the geopotential disturbance, with prime referring to wave quantities. To represent wave dissipation from Newtonian cooling, Rayleigh friction and wave breaking, a linear damping term is added to the right hand side of equations (39) and (40), where \( \alpha \) is the Newtonian cooling rate, \( \beta \) is the Rayleigh dissipation rate, and \( \delta \) is the dissipation rate from planetary wave breaking (method to derive \( \delta \) will be described later). To derive the potential vorticity equation, \( w' \) is eliminated between (39) and (40), and substituted with (41) and (42) to form a single equation of the planetary wave geopotential \( \Phi' \). For a more concise formulation of the potential vorticity equation, the following transformed coordinates are defined:

\[
z = - \ln (p / p_0) \quad \text{log pressure}
\]
\[ s = \frac{R}{4\Omega^2a^2} \left( \frac{\partial T}{\partial z} + \kappa T \right) \quad \text{equivalent buoyancy frequency} \]

\[ \tilde{u} = \frac{\tilde{u}}{a \cos \phi} \quad \text{angular velocity} \]

Note that the log pressure is a dimensionless altitude unit used only within the wave model which is different from the pressure altitude coordinate used throughout SOCRATES. Furthermore, a new variable \( \Psi' \) is introduced to define the geopotential \( \Phi \) at zonal wave number \( m \), such that

\[ \Phi' = \sqrt{s} e^{z/2} \Psi(\phi, z, t)e^{im\lambda}. \]

Thus, the equation can be written as:

\[
\left( \frac{\partial}{\partial t} + \beta' \right) \left( A \Psi + B \frac{\partial \Psi}{\partial \phi} + \frac{\partial^2 \Psi}{\partial z^2} \right) + \left( \frac{\partial}{\partial t} + \alpha' \right) \left( D \frac{\partial^2 \Psi}{\partial z^2} + E \Psi \right) + \epsilon \frac{\partial \Psi}{\partial z} + F \Psi = 0
\]

(43)

where \( \alpha' = \alpha + im\tilde{u} + \delta, \ \beta' = \beta + im\tilde{u} + \delta, \ \epsilon = \frac{\sin^2 \phi}{s} \frac{\partial \alpha}{\partial z} \), and

\[
A = \frac{-m^2}{\cos^2 \phi} \\
B = \frac{-1 + \cos^2 \phi}{\sin \phi \cos \phi} \\
D = \frac{\sin^2 \phi}{s}, \ \text{E}=\frac{1}{4} D \\
F = \frac{im}{\cos \phi \frac{\partial q}{\partial \phi}} + \frac{1}{2} \frac{\sin^2 \phi}{s} \frac{\partial \alpha}{\partial z} + \frac{\partial^2 q}{\partial z^2}
\]

In the current version of the model, we are using \( s=0.02 \), independent of altitude, and only planetary wave one is considered, with \( m=1 \). Then applying implicit method for time integration, Equation (43) can be rewritten as:

\[
AA \frac{\partial^2 \Psi}{\partial z^2} + BB \frac{\partial \Psi}{\partial z} + CC \frac{\partial^2 \Psi}{\partial \phi^2} + DD \frac{\partial \Psi}{\partial \phi} + EE \Psi = FF
\]

(44)

where

\[
AA = 1 + \Delta t \cdot \alpha' \\
BB = \Delta t \cdot \frac{\partial \alpha}{\partial z} \\
CC = (1 + \Delta t \cdot \beta') \frac{s}{\sin^2 \phi}
\]
Using a space-centered differencing scheme, Equation (44) is solved using a numerical technique developed by Lindzen and Kuo (1969). Forcing at the lower boundary (16 km) is specified according to climatological values of wave one geopotential height at 100 mb (Randel, 1987). From the wave stream function, the wave zonal wind $u'$ and meridional wind $v'$ can be derived. The planetary wave momentum flux divergence, or the Eliassen-Palm (EP) flux divergence $\nabla \cdot F'$, is then calculated from

$$ F_R = \frac{1}{\rho_0 a \cos \phi} \nabla \cdot F $$

$$ = -\frac{1}{a \cos^2 \phi} \frac{\partial}{\partial \phi} (u' \cos^2 \phi) + \frac{1}{\rho_0} \frac{f}{4 \Omega^2 a^2} \frac{\partial}{\partial z} \left( \rho_0 \frac{\bar{v}' \bar{\Psi}_t'}{s} \right). \tag{45} $$

The planetary wave diffusion coefficient $K_{yy}$ and the wave breaking dissipation rate $\delta$ are derived according to methods developed by Garcia (1991). Garcia adopted barotropic instability as the criterion for planetary wave breaking, and assumed that there is dissipation when $|q'| \geq \bar{q}_y$, generally when the zonal mean potential vorticity meridional gradient becomes negative. In this case, the dissipation rate $\delta$ is calculated from the WKB approximation [Eq. 17 of Garcia (1991)]:

$$ \delta = c_{gy} \left[ -\frac{5}{4} \frac{\bar{u}_y}{(\bar{u} - c)} \right] + c_{gz} \left[ \frac{1}{2H} - \frac{3}{4} \frac{\bar{u}_z}{(\bar{u} - c)} \right] \tag{46} $$

where $c_{gy}$ and $c_{gz}$ are the horizontal and vertical group velocities given by

$$ c_{gy} = \frac{2kl}{k^2 + l^2 + \frac{f^2}{N^2} (m^2 + \frac{1}{4H^2})} (\bar{u} - c) \tag{47a} $$

$$ c_{gz} = \frac{2km \frac{f^2}{N^2}}{k^2 + l^2 + \frac{f^2}{N^2} (m^2 + \frac{1}{4H^2})} (\bar{u} - c). \tag{47b} $$
The planetary wave diffusion coefficient $K_{yy}$ corresponding to this dissipation rate is derived from \[ Eq. 20 of Garcia (1991) \]

$$K_{yy} = \frac{\delta \bar{v} \bar{v}}{k^2 (\bar{u} - c)^2 + \delta^2} \quad (48)$$

Evaluation of the dissipation rate requires knowledge of the phase speed ($c$), meridional wave number ($l$), and vertical wave number ($m$) for the group velocities. These quantities are likewise derived from Garcia (1991) \[ Eqs. (35) and (36) \]:

$$l = \text{Im} \left( \frac{\Phi_y}{\Phi'} \right)$$

$$m = \text{Im} \left( \frac{\Phi_z}{\Phi'} \right)$$

$$c = -\frac{1}{k} \text{Im} \left( \frac{\Phi_x}{\Phi'} \right)$$

where $\text{Im}$ denotes the imaginary component.

### 4.2 Gravity waves

In the new version of the model, two options are available for the parameterization of the gravity wave breaking process. The default standard run uses the Lindzen-Holton gravity wave breaking scheme (Lindzen 1981, Holton 1982) for estimating the gravity wave forcing and vertical diffusion coefficient. In this case, the gravity wave momentum flux divergence is expressed as:

$$F_G = -A_g (\bar{u} - c)^2 [ (\bar{u} - c) - 3H \frac{\partial \bar{u}}{\partial z} ] \quad (49a)$$

and the vertical eddy diffusion resulting from wave breaking is given by

$$K_{zz} = \frac{A_g (\bar{u} - c)^4}{Pr N^2} \left[ 1 - 3H \frac{\partial \bar{u}}{\bar{u} - c} \right] \quad (49b)$$

where $Pr$ is the Prandtl number and $A_g$ is the amplitude coefficient. These parameters are unchanged from previous versions of SOCRATES (Brasseur and Hitchman 1987, Brasseur et al. 1990).

A second option is to use the parameterization scheme developed primarily by Fritts and Lu (1993) (hereafter FL93), which will be described in more detail here. The Fritts-Lu gravity wave forcing parameterization scheme uses a general gravity wave spectral formulation (Fritts and VanZandt 1993) provided by the observed gravity wave spectrum to deduce how the gravity wave energy flux responds to variation in the background environment. The variation of total gravity
wave energy $E_0$ with height is given by $E_0 \propto e^{dz/H_E}$, where the scale height for energy growth is specified as

$$H_E = [2 + \sin(\frac{\pi z}{60})]H,$$

(50)

with $z$ in kilometers. Equation (50) is slightly different from Equation (28) of Fritts and VanZandt (1993), based on more recent observations of the total energy variations (Wilson et al. 1991a,b), and produces a more realistic estimate of the gravity wave forcing profile. The lower boundary condition for gravity wave energy forcing is currently set at 30 km, and the total energy at 30 km is specified as a function of latitude and season according to Hirota (1984). With the assumption that the total energy is comprised of two component spectra propagating east and west, the energy at the lower boundary is equally split into the east and west components, while their intrinsic phase speeds are calculated from the relation [Eq. (22) of Fritts and VanZandt (1993), $E_0/2$]

$$E_j = \frac{1}{20} c^2_j$$

(51)

where $j$ denotes the east or west direction, and $c_j$ is the intrinsic phase speed.

To determine how the total energy varies with height, with the atmospheric stratification and the local mean wind, the relationship expressed in Eq. (31) of FL93 ($E_0 \propto N^{1/2} e^{z/H_E}$) is used to obtain

$$E^z_0 = E^{z-1}_0 e^{1/H_E (\frac{N^z}{N^{z-1}})^{1/2}}$$

(52)

where the superscript $z$ in this case denotes the altitude grid. Meanwhile, the energy spectra for each directional component (component energy) are assumed to vary with changes in the zonal wind in the vertical direction. When $\partial u / \partial z > 0$, the westerly phase speed $c_{*w}$ increases with height according to the formula given in Eq. 33 of FL93, with $c_{*} = N/m_{*}$:

$$c^z_{*w} = [c^z_{*w} \cdot (\frac{N^{z_0}}{N^{z}}) \cdot (\frac{N^z_{z_0}}{N^{z_0}})^{1/4} \cdot e^{-dz/4H}$$

(53)

with the corresponding easterly component energy $E_e$ calculated from Equation (51). With $E_e$ known, $E_w$ (westerly component energy) can be calculated from $E_0- E_e$. Similar conditions are applied when $\partial u / \partial z < 0$, in which case $c_{*e}$ increases with altitude.

Aside from the constraint of energy (or wave saturation) at large vertical wave number that arise from variation of wave energy with height and static stability as mentioned above, another saturation criteria set by FL93 is provided by the maximum anisotropy ($\alpha$) allowed from wave propagation. Fritts and Lu assumed that no less than a fraction $\alpha$ of the energy may be associated with any one component ($E_j/E_0 < 1-\alpha$), which is motivated by the insensitivity of motions of small
vertical wave number to mean wind changes and the tendency of instability to occur under large wind shear conditions. In the model, we have set $\alpha=0.25$. When conditions are such that $E_j/E_0 < 1-\alpha$, than $E_j$ is adjusted back to $E_j=E_0(1-\alpha)$.

With the variation with altitude of the two energy components calculated, the momentum fluxes and its vertical divergence can be estimated. The relationships between energy ($E_j$), the momentum flux ($F_p$), and energy flux ($F_E$) are expressed according to Eq. 37 - 39 of FL93

$$F_p=1/22*(E_e-E_w)$$

(54)

and

$$F_E = \frac{1}{18}(c_e \cdot E_e + c_w \cdot E_w).$$

(55)

The gravity wave momentum flux divergence $F_G$ and the energy dissipation rate $\varepsilon$ are calculated from

$$F_G = -\frac{1}{\rho_0} \frac{\partial}{\partial z} (\rho_0 F_p)$$

(56)

and

$$\varepsilon = -\frac{N}{\rho_0} \frac{\partial}{\partial z} (\rho_0 N F_E).$$

(57)

With the energy dissipation rate ($\varepsilon$) known, the gravity wave diffusion coefficient ($K_{zz}$) is calculated according to the relationship

$$K_{zz} = A \frac{\varepsilon}{N^2}.$$  

(58)

As discussed in Weinstock (1984), the value of the coefficient $A$ (equivalent to the inverse of Prandtl no.) could be as small as $1/3$ or even less. In the model, we adopt the value of $A=0.2$.

4.3. Tidal waves.

The parameterization of tidal wave forcing and diffusion in the 2-D model is based on the work of Lindzen (1981). Lindzen showed that under the WKBJ approximation of the linear wave equation, the momentum flux divergence from tidal gravity wave can be expressed as

$$F_T = -\frac{1}{\rho_0} \frac{\partial}{\partial z} (\rho_0 w' w') = -\frac{k}{2H} \frac{(-c)^3}{N(1+l^2/k^2)^{3/2}}$$

(59)

and the diffusion coefficient can be written as

$$K_{zz(tides)} = \frac{k c^4}{N^3 (1+l^2/k^2)^{3/2}} \frac{1}{2H}.$$  

(60)

From theoretical calculations, it can be shown that only the first diurnal mode of the tidal waves within $30^\circ$ latitude is able to propagate up into the mesosphere, and break to generate
forcing and turbulence. At 85 km altitude where the waves break, with the tidal wave phase speed of 465 m/s and \( k=\pi/6400 \) for the main diurnal propagating mode, \( F_T=-16.3 \) m/s/day, and \( K_{zz}=183 \) m²/s, according to Eqs. (59) and (60). Above 85 km, we let \( F_T \) and \( K_{zz} \) decrease with altitude to take into account the rapid increase of the contribution from molecular viscosity and conductivity. At level \( z \) (km), above the breaking level, the momentum flux divergence \( F_T \) and diffusion coefficient \( K_{zz} \) calculated at 85 km are multiplied by \( \exp[(85-z)/5] \). Since waves are still expected to generate turbulence below the breaking level, a factor \( \exp[(z-85)/5] \) is applied to \( F_T \) and \( K_{zz} \) below the breaking level (85 km).

Because the tidal wave mode that propagates up to the mesosphere is restricted to latitudes \(-30^\circ < \text{lat} < 30^\circ\), a factor of \( \exp[-(\phi / 20^\circ)^2] \) is applied to \( F_T \) and \( K_{zz} \) beyond the latitudes 30° N and 30° S. Within the latitude of 30°, \( F_T \) and \( K_{zz} \) are assumed to be constant with latitude.

4.4. Tropospheric wave forcing and latent heating specification.

As mentioned in the Section 1, the lower boundary condition for the circulation is applied at 2 km. In order to solve the stream function equation (7), the tropospheric wave momentum flux divergence and the latent heat release rate that is particularly important in the troposphere, needs to be accounted for in the forcing term \( C_F \). In SOCRATES, we chose to specify the EP flux divergence and latent heating rate in the troposphere according to a seasonal monthly-mean climatology.

