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The Karlsruhe Simulation Model of the Middle Atmosphere (KASIMA)
Version 2

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Abstract

The numerical methods of the Karlsruhe Simulation Model of the Middle Atmosphere (KASIMA) are described in detail. KASIMA consists of three major modules: The meteorological module integrates the primitive meteorological equations in time. It is driven by the net heating rate that is computed using the absorbtion of ozone and molecular oxygen in the UV spectrum and of CO_2, O_3, and H_2O in the near infrared. The chemical module consists of 58 chemical species and families which are involved in 101 bi- and termolecular reactions, 39 photodissociations, and 10 heterogeneous reactions taking place on surfaces of polar stratospheric clouds (PSC) and on liquid sulfuric acid aerosols.

Das Karlsruher Simulationsmodell der mittleren Atmosphäre KASIMA, Version 2

Zusammenfassung

Die numerischen Algorithmen des Karlsruher Simulationsmodells der mittleren Atmosphäre (KASIMA) sind detailliert beschrieben. KASIMA besteht aus drei Hauptkomponenten: Die meteorologische Komponente integriert das meteorologische Grundgleichungssystem in die Zeit. Es wird von einem Strahlungsmodell angetrieben, das die Absorption von UV Licht durch Ozon und molekularen Sauerstoff und den Strahlungsaustausch im nahen Infrarot durch CO_2, O_3 und H_2O beschreibt. Die chemische Komponente berücksichtigt 58 chemische Spurenstoffe und Familien in 101 bi- und termolekularen Reaktionen, 39 Photolysen und 10 heterogenen Reaktionen auf Oberflächen polarer Stratosphärenwolken (PSC) und flüssiger Schwefelsäureaerosolen.

Contents

1 The Meteorology

The atmosphere is a shallow envelope of compressible gas surrounding an approximately spherical, rotating planet. The equations of motion in a rotating frame for such a gas are well known, but in their most general form they are far more complicated than necessary or desirable for large scale meteorological phenomena considered by this model. Scale analysis shows that several simplifications to the equations can be made. In particular, the vertical momentum equation can be replaced by hydrostatic balance, the Coriolis force associated with the horizontal component of the earth's rotation vector can be neglected, and the distance r from any point in the atmosphere to the center of the earth can be replaced by a mean radius a. The resulting equations are called the "primitive equations":

1.1 The Differential Equations

The model is based on the full set of the primitive equations with a logarithmic pressure z as vertical coordinate. Following the notation of *Holton* [1975] the horizontal momentum equation, the thermodynamic equation, the hydrostatic equation and the continuity equation are:

$$\frac{D\vec{v}_h}{Dt} + f\vec{k} \times \vec{v}_h + \vec{\nabla}_p \Phi - \vec{F} = 0 \tag{1.1}$$

$$\frac{DT}{Dt} + wT\frac{\kappa}{H} - Q = 0 \tag{1.2}$$

$$\frac{\partial \Phi}{\partial z} = \frac{RT}{H} \tag{1.3}$$

$$\vec{\nabla}_p \cdot \vec{v}_h + \frac{1}{\rho_0}\frac{\partial \rho_0 w}{\partial z} = 0 \tag{1.4}$$

Equation 1.1 can be decomposed into its zonal and meridional component yielding:

$$\frac{Du}{Dt} - \left(f + \frac{u\tan\varphi}{a}\right)v + \frac{1}{a\cos\varphi}\frac{\partial \Phi}{\partial \lambda} - F_\lambda = 0 \tag{1.5}$$

$$\frac{Dv}{Dt} + \left(f + \frac{u\tan\varphi}{a}\right)u + \frac{1}{a}\frac{\partial \Phi}{\partial \varphi} - F_\varphi = 0 \tag{1.6}$$

Instead of having two prognostic equations for the horizontal velocity vector components (equations 1.5, 1.6) two equivalent equations for the scalar quantities $\zeta = \vec{k} \cdot \vec{\nabla}_p \times \vec{v}_h$ (the relative vorticity) and $D = \vec{\nabla}_p \cdot \vec{v}_h$ (horizontal divergence) can be obtained by applying $\vec{k} \cdot \vec{\nabla}_p \times$ and $\vec{\nabla}_p \cdot$ on equation 1.1. From the horizontal momentum equation 1.1 in advection and flux form the following alternative sets of equations are derived:

1. For the advection form it is convenient to rewrite the advection term in equation 1.1 using equation A.2 or A.5:

$$\vec{v}_h \cdot \vec{\nabla}_p \vec{v}_h = \vec{\nabla}_p \left(\frac{\vec{v}_h^2}{2} \right) - \vec{v}_h \times (\vec{\nabla}_p \times \vec{v}_h) = \vec{\nabla}_p \left(\frac{\vec{v}_h^2}{2} \right) + \zeta \vec{k} \times \vec{v}_h \tag{1.7}$$

   The vorticity- and divergence equation thus become in advection form:

$$\frac{\partial \zeta}{\partial t} + \vec{\nabla}_p \cdot (\zeta + f) \vec{v}_h + \vec{k} \cdot \vec{\nabla}_p \times \left[w \frac{\partial \vec{v}_h}{\partial z} - \vec{F} \right] = 0 \tag{1.8}$$

   and

$$\frac{\partial D}{\partial t} - \vec{k} \cdot \vec{\nabla}_p \times (\zeta + f) \vec{v}_h + \vec{\nabla}_p \cdot \left[w \frac{\partial \vec{v}_h}{\partial z} - \vec{F} \right] + \vec{\nabla}_p^2 \left[\Phi + \left(\frac{\vec{v}_h^2}{2} \right) \right] = 0 \tag{1.9}$$

2. Equation 1.7 becomes for the momentum flux:

$$\vec{\nabla}_p \cdot \vec{v}_h \vec{v}_h = \vec{v}_h \cdot \vec{\nabla}_p \vec{v}_h + \vec{v}_h \vec{\nabla}_p \cdot \vec{v}_h \overset{(1.7)}{=} \vec{\nabla}_p \left(\frac{\vec{v}_h^2}{2} \right) + \zeta \vec{k} \times \vec{v}_h + D \vec{v}_h \tag{1.10}$$

   so that the vorticity and divergence equations become in flux form

$$\frac{\partial \zeta}{\partial t} + \vec{\nabla}_p \cdot (\zeta + f) \vec{v}_h + \vec{k} \cdot \vec{\nabla}_p \times \left[\frac{1}{\rho_0} \frac{\partial \rho_0 w \vec{v}_h}{\partial z} + D \vec{v}_h - \vec{F} \right] = 0 \tag{1.11}$$

   and

$$\frac{\partial D}{\partial t} - \vec{k} \cdot \vec{\nabla}_p \times (\zeta + f) \vec{v}_h + \vec{\nabla}_p \cdot \left[\frac{1}{\rho_0} \frac{\partial \rho_0 w \vec{v}_h}{\partial z} + D \vec{v}_h - \vec{F} \right] + \vec{\nabla}_p^2 \left[\Phi + \left(\frac{\vec{v}_h^2}{2} \right) \right] = 0 \tag{1.12}$$

1.2 The Spectral Representation

The model is based on the vorticity equation 1.11 and the divergence equation 1.12 in flux form, the thermodynamic equation 1.2 in flux form, the hydrostatic equation 1.3, and the continuity equation 1.4. Equations for the spherical harmonic coefficients are obtained by multiplying the equations 1.11, 1.12, 1.2, 1.3, and 1.4 with $P_n^m(\mu)e^{-\imath m\lambda}$ and integrating over the sphere (see equation A.25):

$$\frac{\partial \zeta_n^m}{\partial t} = \frac{1}{4\pi a}\int_{-1}^{+1}\int_{0}^{2\pi}\left[-\frac{1}{(1-\mu^2)}\frac{\partial K_V}{\partial \lambda}+\frac{\partial K_U}{\partial \mu}\right]P_n^m(\mu)e^{-\imath m\lambda}d\lambda d\mu + (F_\zeta)_n^m \tag{1.13}$$

$$\begin{aligned}\frac{\partial D_n^m}{\partial t} &= -\frac{1}{4\pi a}\int_{-1}^{+1}\int_{0}^{2\pi}\left[\frac{1}{(1-\mu^2)}\frac{\partial K_U}{\partial \lambda}+\frac{\partial K_V}{\partial \mu}\right]P_n^m(\mu)e^{-\imath m\lambda}d\lambda d\mu \\ &\quad -\frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi}\vec{\nabla}_p^2\left[\Phi+\frac{\vec{v}_h^2}{2}\right]P_n^m(\mu)e^{-\imath m\lambda}d\lambda d\mu + (F_D)_n^m\end{aligned} \tag{1.14}$$

$$\frac{\partial T_n^m}{\partial t} = \frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi} -K_T P_n^m(\mu)e^{-\imath m\lambda}d\lambda d\mu + Q_n^m \tag{1.15}$$

$$\frac{\partial \Phi_n^m}{\partial z} = \frac{RT_n^m}{H} \tag{1.16}$$

$$D_n^m + \frac{1}{\rho_0}\frac{\partial W_n^m}{\partial z} = 0 \tag{1.17}$$

where

$$K_U = -(\zeta+f)V + DU + \frac{1}{\rho_0}\frac{\partial WU}{\partial z} \tag{1.18}$$

$$K_V = +(\zeta+f)U + DV + \frac{1}{\rho_0}\frac{\partial WV}{\partial z} \tag{1.19}$$

$$\begin{aligned}K_T &= \frac{1}{a(1-\mu^2)}\frac{\partial UT}{\partial \lambda}+\frac{1}{a}\frac{\partial VT}{\partial \mu}+\frac{1}{\rho_0}\frac{\partial WT}{\partial z}+wT\frac{\kappa}{H} \\ &= \frac{1}{a(1-\mu^2)}\frac{\partial UT}{\partial \lambda}+\frac{1}{a}\frac{\partial VT}{\partial \mu}+\frac{1}{\gamma\rho_0}\frac{\partial \gamma WT}{\partial z}\end{aligned} \tag{1.20}$$

In equation 1.20, γ is the conversion factor between the temperature and the potential temperature and is defined by equation 1.113.

Using equations A.22, A.26 and A.27 the vorticity equation 1.13 and the divergence equation 1.14 can be written as:

$$\frac{\partial \zeta_n^m}{\partial t} = \frac{1}{4\pi a}\int_{-1}^{+1}\int_{0}^{2\pi} \frac{-imK_V P_n^m(\mu) + K_U H_n^m(\mu)}{(1-\mu^2)} e^{-\imath m\lambda} d\lambda d\mu + (F_\zeta)_n^m \tag{1.21}$$

$$\begin{aligned}\frac{\partial D_n^m}{\partial t} &= -\frac{1}{4\pi a}\int_{-1}^{+1}\int_{0}^{2\pi} \frac{imK_U P_n^m(\mu) + K_V H_n^m(\mu)}{(1-\mu^2)} e^{-\imath m\lambda} d\lambda d\mu \\ &\quad + \frac{n(n+1)}{4\pi a^2}\int_{-1}^{+1}\int_{0}^{2\pi} \left[\Phi + \frac{\vec{v}_h^2}{2}\right] P_n^m(\mu) e^{-\imath m\lambda} d\lambda d\mu + (F_D)_n^m \end{aligned} \tag{1.22}$$

The equations 1.21, 1.22, 1.15, 1.16, and 1.17 are a complete set of equations for the model variables $\zeta_n^m(t,z)$, $D_n^m(t,z)$, $T_n^m(t,z)$, $\Phi_n^m(t,z)$, and $W_n^m(t,z)$,

In order to compute $K_U(\lambda,\mu,z)$, $K_V(\lambda,\mu,z)$, and $K_T(\lambda,\mu,z)$ in equations 1.21, 1.22, and 1.15 the values for $\zeta(\lambda,\mu,z)$, $D(\lambda,\mu,z)$, and $T(\lambda,\mu,z)$ can immediately be obtained from the transformation equation A.24. $U(\lambda,\mu,z)$ and $V(\lambda,\mu,z)$ can be computed from equations 1.108 and 1.110 by means of A.20, A.22, and A.25 yielding:

$$U = a\sum_{n=0}^{\infty}\sum_{m=-n}^{n} \frac{1}{n(n+1)} \left[-imD_n^m P_n^m(\mu) - \zeta_n^m H_n^m(\mu)\right] e^{\imath m\lambda} \tag{1.23}$$

$$V = a\sum_{n=0}^{\infty}\sum_{m=-n}^{n} \frac{1}{n(n+1)} \left[D_n^m H_n^m(\mu) - im\zeta_n^m P_n^m(\mu)\right] e^{\imath m\lambda} \tag{1.24}$$

The spherical harmonic coefficients of the horizontal flux terms in equation 1.20 are computed using equations A.26 and A.27:

$$\begin{aligned} &\int_{-1}^{+1}\int_{0}^{2\pi} \frac{1}{(1-\mu^2)} \left(\frac{\partial UT(\lambda,\mu)}{\partial \lambda} + \left(1-\mu^2\right)\frac{\partial VT}{\partial \mu}\right) P_n^m(\mu) e^{-\imath m\lambda} d\lambda d\mu \\ = &\int_{-1}^{+1}\int_{0}^{2\pi} \frac{1}{(1-\mu^2)} \left(imUTP_n^m(\mu) + VTH_n^m(\mu)\right) e^{-\imath m\lambda} d\lambda d\mu \end{aligned} \tag{1.25}$$

The first integral of the solution of equation A.27 vanishes because all the terms K_U, K_V, and VT in the equations 1.21, 1.22, and 1.25 vanish for $\mu = \pm 1$.

1.3 The Numerical Methods

1.3.1 The Horizontal Truncation

A fully triangular truncation scheme is used in the model: All series are truncated after the degree $n = N_{\max}$, such that $0 \leq n \leq N_{\max}$ and $-n \leq m \leq n$.

The integration with respect to λ is done on an equally spaced grid with at least $I_{grid} = 3N_{\max} + 1$ gridpoints [e.g. *Machenhauer and Rasmussen*, 1972].

The integrals with respect to μ are computed using Gaussian quadrature. The Gaussian grids are obtained from the zeros of the Legendre polynomial $P^0_{N_{grid}}$, where N_{grid} is the number of gridpoints in meridional direction. The Gaussian weights $\Delta\mu_i$ at gridpoint i are obtained from equation 1.115 [e.g. *Korn and Korn*, 1968]). The integrals with respect to μ are therefore approximated by:

$$\int_{-1}^{+1} X(\mu) d\mu = \sum_{i=1}^{J_{grid}} X(\mu_i)\Delta\mu_i \tag{1.26}$$

1.3.2 The Vertical Discretization

The hydrostatic equation 1.16 is integrated vertically from the lower to the upper boundary in order to compute the geopotential. If subscript k denotes the actual model layer, Φ_k is computed by:

$$\frac{\Phi_k - \Phi_{k-1}}{\Delta z} = \frac{R}{H} 0.5 \left(T_k + T_{k-1}\right) \tag{1.27}$$

At the lower boundary the actual temperature and geopotential field is taken from the ECMWF consolidated dataset. These fields are interpolated linearily in time in order to be applied for the actual timestep.

The continuity equation 1.17 is integrated downward from the upper boundary to the lower boundary in order to compute $\rho_0 w$. At the upper boundary it is assumed that $w = 0$:

$$\frac{1}{\rho_{0k}} \frac{W_{k+0.5} - W_{k-0.5}}{\Delta z} = -D_k \tag{1.28}$$

The vertical flux terms in 1.18, 1.19, and 1.20 are approximated by:

$$\frac{\partial \rho_0 w \alpha}{\partial z} \approx \frac{W_{k+0.5}(\alpha_{k+1}+\alpha_k) - W_{k-0.5}(\alpha_k+\alpha_{k-1})}{2{\rho_0}_k \Delta z} \tag{1.29}$$

where $\alpha = \{U, V, \gamma T\}$.

1.3.3 The semi-implicit time integration scheme

The time integration scheme is adapted from the semi-implicit scheme developed by *Haltiner and Williams* [1980]. All the terms that describe fast propagating internal gravity waves are treated implicitly, whereas for the other terms an explicit leapfrog scheme is applied. The terms being treated implicitly are the Laplacian of the geopotential in the divergence equation 1.22 and the vertical heat flux terms in the thermodynamic equation 1.15. Consequently, the continuity equation and the hydrostatic equation have to be treated implicitly. One entire column of model layers has to be computed simultaneously, because the continuity equation and the hydrostatic equation are integrated from the top to the bottom and vise versa, respectively. Therefore the equations have to be written in matrix form. Since the vertical velocity is defined between two model layers, the vertical grid is now defined as being twice as large as the vertical model layers, where the vertical velocity is defined on odd gridpoints and the other variables are defined on even gridpoints.

Because the Laplacian of the geopotential is involved in the semi-implicit formulations, all derivations shown in this section have to be done in terms of the spherical harmonics of the variables, which is straight forward because of the linearity of the equations discussed here. As long as subscripts in the equations describe the vertical model layer considered, their meaning is changed for convenience in this section: even subscripts denote the variable is defined on the model layer and odd subscripts denote their definition between the model layer.

The hydrostatic 1.27 and the continuity equation 1.28 can be written in matrix form with these conventions:

$$\Phi_{2k} = A_{2k,2l} T_{2l} + \Phi^s_k \tag{1.30}$$

$$W_{2k-1} = B_{2k-1,2l} D_{2l} \tag{1.31}$$

In equations 1.30 and 1.31 the subscripts k and l denote the vertical model grid with $1 \leq k, l \leq k_{grid}$, where k_{grid} is the number of model layers and Φ_k^s is specified from the lower boundary condition.

