match no. 5 pp. 3 - 70 1979

ORDINARY DIFFERENTIAL EQUATIONS OF CHEMISTRY

Helmut Knolle

(received: November 1978)

Preface

This paper contains a very short introduction to the theory of ordinary differential equations and an exposition of some special subjects of the mathematical theory of chemical kinetics. Though a section on existence and uniqueness has been included (in a form adapted to the needs of chemistry), our principal aim is to train the chemist in handling differential equations that are frequently met with in chemistry. Therefore we have omitted many subjects (e.g. Bernoulli's equation, Riccati's equation, etc.), that are commonly treated in elementary courses on differential equations. On the other side we have discussed some topics in greater detail than usually.

Of course, the present treatise is not complete. To get bibliographical information on the subject is difficult, because articles from journals of chemistry have not been included in "Mathematical Reviews" (the review journal "Zentralblatt der Mathematik" has not been at our disposal). As a guide we used the bibliographies of [5] (43 titles) and [12] (111 titles).

The symbols $\forall$ (for all), $\exists$ (there exists), $\in$ (element of) and $\subset$ (subset of) are frequently used.

Contents

Acknowledgement

This work has been supported by the Faculty of Sciences of the Universidad Nacional de Colombia, Bogotá.

ORDINARY DIFFERENTIAL EQUATIONS OF CHEMISTRY

1. General Remarks.

A differential equation DE is an equation that relates some derivatives of an unknown function to each other and to this function itself. An ordinary differential equation is a DE, where the unknown function depends on one variable only. We call this variable the independent variable and the unknown function the dependent variable. If the unknown function depends on several independent variables and the equation involves partial derivatives, then we have a partial differential equation. A chemically reacting system without space variations can be described by a set of ordinary DE with time t as independent variable.

The order of a DE is the order of the highest derivative occurring in it. Thus the equation

$$x' = f(t,x) \qquad (' = \frac{d}{dt})$$

is of the first order. In chemistry we are usually concerned with systems of DE of the first order such as

$$\begin{aligned} x_1' &= f_1(t, x_1, x_2, \ldots, x_n) \\ x_2' &= f_2(t, x_1, x_2, \ldots, x_n) \\ &\vdots \\ x_n' &= f_n(t, x_1, x_2, \ldots, x_n) \end{aligned} \tag{1.1}$$

Here n unknown functions of the independent variable t are to be determined. We may introduce the vector $X = (x_1, \ldots x_n)$, $X' = (x_1', \ldots, x_n')$, $F = (f_1, \ldots, f_n)$. Then the system 1.1 can be written as one single vector differential equation

$$X' = F(t,X) \qquad (1.1')$$

A differentiable vector valued function X defined on an t-interval I is called a solution of 1.1', if $X'(t) = F(t,X(t)) \; \forall \; t \in I$. The problem to find a solution of 1.1' that satisfies $X(t_o) = X_o$,, where $t_o \in I$, is known as the initial value problem. Often t_o is the left endpoint of I, but it may also be an interior point or the right endpoint. In order that a DE be suited to describe a deterministic process, the initial value problem should have a unique solution. Therefore we'll give in sec. 2 existence and uniqueness theorems for the initial value problem.

In DE of chemical reactions the x_i mean concentrations and sometimes a component x_{n+1} is included, that means temperature or some other thermodynamic variable. These quantities are always nonnegative. A vector X is called nonnegative, $X \geq O$, if all its components are nonnegative. In order that 1.1' describe a set of chemical reactions, it must have the property, that every solution with nonnegative initial vector remains nonnegative for all time.

We consider a single chemical reaction between n species $A_1,\ldots,A_n$, whose concentrations in a homogeneous mixture of temperature T are $c_1,\ldots,c_n$, and suppose that $c_1' = \frac{dc_1}{dt} = h(c_1,\ldots,c_n,T)$. It was one of the early discoveries of chemistry that $\frac{c_i'}{c_1'} = n_i = \text{const.}$ $(i = 2,\ldots,n)$. Therefore $c_i' = n_i h(c_1,\ldots,c_n,T)$ for $i=2,\ldots,n$. The atomic hypothesis implies that n integers $\nu_1,\ldots,\nu_n$ can be chosen such that

$$c_i' = \nu_i g(c_1,\ldots,c_n,T) \qquad i = 1,\ldots,n \tag{1.2}$$

where $g = \nu_1^{-1} h$. The reaction is then symbolized by $\sum_{i=1}^{n} \nu_i A_i = 0$. The ν_i are the stoichiometric coefficients and the function g is known as the reaction rate. The rate of many reactions is of the form (see [4], p. 19 f.):

$$g = k_o e^{-\frac{E}{RT}} \prod_i c_i^{\nu_i} \tag{1.3}$$

Where k_o, E, R are positive constants. The species A_i is called a reactant or a product of the reaction according to whether $\nu_i < 0$ or $\nu_i > 0$. There is always at least one reactant and at least one product . Therefore n positive numbers γ_i can be chosen such that $\sum_{i=1}^{n} \gamma_i \nu_i = 0$ and thus

$$(\Sigma \gamma_i c_i) = \Sigma \gamma_i c_i' = (\Sigma \gamma_i \nu_i) g(c_1,\ldots,c_n,T) = 0 \tag{1.4}$$

Now consider S reactions with rates $g_j (j = 1,\ldots,S)$ between N homogeneously mixed chemical species $A_1,\ldots,A_N$. Let ν_{ij} be the stoichiometric coefficient of the species A_i in the j-th reaction. The rate of change of c_i in the j-th reaction is $\nu_{ij} g_j$ and therefore the total rate of change is

$$(1.5) \qquad c_i' = \sum_{j=1}^{S} \nu_{ij} g_i(c_1,\ldots,c_N,T) \qquad i = 1,\ldots,N$$

To get a differential equation for T is more difficult. Assuming constant pressure, a comonly used simplified equation is

$$(1.6) \qquad T' = -\frac{1}{C_p} \sum_{j=1}^{S} Q_j g_j(c_1,\ldots,c_N,T) \quad (C_p = \sum_{i=1}^{N} c_i c_{pi})$$

where Q_j is the heat of the j-th reaction amd c_{pi} is the heat capacity at constant pressure of the i-th species. If we adjoin 1.6 to 1.5 and write $n = N + 1$, $x_i = c_i (i = 1,\ldots,n-1)$, $x_n = T$, then we get a system of the form 1.1 with 2^{nd} member independent of t.

2. Existence and Uniqueness

Consider the initial value problem

$$(2.1) \qquad X' = F(t,X) \qquad X(t_o) = X_o$$

In this section we treat the question whether a solution of this problem exists in some interval I and whether it is uni-

que. The famous existence theorem of Cauchy-Peano, which requires only continuity of F, is a local existence theorem, i.e. it guarantees existence of a solution only in a small neighborhood of the intial point. A general procedure which leads to existence theorems in the large is furnished by the theory of completely continuous operators of Leray and Schauder. The following basic theorem, which results from this theory, is stated without proof.

Existence Theorem

Let F be continous. For every vector-valued function X, defined and continuous in I, let $||X|| = \sup_I (|x_1(t)| + |x_2(t)| + \ldots + |x_n(t)|)$. If there exists a number $K > 0$, independent of λ, such that

$$(2.2) \qquad X' = \lambda F(t,X) \quad X(t_o) = \lambda X_o \qquad 0 < \lambda < 1$$

implies $||X|| \leq K$, then the initial value problem 2.1 has at least one solution defined in I.

This general existence theorem is the base of the following theorem, where specific conditions are imposed.

Theorem 2.1

Let $X_o \geq 0$ and let F be continous and satisfy:

(i) $f_i(t, x_1,\ldots,x_{i-1}, 0, x_{i+1},\ldots,x_n) \geq 0$ for $X \geq 0$, $t \geq t_o$, $i = 1,\ldots,n$

(ii) $\exists$ m, M and n positive numbers δ_i such that

$$\sum_{i=1}^{n} \delta_i f_i(t, X) + m \sum_{i=1}^{n} \delta_i X_i \leq M \qquad \forall\, X \geq 0, \forall\, t \geq t_o$$

Then there is at least one solution of 2.1 defined and nonnegative for all $t \geq t_o$.

