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Stratospheric ozone dynamics according to the Chapman mechanism

R. M. Velasco · F. J. Uribe · E. Pérez-Chavela

Abstract The photochemical mechanisms behind the ozone dynamics in the stratosphere have been studied for a long time. Though the differential equations describing the kinetics associated with them are well known, their mathematical properties have not been fully explored. In this work some of these mathematical properties as well as their physical implications are investigated in the simplest photochemical mechanism, namely, Chapman's one.

Keywords Stratospheric ozone · Chapman mechanism · Dynamical systems

1 Introduction

The ozone layer in the stratosphere has become one of the most important scientific problems due to its numerous implications. In order to briefly understand its relevance some well established facts will be mentioned [1–5]. Light coming from the sun can be approximated by a black body radiation at a temperature of about 6,000 K, its spectrum peaks at the visible but contains also a fraction of "high energy" electromagnetic radiation corresponding to the ultraviolet region, part of which is absorbed by the ozone layer and makes life possible as we know it.

The dynamics of stratospheric ozone was mainly elucidated by S. Chapman, P. Crutzen, M. Molina and S. Rowland. In 1930, S. Chapman proposed [6] a chemical mechanism to understand the cycle of stratospheric ozone; in the same year T. Midgley

R. M. Velasco · F. J. Uribe (✉)
Department of Physics, Universidad Autónoma Metropolitana-Iztapalapa,
Av. San Rafael Atlixco 186, Col. Vicentina, Mexico D.F. 09340, Mexico
e-mail: paco@xanum.uam.mx

E. Pérez-Chavela
Departments of Mathematics, Universidad Autónoma Metropolitana-Iztapalapa,
Av. San Rafael Atlixco 186, Col. Vicentina, Mexico D.F. 09340, Mexico

invented a rather useful set of chemicals known as chlorofluorocarbons (CFCs) that due to the work by Rowland and Molina, done some 40 years later, were identified as precursors of stratospheric ozone destruction mainly in the south pole. On the other hand, P. Crutzen realized that nitrogen oxides could be transported to the stratosphere and contribute to the destruction of ozone.
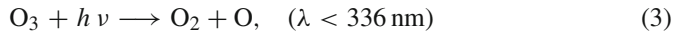
The dynamical evolution of chemical species in the atmosphere is an extremely complicated problem which up to date has not been solved completely. The photochemical mechanisms play an important role in the formation and destruction of several chemical species. In particular the ozone cycle is one of the most relevant ones because of its essential role in the stratospheric dynamics. In 1930 Chapman [6] proposed a photochemical mechanism to understand the formation of ozone in stratospheric conditions. This mechanism considers molecular oxygen (O_2), atomic oxygen (O), ozone (O_3), and another body, usually called a third body or buffer, which is necessary for some of the reactions to take place. In our case the buffer is just the earth atmosphere. Such species, by means of the interaction with high frequency radiation, allow the formation and destruction of ozone [1,2]. Our interest in this work is to study the mathematical properties of the set of differential equations describing the ozone cycle in the stratosphere, which as far we know have remained unexplored. In order to establish a link between the terminology used by chemists and those used by mathematicians, we first analyze the Chapman mechanism under the conditions that the chemical rates are constant. This leads to an autonomous dynamical system for which the steady (critical) points are well defined mathematical concepts. We will show that the Chapman mechanism has three steady states for the species concentrations but only one of them is found experimentally [3,4], a stable node. In this work we are interested in the study of how this critical point is reached from a given initial condition, or in other words what is the basin of attraction. It is also interesting to know if initial positive concentrations can lead to negative concentrations when integrated according to the flow provided by the Chapman mechanism. We have shown that there exists an invariant set (D) which defines the region of non-negative concentrations for which the vector field always points to the interior. The stable node, being inside this region is always reached when the rates are constant. If we take into account the time dependence of rates, the quasi-critical point is also inside the interior of D but its position varies with time.

After this introduction we consider the specific differential equations studied in this work in Sect. 2. In Sect. 3 we perform the local analysis according to the theory of dynamical systems and in Sect. 4 results from global analysis are considered, in particular the existence of a positively invariant set. Finally in Sect. 5 some final remarks are given.