From equations 1.27 and 1.28 the matrix equations 1.30 and 1.31 are explicitly:

$$\begin{bmatrix} \Phi_2 \\ \Phi_4 \\ \Phi_6 \\ \cdots\cdots \\ \Phi_{2k_{grid}-2} \\ \Phi_{2k_{grid}} \end{bmatrix} = \frac{R\Delta z}{2H} \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 & 0 \\ 2 & 1 & 0 & \cdots & 0 & 0 \\ 2 & 2 & 1 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 2 & 2 & 2 & \cdots & 1 & 0 \\ 2 & 2 & 2 & \cdots & 2 & 1 \end{bmatrix} \begin{bmatrix} T_2 \\ T_4 \\ T_6 \\ \cdots\cdots \\ T_{2k_{grid}-2} \\ T_{2k_{grid}} \end{bmatrix} + \begin{bmatrix} \Phi^s \\ \Phi^s \\ \Phi^s \\ \cdot\cdot \\ \Phi^s \\ \Phi^s \end{bmatrix} \tag{1.32}$$

and

$$\begin{bmatrix} W_1 \\ W_3 \\ W_5 \\ \cdots\cdots \\ W_{2k_{grid}-3} \\ W_{2k_{grid}-1} \end{bmatrix} = \Delta z \begin{bmatrix} \rho_{02} & \rho_{04} & \rho_{06} & \cdots & \rho_{02k_{grid}-2} & \rho_{02k_{grid}} \\ 0 & \rho_{04} & \rho_{06} & \cdots & \rho_{02k_{grid}-2} & \rho_{02k_{grid}} \\ 0 & 0 & \rho_{06} & \cdots & \rho_{02k_{grid}-2} & \rho_{02k_{grid}} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & \rho_{02k_{grid}-2} & \rho_{02k_{grid}} \\ 0 & 0 & 0 & \cdots & 0 & \rho_{02k_{grid}} \end{bmatrix} \begin{bmatrix} D_2 \\ D_4 \\ D_6 \\ \cdots\cdots \\ D_{2k_{grid}-2} \\ D_{2k_{grid}} \end{bmatrix} \tag{1.33}$$

Φ^s is specified from the lower boundary condition as:

$$\Phi^s = \frac{R\Delta z}{2H} T_0 + \Phi_0 \tag{1.34}$$

where T_0 and Φ_0 are the lower boundary temperature and Geopotential, defined one model layer below the lower boundary.

The vertical heat flux terms are linearized for the purpose of the semi-implicit treatment by separating the temperature:

$$T(\lambda, \mu, z, t) = T^*(z) + T'(\lambda, \mu, z, t) \tag{1.35}$$

The linearized part of the vertical heat flux K_T^*

$$K_T^* = -\frac{1}{\gamma\rho_0} \frac{\partial \gamma W T^*}{\partial z} - DT^* \tag{1.36}$$

is treated implicitly, whereas the nonlinear part is treated explicitly. Using equations 1.29 equation 1.36 can be written in matrix form:

$$\begin{aligned}
K^*_{T2k} &= Y_{2k,2l-1}W_{2l-1} + T^*_{2k,2k}D_{2k} \\
&= +W_{2k+1}\left[-\frac{\gamma_{2k+2}T^*_{2k+2}+\gamma_{2k}T^*_{2k}}{2\gamma_{2k}\rho_{0\,2k}\Delta z}\right] \\
&\quad +W_{2k-1}\left[+\frac{\gamma_{2k}T^*_{2k}+\gamma_{2k-2}T^*_{2k-2}}{2\gamma_{2k}\rho_{0\,2k}\Delta z}\right] \\
&\quad -T^*_{2k,2k}D_{2k}
\end{aligned} \tag{1.37}$$

For $k = k_{grid}$, $W_{2k+1} = 0$ and for $k = 1$, T^*_0 is taken from the reference temperature.

The Laplacian of the geopotential can immediatly be obtained in spherical harmonic coefficients from equation 1.22:

$$\left[\vec{\nabla}^2_p \Phi_{2k}\right]^m_n = \frac{n(n+1)}{a^2}\left[\Phi_{2k}\right]^m_n \tag{1.38}$$

The semi-implicit formulation of the divergence equation 1.22 and the thermodynamic equation 1.15 can be derived with the matrix equations derived in this section. If the superscripts denote the timestep and the subscripts the vertical gridpoint, one obtains for the relevant terms of the divergence and thermodynamic equation:

$$\begin{aligned}
\frac{D^{n+1}_k - D^{n-1}_k}{2\Delta t} &\overset{(1.38)}{=} \vec{\nabla}^2_p\left(\Phi^{n+1}_k\right) + \text{explicit terms} \\
&\overset{(1.30)}{=} \vec{\nabla}^2_p\left(A_{k,m}T^{n+1}_m + \Phi^{s,n+1}_l\right) + \overset{(1.39)}{\cdots}
\end{aligned} \tag{1.39}$$

$$\begin{aligned}
\frac{T^{n+1}_k - T^{n-1}_k}{2\Delta t} &\overset{(1.37)}{=} Y_{k,l}\left(W^{n+1}_l\right) - T^*_{k,l}\left(D^{n+1}_l\right) + \text{explicit terms} \\
&\overset{(1.31)}{=} \left(Y_{k,l}B_{l,m} - T^*_{k,m}\right)\left(D^{n+1}_m\right) + \overset{(1.40)}{\cdots}
\end{aligned} \tag{1.40}$$

In equation 1.39 the values for Φ_k^s are computed with equation 1.32 using the lower boundary condition 1.34. The explicitly treated terms marked $\overset{(1.39)}{\cdots}$ and $\overset{(1.40)}{\cdots}$ are defined in Section 1.3.4, line item 6. Solving equation 1.40 for T_k^{n+1} and inserting the result into 1.39 gives an equation for D_k^{n+1}:

$$\begin{aligned}
\left(I_{k,l} - X_{k,l}\right) D_l^{n+1} \quad = \quad & + \left(I_{k,l} + X_{k,l}\right) D_l^{n-1} \\
& + (2\Delta t) \vec{\nabla}_p^2 A_{k,m} \left(T_m^{n-1} + (2\Delta t) \overset{(1.40)}{\cdots} \right) \\
& + (2\Delta t) \vec{\nabla}_p^2 \left(\Phi_k^{s,n+1} \right) \\
& + (2\Delta t) \overset{(1.39)}{\cdots}
\end{aligned} \tag{1.41}$$

where

$$X_{l,o} = (2\Delta t)^2 \left(\vec{\nabla}_p^2 I_{l,k} \right) A_{k,m} \left(Y_{m,n} B_{n,o} - T^*_{m,o} \right) \tag{1.42}$$

and $I_{k,l}$ is the identity matrix.

1.3.4 The Finite Difference Equations

A computational overview for the computation of one timestep is presented together with the finite difference equations in the following list:

1. The spherical harmonics of the vorticity and the deviation from the reference temperature T' (see equation 1.35) of the actual timestep is transformed on gridpoints using equation A.24:

$$\zeta(\lambda, \mu) = \sum_{n=0}^{N_{\max}} \sum_{m=-n}^{n} \zeta_n^m P_n^m(\mu) e^{\imath m \lambda} \tag{1.43}$$

$$D(\lambda, \mu) = \sum_{n=0}^{N_{\max}} \sum_{m=-n}^{n} D_n^m P_n^m(\mu) e^{\imath m \lambda} \tag{1.44}$$

$$T'(\lambda, \mu) = \sum_{n=0}^{N_{\max}} \sum_{m=-n}^{n} T'^m_n P_n^m(\mu) e^{\imath m \lambda} \tag{1.45}$$

2. The values of U, V, and W are computed at the actual timestep on gridpoints by means of equations 1.23, 1.24, 1.28 using the transformation A.24:

$$U = a \sum_{n=0}^{N_{\max}} \sum_{m=-n}^{n} \frac{1}{n(n+1)} \left[-imD_n^m P_n^m(\mu) - \zeta_n^m H_n^m(\mu) \right] e^{\imath m\lambda} \tag{1.46}$$

$$V = a \sum_{n=0}^{N_{\max}} \sum_{m=-n}^{n} \frac{1}{n(n+1)} \left[D_n^m H_n^m(\mu) - im\zeta_n^m P_n^m(\mu) \right] e^{\imath m\lambda} \tag{1.47}$$

$$W_{k-0.5} = W_{k+0.5} + \rho_{0k} \Delta z D_k(\lambda, \mu) \tag{1.48}$$

3. The non-linear terms K_U and K_V used in the vorticity equation 1.21 and in the divergence equation 1.22 are computed for the actual timestep on gridpoints from equations 1.18 and 1.19 using 1.29:

$$K_U = -(\zeta + f)V + DU + \frac{W_{k+0.5}(U_{k+1} + U_k) - W_{k-0.5}(U_k + U_{k-1})}{2\rho_0 \Delta z} \tag{1.49}$$

$$K_V = +(\zeta + f)U + DV + \frac{W_{k+0.5}(V_{k+1} + V_k) - W_{k-0.5}(V_k + V_{k-1})}{2\rho_0 \Delta z} \tag{1.50}$$

4. With the separation of the temperature (equation 1.35) and the implicit treatment of the vertical heat flux associated with the reference temperature T^* (see Section 1.3.3) the explicitely treated non-linear terms of the thermodynamic equation 1.15 K_T are computed using T' only in equation 1.20. The spherical harmonic coefficients $(K_{T'})_n^m$ are then computed using 1.25 and 1.107:

$$\begin{aligned} (K_{T'})_n^m \quad = \quad & + \frac{1}{4\pi a} \sum_{j=1}^{J_{grid}} \sum_{i=1}^{I_{grid}} \frac{imUT'P_n^m(\mu_j) + VT'H_n^m(\mu_j)}{(1-\mu_j^2)} e^{-\imath m\lambda_i} \Delta\lambda \Delta\mu_j \\ & + \frac{1}{4\pi} \sum_{j=1}^{J_{grid}} \sum_{i=1}^{I_{grid}} \frac{W_{k+0.5}(\gamma_{k+1}T'_{k+1} + \gamma_k T'_k)}{2\gamma_k \rho_{0k} \Delta z} P_n^m(\mu_j) e^{-\imath m\lambda_i} \Delta\lambda \Delta\mu_j \\ & - \frac{1}{4\pi} \sum_{j=1}^{J_{grid}} \sum_{i=1}^{I_{grid}} \frac{W_{k-0.5}(\gamma_k T'_k + \gamma_{k-1}T'_{k-1})}{2\gamma_k \rho_{0k} \Delta z} P_n^m(\mu_j) e^{-\imath m\lambda_i} \Delta\lambda \Delta\mu_j \end{aligned} \tag{1.51}$$

5. The vorticity equation 1.21 is solved explicitely. Using a leap frog scheme and let the superscript t denote the timestep, one obtaines from equation 1.21:

$$\begin{aligned} \left(\zeta^{t+\Delta t}\right)_n^m \quad = \quad & + \left(\zeta^{t-\Delta t}\right)_n^m \\ & - \frac{2\Delta t}{4\pi a} \sum_{j=1}^{J_{grid}} \sum_{i=1}^{I_{grid}} \frac{imK_V^t P_n^m(\mu_j)}{(1-\mu_j^2)} e^{-\imath m\lambda_i} \Delta\lambda \Delta\mu_j \\ & + \frac{2\Delta t}{4\pi a} \sum_{j=1}^{J_{grid}} \sum_{i=1}^{I_{grid}} \frac{K_U^t H_n^m(\mu_j)}{(1-\mu_j^2)} e^{-\imath m\lambda_i} \Delta\lambda \Delta\mu_j \\ & + 2\Delta t \left(F_\zeta^t\right)_n^m \end{aligned} \tag{1.52}$$

6. The divergence- and thermodynamic equation are already discussed in Section 1.3.3. The explicitely computed terms marked by $\cdots$ in equations 1.40 and 1.41 now become:

$$\begin{aligned}\overset{(1.39)}{\cdots} \quad = \quad & -\frac{1}{4\pi a}\sum_{j=1}^{J_{grid}}\sum_{i=1}^{I_{grid}}\frac{imK_U P_n^m(\mu_j) + K_V H_n^m(\mu_j)}{1-\mu_j^2}e^{-\imath m\lambda_i}\Delta\lambda\Delta\mu_j \\ & +\frac{n(n+1)}{4\pi a^2}\sum_{j=1}^{J_{grid}}\sum_{i=1}^{I_{grid}}\frac{U^2+V^2}{2(1-\mu_j^2)}P_n^m(\mu_j)e^{-\imath m\lambda_i}\Delta\lambda\Delta\mu_j \\ & +(F_D)_n^m \end{aligned} \tag{1.53}$$

$$\overset{(1.40)}{\cdots} = -(K_{T'})_n^m + Q_n^m \tag{1.54}$$

1.4 Miscellaneous

1.4.1 The off-line Model

Despite integrating the primitive equations as described in Section 1, the off-line version interpolates global external analyses to the model architecture. Currently, global analyses provided in terms of spherical harmonic coefficients on pressure surfaces are supported. A linear interpolation of these coefficients is applied in the vertical onto the model pressure surfaces and in time onto the actual model date. This model version is applied for the solution of chemical problems when an direct comparison with measurements is requested.

Since current analysis models have an upper boundary at ≈ 30 km, a hybrid or mixed model can be used. This version combines the on-line and the off-line model using the following alternatives:

- Run the off-line model up to a prescribed layer, use this layer as lower boundary condition for the on-line model.
- Combine the on-line and off-line model by computing the tendencies of the prognostic variables from both models as follows:

$$\frac{\partial X}{\partial t} = \alpha\left[\frac{\partial X}{\partial t}\right]^{\text{Off-Line}} + (1-\alpha)\left[\frac{\partial X}{\partial t}\right]^{\text{On-Line}}, \tag{1.55}$$

where $X \in \{\zeta, D, T\}$ is the set of prognostic variables and $0 \leq \alpha \leq 1$ is the mixing parameter. α is a function of pressure altitude z and the degree n of the spherical harmonic coefficient in use:

$$\alpha(n, z) = \exp\left[-\frac{n^2}{\sigma^2}\right], \text{where } \sigma = \frac{N_{\max}}{2}\frac{z - z_u}{z_u - z_b}, \text{ for } z < z_u \tag{1.56}$$

and $\alpha(n, z) = 0$, for $z \geq z_u$. In equation 1.56 z_u and z_b are the pressure altitude of the upper boundary of the analysis and the lower boundary of the model, respectively. Thus, α has a Gaussian shape centered around $n = 0$, the global means, with a band width σ, which reduces linear from $0.5N_{\max}$ at $z = z_b$ to zero at $z = z_u$.

1.4.2 The Effects of Breaking Gravity Waves

The effects of gravity waves are implemented according to the theory of breaking gravity waves of *Lindzen* [1981]. Lindzen applied the theory of internal gravity waves on a basic flow with weak vertical shear compared to the vertical component of the gravity wavenumber vector in an atmosphere with constant static stability. With these assumptions a simplified set of the primitive equations 1.1-1.4 describing internal gravity waves can be solved analytically. From the solution the following quantities relevant for the parameterization scheme can be derived [*Holton*, 1982]:

- The breaking level z_b is computed from the assumption of momentum and energy conservation of an undamped gravity wave leading to an increase of wave amplitude with height due to the decrease of density. Assuming a non-zero vertical momentum flux of the gravity wave, the static becomes locally unstable at some altitude resulting in convection. This breaking level is computed by:

  $$z_b = 3H \ln\left(\frac{|\bar{u} - c|}{\tilde{u}}\right), \tag{1.57}$$

  where

  $$\tilde{u} = \left(2\,\overline{u'w'}\,\frac{N}{k}\right)^{1/3} \tag{1.58}$$

  is a measure of the wave amplitude, $\bar{u}$ is the component of the horizontal basic flow parallel to the horizontal wavenumber vector, $\overline{u'w'}$ is the vertical momentum flux devided by the basic state density ρ_0, k is the absolute value of the horizontal wave number vector, c is the phase velocity of the gravity wave, and N is the buoancy frequency.

- The critical level is the level where the component of the basic flow parallel to the wavenumber vector is equal to the phase velocity of the gravity wave.

- Between the breaking and the critical level the convection processes are parameterized by vertical diffusion D and an force per unit mass F parallel to the horizontal wavenumber vector:

  $$D = \frac{k(\bar{u}-c)^4}{N^3}\left[\frac{1}{2H} - \frac{3}{2}\frac{\partial\bar{u}/\partial z}{\bar{u}-c}\right], \tag{1.59}$$

  $$F = \frac{N^2 D}{\bar{u}-c}, \tag{1.60}$$

  where k is the absolute value of the horizontal wavenumber vector.

The parameterization scheme described above is actually implemented as follows:

- The vertical momentum flux is an analytical function of the phase velocity and direction of the horizontal wavenumber vector:

  $$\overline{u'w'} = \left(\overline{u'w'}\right)_0 \exp\left[-\frac{(c-c_0)^2}{\sigma^2}\right], \tag{1.61}$$

  where $\left(\overline{u'w'}\right)_0 = 10^{-3}\ m^2/s^2$, $c_0 = 8\ m/s\cos\theta$, and $\sigma = \sqrt{\sigma_x^2+\sigma_y^2}$ with $\sigma_x = 25\ m/s\cos\theta$, and $\sigma_y = 20\ m/s\sin\theta$, is. θ is the angle towards east of the horizontal wavenumber vector.

- The absolut value of the horizontal wavenumber vector is constant:

  $$k = \frac{2\pi}{120\ km}. \tag{1.62}$$

- A spectrum of 12 independent gravity waves is implemented with three phasevelocities (8, 16, and 41 m/s) and four directions of the horizontal wavenumber vector pointing to the four cardinal points.

1.4.3 The Quasi-biennial Oscillation (QBO)

This section describes the implementation of a mechanistically forced quasi-biennial oscillation (QBO) of the zonal wind based on analyzed winds from ECMWF analyses to the on-line version.

The quasi-biennial oscillation in the equatorial lower stratosphere around 25-30 km altitude is described by e. g. *Reed et al.* [1961]; *Veryard and Ebdon* [1961]. From radiosonde observations it is found that the zonal wind changes from westerlies to easterlies with a mean period of 28 (± 2) months and a maximum wind speed between +15 m/s (westerlies) and -35 m/s (easterlies). The phase of the westerly wind moves downward with a nearly constant velocity of around 1.2 km/month whereas the phase of the easterly wind moves slower downward with a mean velocity of around 0.8 km/month and also not so constant in time. The QBO has an effect on the transport and the distribution of long-lived tracers and thus on the stratospheric ozone.

An additional force has been applied to the model wind field of the on-line model in form of a Rayleigh friction type relaxation term proportional to the difference in the zonal wind components of the model wind and an idealized wind u_{QBO}. This idealized QBO wind is derived from the ECMWF analysis of the time period from 1978 to 1994. U_{QBO} is calculated from the amplitudes and phases determined from a harmonical analysis of this oscillation as a function of height and latitude. A band pass filter has been applied to suppress high and low frequent oscillations. We used the following 5 frequencies ν_n:

$$\nu_n = n \cdot 2\pi / 180 months, \tag{1.63}$$

with n = 4,5,6,7,8 what corresponds to the periods from 22.5 to 45 months.

For the calculation of the frequencies the denominator of 180 has to be used, which is the number of months in the used time period of the ECMWF analysis, to guarantee the extention of the integration in time without an attenuation of the amplitude.