Based on the EP flux divergence climatology established in Randel (1992), we formulated the EP flux divergence as a function of latitude, height and season as following:

If \(-\pi/2<\phi<-\pi/6\) or \(\pi/6<\phi<\pi/2\) (mid to high latitudes):

\[
\nabla \cdot F_{trop} = \frac{1}{2} \cos(3\phi - \pi) \left[ -A_{trop} \cdot e^{-(z-8)^2/4} + 4 \cdot e^{-3(z-4)^2/2} \right] \quad (61)
\]

If \(-\pi/6<\phi<\pi/6\) (tropics):

\[
\nabla \cdot F_{trop} = 0
\]

The amplitude of \( A_{trop} \) varies with season and hemisphere:

- Equinox season: \(-\pi/2<\phi<-\pi/6\) \( A_{trop}=15 \) m/s/day
- \(\pi/6<\phi<\pi/2\) \( A_{trop}=28 \) m/s/day
- June solstice season: \(-\pi/2<\phi<-\pi/6\) \( A_{trop}=23 \) m/s/day
- \(\pi/6<\phi<\pi/2\) \( A_{trop}=16 \) m/s/day
- December solstice season: \(-\pi/2<\phi<-\pi/6\) \( A_{trop}=13 \) m/s/day
- \(\pi/6<\phi<\pi/2\) \( A_{trop}=40 \) m/s/day
The tropospheric latent heating rate due to condensation during convection events is specified to vary with latitude, height and season, based on Boville (1985) and Peixoto and Oort (1991). We use the following formulation for condensation heating rate:

At $z < 12$ km:

\[ Q_{LH} = 4 \sin(\pi \frac{z-3}{12}) \exp\left(-\frac{\phi^2}{100}\right) \text{ (K/day)} \]  

(62a)

In the winter hemisphere, at latitudes less than $20^\circ$,

At $z < 5$ km:

\[ Q_{LH} = 5 \cdot \sin(\pi \frac{z+10}{20}) \cdot \cos(\frac{9\phi}{4}) \text{ (K/day)} \]  

(62b)

In the summer hemisphere,

At $z < 5$ km:

\[ Q_{LH} = 8 \cdot \sin(\pi \frac{z+10}{20}) \cdot \cos(\frac{3\phi}{2}) \text{ (K/day)} \].  

(62c)

The latent heating rate $Q_{LH}$ calculated from Eq. (62) is finally processed with the Gaussian filter smoothing routine, with weights of 0.25, 0.5, and 0.25, in both $y$ and $z$ direction for five times.

4.5 The circulation global mass balance correction.

The meridional circulation estimated from the stream function equation (7) is not necessarily in perfect global mass balance, either from inaccuracies in the radiative or dynamical forcing scheme, or from omitted physical processes such as small-scale turbulent processes. Thus, corrections have to be made to ensure that as the model integration proceeds, the integrated zonally-averaged mass flux between poles along a pressure surface remains equal zero. The global mass balance requirement can be written as

\[ \int_{-\pi/2}^{\pi/2} \rho \bar{w}^* \cos \phi \cdot d\phi = 0, \]  

(63)

which is the latitudinal integration of area-weighted vertical residual wind along the log pressure height surface. Since $\bar{w}^*$ does not necessarily meet the condition as shown in Eq.(63), a correction $\alpha$ is applied to $\bar{w}^*$ such that

\[ \int_{-\pi/2}^{\pi/2} \rho(\bar{w}^* - \alpha) \cos \phi \cdot d\phi = 0 \]  

(64)

where $\alpha$ is a function of height only. Thus, the correction factor $\alpha$ can be obtained from
4.6 Molecular diffusivity parameterization

The effect of molecular diffusion on the chemical species and thermal field becomes important above the mesopause. Since the model domain of SOCRATES extends up to 120 km, the effect of molecular diffusion effect is taken into account.

Following Banks and Kockarts (1973), the vertical flux of a minor constituent \(i\) relative to air from molecular diffusion can be written as:

\[
\varphi(i) = -K_{m(i)} \left[ \frac{\partial [n(i)]}{\partial z} + \frac{[n(i)]}{H(i)} + \left(1 + \alpha_T \right) \frac{[n(i)]}{T} \frac{\partial T}{\partial z} \right] \tag{66}
\]

with the molecular diffusion coefficient \(K_m\) for a particular gas \(i\) expressed as:

\[
K_{m(i)} (\text{cm}^2 / \text{s}) = 1.52 \times 10^{18} \left( \frac{1}{m_{\text{air}}} + \frac{1}{m_i} \right)^{0.5} \sqrt{T} \left[ M \right] \tag{67}
\]

where \([n]\) is the number density of the minor constituent, \(H(i) = RT/(m_i g)\) is the scale height for trace species \((i)\), \(\alpha_T\) the thermal diffusion factor (-0.38 for H), \(m_{\text{air}}\) is the molecular weight of air (g/mole) which is specified as a function of altitude, \(m_i\) is the molecular weight of gas \(i\) (g/mole), and \([M]\) is the number density of air (cm\(^3\)). To derive the diffusivity flux formulation of Eq. (66) consistent with the chemical transport equation that will be described in section 2.3 [Equation (79)], \([n]\) in Eq. (66) is substituted by the mixing ratio \(X_i\):

\[
\varphi(i) = -K_{m(i)} [M] \frac{\partial X_i}{\partial z} + X_i K_{m(i)} [M] \left( \frac{1}{H} - \frac{1}{H_i} \right) \tag{68}
\]

where \(\frac{1}{H_i} = \frac{1}{H(i)} + (1 + \alpha_T) \frac{\partial T}{\partial z}\). Thus, if we define the vertical diffusive velocity by

\[
\overline{w}_{D(i)} = K_{m(i)} \left( \frac{1}{H} - \frac{1}{H_i} \right), \tag{69}
\]

the diffusivity flux can be expressed as

\[
\varphi(i) = [M] \left[ -K_{m(i)} \frac{\partial X_i}{\partial z} + X_i \overline{w}_{D(i)} \right] \tag{70}
\]
Since the time rate of change of mixing ratio expressed in flux form is \( \frac{\partial X}{\partial t} = \frac{\partial \bar{\chi}}{\partial z} \), the effect of molecular diffusion on the chemical transport is given by

\[
\frac{\partial \bar{\chi}_i}{\partial t} = \frac{1}{\rho_0} \frac{\partial}{\partial z} \left[ \rho_0 \cdot K_{m(i)} \frac{\partial \bar{\chi}_i}{\partial z} \right] - \frac{1}{\rho_0} \frac{\partial}{\partial z} \left( \rho_0 \cdot \bar{w}_D \bar{\chi}_i \right) \tag{71}
\]

where \( \bar{\chi}_i \) represents the zonally averaged mixing ratio of gas \( i \).

The thermal conductivity coefficient \( K_T \) associated with the molecular diffusion of heat in Equation (6) is adapted from the NCAR Thermospheric General Circulation Model (Alan Burns, private communication), in the form of

\[
K_T\left(\frac{\text{ergs}}{\text{cm} \cdot \text{K} \cdot \text{s}}\right) = \left[(X_{O_2} + X_{N_2}) \cdot 56 + X_O \cdot 75.9\right] \cdot T^{0.69} \tag{72}
\]

where \( X \) represents the mixing ratio. To convert \( K_T \) to units of \( \text{m}^2/\text{s} \) for the model, Equation (72) is multiplied by a factor of \((m_{\text{air}} g^2 H^2)/(P_0 \gamma \rho R T e^{-Z/H})\).

### 4.7. Quasi-ibiennial oscillation simulation

The quasi-ibiennial oscillation (QBO) of the temperature, zonal wind, and meridional circulation in the equatorial stratosphere is simulated in the 2-D model according to Politowitz and Hitchman (1997). An analytical expression for the QBO radiative forcing is derived from a composite of observed zonal wind in the tropics, which is used to obtain the QBO forced circulation and the temperature oscillation in the stratosphere. Since the 2-D model does not explicitly deal with the zonal component of the momentum equation, using a QBO type radiative forcing in the stream function equation (Eq. 7) is a convenient way to simulate QBO processes for temperature and circulation without changes in the logistics of the model physics. The QBO forcing is specified and therefore does not respond to changes in zonal mean conditions. However, with this parameterization, the model can be used to examine various QBO radiative, transport, and chemical feedback effects on stratospheric chemistry.

From radiosonde time series at 15 tropical stations, Politowitz and Hitchman (1997) created a composite QBO for zonal wind at tropical latitudes between 16 to 40 km altitude with the formulation:

\[
\bar{u}_{qbo} = -\bar{u}_{\text{max}} \cdot \exp\left[-\left(\frac{\phi}{\phi_w}\right)^2\right] \cdot \cos\left(\frac{\pi}{2} \frac{\phi}{\phi_w}\right) \cdot \\
\cos\left(\frac{z - z_{\text{max}}}{h_{qbo}} \pi\right) \cdot \cos\left(2\pi \frac{t - \frac{1}{2}}{t_{qbo}} + 2\pi \frac{z - z_{\text{max}}}{z_{hfwd}}\right) \tag{73}
\]
where $h_{qbo}$ is the QBO vertical extent of 24 km and $t$ is the model time (in units of day with $t_{qbo}$ in units of days). The maximum zonal wind QBO perturbation ($\bar{u}_{\text{max}}$) is 25 m/s and is centered over the equator. The perturbation decays exponentially in latitude with a Gaussian latitude width ($\phi_w$) of 15°, with negative tails beyond 15° on either side of the equator with the factor $\cos(\pi\phi / 2\phi_w)$. The perturbation varies sinusoidally in altitude, between 16 km and 40 km, with maximum vertical amplitude at $z_{\text{max}}$, (28 km). A node between easterlies and westerlies descends with time, with a descent period of $t_{qbo}$=27 months (or 821 days) and a half width ($zhfwd$) of 27 km.

A analytical expression for the time rate of change of temperature is derived based on the equatorial $\beta$ plane thermal wind relationship:

$$\frac{\partial \bar{u}}{\partial z} = - \frac{Ra}{2H\Omega y} \frac{\partial \bar{T}}{\partial y}. \tag{74}$$

Assuming $\bar{T} = T_0 \exp(-\phi^2 / \phi_w^2)$, where $T_0$ is the equatorial temperature with $\phi_w$ in radial units, the thermal wind relation can be written as

$$\bar{T} = \frac{H\Omega y}{R} \phi_w^2 \frac{\partial \bar{u}}{\partial z}, \tag{75}$$

or

$$\frac{\partial \bar{T}}{\partial t} = \frac{H\Omega y}{R} \phi_w^2 \frac{\partial \bar{u}}{\partial \phi_w \partial z}. \tag{76}$$

Substituting the expression of \( \bar{u} \) (Eq. 73) into Equation (76), the time rate of change of temperature as a function of time, latitude, and altitude can be written as

$$\frac{\partial \bar{T}}{\partial t} = - \frac{2H\Omega y}{R \cdot t_{qbo}} \frac{\partial u_{\text{max}}}{\phi_w} \exp[-(\phi^2)^2] \cdot \cos\left(\frac{\pi \phi}{2 \phi_w}\right) \cdot \cos\left(\frac{2\pi z - z_{\text{max}}}{zhfwd}\right) \cdot \cos\left(\frac{2\pi z - z_{\text{max}}}{zhfwd}\right). \tag{77}$$

Although in principle, temperature QBO can be derived from Equation (75) knowing the zonal wind profile, the temperature is actually derived from dynamical and thermal equations through the QBO forced meridional circulation. One option is to include the time rate of temperature change from Equation (76) as a diabatic heat forcing in the stream function equation (7) to obtain a meridional circulation forced by the QBO temperature damping rate. Another option is to include in the stream function equation a direct QBO momentum forcing with the formulation:

$$F_{\text{QBO}} = A_{qbo} \cdot \bar{u}_{\text{max}} \cdot \frac{2\pi}{t_{qbo}} \cdot \exp[-(\phi^2)^2] \cdot \cos\left(\frac{\pi \phi}{2 \phi_w}\right) \cdot \cos\left(\frac{z - z_{\text{max}}}{h_{qbo}} \pi\right). \tag{78}$$
where $A_{qbo}$ is an adjustable parameter to optimize the results. The QBO forced circulation is then used to integrate in time the thermodynamic equation (1), which provides the temperature. Through this procedure, both the circulation and temperature can be affected by the QBO.
5. Chemistry

In SOCRATES, the chemical species are grouped into three categories: long-lived species and chemical families, intermediate lifetime species, and short-lived species. For long-lived species or families with chemical lifetimes comparable to or longer than transport timescales, the full chemical continuity/transport equation is solved:

$$\frac{\partial \bar{X}_i}{\partial t} + \bar{v} \cdot \frac{\partial \bar{X}_i}{\partial y} + \bar{w} \cdot \frac{\partial \bar{X}_i}{\partial z} = \frac{P_i}{[M]} - L_i \cdot \bar{X}_i + D_{Xi}$$

(79)

where $\bar{X}_i$ represents the mixing ratio of gas $i$, $P_i$ is the chemical production rate of gas $i$, and $L_i \cdot \bar{X}_i$ is the chemical loss rate of gas $i$. The transport of tracers by small scale mixing process is represented by a diffusive term $D_{Xi}$, written as

$$D_{Xi} = \frac{1}{\cos \phi} \frac{\partial}{\partial y} \left( \cos \phi \cdot K_{yy} \frac{\partial \bar{X}_i}{\partial y} \right) + \frac{1}{\rho_0} \frac{\partial}{\partial z} \left( \rho_0 \cdot (K_{zz} + K_m) \frac{\partial \bar{X}_i}{\partial z} \right)$$

$$- \frac{1}{\rho_0} \frac{\partial}{\partial z} \left( \rho_0 \cdot \bar{w}_D \bar{X}_i \right) - w_d \bar{X}_i$$

(80)

The intermediate species are chemicals with lifetimes shorter than the transport timescales, with timescales relatively insensitive to dynamical process, but sufficiently long that photochemical equilibrium cannot be assumed. These species are solved from the continuity equation without involving transport:

$$\frac{\partial \bar{X}_i}{\partial t} = P_i - L_i \cdot \bar{X}_i$$

(81)

For the short-lived chemical species with lifetimes much shorter than the dynamical time constants, photochemical equilibrium conditions apply and the concentration of the trace gas $i$ is derived from

$$P_i - L_i \cdot \bar{X}_i = 0.$$

(82)

The list of the constituents included in the standard version of SOCRATES is given in Table 4.

5.1 Chemical reactions

More than 160 chemical reactions describing HO$_x$, NO$_x$, Cl$_x$, Br$_x$, O$_x$, and hydrocarbon chemistry are included in SOCRATES. The majority of the chemical reaction rate constants are based on the compilation published by the Jet Propulsion Laboratory (JPL) in 1997 (DeMore et al., 1997). A list of the reactions and rates is given in Table 5.