2 The working equations

Let us go into the details of the Chapman mechanism. Its chemistry is given according to the following kinetics,

$$O_2 + h\nu \longrightarrow 2O, \quad (\lambda < 242\,\text{nm}) \tag{1}$$

$$O + O_2 + M \longrightarrow O_3 + M \tag{2}$$

$$O_3 + h\nu \longrightarrow O_2 + O, \quad (\lambda < 336\,\text{nm}) \tag{3}$$

$$O + O_3 \longrightarrow 2O_2, \tag{4}$$

where λ denotes the wave length of the electromagnetic radiation and M is any molecule in the atmosphere.

The chemical reactions describing the mechanism are just the balance equations for the concentrations of atomic oxygen n_O, molecular oxygen n_{O_2} and ozone n_{O_3} that depend with time. The photolytic rates in Eqs. 1 and 3 are denoted by j_{O_2} and j_{O_3} and depend on the geographical location, the spectral distribution of the radiation coming from the sun and some optical properties of the atmosphere and the earth (the albedo). In particular, they are time dependent and at night they are zero. In this work their values are taken from the literature [4] and we first will consider them as constants so that the dynamical system obtained from Eqs. 1 to 4, can be considered as autonomous and therefore the concept of steady state is well defined. In the chemistry literature one finds the concept of steady state but its meaning may not always be same as the one used by the people working in dynamical systems. However, the assumption of constant rates brings together the different usages and this is why this case is considered first. The rates for reactions (2) and (4) in the mechanism are denoted by $k_{4.2}$ and $k_{4.4}$, respectively, this notation is the one used in [1]. Their values either come from experimental information or from theoretical approaches [1,7], they depend on the temperature, pressure and some characteristics of the molecules involved. The quantity n_M denotes the concentration of the third body which can be any molecule in the atmosphere, in fact this dependence is only a way to take into account the pressure dependence in the rate of the reaction.

The differential equations that follow from Chapman's mechanism are those obtained from mass conservation, namely,

$$
\begin{aligned}
\frac{d}{dt}n_O(t) &= 2\,j_{O_2}n_{O_2}(t) + j_{O_3}n_{O_3}(t) - k_{4.2}n_O(t)n_{O_2}(t)n_M \\
&\quad -k_{4.4}n_{O_3}(t)n_O(t), \\
\frac{d}{dt}n_{O_2}(t) &= j_{O_3}n_{O_3}(t) + 2k_{4.4}n_{O_3}(t)n_O(t) - j_{O_2}n_{O_2}(t) \\
&\quad -k_{4.2}n_O(t)n_{O_2}(t)n_M, \\
\frac{d}{dt}n_{O_3}(t) &= k_{4.2}n_O(t)n_{O_2}(t)n_M - j_{O_3}\,n_{O_3}(t) - k_{4.4}n_{O_3}(t)n_O(t).
\end{aligned}
\tag{5}
$$

They satisfy conservation of mass, which can be seen directly and it represents the conservation of the number of atoms involved in the chemical reactions,