The total mean zonal force per unit mass is then calculated as follows:

$$\bar{F}_{total} = \bar{F}_\lambda + \gamma(\bar{u}_{QBO} - \bar{u}), \tag{1.64}$$

where the overbar denotes the zonal average, γ is the QBO-coefficient and $\bar{u}_{QBO}$ is the zonal mean zonal wind component of the idealized QBO. The QBO-coefficient γ is the relaxation of the QBO signal and has the dimension 1/time. It is applied as a 2-dimensional Gauss function in height and latitude to consider the attenuation of the observed QBO, with a relaxation time of 3 days as maximum value. Thus the QBO-coefficient γ becomes:

$$\gamma = 3.7 \cdot 10^{-6} \cdot \exp\left\{-0.5\left(\left(\frac{\Delta z}{\sigma_z}\right)^2 + \left(\frac{\Delta\varphi}{\sigma_\varphi}\right)^2\right)\right\} \tag{1.65}$$

The width σ_z in height is 7 km and the width σ_φ in latitude is $11°$. With this set of parameters the modelled QBO is close to that observed.

1.4.4 The Transport Algorithm

The behaviour of atmospheric trace constituents is simulated by integrating mass balance equations for their mixing ratios in time of the form:

$$\frac{\partial q}{\partial t} = -\vec{\nabla}_p \cdot (\vec{v}_h q) - \frac{1}{\rho_0} \frac{\partial \rho_0 w q}{\partial z} + S \tag{1.66}$$

where q denotes the mixing ratio and S its sources and sinks (see section 2).

The first two terms on the right hand side of equation 1.66 describe the horizontal and vertical flux divergence. When reduced to an arbitrary one-dimensional problem, the flux divergence is computed by

$$\frac{\partial uq}{\partial x} \approx \frac{f_{i+0.5} - f_{i-0.5}}{\Delta x} \tag{1.67}$$

where $f = uq$ is the flux of q, the subscript i is the actual gridpoint and Δx is the distance between the gridpoints. The flux f is computed using a two step flux corrected transport (FCT) algorithm introduced by *Zalesak* [1979]:

1. A 1. order upwind scheme from *Courant et al.* [1952]:

   $$f^{UP}_{i+0.5} = 0.5\left(u_{i+0.5} + |u_{i+0.5}|\right) q_i + 0.5\left(u_{i+0.5} - |u_{i+0.5}|\right) q_{i+1} \tag{1.68}$$

2. An antidiffusive step based on the difference between the scheme of *Lax and Wendroff* [1960] and the 1. order upwind scheme multiplied by a limiter function $\Phi(r)$:

   $$f^{FC}_{i+0.5} = \Phi(r_{i+0.5}) 0.5 |u_{i+0.5}| \left(1 - \frac{\Delta t}{\Delta x}|u_{i+0.5}|\right)(q_{i+1} - q_i) \tag{1.69}$$

   where the limiter function $\Phi(r)$ is given by *Roe and Baines* [1982]:

   $$\Phi(r) = \max\left(0, \min(2r, 1), \min(r, 2)\right) \tag{1.70}$$

   with

   $$r_{i+0.5} = \begin{cases} \dfrac{q_i - q_{i-1}}{q_{i+1} - q_i} & \text{for} \quad u_{i+0.5} \geq 0 \\[2ex] \dfrac{q_{i+2} - q_{i+1}}{q_{i+1} - q_i} & \text{for} \quad u_{i+0.5} < 0 \end{cases} \tag{1.71}$$

The total flux is given by

$$f_{i+0.5} = f^{UP}_{i+0.5} + f^{FC}_{i+0.5} \tag{1.72}$$

In case of the known fluxes $f_{i+0.5}$ equation 1.72 can be inverted to compute $u_{i+0.5}$:

1. From the requirement that $f > 0 \Leftrightarrow u > 0$ and $f < 0 \Leftrightarrow u < 0$ the following two equations are obtained:

$$u = +\frac{c}{2}\left(1 + \frac{2q_i}{\Phi(r)\Delta q}\right) \pm \sqrt{\frac{c^2}{4}\left(1 + \frac{2q_i}{\Phi(r)\Delta q}\right)^2 - \frac{2c}{\Phi(r)\Delta q}f} \quad \text{for } f > 0 \tag{1.73}$$

$$u = -\frac{c}{2}\left(1 - \frac{2q_{i+1}}{\Phi(r)\Delta q}\right) \pm \sqrt{\frac{c^2}{4}\left(1 - \frac{2q_{i+1}}{\Phi(r)\Delta q}\right)^2 - \frac{2c}{\Phi(r)\Delta q}f} \quad \text{for } f < 0 \tag{1.74}$$

   where $c = \frac{\Delta x}{\Delta t}$, $\Delta q = q_{i+1} - q_i$, and u, f, and $\Phi(r)$ are to be taken at $i + 0.5$.

2. The signs of the roots in equations 1.73 and 1.74 have to be obtained from the condition that $u = 0 \Leftrightarrow f = 0$ and are therefore determined by the sign of the terms in the parenthesis.

When returning to the model grid defined in sections 1.3.1 and 1.3.2, the computation of the fluxes from equation 1.72 requires a finite difference scheme in the horizontal for computing the spatial derivatives. Here centered are differences of the form

$$\left(\frac{\partial\alpha}{\partial\lambda}\right)_{i,j} \approx \frac{\alpha_{i+1,j} - \alpha_{i-1,j}}{2\Delta\lambda} \tag{1.75}$$

and

$$\left(\frac{\partial\alpha}{\partial\mu}\right)_{i,j} \approx \frac{\alpha_{i,j+1} - \alpha_{i,j-1}}{2\Delta\mu_j} \tag{1.76}$$

for an arbitrary scalar quantity α, where the subscripts i and j denote the zonal and meridional gridpoint, respectively. Any scalar or vector component α, that is required to be defined between the gridpoint (e. g. $\alpha_{i+0.5}$), is computed with the arithmetic mean of the neighboured gridpoints:

$$\alpha_{i+0.5} = 0.5(\alpha_{i+1} + \alpha_i) \tag{1.77}$$

With these definitions and in order to fulfil numerically both the constraints A.3 and that the horizontal wind components are nondivergent (free of rotation) if the wind components are computed from the relative vorticity ζ (horizontal divergence D), all the wind components are recomputed by:

1. Compute the spherical harmonic coefficients of the velocity stream function Ψ_n^m and the velocity potential χ_n^m from the relative vorticity and the horizontal divergence with equation A.22. Transform Ψ_n^m and χ_n^m to gridpoints with equation A.24.
2. Compute the horizontal wind components U and V by approximation of equations 1.108 and 1.110 with the definitions 1.75, 1.76, and 1.77:

$$\begin{aligned} U_{i+0.5,j} &= -\left(1-\mu^2\right)_j \frac{\Psi_{i+1,j+1} - \Psi_{i+1,j-1} + \Psi_{i,j+1} - \Psi_{i,j-1}}{4a\Delta\mu_j} \\ &\quad + \frac{\chi_{i+2,j} + \chi_{i+1,j} - \chi_{i,j} - \chi_{i-1,j}}{4a\Delta\lambda} \end{aligned} \tag{1.78}$$

$$\begin{aligned} V_{i,j+0.5} &= \frac{\Psi_{i+1,j+1} - \Psi_{i-1,j+1} + \Psi_{i+1,j} - \Psi_{i-1,j}}{4a\Delta\lambda} \\ &\quad + \left(1-\mu^2\right)_{j+0.5} \left[\frac{\chi_{i,j+1} - \chi_{i,j-1}}{4a\Delta\mu_j} + \frac{\chi_{i,j+2} - \chi_{i,j}}{4a\Delta\mu_{j+1}}\right] \end{aligned} \tag{1.79}$$

3. Analogeous to equation 1.28, the vertical velocity is computed from downward integration of the continuity equation:

$$W_{k-0.5} = W_{k+0.5} + \rho_{0k}\Delta z D_{i,j,k}, \tag{1.80}$$

where k denotes the index of the vertical gridpoint. The horizonal divergence $D_{i,j,k}$ is computed from U an V obtained from equations 1.78 and 1.79:

$$D_{i,j} = \frac{U_{i+0.5,j} - U_{i-0.5,j}}{a(1-\mu^2)_j\Delta\lambda} + \frac{V_{i,j+0.5} - V_{i,j-0.5}}{a\Delta\mu_j} \tag{1.81}$$

where the vertical gridpoint index k is omitted.

1.4.5 Domain filling Trajectories

When computing trajectories the basic problem is the computation of the change of the trajectory position vector $\vec{r}(x, y, z, t)$, a function of position in three-dimensional space and time, in time by integrating the 3-D velocities $\vec{v}(\vec{r}, t)$ along a trajectory path:

$$\frac{D\vec{r}}{Dt} = \vec{v}(\vec{r}, t), \tag{1.82}$$

where $\vec{r}$ is the trajectory position vector and $\vec{v}$ is the 3-dimensional velocity vector. Thus, at each timestep either $\vec{v}(\lambda, \mu, z)$ given at the gaussian grid or its spectral representation in terms of ζ_n^m, D_n^m and the vertical velocity (see section 1.3) has to be interpolated to the trajectory position vector, i. e.:

$$\vec{v}(\lambda, \mu, z) \Longleftrightarrow (\zeta_n^m(z), D_n^m(z), W_n^m(z)) \longrightarrow \vec{v}(\vec{r}) \tag{1.83}$$

The interpolation is done using the spectral transform technique in the horizontal and linear interpolation in the vertical:

1. Transform the vertical velocity W, computed in equation 1.28 on the Gaussian grid to spherical harmonics $W_n^m(z)$.
2. Compute the normalized spherical harmonics $P_n^m(\mu)e^{\imath m\lambda}$ at the horizontal components of the trajectory position vector, where $P_n^m(\mu)$ is computed based on the recurrence relation A.13, starting with

   $$Q_m^m(\mu) = (-1)^m(2m-1)!!\left(1-\mu^2\right)^{m/2}, \tag{1.84}$$

   where the notation $n!!$ denotes the product of all odd integers less than or equal to n [*Press et al.*, 1988].
3. Compute the 3 components of $\vec{v}$ at the horizontal components of $\vec{r}$ based on the transformations 1.46, 1.47 for U and V and A.24 for W using the spherical harmonics computed in step 2.
4. Interpolate the U, V, and W computed in step 3 linearily to the vertical component of $\vec{r}$ yielding to the velocity vector at the trajectory position vector at timestep t, i.e. $\vec{v}(\vec{r}(t), t)$.

The equation of motion 1.82 is integrated in time using the Euler foreward scheme:

$$\frac{\vec{r}(t+1)-\vec{r}(t)}{\Delta t} = \vec{v}(\vec{r}(t), t) \tag{1.85}$$

1.4.6 The Balance Equation

Assuming a horizontally non-divergent flow the divergence equation (1.12) yields the nonlinear balance equation:

$$\vec{\nabla}_p \cdot \left[\left(f + \vec{\nabla}_p^2\Psi\right)\vec{\nabla}_p\Psi\right] = \vec{\nabla}_p^2\left[\Phi + \frac{1}{2}\left(\vec{\nabla}_p\Psi\right)^2\right] \tag{1.86}$$

Equation 1.86 is a diagnostic relationship between the geopotential Φ and the velocity stream function Ψ and is solved in this section to obtain a balanced flow for a given geopotential field. The solution is obtained by linearizing equation 1.86 around a basic state flow Ψ_0 setting

$$\Psi = \Psi_0 + \Psi' \tag{1.87}$$

yielding [e.g. *Haltiner and Williams*, 1980]:

$$\begin{aligned} \vec{\nabla}_p \cdot \left[\left(f + \vec{\nabla}_p^2\Psi_0\right)\vec{\nabla}_p\Psi_0\right] &+ \left(f + 2\vec{\nabla}_p^2\Psi_0\right)\vec{\nabla}_p^2\Psi' \\ &+ \vec{\nabla}_p\left(f + \vec{\nabla}_p^2\Psi_0\right)\cdot\vec{\nabla}_p\Psi' + \vec{\nabla}_p\vec{\nabla}_p^2\Psi'\cdot\vec{\nabla}_p\Psi_0 \\ &= \vec{\nabla}_p^2\left[\Phi + \frac{1}{2}\left(\vec{\nabla}_p\Psi_0\right)^2 + \vec{\nabla}_p\Psi_0\cdot\vec{\nabla}_p\Psi'\right] \end{aligned} \tag{1.88}$$

Assuming in a first approximation a basic state of zero (i.e. $\Psi_0 = 0$) equation 1.88 reduces to

$$f\vec{\nabla}_p^2\Psi' + \vec{\nabla}_p f\cdot\vec{\nabla}_p\Psi' = \vec{\nabla}_p^2\Phi \tag{1.89}$$

In order to solve the equation 1.89 for Ψ' the following steps are applied:

1. The equation 1.89 is developed into coefficients of the spherical harmonics (equation A.24):

$$\left(f\vec{\nabla}_p^2\Psi'\right)_n^m + \left(\vec{\nabla}_p f\cdot\vec{\nabla}_p\Psi'\right)_n^m = \left(\vec{\nabla}_p^2\Phi\right)_n^m \tag{1.90}$$

2. The variables are developed into coefficients of the sperical harmonics (equation A.24). Since $f = 2\Omega\mu$, the following simplifications apply for f and $\vec{\nabla}_p f$:

$$f(\mu) = \sum_{n=0}^{\infty} f_n^0 P_n^0(\mu) \overset{(A.11)}{=} f_1^0 P_1^0(\mu) \qquad \Leftrightarrow \qquad f_1^0 = \frac{f(\mu)}{P_1^0(\mu)} = \frac{2\Omega}{\sqrt{3}} \tag{1.91}$$

$$\vec{j}\cdot\frac{\vec{\nabla}_p f(\mu)}{\sqrt{1-\mu^2}} \overset{(1.118)}{=} \frac{1}{a}\frac{\partial f(\mu)}{\partial\mu} \overset{(f=2\Omega\mu)}{=} \frac{2\Omega}{a} := \beta = \frac{\sqrt{3}f_1^0}{a} \tag{1.92}$$

The streamfunction and the geopotential may be written as:

$$\vec{\nabla}_p^2\Psi'(\lambda,\mu) \overset{(A.22)}{=} \sum_{n=0}^{\infty}\sum_{m=-n}^{n} -\frac{n(n+1)}{a^2}\Psi'^m_n P_n^m(\mu)e^{\imath m\lambda} \tag{1.93}$$

$$\begin{aligned}
\vec{j}\cdot\sqrt{1-\mu^2}\vec{\nabla}_p\Psi'(\lambda,\mu) &\overset{(1.118)}{=} \frac{(1-\mu^2)}{a}\frac{\partial\Psi'(\lambda,\mu)}{\partial\mu} \\
&\overset{(A.24)}{=} \frac{(1-\mu^2)}{a}\frac{\partial}{\partial\mu}\left(\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\Psi'^m_n P^m_n(\mu)e^{\imath m\lambda}\right) \\
&= \frac{(1-\mu^2)}{a}\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\left\{\Psi'^m_n e^{\imath m\lambda}\frac{\partial P^m_n(\mu)}{\partial\mu}\right\} \\
&\overset{(A.20)}{=} -\frac{1}{a}\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\Psi'^m_n H^m_n(\mu)e^{\imath m\lambda} \qquad (1.94)
\end{aligned}$$

$$\vec{\nabla}^2_p\Phi(\lambda,\mu) \overset{(A.22)}{=} \sum_{n=0}^{\infty}\sum_{m=-n}^{n} -\frac{n(n+1)}{a^2}\Phi^m_n P^m_n(\mu)e^{\imath m\lambda} \qquad (1.95)$$

where $H^m_n(\mu)$ is given by equation A.20.

3. Using the equations 1.91-1.95 the single terms of equation 1.90 become by means of equation A.25: The first term of equation 1.90 may be written as:

$$\begin{aligned}
&\left(f\vec{\nabla}^2_p\Psi'\right)^k_l = \\
&= \frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi} f\vec{\nabla}^2_p\Psi' P^k_l(\mu)e^{-\imath k\lambda}d\lambda d\mu \\
&= -\frac{f^0_1}{a^2}\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\left\{\Psi'^m_n\frac{n(n+1)}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi}P^0_1(\mu)P^m_n(\mu)P^k_l(\mu)e^{\imath m\lambda}e^{-\imath k\lambda}d\lambda d\mu\right\} \\
&= -\frac{f^0_1}{a^2}\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\left\{\Psi'^m_n\;[n(n+1)]\;\frac{1}{2}\int_{-1}^{+1}P^0_1(\mu)P^m_n(\mu)P^k_l(\mu)d\mu\;\frac{1}{2\pi}\int_{0}^{2\pi}e^{\imath(m-k)\lambda}d\lambda\right\} \\
&\overset{(A.23)}{=} -\frac{f^0_1}{a^2}\sum_{n=0}^{\infty}\left\{\Psi'^k_n\;[n(n+1)]\;\frac{1}{2}\int_{-1}^{+1}P^0_1(\mu)P^k_n(\mu)P^k_l(\mu)d\mu\right\} \qquad (1.96)
\end{aligned}$$

Since $P^0_1(\mu) = \sqrt{3}\mu$ from equation A.18 using A.11 and A.17, the last integral in equation 1.96 may be written as

$$\frac{1}{2}\int_{-1}^{+1}P^0_1(\mu)P^k_n(\mu)P^k_l(\mu)d\mu$$

$$\overset{(A.19)}{=} \sqrt{3}\frac{1}{2}\int_{-1}^{+1}\left[\epsilon_{n+1}^{k}P_{n+1}^{k}(\mu)+\epsilon_{n}^{k}P_{n-1}^{k}(\mu)\right]P_{l}^{k}(\mu)d\mu$$

$$\overset{(A.23)}{=} \begin{cases} \sqrt{3}\epsilon_{l+1}^{k} & \text{for } n=l+1 \\ \sqrt{3}\epsilon_{l}^{k} & \text{for } n=l-1 \\ 0 & \text{else} \end{cases} \tag{1.97}$$

Combining equations 1.97 and 1.96 yields finally:

$$\left(f\vec{\nabla}_p^2\Psi'\right)_l^k = -\frac{\sqrt{3}f_1^0}{a^2}\left[(l-1)l\Psi'^{k}_{l-1}\epsilon_l^k+(l+1)(l+2)\Psi'^{k}_{l+1}\epsilon_{l+1}^k\right] \tag{1.98}$$

The second term of equation 1.90 may be written as:

$$\left(\vec{\nabla}_p f\cdot\vec{\nabla}_p\Psi'\right)_l^k =$$

$$= -\frac{\beta}{a}\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\left\{\Psi'^{m}_{n}\frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi}H_n^m(\mu)P_l^k(\mu)e^{\imath(m-k)\lambda}d\lambda d\mu\right\}$$

$$\overset{(A.23)}{=} -\frac{\beta}{a}\sum_{n=0}^{\infty}\left\{\Psi'^{k}_{n}\frac{1}{2}\int_{-1}^{+1}H_n^k(\mu)P_l^k(\mu)d\mu\right\}$$

$$\overset{(A.20)}{=} -\frac{\beta}{a}\sum_{n=0}^{\infty}\left\{\Psi'^{k}_{n}\frac{1}{2}\int_{-1}^{+1}\left[n\epsilon_{n+1}^k P_{n+1}^k(\mu)-(n+1)\epsilon_n^k P_{n-1}^k(\mu)\right]P_l^k(\mu)d\mu\right\}$$

$$\overset{(A.23)}{=} -\frac{\beta}{a}\left\{\Psi'^{k}_{l-1}(l-1)\epsilon_l^k-\Psi'^{k}_{l+1}(l+2)\epsilon_{l+1}^k\right\} \tag{1.99}$$

where ϵ_n^m is defined by equation A.21

4. Inserting equations 1.98 and 1.99 into equation 1.90 yields a set of equations for the spherical harmonic coefficients of Ψ' and Φ of the form:

$$\Gamma_{n+1}^m\Psi'^{m}_{n+1}+\Gamma_n^m\Psi'^{m}_{n-1}=\left(\vec{\nabla}_p^2\Phi\right)_n^m \tag{1.100}$$

for $-\infty\leq m\leq\infty$, $|m|\leq n\leq\infty$ and where Γ_n^m are computed from equations 1.98 and 1.99. In equation 1.100 Γ_n^m is defined by

$$\Gamma_n^m=\frac{\beta}{a}\epsilon_n^m\left(1-n^2\right) \tag{1.101}$$

using the equations 1.91 and 1.92.