Proof: Suppose first that in (i) the inequality involving f_i is strict. Choose a number $a > 0$ and let

$$I = [t_o, t_o+a], \quad L = \sum_{i=1}^{n} \delta_i x_{oi}, \quad \delta_o = \min_i \delta_i, \quad K = \frac{n}{\delta_o}(L + \frac{M}{|m|})\ (1 + e^{|m|}$$

Let X be a solution of 2.2 for some λ, $0 < \lambda < 1$. Since $X_o > 0$, the solution cannot leave the positive orthant. For suppose, it does leave it, then for some t_1 and i we have $x_i(t_1) = 0$, $x_i'(t_1) \leq 0$, $x_j(t_1) \geq 0$ $(j = 1,\ldots,n)$. But (i) implies $x_i'(t_1) = \lambda f_i(t, x_1,\ldots,x_{i-1}, 0, x_{i+1},\ldots,x_n) > 0_i$, a contradiction. Now consider the function $v(t) = \Sigma\delta_i x_i(t)$. It satisfies $v' + \lambda mv = \Sigma\delta_i x_i' + \lambda mv = \lambda(\Sigma\delta_i f_i(t, X) + m\Sigma\delta_i x_i) \leq \lambda M$ and $v(t_o) = \lambda L$. Multiplication by $e^{\lambda mt}$ and integration yields

$$\begin{aligned}
(ve^{\lambda mt})' &= (v' + \lambda mv)e^{\lambda mt} \leq \lambda M\, e^{\lambda mt} \\
v(t)e^{\lambda mt} &= v(t_o)e^{\lambda mt_o} + \frac{M}{m}\,(e^{\lambda mt} - e^{\lambda mt_o}) \\
v(t) &= v(t_o)e^{-\lambda m(t-t_o)} + \frac{M}{m}\,(1 - e^{-\lambda m(t-t_o)}) \\
&\leq (\lambda L + \frac{M}{|m|})\ (1 + e^{|m|a})
\end{aligned}$$

Since $x_i \geq 0$, $\delta_o > 0$, it follows

$$x_i(t) \leq \delta_o^{-1}(L + \frac{M}{m})\ (1 + e^{|m|a}) \qquad \forall\ t\in I$$

and hence $||x|| \leq K$.

Thus the conditions of the Existence Theorem are satisfied. Therefore a solution $\tilde{X}(t)$ exists for $t\in[t_o, t_o+a]$ with $\tilde{X}(t_o + a) \geq 0$. In the same way we can show that the initial value problem

$$X' = F(t, X) \qquad X(t_o + a) = \tilde{X}(t_o + a)$$

has a solution in $[t_o + a, t_o + 2a]$. This process is called continuation of the solution $\tilde{X}$. Obviously continuation is possible up to any value of $t \geq t_o$. This proves the theorem, when strict inequality holds in (i).

We'll only sketch the proof for the general case. Let $\{\epsilon_m\}$ be a sequence of positive numbers converging to zero, e.g. $\epsilon_m = 2^{-m}$. The functions $f_i^{(m)} = f_i + \epsilon_m$ have the property (i) with strict inequality. Hence for $m = 1,2,\ldots$ there exists a solution $X^{(m)}(t)$ of 2.1, where f_i is replaced by $f_i + \epsilon_m$, defined and nonegative for all $t \geq t_o$. There is a convergent subsequence of the sequence $X^{(m)}$ whose limit is a nonegative solution of 2.1. (strictly speaking this argument requires a Lipschitz conditon for F).

Definition: A function F(t, X) defined on IxD, where D is a-subset of R^n, is said to satisfy a Lipschitz condition with respect to X for the constant k > O, if for every t,X,Y such that (t,X) and (t,Y) are in IxD

$$\sum_{i=1}^{n} |f_i(t,X)-f_i(t,Y)| \leq k \sum_{i=1}^{n} |x_i-y_i|$$

This condition is satisfied, e.g. if F has continuous partial derivatives with respect to $x_1, x_2, \ldots, x_n$ (see [20], p. 5).

Theorem 2.2

If F satisfies a Lipschitz condition with respect to X, then there exists at most one solution of 2.1.
A proof is given in every text book on DE. We may combine theorem 2.1 and 2.2 and get

Theorem 2.3

If F and x_o satisfy the conditions of theorem 2.1 and 2.2 alltogether, then there is a unique solution of 2.1 defined andnonegative for all $t \geq t_o$.

Example 1

Consider a number of R isothermal reactions in a homogeneousmixture of N > R chemical species. The rate equations are

$$(2.4) \qquad c_i' = \sum_{j=1}^{R} \nu_{ij} g_j(c_1,\ldots,c_n) = f_i \qquad i=1,\ldots,N$$

Gavals ([5], p. 8) has pointed out, that there exist numbers

γ_{il} $(i=1,\ldots,N_j;\ l=1,\ldots,N-R)$ such that $\sum_{i=1}^{N} \gamma_{il}\nu_{ij} = 0$

$(l=1,\ldots,N-R;\ j=1,\ldots,R)$ and $\sum_{l=1}^{N-R} \gamma_{il} > 0$ $(i=1,\ldots,N)$.

Then (ii) is satisfied with m=M=0, $\delta_i = \sum_{l=1}^{N-R} \gamma_{il}$. Indeed,

$$\sum_{i=1}^{N} \delta_i f_i = \sum_{i=1}^{N} \sum_{l=1}^{N-R} \gamma_{il} f_i = \sum_{i=1}^{N} \sum_{l=1}^{N-R} \sum_{j=1}^{R} \gamma_{il} \nu_{ij} g_j = \sum_{l=1}^{N-R} \sum_{j=1}^{R}$$

$$(\sum_{i=1}^{N} \gamma_{il}\nu_{ij}) f_j = 0$$

We will illustrate this with two special examples.

The reactions

$$\nu_1 A \xrightarrow{1} \nu_2 B \xrightarrow{2} \nu_3 C \qquad (\nu_i > 0)$$

are described by the equations

$$(2.5) \qquad \begin{aligned} c_1' &= -\nu_1 g_1 \\ c_2' &= \nu_2 g_1 - \nu_2 g_2 \\ c_3' &= \nu_3 g_2 \end{aligned}$$

Condition (ii) of theorem 2.1 is satisfied because

$\frac{c_1'}{\nu_1} + \frac{c_2'}{\nu_2} + \frac{c_3'}{\nu_3} = -g_1 + (g_1-g_2) + g_2 = 0$. If we assume that $g_i = k_i c_i^{\nu_i}$ $(k_i > 0)$, then condition (i) is satisfied, too.

Next consider the enzymatic reaction (see [8])

$$S + E \underset{-1}{\overset{1}{\rightleftarrows}} C \xrightarrow{2} P + E$$

with the equations

$$\begin{aligned} s' &= -k_1 se + k_{-1} c \\ e' &= -k_1 se + (k_{-1} + k_2) c \\ c' &= k_1 se - (k_{-1} + k_2) c \\ p' &= k_2 c \end{aligned} \qquad (k_1, k_{-1}, k_2 > 0) \tag{2.6}$$

Here $s'+e'+2c'+p' = 0$, and we may put $\delta_1 = \delta_2 = \delta_4 = 1$, $\delta_3 = 2$.

Therefore conditions (i) and (ii) are satisfied.

Example 2

Consider a continuous isothermal stirred tank reactor with constant volume V and constant volumetric flow rate w of input and output streams. Let c_{if} be the input or feed concentrations, which are given functions of time. As a result of the mixing the concentrations in the output stream are the same as those

in the reactor. If R reactions between N species occur, then the equations are (see [5], p. 29)

$$(2.7) \qquad c_i' = \frac{W}{V}(c_{if} - c_i) + \sum_{j=1}^{R} \nu_{ij} g_j = f_i \quad i=1,\ldots,N$$

With γ_{il} and δ_i as in example 1 we get

$$\sum_{i=1}^{N} \delta_i f_i = \frac{W}{V} \sum_{i=1}^{N} \delta_i (c_{if} - c_i)$$

Since the c_{if} are bounded, there is an $M > 0$ such that

$$\frac{W}{V} \sum_{i=1}^{N} \delta_i c_{if} \leq M \text{ and therefore}$$

$$\sum \delta_i f_i + \frac{W}{V} \sum \delta_i c_i \leq M$$

i.e. condition (ii) is satisfied.

An existence proof for non-isothermal reactions is given in sec. 4.

As much as concerns uniqueness let's remark, that F has always continuous partial derivatives and hence satisfies a Lipschitz condition, if the rate functions have the form as in 1.3. The derivative with respect to T, absolute temperature, contains the factor $\frac{E}{RT^2} e^{\frac{-E}{RT}}$ which is continuous even if $T \to 0$.

For later use we prove the following

Comparison Theorem

If $f(t,x)$ is continuous and if in $[t_o,t_o+a]$ the functions x and y are differentiable and satisfy

(i) $x'-f(t,x) < y'-f(t,y) \qquad x(t_o) < y(t_o)$

then $x(t) < y(t)$ in $[t_o,t_o+a]$.

Proof: Consider the function $z(t)=y(t)-x(t)$. Obviously $z(t_o) > 0$. If not $z(t) > 0$ for all $t \in [t_o,t_o+a]$, then there is a t_1 such that $z(t_1)=0$, $z'(t_1) \leq 0$, i.e. $y(t_1) = x(t_1)$, $y'(t_1) \leq x'(t_1)$. But $y(t_1) = x(t_1)$ and (i) imply $x'(t_1) < y'(t_1)$, a contradiction.