$$n_O(t) + 2n_{O_2}(t) + 3n_{O_3}(t) = f, \tag{6}$$

where f is a constant of motion. In our case the existence of this relation (a first integral) allows us to reduce the number of independent variables. Notice should be made that this relation is not valid as soon as we consider mass transport. In fact we
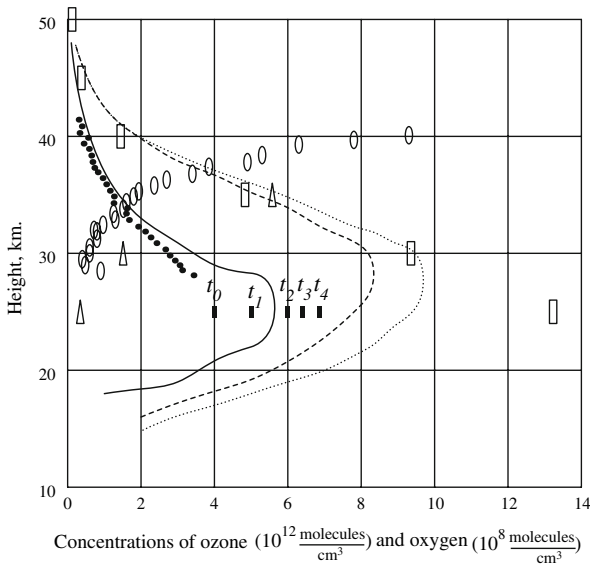
Fig. 1 Height above the sea level in km vs. the concentrations of oxygen in units of 10^8 molecules cm^{-3}, and ozone in units of 10^{12} molecules cm^{-3}. The dotted and dashed lines are the solutions of the Chapman mechanism for ozone at the equator and a latitude of 30 degrees north, respectively [1]. The solid line represents experimental data for ozone taken in November 13 of 1970 at Panama ($9°$ N) and the solid circles are experimental data for ozone taken in December 2, 1977 at Palestina, Texas ($32°$ N), with a solar zenith angle of $50°$; the open circles are experimental data for atomic oxygen at the same location [1]. The rectangles give ozone concentrations as calculated by Eq. (9), the solid ones are calculated using the values of Table 1 and the others using those of Table 2. The solid rectangles give the numerical solution of the Chapman mechanism for different times obtained with Adams' method. The initial conditions used were 4×10^{12} molecules cm^{-3} for ozone and 0.5×10^8 molecules cm^{-3} for monatomic oxygen. The times for which the numerical solution is given are $t_0 = 0$ s, $t_1 \approx 2.5 \times 10^6$ s ($\approx$28 days), $t_2 \approx 6.5 \times 10^6$ s ($\approx$2.5 months), $t_3 \approx 9.7 \times 10^6$ s ($\approx$3.7 months), and $t_4 \approx 3 \times 10^7$ s ($\approx$11.6 months). The triangles are the steady concentrations of monatomic oxygen from Table 2

are working in the so-called photochemical box model for which all the species form a perfect mixture, and the changes in the species concentration are caused only by the chemical mechanism. In Fig. 1 information about the height profiles for monatomic oxygen and ozone and the different scales involved are provided. Using Eq. 6 the system (5) can be written as a two dimensional system given by,

$$\frac{dx}{dt} = df - 3dy - dx + by - \frac{aef}{2}x + \frac{3ae}{2}xy + \frac{ae}{2}x^2 - cxy \equiv g_1(x, y), \quad (7)$$

$$\frac{dy}{dt} = \frac{aef}{2}x - \frac{3ae}{2}xy - \frac{ae}{2}x^2 - by - cxy \equiv g_2(x, y), \quad (8)$$

where $x(t) \equiv n_O(t)$ and $y(t) \equiv n_{O_3}(t)$ are the oxygen and ozone concentrations, $a \equiv k_{4.2}$, $b \equiv j_{O_3}$, $c \equiv k_{4.4}$, $d \equiv j_{O_2}$, and $e \equiv n_M$ have the values given in Table 1.

The critical concentrations corresponding to the steady states or equilibrium points of Eqs. 7–8 can be easily calculated by solving $\frac{dx}{dt} = 0$ and $\frac{dy}{dt} = 0$. Then, the

Table 1 Approximate values for the rates to be used as an example in our calculations. The values of the rates $k_{4.2}$ and $k_{4.4}$ were rounded off, see Table 2 for more detailed information. The values of the photolytic rates were taken from the book by Andrews [4] and correspond to calculated values at mid latitudes under equinox conditions at noon at a height of 25 km. The value of n_M is taken from the standard atmosphere at mid latitudes in the month of March and its value is typical of an altitude of about 27.5 km [8]. These values were choosen so that the interested reader can make quick calculations, more detailed information is given in Table 2

Rate constants	Photolytic rates	Concentrations
$k_{4.2} = 10^{-33}$ cm^6 molecules^{-1} s^{-1}	$j_{O_2} = 3 \times 10^{-12}$ s^{-1}	$n_M = \frac{3}{5} \times 10^{18}$ molecules cm^{-3}
$k_{4.4} = 10^{-15}$ cm^3 molecules^{-1} s^{-1}	$j_{O_3} = 5.5 \times 10^{-4}$ s^{-1}	$f = 0.24 \times 10^{18}$ molecules cm^{-3}

equilibrium points are given by $P_0 = (f, 0)$ and $P^\pm = (x_c^\pm, y_c^\pm)$ where

$$
x_c^\pm = \frac{dc \pm \sqrt{d^2c^2 + 4aecdb}}{2aec} = \frac{j_{O_2} k_{4.4} \pm \sqrt{j_{O_2}^2 k_{4.4}^2 + 4k_{4.2}n_M k_{4.4} j_{O_2} j_{O_3}}}{2k_{4.2}n_M k_{4.4}},
$$
$$
y_c^\pm = \frac{ax_c^\pm e(f - x_c^\pm)}{3aex_c^\pm + 2b + 2cx_c^\pm}. \tag{9}
$$