The equations 1.100 can numerically be solved for Ψ' seperately for the orders m and simulteneously for the degrees n of the associated Legendre polynomials truncating the infinite number of equations after $m = M$ and $n = N$. Since the equations 1.100 can be solved for a given m only if the resulting number of equations for n is even, the triangular truncation scheme described in Section 1.3.1 cannot be applied here. Therefore a rhomboidal truncation scheme is used setting $M = 0.5N_{\max}$ and $N = |m| + M$, ensuring that M is odd.

1.4.7 List of Symbols

a	Radius of the earth $(a = 6366\ km)$
c_p	Specific heat of dry air at constant pressure $(c_p = 1005\ J\ kg^{-1}\ K^{-1})$
D	Horizontal divergence $\begin{aligned} D &= \vec{\nabla}_p \cdot \vec{v}_h = \vec{\nabla}_p^2 \chi \\ &= \frac{1}{a\cos\varphi}\frac{\partial u}{\partial\lambda} + \frac{1}{a\cos\varphi}\frac{\partial v\cos\varphi}{\partial\varphi} \\ &= \frac{1}{a(1-\mu^2)}\frac{\partial U}{\partial\lambda} + \frac{1}{a}\frac{\partial V}{\partial\mu} \qquad (1.102) \end{aligned}$
$\frac{D\alpha}{Dt}$	time rate of change of α following the motion 1.The advection form: $\begin{aligned} \frac{D\alpha}{Dt} &= \frac{\partial\alpha}{\partial t} + \vec{v}_h \cdot \vec{\nabla}_p\alpha + w\frac{\partial\alpha}{\partial z} \\ &= \frac{\partial\alpha}{\partial t} + \frac{u}{a\cos\varphi}\frac{\partial\alpha}{\partial\lambda} + \frac{v}{a}\frac{\partial\alpha}{\partial\varphi} + w\frac{\partial\alpha}{\partial z} \\ &= \frac{\partial\alpha}{\partial t} + \frac{U}{a(1-\mu^2)}\frac{\partial\alpha}{\partial\lambda} + \frac{V}{a}\frac{\partial\alpha}{\partial\mu} + w\frac{\partial\alpha}{\partial z} \qquad (1.103) \end{aligned}$ 2.The flux form is obtained using equation 1.4: $\begin{aligned} \frac{D\alpha}{Dt} &= \frac{\partial\alpha}{\partial t} + \vec{\nabla}_p \cdot (\vec{v}_h\alpha) + \frac{1}{\rho_0}\frac{\partial\rho_0 w\alpha}{\partial z} \\ &= \frac{\partial\alpha}{\partial t} + \frac{1}{a\cos\varphi}\left(\frac{\partial u\alpha}{\partial\lambda} + \frac{\partial v\alpha\cos\varphi}{\partial\varphi}\right) \\ &\quad + \frac{1}{\rho_0}\frac{\partial\rho_0 w\alpha}{\partial z} \\ &= \frac{\partial\alpha}{\partial t} + \frac{1}{a(1-\mu^2)}\frac{\partial U\alpha}{\partial\lambda} + \frac{1}{a}\frac{\partial V\alpha}{\partial\mu} + \frac{1}{\rho_0}\frac{\partial\rho_0 w\alpha}{\partial z} \qquad (1.104) \end{aligned}$

f	Coriolis Parameter $(f = 2\Omega \sin\varphi = 2\Omega\mu)$	
$\vec{F},\ F_\lambda,\ F_\varphi$	Additional forces in zonal and meridional direction, respectively	
F_ζ	$F_\zeta = \vec{k} \cdot \vec{\nabla}_p \times \vec{F}$	(1.105)
F_D	$F_D = \vec{\nabla}_p \cdot \vec{F}$	(1.106)
H	Atmospheric Scale Height $(H = 7\ km)$	
I_{grid}	No. of zonal gridpoints	
J_{grid}	No. of meridional gridpoints	
k_{grid}	No. of model layers	
$\vec{i}$	Zonal unit vector	
$\vec{j}$	Meridional unit vector	
$\vec{k}$	Vertical unit vector	
$N_{\max}$	Maximum degree of associated Legendre polynomials	
p	Pressure	
p_0	Constant reference pressure $(p_0 = 1013\ hPa)$	
T	Temperature	
$T^*(z)$	Reference temperature (US-Standard Atmosphere)	
Q	Net Heating Rate	
R	Gas constant of dry air $(R = 287.04\ J\ kg^{-1}\ K^{-1})$	
u	Zonal component of velocity	
	$u = \frac{1}{a\cos\varphi}\frac{\partial\chi}{\partial\lambda} - \frac{1}{a}\frac{\partial\Psi}{\partial\varphi} = \frac{1}{a\sqrt{1-\mu^2}}\frac{\partial\chi}{\partial\lambda} - \frac{\sqrt{1-\mu^2}}{a}\frac{\partial\Psi}{\partial\mu}$	(1.107)
U		
	$\begin{aligned} U &= u\cos\varphi \\ &= \frac{1}{a}\frac{\partial\chi}{\partial\lambda} - \frac{\cos\varphi}{a}\frac{\partial\Psi}{\partial\varphi} \\ &= \frac{1}{a}\frac{\partial\chi}{\partial\lambda} - \frac{(1-\mu^2)}{a}\frac{\partial\Psi}{\partial\mu} \end{aligned}$	(1.108)

v Meridional component of velocity

$$v = \frac{1}{a}\frac{\partial \chi}{\partial \varphi} + \frac{1}{a\cos\varphi}\frac{\partial \Psi}{\partial \lambda} = \frac{\sqrt{1-\mu^2}}{a}\frac{\partial \chi}{\partial \mu} + \frac{1}{a\sqrt{1-\mu^2}}\frac{\partial \Psi}{\partial \lambda} \tag{1.109}$$

V

$$\begin{aligned} V &= v\cos\varphi \\ &= \frac{\cos\varphi}{a}\frac{\partial \chi}{\partial \varphi} + \frac{1}{a}\frac{\partial \Psi}{\partial \lambda} \\ &= \frac{(1-\mu^2)}{a}\frac{\partial \chi}{\partial \mu} + \frac{1}{a}\frac{\partial \Psi}{\partial \lambda} \end{aligned} \tag{1.110}$$

$\vec{v}$ Three dimensional velocity vector $(\vec{v} = u\vec{i} + v\vec{j} + w\vec{k})$

$\vec{v}_h$ Horizontal velocity vector on pressure surface

$$\vec{v}_h = u\vec{i} + v\vec{j} = \vec{\nabla}_p\chi + \vec{k} \times \vec{\nabla}_p\Psi \tag{1.111}$$

w Vertical component of velocity

W $W = \rho_0 w$ (1.112)

z Vertical coordinate $(z = -H\ln(p/p_0))$

γ Conversion factor between temperature and potential temperature:

$$\theta = \gamma(z)T = \exp\left(\frac{\kappa z}{H}\right)T \tag{1.113}$$

χ Horizontal velocity potential on pressure surface (see equation 1.102)

Δt Timestep

Δz Distance between 2 model layers

$\Delta\lambda$ Distance between 2 zonal gridpoints

$$\Delta\lambda = \frac{2\pi}{I_{grid}} \tag{1.114}$$

$\Delta\mu_i$ Gaussian weight at $\mu = \mu_i$

$$\Delta\mu_i = \frac{2}{(1-\mu_i^2)^2\left[P_n'(\mu_i)\right]^2} \tag{1.115}$$

Φ Geopotential

φ	Geographical latitude
κ	Ratio of gas constant over specific heat at constant pressure of dry air ($\kappa = R/c_p$)
λ	Geographical longitude
μ	Alternate meridional coordinate $\mu = \sin(\varphi)$ $\mu = \sin\varphi \qquad (1.116)$
Ψ	Vertical component of velocity stream function (see equation 1.117)
ρ_0	Basic state density ($\rho_0 \sim \exp(-z/H)$)
Ω	Absolute value of angular velocity of the earth $\Omega = 2\pi day^{-1}$
$\vec{\Omega}$	Angular velocity of the earth
ζ	Relative vorticity $\begin{aligned} \zeta &= \vec{k}\cdot\vec{\nabla}_p \times \vec{v}_h = \vec{\nabla}_p^2 \Psi \\ &= \frac{1}{a\cos\varphi}\frac{\partial v}{\partial\lambda} - \frac{1}{a\cos\varphi}\frac{\partial u\cos\varphi}{\partial\varphi} \\ &= \frac{1}{a(1-\mu^2)}\frac{\partial V}{\partial\lambda} - \frac{1}{a}\frac{\partial U}{\partial\mu} \qquad (1.117) \end{aligned}$
ζ_a	Absolute vorticity ($\zeta_a = \zeta + f$)
$\vec{\nabla}_p\alpha$	Gradient of any scalar α on constant pressure surface $\begin{aligned} \vec{\nabla}_p\alpha &= \frac{1}{a\cos\varphi}\frac{\partial\alpha}{\partial\lambda}\vec{i} + \frac{1}{a}\frac{\partial\alpha}{\partial\varphi}\vec{j} \\ &= \frac{1}{a\sqrt{1-\mu^2}}\frac{\partial\alpha}{\partial\lambda}\vec{i} + \frac{\sqrt{1-\mu^2}}{a}\frac{\partial\alpha}{\partial\mu}\vec{j} \qquad (1.118) \end{aligned}$
$\vec{\nabla}_p\cdot\vec{\alpha}$	Divergence of $\vec{\alpha} = \alpha_\lambda\vec{i} + \alpha_\varphi\vec{j}$ on pressure surface $\begin{aligned} \vec{\nabla}_p\cdot\vec{\alpha} &= \frac{1}{a\cos\varphi}\frac{\partial\alpha_\lambda}{\partial\lambda} + \frac{1}{a\cos\varphi}\frac{\partial\alpha_\varphi\cos\varphi}{\partial\varphi} \\ &= \frac{1}{a\sqrt{1-\mu^2}}\frac{\partial\alpha_\lambda}{\partial\lambda} + \frac{1}{a}\frac{\partial\alpha_\varphi\sqrt{1-\mu^2}}{\partial\mu} \qquad (1.119) \end{aligned}$

$\vec{\nabla}_p \times \vec{\alpha}$ Vertical component of $\vec{\nabla} \times \vec{\alpha}$, $\vec{\alpha} = \alpha_\lambda \vec{i} + \alpha_\varphi \vec{j}$ on pressure surface

$$\begin{aligned}
\vec{\nabla}_p \times \vec{\alpha} &= \vec{k} \cdot \vec{\nabla} \times \vec{\alpha} \\
&= \frac{1}{a\cos\varphi}\frac{\partial \alpha_\varphi}{\partial \lambda} - \frac{1}{a\cos\varphi}\frac{\partial \alpha_\lambda \cos\varphi}{\partial \varphi} \\
&= \frac{1}{a\sqrt{1-\mu^2}}\frac{\partial \alpha_\varphi}{\partial \lambda} - \frac{1}{a}\frac{\partial \alpha_\lambda \sqrt{1-\mu^2}}{\partial \mu} \qquad (1.120)
\end{aligned}$$

$\vec{\nabla}_p^2 \alpha$ Horizontal Laplacian of α on pressure surface

$$\begin{aligned}
\vec{\nabla}_p^2 \alpha &= \vec{\nabla}_p \cdot \vec{\nabla}_p \alpha \\
&= \frac{1}{a^2\cos^2\varphi}\frac{\partial^2 \alpha}{\partial \lambda^2} + \frac{1}{a^2\cos\varphi}\frac{\partial}{\partial \varphi}\left[\cos\varphi \frac{\partial \alpha}{\partial \varphi}\right] \\
&= \frac{1}{a^2(1-\mu^2)}\frac{\partial^2 \alpha}{\partial \lambda^2} + \frac{1}{a^2}\frac{\partial}{\partial \mu}\left[\left(1-\mu^2\right)\frac{\partial \alpha}{\partial \mu}\right] \qquad (1.121)
\end{aligned}$$

2 The Chemistry

2.1 General

Any chemical reaction l can be written as

$$\sum_{i=1}^{n} \nu_{il} Reactant_i \rightarrow \sum_{i=1}^{n} \mu_{il} Product_i \tag{2.1}$$

where n denotes the number of the species. ν_{il} and μ_{il} represent the stoichiometric coefficients of the reactants and products, respectively. The rate of the reaction l at the time t is defined as the product of the concentrations of the reactants $c_i(t)$ which are involved in the reaction l multiplied by the reaction rate constant k_l:

$$r_l(t) = k_l \prod_{i=1}^{n} c_{il}^{\nu_{il}}(t) \tag{2.2}$$

Since most of the species in the atmosphere are produced and destroyed in more than one reaction the production and loss rate of a species i is defined by the sum of the rates of the reactions in which the species i is produced or destroyed:

$$P_i(t) = \sum_{l=1}^{m} \mu_{il} r_l(t) \tag{2.3}$$

$$L_i(t) = \sum_{l=1}^{m} \nu_{il} r_l(t) \tag{2.4}$$

The time development of the concentration c_i of a species i due to chemistry is given by

$$\frac{\partial c_i(t)}{\partial t} = P_i(t) - L_i^{'}(t) c_i(t) \tag{2.5}$$

where $L_i^{'}(t)$ denotes the loss frequency which is obtained by dividing the loss rate $L_i(t)$ by the concentration of the species i:

$$L_i^{'}(t) = \frac{L_i(t)}{c_i(t)} \tag{2.6}$$

The photochemical lifetime τ_i is defined by the reciprocal of the loss frequency.

$$\tau_i = \frac{1}{L_i'(t)} \tag{2.7}$$

2.2 The Numerical Solver in KASIMA

The chemical scheme uses the family concept, which groups related chemical species with short photochemical lifetimes together in order to remove pairs of large reaction rates from the system and thus to increase the chemical timestep. The photochemical lifetime also determines the species which have to be transported. If the photochemical lifetime is large compared to the characteristic time constants for transport the species have to be transported separately whereas the species with a short photochemical lifetime and large production and destruction rate can be grouped together. Within these families the exchange rates are large but the overall rates of exchange between the families are small. Therefore, only the family itself has to be transported.

The method to calculate the concentrations of the advected and non-advected species in KASIMA is as follows:

The changes of the concentration of the chemical species are obtained by the method of operator splitting at the model gridpoints. First, the tendencies of the long-lived tracers due to transport are calculated (see section 1.4.4). Then, the chemical tendencies are calculated in order to modify the long-lived tracer distributions and to get the concentrations of the short-lived species.

The concentrations of the transported (long-lived) species are calculated via an iterative Euler backward approximation of the chemical differential equation (2.5) with the transport timestep Δt and the iteration number k (superscript) with $k = 1, ..., (K-1)$:

$$\frac{c_i^1 - c_i(t)}{\Delta t} = P_i(t) - L_i'(t)c_i(t) \tag{2.8}$$

$$\frac{c_i^{k+1} - c_i(t)}{\Delta t} = P_i^k - L_i'^k c_i^k \tag{2.9}$$

The solution for $k+1 = K$ is considered as the $t + \Delta t$ solution of the Euler backward approximation. Within the iteration the concentrations of the constituents of the families, the diagnostic species, are calculated via the analytical expression of the differential equation first:

$$c_i(t+\Delta t') = \frac{P_i(t)}{L_i'(t)} + \left(c_i(t) - \frac{P_i(t)}{L_i'(t)}\right) \exp^{-L_i'(t)\Delta t'} \tag{2.10}$$

Due to numerical reasons we split the integration of the diagnostic species into N substeps. Intermediate solutions for all diagnostic species are calculated successively with the timestep $\Delta t'$ = $\Delta t/(N * K)$. Sensitivity tests performed using a box-model [*Ruhnke and Röth*, 1995] show that it is adequate to take $K = 3$ and $N = 5$ to coincide with the results of the accurate box model simulations. Due to the finite number of iterations the iterative solution to the calculation of the concentration of the long-lived and short-lived species is not exact and some deviation from mass conservation may occur. Thus, to ensure mass conservation a scaling factor representing the ratio of the concentrations of the family constituents to the family concentration has to be applied. The scaling factor of each family member is defined by dividing the family concentration c_{family} by the sum of the concentrations of the individual members.

$$fac = \frac{c_{family}}{\sum_{i=1}^{n} c_i(t)} \tag{2.11}$$

2.3 The Chemistry Scheme

For the purpose of modeling the behavior of the stratospheric ozone with KASIMA a detailed chemistry scheme was developed. The scheme includes the gas phase reactions of the HO_x, NO_x, ClO_x and BrO_x families and the oxidation of methane as well as a parameterization of heterogeneous reactions on aerosols. The scheme consists of 58 chemical species and families which are involved in 101 bi- or termolecular reactions, 39 photodissociations, and 10 heterogeneous reactions on liquid sulfuric acid, nitric acid trihydrate (NAT) and ice.

