

Non-Equilibrium Phenomena in the Kinetics of Photochemical Ozone Production

J. J. Kozak, G. Nicolis¹, J. W. Kress, M. Sanglier¹

Dept. of Chemistry and Radiation Laboratory University of Notre Dame, Notre Dame, USA

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Abstract

A sequence of photochemical reactions of interest in atmospheric physics is considered. Mass and energy-balance equations are derived and studied both analytically and numerically. It is shown that under certain conditions the approach to the steady state is characterized by considerable overshoots in the composition variables and in the temperature.

Introduction

Nonlinear systems driven away from equilibrium may undergo transitions to regimes showing sustained oscillations of the limit-cycle type, spatial ordering, or excitability phenomena associated with transitions between multiple steady states [1]. One of the best studied examples of this behavior refers to systems undergoing chemical reactions and diffusion [2]. Hitherto such systems – especially in the context of biological applications – have mostly been modeled by assuming that they are *open to mass transfer*, but remain isolated with respect to (any, but the convective) energy transfer from the outside world.

Recently, Ross and co-workers [3] pointed out that the illumination of chemical systems provides the possibility of interesting feedback mechanisms between kinetic and energetic phenomena. They analyzed simple reaction schemes and showed that, even in systems closed to mass transfer, there are possibilities of radiation-induced multiple steady states in the presence of exothermic reaction steps.

The purpose of the present paper is to analyze a sequence of photochemical reactions of interest in atmospheric physics from the standpoint of irreversible thermodynamics and nonlinear kinetics. The model is defined in section 1, and the rate equations are developed in section 2. Section 3 is devoted to the results of numerical simulations of these equations. Possible implications in atmospheric sciences are suggested in section 4.

¹ Faculté des Sciences de l'Université Libre de Bruxelles, Bruxelles, Belgium.

1. The model

Chapman Sequence Reactions

As suggested many years ago by Chapman, in the stratosphere a continuous oxygen-ozone conversion takes place which is driven by the flux of solar energy (see [4] for a recent survey). The detailed steps in the Chapman mechanism are as follows.

a) Oxygen photodissociation:



Here the wavelength λ of the light must be $\lambda \leq 2400 \text{ \AA}$. An absolute upper bound for J_2 is [4],

$$J_2 \leq J_2(100 \text{ km}) = 2 \times 10^{-7} \text{ sec}^{-1}. \quad (1a)$$

b) Three-Body recombination:



with

$$k_2 = 1 \cdot 1 \times 10^{-34} \exp\left(\frac{510}{T}\right) \text{ cm}^6 \text{ sec}^{-1}. \quad (2a)$$

The concentration of the third body M is to be taken as that of the ambient atmosphere, T is the temperature in Kelvin (K).

c) Ozone photolysis:

The photolysis of ozone by visible and UV light (wavelength $\lambda \leq 11,800 \text{ \AA}$) is



with a total rate

$$J_3 = 10^{-2} \text{ sec}^{-1}, \quad (3a)$$

at zero optical depth, or in the visible part of the spectrum

$$J_3 = 3.0 \times 10^{-4} \text{ sec}^{-1}. \quad (3b)$$

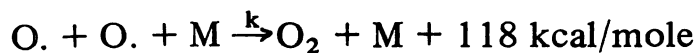
Note that both J_2 and J_3 are complex functions of the state of the system, as they depend crucially on the concentration of O_3 [4]. This additional feedback will not be treated explicitly in the present study.

d) **Bimolecular Recombination:**

with

$$k_3 = 10^{-11} \exp\left(-\frac{2300}{T}\right) \text{ cm}^3 \text{ sec}^{-1} . \quad (4a)$$

The additional reaction



having the rate coefficient

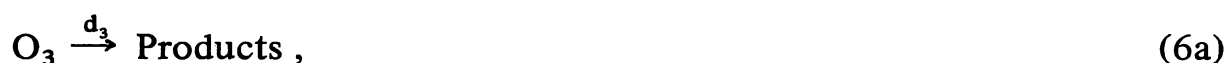
$$k = 4.7 \times 10^{-33} \left(\frac{300}{T}\right)^2 \text{ cm}^6 \text{ sec}^{-1} ,$$

can be envisaged. However, this reaction, which plays a role in the mesosphere, will be neglected in the present analysis.

