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A Multiple Time Scale Solution for the Chapman Mechanism

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Abstract

The rate equations representing the Chapman mechanism are solved analytically in the Multiple Time Scale Approximation by the exploitation of their stiffness. The widely different time scales of the reactions in the mechanism can be used to disentangle their effects on the solution. The reactions which bring oxygen into equilibrium with ozone are responsible for the overall stiffness, because their time scales are on the extreme ends of time scale spectrum for the reactions comprising the Chapman mechanism. Since catalytic cycles have similar equilibration reactions which may have time scales bordering the time scales of other reactions involving the catalysts, the method of multiple time scales can also be used to cure the stiffness in the rate equations governing these cycles. These analytical solutions may be incorporated into a numerical algorithm to improve its efficiency for the computation of the rate equations governing the chemistry of the atmosphere.

The cornerstone of modern theories on the ozone layer in the stratosphere is the the Chapman mechanism[1,2]. Although it is a highly simplified model for the production of stratospheric ozone, the Chapman mechanism predicts the abundance of ozone in the layer surprisingly well. Nevertheless its simplicity begs for an analytic solution, which can add insight into the ozone chemistry described by nonlinear differential equations. An analytical solution may also be incorporated into a numerical algorithm to improve its efficiency for the computation of the equations representing the modern theories.

The photolysis of molecular oxygen by very short wavelength ultraviolet (uv) radiation

can be viewed as the external source for ground state atomic oxygen in the Chapman mechanism. Assuming a pure oxygen atmosphere, atomic oxygen can suffer only three fates. The most likely possibility is for it to combine with molecular oxygen to form ozone in the three body reaction

Since ozone is also unstable to uv radiation, it can reform atomic oxygen through the photolytic reaction

The pair of reactions, R_2 and R_3 , act in concert to drive atomic oxygen and ozone into a state of quasi-equilibrium. These equilibration reactions are responsible for the stiffness of the rate equations representing the Chapman mechanism. A less likely possible outcome for atomic oxygen is for it to react with ozone to reform molecular oxygen in the exchange reaction

The least likely possibility for atomic oxygen is for it to recombine with another atom of oxygen in the three body reaction

to reform molecular oxygen.

Assuming a constant concentration of molecular oxygen, the rate equations for the Chapman mechanism derived from Eqs. (1-5) are

$$\frac{dn(O)}{dt} = -k_2 n(O) + J_3 n(O_3) - k_4 n(O) n(O_3) - 2 k_5 n(O)^2 + 2J_2, \quad (6)$$

$$\frac{dn(O_3)}{dt} = k_2 n(O) - J_3 n(O_3) - k_4 n(O) n(O_3). \quad (7)$$

The shorthand notations, $J_2 = J_1 n(O_2)$, $k_2 = k'_2 n(M) n(O_2)$ and $k_5 = k'_5 n(M)$, are used to express the above equations succinctly. The contributions of the reactions to the derivatives of the differential equations can be estimated by the substitution of the steady state concentrations of atomic oxygen and ozone into the reaction rates on the right hand sides of Eqs. (6) and (7). Taking the point at the height of 50 km as an illustrative example, these abundances[3] are $n(O) = 6 \times 10^9 \text{ cm}^{-3}$ and $n(O_3) = 4 \times 10^{10} \text{ cm}^{-3}$. The parameters in Eqs. (6) and (7) for this height[3] are: $k_2 = 1.7 \times 10^{-2} \text{ s}^{-1}$, $k_4 = 2.5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$, $k_5 = .01 k_4$ [4], $J_2 = 1.4 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$, and $J_3 = 10^{-3} \text{ s}^{-1}$. It is found from these values that the linear terms, $k_2 n(O) \approx 10^8 \text{ cm}^{-3} \text{ s}^{-1}$ and $J_3 n(O_3) \approx 4 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$, are at least an order of magnitude larger than the nonlinear losses, $k_4 n(O) n(O_3) \approx 4 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ and $2k_5 n(O)^2 \approx 1.4 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$, and are of the same order as the source $2J_2 \approx 2.8 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$. Since the nonlinear reactions exact losses on oxygen and ozone at a slow rate, their effect is insignificant on the solution at early times when the quasi-equilibrium between atomic oxygen and ozone is being established by the faster linear reactions. However the losses incurred by the nonlinear reactions are cumulative. After a long period of time these losses may become so large that the slower nonlinear reactions may be the deciding factors of the steady state abundances. Therefore the nonlinear terms while ineffective at early times may control the asymptotic region of the solution where the steady state is formed.

