# Limit Cycles in a Two-Species Reaction\*

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**Abstract** Kinetic differential equations, being nonlinear, are capable of producing many kinds of exotic phenomena. However, the existence of multistationarity, oscillation or chaos is usually proved by numerical methods. Here we investigate a relatively simple reaction among two species consisting of five reaction steps, one of the third order. Using symbolic methods we find the necessary and sufficient conditions on the parameters of the kinetic differential equation of the reaction under which a limit cycle bifurcates from the stationary point in the positive quadrant in a supercritical Hopf bifurcation. We also performed the search for partial integrals of the system and have found one such integral. Application of the methods needs computer help (Wolfram language and the SINGULAR computer algebra system) because the symbolic calculations to carry out are too complicated to do by hand.

Keywords Limit cycles, two-species reaction, third order reaction step.

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## 1. Introduction

After an extremely short review of the history of oscillatory reactions we describe how and why we selected—both from the mathematical and chemical points of view—the model investigated here. Definitions of concepts and formulation of theorems not given here can be found e.g. in [44] and [34].

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### 1.1. Historical remarks

Chemical reactions show all kinds of exotic behavior: oscillation, multistability, multistationarity, or chaos. They are interesting not only from the mathematical point of view, but oscillatory behavior in a reaction may also form the basis of periodic behavior in biological systems that can have different periods: minutes, one day, one year etc., see [14, 30, 31, 47]. Analogous expectations can be expressed in connection with other phenomena. Here we are only concerned with oscillatory behavior.

In his famous 1900 lecture David Hilbert formulated as the second part of his XVI<sup>th</sup> problem to find the number of limit cycles of two-dimensional autonomous polynomial differential systems, see e.g. [28]. The last more than 100 years have shown that this is a very hard problem (see e.g. [28].) However, from the point of view of applications one would need even more: find the number of periodic solutions of polynomial differential equations in any number of variables although one would be content with the solution of the kinetic case, i.e. a subclass of quadratic or cubic polynomials is only relevant. Early attacks by [17, 18] are worth mentioning here.

As it can be seen form history, Hilbert's XVI<sup>th</sup> problem seems to be very difficult even in the case of two-dimensional kinetic differential equations. (It is quite characteristic that according to Schlomiuk and Vulpe [36] in the class of quadratic differential equations—slightly larger than the set of kinetic differential equations—the number of different phase portraits is estimated to be more than two thousand.) We neglected quite important topics: the case of simplest oscillators, see e.g. [41,43,46], reactions with more than two species [1,21,42], etc.

#### 1.1.1. Existence of periodic trajectories

Especially when the experiments of Belousov [7] became widely known—first, through the work by Zhabotinsky [48]—the question emerged what are the structural conditions of the existence of periodic solutions in a kinetic differential equation. (On the difference between structural and parametric conditions see e.g. [5,6].)

A fruitful tool to prove the existence of periodic solutions is the theorem on Andronov–Hopf bifurcation as it has been shown by Hsü [27]: he has rigorously shown that the Oregonator model of the Belousov–Zhabotinsky reaction has periodic solutions. Another early application is shown in [39] containing a reaction similar to the Brusselator—see below: (1.10)—to model synaptic low waves and having periodic solutions as a consequence of the above mentioned theorem.

Another method to prove the existence of closed trajectories is to find first integrals having closed level curves. This is how one can investigate the Lotka– Volterra reaction.

Even before oscillatory chemical reactions became popular in the seventies of the XX<sup>th</sup> century, following the work by Belousov and Zhabotinsky, and later by Field, Kőrös and Noyes [22] and others, the biologically motivated differential equation

$$\dot{x} = k_1 x - k_2 x y, \quad \dot{y} = k_2 x y - k_3 y$$
 (1.1)

was reinterpreted as the induced kinetic differential equation of the reaction

$$X \xrightarrow{k_1} 2X, \quad X + Y \xrightarrow{k_2} 2Y, \quad Y \xrightarrow{k_3} 0$$
 (1.2)

and was used as a model of oscillation in cold flames by Frank-Kamenetsky [23].

Since the Lotka–Volterra equation (1.1) has a nonlinear first integral, it shows conservative oscillations, i.e. to all initial concentrations in the open first quadrant (except the unique positive stationary point) a different closed trajectory is assigned.

#### 1.1.2. Exclusion of periodic trajectories

Given a special mechanism one may try to apply the theorem by Bendixson, or by Bendixson and Dulac, see e.g. [8]. These are enough to show e.g. that the induced kinetic differential system

$$\dot{x} = -k_1 x + k_{-1} y - 2k_2 x^2 + 2k_{-2} y^2 =: f \circ (x, y),$$
  
$$\dot{y} = k_1 x - k_{-1} y + 2k_2 x^2 - 2k_{-2} y^2 = -f \circ (x, y)$$

of the reversible Wegscheider reaction has no periodic trajectory, or to show that periodic trajectories of the Lotka–Volterra reaction necessarily cross a line (having a tangent and an intersection which depends on the reaction rate coefficients).

Based on the Bendixson–Dulac theorem Bautin [4] has shown that within the class of equations

$$\dot{x} = x(ax + by + c), \quad \dot{y} = y(dx + ey + f)$$
(1.3)

(which are often called generalized Lotka–Volterra equations, a subclass of Kolmogorov type equations) only those can have a periodic solution which are of the Lotka–Volterra form (1.1), specifically, they cannot have a limit cycle.

A far reaching generalization of the statement by Bautin is the Póta–Hanusse-Tyson–Light theorem, the full proof of which by Póta [32] has also used an appropriate Dulac function.

**Theorem 1.1.** Suppose that the coefficients of the equation

$$\dot{x} = ax^2 + bxy + cy^2 + dx + ey + f, \quad \dot{y} = Ax^2 + Bxy + Cy^2 + Dx + Ey + F$$
 (1.4)

obey the following inequalities

$$0 \le c, e, f, A, D, F, \tag{1.5}$$

$$0 \ge a, C,\tag{1.6}$$

and

at most one of 
$$b$$
 and  $B$  is positive. (1.7)

Then, the only equation to have periodic solutions is of the form similar to (1.1) above, specifically, limit cycles cannot arise.