Mass and energy sources and sinks

In the sequel, we will introduce in our development some generalizations of the Chapman sequence, eqs. (1) to (4). First, a source of O_2 production will be added. And second, the consumption of the resultant reactive forms of oxygen — i. e. O and O_3 — as well as of O_2 will be taken into account. The main motivation for dealing with a system with *evolving oxygen content* is, that by this we are able to incorporate in the analysis some features simulating realistic atmospheric situations. For instance, it is known that O and O_3 react with other gaseous components of the stratosphere such as nitrogen oxydes. Thus, inclusion of sink terms for these chemicals allows us to consider — admittedly in a rudimentary way — the coupling between a pure oxygen atmosphere described by the Chapman sequence and the much more complex terrestrial atmosphere under stratospheric conditions. Moreover, oxygen is produced mainly by plant photosynthesis. Inclusion of such a term will allow us to discuss possible evolution pathways of a primordial atmosphere brought about by living systems over a long time scale.

We represent the kinetics of these processes in the simplest possible way:



A different kind of process that will also be incorporated in our analysis involves the absorption of radiation, primarily by ozone, and the evacuation of heat through infrared cooling. Both processes together with the heats released by the reactions of the Chapman sequence, determine the system's temperature, which in turn influences the rate of the reactions. Moreover, the intensity of light absorption by O_3 depends on the concentration of this reactant. We are therefore in the presence of strong feedback mechanisms between chemical kinetics and energetics. Again, such mechanisms are known to operate in a variety of atmospheric phenomena [5].

2. Rate equations

We now are prepared to write down a set of rate equations describing the dynamical behavior of our model. To this end, we adopt the picture of a well-stirred medium. Thus, we develop our equations for such intensive quantities as the number of molecules O_2 per cm^3 (designated by X), the number of atoms O per cm^3 (designated by Y) and the number of molecules O_3 per cm^3 (designated by Z). In addition, we deal with the internal energy density per cm^3 , denoted by ρe , where ρ and e are expressed in units of g/cm^3 and cal/g , respectively, ($1\text{ cal} = 4.1815\text{ Joule}$).

Mass balance

From eqs. (1–6) we can write, using the well-known laws of chemical kinetics of dilute mixtures, the following equations:

$$\frac{dX}{dt} = v - J_2 X + J_3 Z - k_2(T) MXY + 2k_3(T) YZ - d_2 X, \quad (7)$$

$$\frac{dY}{dt} = 2J_2 X + J_3 Z - k_2(T) XYM - k_3(T) YZ - d_1 Y, \quad (8)$$

$$\frac{dZ}{dt} = -J_3 Z + k_2(T) XYM - k_3(T) YZ - d_3 Z. \quad (9)$$

An inspection of eqs. (7–9) permits us to realize a characteristic difference of time scales. From the data presented in section 1, the magnitude of a representative linear term in eqs. (7–9), say $J_2 X$, can be estimated using present-day atmospheric values, [6], for the concentration of molecular oxygen in the stratosphere. From these we determine that $J_2 X \sim 10^{10}$ molecules $cm^{-3} sec^{-1}$. In a similar way, we may estimate the magnitude of a representative nonlinear term, say $k_2 XYM$. Again using present-day estimates, [6], for X , Y , M , we find that $k_2 XYM \sim 10^9$ molecules $cm^{-3} sec^{-1}$. These two estimates reflect the chemical and photochemical time scales in the atmospheric problem being considered here.

