QUALITATIVE ANALYSIS OF THE OZONE CYCLE EQUATIONS WITHOUT RADIATION

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Qualitative analysis of the simplest ozone cycle equations without radiation is performed. Complete phase portraits of the systems are drawn for both fixed and arbitrary concentration of the molecular oxygen. Some peculiarities of time behavior of the concentration under different initial conditions are discussed for both cases.

INTRODUCTION

The ozone cycle reactions in the atmosphere have recently become a topic of an increase attention, because the question on irreversibility of changes taking place in the ozone layer unexpectedly became a question of wide public discussions. Computer simulations of vast systems of equations for reactant concentrations can give only limited information about a probable process evolution without answering the above question. The answer to this question, as well as to other similar questions concerning the systems described by nonlinear differential equations may be often obtained using a qualitative theory of differential equations, or, in other words, the theory of dynamical systems, see, e.g., Ref. 1. A result of qualitative analysis can be the phase portrait of the system under study which includes all possible types of its solutions and their dependences on the initial conditions. Therefore addressing to the theory of the dynamical systems as a mean for studying the ozone cycle is quite opportune and justified. It would be logical to obtain first of all the phase portrait of the simplest reaction cycle ensuring the presence of the ozone in the atmosphere, the so–called Chapman ozone cycle:[2]

$$O_2 + h\nu \xrightarrow{J_2} O + O\ ,$$
$$O_3 + h\nu \xrightarrow{J_3} O_2 + O\ ,$$
$$O_2 + O + M \xrightarrow{k_2} O_2 + M\ ,$$
$$O + O_3 \xrightarrow{k_3} 2O_2\ . \qquad (1)$$

To the authors' knowledge, no complete treatment of the problem from the point of view of qualitative analysis is available in the literature, though some its aspects have been considered in Refs. 3–5. However, acomplete phase portrait even of the simplest system has not been obtained so far. In this situation we have repeated qualitative consideration[6,7] of the system of three equations which describe cycle (1) within the framework of the investigation program on qualitative studies of the climatic processes. The steady states in the finite part of the plane and at infinity were found and the character of the trajectory behaviors in their vicinity was determined. A qualitative structure of the system appeared to be quite rich and gave reasons to assume the existence of nontrivial trajectories behavior in a physically meaningful region.

Aiming our further studies at finding the separatix behavior on the whole plane that is necessary for obtaining a complete phase portrait in this paper we consider a particular case of the system of reactions (1), that is, without radiation. In this case the phase portrait can be drawn rather simply. Such an approach is first of all aimed at demonstrating the advantages of a qualitative analysis. Moreover, such a phase portrait can be practical, for example, for studying the ozone dynamics during nighttime.

In the case of absence of radiation from the system of reactions (1) only two last reactions are to be taken into consideration. If the oxygen atmosphere is considered as a closed homogeneously isothermic reactor of ideal mixing the system of nonlinear differential equations for concentrations ($[O_2] = \tilde{x}$, and $[O] = \tilde{y}$, and $[O_3] = \tilde{z}$ $M = O_2$) is given by

$$\dot{\tilde{x}} = \kappa_2\, \tilde{x}^2\tilde{y} + 2\kappa_3\tilde{y}\tilde{z}\ ;$$
$$\dot{\tilde{y}} = -\ \kappa_2\, \tilde{x}^2\tilde{y} - \kappa_3\tilde{y}\tilde{z}$$
$$\dot{\tilde{z}} = \kappa_2\, \tilde{x}^2\tilde{y} - \kappa_3\tilde{y}\tilde{z}\ . \qquad (2)$$

For the sake of convenience of further discussion let us introduced new variables

$$t = \alpha\tilde{t}\ , \qquad x = \beta\tilde{x}\ , \qquad y = \gamma\tilde{y}\ , \qquad z = \delta\tilde{z}\ , \qquad (3)$$

where

$$\alpha = \kappa_3^2/\kappa_2\ ,\ \beta = \gamma = \delta = \kappa_2/\kappa_3\ .$$

Then the system of equations (2) is reduced to the dimensionless form

$$\dot{x} = -\ x^2y + 2yz\ ,$$
$$\dot{y} = -\ x^2y - yz\ ,$$
$$\dot{z} = x^2y - yz\ . \qquad (4)$$

Usually the concentration of O_2 molecules exceeds those of O and O_3 by several orders of magnitude. This fact allows one to consider it to be unchanged during the reaction. Similar approximation is often used in the literature, and following its logic in the case without radiation the system of equations (4) should be replaced by

$$\dot{y} = -\ y(a + z)\ , \qquad \dot{z} = y(a - z)\ . \qquad (5)$$

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Below, systems (4) and (5) will be considered separately.