Since their effects are small, the nonlinear terms in Eqs. (6) and (7) can be treated as perturbations and can also be thought of as inhomogeneities. As a result of this kind of thinking, Eqs. (6) and (7) can be viewed as the linear system of equations $\underline{n}' = -\underline{v} \underline{n} + \underline{f}$. Here $\underline{n}$ is the column vector $[n(O), n(O_3)]^T$, $\underline{v}$ is the 2×2 matrix whose rows are $[k_2, -j_3]$ and $[-k_2, j_3]$, $\underline{f}$ is the column vector $[-k_4 n(O) n(O_3) - 2k_5 n(O)^2 + 2J_2, -k_4 n(O) n(O_3)]^T$, and the superscript ' means differentiation with respect to time. The pair of equilibration reactions R_2 and R_3 are the linear terms of Eqs. (6) and (7). Gear [5] shows that a system of linear differential equations can be stiff if the eigenvalues of the coupling matrix are widely different. This condition holds for the matrix $\underline{v}$, since its eigenvalues are $j_3 + k_2$

and 0 respectively. Diagonalization relieves the stiffness by uncoupling the eigenfunctions, and is also the first step in the Multiple Time Scale (MTS) approximation[7] for solving differential equations.

The matrix v has a zero eigenvalue because the sum of atomic oxygen and ozone is conserved in the pair of equilibrium reactions R_2 and R_3 . Catalytic cycles are similar sets of conservative reactions which occur within other families of atmospheric gases. They maintain a quasi-equilibrium between the members of a family, and in doing so contribute to the stiffness of the rate equations. For example, in the catalytic cycle reactions of NO_x , $NO + O_3 \rightarrow NO_2 + O_2$ and $NO_2 + O \rightarrow NO + O_2$, the sum of NO and NO_2 is constant.

The vector equation $\dot{\mathbf{n}}' = -\mathbf{v} \mathbf{n} + \mathbf{f}$ can be transformed into its uncoupled representation $\dot{\mathbf{x}}' = -\lambda \mathbf{x} + \Phi$, by the change of variables $\mathbf{n} = \mathbf{s} \mathbf{x}$ and $\Phi = \mathbf{s}^{inv} \mathbf{f}$. The matrix $\mathbf{s}$,

$$\mathbf{s} = \frac{1}{1 + k_{eq}} \begin{bmatrix} 1 & k_{eq} \\ -1 & 1 \end{bmatrix}, \quad \text{where } k_{eq} = \frac{j_3}{k_2}, \quad (8)$$

diagonalizes $\mathbf{v}$ by the similarity transformation $\mathbf{s}^{inv} \mathbf{v} \mathbf{s} = \lambda$. The elements of λ are the eigenvalues $j_3 + k_2$ and 0 respectively. The components of the transformed rate equations are

$$\frac{dx_1}{dt} = -(j_3 + k_2) x_1 + \Phi_1, \quad \text{and} \quad (9)$$

$$\frac{dx_2}{dt} = - (0) x_2 + \Phi_2. \quad (10)$$

The inhomogeneities of Eqs. (9) and (10) are $\Phi_1 = -(1 - k_{eq})k_4 n(O)n(O_3) - 2k_5 n(O)^2 + 2J_2$, and $\Phi_2 = -2k_4 n(O)n(O_3) - 2k_5 n(O)^2 + 2J_2$ respectively. In these inhomogeneous terms, the abundances of oxygen and ozone are expressed in term of the new variables, so that $n(O) = (1 + k_{eq})^{-1} (-x_1 + x_2)$ and $n(O_3) = (1 + k_{eq})^{-1} (k_{eq}x_1 + x_2)$.