3. Elementary methods of integration

The process of solving a differential equation is called integration. The simplest DE is $x'=f(t)$. It has the solutions $x = \int f(t)dt + C$, where C is a constant of integration to be determined from the initial value. The unique solution satisfying $x(t_o) = x_o$ is

$$x = x_o + \int_{t_o}^{t} f(s)\, ds \tag{3.1}$$

Now consider the scalar DE $x'=f(t,x)$. If it can be written in the form

(3.2) $$x' = g(x)\, h(t)$$

then the variables are said to be "separated".

If g and h are continuous, then a solution $\tilde{x}$ of 3.2 satisfying $x(t_o) = x_o$ exists in a neighbourhood of t_o, according to the existence theorem of Cauchy-Peano. If $g(x_o)=0$, $x \equiv x_o$ is a solution. If $g(x_o) \neq 0$, then a solution can be obtained by solving the equation

(3.3) $$\int \frac{dx}{g(x)} = \int h(t)\, dt + C$$

for x (it can be shown by the implicit function theorem that this is always possible near t_o) and giving the constant C the appropriate value. One might ask the questions: can the solution $\tilde{x}$ be continued up to any value of $t \geq t_o$. What happens, if $g(\tilde{x}(t_1)) = 0$ for some $t_1 > t_o$? It turns out, that the latter is impossible, if g is Lipschitzian and $g(x_o) \neq 0$. To prove this, suppose that $g(x_1) = 0$ and that $x(t_1) = x_1$ for some $t_1 > t_o$ where x is defined. Then x is a solution of the initial value problem $x' = g(x)\, h(t)$, $x(t_1) = x_1$. But this is impossible because the constant x_1 is also a solution of this problem and the solution must be unique. Therefore it is legitimate to use 3.3 even if g has zeroes. The question concerning continuation will not be discussed here to its full extent, but only applied to examples.

Example 1

(3.4) $\qquad x' = a(t)x$

We have $g(x) = x, h(t) = a(t)$; then equation 3.3 reads

$$\ln|x| = \int \frac{dx}{x} = \int a(t)dt + C$$

If $x(t_o) = x_o$, then

(3.5) $\qquad x(t) = x_o \exp\left(\int_{t_o}^{t} a(s)ds\right)$

Continuation of the solution is not limited.

Example 2

(3.6) $\qquad x' = -ax^n \qquad (a > 0, n > 1)$

We get $at + C = -\int \frac{dx}{x^n} = (n-1)^{-1} x^{-(n-1)}$ or, solved for x:

(3.7) $\qquad x = [(n-1)(at + C)]^{-\frac{1}{n-1}}$

If $x(0) = x_o \neq 0$, then $C = \frac{1}{n-1} x_o^{-(n-1)}$. If $x_o < 0$ and n is even the solution 3.7 is not defined for all $t \geq 0$.

Example 3

Reversible reactions involving two molecules of reactants and/or products, lead to rate equations of the form $x' = g(x)$, where $g(x) = -ax + b(1-x)^2$ or $-ax^2 + b(1-x)^2$. If g has two real zeroes α and β, we may write, neglecting a constant factor,

$$x' = g(x) = (x - \alpha)(x-\beta) \qquad (\alpha < \beta) \tag{3.8}$$

Equation 3.3 yields

$$(*) \quad t + C = \int \frac{dx}{(x-\alpha)(x-\beta)} = \frac{1}{\beta-\alpha} \int \left(\frac{1}{x-\beta} - \frac{1}{x-\alpha} \right) dx =$$

$$\frac{1}{\alpha-\beta} \ln \left| \frac{x-\beta}{x-\alpha} \right|$$

Let $x(0) = x_o$. We set $t = 0$ in $(*)$ and get $(\beta-\alpha)C = \ln \left| \frac{x_o-\beta}{x_o-\alpha} \right|$

Now we take exponentials and get

$$(**) \qquad \left| \frac{x-\beta}{x-\alpha} \right| = \exp\left[(\beta-\alpha)(t+C) \right] = c \exp(\beta-\alpha)t$$

where $c = \exp(\beta-\alpha)C = \left| \frac{x_o-\beta}{x_o-\alpha} \right|$.

Since $g(\alpha) = g(\beta) = 0$, a nonconstant solution never takes the values α or β. Therefore if $x \neq \alpha, \beta$ is a solution defined in I, then only three cases are possible:

$x(t) < \alpha \ \forall t \in I$, $\alpha < x(t) < \beta \ \forall t \in I$, or $x(t) > \beta \ \forall t \in I$.

1st case: $x < \alpha$

We have sign $(x-\alpha)$ = sign $(x-\beta)$ = -1 and hence from (**) $(x-\beta) = (x-\alpha)Y$, where $Y = c \exp(\beta-\alpha)t$. This gives $x-xY = \beta-\alpha Y$, $x = \frac{\beta-\alpha Y}{1-Y}$ i.e.

$$x = \frac{\beta-\alpha c\exp(\beta-\alpha)t}{1-c\ \exp(\beta-\alpha)t}$$

Since $x_o < \alpha$ implies $|x_o-\beta| > |x_o-\alpha|$ or $c > 1$, the denominator is < 0 for all $t \geq 0$, and thus the solution is defined for all $t > 0$. It is easily seen that $x(t) \to \alpha$ for $t \to \infty$.

2nd case: $\alpha < x < \beta$

In this case we have sign $(x-\alpha)$ = -sign $(x-\beta)$ and therefore $(x-\beta) = -(x-\alpha)Y$, $x+xY = \beta+\alpha Y$, i.e.

$$(3.9) \qquad x = \frac{\beta+\alpha c\exp(\beta-\alpha)t}{1+c\ \exp(\beta-\alpha)t} .$$

Since $c > 0$, the deominator is positive and the solution is defined for all $t \geq 0$. Again $x(t) \to \alpha$ for $t \to \infty$.

3rd case: $x > \beta$

Since sign $(x-\alpha)$ = sign $(x-\beta)$, the solution is the same as in the 1st case. But $x_o > \beta$ implies $|x_o-\beta| < |x_o-\alpha|$ or $c < 1$. Therefore a $t^{**} > 0$ exists such that $1-c\ \exp(\beta-\alpha)t^{**} = 0$, hence the solution cannot be continued up to t^{**}.

Example 3'

(3.8') $x' = -(x-\alpha)(x-\beta) \qquad (\alpha<\beta)$

This equation is reduced to 3.8, if t is replaced by -t. We consider only the case $x_o > \beta$, because we'll need it later. The solution is

(3.9') $$x = \frac{\beta-\alpha c \exp[-(\beta-\alpha)t]}{1-c \exp[-(\beta-\alpha)t]}$$

where $c < 1$. Hence the denominator is > 0 and the solution is defined for all $t \geq 0$. We have $\lim_{t\to\infty} x(t) = \beta$. Application of formulas 3.9 and 3.9' will follow in sec. 8a.

There are still many elementary methods of integration which can be applied to particular types of equation. Most of these, however, are not related to any known problem in chemical kinetics.

4. Linear equations and systems

The general linear differential equation of first order has the form

(4.1) $x' + a(t)x = b(t)$

The solutions of this equation are

$$x = e^{-\int a(t)dt} \left[c + \int b(t) e^{\int a(t)dt} dt\right] \tag{4.2}$$

and are defined for all t for which a and b are defined and continous. The solution which satisfies $x(t_o) = x_o$, is given by

$$x(t) = e^{-\int_{t_o}^{t} a(s)ds} \left[x_o + \int_{t_o}^{t} b(s)\, e^{\int_{t_o}^{s} a(u)du}\, ds\right] \tag{4.2'}$$

Now we consider the linear homogeneous system with constant coefficients

$$x_i' = \sum_{j=1}^{n} a_{ij}\, x_j \qquad i = 1,\ldots,n$$

This can be written in vector form

$$X' = \mathcal{A}X \tag{4.3}$$

where $\mathcal{A}$ denotes the (m,n) matrix $[a_{ij}]$.

The general solution of 4.3 is an expression containing n constants such that any solution of 4.3 can be obtained from it by assigning appropriate values to these constants. It is known that the solutions of 4.3 form an n dimensional vector space, i.e. any linear combination of solutions is itself a solution. A set of solutions that is a basis of this vector space, is called a fundamental system of solutions. Thus, if $\{X^1, X^2, \ldots, X^n\}$ is a fundamental system for 4.3, then every solution of

4.3 can be obtained in the form $X = \Sigma\lambda_i X^i$, where the λ_i are real numbers.