THE CASE OF CONSTANT O_2 CONCENTRATION

The system of equations (5) is a dynamical system on the plane and the methods of its qualitative analysis are well known (see, e. g., Refs. 1 and 8). A brief description of the key elements of the qualitative analysis are given, at the editor's request, in Appendix. Its a peculiar feature of the system of equations (5) that the right sides of its equations have a common factor y. Let us consider the system

$$\dot{y} = -(a + z)\,, \qquad \dot{z} = a - z\,, \tag{6}$$

which unlike the system of equations (5) does not contain a common factor. It is evident, that the steady states of system (6) are also those of system (5). The system (6) has no steady states in a finite part of the plane. The investigation done for infinite points with the use of the Poincaré transformation ($y, z \to u, v$) gives two steady states at infinity, one of them B being a degenerative node while another one C, being the saddle–node with a stable node sector. The trajectory behavior in the vicinities of these points is shown in Fig. 1.

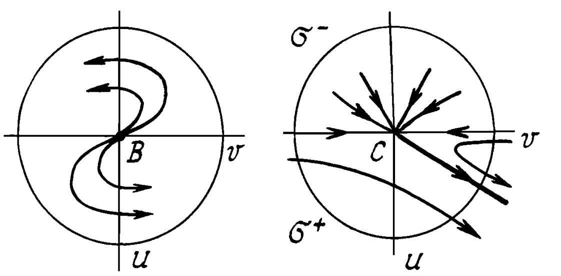
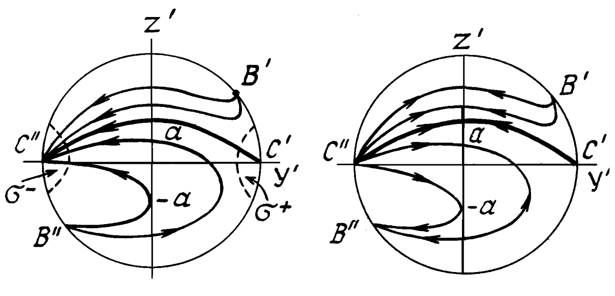


FIG. 1. Trajectory behavior in the vicinity of singular points at infinity for system (6).

This information is sufficient to draw the phase portrait of the system under consideration. It is shown in Fig. 2*a*. Remind that the phase portrait is drawn in a circle, and the entire plane (y, z) is transformed into the interior part of the circle. The infinitely remote points correspond to the points on the circle circumference. The vicinities of the points at infinity being divided into two parts by the "equator" $u = 0$ are transformed into the vicinities of diametrically opposite points of the circumference (see, e. g., σ^+ and σ^- vicinities of the point C in Figs. 1 and 2*a*). The arrows in the figure indicate the direction of motion along the trajectories. Such a transformation conserves the qualitative behavior of trajectories and yields a pleasant visualization. The most distinctive feature of the phase portrait is the existence of the separatrix ($C'aC''$) dividing the phase space into two parts. The separatrix equation $ua = v$ in the (u, v) coordinates has the form $a = z$ in the (y, z) coordinates. The transition of trajectories through the separatrix is forbidden. The appearance of trajectories in one of these parts is determined by initial conditions. For an abstract system described by Eqs. (6) all the trajectories run away to infinity. When the variables have a physical meaning of concentrations only the first quadrant is accessible for the system. There are also two regions in it divided by the separatrix. The trajectories terminate at the quadrant boundaries when the concentration of y, i.e., of the atomic oxygen, is exhausted.



a *b*

FIG. 2. a) Phase portrait for system (6). b) Phase portrait for system (5), which in contrast to system (6) includes the common factor y.

The phase portrait of system (5) can be drawn using the results obtained for system (6). To the stationary points of the system (6) the points are added which appear when the common factor in Eqs. (5) is equal to zero, $y = 0$. In the given case these are the points of the z axis. Thus, we obtain the phase portrait of system (5) from that of system (6) by denoting the z axis as a singular line and changing properly the direction of motion along the trajectories (see Fig. 2*b*). Difference between the data presented in the first quadrant of Figs. 2*a* and *b* is in time behaviors of the system. Thus, in the case 2*b* the points on the z axis are stable stationary states, so that at these points $\dot{y} = 0$, $\dot{z} = 0$ while in the case 2*a* the system approaches the points of the z axis with nonzero velocity.