Using the values given in Table 1 it can be shown that $d^2c^2 \ll 4aecdb$, and therefore Eq. 9 in shorter form can be given as:

$$
x_c^\pm \approx \pm\sqrt{\frac{bd}{ace}} = \pm\sqrt{\frac{j_{O_2} j_{O_3}}{k_{4.2}k_{4.4}n_M}} \approx \pm 0.52 \times 10^8 \text{ molecules cm}^{-3},
$$
$$
y_c^\pm \approx \pm\frac{ax_c^+ ef}{2b} = \pm\frac{f}{2}\sqrt{\frac{k_{4.2}n_M j_{O_2}}{k_{4.4} j_{O_3}}} \approx \pm 0.69 \times 10^{13} \text{ molecules cm}^{-3}. \tag{10}
$$

The coordinates of the point P_0 indicate that the molecular oxygen and ozone are completely destroyed and we will have only atomic oxygen. On the other hand, we notice that the point P^- has not physical meaning because the concentrations are negative. Lastly, the point P^+ is the interesting one since the concentrations are positive and is the one that corresponds to the experimental data (see Fig. 1).

3 Local analysis

The local analysis of the dynamical system given by Eqs. 7–8, with the values of the constants given in Table 1 (see also Table 2), goes along the usual way [9]. First, one calculates the jacobian matrix of the dynamical system given by Eqs. 7–8 at each of the critical points. Secondly, one calculates the corresponding eigenvalues and it turns out that each critical point is hyperbolic (the eigenvalues of the jacobian matrix have real parts not equal zero). Since the stationary points are hyperbolic, the Hartman (or Hartman–Grobman) [9] theorem guarantees that locally, the linearized

Table 2 The values of the photolytic rates were taken from Figure 5.5 in the book by Houghton [8], the variation of the pressure and temperature as a function of the altitude were taken from the standard atmosphere as reported by Seinfeld and Pandis [1], and the values on n_M were calculated using the ideal gas law. The values for the other rates were calculated according to $k_{4.2} = 6 \times 10^{-34}(T/300)^{-2.3}$ molecules cm^{-3}, and $k_{4.4} = 8 \times 10^{-12} \exp(-2060/T)$ cm^3 molecules^{-1} s^{-1} [1,7], x_{cr} and y_{cr} are the critical values corresponding to the stable node

h (km)	25	30	35	40	45	50
p (hPa)	25.49	11.97	5.746	2.871	1.491	0.7978
T (K)	222	227	237	253	264	271
$n_M \left(10^{17} \text{ molecules cm}^{-3}\right)$	8.314	3.818	1.756	0.822	0.4090	0.213
$k_{4.2} \left(10^{-33} \text{ cm}^6 \text{ molecules}^{-1} \text{ s}^{-1}\right)$	1.199	1.139	1.032	0.888	0.805	0.758
$k_{4.4} \left(10^{-16} \text{ cm}^2 \text{ molecules}^{-1} \text{ s}^{-1}\right)$	7.467	9.160	13.434	23.278	32.680	39.977
$J_{O_2} \left(10^{-10} \text{ s}^{-1}\right)$	0.021	0.170	1.032	3.262	6.469	10.316
$J_{O_3} \left(10^{-5} \text{ s}^{-1}\right)$	43.20	53.67	73.30	132.32	306.50	504.30
$x_{cr} \left(10^8 \text{ molecules cm}^{-3}\right)$	0.345	1.512	5.578	15.963	43.0257	90.060
$y_{cr} \left(10^{12} \text{ molecules cm}^{-3}\right)$	13.23	9.356	4.834	1.445	0.376	0.122

Table 3 Specific values for the critical points using the values given in Table 1 and the corresponding eigenvalues (μ) of the Jacobian matrix at each critical point