2.3.1 The Chemical Constituents

The species involved in the reactions are divided into two groups, the prognostic species which are transported and the diagnostic species.

Prognostic Species	Diagnostic Species
H_2O	O_3
H_2O_2	$O(^3P)$
N_2O_5	$O(^1D)$
HONO	OH
HNO_3	H
HO_2NO_2	HO_2
N_2O	N
CH_4	NO

Prognostic Species	Diagnostic Species
CO	NO_2
CH_2O	NO_3
CH_3OOH	CH_3O_2
$CH_3O_2NO_2$	Cl
Cl_2	ClO
OClO	Cl_2O_2
HCl	Br
HOCl	BrO
$ClNO_2$	HO_x
$ClONO_2$	
BrCl	
HBr	
HOBr	
$BrONO_2$	
O_x	
NO_x	
ClO_x	
BrO_x	
NO_y	
Cl_y	
Br_y	
H_2SO_4	

The concentrations of the most important source gases for the ClO_x- and BrO_x-radicals in the stratosphere (i.e. CH_3Cl, CH_3CCl_3, CCl_4, $CFCl_3$, CF_2Cl_2 and CH_3Br) are prescribed as a function of latitude and height according to 2-D-model results.
Trace species with constant mixing ratios:

$$[\mathrm{N_2}] = 0.78 \times [\mathrm{M}] \tag{2.12}$$

$$[\mathrm{O_2}] = 0.21 \times [\mathrm{M}] \tag{2.13}$$

$$[\mathrm{CO_2}] = 3.5 \times 10^{-4} \times [\mathrm{M}] \tag{2.14}$$

$$[\mathrm{H_2}] = 5.0 \times 10^{-7} \times [\mathrm{M}] \tag{2.15}$$

$[\mathrm{M}]$ denotes the air concentration.

2.3.2 The Gas Phase Reactions

The following gas phase reactions are included in the model. The rate constants are taken from the compilation of *DeMore et al.* [1997].

No.	Reaction	Rate Constant
R. 1	$O(^3P) + O(^3P) + M \longrightarrow O_2 + M$	$k_1 = 4.70 \times 10^{-33} (T/300)^{-2.0}$
R. 2	$O(^3P) + O_2 + M \longrightarrow O_3 + M$	$k_2 = 6.00 \times 10^{-34} (T/300)^{-2.3}$
R. 3	$O(^3P) + O_3 \longrightarrow O_2 + O_2$	$k_3 = 8.00 \times 10^{-12} \exp(-2060/T)$
R. 4	$O(^1D) + N_2 \longrightarrow O(^3P) + N_2$	$k_4 = 1.80 \times 10^{-11} \exp(110/T)$
R. 5	$O(^1D) + O_2 \longrightarrow O(^3P) + O_2$	$k_5 = 3.20 \times 10^{-11} \exp(70/T)$
R. 6	$O(^1D) + H_2O \longrightarrow OH + OH$	$k_6 = 2.20 \times 10^{-10}$
R. 7	$O(^1D) + H_2 \longrightarrow OH + H$	$k_7 = 1.10 \times 10^{-10}$
R. 8	$H + O_2 + M \longrightarrow HO_2 + M$	$k_{8,0} = 5.70 \times 10^{-32} (T/300)^{-1.6}$
		$k_{8,\infty} = 7.50 \times 10^{-11}$
R. 9	$H + O_3 \longrightarrow OH + O_2$	$k_9 = 1.40 \times 10^{-10} \exp(-470/T)$
R. 10	$H + HO_2 \longrightarrow OH + OH$	$k_{10} = 6.50 \times 10^{-11}$
R. 11	$H + HO_2 \longrightarrow H_2 + O_2$	$k_{11} = 1.20 \times 10^{-11}$
R. 12	$H + HO_2 \longrightarrow H_2O + O(^3P)$	$k_{12} = 4.00 \times 10^{-12}$
R. 13	$O(^3P) + OH \longrightarrow O_2 + H$	$k_{13} = 2.20 \times 10^{-11} \exp(120/T)$
R. 14	$O(^3P) + HO_2 \longrightarrow OH + O_2$	$k_{14} = 3.00 \times 10^{-11} \exp(200/T)$
R. 15	$OH + HO_2 \longrightarrow H_2O + O_2$	$k_{15} = 4.80 \times 10^{-11} \exp(250/T)$
R. 16	$OH + O_3 \longrightarrow HO_2 + O_2$	$k_{16} = 1.60 \times 10^{-12} \exp(-940/T)$
R. 17	$OH + H_2O_2 \longrightarrow H_2O + HO_2$	$k_{17} = 2.90 \times 10^{-12} \exp(-160/T)$
R. 18	$OH + H_2 \longrightarrow H_2O + H$	$k_{18} = 5.50 \times 10^{-12} \exp(-2000/T)$
R. 19	$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	$k_{19} = 2.30 \times 10^{-13} \exp(600/T)$
R. 20	$HO_2 + O_3 \longrightarrow OH + O_2 + O_2$	$k_{20} = 1.10 \times 10^{-14} \exp(-500/T)$
R. 21	$O(^1D) + N_2O \longrightarrow N_2 + O_2$	$k_{21} = 4.90 \times 10^{-11}$
R. 22	$O(^1D) + N_2O \longrightarrow NO + NO$	$k_{22} = 6.70 \times 10^{-11}$
R. 23	$N + O_2 \longrightarrow NO + O(^3P)$	$k_{23} = 1.50 \times 10^{-11} \exp(-3600/T)$
R. 24	$N + NO \longrightarrow N_2 + O(^3P)$	$k_{24} = 2.10 \times 10^{-11} \exp(100/T)$
R. 25	$O(^3P) + NO_2 \longrightarrow NO + O_2$	$k_{25} = 6.50 \times 10^{-12} \exp(120/T)$
R. 26	$O_3 + NO \longrightarrow NO_2 + O_2$	$k_{26} = 2.00 \times 10^{-12} \exp(-1400/T)$
R. 27	$NO + HO_2 \longrightarrow NO_2 + OH$	$k_{27} = 3.50 \times 10^{-12} \exp(250/T)$
R. 28	$OH + NO_2 + M \longrightarrow HNO_3 + M$	$k_{28,0} = 2.50 \times 10^{-30} (T/300)^{-4.4}$
		$k_{28,\infty} = 1.60 \times 10^{-11} (T/300)^{-1.7}$
R. 29	$OH + HNO_3 \longrightarrow H_2O + NO_3$	$k_{29,0} = 7.20 \times 10^{-15} \exp(785/T)$

No.	Reaction	Rate Constant
		$k_{29,1} = 4.10 \times 10^{-16} \exp(1440/T)$
		$k_{29,2} = 1.90 \times 10^{-33} \exp(725/T)$
R. 30	$OH + HO_2NO_2 \longrightarrow Products(H_2O + NO_2 + O_2)$	$k_{30} = 1.30 \times 10^{-12} \exp(380/T)$
R. 31	$HO_2 + NO_2 + M \longrightarrow HO_2NO_2 + M$	$k_{31,0} = 1.80 \times 10^{-31} (T/300)^{-3.2}$
		$k_{31,\infty} = 4.70 \times 10^{-12} (T/300)^{-1.4}$
R. 32	$O_3 + NO_2 \longrightarrow NO_3 + O_2$	$k_{32} = 1.20 \times 10^{-13} \exp(-2450/T)$
R. 33	$NO_2 + NO_3 + M \longrightarrow N_2O_5 + M$	$k_{33} = 2.20 \times 10^{-30} (T/300)^{-3.9}$
		$k_{33,\infty} = 1.50 \times 10^{-12} (T/300)^{-0.7}$
R. 34	$N_2O_5 + M \longrightarrow NO_2 + NO_3 + M$	$k_{34} = k_{33}/2.70 \times 10^{-27} \exp(11000/T)$
R. 35	$HO_2NO_2 + M \longrightarrow HO_2 + NO_2 + M$	$k_{35} = k_{31}/2.10 \times 10^{-27} \exp(10900/T)$
R. 36	$OH + NO + M \longrightarrow HONO + M$	$k_{36,0} = 7.00 \times 10^{-31} (T/300)^{-2.6}$
		$k_{36,\infty} = 3.60 \times 10^{-11} (T/300)^{-0.1}$
R. 37	$OH + HONO \longrightarrow H_2O + NO_2$	$k_{37} = 1.80 \times 10^{-11} \exp(-390/T)$
R. 38	$O(^1D) + CH_4(+O_2) \longrightarrow OH + CH_3O_2$	$k_{38} = 1.125 \times 10^{-10}$
R. 39	$O(^1D) + CH_4 \longrightarrow H_2 + CH_2O$	$k_{39} = 3.75 \times 10^{-11}$
R. 40	$OH + CO \longrightarrow H + CO_2$	$k_{40} = 1.50 \times 10^{-13} (1 + 0.6 P_{atm})$
R. 41	$OH + CH_4(+O_2) \longrightarrow CH_3O_2 + H_2O$	$k_{41} = 2.45 \times 10^{-12} \exp(-1775/T)$
R. 42	$OH + CH_2O(+O_2) \longrightarrow H_2O + CO + HO_2$	$k_{42} = 1.00 \times 10^{-11}$
R. 43	$OH + CH_3OOH \longrightarrow H_2O + CH_3O_2$	$k_{43} = 2.70 \times 10^{-12} \exp(200/T)$
R. 44	$OH + CH_3OOH \longrightarrow H_2O + CH_2O + OH$	$k_{44} = 1.10 \times 10^{-12} \exp(200/T)$
R. 45	$O(^3P) + CH_2O \longrightarrow Products(OH + CO + HO_2)$	$k_{45} = 3.40 \times 10^{-11} \exp(-1600/T)$
R. 46	$CH_3O_2 + CH_3O_2 \longrightarrow 2 \cdot CH_2O + 2 \cdot HO_2$	$k_{46} = 2.50 \times 10^{-13} \exp(190/T)$
R. 47	$CH_3O_2 + NO(+O_2) \longrightarrow CH_2O + HO_2 + NO_2$	$k_{47} = 3.00 \times 10^{-12} \exp(280/T)$
R. 48	$CH_3O_2 + NO_2 + M \longrightarrow CH_3O_2NO_2 + M$	$k_{48,0} = 1.50 \times 10^{-30} (T/300)^{-4.0}$
		$k_{48,\infty} = 6.50 \times 10^{-12} (T/300)^{-2.0}$
R. 49	$CH_3O_2 + HO_2 \longrightarrow CH_3OOH + O_2$	$k_{49} = 3.80 \times 10^{-13} \exp(800/T)$
R. 50	$CH_3O_2NO_2 + M \longrightarrow CH_3O_2 + NO_2 + M$	$k_{50} = k_{48}/1.30 \times 10^{-28} \exp(11200/T)$
R. 51	$O(^3P) + ClO \longrightarrow Cl + O_2$	$k_{51} = 3.00 \times 10^{-11} \exp(70/T)$
R. 52	$O(^3P) + OClO \longrightarrow ClO + O_2$	$k_{52} = 2.40 \times 10^{-12} \exp(-960/T)$
R. 53	$O(^3P) + HOCl \longrightarrow OH + ClO$	$k_{53} = 1.70 \times 10^{-13}$
R. 54	$O(^3P) + ClONO_2 \longrightarrow Products(OClO + NO_2)$	$k_{54} = 2.90 \times 10^{-12} \exp(-800/T)$
R. 55	$OH + ClO \longrightarrow Products(Cl + HO_2)$	$k_{55} = 1.10 \times 10^{-11} \exp(120/T)$
R. 56	$OH + OClO \longrightarrow HOCl + O_2$	$k_{56} = 4.50 \times 10^{-13} \exp(800/T)$
R. 57	$OH + HCl \longrightarrow H_2O + Cl$	$k_{57} = 2.60 \times 10^{-12} \exp(-350/T)$

No.	Reaction	Rate Constant
R. 58	$\mathrm{OH + HOCl \longrightarrow H_2O + ClO}$	$k_{58} = 3.00 \times 10^{-12} \exp(-500/T)$
R. 59	$\mathrm{HO_2 + Cl \longrightarrow HCl + O_2}$	$k_{59} = 1.80 \times 10^{-11} \exp(170/T)$
R. 60	$\mathrm{HO_2 + Cl \longrightarrow OH + ClO}$	$k_{60} = 4.10 \times 10^{-11} \exp(-450/T)$
R. 61	$\mathrm{HO_2 + ClO \longrightarrow HOCl + O_2}$	$k_{61} = 4.80 \times 10^{-13} \exp(700/T)$
R. 62	$\mathrm{NO + OClO \longrightarrow NO_2 + ClO}$	$k_{62} = 2.50 \times 10^{-12} \exp(-600/T)$
R. 63	$\mathrm{Cl + O_3 \longrightarrow ClO + O_2}$	$k_{63} = 2.90 \times 10^{-11} \exp(-260/T)$
R. 64	$\mathrm{Cl + H_2 \longrightarrow HCl + H}$	$k_{64} = 3.70 \times 10^{-11} \exp(-2300/T)$
R. 65	$\mathrm{Cl + H_2O_2 \longrightarrow HCl + HO_2}$	$k_{65} = 1.10 \times 10^{-11} \exp(-980/T)$
R. 66	$\mathrm{Cl + NO_2 + M \longrightarrow ClNO_2 + M}$	$k_{66,0} = 1.80 \times 10^{-31} (T/300)^{-2.0}$
		$k_{66,\infty} = 1.00 \times 10^{-10} (T/300)^{-1.0}$
R. 67	$\mathrm{Cl + CH_4(+O_2) \longrightarrow HCl + CH_3O_2}$	$k_{67} = 1.10 \times 10^{-11} \exp(-1400/T)$
R. 68	$\mathrm{Cl + CH_2O(+O_2) \longrightarrow HCl + CO + HO_2}$	$k_{68} = 8.10 \times 10^{-11} \exp(-30/T)$
R. 69	$\mathrm{Cl + CH_3O_2(+O_2) \longrightarrow ClO + CH_2O + HO_2}$	$k_{69} = 8.00 \times 10^{-11}$
R. 70	$\mathrm{Cl + CH_3O_2 \longrightarrow HCl + CH_2O + O_2}$	$k_{70} = 8.00 \times 10^{-11}$
R. 71	$\mathrm{Cl + OClO \longrightarrow ClO + ClO}$	$k_{71} = 3.40 \times 10^{-11} \exp(160/T)$
R. 72	$\mathrm{Cl + HOCl \longrightarrow} \; Products(\mathrm{OH + Cl_2})$	$k_{72} = 2.50 \times 10^{-12} \exp(-130/T)$
R. 73	$\mathrm{ClO + NO \longrightarrow NO_2 + Cl}$	$k_{73} = 6.40 \times 10^{-12} \exp(290/T)$
R. 74	$\mathrm{ClO + NO_2 + M \longrightarrow ClONO_2 + M}$	$k_{74,0} = 1.80 \times 10^{-31} (T/300)^{-3.4}$
		$k_{74,\infty} = 1.50 \times 10^{-11} (T/300)^{-1.9}$
R. 75	$\mathrm{ClO + CH_3O_2(+O_2) \longrightarrow Cl + CH_2O + HO_2}$	$k_{75} = 3.30 \times 10^{-12} \exp(-115/T)$
R. 76	$\mathrm{ClO + ClO \longrightarrow Cl_2 + O_2}$	$k_{76} = 1.00 \times 10^{-12} \exp(-1590/T)$
R. 77	$\mathrm{ClO + ClO \longrightarrow Cl + O_2 + Cl}$	$k_{77} = 3.00 \times 10^{-11} \exp(-2450/T)$
R. 78	$\mathrm{ClO + ClO \longrightarrow OClO + Cl}$	$k_{78} = 3.50 \times 10^{-13} \exp(-1370/T)$
R. 79	$\mathrm{ClO + ClO + M \longrightarrow Cl_2O_2 + M}$	$k_{79,0} = 2.20 \times 10^{-32} (T/300)^{-3.1}$
		$k_{79,\infty} = 3.50 \times 10^{-12} (T/300)^{-1.0}$
R. 80	$\mathrm{Cl_2O_2 + M \longrightarrow ClO + ClO + M}$	$k_{80} = k_{79}/1.30 \times 10^{-27} \exp(8744/T)$
R. 81	$\mathrm{O(^3P) + BrO \longrightarrow Br + O_2}$	$k_{81} = 1.90 \times 10^{-11} \exp(230/T)$
R. 82	$\mathrm{O(^3P) + HOBr \longrightarrow OH + BrO}$	$k_{82} = 1.20 \times 10^{-12} \exp(-430/T)$
R. 83	$\mathrm{OH + HBr \longrightarrow H_2O + Br}$	$k_{83} = 1.10 \times 10^{-11}$
R. 84	$\mathrm{HO_2 + Br \longrightarrow HBr + O_2}$	$k_{84} = 1.50 \times 10^{-11} \exp(-600/T)$
R. 85	$\mathrm{HO_2 + BrO \longrightarrow} \; Products(\mathrm{HOBr + O_2})$	$k_{85} = 3.40 \times 10^{-12} \exp(540/T)$
R. 86	$\mathrm{Br + O_3 \longrightarrow BrO + O_2}$	$k_{86} = 1.70 \times 10^{-11} \exp(-800/T)$
R. 87	$\mathrm{Br + CH_2O(+O_2) \longrightarrow HBr + CO + HO_2}$	$k_{87} = 1.70 \times 10^{-11} \exp(-800/T)$
R. 88	$\mathrm{Br + OClO \longrightarrow BrO + ClO}$	$k_{88} = 2.60 \times 10^{-11} \exp(-1300/T)$