5.1.1. Heterogeneous chemistry on polar stratospheric clouds
The parameterization of heterogeneous processes occurring on the surface of polar stratospheric clouds is based on the methods described by Chipperfield et al. (1993). Two types of PSC are considered: type II PSCs, mainly composed of water ice, and type I PSCs mainly composed of nitric acid trihydrate (NAT). For type I PSCs, the formula of Hanson and Mauersberger (1988) is used to estimate the saturation vapor pressure of HNO$_3$ over NAT and hence the number density of condensed HNO$_3$.3H$_2$O species:

$$P_{HNO3} = 10^{[m(T)\cdot \log(P_{H2O})+b(T)]}$$  \hspace{1cm} (83)

where $m(T) = -2.7836 - 0.00088 \cdot T$ and $b(T) = 39.9855 - 11.397/T + 0.009179 \cdot T$. The vapor pressure is converted into units of number density from

$$[HNO_3] = P_{HNO3} \cdot [M] / P.$$  \hspace{1cm} (84)

Thus the number density of condensed HNO$_3$.3H$_2$O species is then estimated by subtracting the "saturation number density" from the total number density of HNO$_3$. In the case of NAT, the condensed particles are assumed to have a radius of 1 µm, with a sedimentation velocity of 0.015 km/day. Similarly, the formula for the saturation vapor pressure over ice from Murray (1967):

$$P_{H2O} = 5.715185606 \times 10^{10} \cdot \exp[-20.947031 \cdot (273.16/T) - 3.56654 \cdot \ln(273.16/T) - 2.01889049 \cdot (T/273.16)]$$  \hspace{1cm} (85)

is used to predict the occurrence of type II PSCs. These type II PSCs are assumed to have a radius of 10 µm, and a sedimentation velocity of 1.5 km/day. The condensed HCl number density is deduced from the mole fractions of condensed HNO$_3$ and H$_2$O according to Hanson and Mauersberger (1990):

$$[HCl(s)] = 0.0035 \cdot [HNO_3(s)] + 0.0001 \cdot [H_2O(s)].$$  \hspace{1cm} (86)

If sedimenting particles reach a level where the ambient temperature is higher than the condensation threshold, evaporation takes place and the condensed species are returned to the gas phase. In the presence of PSCs, the following five heterogeneous reactions are assumed to occur:

- (het1) ClONO$_2$(g)+H$_2$O(s) $\rightarrow$ HOCl(g)+HNO$_3$(s)
- (het2) ClONO$_2$(g)+HCl(s) $\rightarrow$ Cl$_2$(g)+HNO$_3$(s)
- (het3) N$_2$O$_5$(g)+H$_2$O(s) $\rightarrow$ 2HNO$_3$(s)
- (het4) N$_2$O$_5$(g)+HCl(s) $\rightarrow$ ClNO$_2$(g)+HNO$_3$(s)
- (het5) HOCl(g)+HCl(s) $\rightarrow$ Cl$_2$(g)+H$_2$O(s)

The first order rate constant (het 1 ~ het5) for these reactions can be written as $het = \gamma v A / 4$ (Cadle et al. 1975), where $\gamma$ is the reaction probability, $A$ the PSC surface area density, and $v$ the mean molecular velocity given by $v = (8kT / \pi m)^{1/2}$. The reaction probabilities for these reactions are

36
### Table 4a Long-lived species

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>Formula/Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$N_2O$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$CH_4$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$H_2O$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$NO_y = NO + NO_2 + HNO_3 + 2*N_2O_5 + HO_2NO_2 + NO_3 + N^+ ClONO_2 + BrONO_2 + ClINO_2$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$HNO_3$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$N_2O_5$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$Cl_y = ClO + OCIO + 2<em>Cl_2O_2 + HCl + ClONO_2 + HOCI + 2</em>Cl_2 + ClINO_2$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$O_x = O_3 + O(3P) + O(1D)$</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$CO$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$OCIO$</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>TRACER</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>AEROSOLS</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>$HCl$</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>$ClONO_2$</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>$HOCI$</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>$Cl_2$</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>$H_2O_2$</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>$ClNO_2$</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>$HBr$</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>$BrONO_2$</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>$NO_x = NO + NO_2$</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>$HO_2NO_2$</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>$ClO_x = Cl + ClO$</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>$BrO_x = Br + BrO$</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>$Cl_2O_2$</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>$HOBr$</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>$CO_2$</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>$C_2H_6$</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>$C_2H_4$</td>
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<tr>
<td>30</td>
<td>$C_3H_6$</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>$CH_2O$</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>PAN</td>
<td>$(CH_3CO_3NO_2)$</td>
</tr>
<tr>
<td>33</td>
<td>$H_2$</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>$HO_x$</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>CFC-10</td>
<td>$(CCl_4)$</td>
</tr>
<tr>
<td>36</td>
<td>CFC-11</td>
<td>$(CCl_3F)$</td>
</tr>
<tr>
<td>37</td>
<td>CFC-12</td>
<td>$(CCl_2F_2)$</td>
</tr>
<tr>
<td>38</td>
<td>CFC-113</td>
<td>$(C_2Cl_3F_3)$</td>
</tr>
<tr>
<td>39</td>
<td>CFC-114</td>
<td>$(C_2Cl_2F_4)$</td>
</tr>
<tr>
<td>40</td>
<td>CFC-115</td>
<td>$(C_2ClF_5)$</td>
</tr>
<tr>
<td>41</td>
<td>HCFC-22</td>
<td>$(CHClF_2)$</td>
</tr>
<tr>
<td>42</td>
<td>$CH_3CCl_3$</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>$CH_3Cl$</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>$CCl_2O$</td>
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<tr>
<td>45</td>
<td>$CClFO$</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>$CF_2O$</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>Ha-1211</td>
<td>$(CF_2ClBr)$</td>
</tr>
<tr>
<td>48</td>
<td>Ha-1301</td>
<td>$(CF_3Br)$</td>
</tr>
<tr>
<td>49</td>
<td>HF</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>$CH_3Br$</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>$Br_y = Br + BrO + HOBr + HBr + BrONO_2 + BrCl$</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>$CHBr_3$</td>
<td></td>
</tr>
</tbody>
</table>
### Table 4b Intermediate lifetime species

1. \( \text{CH}_3\text{O}_2 \)
2. \( \text{CH}_3\text{OOH} \)
3. \( \text{C}_2\text{H}_5\text{O}_2 \)
4. \( \text{C}_2\text{H}_5\text{OOH} \)
5. \( \text{CH}_3\text{CHO} \)
6. \( \text{CH}_3\text{CO}_3 \)
7. \( \text{CH}_3\text{COOOH} \)
8. \( \text{C}_3\text{H}_6\text{OHO}_2 \)
9. \( \text{C}_3\text{H}_6\text{OHOOH} \)
10. \( \text{BrCl} \)

### Table 4c Short-lived species

1. \( \text{O}(1\text{D}) \)
2. \( \text{OH} \)
3. \( \text{Cl} \)
4. \( \text{O}(3\text{P}) \)
5. \( \text{O}_3 \)
6. \( \text{HO}_2 \)
7. \( \text{NO}_2 \)
8. \( \text{NO} \)
9. \( \text{Br} \)
10. \( \text{N} \)
11. \( \text{ClO} \)
12. \( \text{BrO} \)
13. \( \text{NO}_3 \)
14. \( \text{H} \)
### Table 5 - Chemical reactions and rate constants

Underline rate coefficients denote change from JPL94 to JPL97

#### Odd hydrogen reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1</td>
<td>$H + O_2 + M \rightarrow HO_2 + M$</td>
</tr>
<tr>
<td>a1et</td>
<td>$O_1D + H_2O \rightarrow OH + OH$</td>
</tr>
<tr>
<td>a2</td>
<td>$H + O_3 \rightarrow OH + O_2$</td>
</tr>
<tr>
<td>a2et</td>
<td>$O_1D + CH_4 \rightarrow OH + CH_3O_2$</td>
</tr>
<tr>
<td>a3et</td>
<td>$O_1D + H_2 \rightarrow OH + H$</td>
</tr>
<tr>
<td>a5</td>
<td>$O + OH \rightarrow O_2 + H$</td>
</tr>
<tr>
<td>a6</td>
<td>$OH + O_3 \rightarrow HO_2 + O_2$</td>
</tr>
<tr>
<td>a6b</td>
<td>$HO_2 + O_3 \rightarrow OH + 2O_2$</td>
</tr>
<tr>
<td>a7</td>
<td>$O + HO_2 \rightarrow OH + O_2$</td>
</tr>
<tr>
<td>a17</td>
<td>$OH + HO_2 \rightarrow H_2O + O_2$</td>
</tr>
<tr>
<td>a19</td>
<td>$OH + H_2 \rightarrow H_2O + H$</td>
</tr>
<tr>
<td>a23a</td>
<td>$H + HO_2 \rightarrow OH + OH$</td>
</tr>
<tr>
<td>a23b</td>
<td>$H + HO_2 \rightarrow H_2 + O_2$</td>
</tr>
<tr>
<td>a23c</td>
<td>$H + HO_2 \rightarrow H_2O + O$</td>
</tr>
<tr>
<td>a24</td>
<td>$H_2 + O \rightarrow OH + H$</td>
</tr>
<tr>
<td>a26</td>
<td>$NO + HO_2 \rightarrow NO_2 + OH$</td>
</tr>
<tr>
<td>a27</td>
<td>$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$</td>
</tr>
<tr>
<td>a30</td>
<td>$OH + H_2O_2 \rightarrow H_2O + HO_2$</td>
</tr>
<tr>
<td>a36</td>
<td>$OH + CO \rightarrow CO_2 + H$</td>
</tr>
<tr>
<td>a40</td>
<td>$HO_2+HO_2+H_2O_2 \rightarrow H_2O_2+O_2+H_2O$</td>
</tr>
<tr>
<td>a81</td>
<td>$O+H_2O_2 \rightarrow OH+HO_2$</td>
</tr>
<tr>
<td>a83</td>
<td>$OH+OH+M \rightarrow H_2O_2 + M$</td>
</tr>
</tbody>
</table>

#### Odd nitrogen reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>b3</td>
<td>$O + NO_2 \rightarrow NO + O_2$</td>
</tr>
<tr>
<td>b4</td>
<td>$O_3 + NO \rightarrow NO_2 + O_2$</td>
</tr>
<tr>
<td>b6</td>
<td>$N + NO \rightarrow N_2 + O$</td>
</tr>
<tr>
<td>b7</td>
<td>$N + O_2 \rightarrow NO + O$</td>
</tr>
<tr>
<td>b9</td>
<td>$O_3 + NO_2 \rightarrow NO_3 + O_2$</td>
</tr>
<tr>
<td>b12</td>
<td>$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$</td>
</tr>
<tr>
<td>b22</td>
<td>$OH + NO_2 + M \rightarrow HNO_3 + M$</td>
</tr>
<tr>
<td>b23</td>
<td>$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$</td>
</tr>
<tr>
<td>b24</td>
<td>$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$</td>
</tr>
<tr>
<td>b27</td>
<td>$HNO_3 + OH \rightarrow H_2O + NO_3$</td>
</tr>
<tr>
<td>b28</td>
<td>$OH + HO_2NO_2 \rightarrow H_2O + NO_2 + O_2$</td>
</tr>
<tr>
<td>b32</td>
<td>$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$</td>
</tr>
</tbody>
</table>
b38  O1D + N2O -> N2 + O2  4.9e-11  
b39  O1D + N2O -> NO + NO  6.7e-11  
b71  NO3+O -> NO3+O  1.0e-11  
b72  NO3+OH -> NO2+HO2  2.2e-11  
b73a NO3+HO2 -> OH+NO2+O2  3.5e-12*0.8  
b73b NO3+HO2 -> HNO3+O2  3.5e-12*0.2  
b81  O+NO2+M -> NO3+M  * k0300=9.0e-32  n=2  
                       k∞300=2.2e-11  m=0  
b82  NO+O+M -> NO2+M  * k0300=9.0e-32  n=1.5  
                       k∞300=3.0e-11  m=0  
b84  NO+NO3 -> 2NO2  1.5e-11 exp(170/T)  

Carbon reactions  
c1  CH4 + O1D -> CH3O2 + OH  1.5e-10  
c1a CH4 + O1D -> CH2O + H2  1.5e-11  
c2  CH4 + OH -> CH3O2 + H2O  2.45e-12 exp(-1775/T)  
c5  CH3O2 + NO -> CH3O+HO2+NO2  4.2e-12 exp(180/T)  
c7  CH3O2 + HO2 -> CH3OH+O2   3.8e-13 exp(800/T)  
c8  CH2O + OH -> CO+HO2+H2O  1.e-11  
c9  CH2O + O -> CO+HO2+OH  3.4e-11 exp(-1600/T)  
c10 CH2O + NO3 -> CO+HO2+HNO3  6.e-13 exp(-2058/T)  
c14 CH3O2 + CH3O2 -> 0.6CH3OH+1.4CH2O+0.8HO2  2.5e-13 exp(190/T)  
c17 CH3O2H + OH -> CH3O2+H2O  0.58*3.8e-12 exp(200/T)  
c44 CH3O2H + OH -> CH3O+H2O+OH  0.42*3.8e-12 exp(200/T)  
c50 C2H6 + OH -> C2H5O2+H2O  8.7e-12 exp(-1070/T)  
c51 C2H6 + Cl -> HCl + C2H5  7.7e-11 exp(-90/T)  
c52 C2H5O2 + NO -> CH3CHO+HO2+NO2  2.6e-12 exp(365/T)  
c53 C2H5O2 + HO2 -> C2H5OOH+O2  7.5e-13 exp(700/T)  
c54 C2H5O2 + CH3O2 -> 0.7CH2O+0.8CH3CHO+HO2+0.3CH3OH +0.2C2H5OH  3.75e-13 exp(-40/T)  
c55 C2H5O2 + C2H5O2 -> 1.6C2H5CHO+1.2HO2+0.4C2H5OH+O2  1.5e-13 exp(-270/T)  
c56 C2H5O2H + OH -> 0.5(C2H5O2+CH3CHO+OH)+H2O  7.0e-12 exp(235/T)  
c57 CH3CHO + OH -> CH3COO+H2O  5.6e-12 exp(270/T)  
c57et CH3CHO + NO3 -> CH3CO2O+HNO3  1.4e-12 exp(-1900/T)  
c58 CH3CO3H + OH -> CH3CO2O+H2O  1.e-11  
c59 CH3CO3 + NO -> CH3O2+NO2+CO2  5.3e-12 exp(360/T)  
c60 CH3CO3 + NO2 +M -> PAN + M  * k0300=9.7e-20  n=5.6  
                       k∞300=9.0e-12  m=1.5  
c61 CH3CO3 + HO2 -> 2/3(CH3CO3H+O2)+1/3(CH3COOH+O3)  4.5e-13 exp(1000/T)  
c62 CH3CO3 + CH3O2 -> CH3O2 + CH2O + CO2 + HO2  ***** c62 = k*kratio/(1+kratio)  
c63 CH3CO3 + CH3O2 -> CH3CO2H + CH2O + O2  ***** c63 = k/(1+kratio)  
c64 CH3CO3 + CH3CO3 -> 2CH3O2+2CO2  2.9e-12 exp(500/T)  
c65 PAN + OH -> CH3O2+CO3NO2+H2O  1.1e-12 exp(-650/T)  
c66 PAN + M -> CH3CO2O+N02+M  **** k0=5.2e-2 exp(-12875/T)  
                       k∞=2.2e16 exp(-13435/T)
\[
\begin{align*}
PAN + NO & \rightarrow \text{products} \\
C_2H_4 + OH + M & \rightarrow \frac{2}{3}(C_3H_6OHO_2) + M \\
f_c & = 0.27 \\
1.0 \times 10^{-12} \\
\end{align*}
\]

** \[
\begin{align*}
C_2H_4 + O_3 & \rightarrow CH_2O + 0.4HCOOH + 0.52HO_2 + 0.4OH \\
& + 0.18CO_2 + 0.42CO + 0.12H_2 + 0.02H_2O \\
k_0 & = 9.5 \times 10^{-20} (300/T)^{3.1} \\
k_\infty & = 9.5 \times 10^{-12} \\
f_c & = \exp(-T/840) \\
\end{align*}
\]

** \[
\begin{align*}
C_3H_6 + OH + M & \rightarrow C_3H_6OHO_2 + M \\
k_0 & = 9.0 \times 10^{-26} (300/T)^{3.5} \\
k_\infty & = 3.0 \times 10^{-11} \\
f_c & = \exp(-T/433) \\
\end{align*}
\]