An eigenvector of $\mathcal{A}$ is a real or complex vector $\neq 0$ such that $\mathcal{A}X = \lambda X$ or $(\mathcal{A} - \lambda E)X = 0$ (E = unity matrix), where λ is some real or complex constant. In this case λ is called an eigenvalue of the matrix $\mathcal{A}$ and X an eigenvector belonging to λ. Note, that every scalar multiple of an eigenvector is itself an eigenvector. The eigenvalues are the solutions of the characteristic equation $\det(\mathcal{A} - \lambda E) = 0$.

Theorem 4.1

Corresponding to every eigenvalue λ of $\mathcal{A}$ there exists at least one solution of 4.3 of the form

$$(4.4) \qquad X(t) = (c_1 e^{\lambda t}, c_2 e^{\lambda t}, \ldots, c_n e^{\lambda t})$$

where $(c_1, c_2, \ldots, c_n)$ is an eigenvector belonging to λ. If $\mathcal{A}$ has n distinct eigenvalues, then the corresponding set of solutions forms a fundamental system for 4.3.

Proof: See [20] p. 60 f.

If λ is complex, $\lambda = a + bi$, then $e^{\lambda t} = e^{at}(\cos bt + i \sin bt)$ and the solution is oscillating. On the other hand if $\mathcal{A}$ has n distinct real eigenvalues, then the components of any solution

of 4.3 pass through at most a finite number of maxima and minima.

Example

Let $\mathcal{A} = \begin{pmatrix} -a & 0 \\ a & -b \end{pmatrix}$, $a > 0$, $b > 0$, $a \neq b$, and consider the system $X' = \mathcal{A}X$, i.e.

$$x_1' = -ax_1$$
$$x_2' = ax_1 - bx_2 \tag{4.5}$$

The characteristic equation

$$\det(\mathcal{A} - \lambda E) = \begin{vmatrix} -a-\lambda & 0 \\ a & -b-\lambda \end{vmatrix} = (a + \lambda)(b + \lambda) = 0$$

has the solutions $\lambda_1 = -a$, $\lambda_2 = -b$. In order to get an eigenvector belonging to λ_1, we solve the algebraic system

$$-(a + \lambda_1)c_1 = 0$$
$$a\,c_1 - (b + \lambda_1)c_2 = 0$$

Since $\lambda_1 = -a$, we may choose $c_1 = 1$ and this leads to $c_2 = \frac{a}{b-a}$. For $\lambda = \lambda_2 = -b$ we get $c_1 = 0$ and $c_2 = 1$. Therefore the solutions

$$X_1 = \begin{pmatrix} e^{-at} \\ \frac{a}{b-a}\, e^{-at} \end{pmatrix} \quad \text{and} \quad X_2 = \begin{pmatrix} 0 \\ e^{-bt} \end{pmatrix}$$

form a fundamental system for 4.5, and the general solution is

$$(4.6) \qquad \begin{aligned} x_1 &= c_1\, e^{-at} \\ x_2 &= c_1 \frac{a}{b-a}\, e^{-at} + c_2\, e^{-bt} \end{aligned}$$

where c_1, c_2 are now arbitrary constants.

The system 4.5 can also be solved by integrating the first equation apart, which gives $x_1 = c_1\, e^{-at}$ and replacing this in the 2nd equation, obtaining $x_2' + bx_2 = ac_1\, e^{-at}$ which is of the form 4.1. Applying 4.2 we get

$$x_2 = e^{-bt}[c_2 + \int ac_1\, e^{-at} e^{bt} dt] = e^{-bt}[c_2 + c_1 \frac{a}{b-a}\, e^{(b-a)t}]$$

in accordance with 4.6. This method works also in the case $a = b$ and yields $x_2 = e^{-at}(c_2 + a\, c_1 t)$.

A linear system is called inhomogeneous, if it contain terms that are free of X. Consider the inhomogeneous system

$$(4.7) \qquad x_i' = \sum_{j=1}^{n} a_{ij}\, x_j + b_i \qquad i = 1,\ldots,n$$

The general solution of 4.7 is obtained by adding the general solution of 4.3 to a particular solution of 4.7.

The rest of this section is not needed in the further course of this paper. By means of formula 4.2 and the Comparison Theorem we will prove an existence theorem for non-isothermic reactions in a continuous stirred tank reactor.

We make use of example 2 (sec. 2). The equations 2.7 for c_i' remain unchanged, except that now the g_j depend also on T. The heat balance gives an equation similar to 1.6, but with the term $\frac{W}{V}(T_f - T)$ added. Here T_f is the input or feed temperature. In this way we get the system of DE

$$c_i' = \frac{W}{V}(c_{if} - c_i) + \sum_{j=1}^{R} \nu_{ij} g_j \qquad i = 1,\ldots,N$$

$$T' = \frac{W}{V}(T_f - T) + \frac{1}{C_p} \sum_{j=1}^{R} Q_j g_j \tag{4.8}$$

where $C_p = \sum_{i=1}^{N} c_{pi} c_i$

$$Q_j = Q_{oj} + \left(\sum_{i=1}^{N} \nu_{ij} c_{vj}\right) T \qquad j = 1,\ldots,R \text{ (see [2], p.47)} \tag{4.8a}$$

c_p and c_v denote the specific heat at constant pressure resp. volume.

Theorem 4.2

If the following conditions are satisfied:

(i) the specific heats c_{pi} and c_{vi} $(i = 1,\ldots,N)$ are independent of T

(ii) $\tilde{g}_j(c_1,\ldots,c_N) = \sup_{0<T<\infty} g_j(c_1,\ldots,c_N,T) < \infty$

(iii) $\sum_{j=1}^{R} \nu_{ij} g_j(c_1,\ldots,c_{i-1}, 0, c_{i+1},\ldots,c_N, T) \geq 0$

(iv) $g_j(c_1,\ldots c_N, 0) = 0 \; g_j(c_1,\ldots,c_N, T) \geq 0 \quad (j = 1 \ldots, R)$

(v) $c_{if} > 0 \; (i = 1,\ldots,N), \; T_f > 0 \quad \sum_{i=1}^{N} c_{if} \equiv 1$

Then the system 4.8 has a solution that satisfies given nonnegative initial values and is defined and nonnegative for all $t \geq t_o$.

Proof: We have to derive estimates for solutions of

$$X' = \lambda F(t, X) \qquad X(t_o) = \lambda X_o$$

or explicitly

$$c_i' = \lambda m(c_{if} - c_i) + \lambda \Sigma \nu_{ij} g_j$$

$$T' = \lambda m(T_f - T) + \frac{\lambda}{C_p} \Sigma Q_j g_j \tag{4.9}$$

$$c_i(t_o) = \lambda \, c_{oi} \quad T(t_o) = \lambda \, T_o \quad \text{where } m = \frac{W}{V}$$

Let $(c_1,\ldots,c_N, T)$ be a solution of 4.9. Conditions (iii)-(v)

imply that it is nonnegative. We consider $v(t) = \sum_{i=1}^{N} \delta_i c_i(t)$, where the δ_i have the same meaning as in example 1 of sec. 2. We get $v' = \Sigma\delta_i c_i' = \lambda m\ (\Sigma\lambda_i c_{if} - v)$ and $v' + \lambda m v < \lambda M$ for some $M > 0$. It turns out, that K as defined in the proof of theorem 2.1 is an upper bound for the c_i. In order to get an estimate for T, we need a positive lower bound for C_p and therefore a positive lower bound for the c_i. Since (v) implies $m\Sigma\delta_i c_{if} \geq \epsilon$ for some $\epsilon > 0$, we get $v' + \lambda m v \geq \lambda\epsilon$ and, after multiplication with $e^{\lambda m t}$ and integration

$$v(t) \geq v(t_o)e^{-\lambda m(t-t_o)} + \frac{\epsilon}{m}(1-e^{-\lambda m(t-t_o)}) \geq v(t_o)$$

since $m = \frac{W}{V} > 0$. Therefore $v(t) \geq \lambda L$ for $t \geq t_o$, where $L = \Sigma\delta_i c_{oi}$. But then $c(t) > \frac{\lambda L}{N\delta_k}$ for at least one index k, hence

$$C_p = \sum_i c_{pi} c_i \geq \lambda \frac{C_{pk} L}{N\delta_k} = \lambda C_o > 0 \text{ and from 4.9}$$

$$T' \leq \lambda m\ (T_f - T) + C_o^{-1}\ \Sigma Q_j g_j$$

Now, using $0 < \lambda < 1$, $T_f > 0$, $T \geq 0$ and 4.8 a, and dropping terms with negative Q_{oj} and negative ν_{ij}, we obtain

$$T' < mT_f + C_o^{-1}\ \{\Sigma Q_{oj}\ \tilde{g}_j + T\Sigma\Sigma\nu_{ij}\ c_{vj}\ \tilde{g}_j\}$$

or breefly

$$T' < \Gamma_1(t, c_1,\ldots,c_N) + \Gamma_2(c_1,\ldots,c_N)T$$

Since $(c_1,\ldots,c_N, T)$ is a hypothetically given solution of 4.9, we may consider Γ_1 and Γ_2 as functions of t alone, which are bounded independently of λ. Now choose $x_o > T_o$. According to the comparison Theorem, the solution of

$$x' = \Gamma_1 + \Gamma_2 x \qquad x(t_o) = \lambda x_o$$

satisfies $T(t) < x(t)$ and is given by (see formula 4.2')

$$x(t) = e^{\int^t \Gamma_2 ds} \left[\lambda x_o + \int^t_{\Gamma_1} e^{-\int^s \Gamma_2 du} ds\right]$$

Since $\lambda x_o e^{\int \Gamma_2} < x_o e^{\int \Gamma_2}$, x and T are bounded independently of λ. Therefore the conditions of the general. Existence Theorem (sec. 2) are satisfied and the proof is complete.