No.	Reaction	Rate Constant
R. 89	$BrO + NO \longrightarrow NO_2 + Br$	$k_{89} = 8.80 \times 10^{-12} \exp(260/T)$
R. 90	$BrO + NO_2 + M \longrightarrow BrONO_2 + M$	$k_{90,0} = 5.20 \times 10^{-31} (T/300)^{-3.2}$
		$k_{90,\infty} = 6.90 \times 10^{-12} (T/300)^{-2.9}$
R. 91	$BrO + ClO \longrightarrow Br + OClO$	$k_{91} = 1.60 \times 10^{-12} \exp(430/T)$
R. 92	$BrO + ClO \longrightarrow Br + Cl + O_2$	$k_{92} = 2.90 \times 10^{-12} \exp(220/T)$
R. 93	$BrO + ClO \longrightarrow BrCl + O_2$	$k_{93} = 5.80 \times 10^{-13} \exp(170/T)$
R. 94	$BrO + BrO \longrightarrow Br + Br + O_2$	$k_{94} = 1.50 \times 10^{-12} \exp(230/T)$
R. 95	$O(^1D) + CCl_4 \longrightarrow ClO + Products$	$k_{95} = 3.30 \times 10^{-10}$
R. 96	$O(^1D) + CFCl_3 \longrightarrow ClO + Products$	$k_{96} = 2.30 \times 10^{-10}$
R. 97	$O(^1D) + CF_2Cl_2 \longrightarrow ClO + Products$	$k_{97} = 1.40 \times 10^{-10}$
R. 98	$O(^1D) + CH_3Br \longrightarrow OH + Products$	$k_{98} = 1.80 \times 10^{-10}$
R. 99	$OH + CH_3Cl \longrightarrow H_2O + Products$	$k_{99} = 4.00 \times 10^{-12} \exp(-1400/T)$
R. 100	$OH + CH_3CCl_3 \longrightarrow H_2O + Products$	$k_{100} = 1.80 \times 10^{-12} \exp(-1550/T)$
R. 101	$OH + CH_3Br \longrightarrow H_2O + Products$	$k_{101} = 4.00 \times 10^{-12} \exp(-1470/T)$

The rate constants of the three body reactions are calculated by

$$k_i(M,T) = \left(\frac{k_{i,0}(T)[M]}{1. + \frac{k_{i,0}(T)[M]}{k_{i,\infty}(T)}} \right) 0.6^{\left(1. + \left[log_{10}(\frac{k_{i,0}(T)[M]}{k_{i,\infty}(T)} \right]^2 \right)^{-1}} \tag{2.16}$$

The rate constant of the $\mathrm{OH} + \mathrm{HNO_3}$ reaction is calculated by

$$k(M,T) = k_0(T) + \frac{k_2(T)[M]}{1. + \frac{k_2(T)[M]}{k_1(T)}} \tag{2.17}$$

2.3.3 The Photolysis Reactions

The photodissociation coefficients are interpolated from values in a lookup table. The photodissociation coefficients in the lookup table are calculated by using the photonflux model of *Röth* [1992] and depend on the altitude, the zenith angle (up to 95 degrees) and the ozone column. The cross sections have generally been taken from the compilation of *Röth et al.* [1997a, b]. For the HNO_3 photolysis the cross sections of *Burkholder et al.* [1993] are used.
The following photolysis are included in the model:

No.	Photolysis
J. 1	$O_2 + h\nu \longrightarrow O(^3P) + O(^3P)$

No.	Photolysis
J. 2	$O_3 + h\nu \longrightarrow O(^1D) + O_2$
J. 3	$O_3 + h\nu \longrightarrow O(^3P) + O_2$
J. 4	$H_2O + h\nu \longrightarrow OH + H$
J. 5	$H_2O_2 + h\nu \longrightarrow OH + OH$
J. 6	$NO + h\nu \longrightarrow N + O(^3P)$
J. 7	$NO_2 + h\nu \longrightarrow NO + O(^3P)$
J. 8	$NO_3 + h\nu \longrightarrow NO + O_2$
J. 9	$NO_3 + h\nu \longrightarrow NO_2 + O(^3P)$
J. 10	$N_2O + h\nu \longrightarrow N_2 + O(^1D)$
J. 11	$N_2O_5 + h\nu \longrightarrow NO_2 + NO_3$
J. 12	$HONO + h\nu \longrightarrow OH + NO$
J. 13	$HNO_3 + h\nu \longrightarrow OH + NO_2$
J. 14	$HO_2NO_2 + h\nu \longrightarrow HO_2 + NO_2$
J. 15	$CO_2 + h\nu \longrightarrow CO + O(^3P)$
J. 16	$CH_2O + h\nu(+O_2) \longrightarrow H + HO_2 + CO$
J. 17	$CH_2O + h\nu \longrightarrow H_2 + CO$
J. 18	$CH_3OOH + h\nu(+O_2) \longrightarrow CH_2O + HO_2 + OH$
J. 19	$CH_3O_2NO_2 + h\nu \longrightarrow CH_3O_2 + NO_2$
J. 20	$Cl_2 + h\nu \longrightarrow Cl + Cl$
J. 21	$ClO + h\nu \longrightarrow Cl + O(^3P)$
J. 22	$OClO + h\nu \longrightarrow O(^3P) + ClO$
J. 23	$Cl_2O_2 + h\nu \longrightarrow Cl + Cl + O_2$
J. 24	$HCl + h\nu \longrightarrow H + Cl$
J. 25	$HOCl + h\nu \longrightarrow OH + Cl$
J. 26	$HOCl + h\nu \longrightarrow O(^3P) + HCl$
J. 27	$ClNO_2 + h\nu \longrightarrow Cl + NO_2$
J. 28	$ClONO_2 + h\nu \longrightarrow Cl + NO_3$
J. 29	$ClONO_2 + h\nu \longrightarrow Cl + NO_2 + O(^3P)$
J. 30	$BrO + h\nu \longrightarrow Br + O(^3P)$
J. 31	$HOBr + h\nu \longrightarrow OH + Br$
J. 32	$BrONO_2 + h\nu \longrightarrow Br + NO_3$
J. 33	$BrCl + h\nu \longrightarrow Br + Cl$
J. 34	$CH_3Cl + h\nu(+O_2) \longrightarrow Cl + CH_3O_2$
J. 35	$CH_3CCl_3 + h\nu \longrightarrow 3 \times Cl + Products$

No.	Photolysis
J. 36	$\mathrm{CCl_4} + h\nu \longrightarrow 4 \times \mathrm{Cl} + Products$
J. 37	$\mathrm{CFCl_3} + h\nu \longrightarrow 3 \times \mathrm{Cl} + Products$
J. 38	$\mathrm{CF_2Cl_2} + h\nu \longrightarrow 2 \times \mathrm{Cl} + Products$
J. 39	$\mathrm{CH_3Br} + h\nu(+\mathrm{O_2}) \longrightarrow \mathrm{Br} + \mathrm{CH_3O_2}$

2.3.4 The Heterogeneous Reactions

The heterogeneous reactions included in KASIMA occur both on the surface of frozen polar stratospheric clouds (PSCs) and on liquid sulfuric acid aerosols with an assumed equilibrium of the particels. No microphysics of the particles is contained in the model.

The first order rate constant in s^{-1} of a species X on PSCs and aerosols depends on the surface area A of these particles

$$k_{het} = \gamma \bar{v} \frac{A}{4} \tag{2.18}$$

with the surface reaction probability γ and the mean velocity $\bar{v}$ of the species X which is given by

$$\bar{v} = \sqrt{\frac{8 k_b T}{\pi m_X}} \tag{2.19}$$

k_b is the Boltzmann's constant and m_X the mass of the species X which is calculated from the molar mass M_X and the Avogadro's number N_A:

$$m_X = \frac{M_X}{N_A} \tag{2.20}$$

The heterogeneous scheme on sulfuric acid aerosols assumes that the aerosols remain liquid above the ice point and that they are able to take up species (e.g., $\mathrm{HNO_3}$, HCl) from the gas phase [*Carslaw et al.*, 1995]. By this, the surface reaction probabilities on sulfate aerosols are calculated in dependence on the composition of the liquid aerosols. The initial surface area of the sulfate aerosol is recalculated into mixing ratios of $\mathrm{H_2SO_4}$ which are transported during the model experiment.

The heterogeneous processes on polar stratospheric clouds (NAT and ice) are calculated by using the conventional PSC scheme which was proposed by *Poole and McCormick* [1988]. To predict when polar stratospheric clouds are thermodynamically possible the algorithm given in

Hanson and Mauersberger [1988] is used. Therein, the existence of NAT and ice depends on the temperature, the $\mathrm{HNO_3}$ mixing ratio and the water vapour pressure. The equilibrium vapor pressure of HNO_3 over NAT is given by

$$\begin{aligned}\ln P_{\mathrm{HNO_3}^{eq}} = (-2.7836 - 0.00088T)\ln P_{\mathrm{H_2O}} + 90.8556 \\ -26242.6/T + 0.0213885T\end{aligned} \qquad (2.21)$$

with the partial pressure of water vapor $P_{\mathrm{H_2O}}$. The equilibrium vapor pressure of H_2O over ice is given by

$$\ln P_{\mathrm{H_2O}^{eq}} = 24.306 - 6144.9/T \qquad (2.22)$$

At low temperatures these vapor pressures are lower than the partial pressure of HNO_3 or H_2O and NAT or ice is formed:

$$[\mathrm{NAT}] = [\mathrm{HNO_3}^{gas}] - [\mathrm{HNO_3}^{eq}] \qquad (2.23)$$

$$[\mathrm{ice}] = [\mathrm{H_2O}^{gas}] - [\mathrm{H_2O}^{eq}] \qquad (2.24)$$

Because polar stratospheric cloud particels can be very large the model take gas diffusion limitation for NAT and ice into account. Thus, (2.18) is corrected by the following multiplication factor

$$f = \left(1 + \frac{3\gamma r_{PSC}}{4l}\right)^{-1} \qquad (2.25)$$

with the radius r_{PSC} of the polar stratospheric cloud particel and the mean free path l which can be calculated from

$$l = 2.28 \times 10^{-5}\frac{T}{p} \qquad (2.26)$$

As *Steil et al.* [1998] a constant concentration of 1 particle NAT per cm^3 and 0.01 particle ice per cm^3 [*Drdla and Turco*, 1991] instead of a fixed radius is assumed in order to prevent a strong dependence on the chosen parameterization. With the number concentration n_{PSC} of NAT and ice, respectively, as given in (2.23) and (2.24) and the radius r_{PSC} of these particels the surface area of the PSC is given by

$$A_{PSC} = 4\pi r_{PSC}^2 n_{PSC} \qquad (2.27)$$

Assuming a monodisperse size distribution the radius of NAT and ice is obtained from the NAT and ice concentration, the molar mass M of NAT [117 g/mol] and ice [18 g/mol] and the density ρ of NAT [1.6 g/cm^3] and ice [0.92 g/cm^3], respectively.

$$V_{PSC} = \frac{[PSC]M_{PSC}}{N_A \rho_{PSC} n_{PSC}} \tag{2.28}$$

followed by

$$r_{PSC} = \left(\frac{3V_{PSC}}{4\pi}\right)^{(1/3)} \tag{2.29}$$

The sedimentation of NAT and ice is calculated in dependence on the radius of the particles as given in *Müller and Peter* [1992]. According to *Wofsy et al.* [1990] ice-particles form on NAT. Therefore, if the temperature is below the frost point the sedimentation velocity of NAT is the same as for ice.

The surface reaction probabilities are taken from the compilation of *DeMore et al.* [1997]. The probabilities denoted with $f(T)$ are calculated from the scheme provided by *Carslaw et al.* [1995].

No.	Reaction	$\gamma_{\mathrm{H_2SO_4}}$	γ_{NAT}	γ_{ice}
H. 1	$\mathrm{N_2O_5 + H_2O \longrightarrow HNO_3 + HNO_3}$	0.1	0.0003	0.01
H. 2	$\mathrm{N_2O_5 + HCl \longrightarrow ClNO_2 + HNO_3}$	–	0.003	0.03
H. 3	$\mathrm{ClONO_2 + H_2O \longrightarrow HOCl + HNO_3}$	$f(T)$	0.001	0.3
H. 4	$\mathrm{ClONO_2 + HCl \longrightarrow Cl_2 + HNO_3}$	$f(T)$	0.1	0.3
H. 5	$\mathrm{HOCl + HCl \longrightarrow Cl_2 + H_2O}$	$f(T)$	0.1	0.3
H. 6	$\mathrm{ClONO_2 + HBr \longrightarrow BrCl + HNO_3}$	–	0.3	0.3
H. 7	$\mathrm{HOCl + HBr \longrightarrow BrCl + H_2O}$	$f(T)$	0.1	0.3
H. 8	$\mathrm{BrONO_2 + H_2O \longrightarrow HOBr + HNO_3}$	$f(T)$	0.001	0.3
H. 9	$\mathrm{BrONO_2 + HCl \longrightarrow BrCl + HNO_3}$	–	0.1	0.3
H. 10	$\mathrm{HOBr + HCl \longrightarrow BrCl + H_2O}$	$f(T)$	0.1	0.3

3 The Radiation

Radiation from the sun and its subsequent absorption and reemission within the atmosphere is the main mechanism to drive the circulation in the atmosphere. Even the main absorbing and emitting gases exhibit such a wealth of lines and spectral structures that within a model it is impossible to perform exact calculations of the radiation. Therefore parameterizations are used which summarize in some computational efficient way the properties of the radiation processes. In this chapter first some principles of the treatment of radiation are outlined. Then the parameterizations used within the model to determine the heating rates are described.

3.1 Some Principles and Nomenclature

3.1.1 Heating Rates

The amount of energy absorbed or released in radiative or chemical processes is expressed by the diabatic temperature de- or increase of a certain volume of the atmosphere. In the following the term 'solar heating' is used for absorption of solar radiation and the term 'cooling' for heating terms of atmospheric infrared radiation which are negative in general but may also contribute to heating.

The temperature change of a specific volume element and the radiative heating rate h is given by:

$$\frac{\partial T}{\partial t} = -\frac{1}{c_p \rho(z)} \vec{\nabla} \cdot \vec{F} = \frac{h}{c_p} \tag{3.1}$$

where z is the pressure altitude (see Section 1), $\vec{F} = \int_0^\infty \vec{F_\nu} d\nu$ is the flux, and the projection of $\vec{F_\nu}$ on a unit vector $\vec{s}$ is given by $\int I_\nu(\Omega)\vec{s} \cdot d\vec{A}/dAd\Omega$ with $I_\nu = \frac{dE}{dA \cdot dt \cdot d\Omega \cdot d\nu}$ the specific intensity of the radiation with E energy, A the illuminated area, Ω the solid angle in direction of $\vec{s}$ and ν the frequency of the radiation. The orientation of A is given by the normal vector on A.

I_ν is given by the equation of radiation transfer (ERT):

$$\frac{dI_\nu}{ds} = -e_\nu I_\nu + e_\nu S_\nu \tag{3.2}$$

where s is a linear coordinate in the direction of radiation, $e_\nu = a_\nu + s_\nu$ is the linear extinction coefficient composed of the absorption and scattering coefficient, and S_ν is the source function, which includes scattered and thermally emitted radiation. Often the extinction coefficient is expressed as $e_\nu = \sigma_\nu \cdot n = e_{m,\nu}\rho$ where σ is the extinction cross section and n is the number density of the extinguishing species, and $e_{m,\nu}$ is called the mass extinction coefficient. In case of negligible scattering, S_ν is given by the Planck function if the conditions of local thermodynamical equilibrium (LTE) are fulfilled. This is the case whenever the ratio of population densities of the quantum states of a molecule are given by the Boltzmann distribution.

With the help of eq. 3.2 the total heating rate can also be expressed as:

$$h = \frac{1}{\rho}\int_{\Delta\Omega}\int_0^\infty (e_\nu I_\nu - e_\nu S_\nu) d\nu d\omega \tag{3.3}$$

In a planparallel atmosphere equation 3.1 is reduced to:

$$\frac{\partial T}{\partial t} = -\frac{1}{c_p \rho(z)}\frac{\partial F}{\partial z} \tag{3.4}$$

(Detailed introductions into the field of radiation transfer can be found in *Chandrasekhar* [1960] or *Goody and Yung* [1989].)

3.1.2 Solar Heating

Scattering from molecules, aerosols and clouds is the only source term within the atmosphere in equ. 3.2 for solar radiation but in the middle atmosphere for the UV-radiation with $\lambda < 300\mathrm{nm}$ in a good approximation scattering can be neglected or included in a simple albedo ansatz. In the ERT the source function S_ν then is zero. Eq. 3.3 is reduced to $h = \frac{1}{\rho}\int_{\Delta\Omega}\int_0^\infty a_\nu I_\nu(s) d\nu d\omega$. If in addition the total absorption cross section $\sigma_\nu = \sum_X \sigma_{X,\nu}$ is constant in the whole volume, where X is some gas species, and again a planparallel atmosphere is assumed with a solar zenith angle $\chi = \arccos(\mu)$, equ. 3.2 can be simplified to give an expression for the solar flux:

$$F_\nu(z) = \mu F_\nu^\odot \exp(-\sigma_\nu/\mu \int n_X(z) dz) = \mu F_\nu^\odot \exp(-\sigma_\nu N_X(z)/\mu) \tag{3.5}$$

where N_X is called the atmospheric column density of species X, and $F_\nu^\odot$ is the solar extraterrestial flux. This formulation is especially useful in the UV and visual spectral region.

The solar heating rate may also be expressed with the definition of transmissionfunctions $\mathcal{T}(s_1, s_2)$:

$$\mathcal{T}(s_1, s_2) = e^{-\int_{s_1}^{s_2} a_\nu ds}. \tag{3.6}$$

If the top of the atmosphere is at $s = \infty$ it follows:

$$h_\nu(z) = \frac{\pi}{\rho(z)} \mu F_\nu^\odot \frac{d\mathcal{T}_\nu(z,\infty)}{dz} \tag{3.7}$$

3.1.3 Thermal Emission of the Atmosphere

In the spectral region of the thermal emission of the atmosphere scattering can be neglected. The earth's atmosphere is not optically thick through the whole infrared spectrum even at the ground. LTE conditions assumed S_ν is the Planck function and the strongest contributions to the emissivity of the atmosphere are found in the lines of certain molecules. The formal solution of the equation of radiation transfer is with $\tau = \int e_\nu ds$ then given by:

$$I_\nu(s) = I_\nu(0) \cdot e^{-\tau_\nu} + \int_0^{\tau_\nu} B_\nu(T(\tau'_\nu) e^{-\tau'_\nu} d\tau'_\nu \tag{3.8}$$

With the transmissionfunctions $\mathcal{T}(s, s')$ the formal solution of the ERT can be written as (see for example *Andrews et al.* [1987]):

$$I_\nu(s) = I_\nu(0) \cdot \mathcal{T}(0, s) + \int_0^s B_\nu(s') \frac{\partial \mathcal{T}(s, s')}{\partial s'} ds' \tag{3.9}$$

In an infinite planparallel atmosphere the flux transmissionfunction $\mathcal{T}_f$ is introduced as:

$$\mathcal{T}_f(z_1, z_2) = \frac{\int_0^1 \mu \mathcal{T}_\nu(z_1, z_2, \mu) d\mu}{\int_0^1 \mu d\mu} \tag{3.10}$$

and for a spectral band $\Delta\nu_r$ the average of the flux transmissionfunction in this band $\bar{\mathcal{T}}_f$ is defined as the average of the flux transmissionfunction in a spectral band $\Delta\nu_r$ small enough so that the Planck function can be assumed to be almost constant within the band.