Systems (5) and (6) can be integrated exactly. Their variables y and z satisfy the equation

$$\frac{dz}{dy} = \frac{z - a}{z + a}$$

which has the function

$$y = y_0 + (z_0 - a) + 2a \ln\left(\frac{z - a}{z_0 - a}\right)$$

as its solution under the initial conditions $t = t_0$, $z = z_0$, and $y = y_0$. This solution is shown in Fig. 3. The straight line $z = a$ is the asymptote for the integrated curves. An intercomparison of the exact solution (Fig. 3) and the phase portrait (Fig. 2) convinces that the phase portrait gives a complete information about the system behavior except for quantitative characteristics though inessential for a qualitative interpretation.

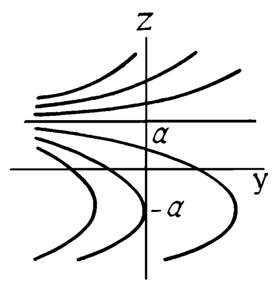


FIG. 3. Exact solutions of systems (5) and (6) in the (y, z) plane.

THE CASE OF AN ARBITRARY O_2 CONCENTRATION

When solving system (4) it is necessary to take into account the limitations imposed on the concentrations by the conservation of the number of atoms during the reaction. In the case considered here we use the only conservation law

$$2x + y + 3z = A \; . \tag{7}$$

The use of Eq. (7) allows one to obtain from Eq. (4) the system of two differential equations for two chosen variables. Thus, the system describing the O and O_3 evolution is

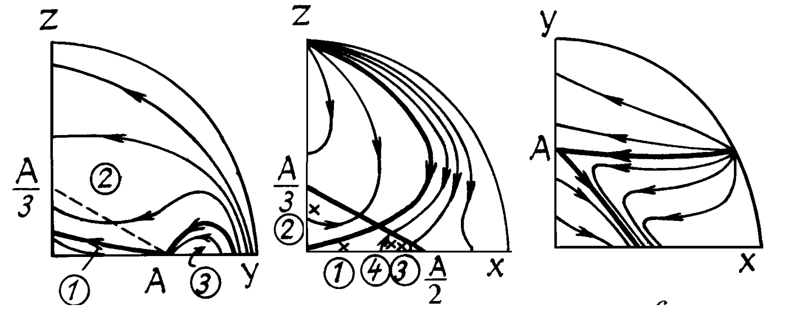
$$\left.\begin{aligned} \dot{y} &= (y/4)\left(-A^2 + 2Ay + (6A - 4)z - y^2 - 9z^2 - 6yz\right) \\ \dot{z} &= (y/4)\left(A^2 - 2Ay - (6A + 4)z + y^2 + 9z^2 + 6yz\right) \end{aligned}\right\}, \tag{8}$$

and the systems describing the evolution of both O_2, O_3 and O_2, O can be reduced to the forms

$$\left.\begin{aligned} \dot{x} &= (-A + 2x + 3z)(-2z + x^2) \\ \dot{z} &= (-A + 2x + 3z)(z - x^2) \end{aligned}\right\}, \tag{9}$$

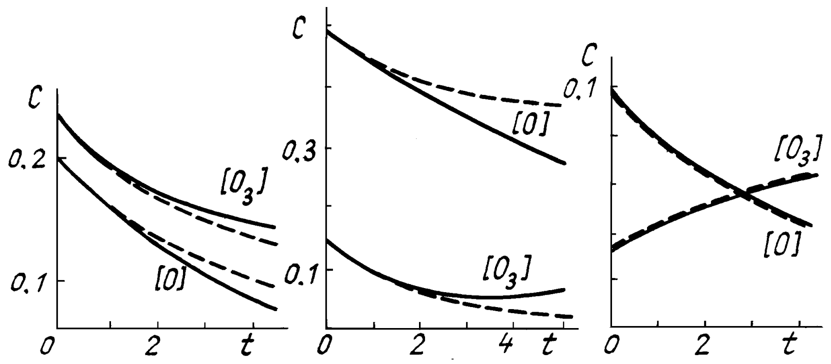
$$\left.\begin{aligned} \dot{x} &= (y/3)(2A - 4x - 2y - 3x^2) \\ \dot{y} &= (y/3)(-A + 2x + y - 3x^2) \end{aligned}\right\}, \tag{10}$$

respectively. Their phase portraits corresponding to the quadrants with positive concentrations are shown in Fig. 4. These portraits clearly demonstrate certain peculiarities in the concentration behavior under different initial conditions. First of all there appears a possibility of elucidating how the assumption on the O_2 concentration constancy affects the qualitative behavior of the system. To do this let us compare the curves shown in Figs. 2*b* and 4*a*.