** \[
\begin{align*}
C_3H_6 + O_3 & \rightarrow 0.1CH_3COOH + 0.08CH_4 + 0.585H_2O_2 + 0.2875CH_3O_2 \\
& + 0.37CO + 0.5325CH_2O + 0.45750H + 0.06H_2 \\
& + 0.18CH_2O + 0.42CO + 0.33C_0_2 \\
k_0 & = 6.5 \times 10^{-14} \exp(-2630/T) \\
k_\infty & = 4.2 \times 10^{-15} \exp(-1900/T) \\
f_c & = \exp(-T/840) \\
\end{align*}
\]

** \[
\begin{align*}
C_3H_6 + NO_3 & \rightarrow C_3H_6NO_3 \\
k_0 & = 8.0 \times 10^{-27} (300/T)^{3.5} \\
k_\infty & = 3.0 \times 10^{-11} \\
\end{align*}
\]

** \[
\begin{align*}
C_3H_6OHO_2 + NO & \rightarrow CH_3CHO + CH_2O + NO_2 + H_2O \\
k_0 & = 4.2 \times 10^{-12} \exp(-700/T) \\
k_\infty & = 4.8 \times 10^{-13} \exp(700/T) \\
f_c & = \exp(-T/840) \\
\end{align*}
\]

** \[
\begin{align*}
C_3H_6OHO_2 + HO_2 & \rightarrow C_3H_6OHOO + O_2 \\
k_0 & = 6.5 \times 10^{-15} \exp(-650/T) \\
k_\infty & = 1.0 \times 10^{-12} \exp(-1590/T) \\
\end{align*}
\]

** Chlorine reactions

\[
\begin{align*}
OH + CH_3Cl & \rightarrow CH_2Cl + H_2O \\
k_0^{300} & = 1.8 \times 10^{-31} \quad n=3.4 \\
k_\infty^{300} & = 1.5 \times 10^{-11} \quad m=1.9 \\
\end{align*}
\]

** \[
\begin{align*}
Cl + CH_3Cl & \rightarrow CHCl + CH_2Cl \\
Cl + CH_3 & \rightarrow CHCl + CH_2 \\
Cl + HOCl & \rightarrow HOCl + Cl \\
Cl + NO_2 & \rightarrow Cl + NO_2 \\
Cl + NO_2 + M & \rightarrow ClNO_2 + M \\
Cl + HOCl & \rightarrow Cl + HCl \\
Cl + HCl & \rightarrow Cl + Cl_2 \\
Cl + Cl_2 & \rightarrow Cl_2 + Cl \\
Cl + Cl & \rightarrow Cl + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

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\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

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\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

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\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]

** Other reactions

\[
\begin{align*}
Cl_2 + Cl & \rightarrow Cl + Cl_2 \\
Cl_2 + Cl_2 & \rightarrow Cl + Cl_2 + Cl \\
Cl_2 + Cl & \rightarrow Cl + Cl_2 + Cl \\
\end{align*}
\]
Cl + OC10 -> ClO + C10
OCIO + O -> ClO + O2
OCIO + NO -> NO2 + ClO
O1D+Cl2 -> ClO+Cl
Cl2O2+Cl -> Cl2+Cl+O2
NO3+Cl -> NO2+ClO
O1D+HCl -> OH+Cl
CH3Br + OH -> H2O + Br + products
CHBr3 + OH -> H2O + 3 Br + products
Br + O3 -> BrO + O2
BrO + O -> Br + O2
BrO + NO -> NO2 + Br
BrO + ClO -> OClO + Br
BrO + Cl -> Br + Cl + O2
BrO + ClO -> BrCl + O2
BrO + BrO -> 2Br + O2
Br + HO2 -> HBr + O2
Br + OClO -> BrO + ClO
Br+CH2O -> HBr+ CO + HO2
OH + HBr -> H2O + Br
BrO + NO2 + M -> BrONO2 + M
BrO + HO2 -> HOBr + O2
O1D+HBr -> OH+Br
BrO+OH -> HOBr+Br
O+HBr -> Br+OH
ha-1301 + O(1D) -> Br + 3HF + prod.
ha-1211 + O(1D) -> Br + Cl + prod.
CH3Br + O(1D) -> Br + prod.

Bromine reactions

\begin{align*}
e0 & \quad \text{CH}_3\text{Br} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Br} + \text{products} & 4.0 \times 10^{-12} \exp(-1470/T) \\
e1 & \quad \text{CHBr}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + 3 \text{Br} + \text{products} & 1.6 \times 10^{-13} \exp(-710/T) \\
e2 & \quad \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 & 1.7 \times 10^{-11} \exp(-800/T) \\
e3 & \quad \text{BrO} + \text{O} \rightarrow \text{Br} + \text{O}_2 & 1.9 \times 10^{-11} \exp(-230/T) \\
e4 & \quad \text{BrO} + \text{NO} \rightarrow \text{NO}_2 + \text{Br} & 8.8 \times 10^{-12} \exp(260/T) \\
e5a & \quad \text{BrO} + \text{ClO} \rightarrow \text{OClO} + \text{Br} & 1.6 \times 10^{-12} \exp(430/T) \\
e5b & \quad \text{BrO} + \text{Cl} \rightarrow \text{Br} + \text{Cl} + \text{O}_2 & 2.9 \times 10^{-12} \exp(220/T) \\
e5c & \quad \text{BrO} + \text{ClO} \rightarrow \text{BrCl} + \text{O}_2 & 5.8 \times 10^{-13} \exp(170/T) \\
e6 & \quad \text{BrO} + \text{BrO} \rightarrow 2 \text{Br} + \text{O}_2 & 1.5 \times 10^{-12} \exp(230/T) \\
e7 & \quad \text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2 & 1.5 \times 10^{-11} \exp(-660/T) \\
e8 & \quad \text{Br} + \text{OClO} \rightarrow \text{BrO} + \text{ClO} & 2.6 \times 10^{-11} \exp(-1300/T) \\
e9 & \quad \text{Br} + \text{CH}_2\text{O} \rightarrow \text{HBr} + \text{CO} + \text{HO}_2 & 1.7 \times 10^{-11} \exp(-800/T) \\
e11 & \quad \text{OH} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br} & 1.1 \times 10^{-11} \\
e13 & \quad \text{BrO} + \text{NO}_2 + \text{M} \rightarrow \text{BrONO}_2 + \text{M} & k_{0}^{300}=5.2 \times 10^{-31} \quad n=3.2 \\
e15 & \quad \text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2 & 3.4 \times 10^{-12} \exp(540/T) \\
e71 & \quad \text{O}1\text{D}+\text{HBr} \rightarrow \text{OH}+\text{Br} & 1.5 \times 10^{-10} \\
e72 & \quad \text{BrO}+\text{OH} \rightarrow \text{HOBr}+\text{Br} & 7.5 \times 10^{-11} \\
e81 & \quad \text{O}+\text{HBr} \rightarrow \text{Br}+\text{OH} & 5.8 \times 10^{-12} \exp(-1500/T) \\
e91 & \quad \text{ha}-1301 + \text{O}(1\text{D}) \rightarrow \text{Br} + 3\text{HF} + \text{prod.} & 1.0 \times 10^{-10} \\
e92 & \quad \text{ha}-1211 + \text{O}(1\text{D}) \rightarrow \text{Br} + \text{Cl} + \text{prod.} & 1.5 \times 10^{-10} \\
e93 & \quad \text{CH}_3\text{Br} + \text{O}(1\text{D}) \rightarrow \text{Br} + \text{prod.} & 1.8 \times 10^{-10} \\
\end{align*}
Oxygen reactions

\[ \begin{align*}
hk1 & \quad O + O + M \rightarrow O_2 + M \quad 4.23e-28 [M]/T^2 \\
hk2 & \quad O + O_2 + M \rightarrow O_3 + M \quad 6.0e-34(300/T)^{2.3}[M] \\
hk3 & \quad O + O_3 \rightarrow O_2 + O_2 \quad 8.0e-12 \exp(-2060/T) \\
hk4 & \quad O_1D + N_2 \rightarrow O + N_2 \quad 1.8e-11 \exp(110/T) \\
hk5 & \quad O_1D + O_2 \rightarrow O + O_2 \quad 3.2e-11 \exp(70/T) \\
hk7 & \quad O_1D + O_3 \rightarrow O_2 + O_2 \quad 1.2e-10 \\
hk21 & \quad O_1D+N_2 +M \rightarrow N_2O +M \quad 3.5e-37(300*T)^{0.6}[M]
\end{align*} \]

Rate constant derived from

\[ k = \left( \frac{k_0[M]}{1 + k_0[M]/k_\infty} \right) \cdot 0.6^{\{1+\log_{10}(k_0[M]/k_\infty)\}^2}^{-1}, \]

with \( k_0 = k_0^{300}(T/300)^{-n} \), and \( k_\infty = k_\infty^{300}(T/300)^{-m} \).

\[ a27 = (k_1 + k_2) \cdot f_{H_2O}. \]

\[ b27 = k_0 + \frac{k_3[M]}{1 + k_3[M]/k_2}. \]

\[ k = \left( \frac{k_0[M]}{1 + k_0[M]/k_\infty} \right) \cdot f_{C}^{\{1+\log_{10}(k_0[M]/k_\infty)\}^2}^{-1}. \]

\[ kratio = 2.2e6 \exp(-3280/T) \]
given in Table 6 for the two types of PSCs. Assuming that the particles are spherical, the surface area density $A$ can be calculated knowing the radius of the two types of PSCs, and their mass and number densities.

<table>
<thead>
<tr>
<th>Table 6 Reaction probabilities for heterogeneous reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>het1</td>
</tr>
<tr>
<td>het2</td>
</tr>
<tr>
<td>het3</td>
</tr>
<tr>
<td>het4</td>
</tr>
<tr>
<td>het5</td>
</tr>
</tbody>
</table>

5.1.2. Sulfate aerosol heterogeneous chemistry

For heterogeneous reactions on sulfate aerosol particles, six reactions are considered:

(g1) $\text{ClONO}_2 + \text{H}_2\text{O}(\text{sulfate aerosol}) \rightarrow \text{HOCl} + \text{HNO}_3(\text{g})$

(g2) $\text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{sulfate aerosol}) \rightarrow 2\text{HNO}_3(\text{g})$

(g3) $\text{ClONO}_2 + \text{HCl (s)} \rightarrow \text{Cl}_2 + \text{HNO}_3(\text{g})$

(g4) $\text{HOC1} + \text{HCl (s)} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$

(g5) $\text{BrONO}_2 + \text{H}_2\text{O (s)} \rightarrow \text{HOBr} + \text{HNO}_3(\text{g})$

(g6) $\text{HOBr} + \text{HCl (s)} \rightarrow \text{BrCl} + \text{H}_2\text{O}$

As for the PSC heterogeneous chemistry, the rate constants for these reactions are estimated from $g = \gamma v A / 4$. The surface area density ($A$) of sulfate aerosols is generally attainable from extinction measurements. The reaction probability of the above reactions are based on works described in Hanson et al. (1994) and Hanson and Ravishankara (1995). The reaction probability for the g1 reaction rate is expressed as a function of sulfate aerosol composition ($W$: $\text{H}_2\text{SO}_4$ weight %) as

$$\gamma_1 = 10^{1.86 - 0.0747W} \quad (87)$$

where the aerosol composition which depends primarily on the temperature and water vapor mixing ratio is evaluated based on the study of Steele and Hamill (1981) and has been fitted to a formula as described in Hanson et al. (1994) as

$$W = \frac{[-14.458 + 0.62456 \cdot \ln(p_{H_2O})] \cdot T + 3565}{44.777 + 1.3204 \cdot \ln(p_{H_2O}) - 0.19988T} \quad (88)$$
where \( p_{H_2O} \) is the partial pressure for water vapor. The reaction probability \((\gamma)\) of \( g_2 \) is specified as 0.14, independent of the aerosol and composition, and hence, of the temperature. The reaction probability for \( g_3 \) reaction is expressed as:

\[
\gamma_3 = 0.018 \sqrt{T \cdot [HCl]^*}
\]

(89)

where \([HCl]^*\) is the HCl solubility in droplets calculated from the equation:

\[
[HCl]^* = p_{HCl(atm)} \cdot 10^{15.514 - 0.1791W}.
\]

(90)

For \( g_4 \), the reaction probability is set to be 19.1 times that of \( \gamma_3 \). For the bromine reactions, the values adopted for the reaction probability are based on the work by Hanson and Ravishankara (1995), with \( \gamma_5 = 0.6 \), and \( \gamma = 10 \gamma_4 \).

### 5.1.3. NO\(_y\) production.

In addition to the major stratospheric NO\(_y\) production resulting from \( N_2O + O(1D) \rightarrow 2NO \) reaction, the production source of NO\(_y\) by lightning, cosmic ray, and ionic reactions are included in the model. The rate of global lightning production is 8.7 Tg/yr, with productions occurring at latitudes less than 60°, and at altitudes between 0 and 16 km. Between latitudes of -30 to 30 deg, the NO\(_y\) production rate is specified as 2000 cm\(^{-3}\)/s. Beyond 30 deg latitude north and south, the NO\(_y\) production is specified to decrease linearly from 2000 cm\(^{-3}\)/s at 30 deg to zero at 60 degrees latitude. Production of NO\(_y\) associated with the deposition of galactic cosmic rays is parameterized as a function of latitude and altitude according to Heaps (1978) for solar maximum condition, with the production of 1.3 NO molecules per ion pair produced by the cosmic rays. At altitudes less than 8 km, NO\(_y\) production by cosmic ray is assumed to be zero. At other altitudes:

If \( 8 \text{ km} < z < 19 \text{ km} \):

\[
P_{cr} = 1.3 \cdot [1.74 \times 10^{-18} + 1.93 \times 10^{-17} \cdot (\sin \phi)^4] \cdot (a + bz + cz^2)
\]

(91a)

where

\[
a = (3.03 \times 10^{17})^{1-0.6-0.8 \cos \phi} [M]^{0.6+0.8 \cos \phi} [14.4 / 7 \times 10^5(0.6 + 0.8 \cos \phi) - 2.24]
\]

\[
b = (3.03 \times 10^{17})^{1-0.6-0.8 \cos \phi} [M]^{0.6+0.8 \cos \phi} [-2.6 / 7 \times 10^5(0.6 + 0.8 \cos \phi) + 0.36]
\]

\[
c = (3.03 \times 10^{17})^{1-0.6-0.8 \cos \phi} [M]^{0.6+0.8 \cos \phi} [0.1 / 7 \times 10^5(0.6 + 0.8 \cos \phi) - 0.01] .
\]

If \( z > 18 \text{ km} \):

\[
P_{cr} = 1.3 \cdot [1.74 \times 10^{-18} + 1.93 \times 10^{-17} \cdot (\sin \phi)^4] \cdot [M] \quad \text{for } [M] < 3.03 \times 10^{17},
\]

(91b)

or
\[ P_{cr} = 1.3 \cdot (1.74 \times 10^{-18} + 1.93 \times 10^{-17} \cdot (\sin \phi)^4) \cdot (3.03 \times 10^{17})^{1-0.6-0.8 \cos \phi} [M]^{0.6+0.8 \cos \phi} \]

for \([M] \geq 3.03 \times 10^{17}\). \hspace{1cm} (91c)

Production of NO\(_y\) by thermospheric ionic process including its production by N\(_2\) photolysis and N\(_2\) reaction with energetic electrons (e\(^*\)) is specified as a function of height and latitude based on data presented by McEwan and Phillips (1975). NO\(_y\) production by particle precipitation near the auroral zone in the thermosphere is confined to latitudes beyond 55 degrees, while the production by extreme UV radiation occurs at all latitudes except for night time conditions. The magnitude of the NO\(_y\) production rate is on the order of 1000 cm\(^{-3}\)/s by N\(_2\) + e\(^*\), and on the order of 10 cm\(^{-3}\)/s by N\(_2\)+hv in the lower thermosphere. NO\(_y\) production rates by these processes are assumed to be negligible below 90 km.

d. Tropospheric species washout rates.