Schuman and Tóth [40] has provided an alternative proof based on the classification of polynomial vector fields which may be more handy to be generalized. (One should remark that Point 4 of their Theorem 2.2 is said to give the conditions for symmetric (time-reversible) centers. However it is not precise, not all systems defined by this condition are time-reversible. Confer it to the details in Section 4 of the paper [35].)

Condition (1.5) restricts the set of equations to the kinetic case (cf. [26]). Condition (1.6) excludes the presence of reaction steps  $2X \longrightarrow 3X$  or  $2Y \longrightarrow 3Y$ , while condition (1.7) excludes the presence of reaction steps  $X + Y \longrightarrow 2X + Y$ and  $X + Y \longrightarrow X + 2Y$ .

An interesting question is if condition (1.5) is enough to exclude the emergence of limit cycles. The answer has been given by Escher [17], who has written the most remarkable early papers on the topics of oscillation in two-species reactions both from the mathematical and chemical points of view. Here we only cite one of his interesting reactions: the one having both conservative oscillations and limit cycles—in different parts of the state space:

$$2 Y \Longrightarrow 2 X \longrightarrow 3 X, \quad X \Longrightarrow 0 \longleftarrow Y \quad X + Y \longrightarrow 0. \tag{1.8}$$

The article [17] of Escher contains chemical examples with two species and second order reactions with even more than one limit cycles, but the author allows long product complexes, as well, thus his examples are in no contradiction to Theorem 1.1. Theorem 1.1 says that among two-species second order reactions the only oscillatory reaction is the Lotka–Volterra model. It is interesting that the same result is obtained if one starts from different premises: if the linearized form of the Lotka–Volterra model is given, then the simplest model with this linearized form is again the Lotka–Volterra model [43].

A serious disadvantage of the Bendixson–Dulac theorem is that it is about planar systems, and cannot easily and naturally be generalized to higher dimensional cases. It may happen that a system can be reduced to a 2D system via first integrals and then one can apply the theorem [42].

Necessary conditions formulated in chemical terms to exclude the existence of periodic solutions can be found in the classical central theorems on regular behavior, see e.g. [44, Subsection 8.7.1].

#### 1.1.3. Limit cycles

People involved in modeling real life phenomena wanted to have a model with a (preferably stable) limit cycle or limit cycles. It was Prigogine and Lefever [33] who constructed the reaction

$$0 \xrightarrow[]{1} X \xrightarrow{b} Y, \quad 2X + Y \xrightarrow{a} 3X \tag{1.9}$$

having the induced kinetic differential equation

$$\dot{x} = 1 - (b+1)x + ax^2y, \quad \dot{y} = bx - ax^2y.$$
 (1.10)

It can be—and has later been—shown that there exists a limit cycle in this model. (One can use the Andronov–Hopf theorem on bifurcation to show this, or construct a Bendixson sack only to show the existence of a periodic solution. [45] shows a Wolfram language animation how a Hopf biurcation emerges in the Brusselator.)

Note the cubic term  $x^2y$  on the right-hand sides.

A similar reaction with a limit cycle called the Autocatalator

$$0 \xrightarrow{k_0} Y \xrightarrow{k_3} X \xrightarrow{k_2} 0, \quad 2X + Y \xrightarrow{k_1} 3X$$
(1.11)

having the induced kinetic differential equation

$$\dot{x} = k_3 y - k_2 x + k_1 x^2 y, \quad \dot{y} = k_0 - k_3 y - k_1 x^2 y$$
 (1.12)

has been proposed and later thoroughly investigated by Gray and Scott [25].

Erle [15] has shown that under the conditions

$$0 \le m' < m; 0 < \beta < n < n'; \alpha > 0$$

for the reaction

$$m \mathbf{X} + n \mathbf{Y} \xrightarrow[]{k_1}{k_1'} m' \mathbf{X} + n' \mathbf{Y}, \quad \alpha \mathbf{X} \xrightarrow[]{k_2}{k_2'} 0 \xrightarrow[]{k_3}{k_3'} \beta \mathbf{Y}$$
 (1.13)

there exist reaction rate coefficients for which the reaction has an asymptotically orbitally stable closed orbit.

In a following paper  $\operatorname{Erle}\left[16\right]$  has dealt with the case when all the reaction steps are reversible and the number of reversible pairs is not larger than the number of species. Although it is a strong restriction (e.g. in the case of combustion reactions the usual ratio of the number of reaction steps to the number of species is five as stated by the—empirical—Law of Law [29]), let us summarize his results in this case. He does not assume mass conservation and neither that the orders of the reaction steps are low. If the number of species and the number of reversible reaction step pairs are equal to two and the stoichiometric matrix is invertible, then no closed trajectory can exist in the open first orthant. If the number of reaction step pairs is not larger than the number of species (and now it can be any number, not only two), then no structurally stable closed orbit can exist in the open first orthant. His result is in accordance with the statement by Schnakenberg [38], who has shown that for exhibiting limit cycle behavior a two-species reaction has to consist of at least three reaction steps among which one must be autocatalytic of the type 2X + $Y \longrightarrow 3X$ . Under this condition, possible candidates having (a) limit cycle(s) are selected by postulating that their stationary state be an unstable focus. He enumerated all the reactions with three reaction steps fulfilling the conditions.

Császár et al. [10] used necessary conditions (for systems of two equations with not necessarily polynomial right-hand sides) provided by Feistel and Ebeling [19] and by Escher to construct candidate reactions with limit cycles, and they obtained a table of reactions similar to, but different from—thus, complementary in a certain sense—that of Schnakenberg. They have shown numerically that some of the reactions seem to have limit cycles.

A graph theoretical necessary condition of periodicity and multistationarity has been given by Schlosser and Feinberg [37].

Finally, we mention that an important mathematical tool for the qualitative analysis performed below is blowing up/down singularities. The reader can consult [3, 13] regarding to this technique.