$x_c(10^8 \text{ molecules cm}^{-3})$	$y_c (10^{12} \text{ molecules cm}^{-3})$	μ_1 (1/s)	μ_2 (1/s)
+0.52	+0.69	-2.1×10^{-7}	−72.00
−0.52	−0.69	$+2.1 \times 10^{-7}$	−72.00
$+0.24 \times 10^9$	0	+75.25	−459.25

field is homeomorphic to the non-linear one. Finally, by looking at the eigenvalues (see Table 3), one infers that P_0, P^- are saddle points (one of the eigenvalues of the jacobian matrix is positive and the other negative) and P^+ is a stable node (both eigenvalues of the jacobian matrix are negative). As it is well known the local analysis is valid only in a neighborhood of the critical points, however it allows for a local qualitative picture of the behavior of the complete (non-linear) system.

In Fig. 2 we have shown the results of integrating numerically the set of differential equations 7–8 for different initial conditions using Adams' method [10] with the values for the rates taken from Table 1.

From the results summarized in Figs. 1 and 2, it follows that there are two very different time scales, one which is of the order of fractions of seconds in which there is a significant variation of monatomic oxygen (this is easy to understand since monatomic oxygen is very reactive) and the concentrations of ozone remain practically constant, and other of the order of months in which the stable node (physical point) is reached.
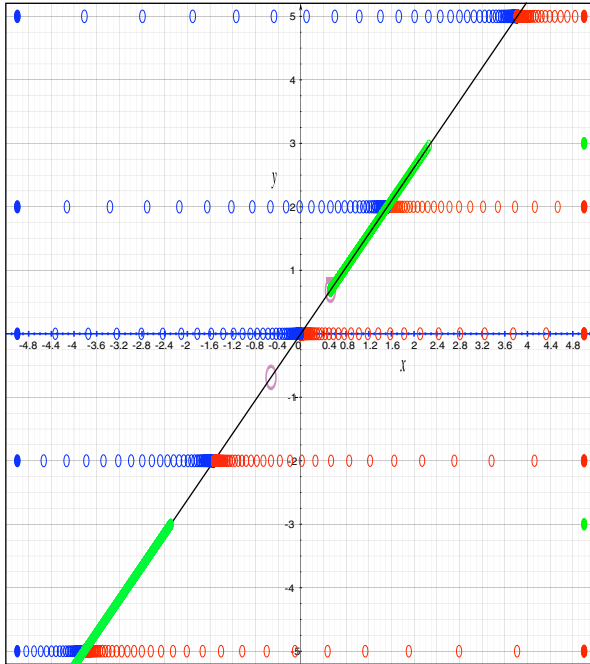
Fig. 2 Concentrations of oxygen (x axis) in units of 10^8 molecules cm^{-3} and of ozone (y axis) in units of 10^{13} molecules cm^{-3}. Initial conditions for solving the dynamical system given by Eqs. 7–8 with values from Table 1; •, •, and •. Numerical solutions for a time step of about 0.002 s; ○ and ○. Numerical solutions for a time step of about 10^3 s (8 h); ○. In the last case the corresponding open circles that represent the numerical solution are so closed that they look like a wide green line. The critical points, $(-0.52, -0.69)$ and $(0.52, 0.69)$ in the units used, are at the centers of the magenta circles. The black line joining them looks like an invariant set that can be identified with an invariant manifold in which the solutions move slowly (see also Fig. 1 to get an idea of the times scales involved)

Let us recall that we assumed that the photolytic rates are constant, however we know that they are zero at night, hence our calculation is not realistic due to the two different time scales involved. Therefore, we would like to analyze the situation when we consider the time dependence of the photolytic rates. If the photolytic rates are zero then, a different dynamical system follows from Eqs. 7 to 8, a similar analysis as we did before can be done to conclude that the dynamical system at night has a line of critical points, which corresponds to $x = 0$. The physical interpretation is easy to infer: monatomic oxygen is very reactive so that it will soon disappear since the reactions at night do not provide a source for it. Therefore, the population of ozone will remain almost the same provided that the amount of monatomic oxygen is small compared with that of ozone. If in the plane $x-y$ we start with positive concentrations then the orbits of the dynamical system at night cannot cross the y axis because it takes an infinite time to reach a critical point due to the local existence and uniqueness theorem for differential equations. This observation will be of use later on.