Consider now the input term v . In a present-day atmosphere, X is of the order of 10^{18} atom cm^{-3} in the troposphere [4]. Moreover, it has been estimated that the turnover time for the biotic production of O_2 is approximately 2000 years [7]. Thus, a present-day estimate of v is something like:

$$v = \frac{10^{18} \text{ atoms } cm^{-3}}{2000 \text{ years}} \sim 10^7 \text{ atoms } cm^{-3} sec^{-1}. \quad (10)$$

This value corresponds to an evolution *slower* than most of the remaining terms in the rate equations, eqs. (7–9). The contrast becomes even more striking if one considers the problem of the evolution of a primordial atmosphere. First, in this case one expects that v will be much smaller because of the scarcity of plant life. In fact, one might even argue that v could then become inversely proportional to the *size* of the earth's surface, as the biotic production of O_2 might have occurred in certain preferred regions. And second, if X, Y, Z, M are all small at a certain initial stage, the nonlinear terms in eqs. (7–9) can in turn become exceedingly small. In either case, the time scale of evolution can easily become 10^3 fold (or more) larger, which would bring us just into the regime of a *geological* time scale.

Energy balance

In the presence of an electromagnetic field, the energy balance equation reads ([5], [8]):

$$\rho \frac{de}{dt} = \text{Net flux } F = \int d\nu [F_S(\nu) + F_{IR}(\nu)] . \quad (11)$$

Here the (frequency dependent) net flow term F is decomposed into an (incoming) absorbed part F_S and an infrared contribution F_{IR} . The time derivative de/dt can be evaluated using a local equilibrium assumption as follows:

$$\rho \frac{de}{dt} = \rho c_p \frac{dT}{dt} + \sum_{i=X,Y,Z} \left(\frac{\partial e}{\partial \rho_i} \right) \frac{d\rho_i}{dt} . \quad (12)$$

where ρ is the density of the mixture, c_p is the specific heat at constant pressure, and $(\partial e/\partial \rho_i)$ are the enthalpy changes arising from the various reactions.

We may now use the rate equations, (7–9), to eliminate $d\rho_i/dt$ in eq. (12). Moreover, we assume that the main absorbers of radiation are O_2, O_3 and that the infrared flux can be modeled by a Newton-like cooling law. We thus obtain:

$$\begin{aligned} \rho c_p \frac{dT}{dt} = & |\Delta H_2| k_2(T) XYM + |\Delta H_3| k_3(T) YZ + \alpha(T_0 - T) + \\ & + \alpha_2 X + \alpha_3 Z . \end{aligned} \quad (13)$$

$\Delta H_2, \Delta H_3$ are the heats of reaction in steps (2) and (4), α is Newton's cooling coefficient, T_0 is the ambient temperature, and α_2, α_3 the absorption coefficients of O_2 and O_3 respectively.

3. Numerical simulations

The structure of the rate equations under isothermal conditions, eqs. (7–9), was investigated analytically. It was shown that they admit a single physically acceptable steady-state solution which is asymptotically stable. Moreover, damped oscillations around this state seem to be ruled out. We therefore focus from now on the full chemical-dynamical system described by eqs. (7), (8), (9) and (13).

The time evolution of this system was followed numerically. It becomes immediately clear that, owing to the large order-of-magnitude difference between the time scales characterizing the various processes, the system was *stiff* (cp. [9]). Because of this, the evolution could only be followed for a relatively limited period of time. In all simulations however, there was a clear tendency to achieve a unique steady state. The conclusion seems to be therefore that for a wide range of parameter values the augmented Chapman sequence described in the preceding sections cannot give rise to self-organization phenomena in the form of limit cycles or of multiple steady-state transitions. As we see presently however the *transient* evolution toward the steady state presents some highly non-trivial features.