Computation of the rainfall rate and wet removal rate of soluble species in the troposphere for HNO\(_3\), H\(_2\)O\(_2\), CH\(_3\)OOH, HCl, HO\(_2\)NO\(_2\), and CH\(_2\)O, is based on the parameterization described by Hough (1991). For HBr, CCl\(_2\)O, CCl\(_2\)FO, CF\(_2\)O, HF, Br\(_y\) and Cl\(_y\), the washout rate for HCl is used; for C\(_2\)H\(_5\)OOH, CH\(_3\)COOOH, and C\(_3\)H\(_6\)OHOOH, the washout rate for CH\(_2\)O is used; and for NO\(_y\), the washout rates for HNO\(_3\) and HO\(_2\)NO\(_2\) is used.

As described in Appendix B of Hough (1991), the rainfall rate of water vapor is written as:

\[
\frac{d[H_2O]}{dt} = -\frac{[H_2O]}{7200\Delta z} \cdot \exp\left[\frac{2([H_2O] - [H_2O]_{sat})}{[H_2O]}\right] \text{ cm}^{-3}\text{s}^{-1},
\]

and the water from the rainout is assumed to move vertically down to the immediate lower layer and evaporate. The washout rates of species \(i\) is then:

\[
\frac{d[n_i]}{dt} = -\frac{1}{7200\Delta z} fx_i
\]

where \(fx_i\) is the fraction of species \(i\) in the aqueous phase derived from

\[
fx_i = \left(\frac{\text{lwc}}{d_{h_2o}}\right)\left(H_i + \frac{\text{lwc}}{d_{h_2o}}\right),
\]

and \(d_{h_2o}\) is the density of liquid water (g/cm\(^3\)), while \(\text{lwc}\) is the liquid water content (g/cm\(^3\)) of the clouds.

\(H_i\) is the dimensionless Henry’s Law coefficient, derived from

\[
H_i = 273.15 \cdot \frac{p}{(k_i \cdot 22.4 \cdot T \cdot p_0)}
\]

where \(k_i\) is the Henry Law coefficients, listed in Table 7 for different rainout species, while \(p\) is the local pressure and \(p_0\) is the standard surface pressure, both in units of Pascal. The liquid water content, \(\text{lwc}\) (g/cm\(^3\)), is calculated from the formula
\[ lwc = \exp\left[2\left(\frac{[H_2O] - [H_2O]_{(sat)}}{[H_2O]}\right)\right] \cdot [H_2O] \cdot \frac{m_{H_2O}}{6 \times 10^{23}} \]  

(96)

where \( m_{H_2O} \) is the mean molecular mass of water (18 g/mole), and \([H_2O]_{(sat)}\) is the saturated concentration of water vapor derived from

\[ [H_2O]_{(sat)} = \left[M\right] \cdot \frac{100 \cdot 10^{\left(-2937.4/T - 4.9283 \log T + 23.552\right)}}{p - 100 \cdot 10^{\left(-2937.4/T - 4.9283 \log T + 23.552\right)}}, \]  

(97)

where \( p \) is the pressure in units of Pascal.

<table>
<thead>
<tr>
<th>Table 7. Values of Henry's Law coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>HNO(_3)</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
</tr>
<tr>
<td>CH(_3)OOH</td>
</tr>
<tr>
<td>HCl</td>
</tr>
<tr>
<td>HO(_2)NO(_2)</td>
</tr>
<tr>
<td>CH(_2)O</td>
</tr>
</tbody>
</table>

5.2 **Vertical transport in the troposphere associated with convection and fronts.**

Tropospheric vertical transport produced by convective and frontal activity is formulated in the 2-D model by a simple parameterization which ensures mass continuity. Assuming that the convective upward mass flux at the first model layer is known (which we shall call \( \Phi \) in units of g/m2/s), mass continuity dictates that at layer \( i \):

\[ \alpha_i \Phi + \varphi_{i+1} = \varphi_i \]  

(98)

if \( \alpha_i \) is the fraction of boundary mass flux that is detrained into the layer \( i \) (\( \sum_{i=1}^{N} \alpha_i = 1 \)) and \( \varphi_i \) is the downward mass flux out of layer \( i \). At the top layer of the convective layer (denote by layer N), the continuity can be written as

\[ \varphi_N = \alpha_N \Phi. \]  

(99)

Substituting into Eq.98 for layer \( N-1 \) yields:

\[ \varphi_{N-1} = (\alpha_N + \alpha_{N-1}) \Phi. \]  

(100)
By the same token, at layer \( i \), a recursive relationship can be obtained for the downward flux out of layer \( i \):

\[
\varphi_i = (\sum_{j=i}^{N} \alpha_j) \cdot \Phi_i.
\] (101)

The time rate of change of the transported chemical species, knowing the mass flux in and out of the layer \( i \), can be written as:

\[
\frac{\partial [n_i]}{\partial t} = \alpha_i \frac{\Phi}{\Delta z} X_1 + \varphi_{i+1} \frac{\Phi}{\Delta z} X_{i+1} - \varphi_i \frac{\Phi}{\Delta z} X_i
\] (102)

where \([n_i]\) is the number density of species \( i \), and \( X_i \) the mixing ratio of the transported species at layer \( i \). Substituting the relationship (101) into (102), and after converting mass flux in units of \( \text{g/m}^2/\text{s} \) to units of \( \text{(cm}^{-3}\text{s}^{-1}) \) by multiplying it with \( N_A/m_{\text{air}} \times 10^9 \) yields

\[
\frac{\partial [n_i]}{\partial t} = \alpha_i \frac{\Phi}{\Delta z} X_1 + \varphi_{i+1} \frac{\Phi}{\Delta z} (\sum_{j=i+1}^{N} \alpha_j) X_{i+1} - \varphi_i \frac{\Phi}{\Delta z} (\sum_{j=i}^{N} \alpha_j) X_i
\] (103)

which can be rewritten as

\[
\frac{\partial [n_i]}{\partial t} = \frac{\Phi}{\Delta z} [\alpha_i \cdot X_1 + (\sum_{j=i+1}^{N} \alpha_j) X_{i+1}] - \frac{\Phi}{X_{\text{air}\Delta z}} (\sum_{j=i}^{N} \alpha_j) [n_i].
\] (104)

Thus, the convective transport effect is equivalent to a chemical production term: represented by the first term in the right-hand side of Eq. (104), and a chemical loss coefficient, represented by the coefficient of the second term on the right-hand side. These convective "production" and "loss" terms are added to the chemical production and loss rates in the continuity equation (79).

The input information needed for the transport parameterization is the upward boundary mass flux \( \Phi \), and the fraction of \( \Phi \) that enters layer \( i \) \( (\alpha_i) \). The convective mass flux out of the boundary layer for both deep convection and frontal circulation process is taken from Langner et al. (1990) (Table 7 in the paper). The detrainment percentages (or \( \alpha_i \)) of the convective and frontal process as a function of season, altitude and latitude are also obtained from Langner et al. (1990) (Table 1 and 2 in the paper). The same data is used to estimate the top level \( (N) \) reached by convective and frontal vertical transport.
6. Initial and Boundary conditions

6.1 Chemical Species

The initial conditions for the concentration of chemical species are obtained from a standard model run of four years of the date January 1st. Results of selected species are shown in Section 8.

Boundary conditions for the chemical species can be specified as flux or mixing ratio boundary conditions. Listed in Table 8 are the specifications of upper and lower boundary conditions for the transported species, including the dry deposition velocity \((w_d)\) at the surface. The lower boundary conditions adapted in the model are those of Hauglustaine et al. (1994) but will be described in more detail here. When fluxes are specified as boundary flux conditions (Table 8), they are generally based on Hough (1991). An uptake of methane by soils is assumed to be 30 Tg-CH$_4$ yr$^{-1}$, with a latitudinal distribution adopted from Fung et al. (1991). The surface emissions of these gases are estimated based on the relative contribution of each emission category listed in Table 9, and the latitudinal distribution of each emission category and of methane soil absorption are presented in Table 10. The boundary fluxes of each emission category expressed in units of Tg yr$^{-1}$ m$^{-2}$ are obtained by multiplying the values listed in Table 9 with values listed in Table 10. The latitudinal distribution of the boundary fluxes for each species are then the addition of all emission categories. For the net surface flux of methane, the soil absorption flux is subtracted out from the emission flux. The boundary fluxes are then converted to units of cm$^{-2}$s$^{-1}$ and used in the chemical transport equation.

Source gases whose lower boundary conditions that are currently specified as mixing ratios according to 1990 conditions are: CO$_2$, CFC-10, CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, HCFC-22, CH$_3$CCl$_3$, CH$_3$Br, CHBr$_3$, Ha-1211, Ha-1301, and HF. For those with values varying with latitude, their surface mixing ratio are specified as: CO$_2$: [356.+$b$(CO$_2$)] ppmv; for CFC-10: 108*$b$(CFC-10) pptv; for CFC-11: 270*$b$(CFC-11) pptv; for CFC-12: 465*$b$(CFC-12) pptv; for CFC-113: 70*$b$(CFC-12) pptv; for CFC-114: 10*$b$(CFC-12) pptv; for CFC-115: 5*$b$(CFC-12) pptv; for HCFC-22: 106*$b$(CFC-12) pptv; for CH$_3$CCl$_3$: 153*$b$(CH$_3$CCl$_3$) pptv; for Ha-1211: 2.9*$b$(CFC-12) pptv; and for Ha-1301: 1.7*$b$(CFC-12) pptv. The values for the $b$ coefficients as a function of latitude are listed in Table 11. CH$_3$Br is specified as 9 pptv in the S.H. and 11.5 pptv in the N.H.

As listed in Table 8, dry deposition surface velocity are considered for species NO$_y$, NO$_x$, HNO$_3$, N$_2$O$_5$, O$_x$, CO, H$_2$O$_2$, CH$_2$O, PAN, and H$_2$. The velocities for different surface types are as listed in Table 2 of Hauglustaine et al. (1994). To estimate the fraction of land, ocean, snow and sea ice as a function of surface temperature, the parameterization from Robock (1983) is used.

The upper boundary conditions at 120 km for the majority of chemical species are specified as zero fluxes (see Table 8), except for NO$_y$, NO$_x$, O$_x$, H$_2$ and H. Downward flux of NO$_x$ and
Table 8. Lower and upper boundary conditions for the transported species and families. Flux in units of cm\(^{-2}\)s\(^{-1}\).

<table>
<thead>
<tr>
<th>Boundary Conditions</th>
<th>0 km</th>
<th>120 km</th>
<th>dry deposition at surface</th>
</tr>
</thead>
<tbody>
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<td>N(_2)O</td>
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<td>flux = 0.</td>
<td>(w_d = 0.)</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>flux (see text)</td>
<td>flux = 0.</td>
<td>(w_d = 0.)</td>
</tr>
<tr>
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<td>m.r. (see text)</td>
<td>flux = 0.</td>
<td>(w_d = 0.)</td>
</tr>
<tr>
<td>NO(_y)</td>
<td>flux (see text)</td>
<td>m.r. of NO</td>
<td>(w_d) (see text)</td>
</tr>
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<td>flux = 0.</td>
<td>(w_d) (see text)</td>
</tr>
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<td>flux = 0.</td>
<td>(w_d) (see text)</td>
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<tr>
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<td>(w_d = 0.)</td>
</tr>
<tr>
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<td>m.r. of O(3P)</td>
<td>(w_d) (see text)</td>
</tr>
<tr>
<td>CO</td>
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<td>flux = 0.</td>
<td>(w_d) (see text)</td>
</tr>
<tr>
<td>OC(_1)O</td>
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<td>flux = 0.</td>
<td>(w_d = 0.)</td>
</tr>
<tr>
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<td>flux = 0.</td>
<td>(w_d = 0.)</td>
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<td>(w_d = 0.)</td>
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<td>flux = 0.</td>
<td>(w_d) (see text)</td>
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<td>flux = 0.</td>
<td>(w_d = 0.)</td>
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<td>(w_d = 0.)</td>
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<td>(w_d = 0.)</td>
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<td>(w_d = 0.)</td>
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<td>(w_d = 0.)</td>
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<td>(w_d = 0.)</td>
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<td>(w_d = 0.)</td>
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<td>(w_d = 0.)</td>
</tr>
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<td>(w_d = 0.)</td>
</tr>
<tr>
<td>C(_3)H(_6)</td>
<td>flux (see text)</td>
<td>flux = 0.</td>
<td>(w_d = 0.)</td>
</tr>
<tr>
<td>CH(_2)O</td>
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<td>flux = 0.</td>
<td>(w_d) (see text)</td>
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continue next page
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<th>120 km</th>
<th>dry deposition at surface</th>
</tr>
</thead>
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<td>wd (see text)</td>
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<td>wd = 0.</td>
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<td>wd = 0.</td>
</tr>
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</tr>
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<td>wd = 0.</td>
</tr>
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</tr>
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<td>wd = 0.</td>
</tr>
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<td>HCFC-22</td>
<td>m.r. (see text)</td>
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<td>wd = 0.</td>
</tr>
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<td>CH₃CCl₃</td>
<td>m.r. (see text)</td>
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<td>wd = 0.</td>
</tr>
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</tr>
<tr>
<td>CClFO</td>
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<td>Ha-1211</td>
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<td>wd = 0.</td>
</tr>
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<td>Ha-1301</td>
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<td>wd = 0.</td>
</tr>
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<td>m.r. Cl₂ *0.25</td>
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<td>wd = 0.</td>
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<td>CH₃Br</td>
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<td>wd = 0.</td>
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<td>wd = 0.</td>
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<td>CHBr₃</td>
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<td>wd = 0.</td>
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<tr>
<td>O(3P)</td>
<td>flux = 0.</td>
<td>m.r. = 0.99 - N₂ - O₂</td>
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<td>O₃</td>
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<td>flux = 0.</td>
<td>wd (see text)</td>
</tr>
<tr>
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<td>flux = 0.</td>
<td>wd (see text)</td>
</tr>
<tr>
<td>NO</td>
<td>flux (see text)</td>
<td>m.r. = 5.e-5</td>
<td>wd (see text)</td>
</tr>
<tr>
<td>H</td>
<td>flux = 0.</td>
<td>m.r. = 5.e-6</td>
<td>wd = 0.</td>
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### Table 9. Global surface emission of source gases

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<tr>
<th>Species</th>
<th>industrial</th>
<th>ruminants</th>
<th>veget.</th>
<th>soil/fauna</th>
<th>wetland</th>
<th>paddy</th>
<th>biomass b.</th>
<th>ocean</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O (Tg N yr$^{-1}$)</td>
<td>1.2</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.05</td>
<td>0.3</td>
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<tr>
<td>CH$_4$ (Tg yr$^{-1}$)</td>
<td>130.9</td>
<td>76</td>
<td>0</td>
<td>34</td>
<td>91</td>
<td>88</td>
<td>42.8</td>
<td>9.8</td>
</tr>
<tr>
<td>H$_2$ (Tg yr$^{-1}$)</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>CO (Tg yr$^{-1}$)</td>
<td>381.6</td>
<td>0</td>
<td>666</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>710.5</td>
<td>13</td>
</tr>
<tr>
<td>NO$_x$ (Tg N yr$^{-1}$)</td>
<td>23.3</td>
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<td>0</td>
<td>6.6</td>
<td>0</td>
<td>0</td>
<td>4.9</td>
<td>0</td>
</tr>
<tr>
<td>C$_2$H$_6$ (Tg C yr$^{-1}$)</td>
<td>6</td>
<td>0</td>
<td>0.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.7</td>
<td>0.8</td>
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<tr>
<td>C$_2$H$_4$ (Tg C yr$^{-1}$)</td>
<td>4.3</td>
<td>0</td>
<td>4.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14.8</td>
<td>8.2</td>
</tr>
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<td>C$_3$H$_6$ (Tg C yr$^{-1}$)</td>
<td>1.7</td>
<td>0</td>
<td>0.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6.5</td>
<td>9.9</td>
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</table>
Table 10. Latitudinal distribution of emissions and methane soil uptake (in units of m^-2).