Fig. 3 The physical region D, in which all the concentration species are positive, in the n_O–n_{O_3} plane in arbitrary units
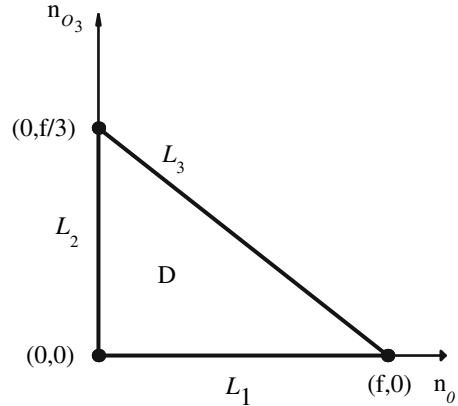
4 Global analysis

Coming back to the question of the physical region for the range of concentrations, we would like to point out that positive concentrations (including molecular oxygen) only occur in the set $D = \{(x, y)|0 \leq x \leq f, 0 \leq 3y + x \leq f\}$ (see Fig. 3). An interesting question is if initial conditions in D can give rise to un-physical conditions when this initial condition is followed as a function of time. If this were the case then we would think of the mathematical model as not being valid from a physical point of view. Notice that we allow that initial un-physical conditions can give origin to physical ones. A mathematical way to answer this requirement is to see if the vector field at the boundary of D always points towards its interior. To stress that we are dealing with the case of photolytic rates depending on time we will denote them by capital J. The boundary of D is the union of the segments $L_1 = \{(x, y)|0 \leq x \leq f, y = 0\}$, $L_2 = \{(x, y)|x = 0, 0 \leq y \leq f/3\}$, and $L_3 = \{(x, y)|0 \leq x \leq f, y = (f - x)/3\}$. We rewrite Eqs. 7–8 as $\frac{d\sigma}{dt} = \mathbf{g}(\sigma(t))$, where $\sigma(t) = (x(t), y(t))$, and the vector field $\mathbf{g}$ has components $\mathbf{g} = (g_1, g_2)$. For L_1 it follows that

$$g_2(x, 0) = \frac{axe}{2}(f - x) = \frac{k_{4.2}xn_M}{2}(f - x), \tag{11}$$

so that the vector field points towards the interior of D if $0 < x < f$ at day or night. Notice that there is one point in which the vector field is zero; for the hyperbolic saddle $(f, 0)$ and that at $(0, 0)$ the information is not enough to conclude that the field points towards the interior of D, but since $g_1(0, 0) = df = J_{O_2}f$ it follows that in $L_1 \setminus \{(f, 0)\}$, the vector field points towards the interior of D at day time, here we have used that even when the J's are time dependent, they maintain the same sign. At night we know that $(0, 0)$ is a critical point and therefore for initial conditions in the interior of D the orbits cannot cross L_1 at night. The same argument applies to $(f, 0)$ that is a true stationary point since it does not move as a function of time. Therefore, we conclude that there are no orbits whose initial conditions are in the interior of D that can cross L_1 at day or night.

For L_2 it follows that

$$g_1(0, y) = (f - 3y)d + by = (f - 3y)J_{O_2} + J_{O_3} y, \tag{12}$$

which is also greater or equal than zero in L_2 at day time, and so the vector field also points to the interior of D except for the point $(0, f/3)$ for which the previous information is not conclusive. However, $g(0, f/3) = bf/3(1, -1)$ and it follows that the vector points to the interior of D at day time. At night all the points in L_2 are critical points of the corresponding dynamical system and therefore there are no orbits crossing L_2 if the initial conditions are in the interior of D.

For L_3, let us observe that a normal vector to L_3 that points towards the exterior of D is $\mathbf{e} = (1/3, 1)$ and we have,

$$\mathbf{e} \cdot \mathbf{g}(x, (f - x)/3) = \frac{4}{9}xc(x - f) + \frac{2}{9}b(x - f) < 0, \tag{13}$$

if $x < f$ at day or night. The above inequality implies that the angle θ formed by $\mathbf{e}$ and the vector field $\mathbf{g}$ satisfies that $|\theta| > \pi/2$, therefore the vector field $\mathbf{g}$ always points towards the interior of D except for two points: $(f, 0)$ at which the vector field is zero and at $(0, f/3)$. Since the vector field is zero at $(f, 0)$ and we have the constant solution $\sigma(t) = (f, 0)$, it follows by uniqueness that no integral curves can cross the boundary of D at $(f, 0)$. The case of the point $(0, f/3)$ has been analyzed previously.