Remark: The principal ideas of the preceding proof are due to [5], p. 28 f., where, however, the rather restrictive conditions, that C_p and the heats of reaction be constant, are imposed.

5. Series expansion and singular perturbations.

If an explicit expression such as 4.3 for the solutions of a DE has been found, then we say that the equation has been solved in closed form. Most nonlinear equations and in particular, systems of nonlinear equations cannot be solved in closed form. Therefore we have to look for methods that provide at least approximate solutions in those cases. This task belong to the branch of Numerical Analysis and is extensively treated in any text book on the subject. Here we'll only discuss series expansions, and especially the method of singular perturbations and its connection with the quasi-steady-state approximation introduced in 1924 by Bodenstein and Lutkemayer.

We recall that a function is called analytic, if it is represented by an absolutely convergent power series. Let's consider the equations

(5.1) $x' = f(t,x)$

(5.2) $x' = h(t,x,\lambda)$

If f is analytic in t and x, i.e. $f(t,x) = a_o + a_{10}t + a_{01}x + a_{20}t^2 + 2a_{11}tx + a_{02}x^2 + \ldots$, then the solutions of 5.1 can be obtained in the form $x = \sum_{m=o}^{\infty} c_m t^m$. The coefficients c_m are calculated by replacing x by $\Sigma c_m t^m$ and x' by $\Sigma m c_m t^{m-1}$ in 5.1 and equating coefficients of equal powers of t. This is the most common method of solution by series expansion. It can also be applied to 5.2, if h is analytic in t and x, with the difference, that c_m will then become a function of λ. If h is analytic in t and λ then a solution of 5.2 can also be obtained in the form

(5.3) $$x(t,\lambda) = \sum_{m=o}^{\infty} x(t)^m \lambda^m$$

If this series is troncated at m = k, then we call it the solution of order k.

We consider the simple example

(5.4) $x' = \lambda f(x) \qquad x(0) = \xi$

where

$$(5.5) \qquad f(x) = A_o + A_1 x + A_2 x^2 + \ldots$$

We insert 5.3 into 5.5 and obtain after reordering

$$f(x) = [A_o + \overset{0}{x}A_1 + \overset{0}{x}\,\overset{0}{x}\,A_2 + \ldots]\,\lambda^0$$

$$+ [\overset{1}{x}A_1 + 2\,\overset{0}{x}\,\overset{1}{x}\,A_2 + \ldots.]\lambda^1$$

$$+ [\overset{2}{x}\,A_1 + (\overset{1}{x}\,\overset{1}{x} + 2\,\overset{0}{x}\,\overset{2}{x})\,A_2 + \ldots]\lambda^2$$

$$+ \ldots$$

On the other hand $x' = \overset{0}{x}' + \lambda\overset{1}{x}' + \lambda^2\overset{2}{x}' + \ldots$

Thus, applying 5.4 and comparing the coefficients of λ^m on both sides, we get the infinite sequence of DE

$$\overset{0}{x}' = 0$$

$$\overset{1}{x}' = A_o + \overset{0}{x}\,A_1 + \overset{0}{x}\,\overset{0}{x}\,A_2 + \ldots = \overset{0}{f}(x)$$

(5.6)

$$\overset{2}{x}' = \overset{1}{x}\,A_1 + 2\,\overset{0}{x}\,\overset{1}{x}\,A_2 + \ldots$$

$$\overset{3}{x}' = \overset{2}{x}\,A_1 + (\overset{1}{x}\,\overset{1}{x} + 2\,\overset{0}{x}\,\overset{2}{x})\,A_2 + \ldots$$

In we impose the initial conditions $\overset{0}{x}(0) = \xi$, $\overset{m}{x}(0) = 0$ ($m \geq 1$), then 5.3 will satisfy $x(0, \lambda) = \xi \ \forall\lambda$. The equation 5.6 can be solved recursively, i.e. we first calculate $\overset{0}{x}$, insert it into the 2nd calculate $\overset{1}{x}$, etc. Each equation of the system 5.6 is simpler than the original equation 5.4, because its second member depends only on known (previously calculated) functions and therefore only on t. Now we consier instead of 5.4 the system

$$x' = \lambda f(x,y) \qquad y' = g(x,y)$$

Suppose that f and g are analytic in x and y,

$$f(x,y) = \sum_{i,k=0}^{\infty} A_{ik}\, x^i y^k \qquad g(x,y) = \sum_{i,k=0}^{\infty} B_{ik}\, x^i y^k$$

Inserting 5.3 and $y = \sum \overset{m}{y}\, \lambda^m$ into 5.7 and comparing the coefficients of λ^m we obtain

(5.8)

$$(\alpha_0) \qquad \overset{0}{x}' = 0$$

$$(\beta_0) \qquad \overset{0}{y}' = \Sigma B_{ik}\, \overset{0}{x}^i\, \overset{0}{y}^k = g(\overset{0}{x}, \overset{0}{y})$$

$$(\alpha_1) \qquad \overset{1}{x}' = f(\overset{0}{x}, \overset{0}{y})$$

$$(\beta_1) \qquad \overset{1}{y}' = B_{10}\overset{1}{x} + B_{01}\overset{1}{y} + 2[B_{20}\overset{0}{x}\,\overset{1}{x} + B_{11}(\overset{0}{x}\,\overset{1}{y} + \overset{1}{x}\,\overset{0}{y}) + B_{02}\,\overset{0}{y}\,\overset{1}{y}] + \ldots$$

This system is again recursive. Once $\overset{0}{x}$ = const. has been determined, equation β_0 reduces to an equation with seperated variables (see sec. 3). Once $\overset{0}{x}$ and $\overset{0}{y}$ are determined, the sec-

and member of α_1 depends only on t, and x^1 can be calculated by simple integration. Furthermore equation β_1 is linear in y^1. Generally speaking: equation α_m requires only the integration of known(previously calculated) functions, and equation $\beta_m (m \geq 1)$ is linear. Thus the system 5.8 is essentially solvable, though the actual computation may become tedious when m increases. This method is particularly useful, if λ is small and higher order terms may be neglected. The same method, applied to

$$x' = f(x,y) \tag{5.9}$$
$$\lambda y' = g(x,y)$$

where λ is small, is called singular pertubation. The system 5.9 is considered as a pertubation of the system

$$x' = f(x,y) \tag{5.10}$$
$$0 = g(x,y)$$

where one equation is degenerated into an algebraic equation. If $y = \phi(x)$ is a root of $g(x,y) = 0$, than 5.10 may be written

$$x' = f(x, \phi(x)) \tag{5.10'}$$

We may impose the initial condition $x(0) = x_o$ on 5.10' and the initial conditions $x(0) = x_o$, $y(0) = y_o$ on 5.9 A Theorem of A. N. Tikhonov (see [8], [18]) states, that under certain conditions, which are usually satisfied in chemical kinetics, the solution (x,y) of the initial value problem for 5.9 tends to the solution $(x, \phi(x))$ of the initial value problem for 5.10 except for $t = 0$. Clearly, we cannot expect convergence for $t = 0$, since in general $\phi(x_o) \neq y_o$.

Now let's consider an example. The equations 2.5 can be reduced to a system of 2 equations, if only the equations for s' and c' are retained and e is eliminated using $e' + c' = 0$, i.e. $e + c = \text{const}$. These reduced equations contain the initial value $e(0) = e_o$, $s(0) = s_o$ and $c(0) = c_o$ as parameters and can be further reduced to the form (see [8])

$$\frac{dx}{d\tau} = -x + (x + K - L)y$$

(5.11)

$$\lambda\frac{dy}{d\tau} = x - (x + K)y$$

where $x = \frac{s}{s_o}$, $y = \frac{c}{c_o}$, $\lambda = \frac{e_o}{s_o}$, $\tau = k_1 e_o t$ and K, L are parameters independent of λ. In enzymatic reactions λ is small. If we set $\lambda = 0$ and eliminate y, we get from 5.11 the so-called Michaelis-Menten kinetic law

(5.12)
$$\frac{dx}{d\tau} = -\frac{Lx}{x+K}$$

The solution of 5.12 is called the quasi-steady state approximation to 5.11. For $t > 0$ the exact solution of 5.11 tends to the solutions of 5.12 as λ tends to zero (Tikhonov's theorem).