<table>
<thead>
<tr>
<th>Latitude</th>
<th>industrial</th>
<th>ruminants</th>
<th>veget.</th>
<th>soil/fauna</th>
<th>wetland</th>
<th>paddy</th>
<th>biomass b.</th>
<th>ocean</th>
<th>CH4 soil abs.</th>
</tr>
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<tbody>
<tr>
<td>-85</td>
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<td>0</td>
<td>0</td>
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Table 11. Boundary coefficients as a function of latitude.

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NO\textsubscript{y} at 120 km can be specified as a function of latitude and season according to Solomon et al. (1982):

\begin{equation}
\text{Flux}_{\text{NO}_x} = -1 \cdot 10^8 - 3.5 \cdot 10^8 \cdot \cos[\phi + 17 \cdot \cos(\frac{\text{day} - 172}{365} \cdot 2\pi)] \text{ (cm}^2\text{s}^{-1})
\end{equation}

except at polar night, where \text{Flux}_{\text{NO}_x}=0. In the current version of the model, the NO, NO\textsubscript{x}, and NO\textsubscript{y} is specified as fixed mixing ratio of 5.e-5. Likewise, O\textsubscript{x} and O(3P) is currently specified as mixing ratio. However, they can also be specified as flux at the upper boundary according to Kasting and Roble (1981) as:

\begin{equation}
\text{Flux}_{\text{O}_x} = (-1 + h_{1/2\text{day}}) \cdot 1.5 \cdot 10^8 - 2 \cdot h_{1/2\text{day}} \cdot 2.5 \cdot 10^{11} \text{ (cm}^2\text{s}^{-1})
\end{equation}

where \(h_{1/2\text{day}}\) is the half day hour angle in units of radius as mentioned in section 2.1.1.

6.2 Temperature, wind and stream function

6.2.1 Initial and boundary conditions for temperature.

The model integration time starts at January 1st, and the steady state model calculation of the temperature distribution at January 1st is used as the initial condition of temperature (Fig. 2). The temperature at and below the lower boundary of the dynamical model (0, 1 and 2 km) is specified as a function of latitude and month according to Randel (1987).

6.2.2 Boundary conditions for zonal wind, and stream function.

The zonal wind in the 2-D model is derived by vertically integrating the thermal wind equation (Eq. 4), knowing the temperature distribution. The zonal wind at the surface needed to start the vertical integration is specified as a function of latitude and month according to Fleming et al. (1988).

The boundary condition for the stream function at 2 km is calculated interactively with the cumulative wave forcing above the boundary. According to the ‘downward control principle’ of Haynes et al. (1991), the mass flow across an isentropic surface is controlled exclusively by the amount of eddy forcing above that surface. As in Garcia et al. (1992), the stream function at the lower boundary (\(z_b=2\text{km}\)) is calculated from:

\begin{equation}
\chi_{z_b} = \frac{\cos \phi}{f \cdot \exp(-z_b/H)} \int_{z_b}^{\infty} \exp(-z/H) \cdot F_{\text{tot}} \cdot dz.
\end{equation}

This expression is derived from a linearized, steady state momentum equation \(-f\overline{v}^* = F_{\text{tot}}\), where \(F_{\text{tot}}\) is the combination of all types of wave forcing as calculated by the model, including gravity and planetary wave forcing, tropospheric wave forcing (\(F_{\text{tot}}=F_R+F_G+F_T\ldots\)).
7. Numerical techniques

7.1 Thermodynamic and stream function equations (temp.f, strcal.f)

The potential temperature thermodynamic equation is solved by first applying standard 2nd order finite difference approximations to the spatial derivative. The solution and the resultant system of ODE's is approximated with a spatially split, fourth order, multi-step, backward difference scheme from Van Der Houwen (1980). In this implementation the predictor value is taken as the last known solution. The split, discrete ODE system is iterated exactly four times. When starting a calculation without using prior results the first three solutions are obtained using a simple backward Euler temporal treatment rather then the full fourth order backward formula. The resultant linear system is solved directly by a specialized banded matrix solver 'band_slv.f'.

The stream function equation, which is a 2nd-order partial differential diagnostic equation is discretized by a center finite differencing scheme. The Jacobian matrix system of equation is solved using the band system solver in the file 'band_slv.f'.

7.2 Chemical transport equation

The chemical transport equation (Eq. 79) can be written in a numerical operator form each representing contribution from advection, diffusion, and chemistry:

\[
\frac{\partial \tilde{X}_i}{\partial t} = L_{adv} \cdot \tilde{X}_i + L_{diff} \cdot \tilde{X}_i + L_{chem} \cdot \tilde{X}_i
\]

where \( L_{adv} \) is the advection operator, \( L_{diff} \) is the diffusion operator, and \( L_{chem} \) is the chemical operator. We solve for the discrete analogue to Eq. 108 by:

\[
\tilde{X}_i^{n+1} = \prod_{l=1}^{3} \Phi_l(\Delta t) \cdot \tilde{X}_i^n,
\]

where \( \Phi_1 = \Phi_{SLT} \) is the discrete analogue to \( L_{adv} \), \( \Phi_2 = \Phi_{chem} \) is the discrete analogue to \( L_{chem} \), and \( \Phi_3 = \Phi_{diff} \) is the discrete analogue to \( L_{diff} \). The following sections detail the numerical schemes used by each discrete operator.

7.2.1 Advection: Semi-Langrangian transport (slt.f)

The solution for the transport of chemicals by advection is obtained with the semi-Lagrangian technique (Robert, 1981). This method requires a backward tracing of air parcels utilizing the residual wind (\( \vec{v}^*, \vec{w}^* \)) information, with the assumption that the tracer mixing ratio value is conserved along the trajectory. A 1 day timestep is the default for the back tracing calculation in the standard model run. Since the point of departure of a tracer parcel generally does not coincide with the model grid point, interpolations of the residual wind and the tracer mixing ratio value are necessary. The interpolation is done in subroutine LE3. To initialize for the diurnal chemistry, only the long-lived species at noon time are advected.
7.2.2 Chemical loss and production (chem_resol.f)

The changes in the concentration of long-lived and intermediate species \( \frac{\partial \overline{X}_i}{\partial t} \) by photochemical sources are calculated by the Euler-backward iterative method:

\[
\overline{X}_{i+1}^t = \overline{X}_i^t + \frac{P_i \Delta t}{1 - L_i \Delta t} \quad (110)
\]

where \( \Delta t \) is the time step. The method is iterated (for a maximum of 10 times) until it is converged within 0.1%.

A different numerical method is used for selected species (O(3P), O₃, OH, HO₂, NO, NO₂, NO₃, H) during night time (night_sub.f). They belong in a special category due to large diurnal variations in their chemical lifetimes. These species which are in photochemical equilibrium in the presence of sunlight must be explicitly time integrated during the night. The system of non-linear chemical equations are transformed to a system of non-linear algebraic equations through an implicit Euler time scheme with Newton Raphson iteration:

\[
F(X) = \frac{X_{i+1}^t - X_i^t}{\Delta t} - (P - LX_{i+1}^t) \quad (112)
\]

\[
X_{it+1} = X_{it} - \frac{F(X_{it})}{F'(X_{it})} \quad (113)
\]

where \( F'(X) \) is the Jacobian Matrix \( \frac{\partial F}{\partial X} \) and \( it \) is the iteration number. The timesteps for the chemical equations varies according to the length of day and night, with 8 timesteps every 24 hours. For the timestep during daylight hours, the length of daylight is divided by 4; likewise, night timestep is the duration of the night divided by 4.

7.2.3 Diffusion (diffus.f)

The molecular and eddy diffusion component of transport is solved like the potential temperature by first applying standard finite difference analogues to the spatial derivatives. The resultant linear ODE system is solved through a straight forward application of backward Euler with modifications to incorporate splitting along the spatial coordinates (y and z). The combined splitting, backward Euler algorithm is iterated three times.
8. Selected example of model results.

In order to illustrate the type of results provided by the model, we present selected two-dimensional distributions of model output. These distributions have been obtained with a prototype of the model after 4 years of integration, shown here for the month of January, with 1992 boundary conditions. The results are expected to change in the future as model parameters, boundary conditions, and other inputs are modified.

8.1 Dynamics

Figures 2 thru 9 present the calculated zonally averaged distributions of temperature, zonal wind, meridional and vertical wind velocities (TEM circulation), solar UV heating, terrestrial IR cooling, Rossby wave forcing, and gravity wave forcing.

8.2 Chemistry

Figures 10 thru 21 show the calculated zonally averaged distributions of selected chemical constituents (24 hour averaged mixing ratios) of N₂O, CH₄, O₃, HNO₃, NOₓ, ClONO₂, HCl, ClOₓ, BrOₓ, BrONO₂, CFC-10, CH₃Br.
Figure 2. Temperature

Figure 3. Zonal wind
Figure 4. Meridional residual wind

Figure 5. Vertical residual wind
Figure 6. Solar heating rate

Figure 7. Infrared cooling rates
Figure 8. Rossby wave forcing

Figure 9. Gravity wave forcing
Figure 10. N2O

Figure 11. CH4
Figure 12. O3

Figure 13. HNO3
Figure 14. NOx

Figure 15. ClONO2
Figure 16. HCl

Figure 17. ClOx
Figure 18. BrOx

Figure 19. BrONO2
Figure 20. CFC-10

Figure 21. CH3Br

9.1 Introduction

The SOCRATES model is written in the Fortran 90. This allows:
- use of array-syntax;
- use of "module" instructions;
- use of structured data variables, especially for date representation;
- use of namelist-directed input files.

It is important to understand the two last features and their implementation in the model before attempting execution. The structure of TIMING and IO_TIMING variables is explained in subsection 9.5. The format of the namelist-directed input file (e.g. "socrates.inp") where these variables are set is explained in subsection 9.6.

Another modern computing technique used by SOCRATES is netCDF, the Network Common Data Format. These libraries must be installed on the computer where the simulation is executed, because the initial conditions file is written in this format. Utilities built in the Fortran 90 source code are also provided for convenient output of the SOCRATES model to netCDF format.

The sequence of actions to install, compile, run and use the SOCRATES model is:
- Download and install the netCDF library (9.2)
- Download, install and compile the source code (9.4)
- Download and install the data files (9.4)
- Adapt the input file to the desired simulation (9.5 and 9.6)
- Eventually, download and install the IDL application "view2d" to visualize the output files (9.3)

9.2 NetCDF

NetCDF (Network Common Data Format) is a format standard for binary data files. The binary format used is completely platform-independent. The data is self-describing and structured to allow easy reading and analyzed by programs written in C or Fortran, or by commercial packages (e.g. IDL, Matlab). Unidata, a division of UCAR, has developed this format and the Fortran library to read and write data to this format. This library is available for free on all platforms: PC, Mac, UNIX workstations and CRAY computers. Your UNIX administrator should retrieve and install this library before you compile the SOCRATES model. To download the library, point a World Wide Web browser to:

http://www.unidata.ucar.edu/packages/netcdf/index.html

and follow the instructions.
The examples given here assume that the netCDF compiled library is available with the following path and filename: /usr/local/lib/netcdf. The recommended filename extension for netCDF files is *.nc.

**CAUTION!** The current version of netCDF is 3.3. Although it allows faster read/write operations, a bug prevents it from being backward-compatible with previous versions. If you are using version 3.3 of the netCDF library, please compile the SOCRATES model using the module file `src/modules/netcdf33.mod.f`. If you are using a version of netCDF with a smaller version number, compile the SOCRATES model using the module file `src/modules/netcdf.mod.f`. If you have already installed the NetCDF library, but it is a version older than 2.4.2, please update the library at the Unidata Web site given above.

### 9.3 Post-processing of NetCDF files through IDL application

A direct advantage of using netCDF is the ability to write powerful and fast applications to perform graphical analysis on model data output. Such an application has been written for the SOCRATES model. It is a set of IDL routines (IDL is a commercial product for scientific and graphical data analysis). The name of the application is "view2d", packed to the file `view2d.tar.gz`. "view2d" allows the user to draw contour plots or one-dimensional plots from a netCDF output file from SOCRATES, and to compare two different netCDF files, through a Graphical User Interface. The documentation is contained in the package (file `README.txt`). If your institution does not own an IDL license but uses a similar product (e.g. Matlab, or NCAR graphics), "view2d" can be used as a template to write a similar application.

### 9.4 Installation, compilation, and execution of SOCRATES

The file `socrates.tar.gz` contains all the source code of SOCRATES version 1.0. After uncompressing (e.g. "gunzip socrates.tar.gz") and unpacking (e.g. "tar -xlf socrates.tar") the contents are:

- `./socrates.inp` --> a typical simulation input file (see section 9.6)
- `./2dsoc.sh` --> A C-shell script to compile and execute the model on CRAY computers
- `./src/*.f` --> Fortran 90 source code for the main, subroutines and functions
- `./src/Makefile.ibm` --> to compile the model on an IBM RS/6000 workstation
- `./src/modules/*.mod.f` --> Fortran 90 source code for the modules
- `./src/modules/Makefile.ibm` --> to compile the model on an IBM RS/6000 workstation

To compile and execute the model on a CRAY computer, adapt and execute `2dsoc.sh`. 
To compile and execute the model on a UNIX workstation, adapt the Makefiles to your environment (fortran 90 compiler command and options). The sequence of commands on an IBM RS/6000 workstation is:

```
$HOME/.../src/modules> make -f Makefile.ibm
$HOME/.../src> make -f Makefile.ibm
$HOME/...> xlf src/*.o src/modules/*.o -o socrates -L/usr/local/lib -lnetcdf
$HOME/...> nohup socrates < socrates.inp > socrates.out &
```

Makefiles for DEC alpha computers are available as well.