Then, D is positively invariant, meaning that if the initial conditions are in D, then the orbit when integrated forward in time will always remain in D. Using the fact that we know all critical points of Eqs. 7–8 for the case of constants rates at day time, we apply the Poincaré–Bendixon theorem [9,11] to the dynamical system given by (7–8) restricted to the set D, obtaining that since the equilibrium point P^+ is at the interior of D any solution curve (except the saddle point) whose initial condition is in D, will always reach asymptotically the stable node P^+. In particular, one of the unstable branches of the saddle point is in D and therefore we have a heteroclinic connection (an orbit joining two critical points).

More challenging is the case where we take into account the time variation of the photolytic rates. D is a positively invariant set but except for the saddle $(f, 0)$ there are not true steady points inside D. There is experimental information for the time dependence of the photolytic rates that has been compared with theoretical calculations [12] in the troposphere. In the absence of information in the stratosphere we make the "reasonable" assumption that the time variation of the photolytic rates is the same, meaning that

$$J_{O_2}(t) = j_{O_2}\phi(t), \quad J_{O_3}(t) = j_{O_3}\phi(t), \tag{14}$$

where the lower case j's are constants and the positive function $\phi(t)$ takes into account the variation with time and its form will not be specified. In fact, it can be determined from the results for the photolytic rates at the troposphere and assuming that its form remains the same or nearly the same for the stratosphere. The values at which the

vector field **g** is zero (out of the saddle point), denoted by $x^{\pm}$ and $y^{\pm}$ are given by:

$$x^{\pm} = x_c^{\pm}\phi(t), \quad y^{\pm} = \frac{ax_c^{\pm}e(f - x_c^{\pm}\phi(t))}{3aex_c^{\pm} + 2b + 2cx_c^{\pm}}, \tag{15}$$

where the values of a, b, c, d, and e are constant. Then, the same approximation used for the autonomous case holds once we note that the maximum value of the dimensionless function ϕ is about one (the maximum photolytic rates occur about one hour later than noon) and we conclude that,

$$x^{\pm} \approx \pm\sqrt{\frac{j_{O_2} j_{O_3}}{k_{4.2}k_{4.4}n_M}}\phi(t),$$

$$y^{\pm} \approx \pm\frac{f}{2}\sqrt{\frac{k_{4.2}n_M j_{O_2}}{k_{4.4} j_{O_3}}}, \tag{16}$$

the interesting feature of these equations is that although there are no true steady states since the concentration of monatomic oxygen changes with time, that of ozone remains the same. This means that as far as ozone is concerned one may speak of an equilibrium concentration and is the same as if one assumes an autonomous dynamical system.

5 Final remarks

To conclude, we would like to stress that in our opinion the results just described exhaust the considerations from a physical point of view. We have shown that in the physical region D, all the orbits with initial conditions in D will always remain in it, therefore initial conditions with physical meaning lead always to orbits that have physical meaning. In this sense the Chapman's mechanism is robust. It is possible to ask for more general regions that remain invariant but they must necessarily have points that do not have physical meaning, and while the question is interesting from a mathematical point of view it is not interesting on physical grounds because it leads to the consideration of negative concentrations. We have also shown that the set $D/\{(f, 0)\}$ is contained in the basin of attraction of the stable node, other regions that contain the set and belong to the basin necessarily have points that lack physical meaning. A local analysis of the Chapman mechanism has been given and in particular the critical point that is considered in the literature has been shown to correspond to a stable node. The numerical computations using Adams' method show that there are two time scales that need to be considered, this conclusion can also be reached from Table 3. Also, near the two critical points shown in Fig. 2, there is an attracting one dimensional manifold that corresponds to the line joining the two critical points, where the orbits move slowly. When the time variation of the photolytic rates are taken into account it has been shown that the concentrations of ozone will evolve towards the critical concentration of ozone given by the autonomous case.

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