The interpretation of $\mathbf{x}$ can be simplified by expressing the inverse transformation $\mathbf{x} = \mathbf{s}^{inv} \mathbf{n}$ in component form: $x_1 = n(O) - k_{eq}n(O_3)$ and $x_2 = n(O) + n(O_3)$. The second component x_2 an eigenfunction of $\dot{\mathbf{n}}' = -\mathbf{v} \mathbf{n}$ is O_x ! This result is expected because the sum of Eqs. (6) and (7) diagonalizes $\dot{\mathbf{n}}' = -\mathbf{v} \mathbf{n}$ with the eigenvalue of zero. Equation (10) shows that O_x is conserved on a short time scale, because its rate of change is determined solely by the slow nonlinear reactions in Φ_2 . The first component, x_1 , can be considered the

nonequilibrium transient of O_x . Even though the total concentration of oxygen and ozone is conserved, their concentrations may change until they adjust to their steady state values. The eigenfunction, x_1 , describes the relaxation of the initial nonequilibrium apportionment of oxygen and ozone to its steady state distribution. It vanishes exponentially at the rate of j_3+k_2 , which is the sum of the forward and backward equilibrium reactions rates.

The (MTS) approximation assumes that the solution of the differential equation $\underline{x}' = -\lambda \underline{x} + \underline{\Phi}$, where $\underline{\Phi}$ is a small term of the order ϵ , can be described by the time variables: $t_0 = t$, $t_1 = \epsilon t$, $t_2 = \epsilon^2 t$, $t_3 = \epsilon^3 t$, Here t_0 is the fastest variable, t_1 is the second fastest, t_2 is the third fastest variable, and etc Since these time variables are assumed to be independent, then by the chain rule of differentiation the total derivative with respect to time becomes the partial derivatives with respect to these new variables, i.e.

$$\frac{d}{dt} = \frac{\partial}{\partial t_0} + \epsilon \frac{\partial}{\partial t_1} + \epsilon^2 \frac{\partial}{\partial t_2} + \epsilon^3 \frac{\partial}{\partial t_3} + \dots \quad (11)$$

The MTS approximation assumes also that the exact solution can be expanded in the power series $\underline{x} = \underline{x}^{(0)} + \epsilon \underline{x}^{(1)} + \epsilon^2 \underline{x}^{(2)} + \epsilon^3 \underline{x}^{(3)} + \dots$. Substituting this power series and Eq. (11) into Eqs. (9) and (10), and then equating terms of equal powers of ϵ , and keeping in mind that the inhomogeneity $\underline{\Phi}$ is of order ϵ , yields sets of perturbation equations of increasing orders of ϵ . The resulting equations in the first two orders of ϵ are:

$$\frac{\partial x_1^{(0)}}{\partial t_0} = - (j_3+k_2) x_1^{(0)} \quad (12)$$

$$\frac{\partial x_2^{(0)}}{\partial t_0} = - (0) x_2^{(0)} \quad (13)$$

and

$$\frac{\partial x_1^{(1)}}{\partial t_0} + \frac{\partial x_1^{(0)}}{\partial t_1} = - (j_3+k_2) x_1^{(1)} + \Phi_1(x_1^{(0)}, x_2^{(0)}) \quad (14)$$

$$\frac{\partial x_2^{(1)}}{\partial t_0} + \frac{\partial x_2^{(0)}}{\partial t_1} = - (0) x_2^{(1)} + \Phi_2(x_1^{(0)}, x_2^{(0)}) \quad (15)$$

respectively. Higher order accuracy can always be obtained from the higher order equations of the perturbation series, but may not be needed for practical applications. Therefore the perturbation series is terminated after the first two orders.