The net cooling flux in the band is then formally given by:

$$F_{net} = \pi B_r(0_-) \bar{\mathcal{T}}_f(0, z) + \pi \int_0^\infty B_r(z') \frac{\partial \bar{\mathcal{T}}_f(z, z')}{\partial z'} dz' \tag{3.11}$$

where B_r denotes the integral of the Planck function over the band and 0_- denotes the solid surface.

With equ. 3.4 it follows in the formulation of exchange integrals (*Andrews et al.* [1987]):

$$
\begin{aligned}
h_r(z) \quad = \quad & \frac{\pi}{\rho(z)} \left\{ -B_r(z) \frac{d\bar{\mathcal{T}}_f(z,\infty)}{dz} \right. \\
& -[B_r(0_-) - B_r(z)] \frac{d\bar{\mathcal{T}}_f(z,0)}{dz} \\
& - \int_0^z [B_r(z') - B_r(z)] \frac{\partial^2 \bar{\mathcal{T}}_f(z,z')}{\partial z \partial z'} dz' \\
& \left. - \int_z^\infty [B_r(z') - B_r(z)] \frac{\partial^2 \bar{\mathcal{T}}_f(z,z')}{\partial z \partial z'} dz' \right\}
\end{aligned}
\tag{3.12}
$$

and the total cooling rate is the sum over all relevant bands.

In the case of small temperature gradients the dominant term in the exchange formulation is the radiation to space term.

$$
h_r(z) \approx \frac{\pi}{\rho(z)} B_r(z) \frac{d\bar{\mathcal{T}}_f(z,\infty)}{dz} \tag{3.13}
$$

This is called the cooling-to-space-approximation. For small temperature differences from the start profile $\Delta T = T - T_e$ the Planck function can be linearized and one can write:

$$
\frac{\partial \Delta T}{\partial t} \approx -\frac{\pi}{\rho c_p} \left\{ \sum_r \left(\frac{dB_r}{dT}\right)_{T=T_e} \frac{d\bar{\mathcal{T}}_f(z,\infty)}{dz} \right\} \Delta T \equiv -K_{rad}(z, T_e) \Delta T \tag{3.14}
$$

This is the so called Newtonian-cooling approximation and the coefficient K_{rad} is called Newtonian-cooling coefficient.

For numerical calculations with discrete levels z_i it follows from equ. 3.12 that the heating rates can be expressed in the form:

$$
h_r(z_i) = \sum_j R_{ij} B_r(z_j) \tag{3.15}
$$

where the coefficients R_{ij} follow from the transmission coefficients:

$$
R_{i,j} = R(z_i, z_j) \sim \frac{\partial^2 \bar{\mathcal{T}}_f(z_i, z_j)}{\partial z_i \partial z_j} \tag{3.16}
$$

The R_{ij} constitute a matrix, the so called Curtis-Matrix. When the transmission functions depend only slightly on the temperature the coefficients can be chosen to be constant. More

Table 3.1: **Coefficients for solar heating**

Band	Species	ϵ	$F_r^\odot$ [erg cm^{-2}s^{-1}]	σ_r [cm^2]
Chappuis	O_3	1.0	3.7×10^5	2.85×10^{-21}
Hartley	O_3	1.0	4600	8.8×10^{-18}
Herzberg	O_3	1.0	1.2×10^3	4.9×10^{-18}
	O_2	1.0		6.6×10^{-24}
$\mathrm{Schumann - Runge_a}$	O_2	0.3	1.1	1.0×10^{-17}

exact solutions incorporate the temperature dependence, for example the matrix is expanded to a temperature dependend series.

For Non-LTE conditions the source function is not given by the Planck function and has to be determined by a detailed examination of the population densities of the levels which contribute to the radiation field.

3.2 Parameterization of Solar Radiation

The absorption of ultraviolet radiation is parameterized by the scheme of *Strobel* [1978] with modifications according *Apruzese et al.* [1982]. It takes into account the Hartley band (200-300 nm), Huggins bands (300-350 nm), and Chappuis bands (450-750 nm) of ozone, absorption in the Schumann-Runge bands (175-205 nm) and the Schumann-Runge continuum (125-175 nm) of O_2, and the Herzberg continuum of both molecules. If the reaction product ends in an excited state the lifetime of which is long compared to the transport timescale, a correction factor $\epsilon \leq 1$ is used which describes the efficiency of the reaction. This factor is used only for molecular oxygen.

The absorption cross sections are assumed not to depend on temperature or pressure. This is an approximation especially for the Huggins bands of ozone. For the Chappuis bands, the Hartley band and the Herzberg continua the band absorption is characterized by an average value. Then, using eq. 3.5 the heating rate by species X in band r is given by:

$$h_{r,X} = \epsilon_{r,X} F_r^\odot \, n_X \, \sigma_{r,X} \exp(-\sum_X \sigma_{r,X} N_X) \tag{3.17}$$

where $F_r^\odot$ is the solar flux integrated over the band r. Table 3.1 gives the coefficients as used in the model.

For the Huggins bands the spectral shape of the absorption is approximated by an exponential function in the interval $[\lambda_{short}, \lambda_{long}]$. This yields:

$$h_{Hu} = \frac{n_{\mathrm{O}_3}}{N_{\mathrm{O}_3}} \frac{1}{M} \{I_1 + (I_2 - I_1) \exp(-\sigma_{Hu} N_{\mathrm{O}_3} e^{-M\lambda_{long}}) \\ - I_2 \exp(-\sigma_{Hu} N_{\mathrm{O}_3} e^{-M\lambda_{short}})\} \tag{3.18}$$

with $I_1 = 59.2$ ergs cm^{-2} s^{-1} Å^{-1}, $I_2 = 40.0$ ergs cm^{-2} s^{-1} Å^{-1}, $M = 0.0127$Å^{-1}, $\lambda_{short} = 2805$ Å, $\lambda_{long} = 3055$ Å, and $\sigma_{Hu} = 0.0125\ \mathrm{cm}^2$.

The Schumann-Runge continuum is computed in two terms:

$$\begin{aligned} h_{SRC} &= n_{\mathrm{O}_2} F_{SRC} \sigma_{SRC} \exp\{-\sigma_{SRC} N_{\mathrm{O}_2}\} \\ &+ \frac{n_{\mathrm{O}_2}}{N_{\mathrm{O}_2}} \left\{ \frac{I_l}{M} e^{-\sigma_l N_{\mathrm{O}_2}} + \frac{I_s - I_l}{M} e^{-\sigma_m N_{\mathrm{O}_2}} - \frac{I_s}{M} e^{-\sigma_s N_{\mathrm{O}_2}} \right\} \end{aligned} \tag{3.19}$$

with the parameters for the first term given in Table 3.1 and: $\frac{I_l}{M} = 3.43$ erg cm^{-2} s^{-1}, $\frac{I_s}{M} = 1.35$ erg cm^{-2} s^{-1}, $\sigma_l = 2.9 \times 10^{-19}\mathrm{cm}^2$, $\sigma_m = 1.7 \times 10^{-18}\mathrm{cm}^2$, and $\sigma_s = 1.1 \times 10^{-17}\mathrm{cm}^2$.

For the Schumann-Runge bands a rough approximation is used:

$$h_{SRB} = n_{\mathrm{O}_2} \begin{cases} 1/(aN_{\mathrm{O}_2} + bN_{\mathrm{O}_2}^{0.5}) & \text{for} \quad N_{\mathrm{O}_2} \geq 10^{18}\ \mathrm{cm}^{-2} \\ 2.43 \times 10^{-19} \mathrm{erg\ s}^{-1} & \text{for} \quad N_{\mathrm{O}_2} < 10^{18}\ \mathrm{cm}^{-2} \end{cases} \tag{3.20}$$

with $a = 0.67$, and $b = 3.44 \times 10^{-19}$ (in cgs units).

The solar heating rate $h^{\odot}$ in the UV is then determined by the sum of the individual heating terms.

3.2.1 Solar Heating in the Near IR by CO_2 and $\mathrm{H}_2\mathrm{O}$

Solar heating rates in the infrared spectral region in absorption lines of CO_2 and $\mathrm{H}_2\mathrm{O}$ are determined using parameterizations for the transmission according *Lacis and Hansen* [1974] modified according *Ramaswamy and Freidenreich* [1992] and *Freidenreich and Ramaswamy* [1993]. It is based on the product approximation for transmission of radiation through multiple gases. The total transmission of radiation between the top of the atmosphere to a level z due to CO_2 and $\mathrm{H}_2\mathrm{O}$ is then given by:

$$\mathcal{T}_{tot}(z) = \mathcal{T}_{\mathrm{CO}_2}(z) \cdot \mathcal{T}_{\mathrm{H}_2\mathrm{O}}(z) \tag{3.21}$$

Table 3.2: **Coefficients and weights for the pseudo monochromatic intervals used for $\mathrm{H_2O}$ transmission**

Interval	Coefficient $\mathrm{m^2/kg}$	Weight
1	4.0000E-6	0.6214
2	2.0000E-4	0.0698
3	3.5000E-3	0.1558
4	3.7700E-2	0.0631
5	1.9500E-1	0.0362
6	9.4000E-1	0.0243
7	4.4600E0	0.0158
8	1.9000E1	0.0087
9	9.8900E1	1.467E-3
10	2.7060E2	2.342E-3
11	3.9011E3	1.075E-3

The transmission for $\mathrm{CO_2}$ is given by:

$$\mathcal{T}_{\mathrm{CO_2}} = 1 - c_1 \left[\left(c_2 \tilde{N}_{\mathrm{H_2O}} + 1 \right)^{\gamma} - 1 \right] \tag{3.22}$$

with $c_1 = 5.8 \times 10^{-4}$, $c_2 = 758$ and $\gamma = 0.28$, and $\tilde{N}_{\mathrm{H_2O}}$ the Curtis-Godson scaled column density from the top of the atmosphere.

The transmission for $\mathrm{H_2O}$ is given by:

$$\mathcal{T}_{\mathrm{H_2O}} = \sum w_k \mathcal{T}_{\mathrm{H_2O,k}}(z) \tag{3.23}$$

where k denotes some pseudomonochromatic intervals in the water vapour spectrum, w_k a weight with $\sum w_k = 1$, and $\mathcal{T}_{\mathrm{H_2O,k}}(z) = \exp(-k_k \tilde{N}_{\mathrm{H_2O}}$ the transmission in this interval. In total 11 intervals are used. The used numerical values are given in Table 3.2. The heating rates are determined using eq. 3.7.

3.3 Parameterization of Cooling Rates

Several versions of parameterizations of the cooling rates can be used: a simplified version using a Newtonian cooling scheme, and parameterizations for cooling by the most important molecules based on Curtis matrix representations including $\mathrm{CO_2}$, $\mathrm{O_3}$, NO and $\mathrm{H_2O}$. Cooling by these gases have been implemented by two versions: one using a combination of simplified Curtis-Matrix representations published by Fomichev and co-workers together with an exchange integral representation for $\mathrm{H_2O}$ (see following sections); the second version uses the code of *Zhu* [1994] which incorporates a Curtis matrix interpolation scheme including an explicit temperature dependence for $\mathrm{CO_2}$, Curtis matrix interpolation for $\mathrm{O_3}$ and a cooling-to-space approximation for $\mathrm{H_2O}$. For most purposes, a combination of the two versions, using the cooling-to-space approximation for $\mathrm{H_2O}$ of Zhu and the parameterizations for $\mathrm{CO_2}$ and $\mathrm{O_3}$ of Fomichev and co-workers give satisfactorily results at a high numerical efficiency. Here only the parameterizations are described, for which the code was developed by IMK. For a detailed description of the parameterization of Zhu the reader is referred to the original publication (see citation above).

3.3.1 Version with Newtonian Cooling

This version uses a simplified radiation scheme. The cooling rate is given by the sum of the horizontal mean of the solar heating term and a Newtonian cooling term. As the horizontal mean of the solar heating rate does not depend on the declination of the sun this first term is constant in time in a first approximation.

$$h(z,t) = -\frac{1}{4\pi}\int_{-\pi/2}^{+\pi/2}\int_{0}^{2\pi} h^{\odot}(\lambda,\varphi,z,t)d\lambda cos\varphi d\varphi - K_{rad}(z)(T(\lambda,\varphi,z) - T_{equ}(z)) \tag{3.24}$$

The Newtonian cooling coefficient $K_{rad}(z)$ is taken from *Wehrbein and Leovy* [1982], with T_{equ} taken from the US-Standard Atmosphere *U. S. standard atmosphere* [1976].

3.3.2 Version with Parameterizations for the relevant Molecules

These parameterizations include $\mathrm{CO_2}$-15μm band, $\mathrm{O_3}$-9.6μm band, NO for altitudes above about 90 km and $\mathrm{H_2O}$.

Cooling by $\mathrm{CO_2}$

The $\mathrm{CO_2}$ parameterization is based on the formulation given by *Fomichev et al.* [1993]. It uses a LTE model for the height below 70 km and includes NLTE effect above.

In the range of 15 - 80 km the parameterization is based on a LTE formulation of *Akmaev and Shved* [1982]. It is an extension of a parameterization in the form of a Curtis matrix (see eq. 3.15). For the height x_0 the radiative cooling rate is given by (in units of $\mathrm{cm^2 s^{-3}}$):

$$h_{\mathrm{CO_2}} = (1-3\varphi_0)\sum_{j=-7}^{4}\left[a_j(x_0)+\varphi_0 b_j(x_0)+\varphi_0^2 c_j(x_0)\right]\varphi_j \tag{3.25}$$

where

$$\varphi_i = \exp(-960.24/T_i)$$

describes the approximately constant Planck function over the band with T_i the temperature at altitude $x_i H$ where H is the scale height.. The x_i's are given by:

$$x_i(x_0) = x_0 + \Delta x_i$$

with $\Delta x_i = \{-4.75, -2.75, -1.75, -1.25, -0.75, -0.25, 0.0, 0.25, 0.75, 1.75, 3.75\}$ for $i \in [-6, 4]$, where x_{-7} is the surface. The formula 3.25 can be understood as a polynom series for the derivateives of the transmission functions with the Planck emission as independent variable. Radiation exchange of different levels is approximated by restricting the number of the involved altitude levels. In total 14 vibrational transitions are included.

Below 30 km the method of *Aoki* [1980] is applied to compute the coefficients a, b, c using a quasi random band model with a modified Lorentz profile to account for line overlap. In the altitude range 70 - 80 km the coefficients were computed including NLTE deviations.

Above 80 km the parameterization is based on the recurrence formula of *Kutepov and Fomichev* [1993]. Here the cooling rate is given by:

$$h_{\mathrm{CO_2}}(x_j) = 8.63\cdot 10^9\, c_{\mathrm{CO_2}}(1-\lambda_j)\tilde{\epsilon}(x_j) \tag{3.26}$$

where

$$\lambda_j = \lambda(x_j) = \frac{1.5638}{1.5638+\exp(-x_j)\left[c_{\mathrm{N}_{2j}}k_{\mathrm{N_2}}+c_{\mathrm{O}_{2j}}k_{\mathrm{O_2}}+c_{O_j}k_{\mathrm{O}}\right]}$$

is the mean lifetime of the excited level with:

$$k_{\mathrm{N}_2} = (2.9T_j^2 - 1060T_j + 145000)$$

$$k_{\mathrm{O}_2} = (4.23T_j^2 - 1490T_j + 180000)$$

$$k_{\mathrm{O}} = 5 \times 10^6$$

and c_{Z_j} the volume mixing ratio of species Z at level x_j, and k_Z the rate coefficient for the collisional deexcitation of the $\mathrm{CO}_2(01^10)$-level in atm^{-1}. The value of $\tilde{\epsilon}$ is determined by the recurrence formula:

$$A_j\tilde{\epsilon}(x_j) = A_{j-1} + D_{j-1}\varphi_{j-1} - D_j\varphi_j \tag{3.27}$$

with the boundary condition for $x = 11.5$:

$$\tilde{\epsilon}(11.5) = 1.1008 \cdot 10^{-10}\frac{h_{\mathrm{CO}_2}(11.5)}{c_{\mathrm{CO}_2}(11.5)[1-\lambda(11.5)]} \tag{3.28}$$

where $h(11.5)$ is determined by the LTE method. The coefficients A_j are given by:

$$\begin{aligned}
A_j &= 1 - \lambda_j\left(1 - \frac{1}{4}d_{j-1} - \frac{1}{4}d_j\right)\\
A_{j-1} &= 1 - \lambda_{j-1}\left(1 - \frac{3}{4}d_{j-1} - \frac{1}{4}d_j\right)\\
D_j &= \frac{1}{4}\left(d_{j-1} + 3d_j\right)\\
D_{j-1} &= \frac{1}{4}\left(3d_{j-1} + d_j\right)
\end{aligned}$$

The coefficients a_j, b_j, c_j are given in *Fomichev et al.* [1993] for $x = 2 - 11.5$ for a stepsize of 0.25, the same for the d_j above $x = 11.5$. The coefficients are given for the standard concentration of 330 ppmv of CO_2.

In order to use this parameterization the temperature field is interpolated to the grid of this parameterization, the heating rates are calculated and transformed back to the model grid.

Cooling by Ozone

For ozone the parameterization of *Fomichev and Shved* [1985] is used. It is based on a Curtis matrix formulation again restricting the number of involved levels:

$$h_{\mathrm{O_3}} = 2.37 \cdot 10^4 \, c_{v_0} \sum_{j=-I}^{J} C_j(x_0) \exp(-\frac{1500}{T_j}) \tag{3.29}$$

where h is given in $\mathrm{cm^2 s^{-3}}$, x_j and T_j are defined as for the parameterization of $\mathrm{CO_2}$ and c_v is the volume mixing ratio of ozone in ppmv. The indices $j = -I \dots J$ correspond to different heights, where $x(-I) = 0$ and $x(J) = 11$, and

$$x_j = x_0 + \Delta x_j$$

with $\Delta x_j = \{-6.25, -4.25, -3.0, -1.75, -0.25, 0.25, 0.5, 1.0\}$ if x_j is inside the vertical interval where coefficients are given for the parameterization. Depending on the value of x_0 the number I varies from 4 to 7, and J from 0 to 4.