Consider first the case where initially, X, Y, Z are set to the values corresponding to a steady-state solution of eqs. (7–9) for a temperature $T = 220\text{ K}$ and for $d_3 = 10^{-4}\text{ sec}^{-1}$, $d_2 = 0$, $d_1 = 1\text{ sec}^{-1}$. To assess the possible influence of thermal perturbations we set the initial temperature to 230 K and follow the simultaneous composition *and* temperature evolution from eqs. (7–9) and (13). In the latter equation we choose $\alpha_2 \simeq 0$, $\alpha_3 = 0.33 \times 10^{-21}\text{ cal molecule}^{-1}\text{ sec}^{-1}$,

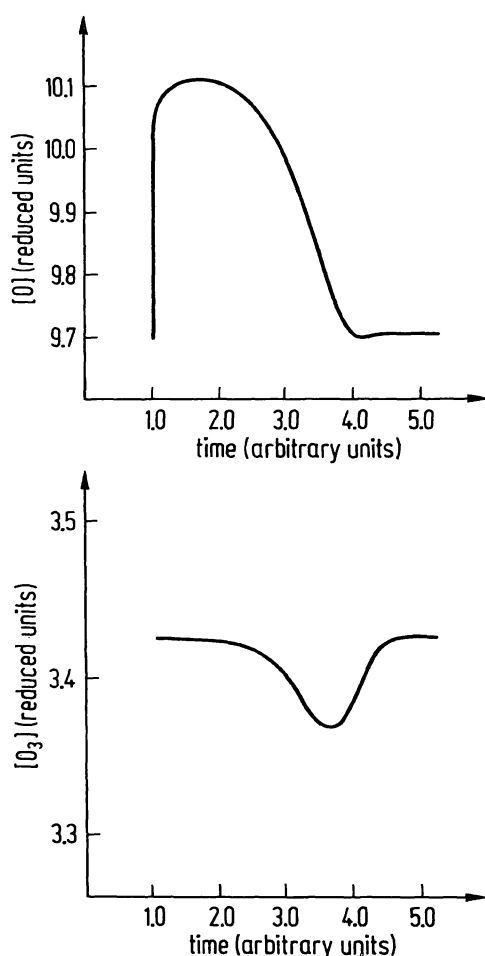


Fig. 1: Response of the system to a thermal perturbation. Displayed are the atomic oxygen and ozone profiles, generated by using the set of parameters given in the text and initialized at the steady-state concentrations corresponding to the temperature $220\text{ }^\circ\text{K}$; with the initial temperature set at $230\text{ }^\circ\text{K}$. The concentrations reported in this figure are reduced with respect to the factor $M = 10^{17}\text{ molecules/cm}^3$, the approximate ambient concentration in the ozonosphere.

$\alpha = 1.16 \times 10^{-9} \text{ cal cm}^{-3} \text{ sec}^{-1} \text{ K}^{-1}$, $c_p = 0.24 \text{ cal g}^{-1} \text{ K}^{-1}$ and $\rho = 4 \times 10^{-5} \text{ g/cm}^3$. These numerical estimates were motivated by atmospheric data, [10].

The results of this simulation are as follows. First, the temperature drops monotonously to about 220 °K. Next, atomic oxygen O. experiences a rapid overshoot of a few percent relative to the initial state, followed by a slower decay as seen in Fig. 1. Finally, the O₃ concentration experiences an undershoot of a few percent as shown in Fig. 1. The molecular oxygen concentration remains practically unaffected.

A different situation is depicted in Fig. 2. It corresponds to the values $d_3 = 10^{-8} \text{ sec}^{-1}$, $d_2 = 0$, $d_1 = 10^{-3} \text{ sec}^{-1}$, $\alpha_2 \simeq 0$, $\alpha_3 = 0.33 \times 10^{-21} \text{ cal molecule}^{-1} \text{ sec}^{-1}$, $\alpha = 5.8 \times 10^{-11} \text{ cal cm}^{-3} \text{ sec}^{-1} \text{ K}^{-1}$, and c_p and ρ as before. The initial conditions are $T = 235 \text{ °K}$, and values of X, Y, Z corresponding to a steady state solution of eq. (7–9) with $T = 235 \text{ °K}$. As is apparent from the Figure, the O. overshoot and the concomitant O₃ decrease are qualitatively the same as in Fig. 1, although quantitatively they are more pronounced. On the other hand, the temperature behaves in a qualitatively different way. It rises rapidly to 285 °K and subsequently levels off to a value of about 380 °K.