**NOTE:** If any of the module files is changed, it is advisable that all the source code be re-compiled again.

The SOCRATES model requires a set of data files to run. These are packed in the file `socrates_data.tar.gz`. It should be downloaded, decompressed and unpacked to a separate directory. The simulation input files provided here assume that the data files are in the directory `./data`, at the same directory level of `./src`.

### 9.5 Structured variables of type TIMING and IO_TIMING

In SOCRATES, structured variables have been used to specify the date of the beginning of the simulation, the date of the end of the simulation, and the dates of desired output. A date in the model is described by a structured variable of type TIMING (defined in the module `TIME_CONTROLS`, file `src/modules/main.mod.f`). A structured variable is a group of subvariables, called "fields" of the structured variable. Each variable of type TIMING contains eight fields:

```
type TIMING
  integer :: year        --> Full year, e.g. 1996
  integer :: month       --> From 1 to 12
  integer :: day         --> If mode="date", day of the month (1 to 31).
                          If mode='days', number of days since the beginning of simulation.
  integer :: days0       --> Absolute measure of time: number of days since date 0/0/0000. Managed within the model.
  integer :: cal_day     --> Julian day of the year (1 to 365)
  integer :: index       --> Number of 5-day timesteps since beginning of simulation
  logical :: active      --> Managed by the model: will be set to .true. if the variable has been specified by the user and checked valid by the model.
  character(len=5) :: mode --> set to "index", "days" or "date" depending
```
of the way the variable is specified

The three different modes allow the user to define a date in several different ways. For example, assuming that the simulation begins January 1, 1995, the three following settings define the same date for the end of the simulation:

\[
\begin{align*}
\text{sim\_stop\_time} &= 1997, 1, 0, 0, 0, \text{.true.}, \text{'date'}, \quad \text{...or...} \\
\text{sim\_stop\_time} &= 0, 0, 730, 0, 0, \text{.true.}, \text{'days'}, \quad \text{...or...} \\
\text{sim\_stop\_time} &= 0, 0, 0, 0, 146, \text{.true.}, \text{'index'}
\end{align*}
\]

The values 0 are just blank fields which will be calculated by the model, depending on the mode ('date', 'days' or 'index') specified by the user. Note that when using the 'date' mode, the first integer sets the year, the second integer sets the month and the third integer sets the day of the month.

The model has two important variables of type TIMING: \text{sim\_start\_time} and \text{sim\_stop\_time}. Both must be specified by the user as elements of the namelist \text{CONTROL\_PARMS} in the simulation input file (see next subsection). Contrary to \text{sim\_stop\_time} (see example above), \text{sim\_start\_time} must be specified with the mode 'date'. Furthermore, the "internal" initial conditions contained in the file data/initcond.nc correspond to the date January 1. If the user starts from these conditions and not from a restart file calculated previously, the date set by \text{sim\_start\_time} must be January 1. The year can be chosen freely by the user, keeping in mind that the initial conditions correspond to the atmospheric composition typical of the 1990's. The usual starting date is thus:

\[
\text{sim\_start\_time} = 1995, 1, 0, 0, 0, \text{.true.}, \text{'date'}
\]

The user can set precise simulation dates at which printed, archived (diurnal averages or diurnal variations) or saved output are required (see next subsection). These variables have the type TIMING, and are named respectively \text{ran\_printout}, \text{ran\_archive}, \text{ran\_dvarch} and \text{ran\_save}. It is also possible to output data at regular intervals between two specified dates, through the variables \text{intv\_printout}, \text{intv\_archive} and \text{intv\_save}. These variables have the type IO\_TIMING, defined in the module \text{TIME\_CONTROLS} (file .src/modules/main.mod.f):

```fortran
type IO\_TIMING
  type( TIMING ) :: start\_time --> set by any of the three modes
  type( TIMING ) :: stop\_time --> set by any of the three modes
  integer :: increment --> in 5-days timesteps
  logical :: active --> must be set to .true.
  character(len=5) :: mode --> must be set to 'index'
end type IO\_TIMING
```

Although these variables are vectors dimensioned to 10, only the first element of the vector is taken in account in the present version of the model.
9.6 Writing the namelist-directed simulation input files

Runs of the SOCRATES model require an input file, named 'socrates.inp' in the present description. This file contains the settings of basic parameters of the simulation, and the settings of variables of type TIMING and IO_TIMING. These variables are set through the use of namelists, a feature of Fortran90 which allows setting variables in a random order, with no formatting, by naming the variables to set. 'socrates.inp' contains two namelists: CONTROL_PARMS and IO_PARMS. CONTROL_PARMS contains the settings of the simulation start date, stop date and basic parameters, whose names and possible values are given in the headers of the file src/main.f.

IO_PARMS contains the settings of the data directory name, and of the variables to specify what, when and where to output data. There are four possible output files, described in Table 12.

Table 12. Characteristics of SOCRATES-generated output files

<table>
<thead>
<tr>
<th>Type of output</th>
<th>Format</th>
<th>output to file</th>
<th>data written in file</th>
<th>TIMING variable</th>
<th>IO_TIMING variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>printed</td>
<td>ASCII</td>
<td>Standard out</td>
<td>dynamical and/or chemical variables (diurnally averaged)</td>
<td>ran_printout</td>
<td>intv_printout</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(50)</td>
<td>(10)</td>
</tr>
<tr>
<td>archived (diurnally averaged)</td>
<td>NetCDF</td>
<td>set by arch_filespec</td>
<td>dynamical and chemical variables (diurnally averaged)</td>
<td>ran_archive</td>
<td>intv_archive</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(10)</td>
<td>(10)</td>
</tr>
<tr>
<td>archived (diurnal cycle)</td>
<td>NetCDF</td>
<td>set by dvarch_filespec</td>
<td>temperature and chemical variables (diurnal cycles)</td>
<td>ran_dvarch</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(10)</td>
<td></td>
</tr>
<tr>
<td>saved</td>
<td>NetCDF</td>
<td>set by save_filespec</td>
<td>Everything needed to restart from last saved date</td>
<td>ran_save(50)</td>
<td>intv_save(10)</td>
</tr>
</tbody>
</table>

To explain the structure of an input file, we will comment the example input file named "socrates.inp", a typical two-year simulation requiring all the possible output files.

&controlParms
sim_start_time%year = 1995, --> arbitrary, left to user's choice.
sim_start_time%month = 1, --> mandatory to use internal initial conditions
sim_start_time%day = 1, --> mandatory to use internal initial conditions
sim_stop_time%year = 1997, --> simulation will end for year 1997...
sim_stop_time%month = 1, --> ... month of January...
sim_stop_time%day = 6, -> ... first day of that month
sim_stop_time%mode = 'date', -> this is an absolute date
particle = 1, -> turn ON sulfate aerosol heterogeneous chemistry
aero = .false., -> turn OFF aerosol effect on photodissociation
and heating rates calculation
polar = 1, -> turn ON heterogeneous chemistry on PSCs.
liste = .true., -> output the initial values
/
&ioParms
data_dir = 'data/', -> name of the directory containing data files
run_label = 'run30', -> label to identify version number
prntsw = 1, -> generate ASCII output...
dynprt = 1, -> ... of dynamical variables ...
chmprt = 0, -> ... but not of chemical variables
intv_printout(1) = 1995, 1, 1, 0, 0, 0, .true., 'date',
-> ASCII output begins 1st day of simulation...
0, 0, 0, 0, 0, 12, .true., 'index',
-> ... and ends after 12 (5-days) timesteps
1, -> between these two dates, write at each timestep
', .true., -> mandatory for variables of type IO_TIMING
'index', -> mandatory for variables of type IO_TIMING
ran_printout(1:3) = 1996, 6, 20, 0, 0, 0, .true., 'date',
-> add ASCII printout for 20 June 1996
0, 0, 90, 0, 0, 0, .true., 'days',
-> add ASCII printout 90 days after simulation begins
0, 0, 0, 0, 0, 73, .true., 'index',
-> ... and 73 (5-days) timesteps after simulation begins
filesw = 1, -> do NetCDF output of all diurnally averaged
variables
arch_filespec = 'results/archive.nc',
-> directory and file name for NetCDF archive file
intv_archive(1) = 1995, 1, 1, 0, 0, 0, .true., 'date',
-> archived output begins 1st day of simulation...
1997, 1, 6, 0, 0, 0, .true., 'date',
-> ... and ends last day of simulation
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2, \text{-- } \text{between those two dates, output every other timestep}\n\text{.true., \text{-- } \text{mandatory for variables of type IO\_TIMING}}\n\text{'index', \text{-- } \text{mandatory for variables of type IO\_TIMING}}\ndvarchsw = 1, \text{-- } \text{do NetCDF output of diurnal cycles of chemicals}\ndiuvarch_filespec = 'results/diuvarch.nc', \text{-- } \text{directory and file name for NetCDF archive file}\nran_dvarch(1:2) = 1996, 6, 20, 0, 0, 0, \text{.true., 'date'}, \text{-- } \text{output for 20 June 1996}\n1996, 12, 17, 0, 0, 0, \text{.true., 'date'}, \text{-- } \text{output for 17 December 1996}\nsavesw = 1, \text{-- } \text{save all variables to restart from a "restart" file}\nsave_filespec = 'results/save30.nc', \text{-- } \text{directory and file name for NetCDF "restart" file}\nintv_save(1) = 1995, 3, 1, 0, 0, 0, \text{.true., 'date'}, \text{-- } \text{begin to save at 1 March 1995}\n1997, 1, 6, 0, 0, 0, \text{.true., 'date'}, \text{-- } \text{stop saving at end of simulation}\n12, \text{-- } \text{save every 12 (5-days) timesteps}\n\text{.true., \text{-- } \text{mandatory for variables of type IO\_TIMING}}\n\text{'index', \text{-- } \text{mandatory for variables of type IO\_TIMING}}\nran_save(1) = 1997, 1, 1, 0, 0, 0, \text{.true., 'date'}, \text{-- } \text{make sure to save simulation at 1 January 1997}\n\text{-- } \text{end of IO\_PARMS namelist}\n
The example provided above makes use of the "internal" initial conditions file 'data/initcond.nc'. The user can start the simulation with any other "restart" file saved from previous runs, provided that he knows the date of the last conditions saved in the "restart" file generated by the previous run.

Suppose the user wants to use a restart file containing the conditions saved by a previous run, for the date 20 June 1995. First, this must be the date of the start of the run:

\&control_parms
sim_start_time\$year = 1995,\nsim_start_time\$month = 1,\nsim_start_time\$day = 1,\nThe following line must be inserted in the CONTROL\_PARMS namelist settings: restrt = .true.,
The path and name of the "restart" file must be set in the IO\_PARMS namelist. If the "restart"
file is named 'save29.nc' and is in the directory 'results', the next line should be inserted in the
IO_PARMS namelist settings: `rstrt_filespec = 'results/save29.nc'`. 
Appendix A. List of Symbols.

\(a\) earth radius
\(day\) day number
\(D_\theta\) heating rate associated with diffusion
\(f\) Coriolis parameter
\(F_G\) gravity wave momentum flux divergence
\(F_R\) Rossby wave momentum flux divergence
\(F_T\) tidal wave momentum flux divergence
\(g\) gravitational acceleration
\(H\) atmospheric scale height
\(J\) photolysis rate
\(K_T\) thermal conductivity coefficient
\(K_{yy}\) meridional eddy diffusivity coefficient
\(K_{zz}\) vertical eddy diffusivity coefficient
\(Q_{IR}\) Infrared heating rate
\(Q_S\) Solar heating rate
\(N\) static stability (Brunt-Vaisala frequency)
\(R\) universal gas constant
\(\bar{u}\) zonally-averaged zonal wind velocity
\(v\) meridional wind velocity
\(v^*\) meridional residual wind velocity
\(w\) vertical wind velocity
\(\bar{w}^*\) vertical residual wind
\(X\) mixing ratio
\(y\) meridional coordinate
\(z\) log-pressure height coordinate
\(\phi\) latitude
\(\rho_0\) basic atmospheric mass density \((\rho_0 = \rho_s \exp(-z/H))\)
\(\theta\) potential temperature
\(\chi\) velocity stream function
\(\Omega\) earth rotational frequency
### Appendix B. Subroutine description

<table>
<thead>
<tr>
<th>File name</th>
<th>Purpose of file and subroutines included</th>
</tr>
</thead>
<tbody>
<tr>
<td>absdep.f</td>
<td>Calculates absorption optical depth. Subroutine absdep</td>
</tr>
<tr>
<td>acc_loss.f</td>
<td>Calculates the global lifetime at each diurnal time step. Subroutine acc_loss</td>
</tr>
<tr>
<td>adam.f</td>
<td>Calculates coefficients for stream function equation. Subroutine adam</td>
</tr>
<tr>
<td>adj_nox.f</td>
<td>Fix initial NOx to include atomic nitrogen. Subroutine adj_nox</td>
</tr>
<tr>
<td>aero_init.f</td>
<td>Initialization of aerosol related variables. Subroutine aero_init</td>
</tr>
<tr>
<td>aero_surf_area.f</td>
<td>Read aerosol surface area. Subroutine aero_surf_area</td>
</tr>
<tr>
<td>aerosol2.f</td>
<td>Calculates aerosol optical parameters. Subroutine aerosol</td>
</tr>
<tr>
<td></td>
<td>wavaero</td>
</tr>
<tr>
<td></td>
<td>wavaero2</td>
</tr>
<tr>
<td>alpham.f</td>
<td>Read convective and frontal flux data. Subroutine alpham</td>
</tr>
<tr>
<td>arch.f</td>
<td>Archive model results in netCDF format. Subroutine archive_init</td>
</tr>
<tr>
<td></td>
<td>save_init</td>
</tr>
<tr>
<td></td>
<td>arch</td>
</tr>
<tr>
<td></td>
<td>save</td>
</tr>
<tr>
<td></td>
<td>read_save</td>
</tr>
<tr>
<td>asg.f</td>
<td>Adjust initial conditions to specified lower boundary mixing ratio. Subroutine asgfic</td>
</tr>
<tr>
<td>atmcond.f</td>
<td>Calculates atmospheric density. Subroutine atmcond</td>
</tr>
<tr>
<td>balance.f</td>
<td>Global mass balance adjustment. Subroutine balance</td>
</tr>
<tr>
<td>boundy.f</td>
<td>Boundary conditions. Subroutine boundy</td>
</tr>
<tr>
<td></td>
<td>fractions</td>
</tr>
<tr>
<td>bvfreq.f</td>
<td>Computes BV frequency. Subroutine bvfreq</td>
</tr>
</tbody>
</table>
calc_chem_rates.f:  Calculates chemical rate coefficients
   subroutine  calc_chem_rates

ccmrd1_aero.f :  Long wave radiation (1)
   subroutine  hecol
dataout
radset
radinp
radot
dimchk
chrcms
setcms

ccmrd2_aero.f :  Long wave radiation (2)
   subroutine  radalb
radcsw
radini
radpth
radtpl

chapman.f :  Chapman correction of UV radiation
   function  chapman
erfcexp

check_ctrls.f :  Check basic simulation control parameters.
   subroutine  check_ctrls

chem_aero.f :  Aerosol heterogenous chemical reactions calculation.
   subroutine  chem_aero

chem_diavg.f :  Calculates diurnal average and check conservation.
   subroutine  chem_diavg

chem_psc.f :  Polar stratospheric cloud heterogeneous chemical reactions.
   subroutine  chem_psc

chem_resol.f :  Calculates species diurnal variation.
   subroutine  chem_resol

chem_subs.f :  Chemical utility subroutines
   subroutine  prtchm
seajou
smoothl
smoothv
adj
column