During the last 20 years the quasi-steady state approximation has been refined in two respects. First, the approximate solution of 5.9 has been splitted into two functions, one the "inner solution", defined for small t and satisfying the initial conditions, and the other, the "outer solution", defined for greater t and equal to the solution of 5.10. Secondly, the solution of 5.10 has been replaced by a series expansion in powers of λ.

The inner solution is obtained as follows. Introduce a new independent variable s by $s\lambda = t$. Since $\frac{d}{ds} = \lambda \frac{d}{dt}$, 5.9 is transformed to

$$(5.7') \qquad \frac{dx}{ds} = \lambda f(x,y) \qquad \frac{dy}{ds} = g(x,y)$$

This system can be solved in the way outlined above. The problem is then, to join the inner and outer solution smoothly. We denote the inner solution with x, y and the outer solution with $\hat{x}$, $\hat{y}$. If $t > 0$, then $\lambda \to 0$ is equivalent to $s \to \infty$. Therefore we require

$$(5.13) \qquad \hat{x}(+0) = \lim_{s \to \infty} x(s)$$

$$\hat{y}(+0) = \lim_{s\to\infty} y(s) \tag{5.14}$$

The series expansion of the outer solution in obtained as follows. If we introduce the series 5.3 and $y = \sum^{m} y\,\lambda^m$ into 5.9 and compare the coefficients of λ^m, then we get

$$(\beta_0) \qquad {}^{0}_{0} = g({}^{0}_{x}, {}^{0}_{y}) \tag{5.15}$$

$$(\alpha_0) \qquad {}^{0}_{x}{}' = f({}^{0}_{x}, {}^{0}_{y})$$

$$(\beta_1) \qquad {}^{0}_{y}{}' = B_{10}\,{}^{1}_{x} + B_{01}\,{}^{1}_{y} + 2[B_{20}\,{}^{0}_{x}\,{}^{1}_{x} + B_{11}({}^{0}_{x}\,{}^{1}_{y} + {}^{0}_{x}\,{}^{1}_{y}) + B_{02}\,{}^{0}_{y}\,{}^{1}_{y}] + \ldots$$

$$(\alpha_1) \qquad {}^{1}_{x}{}' = A_{10}\,{}^{1}_{x} + A_{01}\,{}^{1}_{y} + 2[A_{20}\,{}^{0}_{x}\,{}^{1}_{x} + A_{11}({}^{0}_{x}\,{}^{1}_{y} + {}^{0}_{x}\,{}^{1}_{y}) + A_{02}\,{}^{0}_{y}\,{}^{1}_{y}] + \ldots$$

From β_0, which is no longer a DE, we get ${}^{0}_{y}$ as a function ϕ of ${}^{0}_{x}$, and then we can solve equation α_0 for ${}^{0}_{x}$, replacing ${}^{0}_{y}$ by $\phi({}^{0}_{x})$. (Note that $({}^{0}_{x}, {}^{0}_{y})$ is nothing else than the quasi-steady state approximation). In equation β_1 ${}^{0}_{y}{}'$ is known since ${}^{0}_{y}$ is known, and no derivative of ${}^{1}_{y}$ is present. Therefore α_1 can be solved for ${}^{1}_{x}$ after algebraic elimination of ${}^{1}_{y}$, and then ${}^{1}_{y}$ can be obtained from equation β_1, etc. Obviously initial values are needed only for the ${}^{m}_{x}$. How to obtain these initial values such that 5.13 is satisfied, is explained in [8]. In [3] it is shown by means of an example, how the constants of inte-

gration that occur in the outer solution, are determined by condition 5.13, and that condition 5.14 is then satisfied automatically for the 2nd order solution.

It may happen, that the outer solution breaks down for very large times, because the series 5.3 is not longer convergent. This possibility is considered in [3] and a way to circumvent this difficulty by the construction of a third function, the "far out" solution is indicated.

6. Stability

In many applications it is not necessary to calculate an exact or an approximate solution of a DE, but it is sufficient to know the behaviour as $t \to \infty$ (asymptotic behaviour) of a certain set of solutions. One of the most important concepts in this area is the concept of stability. The short exposition of stability theory given here differs somewhat from the usual way, due to the fact that we are frequently interested only in nonnegative solutions.

Definition 1. A subset $\Omega \subset R^n$ is called an invariant set with respect to 1.1, if for every $X_o \in \Omega$ the solution X of 1.1 that satisfies $X(t_o) = X_o$ is defined amd remains in Ω for all $t \geq t_o$. For example, $\Omega = \{X \in R^n : X \geq 0\}$ is invariant with respect to 1.1, if F satisfies the conditions of Th. 2.3.

Definition 2. A norm in R^n is a function $||\ ||: R^n \to R$ that satisfies $||X|| > 0 \forall X \neq 0$, $||aX|| = |a|\ ||X||$, $||X+Y|| < ||X|| + ||Y||$ for all $X, Y \in R^n$, $a \in R$.

For example, $||X|| = \sum_{i=1}^{n} |x_i|$ and $||X|| = \max_i |x_i|$ are norms in R^n.

Definition 3. Let Ω be an invariant set with respect to 1.1. A solution ψ of 1.1 with $\psi(t_o) \in \Omega$ is said to be Ω-stable, or simply stable, if given any $\varepsilon > 0$, there exists a $\delta > 0$ such that any solution ϕ of 1.1 satisfying $\phi(t_o) \in \Omega$ and $||\phi(t_o) - \psi(t_o)|| < \delta$ satisfies $||\phi(t) - \psi(t)|| < \varepsilon$ for all $t > t_o$. ψ is called asymptotically stable, if it is stable and if there exists a $\delta > 0$ such that any solution of 1.1 satisfying $\phi(t_o) \in \Omega$ and $||\phi(t_o) - \psi(t_o)|| < \delta$ satisfies $||\phi(t) - \psi(t)|| \to 0$ as $t \to \infty$.

Remark: These concepts coincide with the usual stability concepts, if $\Omega = R^n$.

Theorem 6.1

Let A be a(n.n) matrix and let $\Omega = R^n$. If all eigenvalues of A have negative real parts, then the identically zero solution of the system

(6.1) $\qquad X' = AX$

is asymptotically stable.

Proof: If A has n distinct eigenvalues $\lambda_1,\ldots,\lambda_n$, then any solution of 6.1 is a vector whose components are $x_k = \sum_{i=1}^{n} c_{ik}\, e^{\lambda_i t}$, where the c_{ik} are complex numbers (Theorem 4.1). If $\mathrm{Re}(\lambda) = \alpha < 0$, then $|e^{\lambda t}| = e^{\alpha t} \to 0$ as $t \to \infty$. Therefore $x_k \to 0$, if all λ_i have negative real parts. If A has mutiple eigenvalues, then $x_k = \sum_i P_{ik}(t)\, e^{\lambda_i t}$, where P_{ik} is a polynomial in t (see [20], p. 63). But it is known that $\lim_{t\to\infty} P(t)e^{\alpha t} = 0$ for any polynomial P, if $\alpha < 0$.

The eigenvalues of A are the roots of the characteristic equation $\det(A-\lambda E) = 0$, which may be written in the form

$$\lambda^n + m_1 \lambda^{n-1} + \ldots + m_n = 0 \qquad (m_1,\ldots,m_n \in \mathbb{R}) \tag{6.2}$$

We define the determinants $D_1 = m_1$ and

$$D_k = \begin{vmatrix} m_1 & m_3 & m_5 & \cdots & m_{2k-1} \\ 1 & m_2 & m_4 & \cdots & m_{2k-2} \\ 0 & m_1 & m_3 & \cdots & m_{2k-3} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & m_k \end{vmatrix} \qquad k = 2,3,\ldots,n$$

where $m_j = 0$ for $j > n$. We have e.g. for $n = 3$

$$D_2 = \begin{vmatrix} m_1 & m_3 \\ 1 & m \end{vmatrix} \qquad D_3 = \begin{vmatrix} m_1 & m_3 & 0 \\ 1 & m_2 & 0 \\ 0 & m_1 & m_3 \end{vmatrix} = m_3(m_1m_2-m_3)$$

Theorem 6.2 (Routh-Hurwitz criterion)

If all the determinants D_k are positive, then all roots of 6.2 have negative real parts.

It is therefore possible to get information on stability without calculating the roots of 6.2. The proof of Theorem 6.2 cannot be given here. Applications of the Routh-Hurwitz criterion can be found in [1] and [9].