Since the derivatives of Eqs. (12) and (13) are with respect to the fast time variable t_0 , then the "constants" of integration, $\hat{x}_1(t_1)$ and $\hat{x}_2(t_1)$, for the solutions of Eqs. (12) and (13), $x_1^{(0)} = \hat{x}_1(t_1)\exp(-(j_3+k_2)t_0)$ and $x_2^{(0)} = \hat{x}_2(t_1)$, can be dependent on the slow time variable t_1 . This dependence allows these constants to vary on a time scale which is long compared to the time scale of $\exp(-(j_3+k_2)t_0)$, the function representing the time dependence of the fast reactions. The abundances of oxygen and ozone of order ϵ^0 are therefore $n(O) \approx (1+k_{eq})^{-1} [\hat{x}_1(t_1)\exp(-(j_3+k_2)t_0) + k_{eq}\hat{x}_2(t_1)]$ and $n(O_3) \approx (1+k_{eq})^{-1} [-\hat{x}_1(t_1)\exp(-(j_3+k_2)t_0) + \hat{x}_2(t_1)]$. Suppressing the t_1 dependence of $\hat{x}_1(t_1)$ and $\hat{x}_2(t_1)$ for the moment, that is fixing $\hat{x}_1(t_1)$ and $\hat{x}_2(t_1)$ to their initial values, the lowest order approximations for oxygen and ozone are compared to the true abundances in Figs. (1) and (2) respectively. The true solution is obtained from a stiff solver⁶ which uses the backward Euler differencing algorithm to compute Eqs. (6) and (7) numerically.

The lowest order approximations labelled as the linear graphs in Figs. (1) and (2) lie on top of the exact solutions at early times. This result is expected because the lowest order approximation accounts for all the fast reactions in the Chapman mechanism completely. The plots in Figs. (1) and (2) also show that oxygen and ozone equilibrate on the time scale of $1/(j_3+k_2) \approx 56$ s. On the other hand, the comparison of these functions shows that the lowest order approximation departs from the true steady state abundances. This departure is expected because the lowest order solution does not account for any nonlinear losses in the Chapman mechanism. The lowest order approximation predicts the absolute values of the steady state abundances incorrectly. Its prediction for the steady state abundance ratio $n(O)/n(O_3) = j_3/k_2 = .0588$ is however off by less than two percent from .0597 the true partitioning ratio of O_x . This result means that the linear reactions maintain a state of quasi-equilibrium between oxygen and ozone as they are depleted by the nonlinear losses. The nonlinear reactions can therefore reduce the total amount of O_x but are ineffective in changing the partitioning of its components. The results in Figs. (1) and (2) also illustrate that the linear reactions' region of influence is separated from the nonlinear reactions' region of influence. This separation of time domains makes the MTS assumption of the independence between t_0 and t_1 plausible.

It can be hypothesized from the comparisons made in Fig. (1) and (2) that if the "constants" of integration, $\hat{x}_1(t_1)$ and $\hat{x}_2(t_1)$, decay on a time scale much longer than $1/(j_3+k_2)$, then the lowest order approximation can be brought back into coincidence with the true solution at later times. These slowly varying functions can be determined from the subsidiary equations which result from the elimination of the secular terms in Eqs. (14) and

(15) respectively. A secular term occurs when the inhomogeneity of a differential equation is in resonance with the homogeneous solution of the undriven equation. For example, an inhomogeneity of Eq. (14) which is in resonance with $x_1^{(1)}$ is the exponential function $\exp(-(j_3+k_2)t_0)$, because this exponential function is also the homogeneous solution of Eq. (14). The forcing function Φ_1 has three types of bilinear products: 1) $x_1^{(0)}x_2^{(0)}$, 2) $(x_1^{(0)})^2$, and 3) $(x_2^{(0)})^2$. Their time dependences are respectively: 1) $\exp(-(j_3+k_2)t_0)$, 2) $\exp(-2(j_3+k_2)t_0)$, and 3) $\exp(-0)$. The resonant forcing of $x_1^{(0)}x_2^{(0)}$ can be eliminated from Eq. (14) by setting it equal to the second term on the left hand side $\partial x_1^{(0)}/\partial t_1$. This cancellation leads to the differential equation which govern the slow variation of $\hat{x}_1(t_1)$

$$\frac{\partial \hat{x}_1}{\partial t_1} = - \frac{k_4 (1-k_{eq})^2 + 4k_5 k_{eq}}{(1 + K_{eq})^2} \hat{x}_2 \hat{x}_1 . \quad (16)$$

The secular term in Eq. (15) is eliminated in the same way to yield

$$\frac{\partial \hat{x}_2}{\partial t_1} = 2J_2 - 2 \frac{k_4 k_{eq} + k_5 k_{eq}^2}{(1 + K_{eq})^2} (\hat{x}_2)^2 . \quad (17)$$

Equation (17) has been deduced earlier by Brassuer and Solomon [8] to describe the production of atomic oxygen in the upper stratosphere, a region where the majority component of O_x is atomic oxygen.