### 1.2. The model with limit cycles

The dynamical system considered in this paper comes from a chemical model published in [10] that numerically shows limit cycle behavior for certain parameter values. The reaction scheme is called 'model A1' in [10], it contains two species, Uand V and the following set of reactions:

$$0 \xrightarrow{K_1} V, \ U \xrightarrow{K_2} 0, \ V \xrightarrow{K_3} U, \ 2U \xrightarrow{K_4} V, \ 2U + V \xrightarrow{K_5} 3U$$
(1.14)

where '0' is the so-called zero complex representing the environment (see, e.g. [44]), and  $K_i > 0$  for i = 1, ..., 5 are the reaction rate coefficients. (Contrary to the usual

custom uppercase K here does not mean equilibrium constant.) The model was further analyzed in [2], where it was shown that precisely 17160 reaction graphs with different structure—including the original model (1.14)—can produce exactly the same dynamical behavior: they induce the same mass action type kinetic differential equations. However, the computed structures could not be used to show important dynamical properties of the model (e.g. the existence of positive equilibria or the boundedness of solutions).



Figure 1. Graph of the reaction (1.14)

This reaction induces the following two-dimensional system of ordinary differential equations with five parameters:  $K_1, K_2, K_3, K_4, K_5$ ; where u, v are concentrations of two species:

$$\dot{u} = -K_2 u - 2K_4 u^2 + K_3 v + K_5 u^2 v,$$
  

$$\dot{v} = K_1 + K_4 u^2 - K_3 v - K_5 u^2 v.$$
(1.15)

From now on we only assume that all parameters of the system are non-negative (contrary to the usual custom according to which only reaction steps which do take place are only shown).

In this paper we explain the reason for the existence of the limit cycle detected in [10]. Moreover, we find all systems in the family in which a limit cycle appears as a result of a Hopf bifurcation at the stationary point in the first quadrant, and show that it is always stable.

We also have looked for integrals of the system, which from the point of view of chemical kinetics can be considered as conservation laws of the model. Here our result is mostly negative—it appears that the system cannot admit an analytic first integral, and we have found only one partial integral for chemically relevant values of parameters.

The paper is organized as follows. After preparatory calculations we investigate in details the behavior of trajectories in the first quadrant. Then we study the stationary singular point in this quadrant and find the systems admitting the Hopf bifurcation. Finally we look for algebraic invariant curves of the system.

### 2. Preparation for the analysis of the model

We note that the number of parameters in system (1.15) can be decreased by two in the following way. Let us introduce new variables, x and y, such that  $u(t) = ax(t\tau)$ and  $v(t) = by(t\tau)$  where a, b and  $\tau$  are parameters. Then  $u'(t) = a\tau x'(t\tau)$  and  $v'(t) = b\tau y'(t\tau)$  so the new equation system is

$$\dot{x} = -\frac{K_2 x}{\tau} - \frac{2aK_4 x^2}{\tau} + \frac{bK_3 y}{a\tau} + \frac{abK_5 x^2 y}{\tau},$$
  

$$\dot{y} = -\frac{K_1}{b\tau} + \frac{a^2 K_4 x^2}{b\tau} - \frac{K_3 y}{\tau} - \frac{a^2 K_5 x^2 y}{\tau}.$$
(2.1)

If b = a and  $\tau = a^2 K_5$  then the coefficient of  $x^2 y$  will be equal to 1, and if  $a = K_4/K_5$  then the coefficient of  $x^2$  will also be equal to 1. With these substitutions the system will be

$$\dot{x} = -\frac{K_2 K_5 x}{K_4^2} - 2x^2 + \frac{K_3 K_5 y}{K_4^2} + x^2 y,$$
  

$$\dot{y} = -\frac{K_1 K_5^2}{K_4^3} + x^2 - \frac{K_3 K_5 y}{K_4^2} - x^2 y.$$
(2.2)

If 
$$k_1 = \frac{K_1 K_5^2}{K_4^3}$$
,  $k_2 = \frac{K_2 K_5}{K_4^2}$  and  $k_3 = \frac{K_3 K_5}{K_4^2}$  then the system will have the form  
 $\dot{x} = -k_2 x - 2x^2 + k_3 y + x^2 y$ ,  
 $\dot{y} = k_1 + x^2 - k_3 y - x^2 y$ ,
(2.3)

which can also be obtained from system (1.15) if  $K_4 = K_5 = 1$ , and the notation is changed appropriately.

Thus, without loss of generality, instead of system (1.15) we will study system (2.3).

# **3.** Limit cycles of system (2.3)

Straightforward computations show that system (2.3) has two singular points:

$$A\left(\frac{-k_2 + \sqrt{k_2^2 + 4k_1}}{2}, \frac{2k_1\sqrt{k_2^2 + 4k_1}}{k_2\left(k_3 - k_1\right) + \sqrt{k_2^2 + 4k_1}\left(k_3 + k_1\right)}\right)$$
(3.1)

and

$$B\left(-\frac{k_2+\sqrt{k_2^2+4k_1}}{2},\frac{2k_1\sqrt{k_2^2+4k_1}}{k_2(k_1-k_3)+\sqrt{k_2^2+4k_1}(k_3+k_1)}\right).$$

Clearly, when all parameters are positive, then A is located in the first quadrant and B is in the fourth one, so only the point A is of interest for us.

The following theorem shows that all trajectories of system (2.3) in the first quadrant are bounded and tend either to the singular point A or to a limit cycle surrounding A when time increases.

**Theorem 3.1.** For any positive values of parameters  $k_i$  the corresponding system (2.3) has a unique singular point in the first quadrant and all trajectories of this quadrant tend to this point or to a limit cycle surrounding it when  $t \to +\infty$ .

**Proof.** As it is shown above the point A is the unique singular point in the first quadrant. The vector field on the coordinate axes bounding the first quadrant is directed inside the quadrant. Thus, to understand the behavior of the trajectories in the quadrant we have to study the singular points of the system at infinity.

Performing the substitution

$$u = y/x, \quad z = 1/x$$

and the time rescaling  $dt \rightarrow dt/z^2$  we obtain from (2.3) the system

$$\dot{u} = -u - u^2 + z + 2uz + k_2 uz^2 - k_3 uz^2 - k_3 u^2 z^2 + k_1 z^3 = U(u, z),$$
  

$$\dot{z} = z(-u + 2z + k_2 z^2 - k_3 uz^2) = Z(u, z).$$
(3.2)

The line z = 0 corresponds to the equator of the Poincaré sphere of system (2.3). Obviously, system (3.2) has two singular points at the equator z = 0: points C(0,0) and D(-1,0). Clearly, only point C corresponds to the first quadrant and it is located at the ends of the Ox axis of system (2.3).

The point C is a degenerate singular point of system (3.2). Since the first degree approximation of the polynomial U(u, z) is the polynomial  $U_1 = -u + z$  and the lowest terms in Z(u, z) have the second degree,  $Z_1 \equiv 0$ , we consider the function

$$F = uZ_1 - zU_1 = z(u - z).$$
(3.3)

The function F vanishes when z = 0 and z = u. Therefore, trajectories of system (3.2) tend to the singular point C tangentially to the lines z = 0 and z = u (see, e.g. [3]). To investigate the behavior of the trajectories more precisely we blow up the singularity at the origin of system (3.2) using the substitution

$$X = u, \quad Y = z/u.$$

The transformation yields the system

$$\dot{X} = -X(1 + X - Y - 2XY - k_2X^2Y^2 + k_3X^2Y^2 + k_3X^3Y^2 - k_1X^2Y^3),$$
  
$$\dot{Y} = -Y(-1 + Y - k_3X^2Y^2 + k_1X^2Y^3).$$
(3.4)

Singular points of (3.4) on the axis X = 0 are X = 0, Y = 0 and X = 0, Y = 1. Clearly, the point X = 0, Y = 0 is a saddle. Moving the origin into the point X = 0, Y = 1 using the substitution w = X, v = Y - 1 and rescaling the time by  $dt \rightarrow -dt$ , we obtain the system

$$\dot{w} = -vw - w^{2} - 2vw^{2} - k_{1}w^{3} - k_{2}w^{3} + k_{3}w^{3} - 3k_{1}vw^{3} - 2k_{2}vw^{3} + 2k_{3}vw^{3} - 3k_{1}v^{2}w^{3} - k_{2}v^{2}w^{3} + k_{3}v^{2}w^{3} - k_{1}v^{3}w^{3} + k_{3}w^{4} + 2k_{3}vw^{4} + k_{3}v^{2}w^{4} = P(w, v),$$
  
$$\dot{v} = v + v^{2} + k_{1}w^{2} - k_{3}w^{2} + 4k_{1}vw^{2} - 3k_{3}vw^{2} + 6k_{1}v^{2}w^{2} - 3k_{3}v^{2}w^{2} + 4k_{1}v^{3}w^{2} - k_{3}v^{3}w^{2} + k_{1}v^{4}w^{2} = v + Q(w, v).$$
  
(3.5)



Figure 2. Phase portrait of system (3.5) for fixed values of  $k_1$  and  $k_3$  (when  $k_2=1$ ), generated by Wolfram Mathematica.

If  $v = \phi(w)$  is the solution to the equation v + Q(w, v) = 0 then  $P(w, \phi(w)) = -w^2 + h.o.t$ . By Theorem 65 of [3] the singular point at the origin of (3.5) is a saddle-node and the phase portrait qualitatively looks as shown in Figure 2 or Figure 3a. Taking into account that we have changed the direction on trajectories dividing by the negative number -1 after the blow-down we obtain that the phase portrait near the origin of system (3.2) looks as in Figure 3b.



Figure 3. (a) Phase portrait of system (3.5) and (b) phase portrait of system (3.2).

To study the behavior of the trajectories of system (2.3) at the ends of the axis Oy, we perform the substitution

$$u = x/y, \quad z = 1/y$$

and time rescaling  $dt \rightarrow dt/z^2$  and thus we obtain the system

$$\dot{u} = u^2 + u^3 - 2u^2 z - u^3 z + k_3 z^2 - k_2 u z^2 + k_3 u z^2 - k_1 u z^3 = U(u, z),$$
  

$$\dot{z} = u^2 z - u^2 z^2 + k_3 z^3 - k_1 z^4 = Z(u, z).$$
(3.6)

The origin of system (3.6) corresponds to the singular point at the ends of the Oy axis of system (2.3).

For system (3.6) the function (3.3) is identically equal to zero and

$$uZ_2 - zU_2 = -z(u^2 + k_3 z^2).$$

Hence, the characteristic direction is z = 0 and the *u*-directional blow-up needs to be done. Thus, to blow up the singularity at the origin of (3.6) we use the substitution

$$u = X, \quad z = XY.$$

After the transformation and the rescaling of time

$$dt \to X dt$$
 (3.7)

the system has the form

$$\dot{X} = -X(-1 - X + 2XY + X^2Y - k_3Y^2 + k_2XY^2 - k_3XY^2 + k_1X^2Y^3),$$
  
$$\dot{Y} = Y(-1 + 2XY - k_3Y^2 + k_2XY^2).$$
(3.8)

The only singularity of system (3.8) at the origin is a saddle shown in Figure 4. Taking into account rescaling (3.7) we obtain that the phase portrait of system (3.6) near the origin looks like the right picture of Figure 4.



Figure 4. Phase portrait of system (3.8) and phase portrait of system (3.6) after the blow-down.

System (2.3) has exactly one singular point, the point A, in the first quadrant. Thus, the phase portrait of system (2.3) in the first quadrant up to some number of limit cycles surrounding A is qualitatively equivalent to the one shown in Figure 5.

That is, when the time increases, each trajectory of the first quadrant either reach the singular point A or a limit cycle surrounding A.

To simplify the further analysis of system (2.3) we rescale the Ox axis such that the singular point  $A(x_0, y_0)$  (defined in (3.1)) is moved to a singular point  $A'(x'_0, y'_0)$ with  $x'_0 = 1$ , that is we perform the transformation

$$X = \frac{x}{x_0}, \qquad Y = y.$$

Writing in the obtained system x, y instead of X, Y we have

$$\dot{x} = -k_2 x - 2x^2 x_0 + \frac{k_3 y}{x_0} + x^2 x_0 y,$$
  

$$\dot{y} = k_1 + x^2 x_0^2 - k_3 y - x^2 x_0^2 y.$$
(3.9)

Since the point  $A'(x'_0, y'_0)$ , where  $x'_0 = 1$  is a singular point of system (3.9), we obtain that

$$k_1 = x_0(k_2 + x_0) \tag{3.10}$$



Figure 5. Phase portrait of system (2.3) based on Figure 3b and Figure 4.

and the coordinates of the singular point A' are

$$x'_0 = 1, \quad y'_0 = \frac{x_0(k_2 + 2x_0)}{k_3 + x_0^2}$$

Let  $\mathcal{A}$  be the matrix of the linearization of system (3.9) at the point  $\mathcal{A}'$ . The necessary condition for the existence of Hopf and degenerate Hopf bifurcation at the point  $\mathcal{A}'$  (and, therefore, also at the point  $\mathcal{A}$ ) is that the trace of the matrix  $\mathcal{A}$  is zero, or, equivalently, the real parts of the eigenvalues  $\lambda_{1,2}$  of  $\mathcal{A}$  are equal to zero. Computing we find

$$Re\lambda_{1,2} = \frac{x_0^3(k_2 - 2k_3) - k_3x_0(k_2 + k_3) - 4k_3x_0^2 - x_0^5}{2x_0(k_3 + x_0^2)}.$$
(3.11)

Therefore  $Re\lambda_{1,2} = 0$  if and only if

$$k_2 = (-k_3^2 - 4k_3x_0 - 2k_3x_0^2 - x_0^4)/(k_3 - x_0^2).$$
(3.12)

**Theorem 3.2.** If in system (2.3) all parameters and the coordinates of the point A are positive, and the trace of the matrix of the linearization of system (2.3) at A is equal to zero, then the point A is a stable focus.

**Proof.** As it is shown above the conditions of the theorem are fulfilled if and only if conditions (3.10) and (3.12) hold. Since the numerator of (3.12) is negative, but  $k_2$  should be positive, we have that  $k_3$  should satisfy the condition

$$k_3 < x_0^2$$
. (3.13)

Taking into account these conditions and moving the origin of system (3.9) at the origin by the substitution  $u = x - x'_0$ ,  $v = y - y'_0$  we obtain the system

$$\dot{u} = (k_3^2 v + k_3^2 u x_0 - 2k_3 u^2 x_0^2 + 2k_3 u v x_0^2 + k_3 u^2 v x_0^2 - k_3 u^2 x_0^3 - v x_0^4 - 2u v x_0^4 - u^2 v x_0^4 - u x_0^5 - u^2 x_0^5) / (x_0 (k_3 - x_0^2)), \dot{v} = - (k_3^2 v - 2k_3 u x_0^2 - k_3 u^2 x_0^2 + 2k_3 u v x_0^2 + k_3 u^2 v x_0^2 - 2k_3 u x_0^3 - k_3 u^2 x_0^3 - 2u x_0^4 - u^2 x_0^4 - v x_0^4 - 2u v x_0^4 - u^2 v x_0^4 - 2u x_0^5 - u^2 x_0^5) / (k_3 - x_0^2).$$

$$(3.14)$$

Eigenvalues of the linearized system are

$$\omega_{1,2} = \pm \frac{\left(k_3 + x_0^2\right)\sqrt{k_3^2 + 2k_3x_0 - x_0^4 - 2x_0^3}}{k_3 - x_0^2}.$$

By (3.13) the expression under the radical is always negative, therefore the singular point at the origin of (3.14) is either a center or a focus (and the same conclusion holds for the point A of system (1.15)).

We look for a polynomial

$$\Phi(u,v) = \sum_{k+s=2}^{4} \phi_{ks} u^k v^s$$
(3.15)

such that

$$\frac{\partial \Phi}{\partial u}\dot{u} + \frac{\partial \Phi}{\partial v}\dot{v} = g_1(u^2 + v^2)^2 + h.o.t.$$
(3.16)

The computation yield that the quadratic part of (3.15) is

$$\Phi_2 = \frac{1}{2}\phi_{11} \left( \frac{2u^2 x_0^2 (x_0 + 1)}{x_0^2 - k_3} + 2uv + \frac{v^2}{x_0} \right), \tag{3.17}$$

where  $\phi_{11}$  can be chosen arbitrary. We set  $\phi_{11} = 1$ , then, in view of (3.13),  $\Phi_2$  is a positive defined quadratic form. Performing the further computations we find that

$$g_1 = -((x_0^3(-4k_3^2 - 3k_3^3 - 8k_3^2x_0 + 12k_3x_0^2 + 3k_3^2x_0^2 + 24k_3x_0^3 + 7k_3x_0^4 + x_0^6)) \\ /((k_3 + x_0^2)(3k_3^2 - 6k_3x_0^2 + 4k_3^2x_0^2 - 4k_3x_0^3 + 3x_0^4 - 12k_3x_0^4 + 4x_0^5 + 20x_0^6 + 24x_0^7 + 12x_0^8))).$$

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$$g1 \ge 0 \land k_3 - x_0^2 < 0 \land k_3 > 0 \land x_0 > 0$$

we find that it does not have solution. Therefore,  $g_1$  is always negative.

Since  $\Phi_2$  defined by (3.17) is positive defined quadratic form the function (3.15) is positive defined Lyapunov function in a sufficiently small neighborhood of the origin of system (3.14). Since  $g_1 < 0$ , in view of (3.16) its derivative with respect to the vector field is negative defined. Therefore by the Lyapunov theorem the singular point at the origin of (3.14) is asymptotically stable, that means, it is a stable focus.

The next theorem gives the necessary and sufficient conditions for existence of a Hopf bifurcation in system (2.3).

**Theorem 3.3.** If in system (2.3) all parameters are positive, then the point  $A(x_0, y_0)$  defined in (3.1) is the only singular point in the first quadrant and a Hopf bifurcations occur at A, if and only if the coefficients of (2.3) satisfy the conditions (3.10) and (3.10). The bifurcation is always supercritical, that is, a stable limit cycle is born from the point A.

**Proof.** As it is shown in the proof of the previous theorem the eigenvalues of system (2.3) linearized at A are pure imaginary if and only if the coefficients of (2.3) satisfy the conditions (3.10) and (3.10), and in this case A is a stable focus. From (3.11) and (3.12) we see that taking  $k_2$  as perturbation parameter we can



Figure 6. Trajectory going inward, approaching the big cycle and the components of the solution. The distance of the initial point from the singular point is 1.



Figure 7. Trajectory going outward, approaching the big cycle and the components of the solution. The distance of the initial point from the singular point is  $10^{-5}$ .

slightly perturb the system in such a way, that the real parts of  $\lambda_1$  and  $\lambda_2$  (defined by (3.11)) became positive. It means that the point A becomes an unstable focus and a limit cycles is born as the result of a supercritical Hopf bifurcation.

The figures were created with Wolfram Mathematica and together with the calculations these can be found in [20]. The parameter values are  $k_3 = 0.3, k_2 = -((k_3^2 + 6k_3 + 1)/(k_3 - 1)) - 10^{-5}$  and  $k_1 = k_2 + 1$ .

# 4. Invariant algebraic curves of system (2.3)

We first recall a few notions and one of the main results of the elimination theory. Consider a system of polynomials with coefficients in some field k,

$$f_1(x_1, \dots, x_n) = \dots = f_k(x_1, \dots, x_n) = 0,$$
 (4.1)

and the corresponding ideal  $I = \langle f_1, \ldots, f_k \rangle \subset k[x_1, \ldots, x_n].$ 

**Definition 4.1.** Let I be an ideal in  $k[x_1, \ldots, x_n]$  (with the implicit ordering of the variables  $x_1 > \cdots > x_n$ ) and fix  $\ell \in \{0, 1, \ldots, n-1\}$ . The  $\ell$ -th elimination ideal of I is the ideal  $I_\ell = I \cap k[x_{\ell+1}, \ldots, x_n]$ .

To eliminate  $x_1, \ldots, x_\ell$   $(0 \le \ell < n)$  from the system one can use the following theorem (see e.g. [9,34] for the proof).

**Theorem 4.1** (Elimination Theorem). Fix the lexicographic term order on the ring  $k[x_1, \ldots, x_n]$  with  $x_1 > x_2 > \cdots > x_n$  and let G be a Groebner basis for an ideal I

of  $k[x_1, \ldots, x_n]$  with respect to this order. Then for every  $\ell$ ,  $0 \leq \ell \leq n-1$ , the set

 $G_{\ell} := G \cap k[x_{\ell+1}, \dots, x_n]$ 

is a Groebner basis for the  $\ell$ -th elimination ideal  $I_{\ell}$ .

In this section using the theorem we determine invariant algebraic curve of degree 2 of the form  $L = f_0 + f_1 x + f_2 y + f_3 x^2 + f_4 x y + f_5 y^2$  of system (2.3).

Consider the system

$$\dot{x} = A(x, y), \tag{4.2}$$

$$\dot{y} = B(x, y). \tag{4.3}$$

Let

$$\mathcal{X} = \frac{\partial}{\partial x}A + \frac{\partial}{\partial y}B \tag{4.4}$$

be the vector field associated to (4.3) and let L be a polynomial in the variables x, y. The polynomial L defines an invariant algebraic curve L = 0 of system (4.3) if

$$\mathcal{X}L = KL \tag{4.5}$$

for some polynomial K(x, y). The polynomial K is called the cofactor of L and has degree at most n - 1, if the maximal degree of A, B is n.

In the next theorem we list cases when system (2.3) has at least one invariant algebraic curve of degree one or two.

**Theorem 4.2.** System (2.3) has invariant algebraic curves of degree at most two if one of the following conditions holds:

(i) 
$$k_3 = 0;$$
  
(ii)  $k_2^2 + 4k_3 = 0;$   
(iii)  $k_1 - k_3 = k_2^2 + 4k_3 = 0;$   
(iv)  $k_3 = k_1 = 0;$   
(v)  $k_3 - k_1 = 0.$ 

**Proof.** We look for an algebraic invariant curve of the system (2.3) in the form

$$L(x,y) = f_0 + f_1 x + f_2 y + f_3 x^2 + f_4 x y + f_5 y^2$$
(4.6)

with the corresponding cofactor

$$K(x,y) = c_0 + c_1 x + c_2 y + c_3 x^2 + c_4 x y + c_5 y^2.$$
(4.7)

For the computations we substitute L(x, y) and K(x, y) from (4.6) and (4.7) into the equation (4.5) (with the vector field  $\mathcal{X}$  corresponding to system (2.3)). Then we compare the coefficients of similar terms on both sides of (2.3) and obtain the system of polynomials

$$f_1 = f_2 = \dots = f_{15} = 0,$$

where

$$f_1 = -c_3 f_3;$$

$$\begin{split} f_2 &= -c_5 f_5; \\ f_3 &= -c_5 f_1 - c_4 f_2 - c_2 f_4 - c_1 f_5; \\ f_4 &= -c_5 f_2 - c_2 f_5; \\ f_5 &= -c_5 f_4 - c_4 f_5; \\ f_6 &= -c_0 f_0 + f_2 k_1; \\ f_7 &= -c_1 f_0 - c_0 f_1 + f_4 k_1 - f_1 k_2; \\ f_8 &= -c_2 f_0 - c_0 f_2 + 2 f_5 k_1 + f_1 k_3 - f_2 k_3; \\ f_9 &= -c_4 f_0 - c_2 f_1 - c_1 f_2 - c_0 f_4 - f_4 k_2 + 2 f_3 k_3 - f_4 k_3; \\ f_{10} &= -c_5 f_0 - c_2 f_2 - c_0 f_5 + f_4 k_3 - 2 f_5 k_3; \\ f_{11} &= -c_3 f_0 - c_1 f_1 - c_0 f_3 - 2 f_3 k_2 - 2 f_1 + f_2; \\ f_{12} &= -c_3 f_1 - c_1 f_3 - 4 f_3 + f_4; \\ f_{13} &= -c_4 f_1 - c_3 f_2 - c_2 f_3 - c_1 f_4 - 2 f_4 + 2 f_5 + f_1 - f_2; \\ f_{14} &= -c_4 f_3 - c_3 f_4 + 2 f_3 - f_4; \\ f_{15} &= -c_5 f_3 - c_4 f_4 - c_3 f_5 + f_4 - 2 f_5. \end{split}$$

Denote by  $I := \langle f_1, f_2, \ldots, f_{15} \rangle$  the ideal generated by polynomials given above. To obtain conditions for existence of invariant curves we have to eliminate from the system the variables  $f_i$  and  $c_i$ . We observe that (4.5) always has the solution L = 1, K = 0. Thus, computing the 12-th elimination ideal of I we obtain the zero polynomial, which means that the elimination is always possible. To overcome this difficulty we should impose the condition that  $L \not\equiv const$ . To this end we add to the ideal I the polynomial  $1 - wf_3$  and thus we obtain the ideal  $J = \langle 1 - wf_3, I \rangle$ . Ordering variables using a lexicographic ordering with  $\{w, f_0, f_1, f_2, f_3, f_4, f_5, c_0, c_1, c_2, c_3, c_4, c_5\} > \{k_1, k_2, k_3, k_4, k_5\}$  with eliminate of SINGULAR [12] we compute the 13-th elimination ideal  $J_{13}$  of J. Then, we compute the decomposition of the variety of  $J_{13}$  with the routine minAssGTZ<sup>\*</sup> of primdec library [11] of SINGULAR and obtain conditions (i) and (ii) of Theorem 4.2.

Computing the decomposition of the variety of the 13-th elimination ideal of  $\hat{J} = \langle 1 - wf_4, I \rangle$  yields additionally conditions (*iii*) and (*iv*) of Theorem 4.2. Condition (*v*) is obtained by computing the 13-th elimination ideal of  $\hat{J} = \langle 1 - wf_5, I \rangle$ .

We now show that if each of conditions (i) - (v) of the theorem is satisfied, then system (2.3) admits an invariant curve of the form (4.6). We prove this by finding an invariant curve for each case.

**Case** (*i*): In this case the corresponding system has invariant line  $l_1 = x$  with the corresponding cofactor  $K_1 = x(y-2) - k_2$  and invariant curve of degree two  $l_2 = l_1^2$ . **Case** (*ii*): The system has the invariant line  $l_1 = \frac{k_2}{2} + x$  with the corresponding cofactor  $K_1 = x(y-2) - \frac{k_2}{2}y$ .

**Case** (*iii*): The corresponding system admits two invariant lines  $l_1 = \frac{k_2}{2} + x$  and  $l_3 = y - 1$  with the corresponding cofactors  $K_1 = x(y-2) - \frac{k_2}{2}y$  and  $K_2 = x^2 - \frac{k_2^2}{4}$ , respectively.

**Case** (*iv*): In this case the system has two invariant lines  $l_1 = x$  and  $l_2 = y - 1$  with the corresponding cofactors  $K_1 = x(y-2) - k_2$  and  $K_2 = -x^2$ , respectively.

<sup>\*</sup>The routine eliminate is based on Theorem 4.2 and minAssGTZ on the algoritheorem of [24]

**Case** (v): System under this condition admits invariant line  $l_1 = y - 1$  with the corresponding cofactor

$$K_1 = -k_1 - x^2$$
.

Note that in all five cases of Theorem 4.2 the corresponding system admits also invariant curves of degree two but they are only products of invariant lines listed above.  $\hfill \Box$ 

### References

- E.O. Abdel-Rahman, Z.S.A. Malki and S.A. Dakroury, An algorithmic global criterion excluding oscillations based on algebraic first integrals, Journal of Computational and Theoretical Nanoscience, 2015, 12(11), 4674–4678.
- [2] B. Acs, G. Szederkényi, Z. Tuza and Z.A. Tuza, Computing all possible graph structures describing linearly conjugate realizations of kinetic systems, Computer Physics Communications, 2016, 204, 11–20.
- [3] A.A. Andronov, E.A. Leontovich, I.I. Gordon and A.G. Maier, *Qualitative Theory of Second Order Differential Equations*, John Wiley and Sons, New York, Toronto and Israel Program for Scientific Translations, Jerusalem, London, 1973.
- [4] N.N. Bautin, On periodic solutions of a system of differential equations, Prikl. Mat. Mekh., 1954, 18, 128–134.
- [5] M.T. Beck, Mechanistic and parametric conditions of exotic chemical kinetics, Reaction Kinetics and Catalysis Letters, 1990, 42(2), 317–323.
- [6] M.T. Beck, Mechanistic and parametric conditions of exotic chemical kinetics. Why are there so few oscillatory reactions?, Acta Chimica Hungarica, 1992, 129, 519–529.
- [7] B.P. Belousov, A periodic reaction and its mechanism, Sb. Ref. Radiats. Med. Moscow, 1958, 145–147.
- [8] L.A. Cherkas, A.A. Grin and V.I. Bulgakov, Constructive methods of investigation of limit cycles of second order autonomous systems (numerical-algebraic approach), Grodno, 2013, 489. (in Russian).
- [9] D. Cox, J. Little and D. O'shea, *Ideals, Varieties, and Algorithms*, 3, Springer, New York, 2007.
- [10] A. Császár, L. Jicsinszky and T. Turányi, Generation of model reactions leading to limit cycle behavior, Reaction Kinetics and Catalysis Letters, 1982, 18(1–2), 65–71.
- [11] W. Decker, S. Laplagne, G. Pfister and H.A. Schonemann, Singular 3-1 library for computing the prime decomposition and radical of ideals, primdec.lib, 2010.
- [12] W. Decker, S. Laplagne, G. Pfister and H.A. Schönemann, Singure 3-1-6 a computer algebra system for polynomial computations, 2012. http://www. singular.uni-kl.de.
- [13] F. Dumortier, J. Llibre and J. Artes, Qualitative Theory of Planar Differential Systems, Universitext. Springer-Verlag, Berlin, 2006.
- [14] L. Edelstein-Keshet, Mathematical Models in Biology, 46 of Classics in Applied Mathematics, SIAM, 1988.

- [15] D. Erle, A boundedness theorem with application to oscillation of autocatalytic chemical reactions, J. Math. Chem., 1998, 24(4), 365–378.
- [16] D. Erle, Nonoscillation in closed reversible chemical systems, J. Math. Chem., 2000, 27(4), 293–302.
- [17] C. Escher, Models of chemical reaction systems with exactly evaluable limit cycle oscillations and their bifurcation behaviour, Berichte der Bunsengesellschaft für physikalische Chemie, 1980, 84(4), 387–391.
- [18] C. Escher, Bifurcation and coexistence of several limit cycles in models of open two-variable quadratic mass-action systems, Chemical Physics, 1981, 63(3), 337–348.
- [19] R. Feistel and W. Ebeling, Deterministic and stochastic theory of sustained oscillations in autocatalytic reaction systems, Physica A: Statistical Mechanics and its Applications, 1978, 93(1-2), 114–137.
- [20] B. Ferčec, I. Nagy, V.G. Romanovski, G. Szederkényi and J. Tóth, Calculations for two limit cycles in a two-species reaction with wolfram mathematica, (available 27 June 2018). http://math.bme.hu/~nagyi/Mathematica\_notebooks/ index.html.
- [21] A. Ferragut, C. Valls and C. Wiuf, On the liouville integrability of Edelstein's reaction system in r3, Chaos, Solitons & Fractals, 2018, 108, 129–135.
- [23] D.A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics, USSR Academy of Science Press, Moscow, Leningrad, 1947. In Russian.
- [24] P. Gianni, B. Trager and G. Zacharias, Gröbner bases and primary decomposition of polynomial ideals, Journal of Symbolic Computation, 1988, 6(2-3), 149–167.
- [25] P. Gray and S.K. Scott, A new model for oscillatory behaviour in closed systems: The autocatalator, Berichte der Bunsengesellschaft für physikalische Chemie, 1986, 90(11), 985–996.
- [26] V. Hárs and J. Tóth, On the inverse problem of reaction kinetics, in Colloquia Mathematica Societatis János Bolyai, 30 (Edited by M. Farkas), Qualitative Theory of Differential Equations, 1979, 363–379.
- [27] I.D. Hsü, Existence of periodic solutions for the Belousov-Zaikin-Zhabotinskii reaction by a theorem of Hopf, Journal of Differential Equations, 1976, 20(2), 399–403.
- [28] Y.S. Ilyashenko, Centennial history of hilbert's 16th problem, American Mathematical Society, 2002, 39(3), 301–354.
- [29] C.K. Law, Combustion at a crossroads: Status and prospects, Proceedings of the Combustion Institute, 2007, 31(1), 1–29.
- [30] J.D. Murray, Mathematical biology. II Spatial Models and Biomedical Applications, 18 of Interdisciplinary Applied Mathematics, Springer-Verlag, New York, 2001.
- [31] J.D. Murray, Mathematical Biology. I, 2002.

- [32] G. Póta, Two-component bimolecular systems cannot have limit cycles: A complete proof, J. Chem. Phys., 1983, 78, 1621–1622.
- [33] I. Prigogine and R. Lefever, Symmetry breaking instabilities in dissipative systems, II., J. Chem. Phys., 1968, 48, 1695–1700.
- [34] V. Romanovski and D. Shafer, The Center and Cyclicity Problems: A Computational Algebra Approach, Birkhäuser, Boston, Basel, Berlin, 2009.
- [35] V.G. Romanovski, *Time-reversibility in 2-dimensional systems*, Open Systems & Information Dynamics, 2008, 15(04), 359–370.
- [36] D. Schlomiuk and N. Vulpe, Global topological classification of Lotka-Volterra quadratic differential systems, Electr. J. Diff. Eqs., 2012, 2012(64), 1–69.
- [37] P.M. Schlosser and M. Feinberg, A theory of multiple steady states in isothermal homogeneous CFSTRs with many reactions, Chem. Eng. Sci., 1994, 49(11), 1749–1767.
- [38] J. Schnakenberg, Simple chemical reaction systems with limit cycle behaviour, J. Theor. Biol., 1979, 81(3), 389–400.
- [39] K.R. Schneider, B. Wegner and J. Tóth, Qualitative analysis of a model for synaptic slow waves, J. Math. Chem., 1987, 1, 219–234.
- [40] B. Schuman and J. Tóth, No limit cycle in two species second order kinetics, Bull. sci. math., 2003, 127, 222–230.
- [41] H.L. Smith, Global dynamics of the smallest chemical reaction system with Hopf bifurcation, J. Math. Chem., 2012, 50(4), 989–995.
- [42] J. Tóth, Bendixson-type theorems with applications, Zeitschrift für Angewandte Mathematik und Mechanik, 1987, 67(1), 31–35.
- [43] J. Tóth and V. Hárs, Specification of oscillating chemical models starting form a given linearized form, Theor. Chim. Acta, 1986, 70, 143–150.
- [44] J. Tóth, A.L. Nagy and D. Papp, *Reaction Kinetics: Exercises, Programs and Theorems*, Springer Nature, Berlin, Heidelberg, New York, 2018. In press.
- [45] J. Várdai and J. Tóth, Hopf Bifurcation in the Brusselator, 2008. From The Wolfram Demonstrations Project.
- [46] T. Wilhelm and R. Heinrich, Smallest chemical reaction system with Hopf bifurcation, J. Math. Chem., 1995, 17(1), 1–14.
- [47] A.T. Winfree, The Geometry of Biological Time, 12, Springer Science & Business Media, 2001.
- [48] A.M. Zhabotinsky, Periodic liquid-phase oxidation reactions, Doklady Akademii Nauk SSSR, 1964, 157, 392–395.