A very powerful tool in the study of stability, especially in nonlinear systems, is the direct method of liapunov. t consists in the use of certain auxiliary functions, called liapunov functions, which will be defined now.

Definition 4.

A function $V:R^n \to R$ is called positive (negative) definite in a subset $\Omega \subset R^n$, if $V(X) \geq 0$ (≤ 0) for all $X \in \Omega$ and $V(X) = 0$ if and only if $X = 0$.

Definition 5.

Let Ω be an invariant set with respect to 1.1. A liapunov function for the equation 1.1 is a function $V:R^n \to R$ with continuous partial derivatives and the following properties:

(L 1) V is positive definite in Ω

(L 2) $\sum_{i=1}^{n} \frac{\partial V}{\partial x_i} f_i \leq 0$ for all $t > t_o$ and $x \in \Omega$

Note: If X(t) is a solution of 1.1 that remains in Ω, and V is a liapunov function for 1.1, then W(t): = V(X(t)) is descreasing, since

$$W'(t) = \sum_{i=1}^{n} \frac{\partial V}{\partial x_i} x_i' = \sum_{i=1}^{n} \frac{\partial V}{\partial x_i} f_i \leq 0$$

As an example we consider the system 4.5 for which $V = ax_1^2 + bx_2^2$ is a liapunov function. Indeed, $\frac{\partial V}{\partial x_1} f_1 + \frac{\partial V}{\partial x_2} f_2 = -2(a^2x_1^2 + abx_1x_2 + b^2x_2^2) = -(ax_1^2 + bx_2^2) - (ax_1 + bx_2)^2 \leq 0$.

Theorem 6.3

Let $F(t,0) = 0$ for all t and let Ω be an invariant set with respect to 1.1 such that $0 \in \Omega$ and the intersection of Ω with any set $\{X: ||X|| = c\}$ is compact. If there exists a liapunov function such that L 2 is satisfied for all $X \in \Omega$,

then the identically zero solution of 1.1 is Ω-stable.

Note: The compactness condition is satisfied, if, e.g.
$\Omega = \{X \in R^n : X \geq 0\}$

Proof: Given $\varepsilon > 0$, consider the set S of all $X \in \Omega$ such that $||X|| = \varepsilon$. S is compact and therefore $\omega := \min_S V(X)$ exists and is > 0, since $V(X) > 0$ for $X \neq 0$. Now choose δ, $0 < \delta < \varepsilon$ such that $V(X) < \omega$ for $||X|| < \delta$. If $X(t)$ is a solution of 1.1 with $X(t_0) = X_0 \in \Omega$, $||X_0|| < \delta$, then $V(X_0) < \omega$. Since Ω is invariant, $X(t)$ remains in Ω and $V(X(t))$ is decreasing for all $t > t_0$, hence $V(X(t)) < \omega$ and hence $||X(t)|| \neq \varepsilon$ for all $t > t_0$. But $||X_0|| < \varepsilon$ and therefore $||X(t)|| < \varepsilon$ for all $t > t_0$.

In the next theorem we suppose that F doesn't depend on t. Hence we consider

(6.4) $\qquad X' = F(X)$

Theorem 6.4

Let $F(0) = 0$ and let Ω be an invariant set with respect to 6.4 such that $0 \in \Omega$ and the intersection of Ω with any set $\{X : a < ||X|| < b\}$ is compact (e.g. $\Omega = R^n$ or $\Omega = \{X : X \geq 0\}$). If there exists a liapunov function V such that $\sum_{i=1}^{n} \frac{\partial V}{\partial x_i} f_i$ is negative definite in Ω, then the zero solution of 6.4 is asymptotically Ω-stable.

Proof: Since the conditions of Theorem 6.3 are satisfied, the zero solution is Ω-stable. Hence, given $\varepsilon > 0$, there exists a $\delta > 0$, such that any solution $X(t)$ with $X(t_o) = X_o \in \Omega$, $||X(t_o)|| < \delta$ satisfies $||X(t)|| < \varepsilon \; \forall \; t > t_o$. For such a solution $V(X(t))$ is decreasing. Suppose there exists an $\eta > 0$ such that $V(x(t)) \geq \eta \; \forall \; t > t_o$. Since $V(0) = 0$ and V is continuous, to η there exists an $\tilde{\eta}$ such that $||X|| < \tilde{\eta}$ implies $V(X) < \eta$. But then $V(X)) \geq \eta$ implies $||X(t)|| \geq \tilde{\eta}$ $\forall \; t > t_o$. Let S be the set of all $X \in \Omega$ such that $\tilde{\eta} \leq ||X|| \leq \varepsilon$. Then $\omega := \max_S \sum \frac{\partial V}{\partial x_i} f_i < 0$, and $V(X(t))-V(X(t_o)) = \int_{t_o}^{t} \sum \frac{\partial V}{\partial x_i} f_i \, dt < \omega(t - t_o) \; \forall \; t > t_o$, hence $V(X(t)) \to -\infty$ which is impossible. Therefore such an η cannot exist, i.e. $\lim_{t\to\infty} V(X(t)) = 0$.

Now suppose that $\lim_{t\to\infty} X(t) \neq 0$ or that this limit doesn't exist, then there is a convergent sequence $X(t_1), X(t_2), \ldots$, such that $\lim_{n\to\infty} X(t_n) = X^{*} \neq 0$, and then $\lim_{n\to\infty} V(X(t_n)) = V(X^{*}) \neq 0$ because V is continous and positive definite. This is a contradiction therefore $X(t)$ tends to zero as t tends to ∞.

There is no general procedure to construct liapunov functions for arbitrary systems, but some succenful recipes are proposed in [17]. An interesting application of Theorem 6.4 is given in [14] (see also sec. 8 b).

7. Two dimensional system.

The system 1.1 is called autonomous, if F doesn't depend on t. We consider the autonomous system

(7.1) $\qquad x' = f(x,y) \qquad y' = g(x,y)$

A solution of 7.1 may be represented as a curve in (x,y,t) space with tangent vector (x',y',1). Its projection onto the (x,y) plane, the phase plane, has tangent vector (x',y') and direction $\frac{y'}{x'} = \frac{g(x,y)}{f(x,y)}$. This projection is called the path or trajectory of the solution and satisfies the DE

(7.2) $\qquad \frac{dy}{dx} = \frac{g(x,y)}{f(x,y)}$

A design which exhibits the shape of the solution paths in the phase plane, is called a phase potrait of 7.1. A singular point of 7.2 is a point, where f and g both are zero. The singular points of 7.2 are steady states of 7.1. The theory of stability gives sufficient conditions, that solutions near a steady state tend to this steady state. The following classification of singular points is a refinement of stability theory for two dimensional systems.

We start with the linear system

(7.3) $\qquad x' = ax + by \qquad y' = cx + dy$

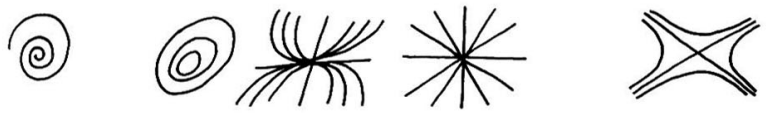
where $ad - bc \neq 0$. The only singular point is (0, 0).

The characteristic equation of 7.3 is

$$(7.4) \qquad \begin{vmatrix} a-\lambda & b \\ c & d-\lambda \end{vmatrix} = \lambda^2-(a + d)\lambda + (ad-bc) = 0$$

We saw in sec. 4 how to determine the solutions of 7.3 from the roots λ_1, λ_2 of 7.4. It can be proved, that the nature of the singularity (0,0) is completely determined by the values of λ_1 and λ_2 (see e.g. [20], p. 75 f). The singular point is called

a) focus (or spiral point)	if λ_1 and λ_2 are complex
b) vortex (or center)	if λ_1 and λ_2 are purely imaginary
c) node	if λ_1 and λ_2 are real and of equal sign
d) degenerate node	if $\lambda_1 = \lambda_2$
e) saddle point	if λ_1 and λ_2 are real and of opposite sign



a) focus b) vortex c) node d) degenerate node e) saddle point

a)-e): Phase protraits near singular points

Now we consider the general nonlinear system 7.1 and suppose that f and g are twice differentiable and that (0,0) is an isolated singular point. Applying Taylor's theorem we get

$$(7.5) \qquad \begin{aligned} x' &= ax + by + \phi(x,y) \\ y' &= cx + dy + \psi(x,y) \end{aligned}$$

where $a = \frac{\partial f(0,0)}{\partial x}$, $b = \frac{\partial f(0,0)}{\partial y}$, $c = \frac{\partial g(0,0)}{\partial x}$, $d = \frac{\partial g(0,0)}{\partial y}$

$$\lim_{|x| + |y| \to 0} \frac{|\phi(x,y)| + |\psi(x,y)|}{|x| + |y|} = 0 \qquad ad - bc \neq 0$$

Except for the case of the vortex and the degenerate node, the phase protraits of 7.5 and 7.3 are topologically equivalent. This means that perhaps straight lines become distorted in the nonlinear case, but e.g. intersection properties don't change. Sometimes but not always, this is also true for the vortex. Let's consider the system

$$(7.6) \qquad \begin{aligned} x' &= x(a_1 - b_1 y) \\ & \qquad\qquad a_i, b_i > 0 \\ y' &= y(-a_2 + b_2 x) \end{aligned}$$

which has, besides (0,0), the singular point $x = \frac{a_2}{b_2}$, $y = \frac{a_1}{b_1}$.