a *b* *c*

FIG. 4. Fragments of phase portraits of systems of equations: a) (8), b) (9), and c) (10).



a *b* *c*

FIG. 5. Variants of time behavior of concentrations for systems in the (y, z) plane with constant dashed curve) and arbitrary (solid curve) concentration of O_2 *for* $A = 1$. *a, b)* $x_0^2 = 0{,}0025$ *and c)* $x_0^2 = 0{,}16$.

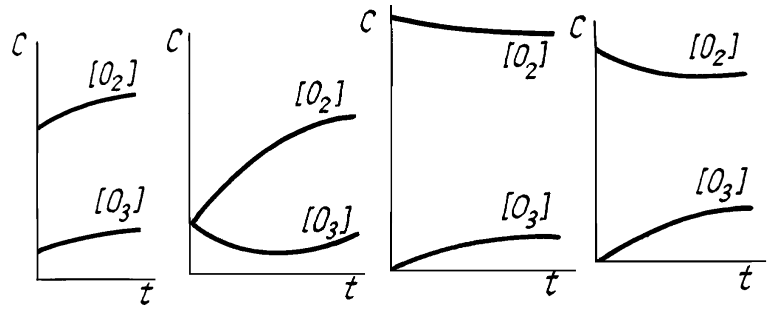


FIG. 6. Variants of time behavior of concentrations for the system of equations (9).

The number and the character of steady states remain unchanged, however their location becomes essentially different. For example, the saddle node moves from the infinity to the finite part of the plane, and the node points at the infinity are now in different quadrants. If the case of constant O_2 concentration there are two regions in the first quadrant divided by the separatrix, in the case of an arbitrary O_2 concentration we have as many as three such regions denoted in Fig. 4*a* by the figures 1, 2, and 3. Existence of a conservation law in the case of an arbitrary O_2 concentration imposes some limitations on the range of concentration variations. Thus, for example, in Fig. 4*a*, the permissible region of the phase space is restricted from above with the straight line $3z_0 + y_0 = A - 2x_0 = B \le A$. For this reason the region 3 is not permitted for the given system. In the case of a constant $[O_2]$ there are no similar restrictions. Figure 5 illustrates the time behaviors of systems (5) and (8) with $A = 1$ under different initial conditions. The graphs show the results of numerical simulations that have been done for these systems. However, their qualitative behavior immediately follows from the phase portraits and the initial conditions for the above–illustrated examples were chosen using these qualitative pictures. The data presented in Fig. 6 underlines once more that the information that can be extracted from the phase portraits is quite sufficient to distinguish between different types of trajectory behavior. Shown in this figure are the variants of time behavior of the trajectories from different parts of the physically allowed region (see Fig. 4*b*, in which the relevant initial conditions are indicated by crosses).

CONCLUSION

The above results clearly shown that the phase portraits give quite a complete information about the trajectories of a system under consideration, and show the regions with qualitatively different trajectory behaviors depending on the initial conditions and the tendencies in the long–term evolution of the solutions. Note that such a great bulk of information could not be obtained by any other method.

In addition to the illustration of some possibilities of a qualitative analysis the investigation of the ozone cycle equations in the absence of radiation allows one to arrive at the following conclusions. Solutions of the system of equations (5), at a constant O_2 concentration are monotonic functions of time in a physically permissible region. Solutions of the system of equations (8) at an arbitrary O_2 concentration show under some initial conditions nonmonotonic time behavior of the O_3 concentration. The atmospheric O_2 concentrations correspond to the region in the phase space near the origin of coordinates where solutions of systems of equations (5) and (8) are practically indistinguishable. Nontrivial concentration behavior in the system of equations (8) may be interesting for studying the processes in chemical reactors. The results obtained in this paper will surely be used in our further studies of the ozone cycle in the presence of radiation.

APPENDIX

Let us consider the system of two nonlinear differential equations

$$\left.\begin{aligned} \dot{x} &= P(x, y) \\ \dot{y} &= Q(x, y) \end{aligned}\right\} , \tag{A1}$$

the right sides of which are independent of time explicitly and are defined on the entire plane (x, y) or in some region G of the plane. Such a system satisfying the conditions of the existence and uniqueness of the solutions is referred to as an autonomous dynamic system of the second order in the region G that can coincide with the entire (x, y) plane. Every pair of (x, y) coordinates characterizes a state of the system. The set of all states of the system spans its phase space. Under given initial conditions the point b of the phase space is moving along a curve named the phase trajectory. Only one phase trajectory passes through a point in the phase space. The points where

$$P(x, y) = 0 , \quad Q(x, y) = 0 , \tag{A2}$$

i.e., where the state of the system does not change with time, are steady states of the system. A steady state itself is a separate trajectory. The periodic solutions are obviously represented by closed trajectories.

By specifying the dynamical system in the region G we thereby specify a set of trajectories, or, in other words, divide the region G into trajectories.

When imaging the plane into itself the type of trajectories can significantly change. Let us choose, among possible images, the so–called topological images of the plane into itself which are in the one–to–one relation with each other and are the two–way continuous images of the plane. There exist such characteristics of the division into trajectories which remain unchanged under topological imaging, or, as they say, topologically invariant. Thus, the closed trajectories remain closed under topological imaging. The number and type of steady states, mutual location of closed and unclosed trajectories etc. also remain unchanged.

Qualitative analysis of a dynamical system or, what is the same, qualitative picture of the phase trajectories implies finding of all properties of a division into trajectories which are topologically invariant.

Qualitative analysis means seeking for the number and types of steady states in the finite part of the plane and at infinity, as well as for the existence of limit cycles and location of separartices. The coordinates of steady states are found from Eqs. (A2). If at a small perturbation, which displaces the system from a steady state, the imaging–it point does not leave the steady state, it is stable. As to an unstable state, the point leaves it being once displaced from it. The question on stability of a steady state (x_0, y_0) is resolved with the help of the first Lyapunov method.

By expanding the right sides of Eqs. (A1) into series over deviations from a steady state and transferring the origin of coordinates into the reference state from Eq. (A1) we obtain

$$\begin{aligned} d\xi/dt &= a\xi + b\eta + \varphi(\xi, \eta) , \\ d\eta/dt &= c\xi + d\eta + \psi(\xi, \eta) , \end{aligned} \tag{A3}$$

where $\xi = x - y_0$, $\eta = y - y_0$, $a = P'_x(x_0, y_0)$, $b = P'_y(x_0, y_0)$, $C = Q'_x(x_0, y_0)$, $d = Q'_y(x_0, y_0)$, and the functions φ and ψ involve the terms with the power not lower than the second order of ξ and η. The general solution of the system of equations (A3) excluding nonlinear terms has the form

$$\begin{aligned} \xi &= C_1 e^{\lambda_1 t} + C_2 e^{\lambda_2 t}, \\ \eta &= C_1\lambda_1 e^{\lambda_1 t} + C_2\lambda_2 e^{\lambda_2 t}, \end{aligned} \tag{A4}$$

where λ_1 and λ_2 are the roots of the so–called characteristic equation

$$\lambda^2 - T\lambda + \Delta = 0\ , \qquad \text{(A5)}$$

with $T = a + d$ and $\Delta = ad - bc$. At $\Delta \neq 0$ a steady state is simple. The following types of simple steady states are possible:

1. $\Delta > 0$, $T^2 - 4\Delta > 0$. The roots of the characteristic equation are real and have the same signs. The steady state is a stable node when $\lambda_1 < 0$ and $\lambda_2 < 0$ and the unstable one when $\lambda_1 > 0$ and $\lambda_2 > 0$ (see Fig. 7*a*). Arrows on trajectories indicate the direction of time. It can be seen from relations (A4) that in the first case the coordinates of the representative point remain to be in the vicinity of a steady state, and in the second case they are removed from it unrestrictedly.