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onedim

chemdr.f : Interface chemistry subroutine from main program.
   subroutine chemdr

co2.f : NLTE 15 µm CO2 cooling
   subroutine co2coolnew
       atmosnew
       coolnew

co2_cool.f : Call co2 cooling calculation and combines
IR cooling of two regions above and below 50 km.
   subroutine co2_cool

colden.f : Calculate O2 and air column density.
   subroutine colden

conserv_diag.f : Ensure mass conservation of NOy, Cly, and Bry.
   subroutine conserv_diag

const.f : Assign chemical coefficient constants.
   subroutine const

convl.f : Convection and frontal vertical transport.
   subroutine convl

cosmic.f : Cosmic ray production of NOy
   subroutine cosmic

crscor.f : Correct absorption cross section and quantum yield.
   subroutine crscor

crsget.f : Read cross sections, solar flux, and quantum yield.
   subroutine crsget

day_sub.f : Daytime short-lived species chemistry calculation
   subroutine day_sub

describe_sim.f : Describes the simulation
   subroutine describe_sim

diffus_hori.f : Horizontal diffusion of chemical continuity equation.
   subroutine diffus_hori

diffus_vert.f : Vertical diffusion of chemical continuity equation.
   subroutine diffus_vert

diftra.f : Calculates small scale diffusive transport of heat.
   subroutine diftra

diurnal_adj.f : Adjust diurnal averages after transport.
   subroutine diurnal_adj
diuvarch.f : Set up the archive netCDF file for diurnal variation of chemical species.

subroutine diuvarch_init
subroutine diuvarch

dwcntrl.f : Calculates lower boundary stream function.

subroutine dwcntrl

eddy.f : Calculates eddy diffusion coefficients when wave parameterization not in use.

subroutine eddy

eddy2.f : Eddy diffusion (heat) in troposphere

subroutine eddy2


subroutine eddy3

eff.f : Calculates UV heating efficiency due to airglow heat loss.

subroutine effic

families.f : Recalculate noon values of family from its member.

subroutine families

force1.f : Calculates forcing term for stream function equation.

subroutine force1

frdrag.f : Gravity wave parameterization (Fritts and Lu)

subroutine frdrag
function wwl

gltime.f : Calculates globally averaged lifetime of chemical species.

subroutine gltime

gravity.f : Gravity wave parameterization (Lindzen)

subroutine gravity

hderiv.f : Calculates vertical derivative

subroutine hderiv

heacoo.f : Calculates Newtonian cooling coefficient

subroutine heacoo

heat_diavg.f : Calculates diurnal average of solar heating rate

subroutine heat_diavg

heat_rate.f : Combine heating and cooling rates and interpolate

subroutine heat_rate

interp.f : Cubic spline interpolation

subroutine spline
splint

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<table>
<thead>
<tr>
<th>File</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>it_conserv.f</td>
<td>Mass conservation.</td>
</tr>
<tr>
<td>subroutine it_conserv</td>
<td></td>
</tr>
<tr>
<td>kockart.f</td>
<td>SR parameterization of UV</td>
</tr>
<tr>
<td>subroutine kockart</td>
<td></td>
</tr>
<tr>
<td>lat_heat.f</td>
<td>Latent heat release in troposphere.</td>
</tr>
<tr>
<td>subroutine lat_heat</td>
<td></td>
</tr>
<tr>
<td>lightning.f</td>
<td>Lightning production of NOy.</td>
</tr>
<tr>
<td>subroutine lightning</td>
<td></td>
</tr>
<tr>
<td>linpol.f</td>
<td>Linear interpolation.</td>
</tr>
<tr>
<td>subroutine linpol</td>
<td></td>
</tr>
<tr>
<td>ls currentPlayer</td>
<td>Skip lines when reading files.</td>
</tr>
<tr>
<td>subroutine ls currentPlayer</td>
<td></td>
</tr>
<tr>
<td>minsch.f</td>
<td>NO photolysis calculation</td>
</tr>
<tr>
<td>subroutine minsch</td>
<td></td>
</tr>
<tr>
<td>function pjno</td>
<td></td>
</tr>
<tr>
<td>moldiff.f</td>
<td>Calculates molecular diffusion coeff. and velocities.</td>
</tr>
<tr>
<td>subroutine moldiff</td>
<td></td>
</tr>
<tr>
<td>neg_da.f</td>
<td>Report negative mixing ratios.</td>
</tr>
<tr>
<td>subroutine neg_da</td>
<td></td>
</tr>
<tr>
<td>night_sub.f</td>
<td>Nighttime short-lived species chemistry calculation</td>
</tr>
<tr>
<td>subroutine night_sub</td>
<td></td>
</tr>
<tr>
<td>noyion.f</td>
<td>Production of NOy by thermospheric processes.</td>
</tr>
<tr>
<td>subroutine noyion</td>
<td></td>
</tr>
<tr>
<td>nwind.f</td>
<td>Calculate zonal wind from thermal wind equation.</td>
</tr>
<tr>
<td>subroutine nwind</td>
<td></td>
</tr>
<tr>
<td>opticp.f</td>
<td>Summarizes UV optical properties of medium.</td>
</tr>
<tr>
<td>subroutine opticp</td>
<td></td>
</tr>
<tr>
<td>outdob.f</td>
<td>Print dobson unit table.</td>
</tr>
<tr>
<td>subroutine outdob</td>
<td></td>
</tr>
<tr>
<td>pho.f</td>
<td>Calculates photolysis and solar heating rates (1)</td>
</tr>
<tr>
<td>subroutine phoStam</td>
<td></td>
</tr>
<tr>
<td>phodis.f</td>
<td>Calculates photolysis and solar heating rates (2)</td>
</tr>
<tr>
<td>subroutine phodis</td>
<td></td>
</tr>
<tr>
<td>phorat.f</td>
<td>Calculates photolysis and solar heating rates (3)</td>
</tr>
<tr>
<td>subroutine phorat</td>
<td></td>
</tr>
<tr>
<td>prod_loss_day.f</td>
<td>Calculates production and loss rates during the day for long-live species.</td>
</tr>
</tbody>
</table>

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prod_loss_night.f: subroutine prod_loss_day
Calculates production and loss rates during the night for long-live species.

subroutine prod_loss_night
prtven.f : subroutineprtven
Print dynamical quantities.

subroutine psc_partition
psc_partition.f : subroutine psc_partition
Compute the loss rates due to PSC.

subroutine qbo
qbo.f : subroutine qbo
QBO forcing calculation.

subroutine radnew_aero
radnew_aero.f : subroutine radnew_aero
Long wave radiation (3)

subroutine radclw
  xface
  nbabem
  path
  ph2ocn
  taugas
  acctau

subroutine scadep
scadep.f : subroutine scadep
Calculates scattering optical depth for UV radiation.

subroutine secjou_chap
secjou_chap.f : subroutine secjou_chap
solar angle properties with chapman correction.

subroutine shap
shap.f : subroutine shap
shapiro filter for temperature.

subroutine sigcfc
sigcfc.f : subroutine sigcfc
cross sections for CFCs.

subroutine slt
slt.f : subroutine slt
Semi-Langrangian transport.

subroutine sol_chm_heat
sol_chm_heat.f : subroutine sol_chm_heat
Calculates solar and chemical heating.

subroutine sol_day
sol_day.f : subroutine sol_day
Photolysis and solar heating interface

subroutine strcal
strcal_lb.f : subroutine strcal
Solves the stream function equation.
Solves the thermodynamic equation.

**subroutine** tempfa2

Gravity wave heat coefficient.

**subroutine** tgravity

Tidal wave momentum forcing.

**subroutine** tide

Trimolecular chemical reaction rates

**subroutine** troev

Two-stream delta eddington method for UV radiation.

**subroutine** twstr

Utilities

**subroutine** mdy
  *date2time*
  *time2date*
  *check_io*
  *swprt*
  *describe_sim*

**function** time_mode
  *do_io*
  *lenof*

calculates vertical derivative

**subroutine** vderiv

General purpose vector print routine.

**subroutine** vec_out

washout rates for soluble species in troposphere.

**subroutine** washout

Wave model for planetary waves.

**subroutine** wave94
  *buoy*
  *diffb*
  *cdiffb*
  *diffn*
  *cdiffn*
  *pwave_o*
  *steady*
  *lkuos*
  *prewm*
wup.f : Correction for vertical velocity for global mass balance

subroutine wup
### Appendix C: Selected variables in SOCRATES

1 = 1, 35 : latitude index
iz = 1, 121 : altitude index
iv = 1, 171: UV wavelength index
k = 1, 2 : solar angle index
ispec : chemical species index
ilon = 1, 8 : diurnal time index

<table>
<thead>
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<th>Variable</th>
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<th>Explanation [units]</th>
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<td>PHO_AERO, module.f</td>
<td>aerosol extinction coefficient (1/km) for UV radiation</td>
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<tr>
<td>aeabs(l,iz)</td>
<td>PHO_AERO, modules.f</td>
<td>aerosol absorption coefficient (cm²/g) for IR radiation</td>
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<td>aerabs(l,iz,iv)</td>
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<td>PHO_AERO, module.f</td>
<td>aerosol mass density (g/cm³) for IR radiation</td>
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<td>alpha(l,iz)</td>
<td>ALP, main.mod.f</td>
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<td>alphadr(l,iz)</td>
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<td>CO chemical loss by convective and frontal vertical transport in Boundary layer [1/s]</td>
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<td>bv(l,iz)</td>
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<td>bw(l,iz,ispec)</td>
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<td>Washout loss term for soluble species HNO₃, H₂O₂, CH₃OOH, Clx, HO₂NO₂, CH₂O [1/s]</td>
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<td>TROPIC, main.mod.f</td>
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<td>coeff(iv)</td>
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<td>cool(l,iz)</td>
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<td>I.R. cooling rate [K/day]</td>
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<td>index for day of the year: Jun/21 =&gt; daynum=0 Dec/31 =&gt; daynum = 193 ; Jun/20 =&gt; daynum = 364</td>
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<td>dh(l,iz)</td>
<td>VEN4, main.mod.f</td>
<td>small scale diffusive transport of heat [K/s]</td>
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<td>dkt(l,iz)</td>
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<td>diffusion coefficient from tidal wave breaking [m²/s]</td>
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<td>dtt(l,iz)</td>
<td>TIDE1, main.mod.f</td>
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<td>ffr(l,iz)</td>
<td>ROSS, main.mod.f</td>
<td>momentum flux from Rossby (planetary) wave [m²/s²]</td>
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<td>fx(l,iz)</td>
<td>VEN5, main.mod.f</td>
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<td>mfcv(l)</td>
<td>Convective and frontal molecular flux (molec/cm^3 s)</td>
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<td>o2dz(iz)</td>
<td>O2 and O3 column above iz, initial condition (molec/cm^2)</td>
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<td>omaer(iv)</td>
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<td>pch(l,iz)</td>
<td>Solar heating rate [K/day]</td>
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<td>pcr(l,iz)</td>
<td>NO\textsubscript{y} production by cosmic rays, z&gt;7km (molec/cm^3 s)</td>
<td>cosmic.f</td>
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<tr>
<td>pcv(l,iz)</td>
<td>CO chemical production by convective and frontal vertical transport in Boundary layer (molec/cm^3 s)</td>
<td>main.f</td>
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<td>pio(l,iz)</td>
<td>NO\textsubscript{y} production in thermosphere by N\textsubscript{2}+e\textsuperscript{-} and N\textsubscript{2}+hn, z&gt;89km (molec/cm^3 s)</td>
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<td>NO\textsubscript{y} production by lightnings, z&lt;16km (molec/cm^3 s)</td>
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<td>q(l,iz)</td>
<td>Net heating rate [K/day]</td>
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<td>q4(l,iz)</td>
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<td>CO2COOLNE</td>
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<td>qc(l,iz)</td>
<td>Volume mixing ratio of short-lived species ispec</td>
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<td>qvd(l,iz)</td>
<td>Volume mixing ratio of intermediate-lived species ispec</td>
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<td>qn2(l,iz)</td>
<td>Volume mixing ratio of long-lived species ispec</td>
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<td>srheat1(l,iz)</td>
<td>Diurnal avg of solar heating rate by O\textsubscript{3} absorption [K/day]</td>
<td>SOLTEST, main.mod.f</td>
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<td>srheat2(l,iz)</td>
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<td>srheat3(l,iz)</td>
<td>Heating rate by exothermical chemical reactions [K/day]</td>
<td>main.mod.f</td>
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<td>t2d(l,iz)</td>
<td>Diurnal averaged temperature [K]</td>
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<td>tj(l,iz)</td>
<td>Photodissociation coefficient for process iproc [1/s]</td>
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<td>try(l,iz)</td>
<td>Relaxation temperature [K]</td>
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<td>tl(l,iz)</td>
<td>Latitudinal derivative of t2d [K/rad]</td>
<td>main.mod.f</td>
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<tr>
<td>tz(l,iz)</td>
<td>Vertical derivative of t2d [K/m]</td>
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<td>u(l,iz)</td>
<td>Zonal wind [m/s]</td>
<td>main.mod.f</td>
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<td>v(l,iz)</td>
<td>Meridional residual wind [m/s] ([cm/s] in chemistry part)</td>
<td>module.f</td>
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<td>( w(l,iz) )</td>
<td>VEN6, main.mod.f</td>
<td>vertical residual wind [m/s] ([cm/s] in chemistry part)</td>
<td>strcal_lb.f, balance.f</td>
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</tr>
<tr>
<td>( vv(l,iz), ww(l,iz) )</td>
<td>ROSS, main.mod.f</td>
<td>meridional and vertical perturbations to residual wind due to Rossby (planetary) wave</td>
<td>WAVE94, wave.f</td>
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<tr>
<td>( wu(l) )</td>
<td>UPPER, main.mod.f</td>
<td>diabatic vertical wind at upper boundary [m/s]</td>
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<td>( xu(l) )</td>
<td>VEN6, main.mod.f</td>
<td>stream function at upper boundary</td>
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<td>( x(l,iz), xm(l,iz) )</td>
<td>VEN6, main.mod.f</td>
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<td>( xa(l,iz); xb(l,iz), xc(l,iz), .xg(l,iz) )</td>
<td>VEN7, main.mod.f</td>
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<td>( xky(l,iz), xkyl(l,iz) )</td>
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<td>coefficients of the stream function equation</td>
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<td>( xkz(l,iz), xkzz(l,iz) )</td>
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<td>( K_{yy} ): horizontal eddy diffusion coefficient from Rossby wave ([m^2/s]) and latitudinal derivative</td>
<td>WAV94,wave.f, eddy2.f, eddy3.f</td>
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<tr>
<td>( xkz(l,iz), xkzz(l,iz) )</td>
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<td>frdrag.f, eddy2.f, eddy3.f</td>
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</table>
Reference:


