III. CHEMICAL REACTIONS DESCRIBED BY AUTONOMOUS ORDINARY DIFFERENTIAL EQUATIONS

In this chapter we present some aspects of the theory of ordinary differential equations describing chemically reacting systems. The main topics are the a priori bounds of solutions and the existence and stability of equilibrium points, the latter aspect being considered by using degree theory developed in chapter II. As a general reference to the present chapter we mention the monograph of GAVALAS [1].

1. CHEMICAL REACTIONS

We consider a system of r simultaneous chemical reactions, symbolized by:

$$(1.1) \qquad \sum_{j=1}^{n} \nu_{ij} M_j = 0, \qquad i = 1,\ldots,r,$$

where ν_{ij} are integers and M_j are chemical species. The numbers ν_{ij} constitute an $(r\times n)$-matrix ν. The species M_j consists of a number of atomic species $A_1,\ldots,A_m$, and β_{ij} will denote the number of atoms A_j in the species M_i. The non-negative numbers β_{ij} constitute an $(n\times m)$-matrix β. Since each chemical species contains at least one atomic species we have

$$(1.2) \qquad \sum_{j=1}^{m} \beta_{ij} > 0, \qquad i = 1,\ldots,n$$

EXAMPLE 1.1. To illustrate the concepts in this section we shall consider the two reactions

$$\begin{aligned} &2NO_2 - N_2O_4 = 0, \\ &2NO + O_2 - 2NO_2 = 0. \end{aligned} \tag{1.3}$$

The four chemical species O_2, NO, NO_2, N_2O_4 will be denoted by M_1, M_2, M_3, M_4 respectively, and the atomic species O, N are denoted by A_1 and A_2. The matrices ν and β are in this case

$$\nu = \begin{pmatrix} 0 & 0 & 2 & -1 \\ 1 & 2 & -2 & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 2 & 0 \\ 1 & 1 \\ 2 & 1 \\ 4 & 2 \end{pmatrix} \tag{1.4}$$

REMARK 1.2. (Notation) The rank of a matrix α will be denoted by $r(\alpha)$ and the transpose of α by α^T. With I_n we denote the $(n\times n)$ unit matrix, and with 0_{nm} we denote the $(n\times m)$-matrix containing only zero elements.

REMARK 1.3. We suppose throughout that

$$r(\nu) = r; \tag{1.5}$$

in other words, we only consider a system of r independent reactions. In general, the chemical equations are presented as $\sum \lambda_j M_j \overset{\leftarrow}{\rightarrow} \sum \mu_j M_j$ where the direction also is important, but in the mathematical treatment these aspects may be ignored.

REMARK 1.4. The r reactions (1.1) are said to be *proper* if

$$\nu\beta = 0_{rm}. \tag{1.6}$$

The condition for a reaction to be proper is known in chemistry as "balancing the equations", and

$$\sum_{j=1}^{n} \nu_{ij}\, \beta_{jk} = 0 \qquad (i=1,\ldots,r,\ k=1,\ldots,m) \tag{1.7}$$

corresponds to the conservation of atomic species A_k in the i-th reaction.

We only consider systems for which (1.6) is fulfilled.

The following lemma is important for the construction of invariant manifolds of the differential equations describing chemical reactions. It is an extension of relation (1.6).

LEMMA 1.5. *There is an* $n \times (n-r)$ *matrix* γ *of rank* $(n-r)$ *such that*

$$\nu\gamma = 0_{r,n-r}. \tag{1.8}$$

PROOF. The proof simply follows from the observation that the linear homogeneous equation $\nu x = 0$, $x \in \mathbb{R}^n$ has $(n-r)$ linearly independent solutions; here (1.5) is used. □

On account of (1.6) or (1.7), the first $r(\beta)$ columns of γ will be taken from the columns of β. If the elements of γ are denoted by γ_{ij}, then it follows from (1.2) that

$$p_i = \sum_{j=1}^{r(\beta)} \gamma_{ij} > 0, \qquad i = 1,\ldots,n. \tag{1.9}$$

Moreover we have

$$r = r(\nu) \leq n - r(\beta) \tag{1.10}$$

giving an upper bound for the number of linearly independent reactions.

It is supposed that the systems considered are *homogeneous*, that is, we suppose that only one phase in the system will occur. The concentration of the chemical species M_i will be denoted by c_i, $i = 1,\ldots,n$. During a reaction process the quantities c_i, which are called the *state variables*, will vary with time, and the evolution of a chemical system can be described by these variables as functions of time. The initial values (at t=0) are denoted by $c_{i0}, i = 1,\ldots,n$. The state vector c and its initial value c_0

$$c = \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix}, \qquad c_0 = \begin{pmatrix} c_{10} \\ \vdots \\ c_{n0} \end{pmatrix} \tag{1.11}$$

are the elements of the n-dimensional real vector space $\mathbb{R}^n$, and $\mathbb{R}^n_+$ is its positive orthant

$$\mathbb{R}^n_+ = \{c \mid c_i \geq 0, \quad i = 1,\ldots,n\} \tag{1.12}$$

The inner product $(.,.)$ and the norm $|.|$ in $\mathbb{R}^n$ are given by

$$(x,y) = x_1y_1 + \ldots + x_ny_n, \quad |x| = (x,x)^{\frac{1}{2}}.$$

REMARK 1.6. If we interpret the r rows of ν as vectors of $\mathbb{R}^n$, the subspace spanned by these rows is denoted by Λ_0. On account of (1.5), dim $(\Lambda_0) = r$, and (1.8) implies that the column vectors of γ are elements of the orthogonal complement of Λ_0.

COROLLARY 1.7. *Let* $x \in \mathbb{R}^n$, *then* $x \in \Lambda_0$ *if and only if* $\gamma^T x = 0$.

EXAMPLE 1.8. For the chemical system in example 1.1 we have

$$\Lambda_0 = \{\lambda \begin{pmatrix} 0 \\ 0 \\ 2 \\ -1 \end{pmatrix} + \mu \begin{pmatrix} 1 \\ 2 \\ -2 \\ 0 \end{pmatrix} \mid \lambda, \mu \in \mathbb{R}\}. \tag{1.13}$$

In this case $r = 2$, $n = 4$, $r(\beta) = r(\gamma) = 2$. As a consequence we can take $\gamma = \beta$.

In this chapter, we only consider *uniform systems*, i.e., systems having no space variations. A uniform system is specified by the values of the state variables at a single point of the reactor tank.

2. DIFFERENTIAL EQUATIONS OF CHEMICAL REACTIONS

In this and the following sections we consider two types of ordinary differential equations associated with homogeneous and uniform chemical systems. In each case the equations are formulated in terms of the *reaction rates* f_j, $j = 1,\dots,r$ of the r reactions in (1.1). These *rate functions* (or *rate laws* or *kinetics*) are functions of the state variables $c_1,\dots,c_n$. Also the vector functions $f(c)$ and $F(c)$,

$$(2.1) \qquad f = \begin{pmatrix} f_1 \\ \vdots \\ f_r \end{pmatrix}, \qquad F = \begin{pmatrix} F_1 \\ \vdots \\ F_n \end{pmatrix},$$

related by

$$(2.2) \qquad F = \nu^T f,$$

are used. F_i is the total production of M_i in moles per unit volume per unit time due to chemical reactions. Explicitly we have

$$(2.3) \qquad F_j(c) = \sum_{i=1}^{r} \nu_{ij} f_i(c), \qquad j = 1,\dots,n.$$

REMARK 2.1. A more realistic model is obtained by regarding the temperature T of the system as a state variable as well. In that case the functions f_j are given as functions of T. In this chapter, however, the temperature, and effects of its variations with time, will not be considered. The suppression of T from the formulas does not change the discussion in a relevant way. The reason for the simplification of the model is only based on the wish of considering a convenient mathematical model.

A *closed system* is a system (1.1) of constant volume which does not exchange mass or energy with its surroundings. It is convenient, to consider a closed system of unit volume. The time evolution of this system is described by the system of differential equations

$$(2.4) \qquad \frac{dc}{dt} = F(c), \qquad c(0) = c_0$$

We also consider in this chapter *open systems*, but the discussion will

be limited to simple open systems known in chemical engineering as a *continuous stirred tank reactor*. Figure 1 shows such a system in which mass is exchanged with the surroundings.

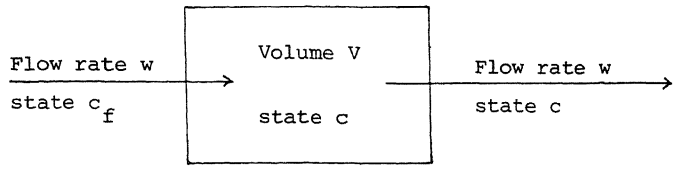


Figure 1

The volume V and the volumetric flow rate w of input and output streams are kept constant; $\theta = V/w$ is called the *holding time* of the reactor; c_f is the input or *feed state* variable and, as c, $c_f \in \mathbb{R}^n_+$. Its components are denoted by $c_{1f},\dots,c_{nf}$, that is

$$c_f = \begin{pmatrix} c_{1f} \\ \vdots \\ c_{nf} \end{pmatrix} . \tag{2.5}$$

The feed state may vary with time in which case we have a variable inflow.

The conservation equations for the chemical species can be written as

$$\frac{dc}{dt} = \frac{1}{\theta}(c_f - c) + F(c), \qquad c(0) = c_0 \tag{2.6}$$

For both closed and open systems we impose the following condition on the function F.

POSTULATE 2.2.

(i) The function $F: \mathbb{R}^n \to \mathbb{R}^n$ is continuous in $\mathbb{R}^n_+$.

(ii) For any $c_j = 0$, $F_j \geq 0$.

REMARK 2.3. On account of condition (i) a conclusion may be drawn concerning the existence of solutions of (2.4) and (2.6). According to a result of Peano, the existence on some interval $[0,t_1)$ can be proved. See HALE [2] for a proof based on a fixed point theorem of Schauder, which is not proved by Hale. Gavalas, also using this fixed point theorem, gives a proof based on degree theory for completely continuous operators; this theory will be

given in chapter VI. A more elementary proof of the existence of solutions can be found in CODDINGTON & LEVINSON [3]. See also remark 3.4. As for uniqueness of the solutions, which is expected on physical grounds, the conditions of postulate 2.2 are not sufficient. If, however, F is Lipschitzian in $\mathbb{R}^n_+$ the initial value problem has at most one solution.

REMARK 2.4. On physical grounds, all state variables have to be non-negative, that is, c has to be an element of $\mathbb{R}^n_+$. Condition (ii) of the postulate insures the non-negativity of the state variables for all $t \geq 0$, if the initial value is chosen in $\mathbb{R}^n_+$.

REMARK 2.5. Condition (ii) of the postulate can be written as $(F,n) \geq 0$ on $\partial\mathbb{R}^n_+$, where n is the inward normal on the boundaries of $\mathbb{R}^n_+$.

In chemical experiments, often there are more than one equivalent systems of reactions (1.1) capable of describing a given chemical change, each system having its own rates f_j. The rates F_i, however, are the same for all equivalent systems. The descriptions in terms of f and F are both useful. The quantities that can be directly measured during the experiment are, among others, the pressure, temperature, concentrations and the thermal and electrical conductivity. From such measurements it is possible to determine the number of independent reactions, but no distinction can be made among equivalent systems of reactions. The determination of the rates f and F from experimental data is a task both difficult and of limited accuracy. Summarizing, the construction of a mathematical or chemical model of chemical reactions falls apart into the choice of (1.1) and into the choice of the rates f_j.

3. CLOSED SYSTEMS

We consider the differential equation (2.4) and we suppose that F satisfies the conditions of postulate 2.2. As noted in remark 2.4, a trajectory starting in $\mathbb{R}^n_+$ will remain in this region at all subsequent times. In the following subsection it will be shown that trajectories remain in a bounded r-dimensional region of $\mathbb{R}^n_+$.

3.1. INVARIANT MANIFOLDS

From (2.4), (1.8), (2.2) and $(\nu\gamma)^T = \gamma^T\nu^T$ we derive

$$\gamma^T \frac{dc}{dt} = \gamma^T F(c) = \gamma^T \nu^T f(c) = 0 \tag{3.1}$$

and integration gives

$$\gamma^T c(t) = \text{constant}.$$

The constant can be expressed in the initial value c_0 of c, giving

$$\gamma^T c(t) = \gamma^T c_0, \tag{3.2}$$

or

$$\gamma^T (c(t)-c_0) = 0. \tag{3.3}$$

Hence, as follows from corollary 1.7, any solution of (2.4) with initial value c_0 satisfies

$$c(t) - c_0 \in \Lambda_0, \tag{3.4}$$

or

$$c(t) \in \Lambda(c_0), \tag{3.5}$$

where $\Lambda(c_0)$ is the r-dimensional linear manifold

$$\Lambda(c_0) = \{x \in \mathbb{R}^n \mid x = c_0 + y,\ y \in \Lambda_0\}, \tag{3.6}$$

which can also be denoted by

$$\Lambda(c_0) = c_0 + \Lambda_0, \tag{3.7}$$

where in the notation the dependence on c_0 is emphasized.

The linear manifold $\Lambda(c_0)$ in $\mathbb{R}^n$ extends to values outside the positive orthant $\mathbb{R}^n_+$. Since we are only interested in values of the state variables in $\mathbb{R}^n_+$, it is convenient to consider only the intersection of $\Lambda(c_0)$ with $\mathbb{R}^n_+$.

DEFINITION 3.1. The set

$$\Lambda^+(c_0) = \mathbb{R}^n_+ \cap \Lambda(c_0) \tag{3.8}$$

is called the *invariant manifold corresponding to the point* c_0.

REMARK 3.2. The invariant manifold $\Lambda^+(c_0)$ is constructed without knowledge of the right-hand side of (2.4), that is, without the reaction rates f_j.

In terms of the elements of γ_{ij} of the matrix γ, the elements c of $\Lambda(c_0)$ satisfy the relations

$$\sum_{j=1}^{n} \gamma_{jk}\, c_j(t) = \sum_{j=1}^{n} \gamma_{jk}\, c_{j0}, \quad k = 1,\ldots,n-r. \tag{3.9}$$

LEMMA 3.3. $\Lambda^+(c_0)$ *is closed, convex and bounded in* $\mathbb{R}^n_+$.

PROOF. The closedness follows from (1.12), (3.8) and (3.9). To show the convexity, let x and y be any two points of $\Lambda^+(c_0)$, then $c(s) = s\,x + (1-s)\,y \in \mathbb{R}^n_+$ and $\gamma^T c(s) = \gamma^T c_0$, $s \in [0,1]$. Hence $c(s) \in \Lambda^+(c_0)$. The boundedness follows from (1.9) and (3.9). Namely,

$$\sum_{k=1}^{r(\beta)} \sum_{j=1}^{n} \gamma_{jk}\, c_j(t) = \sum_{j=1}^{n} p_j\, c_j(t) = \sum_{j=1}^{n} p_j\, c_{j0}$$

and, since all p_j are positive, $c_j(t)$ must be bounded for all $t \geq 0$. □

Since a trajectory of equation (2.4) departing from c_0 lies entirely in $\Lambda^+(c_0)$, we can find c_{im}, $i = 1,\ldots,n$ such that for any t

$$0 \le c_i(t) \le c_{im}, \qquad i = 1,\ldots,n$$

or, if c_m is the vector with components c_{im},

$$|c(t)| \le |c_m|. \tag{3.10}$$

The vector c_m is independent of the reaction rates f_j and is obtained without knowledge of the solution of (2.4). Hence $|c_m|$ is an a priori bound for $|c(t)|$ and this bound depends only on the initial condition.

REMARK 3.4. With this a priori bound we can verify that a solution is defined for all $t \ge 0$, and not only, as noted in remark 2.3, on some interval $[0,t_1]$. See HALE [2,pp. 17-18].

3.2 EXTENTS OF REACTIONS

As we have seen in the foregoing subsection, the action takes place in an r-dimensional linear manifold $\Lambda(c_0)$ of $\mathbb{R}^n_+$. In the subspace Λ_0 we can use intrinsic coordinates $\{\xi_1,\ldots,\xi_r\}$ and, if $c \in \Lambda(c_0)$, c can be expressed in terms of c_0 and $\xi_1,\ldots,\xi_r$. A convenient way of doing this is using the matrix ν. Since $r(\nu) = 4$, we can associate with ν a linear mapping, which induces an isomorphism between $\Lambda(c_0)$ and its image $\tilde{\Lambda}$, the r-dimensional ξ-space. Let us take, if $c-c_0 \in \Lambda_0$,

$$c - c_0 = \nu^T \xi, \tag{3.11}$$

where

$$\xi = \begin{pmatrix} \xi_1 \\ \vdots \\ \xi_r \end{pmatrix} \tag{3.12}$$

is an element of $\mathbb{R}^r$. The connection between the c and the ξ vector is as follows. Since $c-c_0 \in \Lambda_0$, it can be written as $c-c_0 = \lambda_1\nu_1 + \ldots + \lambda_r\nu_r$, where ν_i are the row vectors of the matrix ν (see remark 1.6) and $\lambda_i \in \mathbb{R}$, $i = 1,\ldots,r$. From (3.11) it follows that $\lambda_i = \xi_i$, $i = 1,\ldots,r$.

REMARK 3.5. The variable ξ_j represents the contribution of the j-th reaction in the change from the state c_0 to the state c and is called the *extent of the j-th reaction*. The extents may be interpreted as degrees of freedom in

the thermodynamic sense.

The image of $\Lambda^+(c_0)$ under the mapping (3.11) will be denoted by $\tilde{\Lambda}(c_0)$. From its construction it is clear, that $\tilde{\Lambda}(c_0)$ is a simplex in $\mathbb{R}^r$, that is a line segment if r = 1, a triangle (including the plane region with its bounds) if r = 2; a three-dimensional simplex is a tetrahedron. The simplex $\tilde{\Lambda}(c_0)$ contains the origin. The elements ξ of $\tilde{\Lambda}(c_0)$ satisfy, since $c \in \mathbb{R}^n_+$,

$$c_{j0} + \sum_{i=1}^{n} \nu_{ij}\, \xi_i \geq 0, \qquad j = 1,\ldots,n. \tag{3.13}$$

EXAMPLE 3.6. The extents for the reactions in example 1.1 with

$$c_0 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \\ c_{40} \end{pmatrix}$$

are given by

$$\begin{aligned} c_1 &= \xi_2, \\ c_2 &= 2\xi_2, \\ c_3 &= 2\xi_1 - 2\xi_2, \\ c_4 - c_{40} &= -\xi_1. \end{aligned}$$

These equations can be solved uniquely for ξ in terms of c, provided $c-c_0 \in \Lambda_0$, where Λ_0 is given in (1.13). The simplex $\tilde{\Lambda}(c_0)$ in this example is determined by the inequalities $c_i \geq 0$, giving

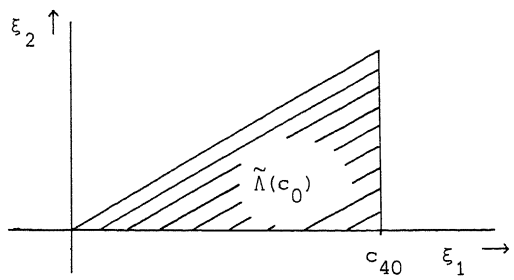


Figure 2

In terms of the extents ξ_j, the system (2.4) of equations reduces to a system of r equations (see 2.2) and (3.11))

$$\frac{d\xi}{dt} = \tilde{f}(\xi), \quad \xi(0) = 0, \tag{3.14}$$

where $\tilde{f}(\xi) = f(c)$, $c \in \Lambda^+(c_0)$ and $c = \nu^T\xi + c_0$. If $c \in \Lambda(c_0)$, (2.4) and (3.14) are equivalent.

REMARK 3.7. Condition (ii) of postulate 2.2 can be written as $(\tilde{f},n) \geq 0$ on $\partial\Lambda(c_0)$; see remark 2.5; n is the inward normal on $\partial\Lambda(c_0)$. The inner product and norm in $\mathbb{R}^r$ are as in $\mathbb{R}^n$.

3.3 EQUILIBRIUM POINTS

DEFINITION 3.8. A *kinetic equilibrium point* (or *equilibrium point* or *equilibrium state*) of a chemical system described by the differential equation (2.4) is a solution of the equation

$$F(c) = 0. \tag{3.15}$$

LEMMA 3.9. *Let* f *and* F *be related by* (2.2). *Then* f *and* F *have the same zeros.*

PROOF. Suppose $f(c) = 0$, than trivially $F(c) = 0$. Conversely, suppose $F(c) = 0$, than $\nu^T f(c) = 0$, hence $f_1 \nu_1 + \ldots . f_r \nu_r = 0$, where $\{\nu_1, \ldots, \nu_r\}$ are the linearly independent row vectors of ν. Hence $f_i = 0$, $i = 1,\ldots,r$, and thus $f(c) = 0$. □

REMARK 3.10. Let c be an equilibrium state in $\Lambda(c_0)$, then $\tilde{f}(\xi) = 0$, where c and ξ are related by (3.11). Conversely, $\tilde{f}(\xi) = 0$ implies $f(c) = 0$. The corresponding point ξ will also be called an equilibrium point.

Of course, we are interested in equilibrium states in $\Lambda^+(c_0)$, or equivalently, in the simplex $\tilde{\Lambda}(c_0)$. In order to prove that equilibrium points exist, we calculate the degree of $\tilde{f}$ with respect to the simplex $\tilde{\Lambda}(c_0)$. The interior of the closed simplex will be denoted by $\tilde{\Lambda}^\circ(c_0)$; that is,

$$\tilde{\Lambda}^\circ(c_0) = \tilde{\Lambda}(c_0) - \partial\tilde{\Lambda}(c_0).$$

THEOREM 3.11. *A chemical system with differential equation* (2.4) *has at least one equilibrium point in* $\Lambda(c_0)$.

PROOF. We will prove that if $F \neq 0$ on $\partial\Lambda^+(c_0)$, or equivalently, $\tilde{f} \neq 0$ on $\partial\tilde{\Lambda}(c_0)$, $\tilde{f}$ has at least one zero in $\tilde{\Lambda}^\circ(c_0)$. Let us suppose $F \neq 0$ on $\partial\Lambda^+(c_0)$. The function $\tilde{f}$ is continuous and $\tilde{\Lambda}^\circ(c_0)$ is bounded. According to definition II.2.15, $\deg(\tilde{f},\tilde{\Lambda}^\circ(c_0),0)$ is defined, and we will prove that the degree is not zero. Let us consider the function $(\xi,t) \to h_t(\xi)$ given by

$$h_t(\xi) = (1-t)\,\tilde{f}(\xi) - t\,g(\xi) \tag{3.16}$$

where $g(\xi) = \xi - \xi^*$ and $\xi^* \in \tilde{\Lambda}^\circ(c_0)$; $h_t(\xi)$ is continuous on $\tilde{\Lambda}(c_0) \times [0,1]$ and, in order to apply theorem II.3.4, we verify if it has zeros in $\partial\tilde{\Lambda}(c_0) \times [0,1]$. The values $t = 0$, $t = 1$ are easily verified, since $h_0 = \tilde{f}$ and $h_1 = -g$ are supposed to be nonzero on $\partial\tilde{\Lambda}(c_0)$. Suppose now $h_t(\xi) = 0$ on $\partial\tilde{\Lambda}(c_0) \times (0,1)$. Then we obtain from (3.16)

$$\tilde{f}(\xi) = \frac{t}{1-t}\,(\xi-\xi^*).$$

Left side multiplication by ν^T yields

$$F(c) = \frac{t}{1-t}\,(c-c_0-c^* + c_0) = \frac{t}{1-t}\,(c-c^*),$$

where c^* is defined by $\nu^T\xi^* = c^* - c_0$; c^* is an interior point of $\mathbb{R}^n_+$ and $c \in \partial\,\mathbb{R}^n_+$. Some component of c, say c_k is zero, giving

$$F_k = \frac{t}{1-t}\,(-c_k^*).$$

But $c_k^* > 0$, and hence we have a contradiction with postulate 2.2. From theorem II.3.4 we obtain $\deg(h_t,\tilde{\Lambda}^\circ(c_0),0) =$ constant for $t \in [0,1]$ and hence $\deg(h_0,\tilde{\Lambda}^\circ(c_0),0) = \deg(h_1,\tilde{\Lambda}^\circ(c_0),0)$ giving

$$\deg(\tilde{f},\tilde{\Lambda}^\circ(c_0),0) = \deg(-g,\tilde{\Lambda}^\circ(c_0),0).$$

The right-hand side is easily computed using theorem II.3.5. The result is

$$\deg(\tilde{f},\tilde{\Lambda}^\circ(c_0),0) = (-1)^r. \tag{3.17}$$

An immediate consequence is, (see theorem II.3.2(b)) that equation (3.15) has at least one zero in $\Lambda^+(c_0)$. □

Figure 3 shows schematically the homotopic vector fields $\tilde{f}$ and -g, $g(\xi) = \xi - \xi^*$ with $\xi^* = 0$, for the case of two chemical reactions.

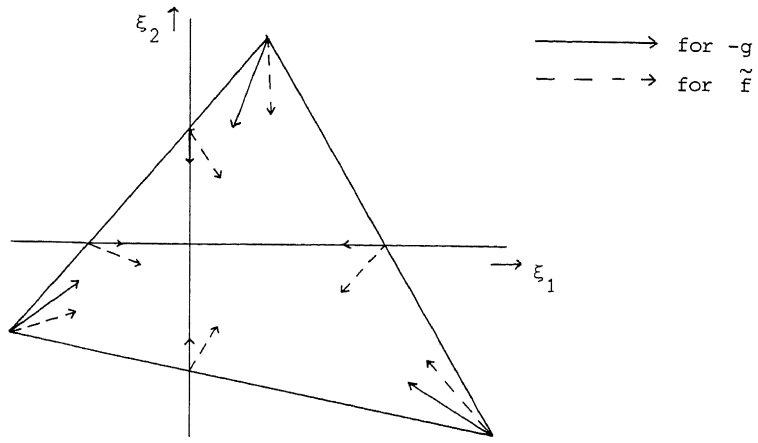


Figure 3

In the proof of theorem 3.11 $\deg(\tilde{f},\tilde{\Lambda}^\circ(c_0),0)$ is not computed if $\tilde{f}$ has zeros at $\partial\tilde{\Lambda}(c_0)$; in that case the degree is not defined. In order to obtain information about the zeros at $\partial\tilde{\Lambda}(c_0)$ we may attempt to compute the degree of $\tilde{f}$ with respect to a sufficiently large open ball B surrounding $\tilde{\Lambda}(c_0)$.

In calculating the degree of $\tilde{f}$ with respect to B, zeros of $\tilde{f}$ outside $\tilde{\Lambda}(c_0)$ must be considered as well. Such equilibrium points, however, do not have any physical significance, since all trajectories originating in $\tilde{\Lambda}(c_0)$ never leave this region, but these points do contribute to the degree of $\tilde{f}$. However, it is possible to extend the function $\tilde{f}$ outside $\tilde{\Lambda}(c_0)$ to a function $\tilde{\phi}$, such that

(i) $\tilde{\phi}(\xi) = f(\xi)$, $\xi \in \tilde{\Lambda}(c_0)$,

(ii) $\tilde{\phi}$ is continuous in $\bar{B}$,

(iii) $\tilde{\phi} \neq 0$ outside $\tilde{\Lambda}(c_0)$.

The differential equation

$$\frac{d\xi}{dt} = \tilde{\phi}(\xi), \quad \xi(0) = 0 \tag{3.18}$$

has the same solutions as (3.14) and the same equilibrium points in $\tilde{\Lambda}(c_0)$.

Before defining $\tilde{\phi}$, we introduce two auxiliary functions. The first one is the distance function $d: \mathbb{R}^r \to \mathbb{R}$ given by

$$d(\xi) = \inf\{|\xi-\xi^*| \mid \xi^* \in \tilde{\Lambda}(c_0)\},$$

the distance between ξ and the closed simplex $\tilde{\Lambda}(c_0)$. The second auxiliary function is $p: \mathbb{R}^r \to \mathbb{R}^r$, defined as the point of intersection of the line segment (ξ^*,ξ) with $\partial\tilde{\Lambda}(c_0)$, where $\xi^* \in \tilde{\Lambda}^\circ(c_0)$. In two dimensions the situation is as in figure 4.

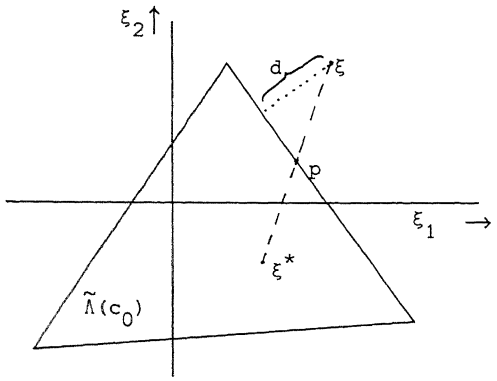


Figure 4

Let us now define $\tilde{\phi}$ as

$$\tilde{\phi}(\xi) = \begin{cases} \tilde{f}(\xi), & \text{if } \xi \in \tilde{\Lambda}(c_0), \\ \tilde{f}(p(\xi)) - d(\xi)(\xi-\xi^*), & \text{if } \xi \notin \tilde{\Lambda}(c_0). \end{cases} \tag{3.19}$$

From its definition it is clear that $\tilde{\phi}$ is continuous if $\tilde{f}$ is continuous. Suppose $\tilde{\phi}(\xi) = 0$ outside $\tilde{\Lambda}(c_0)$. Then $\tilde{f}(p(\xi)) = d(\xi)(\xi-\xi^*)$, or by multiplying

with ν^T, $F(p(c)) = d(\xi)(c-c^*)$, where $p(c)$ is the point in $\mathbb{R}^n$ corresponding to $p(\xi)$, and $c^*-c_0 = \nu^T\xi^*$. Since $p(\xi) \in \partial\tilde{\Lambda}(c_0)$, $p(c) \in \partial\mathbb{R}^n_+$; c^* is an interior point of $\Lambda(c_0)$. Moreover, since $\xi \notin \tilde{\Lambda}(c_0)$, $c \notin \mathbb{R}^n_+$, and hence, some component of c, say c_k, is negative, giving $F_k(p(c)) = d(c_k-c_k^*)$; since $c_k^* > 0$, $F_k(p(c)) < 0$, in contradiction with postulate 2.2. It follows that $\tilde{\phi}$ does not have any zeros outside $\tilde{\Lambda}(c_0)$. Hence $\deg(\tilde{\phi},B,0)$ is defined if $\tilde{\Lambda}(c_0)$ lies wholly in the ball B. As in the proof of theorem 3.11 we now can compute the degree which is left to the reader as an exercise. The result is given in the following theorem.

THEOREM 3.12. *Let F satisfy the conditions of postulate 2.2, let $\tilde{\phi}$ be an extension of $\tilde{f}$ as given in* (3.19), *and let $\Omega \subset \mathbb{R}^r$ be any open bounded set containing $\tilde{\Lambda}(c_0)$, then*

$$\deg(\tilde{\phi},\Omega,0) = (-1)^r.$$

The extension $\tilde{\phi}$ defined on the ξ-space $\mathbb{R}^r$ induces a function $\phi\colon \Lambda(c_0) \to \mathbb{R}^r$ by writing $\phi(c) = \tilde{\phi}(\xi)$, where c and ξ are related by $c-c_0 = \nu^T\xi$, $c \in \Lambda(c_0)$. The function ϕ is an extension of f outside $\Lambda^+(c_0)$, such that $\phi(c) \neq 0$ outside $\Lambda^+(c_0)$. The function $\Phi\colon \Lambda(c_0) \to \mathbb{R}^n$, given by $\Phi = \nu^T\phi$ is an extension of F. It should be noted that ϕ and Φ are defined only on $\Lambda(c_0)$.

REMARK 3.13. In general, the zeros of f are not isolated. To see this, we observe that f is a mapping $\mathbb{R}^n \to \mathbb{R}^r$ and $r < n$. Hence, generally, the equation $f(c) = 0$ defines a $(n-r)$-dimensional closed manifold $N(f) \subset \mathbb{R}^n$ of zeros of f. From theorem 3.11, it follows that $\Lambda^+(c_0)$ and $N(f)$ have at least one common point, whatever $c_0 \in \mathbb{R}^n$. Since c_0 may be arbitrarily close to 0, f is continuous and $N(f)$ is closed, 0 is an element of $N(f)$; that is, $f(0) = F(0) = 0$. Also $N(f)$ is unbounded.

3.4 THE NUMBER AND STABILITY OF EQUILIBRIUM POINTS

Theorem 3.11 gives the existence of at least one equilibrium point, but nothing is said about the exact number of such points. If we impose certain conditions on the rate functions f_j it is possible to prove that all trajectories in Λ^+ converge to a single equilibrium point. These conditions can be interpreted in a thermodynamical sense and are related to the consistency

between thermodynamics and kinetics. The entropy function of the closed system plays the role of a Lyapunov function by which the convergence of the trajectories can be proved. For details, the reader is referred to GAVALAS [1, §1.5].

In the general case, when the reaction rates are only restricted by postulate 2.2, each invariant manifold may include more than one equilibrium point and it is interesting to obtain information about the number and stability of these points.

In order to give qualitative information, however, we need the differentiability of the rate functions. So, apart from the conditions in postulate 2.2, we demand that

$$\tilde{f} \in C(\tilde{\Lambda}(c_0)) \cap C^1(\tilde{\Lambda}^\circ(c_0)). \tag{3.20}$$

In the discussion of stability, the Jacobian matrix of a mapping, introduced in section II.2.1, plays an important role. For convenience, we give the following definition and notation for this matrix and its determinant.

DEFINITION 3.14. Let Ω be an open bounded set in $\mathbb{R}^n$; let $f \in C^1(\Omega)$. Then the linear operator $f'(x)\colon \mathbb{R}^n \to \mathbb{R}^n$, called *the derivative of f at x*, is given by the Jacobian matrix

$$f'(x) = \begin{pmatrix} \frac{\partial f_1(x)}{\partial x_1} & \cdots & \frac{\partial f_1(x)}{\partial x_n} \\ \vdots & & \vdots \\ \frac{\partial f_n(x)}{\partial x_1} & \cdots & \frac{\partial f_n(x)}{\partial x_n} \end{pmatrix} \tag{3.21}$$

and $J_f(x) = \det(f'(x))$ is the Jacobian determinant.

3.4.1 THE NUMBER OF EQUILIBRIUM POINTS

We know from theorem 3.12 and theorem II.3.14 that, for the case that $\tilde{f}(\xi) = 0$ has only a finite number of solutions,

$$\deg(\tilde{f},\Omega,0) = (-1)^r = \sum_{\xi \in \tilde{f}^{-1}(0)} \operatorname{ind}(\tilde{f},\xi,0), \tag{3.22}$$

where Ω is any open bounded set containing $\tilde{\Lambda}(c_0)$. Moreover, if $J_{\tilde{f}}(\xi^*) \neq 0$ at an isolated zero $\xi^* \in \tilde{\Lambda}^\circ(c_0)$, then as follows from theorem II.3.13

$$\text{(3.23)} \qquad \operatorname{ind}(\tilde{f},\xi^*,0) = (-1)^\sigma$$

where σ is the sum of the algebraic multiplicities of the real negative eigenvalues of $\tilde{f}'(\xi^*)$. Suppose now that all equilibrium points are in $\tilde{\Lambda}^\circ(c_0)$.

LEMMA 3.15. *If the number of equilibrium points in $\tilde{\Lambda}^\circ(c_0)$ is finite, and if $J_{\tilde{f}}(\xi) \neq 0$ at each equilibrium point, then the number of equilibrium points is odd, 2m+1 say, among which m+1 have index $(-1)^r$ and the remaining m have index $(-1)^{r+1}$.*

PROOF. The index of each equilibrium point is +1 or -1, and the proof easily follows from (3.22). □

EXAMPLE 3.16. Consider a single reaction (r=1) in a closed system

$$M_1 - 2M_2 = 0.$$

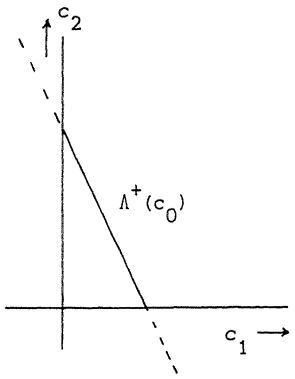
The ν-matrix is (1 -2) and suppose that the system is described by the differential equation

$$\frac{dc}{dt} = F(c), \quad c(0) = c_0,$$

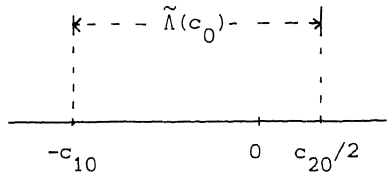
where $F(c) = \nu^T f(c) = \begin{pmatrix} f(c) \\ -2f(c) \end{pmatrix}$; $f: \mathbb{R}^2_+ \to \mathbb{R}$ is a given function such that F satisfies postulate 2.2. We introduce the extent ξ by writing $c-c_0 = \nu^T\xi$, hence

$$c_1-c_{10} = \xi, \quad c_2-c_{20} = -2\xi;$$

$\Lambda(c_0)$ is the line $2c_1 + c_2 = 2c_{10} + c_{20}$ and $\Lambda^+(c_0)$ is its intersection with $\mathbb{R}^2_+$. The simplex $\tilde{\Lambda}(c_0)$ is the segment $[-c_{10}, \frac{1}{2}c_{20}]$ on the ξ-axis and $\tilde{f}(\xi) = f(c_1,c_2) = f(\xi+c_{10}, -2\xi+c_{20})$. If $(F,n) \geq 0$ at $\partial\Lambda^+(c_0)$ (the points $(c_{10}+\frac{1}{2}c_{20},0)$ and $(0,2c_{10}+c_{20})$) then $\tilde{f}(-c_{10}) \geq 0$, $f(\frac{1}{2}c_{20}) \leq 0$. The following figures may be illustrative. Figure 5 gives the manifolds $\Lambda^+(c_0)$ and $\tilde{\Lambda}(c_0)$ in c-space and ξ-space. Figure 6 gives two possible functions $\tilde{f}$, which indeed are homotopic with $g(\xi) = -\xi$. Also the indices (+1) and(-1) of the equilibrium points are shown.

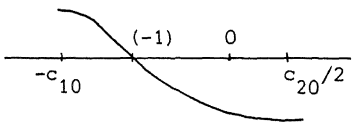


c-space



ξ-space

Figure 5



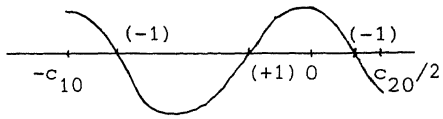


Figure 6

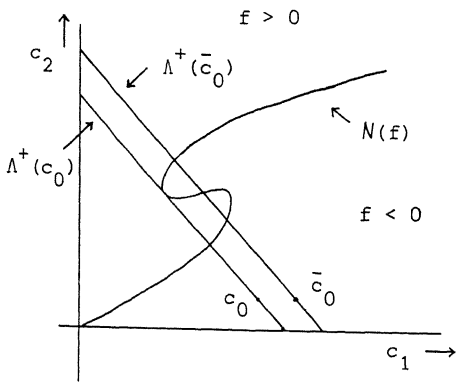
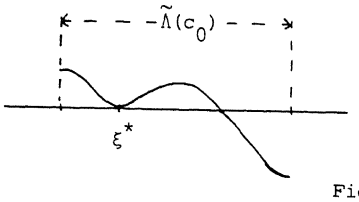


Figure 7



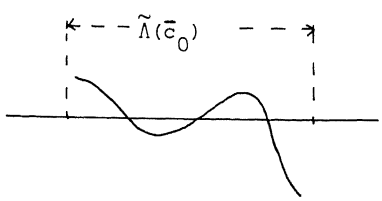


Figure 8

The vanishing of $J_{\tilde{f}}(\xi)$ at the equilibrium points may be illustrated by the set $N(f)$, introduced in remark 3.13. Figure 7 shows a situation where $J_{\tilde{f}}(\xi)$ will vanish at an equilibrium point in $\tilde{\Lambda}(c_0)$, while in $\tilde{\Lambda}(\bar{c}_0)$ this will not be the case.

The corresponding pictures in the ξ-space are shown in figure 8. It follows that, locally, the number of equilibrium points is 0, 1 or 2, according as the position of $\bar{c}_0$ with respect to $\Lambda(c_0)$. Generally, quite different situations may occur. In fact, in chapter IV an example will be given where the number of equilibrium points changes (locally) from 1 to 3.

3.4.2. THE STABILITY OF EQUILIBRIUM POINTS

We first give a definition of stability of an equilibrium point of a general differential equation

$$\frac{dx}{dt} = F(x) \qquad x \in \mathbb{R}^n,\ F: \mathbb{R}^n \to \mathbb{R}^n, \tag{3.24}$$

and we suppose that x^* is an equilibrium point, that is, $F(x^*) = 0$.

DEFINITION 3.17. The solution x^* is called *stable* if for any $\varepsilon > 0$ there exists a $\delta > 0$, such that any solution $x(t)$ of (3.24) with $x(0) = x_0$ satisfying $|x_0 - x^*| < \delta$, satisfies $|x(t) - x^*| < \varepsilon$, $t \geq 0$. The equilibrium point is said to be *asymptotically stable* if, in addition to being stable $|x(t) - x^*| \to 0$ as $t \to \infty$.

According to the Poincaré–Lyapunov theorem, the stability of an equilibrium point of (3.24) can be discussed by considering the eigenvalues of the Jacobian matrix $F'(x)$, defined in definition 3.14, at the equilibrium points. A sufficient condition for the stability (even asymptotic stability) of x^* is that all eigenvalues of $F'(x^*)$ have negative real parts. Conversely, if $F'(x^*)$ has one or more eigenvalues with positive real parts, the equilibrium point x^* is unstable. Finally, when $F'(x^*)$ has eigenvalues with zero real parts, no definitive statement about stability can be made without further information on $F(x)$.

Now suppose c^* is a kinetic equilibrium point of (2.4). This point defines a linear manifold $\Lambda(c^*)$, $c^* \in \Lambda(c^*)$. The image of $\Lambda^+(c^*)$ under the transformation of $c-c^* = \nu^T\xi$, with $c \in \Lambda^+(c^*)$, is a simplex $\tilde{\Lambda}(c^*)$ in the ξ-space. The point $\xi = 0$ corresponds to $c = c^*$; $\tilde{f}(0) = 0$, and hence $\xi = 0$ is an equilibrium point of (3.14). Suppose that the eigenvalues of $\tilde{f}'(0)$ have negative real parts. Then, according to Poincaré-Lyapunov, $\xi = 0$ is asymptotically stable. That is, given $\varepsilon > 0$, there exists a $\delta > 0$, such that $|\xi_0| < \delta$, $\xi_0 \in \tilde{\Lambda}(c^*)$, implies that a solution of (3.14), with $\xi(0) = \xi_0$ satisfies $|\xi(t)| < \varepsilon (t \geq 0)$ and moreover $\xi(t) \to 0$ as $t \to \infty$. The point ξ_0 corresponds to a point $c_0 \in \Lambda(c^*)$; c_0 is given by $c_0 - c^* = \nu^T\xi_0$. Hence, in $\Lambda(c^*)$, if $|c_0 - c^*|$ is small, then $c(t) \to c^*$, as $t \to \infty$, if $c(t)$ is a solution of (2.4) with $c(0) = c_0$.

The question arises: is c^* in the c-space asymptotically stable? The answer is negative. Take for instance an initial value $c_0 \notin \Lambda(c^*)$. Then the closed manifolds $\Lambda^+(c^*)$ and $\Lambda^+(c_0)$ have empty intersection. But $c(t) \in \Lambda^+(c_0)$ for all $t \geq 0$, and hence

$$\lim_{t\to\infty} c(t) \neq c^*. \tag{3.25}$$

So, c^* is not asymptotically stable. (It is not possible to describe this situation in the ξ-space, since, if $c_0 \notin \Lambda^+(c^*)$, there is no corresponding initial value $\xi_0 \in \tilde{\Lambda}(c^*)$.)

From (3.25) it follows that $c(t)$ does not converge to c^*. But c^* is still stable, as will be proved in theorem 3.18.

Here arises another question. If c_0 is close to c^*, $c_0 \notin \Lambda(c^*)$, does the function $c(t)$ converge to a point $c_0^* \in \Lambda(c_0)$ close to c^* and is the corresponding point $\xi_0^* \in \tilde{\Lambda}(c_0)$, $c_0^* - c_0 = \nu^T\xi_0^*$, asymptotically stable? If the answer is affirmative, as indeed it is, then for the purpose of stability analysis there is no loss of generality in considering perturbations lying in the linear manifold of the equilibrium state, i.e., $c_0 \in \Lambda(c^*)$, or, equivalently, to discuss stability in the ξ-space.

THEOREM 3.18. *Let $c^* \in \Lambda^+(c^*)$ be an equilibrium point of (2.4) and let $\xi = 0$ be the corresponding equilibrium point of (3.14), where $c-c^* = \nu^T\xi(c,c^*)$. Let the real parts of the eigenvalues of $\tilde{f}'(0)$ be negative. Then the point c^* is a stable equilibrium point. Moreover it can be shown that if $|c^*-c_0|$ is small enough, then there exists a point $c_0^* \in \Lambda^+(c_0)$, such that $c(t) \to c_0^*$, where $c(t)$ is a solution of (2.4) with $c(0) = c_0$, and*

$|c^*-c_0^*| \to 0$. *The point* $\xi_0^* \in \tilde{\Lambda}(c_0)$, *where* c *and* ξ *are now related by* $c-c_0 = \nu^T\xi(c,c_0)$, $c \in \Lambda(c_0)$ *and* $c_0^*-c_0 = \nu^T\xi_0^*$, *is an asymptotically stable equilibrium point of* (3.14).

PROOF. Consider the equation $\tilde{f}(\xi(c,c^*)) = 0$. It has a solution $\xi = \xi(c^*,c^*) = 0$. The function $\tilde{f}$ can be considered as a function depending on ξ and on c^*. Let us make this clear by writing $\tilde{f}(\xi(c,c^*)) = \tilde{\phi}(\xi,c^*)$, where $\tilde{\phi}$: $\mathbb{R}^r \times \mathbb{R}^n \to \mathbb{R}^r$. The equation $\tilde{\phi}(\xi,c) = 0$ has a solution at $\xi = 0$, $c = c^*$. Moreover, the Jacobian matrix $\partial\tilde{\phi}(\xi,c)/\partial\xi$ of $\tilde{\phi}$ with respect to ξ satisfies $\det(\partial\tilde{\phi}(\xi,c^*)/\partial\varepsilon) \neq 0$ at $\xi = 0$. According to the implicit function theorem, for which the reader is referred to HALE [2,p.8], there exist neighbourhoods U and V of 0 and c^* in $\mathbb{R}^r$ and $\mathbb{R}^n$, respectively, such that for each fixed c in V the equation $\phi(\xi,c) = 0$ has a unique solution ξ in U. Furthermore, this solution can be given as $\xi = g(c)$, where g is continuous and $g(c^*) = 0$.

In $\mathbb{R}^n$ we choose an open ball $B_\delta(c^*) = \{c \in \mathbb{R}^n \mid |c-c^*| < \delta\}$. There exists a $\delta_1 > 0$ such that $\delta < \delta_1$ implies $B_\delta(c^*) \subset V$. Suppose now, $\delta < \delta_1$ and $c_0 \in B_\delta(c^*)$. There is a unique $\xi_0 = g(c_0)$ such that $\tilde{f}(\xi_0) = 0$. Since g is continuous and $g(c^*) = 0$, the smallness of $|c_0-c^*|$ implies the smallness of $|\xi_0|$, or, as needed in the future, that of $|\nu^T\xi_0|$. That is to say, given any $\varepsilon > 0$ we can find $\delta_2 > 0$ such that $\delta < \delta_2$ implies

$$|\nu^T\xi_0| < \varepsilon/3. \tag{3.26}$$

Define $c_0^* \in \Lambda^+(c_0)$ as

$$c_0^* = c_0 + \nu^T\xi_0, \tag{3.27}$$

giving an equilibrium point $c_0^* \in \Lambda^+(c_0)$ for (2.4).

Furthermore, we can find $\delta_3 > 0$ such that $\delta < \delta_3$ implies that for all $c \in B_\delta(c^*)$ the real parts of the eigenvalues of $\partial\tilde{\phi}(\xi,c)/\partial\xi$ evaluated at $\xi = g(c)$ are negative. This can be achieved since the eigenvalues depend continuously on c. Hence, if $\delta < \min(\delta_1,\delta_2,\delta_3)$, ξ_0 is asymptotically stable, and the point ξ_0^* mentioned in the theorem is ξ_0. Moreover, $|c^*-c_0^*| = |c^*-c_0 + c_0 - c_0^*| = |c^*-c_0 - \nu^T\xi_0| \to 0$ if $|c^*-c_0| \to 0$.

Let us now prove the stability of c^*. Since ξ_0 is asymptotically stable, we can find $\delta_4 > 0$ such that, for any initial value $\eta_0 \in \tilde{\Lambda}(c_0)$, $|\eta_0-\xi_0| < \delta_4$

implies $\xi(t) \to \xi_0$, where $\xi(t)$ is a solution of (3.14) with $\xi(0) = \eta_0$. So, with $\varepsilon > 0$ introduced earlier, we can choose δ_4 such that $|\eta_0-\xi_0| < \delta_4$ implies

$$|\nu^T(\xi(t) - \xi_0)| < \varepsilon/3. \tag{3.28}$$

Define $\Gamma = \{c \in \Lambda^+(c_0) \mid c = c_0 + \nu^T\xi, |\xi-\xi_0| < \delta_4\}$.
Any solution with initial value $c_0 \in \Gamma$ satisfies $c(t) \to c_0^*$ as $t \to \infty$.
Take $c_0 \in \Gamma \cap B_\delta(c^*)$ with $\delta < \min(\delta_1,\delta_2,\delta_3,\delta_4,\varepsilon/3)$. Observe that
$|c(t) - c^*| = |c(t) - c_0^* + c_0^* - c_0 + c_0 - c^*| \le |c(t) - c_0^*| + |c_0^*-c_0|$
$+ |c_0-c^*|$. By using (3.26), (3.28), $c(t) - c_0^* = \nu^T(\xi-\xi_0)$ and $c_0^*-c_0 = \nu^T\xi_0$, we obtain $|c(t) - c^*| < \varepsilon$, $t \ge 0$, which proves the stability of c^*. □

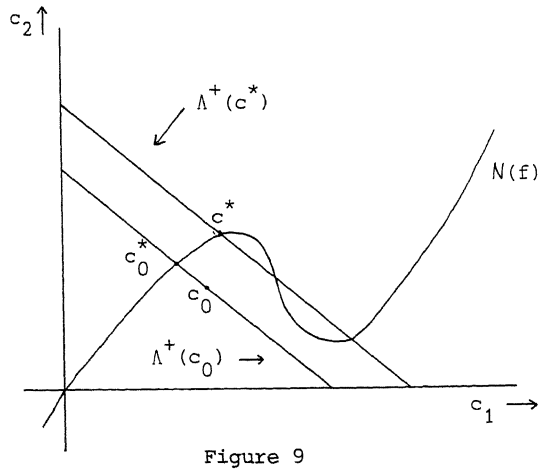


Figure 9

In figure 9 the situation is described for the case of one chemical reaction.

To obtain the relationship between the index and the stability in $\tilde{\Lambda}(c_0)$ of an equilibrium point ξ^* of the system (3.14), let us consider first an odd number r of chemical reactions. Then $\tilde{f}'(\xi^*)$ has an odd number of real eigenvalues. An index +1 implies, according to lemma 3.15, an even number of eigenvalues in $(-\infty,0)$ and hence an odd number of eigenvalues in $(0,\infty)$, so that the equilibrium state ξ^* is unstable. An index -1 implies an even number of positive eigenvalues. If $r = 1$, ξ^* is stable but if $r = 3,5,\ldots$ no conclusion about stability can be made. In any case, if the number of equilibrium points is $2m+1$, at least m of them are unstable.

When r is even, $\tilde{f}'(\xi^*)$ has an even number of eigenvalues. An index -1 implies an odd number of eigenvalues in $(-\infty,0)$ and an odd number in $(0,\infty)$, hence the equilibrium state ξ^* is unstable. An index +1 does not allow a conclusion about stability. Again, at least m among the 2m+1 states are unstable. We have proved the following theorem

THEOREM 3.19. *An equilibrium state of* (3.14) *such that* $J_{\tilde{f}}(\xi^*) \neq 0$, *is unstable if its index satisfies* $\operatorname{ind}(\tilde{f},\xi^*,0)\times(-1)^r < 0$. *If* $J_{\tilde{f}}(\xi^*) \neq 0$ *for all the equilibrium states of a given manifold* $\tilde{\Lambda}$, *the number of these points is odd,* 2m+1, *among which* m *at least are unstable.*

COROLLARY 3.20. *In the case of one chemical reaction,* r = 1, *m of the states are unstable and the remaining* m+1 *are stable. Thus for* r = 1, m = 0 *the unique equilibrium point is always stable. In figure* 6 *the cases* r = 1, m = 0 *and* r = 1, m = 1 *are drawn, respectively. An equilibrium point with index* -1 *is stable.*

4. OPEN SYSTEMS

As in section 3 we can use the matrix γ and we obtain in this case from (2.6)

$$(4.1)\qquad \begin{cases} \dfrac{da}{dt} + \dfrac{1}{\theta}\, a = \dfrac{1}{\theta}\, a_f \\ a(0) = a_0, \end{cases}$$

where $a = \gamma^T c$, $a_f = \gamma^T c_f$, $a_0 = \gamma^T c_0$ and the a-vectors are elements of $\mathbb{R}^{n-r}$.

Equation (4.1) gives on integration

$$(4.2)\qquad a(t) = e^{-t/\theta} a_0 + \theta^{-1} \int_0^t e^{-(t-\tau)/\theta} a_f(\tau)\, d\tau.$$

Hence we now have

$$(4.3)\qquad \gamma^T c(t) = a(t),$$

defining an integral manifold depending on t in contrast with closed systems, where the corresponding right-hand side of (4.3), see (3.2), is a constant. Again (4.3) defines a linear manifold $\Lambda^+(c_0, c_f, t)$. Considering bounded inputs $|a_f(t)| \le a_M$, $t \ge 0$, we obtain

$$|a| \le |a_0| + a_M.$$

Hence $|\gamma^T c(t)|$ is bounded and using the same argumentation as in section 3 we can prove that $\Lambda^+(c_0, c_f, t)$ is bounded for all t. From this it follows that the concentrations are subjected to a priori bounds and hence, if F in (2.6) satisfies the conditions of postulate 2.2, the existence of solutions can be proved.

4.1. STEADY STATES

From now on we suppose that the feed state c_f is a constant, which implies that (4.2) becomes

$$a(t) = e^{-t/\theta} a_0 + (1 - e^{-t/\theta})\, a_f,$$

or

$$\gamma^T c(t) = \gamma^T\{e^{-t/\theta}c_0 + (1-e^{-t/\theta})c_f\}. \tag{4.4}$$

Hence the effect of the initial condition c_0 quickly disappears and the state of the system is eventually determined by the input variables c_f alone. More precisely, as $t \to \infty$ the state trajectories rapidly approach the r-dimensional linear manifold $\Lambda^+(c_f)$. These trajectories lie outside $\Lambda^+(c_0)$, except when $a_0 = a_f$, or $\gamma^T c_0 = \gamma^T c_f$, that is, when $c_0 \in \Lambda^+(c_f)$.

DEFINITION 4.1. A *steady state* is the solution of the time independent equation

$$c - c_f = \theta F(c). \tag{4.5}$$

In the ξ-space the steady states follow from

$$\xi = \theta\tilde{f}(\xi), \tag{4.6}$$

where the extents ξ are defined by (cf. 3.11)

$$c - c_f = \nu^T\xi, \qquad c \in \Lambda(c_f). \tag{4.7}$$

THEOREM 4.2. *If* F *satisfies the conditions of postulate* 2.2, *then the chemical system with differential equation* (2.6) *has one or more steady states in* $\Lambda^+(c_f)$.

PROOF. Let us write

$$g(\xi) = \xi - \theta\tilde{f}(\xi), \qquad h(\xi) = \xi - \xi_0, \tag{4.8}$$

where $\xi_0 \in \tilde{\Lambda}^\circ(c_f)$, and consider the mapping $(\xi,t) \to H_t(\xi)$ given by

$$H_t(\xi) = tg(\xi) + (1-t)h(\xi).$$

Proceeding as in theorem 3.11 we obtain, if $g \neq 0$ on $\partial\tilde{\Lambda}(c_f)$,

$$\deg(g,\tilde{\Lambda}^\circ(c_f),0) = \deg(h,\tilde{\Lambda}^\circ(c_f),0) = 1.$$

This proves the theorem. □

REMARK 4.3. As in section 3, we can extend the function $\tilde{f}$, or g, in such a way that the extension does not vanish outside $\tilde{\Lambda}(c_f)$. For any open bounded set $\Omega \supset \tilde{\Lambda}(c_f)$ we have $\deg(g,\Omega,0) = 1$, where g and its extension are denoted by the same symbol.

4.2. UNIQUENESS AND STABILITY OF STEADY STATES

The following lemma is the analogue of lemma 3.15; g is given by (4.8).

LEMMA 4.4. *If the number of steady states in $\tilde{\Lambda}^\circ(c_f)$ is finite, and if $J_g(\xi_s) \neq 0$ for all steady states $\xi_s \in \tilde{\Lambda}^\circ(c_f)$ and $g \neq 0$ on $\partial\tilde{\Lambda}(c_f)$ then the number of the steady states is odd, $2m + 1$ say, with m having index -1 and $m + 1$ having index $+1$. The index of the steady state ξ_s is equal to $(-1)^\sigma$, where σ is the sum of the algebraic multiplicities of the real eigenvalues of $f'(\xi_s)$ in the interval $(1/\theta,\infty)$.*

PROOF. Remark that the eigenvalues of $f'(\xi)$, say λ_i, and the eigenvalues of $\frac{1}{\theta} I_r - \tilde{f}'(\xi)$, say μ_i, satisfy $\mu_i = \lambda_i - \frac{1}{\theta}$. □

If θ is small, it may be expected that for each steady state ξ_s none of the real eigenvalues of $\tilde{f}'(\xi)$ are situated in $(1/\theta,\infty)$. In that case, the index of each point ξ_s, that is, $\mathrm{ind}(\mathrm{id}-\theta\tilde{f},\xi_s,0)$, is $+1$ from which follows that we have only one steady state. In order to prove this, we construct an upper bound for the real eigenvalues of $\tilde{f}'(\xi)$ which does not depend on σ. It is supposed that $\tilde{f} \in C^1(\tilde{\Lambda}(c_f))$.

First we introduce the real functional $B: \tilde{\Lambda}(c_f) \times \mathbb{R}^r \to \mathbb{R}$, defined by

$$B(\xi,\rho) = \rho^T \tilde{f}'(\xi)\rho \tag{4.9}$$

where $\xi \in \tilde{\Lambda}(c_f)$ and $\rho \in \mathbb{R}^r$. B can be written as

$$B(\xi,\rho) = \sum_{i,j=1}^{r} \frac{\partial \tilde{f}_i(\xi)}{\partial \xi_j} \rho_i \rho_j, \qquad \rho = \begin{pmatrix} \rho_1 \\ \vdots \\ \rho_r \end{pmatrix}.$$

Furthermore we write

$$b(\xi) = \max_{|\rho|=1} B(\xi,\rho), \qquad b_m = \max_{\xi \in \tilde{\Lambda}(c_f)} b(\xi). \tag{4.10}$$

Suppose λ is a real eigenvalue of $\tilde{f}'(\xi_s)$ for some steady state ξ_s, and ρ_λ the corresponding eigenvector normed as $|\rho_\lambda| = 1$. Then

$$\lambda = B(\xi_s,\rho_\lambda) \leq b(\xi_s) \leq b_m.$$

Hence, if $\theta b_m < 1$, then $\lambda < 1/\theta$, giving an explicit bound of θ such that all real eigenvalues of $\tilde{f}'(\xi)$ are outside $(1/\theta,\infty)$. As a consequence, the index of any steady state is +1 if $\theta b_m < 1$. So we have proved the following theorem.

THEOREM 4.5. *Let* b_m *be defined as in* (4.9) *and* (4.10). *If* $\theta b_m < 1$, *then there is one and only one steady state* $\xi_s \in \tilde{\Lambda}(c_f)$.

For large θ we can also give information on the uniqueness of a steady state. Let us recall that an equilibrium point is a solution of $\tilde{f}(\xi) = 0$ and a steady state is a solution of (4.6) and depends on θ and c_f. The vector c_f defines a linear manifold $\Lambda(c_f) \subset \mathbb{R}^n$ and, if c and ξ are related by (4.7), each simplex $\tilde{\Lambda}(c_f)$ contains at least one equilibrium point (theorem 3.11) and at least one steady state (theorem 4.2). With these preliminaries we are ready to prove the following theorem.

THEOREM 4.6. *Let* $\xi_0 \in \tilde{\Lambda}(c_f)$ *be a unique equilibrium point and suppose that the eigenvalues of* $\tilde{f}'(\xi_0)$ *have negative real parts. Then there exists* $\theta^* > 0$, *such that* $\theta > \theta^*$ *implies that* $\tilde{\Lambda}(c_f)$ *contains a unique steady state* ξ_s *and the eigenvalues of* $\tilde{f}'(\xi_s)$ *have negative real parts.*

PROOF. If we set

$$\xi_m = \max_{\xi\in\tilde{\Lambda}(c_f)} |\xi|$$

then

$$|\tilde{f}(\xi_s)| \leq \xi_m/\theta$$

for any solution $\xi_s \in \tilde{\Lambda}(c_f)$ of (4.6). But $\tilde{f}(\xi_0) = 0$, and ξ_0 is the only equilibrium point in the closed manifold $\tilde{\Lambda}(c_f)$. So, $|\xi_s-\xi_0|$ is small if θ is large. That is, for any $\varepsilon > 0$, there exists θ^* such that $\theta > \theta^*$ implies $|\xi_s-\xi_0| < \varepsilon$. But if ε is small enough, the eigenvalues of $\tilde{f}'(\xi_s)$

have negative real parts. In that case, $\mathrm{ind}(g,\xi_s,0) = 1$, and hence ξ_s is unique. □

In open systems it is natural to consider perturbations in the initial state and the feed state, which suggests the following definition of stability.

DEFINITION 4.7. A steady state $c_s \in \Lambda(c_f)$ will be called stable if given any $\varepsilon > 0$ there exists a $\delta > 0$ such that $|c_0-c_s| < \delta$, $|c_f'-c_f| < \delta$ imply that the solution $c(t)$ of the equation

$$(4.11) \qquad \frac{dc}{dt} = \frac{1}{\theta}(c_f'-c) + F(c), \qquad c(0) = c_0$$

satisfies $|c(t)-c_s| < \varepsilon, \quad t \geq 0.$

In fugure 10 the situation is illustrated for one chemical reaction (r=1). Since the solution is attracted by $\Lambda(c_f')$, if $c_f' \notin \Lambda(c_f)$ the solution will never reach the point c_s.

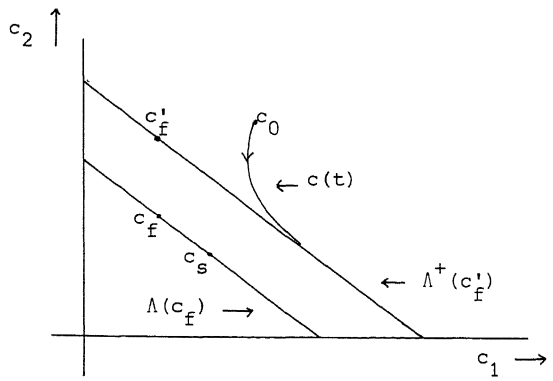


Figure 10

Under the condition of theorems 4.5 and 4.6, for small θ and for large θ, the steady state is unique. As in theorem 3.18 it can be proved that in these cases c_f is stable. Multiple steady states and instabilities are possible when the flow rate (corresponding to c_f) and the reaction rate (corresponding to F) balance each other. If either of the two rates predominates the steady state is unique and stable.

As in the previous section it can be shown that the stability of the steady state $c_s \in \Lambda(c_f)$ (under the perturbations c_0, c_f') is equivalent to the stability of the steady state $c_s' \in \Lambda(c_f')$ under the perturbation c_0, which again is equivalent to the asymptotic stability of c_s' under perturbation $c_0 \in \Lambda(c_f'))$.

REMARK 4.8. It should be emphasized that, if $c_0 \in \Lambda^+(c_f')$, corresponding to c_0 there is no point in $\tilde{\Lambda}(c_f)$ under the transformation $c - c_f' = \nu^T\xi$, $c \in \Lambda(c_f')$. Therefore, it is not possible to give a differential equation in terms of ξ in the simples $\tilde{\Lambda}(c_f')$ analogous with (3.14).

Using lemma 4.4 and the Poincaré-Lyapunov theorem we can prove the following theorem, the analogue of theorem 3.19.

THEOREM 4.9. *Under the conditions of lemma* 4.4, *at least* m *of the* 2m + 1 *steady states of a given manifold are unstable.*

EXAMPLE 4.10. Consider example 3.16. The simplex $\Lambda(c_f)$ is obtained by replacing c_0 by c_f. The steady state equation is $\xi = \theta\tilde{f}(\xi)$. An appropriate choice of f(c) gives the following picture.

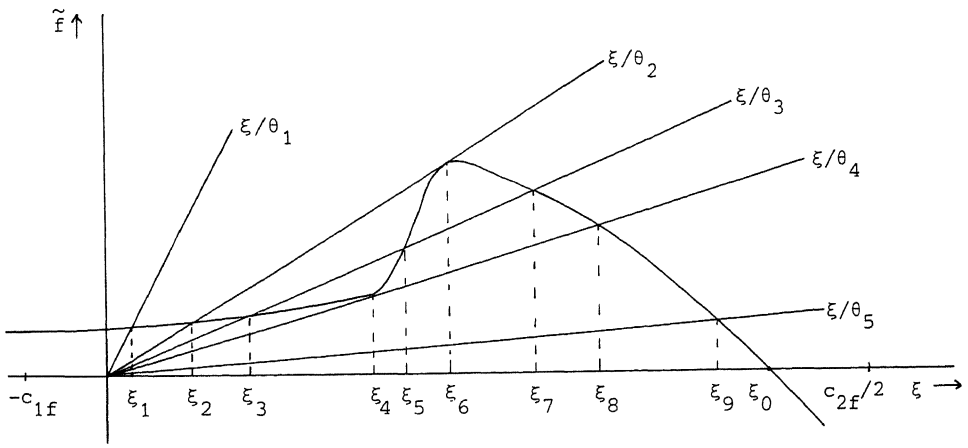


Figure 11

When θ is smaller than θ_2 or larger than θ_4 the steady state (e.g. ξ_1, ξ_9) is unique and stable. When $\theta = \theta_4$, or $\theta = \theta_2$, $d\tilde{f}/d\xi = 1/\theta$ and the index of the points ξ_4, ξ_6 is zero. For values of θ between θ_2, θ_4 there are three steady states. Steady states, such as ξ_5 have index -1, as $d\tilde{f}/d\xi > 1/\theta$, and are unstable. Steady states such as ξ_3 and ξ_9 have index +1, as $d\tilde{f}/d\xi < 1/\theta$, and are stable.

Figure 12 shows the curve of steady states in the ξ - θ plane. From this curve the regions of stability and instability are easily determined. A point on the curve is stable if $d\xi/d\theta > 0$.

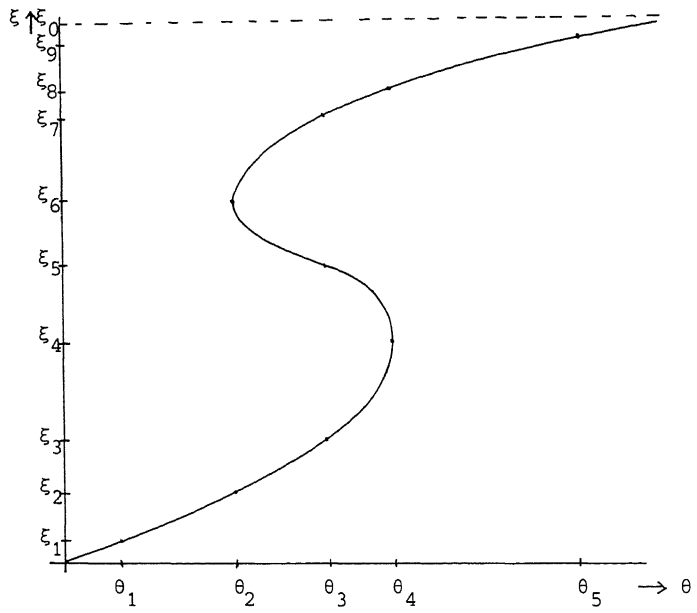


Figure 12

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