Equations (16) and (17) can be simplified by the Riccati transformation[9]

$$\hat{x}_2 = \frac{1}{2} \frac{(1+k_{eq})^2}{k_4 k_{eq} + k_5 k_{eq}^2} \frac{1}{\psi} \frac{\partial \psi}{\partial t_1} . \quad (18)$$

The substitution of Eq. (18) into Eq. (17) leads to the second order differential equation of constant coefficients for ψ

$$\frac{\partial^2 \psi}{\partial t_1^2} = 4 J_2 \frac{k_4 k_{eq} + k_5 k_{eq}^2}{(1 + K_{eq})^2} \psi \equiv J^2 \psi . \quad (19)$$

Equation (19) is solved by $\psi(t_1) = \exp(J t_1) + \psi_0 \exp(-J t_1)$, where ψ_0 is a constant [10] which is related to the initial value of $\hat{x}_2(t_1)$. The substitution of $\psi(t_1)$ into Eq. (18) gives $\hat{x}_2(t_1)$ explicitly. Equation (16) can be simplified into the form of a complete integral

$$\frac{\partial \ln \hat{x}_1}{\partial t_1} = - \frac{k_4 (1-k_{eq})^2 + 4 k_5 k_{eq}}{(1 + K_{eq})^2} \frac{(1 + k_{eq})^2}{2 (k_4 k_{eq} + k_5 k_{eq}^2)} \frac{\partial \ln \psi}{\partial t_1} \equiv - \alpha \frac{\partial \ln \psi}{\partial t_1} \quad (20)$$

for $\hat{x}_1(t_1)$ by the substitution of Eq. (18), the Riccati transformation, for $\hat{x}_2(t_1)$.

Up to this point the fast and slow variations in the abundances of oxygen and ozone are known only up to ϵ^0 . The analytical expressions, $\hat{x}_1(t_1) = \hat{x}_1(0) [1 + \psi_0]^\alpha / [\exp(Jt_1) + \psi_0 \exp(-Jt_1)]^\alpha$ and $\hat{x}_2(t_1) = (1+k_{eq}) \sqrt{J_2 (k_4 k_{eq} + k_5 k_{eq}^2)} [\exp(Jt_1) - \psi_0 \exp(-Jt_1)] / [(\exp(Jt_1) + \psi_0 \exp(-Jt_1))]$, describe the composite effects of the slower nonlinear sinks of Eqs. (4) and (5) and the external source of Eq. (1) on the abundances of oxygen and ozone. Their effects on $n(O)$ and $n(O_3)$ are illustrated in Figs. (1) and (2) respectively. The examination of Figs. (1) and (2) shows that these functions to be inoperative at early times but to be important at later times. Further examination of these figures shows that these functions bring the approximate solutions into coincidence with the true steady state values of oxygen and ozone. The approximation breaks down at intermediate times, because the approximation up to this point has not yet been corrected to any order of ϵ nor has any slower time scale beyond t_1 been deduced to resolve the three slower reactions. Since $\psi(t_1)$ controls both $\hat{x}_1(t_1)$ and $\hat{x}_2(t_1)$, then the time scales of the variations in these function can be deduced from the exponential function $\exp(-Jt_1)$ of $\psi(t_1)$. The time scales of $\hat{x}_1(t_1)$ and $\hat{x}_2(t_1)$ are approximately $(\alpha J)^{-1} \approx 4,400$ s and $J^{-1} \approx 34,800$ s respectively, which prove a posteriori that the time scale of t_1 is considerably longer than $(j_3 + k_2)^{-1}$ the 56 second time scale of t_0 .