The coefficients C_j are essentially the second derivative of the transmission function which is evaluated using a random band model. Only the fundamental transitions 100-000 and 001-000 are considered with a Voigt profile uniform for all lines in the band. The C_j are given by:

$$2C_j(x_0) = \left\{ \begin{array}{rcl} L_b(x_0, x_{j+1}) + L_b(x_0, x_j) & : & j = -I \\ L_b(x_0, x_{j+1}) - L_b(x_0, x_{j-1}) & : & -I < j < 0 \\ -2 - L_b(x_0, x_{j+1}) - L_b(x_0, x_{j-1}) & : & j = 0 \wedge J \neq 0 \\ -3 - L_b(x_0, x_{j-1}) & : & j = J = 0 \\ L_b(x_0, x_{j-1}) - L_b(x_0, x_{j+1}) & : & 0 < j < J \\ L_b(x_0, x_{j-1}) - L_b(x_0, x_j) & : & j = J \wedge J \neq 0 \end{array} \right. \tag{3.30}$$

The function L_b is parameterized by:

$$L_b(x_0, x_j) = \left\{ \begin{array}{rcl} A_j(x_0) \exp[-B_j(x_0) N(x_0, x_j)] & : & j \neq 0 \\ 1 & : & j = 0 \end{array} \right. \tag{3.31}$$

where $N(x_0, x_j)$, the column density of ozone is given by

$$2N(x_0, x_j) = \left\{ \begin{array}{lcl} \sum_{i=j}^{-1} (c_{v_{i+1}} e^{-x_{i+1}} + c_{v_i} e^{-x_i})(x_{i+1} - x_i) & : & j < 0 \\ \sum_{i=1}^{j} (c_{v_i} e^{-x_i} + c_{v_{i-1}} e^{-x_{i-1}})(x_i - x_{i-1}) & : & j > 0 \end{array} \right. \tag{3.32}$$

The coefficients A_j and B_j are given with a step size in x of 0.25 from 3 to 11. As for $\mathrm{CO_2}$ the heating rates are determined in this paramerization grid and then interpolated to the model grid.

NO

NO is the major cooling gas in the lower thermosphere. Here the parameterization of *Kockarts* [1980] is used which describes NO emission as a two-level system:

$$h_{\mathrm{NO}} = \frac{\epsilon_\nu}{\rho} = \frac{1}{\rho}\mathrm{h}\nu\, n_1 A_{10} \tag{3.33}$$

Neglecting the radiation field one can write:

$$h_{\mathrm{NO}} = -\frac{1}{\rho}\mathrm{h}\nu\, n_{NO}\frac{A_{10}C_{10}}{C_{10}+A_{10}}\exp(-\mathrm{h}\nu/T) \tag{3.34}$$

As the most effective collision partner is atomic oxygen, it follows $C_{10} = k_{10}n_{\mathrm{O}}$ where k_{10} is the dexcitation rate for collisions with atomic oxygen. The heating rate for NO in $\mathrm{cm}^2\ \mathrm{s}^{-3}$ is then given by:

$$h_{\mathrm{NO}} = \frac{1}{\rho}3.7\times 10^{-13} n_{\mathrm{NO}}\frac{k_{10}n_{\mathrm{O}}A_{10}}{k_{10}n_{\mathrm{O}}+A_{10}}\exp(-2699/T) \tag{3.35}$$

with $k_{10} = 6.5^{-11}\ \mathrm{cm^3 s^{-1}}$ and $A_{10} = 13.3\ \mathrm{s}^{-1}$.

$\mathrm{H_2O}$

Cooling by water vapour is expressed by using the exchange integral formulation given in equation 3.12.

The transmission function are computed using a statistical band model where the transmission function is expressed by:

$$\bar{T}_{\Delta\nu} = \exp\left[-\frac{\bar{S}N_{\mathrm{H_2O}}}{\delta}\left(1+\frac{\bar{S}N_{\mathrm{H_2O}}}{\pi\alpha}\right)^{-1/2}\right] \tag{3.36}$$

where $\frac{\bar{S}}{\delta}$ and $\frac{\bar{S}}{\pi\alpha}$ are band specific parameters taken from *Rodgers and Walshaw* [1966]. In addition, the pressure and temperature dependence of the Voigt profile has been taken into

Table 3.3: **Random Model Band Parameters for** $\mathrm{H_2O}$

Band	Interval	$\bar{S}/\delta$	$\pi\alpha/\delta$	C
rotational	40-160	7210.30	0.182	1.E-3
	160-280	6024.80	0.094	1.E-3
	280-380	1614.10	0.081	1.E-3
	380-500	139.03	0.0080	1.E-3
	500-600	21.64	0.068	1.E-3
	600-720	2.919	0.060	1.E-3
	720-800	0.386	0.059	1.E-3
	800-900	0.0715	0.067	1.E-3
	-			
6.3 μm	1200-1350	12.65	0.089	4.E-3
	1350-1450	134.4	0.230	4.E-3
	1450-1550	632.9	0.320	4.E-3
	1550-1650	331.2	0.296	4.E-3
	1650-1750	434.1	0.452	4.E-3
	1750-1850	136.0	0.359	4.E-3
	1850-1950	35.65	0.165	4.E-3
	1950-2050	9.015	0.104	4.E-3
	2050-2200	1.529	0.116	4.E-3

account by scaling α by $\frac{N_{\mathrm{H_2O}}}{\tilde{N}_{\mathrm{H_2O}}+CN_{\mathrm{H_2O}}}$ where C is effectively representing a finite Doppler width of the line. The used coefficients are given in Tab. 3.3. For the rotational lines, the parameter $\frac{\bar{S}}{\pi\alpha}$ was reduced by 15% to achieve better agreement with line-by-line computations.

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A Mathematical Symbols and Relations

A.1 Vector Operations

If $\vec{A}$, $\vec{B}$, $\vec{C}$ denote arbitrary three-dimensional vectorfields and α denotes an arbitrary scalar field, the following vector operations apply (partly adapted from *Haltiner and Williams* [1980]).

$$\begin{aligned} \vec{A}\cdot(\vec{B}\times\vec{C}) &= (\vec{A}\times\vec{B})\cdot\vec{C} \\ &= (\vec{C}\times\vec{A})\cdot\vec{B} \end{aligned} \tag{A.1}$$

$$\vec{A}\times(\vec{B}\times\vec{C}) = (\vec{A}\cdot\vec{C})\vec{B} - (\vec{A}\cdot\vec{B})\vec{C} \tag{A.2}$$

$$\begin{aligned} \vec{\nabla}\times\vec{\nabla}\alpha &= 0 \\ \vec{\nabla}\cdot\vec{\nabla}\times\vec{A} &= 0 \end{aligned} \tag{A.3}$$

$$\begin{aligned} \vec{\nabla}\cdot(\alpha\vec{A}) &= \alpha\vec{\nabla}\cdot\vec{A} + \vec{A}\cdot\vec{\nabla}\alpha \\ \vec{\nabla}\times(\alpha\vec{A}) &= \alpha\vec{\nabla}\times\vec{A} - \vec{A}\times\vec{\nabla}\alpha \end{aligned} \tag{A.4}$$

$$\vec{\nabla}(\vec{A}\cdot\vec{B}) = (\vec{A}\cdot\vec{\nabla})\vec{B} + (\vec{B}\cdot\vec{\nabla})\vec{A} + \vec{A}\times(\vec{\nabla}\times\vec{B}) + \vec{B}\times(\vec{\nabla}\times\vec{A}) \tag{A.5}$$

$$\vec{\nabla}\cdot(\vec{A}\vec{B}) = \vec{B}\vec{\nabla}\cdot\vec{A} + \vec{A}\cdot\vec{\nabla}\vec{B} \tag{A.6}$$

$$\vec{\nabla}\cdot(\vec{A}\times\vec{B}) = \vec{B}\cdot\vec{\nabla}\times\vec{A} - \vec{A}\cdot\vec{\nabla}\times\vec{B} \tag{A.7}$$

$$\vec{\nabla}\times(\vec{A}\times\vec{B}) = \vec{A}\vec{\nabla}\cdot\vec{B} - \vec{B}\vec{\nabla}\cdot\vec{A} + (\vec{B}\cdot\vec{\nabla})\vec{A} - (\vec{A}\cdot\vec{\nabla})\vec{B} \tag{A.8}$$

$$\vec{\nabla}\times(\vec{\nabla}\times\vec{A}) = \vec{\nabla}(\vec{\nabla}\cdot\vec{A}) - \vec{\nabla}^2\vec{A} \tag{A.9}$$

Let $\vec{A} = \vec{A}_\psi + \vec{A}_\chi$, where $\vec{\nabla}\times\vec{A}_\chi = 0$ and $\vec{\nabla}\cdot\vec{A}_\psi = 0$, then:

$$\begin{aligned} \vec{A}_\chi = \vec{\nabla}\chi \quad &, \quad \vec{A}_\psi = -\vec{\nabla}\times\vec{\psi} \\ \vec{\nabla}^2\chi = \vec{\nabla}\cdot\vec{A}_\chi = \vec{\nabla}\cdot\vec{A} \quad &, \quad \vec{\nabla}^2\vec{\psi} = \vec{\nabla}\times\vec{A}_\psi = \vec{\nabla}\times\vec{A} \end{aligned} \tag{A.10}$$

A.2 The Spherical Harmonics

The associated Legendre polynomials $Q_n^m(\mu)$ can be computed by:

$$\begin{aligned} Q_n^m(\mu) &= \frac{1}{2^m}\frac{(n+m)!}{(n-m)!m!}\left(1-\mu^2\right)^{m/2}\cdot F\left(m-n, m+n+1; m+1; \frac{1-\mu}{2}\right) \\ &= \left(1-\mu^2\right)^{m/2}\frac{d^m}{d\mu^m}Q_n(\mu) \\ &= \frac{(1-\mu^2)^{m/2}}{2^n n!}\frac{d^{n+m}}{d\mu^{n+m}}(\mu^2-1)^n \\ &= (-1)^{n+m}Q_n^m(-\mu) \end{aligned} \tag{A.11}$$

for $(-1 < \mu < 1)$, $n = 0, 1, 2, ...$, and $-n \leq m \leq n$ [*Korn and Korn*, 1968]. F is the hypergeometric series defined by

$$\begin{aligned} F(\alpha, \beta, \gamma, \mu) &= 1 + \frac{\alpha\cdot\beta}{1\cdot\gamma}\mu + \frac{\alpha(\alpha+1)\beta(\beta+1)}{1\cdot 2\cdot\gamma(\gamma+1)}\mu^2 + ... \\ &\quad + \frac{\alpha(\alpha+1)\cdot ...\cdot(\alpha+n)\beta(\beta+1)\cdot ...\cdot(\beta+n)}{1\cdot 2\cdot ...\cdot(n+1)\gamma(\gamma+1)\cdot ...\cdot(\gamma+n)}\mu^{n+1} + ... \end{aligned} \tag{A.12}$$

[e.g. *Bronstein and Semendjajew*, 1975]. The non-normalized $Q_n^m(\mu)$ defined by equation A.11 satisfy the following recurrence relations [*Korn and Korn*, 1968]:

$$(2n+1)\mu Q_n^m(\mu) - (n-m+1)Q_{n+1}^m(\mu) - (n+m)Q_{n-1}^m(\mu) = 0 \tag{A.13}$$

$$-\left(1-\mu^2\right)\frac{dQ_n^m(\mu)}{d\mu} - (n-m+1)Q_{n+1}^m(\mu) + (n+1)\mu Q_n^m(\mu) = 0 \tag{A.14}$$

Combining A.13 and A.14 yields:

$$\begin{aligned} \left(1-\mu^2\right)\frac{dQ_n^m(\mu)}{d\mu} &= -\frac{n(n-m+1)}{2n+1}Q_{n+1}^m(\mu) \\ &\quad + \frac{(n+1)(n+m)}{(2n+1)}Q_{n-1}^m(\mu) \end{aligned} \tag{A.15}$$

The norm Y_n^m of $Q_n^m(\mu)$ is obtained from the orthogonality relation:

$$\int\limits_0^{+1} Q_n^m(\mu)Q_l^m(\mu)d\mu = \frac{1}{2n+1}\frac{(n+m)!}{(n-m)!}\delta_n^l \tag{A.16}$$

$$Y_n^m = \sqrt{\frac{1}{2n+1}\frac{(n+m)!}{(n-m)!}} \tag{A.17}$$

Hereafter and throughout the text of this document $P_n^m(\mu)$ refers to the normalized associated Legendre polynomial:

$$P_n^m(\mu) = \frac{Q_n^m(\mu)}{Y_n^m} \tag{A.18}$$

The equations A.13 and A.15 become for the normalized associated Legendre Polynomials $P_n^m(\mu)$ using equation A.17 and A.18:

$$\mu P_n^m(\mu) - \epsilon_{n+1}^m P_{n+1}^m(\mu) - \epsilon_n^m P_{n-1}^m(\mu) = 0 \tag{A.19}$$

$$\begin{aligned} H_n^m(\mu) &= -\left(1-\mu^2\right)\frac{dP_n^m(\mu)}{d\mu} \\ &= n\epsilon_{n+1}^m P_{n+1}^m(\mu) - (n+1)\epsilon_n^m P_{n-1}^m(\mu) \end{aligned} \tag{A.20}$$

where

$$\epsilon_n^m = \sqrt{\frac{n^2-m^2}{4n^2-1}} \tag{A.21}$$

The spherical harmonics of degree n and order m $P_n^m(\mu)e^{\imath m\lambda}$ are solutions of the differential equation:

$$\vec{\nabla}_p^2\left[P_n^m(\mu)e^{\imath m\lambda}\right] + \frac{n(n+1)}{a^2}P_n^m(\mu)e^{\imath m\lambda} = 0 \tag{A.22}$$

They obey the orthogonality relation (using A.16):

$$\frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi} P_n^m(\mu)e^{\imath m\lambda}P_l^k(\mu)e^{-\imath k\lambda}d\lambda d\mu = \delta_k^m\delta_l^n \tag{A.23}$$

Any steady and differentiable field on a sphere can be developed in an infinite series of spherical harmonics:

$$X(\lambda,\mu) = \sum_{n=0}^{\infty}\sum_{m=-n}^{n} X_n^m P_n^m(\mu)e^{\imath m\lambda} \tag{A.24}$$

where the complex coefficients X_n^m are given by:

$$X_n^m = \frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi} X(\lambda,\mu)P_n^m(\mu)e^{-\imath m\lambda}d\lambda d\mu \tag{A.25}$$

Some properties of spherical harmonics are derived below:

$$\begin{aligned}
\left[\frac{\partial X(\lambda,\mu)}{\partial\lambda}\right]_l^k &= \frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi}\frac{\partial X(\lambda,\mu)}{\partial\lambda}P_l^k(\mu)e^{-\imath k\lambda}d\lambda d\mu \\
&\overset{(A.24)}{=} \frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi}\frac{\partial}{\partial\lambda}\left[\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\left(X_n^m P_n^m(\mu)e^{\imath m\lambda}\right)\right]P_l^k(\mu)e^{-\imath k\lambda}d\lambda d\mu \\
&= \frac{1}{4\pi}\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\left[imX_n^m\int_{-1}^{+1}\int_{0}^{2\pi}P_n^m(\mu)P_l^k(\mu)e^{\imath m\lambda}e^{-\imath k\lambda}d\lambda d\mu\right] \\
&\overset{(A.23)}{=} ikX_l^k \\
&\overset{(A.25)}{=} \frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi} ikX(\lambda,\mu)P_l^k(\mu)e^{-\imath k\lambda}d\lambda d\mu
\end{aligned} \tag{A.26}$$

Integration by parts (i.e.: $\int f'(x)g(x)dx = f(x)g(x) - \int f(x)g'(x)dx$), with $f(\mu) = X(\lambda,\mu)$ and $g(\mu) = P_n^m(\mu)$ yields using A.20

$$\begin{aligned}
\left[\frac{\partial X(\lambda,\mu)}{\partial\mu}\right]_n^m &\overset{(A.25)}{=} \frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi}\frac{\partial X(\lambda,\mu)}{\partial\mu}P_n^m(\mu)e^{-\imath m\lambda}d\lambda d\mu \\
&\overset{(A.20)}{=} +\frac{1}{2\pi}\int_{0}^{2\pi}\left[X(\lambda,\mu)P_n^m(\mu)\right]_{\mu=-1}^{\mu=+1}e^{-\imath m\lambda}d\lambda \\
&\quad +\frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi}\frac{X(\lambda,\mu)}{(1-\mu^2)}H_n^m(\mu)e^{-\imath m\lambda}d\lambda d\mu
\end{aligned} \tag{A.27}$$

The product of two functions $X(\lambda, \mu)$ and $Y(\lambda, \mu)$ can be computed as:

$$\begin{aligned}
[XY]_n^m &\overset{(A.25)}{=} \frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi} X(\lambda,\mu)Y(\lambda,\mu)P_n^m(\mu)e^{-\imath m\lambda}d\lambda d\mu \\
&\overset{(A.24)}{=} \frac{1}{4\pi}\int_{-1}^{+1}\int_{0}^{2\pi} \sum_{l=0}^{\infty}\sum_{k=-l}^{l}\left[X_l^k P_l^k(\mu)e^{\imath k\lambda}\right]\sum_{l=0}^{\infty}\sum_{k=-l}^{l}\left[Y_l^k P_l^k(\mu)e^{\imath k\lambda}\right]P_n^m(\mu)e^{-\imath m\lambda}d\lambda d\mu \\
&= \frac{1}{4\pi}\sum_{i=0}^{\infty}\sum_{j=-i}^{i}\sum_{l=0}^{\infty}\sum_{k=-l}^{l} X_i^j Y_l^k \int_{-1}^{+1}\int_{0}^{2\pi} P_i^j(\mu)P_l^k(\mu)e^{\imath(j+k)\lambda}P_n^m(\mu)e^{-\imath m\lambda}d\lambda d\mu \\
&\overset{(A.23)}{=} \frac{1}{2}\sum_{i=0}^{\infty}\sum_{l=0}^{\infty}\sum_{k=m-\Gamma}^{\Gamma} X_i^{m-k}Y_l^k\int_{-1}^{+1}P_i^{m-k}(\mu)P_l^k(\mu)P_n^m(\mu)d\mu
\end{aligned} \tag{A.28}$$

for $\Gamma = \min(i, l)$.