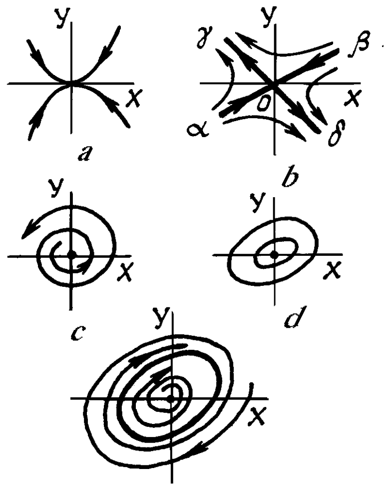


FIG. 7. Types of steady states: a) stable node, b) saddle, c) unstable focus, d) center, and e) stable limit cycle.

2. $\Delta < 0$. The roots of the characteristic equation are real and have different signs: $\lambda_1\lambda_2 < 0$. The corresponding steady state is a saddle. In this case there are four singular phase trajectories, the so–called saddle separatrices, along two of them the representative point approaches the steady state, and along the other two the point removes from it (see Fig. 7*b*). When moving along the trajectories different from the separatrices the representative point eventually leaves the steady state. Thus the saddle is an unstable steady state. The separatrices divide the phase space into parts, so that the trajectories cannot penetrate from one part into the other.

3. $\Delta > 0$, $T^2 - 4\Delta < 0$ for $T \neq 0$. The roots of the characteristic equation are complex conjugate, and their real parts are nonvanishing. The steady state is a focus stable in the negative real parts and unstable in the positive real parts (Fig. 7*c*). The trajectories are spirals. They obviously correspond to a periodic motion with varying amplitude. When all roots are imaginary the steady state is called the center. The trajectories in the vicinity of a steady state are closed and correspond to periodical motions with an amplitude given by the initial conditions.

In nonlinear systems closed trajectories can also exist whose characteristics is independent of the initial conditions being an inherent property of the system itself. Similar trajectories are known as limit cycles. The trajectory behavior in the vicinity of a limit cycle is shown in Fig. 7*e*. The methods of finding the limit cycles are, to a certain extent, the skill problem.

In the case $\Delta = 0$ the steady states are too complicated. For studying their stability it is not enough to use equations of the first approximation (A3), and a more detailed consideration is required.

The set of phase trajectories forms the so–called phase portrait of a dynamical system. Figures 7*a–e*, show the examples of the phase portraits.

The above methods allow one to determine a system behavior in the finite part of the plane. To obtain the entire picture it is needed to examine the infinitely removed points of the plane as well. When the right sides of Eqs. (A1) are polynomials this can be done using the standard Poincaré transformations. These transformations are explained in Fig. 8.

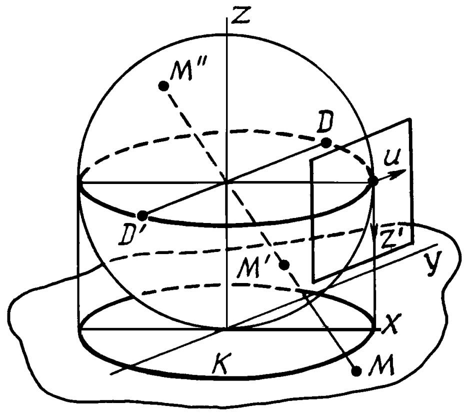


FIG. 8. Poincaré transformations.

Every point of the plane is put into correspondence with two points M' and M' located on the sphere of unit radius touching the plane at the origin of coordinates at the intersection of the sphere with a straight line connecting the point M with the center of the sphere. The points on equator correspond to infinitely removed points of the plane. The finite part of the plane is topologically involved into the sphere surface, i.e., the number and the character of singular points is conserved on the sphere. However, there can appear new singular points on the equator. The transformation $x = 1/z'$, $y = u/z'$ allows one to study the singular points lying on the equator except for the "ends" of the y axis. The plane touching the sphere where u and z' are the Cartesian coordinates is perpendicular to the (x, y) plane and parallel to the y axis. For studying the ends of the y axis (the points D and D') it is necessary to use the transformation $x = v/z'$ and $y = 1/z'$. In this case the plane (v, z') will be parallel to the x axis. The transformed systems of equations are further investigated for establishing the existence of a steady state using the above–described methods. The lower hemisphere is then projected orthogonally on the circle K on the (x, y) plane. In this way the entire phase portrait, i.e., the picture of singular points and trajectories together with the infinity is obtained in the interior of the circle. The phase portrait actually represents the complete qualitative information about the system, in other words, about possible types of motion and the initial conditions under which they can occur.

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