As expected $J = 2 (1+k_{eq})^{-1} \sqrt{J_2 (k_4 k_{eq} + k_5 k_{eq}^2)}$ the composite depletion rate for x_2 odd oxygen increases with k_4 and k_5 the lose rates of atomic oxygen and ozone for the nonlinear reactions represented in Eqs. (4) and (5). It is somewhat surprising to find that J the depletion rate increases with J_2 the source rate for odd oxygen in the Chapman mechanism. This odd result can be accounted for by noting that the odd oxygen depletion reactions R_4 and R_5 can be increased in two ways: 1) by increasing the thermal rate coefficients k_4 and k_5 , or 2) by increasing the abundances of atomic oxygen and ozone. An increase in the source rate J_2 speeds up the overall depletion of odd oxygen because it supplies more atomic oxygen to be destroyed. The composite depletion J is also a function of k_{eq} the partitioning of odd oxygen, and the function has a maximum.

Equations (14) and (15) can now be solved because they have been cured of their secular behavior by the elimination of the resonant forces driving them. The homogeneous solutions of Eqs. (14) and (15) need not be rederived because they have already been determined by solving Eqs. (12) and (13). The particular solutions of Eqs. (14) and (15) satisfying the null initial values can be expressed as the integrals $x_1^{(1)} = \int_0^{t_0} dt_0'' \exp(-(j_3+k_2)(t_0-t_0''))(\Phi_1 - \partial x_1^{(0)}/\partial t_1)$ and $x_2^{(1)} = \int_0^{t_0} dt_0'' (\Phi_2 - \partial x_2^{(0)}/\partial t_1)$ respectively. Since their integrands are exponential functions of t_0'' , these integrals are

$$x_1^{(1)} = A \frac{1 - \exp(-(j_2+k_3)t_0)}{j_2+k_3} + B \frac{\exp(-(j_3+k_2)t_0) - \exp(-2(j_3+k_2)t_0)}{j_3+k_2}, \quad (21)$$

and

$$x_2^{(1)} = C \frac{1 - \exp(-(j_2+k_3)t_0)}{j_2+k_3} + D \frac{1 - \exp(-2(j_2+k_3)t_0)}{2(j_2+k_3)} \quad (22)$$

respectively. The coefficients in Eqs. (21) and (22) are respectively: 1) $A = 2J_2 - \hat{x}_2(t_1)^2 [k_4(1-k_{eq})k_{eq} + 2k_5k_{eq}^2] / [1+k_{eq}]^2$, 2) $B = \hat{x}_1(t_1)^2 [k_4(1-k_{eq}) - 2k_5] / [1+k_{eq}]^2$, 3) $C = -2\hat{x}_1(t_1)\hat{x}_2(t_1) [k_4(1-k_{eq}) + 2k_5k_{eq}] / [1+k_{eq}]^2$, and 4) $D = \hat{x}_1(t_1)^2 [k_4 - k_5] / [1+k_{eq}]^2$. Equations (21) and (22) completes the derivation of the solution to the Chapman mechanism to first order in ϵ . The first order corrections are added to the zeroth order approximations, and the results are illustrated in Figs. (1) and (2) respectively. The first order corrections improve the approximations in the intermediate time region.

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Figure 1. Atomic oxygen $n(O)$ is plotted against time for four different functions. The first graph labelled as exact was obtained from the numerical computation of Eqs. (6) and (7). The second graph designated as linear is the solution of the linear system expressed in Eqs. (12) and (13). This graph illustrates the fast variation of $\exp(-(j_3+k_2)t_0)$ by holding the slowly varying functions $\hat{x}_1(t_1)$ and $\hat{x}_2(t_1)$ to their initial values. When $\hat{x}_1(t_1)$ and $\hat{x}_2(t_1)$ are allowed to vary according to Eqs. (16) and (17) the subsidiary equations resulting from the suppression of the secular terms in Eqs. (14) and (15), then their effects are illustrated in the third graph listed as the zero(th). This graph shows two results of the subsidiary equations: 1) their steady states are correct, 2) their time scales are considerably longer than the time scale of the faster equilibration reactions. The fourth graph designated as zero(th)+first is the sum of the third graph and the first order corrections provided by Eqs. (21) and (22).

Figure 2. These graphs of ozone $n(\text{O}_3)$ are designated in the way as in Figure 1.

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