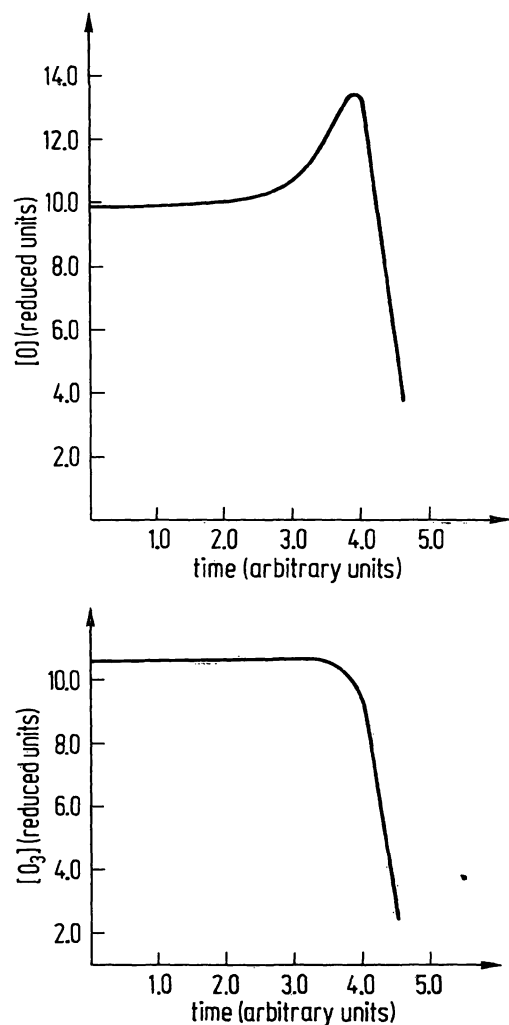


Fig. 2: Response of the system to simultaneous thermal and concentration perturbations. Displayed are the atomic oxygen and ozone profiles, generated by using the choice of parameters given in the text, and initialized at the steady-state concentrations corresponding to the temperature 235 °K, with the initial temperature set at 235 °K. The normalization adopted here is the same as in Fig. 1.

This catastrophic behavior, which is to be contrasted to the self-regulating behavior of temperature found in the preceding simulation, is reminiscent of the *climatic catastrophes* whose possibility was pointed out recently and analyzed on simple models by Budyko [11] and Sellers [12].

4. Concluding remarks

In this paper we analyzed the effects of energy and mass fluxes on the nonequilibrium behavior of the photochemical production of ozone. We have shown that the approach to the steady state is characterized by interesting transient behavior in the form of composition or temperature overshoots, which under some conditions take catastrophic proportions.

Given that the photochemical reactions of the Chapman sequence studied here constitute a basic component of atmospheric dynamics at the stratospheric level, it is difficult to avoid the feeling that the analysis undertaken here should have some implications both for present-day atmospheric dynamics as well as for the understanding of atmospheric evolution, in the early biological era. These problems will be pursued in future investigations.

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Professor Dr. J. J. Kozak
 Dr. J. W. Kress
 Dept. of Chemistry and
 Radiation Laboratory
 University of Notre Dame
 Notre Dame, Indiana 46556, USA

Professor Dr. G. Nicolis
 Dr. M. Sanglier
 Faculte de Sciences de l'Université
 Libre de Bruxelles
 Code Postal N° 226
 Boulevard du Triomphe
 B-1050 Bruxelles