By the substitution $\bar{x} = x - \frac{a_2}{b_2}$, $\bar{y} = y - \frac{a_1}{b_1}$ we get the system

(7.6') $x' = -b_1 y \left(x + \frac{a_2}{b_2}\right)$

$y' = b_2 x \left(y + \frac{a_1}{b_1}\right)$

with linear part $x' = -b_1 \frac{a_2}{b_2} y$, $y' = b_2 \frac{a_1}{b_1} x$ and the characteristic equation $\lambda^2 + a_1 a_2 = 0$. Hence the roots are purely imaginary and the singular point of the linearized equation is a vortex. The solutions are ellipses with (0,0) as center. Lotka ([10]) has shown that the nonlinear system 7.6 has an infinite family of periodic solutions, whose paths in the phase plane are closed nested curves surrounding the singular point. Hence this point is a vortex (see also sec. 8c).

At greater distance from a singular point, however, the nonlinear system in general exhibits qualitatively distinct features. Consider for example, the system

(7.7) $x' = y + x(1 - x^2 - y^2)$ $y' = -x + y(1 - x^2 - y^2)$

For the linearized system

(7.7a) $x' = x + y$ $y' = -x + y$

the singular point (0,0) is a focus. In polar coordinates

$x = r \cos \phi$ $r^2 = x^2 + y^2$ $r' = \frac{xx' + yy'}{r}$

$y = r \sin \phi$ $\phi = \operatorname{artg}(y/x)$ $\phi' = \frac{y'x - yx'}{r^2}$

the nonlinear system becomes

(7.7') $\qquad r' = r(1 - r^2) \qquad \phi' = -1$

According to 3.3, $t + C = \int \frac{dr}{r(1-r^2)} = \int \{\frac{1}{r} + \frac{r}{1-r^2}\}\, dr = \ln|r| - \frac{1}{2}\ln|1 - r^2|$, which yields, after some algebra,

$$r = \frac{1}{\sqrt{1+kc^{-2t}}} \qquad k \text{ arbitrary}$$

Hence the solutions are spirals, which approach the circle $r = 1$ from inside if $k > 0$, and from outside if $k < 0$. The circle $r = 1$ is itself the path of a periodic solution, corresponding to $k = 0$. A closed path such as the circle $r = 1$ in this example is called a limit cycle. Linear systems cannot posses limit cyles.

The following condition for the existence of a limit cycle is due to Poincaré and Bendixson: If there is an annular region free from singularities, such that all solution paths cross the boundary towards the interior of the annulus, then there exists at least one limit cycle in the annulus.

A new technique for stability and limit cycle analysis for two dimensional systems has been developped in [11]. The system is transformed to polar coordinates with a singular point as center. If this point is a focus or a vortex, then the solutions perform turns around it. The method consists then of calculating and studying the average radius of a path during

one turn. If the average radius is decreasing to zero, then the singular point is asymptotically stable; if it tends to a positive limit, then there exists a limit cycle.

Interesting applications of the theory of two dimensional systems are given in [15] and [16].

8. Some applications

a) Solutions in closed form

We consider the isothermal reversible reaction

$$(8.1) \qquad \alpha_1 A_1 + \ldots + \alpha_r A_r \underset{-1}{\overset{1}{\rightleftharpoons}} \beta_1 B_1 + \ldots + \beta_s B_s$$

Let's denote the concentration of A_i by c_i $(i=1, \ldots, r)$ and the concentration of B_i by c_{r+i} $(i=1, \ldots, s)$. The reaction rates of the forward and the reverse reaction are given by

$$g_1 = k_1 c_1^{\alpha_1} \ldots c_r^{\alpha_r}$$

$$g_{-1} = k_{-1} c_{r+1} \ldots c_{r+s}$$

The stoichiometric coefficients of the reverse reaction are the negatives of those of the forward reaction. Therefore, according to 1.5, we get

(8.2a) $$c_i' = -\alpha_i k_1 c_1^{\alpha_1} \ldots c_r^{\alpha_r} + \alpha_i k_{-1} c_{r+1}^{\beta_1} \ldots c_{r+s}^{\beta_s} =$$

$$-\alpha_i (g_1 - g_{-1}) \qquad i = 1, \ldots, r$$

(8.2b) $$c_{r+j}' = \beta_j (g_1 - g_{-1}) \qquad j = 1, \ldots, r$$

and therefore $c_i'/\alpha_i - c_k'/\alpha_k = 0 \qquad (i,k = 1, \ldots, r)$

$$c_i'/\alpha_i + c_{r+k}'/\beta_k = 0 \qquad (i=1, \ldots, r;\ k=1, \ldots, s)$$

We let i = 1 and get by integration

(8.3a) $$c_k = \frac{\alpha_k}{\alpha_1} c_1 + c_k (t_o) - \frac{\alpha_k}{\alpha_1} c_1 (t_o) \qquad k = 2, \ldots, r$$

(8.3b) $$c_{r+j} = -\frac{\beta_j}{\alpha_1} c_1 + c_{r+j} (t_o) + \frac{\beta_j}{\alpha_1} c_1 (t_o) \qquad j = 1, \ldots, s$$

Substituting $c_2, \ldots, c_{r+s}$ from 8.3 and writing x instead of c_1, we get from 8.2a

$$x' = -P (X) + Q (X)$$

where P (X) and Q (X) are polynomials of degree $\alpha = \alpha_1 + \ldots + \alpha_r$ and $\beta = \beta_1 + \ldots + \beta_s$ resp.

Now we consider more special examples. First we let r=s=1, $\alpha_1 = \beta_1 = 1$, i.e. we consider the reaction

(8.1-1) $$A \underset{-1}{\overset{1}{\rightleftharpoons}} B$$

From 8.3b we get $c_2 = -c_1 + c_2(0) + c_1(0)$. With $c_2(0) + c_1(0) = 1$ and $x = c_1$ we obtain the equation

$$x' = -ax + b(1-x) = b-(a + b)x \qquad (a=k_1,\ b=k_{-1})$$

Formula 4.2' gives the solution

$$x(t) = e^{-(a+b)t}\, x(0) + \frac{b}{a+b}\,(1-e^{-(a+b)t})$$

We observe that $\lim_{t\to\infty} x(t) = \frac{b}{a+b}$, which is the unique steady state.

Next consider the reaction

(8.1-2) $\qquad A \underset{<}{\rightleftharpoons} 2B$

where $c_1(0) = 1$, $c_2(0) = 0$ is supposed. According to 8.3b $c_2(t) = -2c_1(t) + 2$. Therefore c_1 satisfies the equation

(8.4) $\qquad x' = -k_1x + 4k_{-1}\,(1-x)^2$

In the same way it is seen, that the concentration of A in the reaction $A \underset{<}{\rightleftharpoons} B_1 + B_2$ satisfies the equation

(8.4') $\qquad x' = -k_1x + k_{-1}(1-x)^2$

if $c_1(0) = 1$, $c_2(0) = c_3(0) = 0$ is assumed.

At last consider the reactions

$2A \rightleftarrows 2B$	with	$c_1(0) = 1$	$c_2(0) = 0$
$A_1+A_2 \rightleftarrows 2B$	with	$c_1(0) = c_2(0) = 1$	$c_3(0) = 0$
$A_1+A_2 \rightleftarrows B_1+B_2$	with	$c_1(0) = c_2(0) = 1$	$c_3(0) = c_4(0) = 0$

Here c_1, the concentration of A resp. A_1 satisfies

$$x' = -k_1x^2 + mk_{-1}(1-x)^2 \tag{8.5}$$

where m=1, m=4, m=1 respectively.

We are going to show that the right member of 8.4, 8.4' and 8.5 has exactly one zero in (0, 1) and that the solution tends to this zero if the initial condition is x(0) = 1. We'll use Vieta's theorem, whereby the product of the two roots of $x^2 + rx + s = 0$ is s.

Consider $f(x) = -ax^{\alpha} + b(1-x)^{\beta}$ with $a, b > 0$; $\alpha, \beta \geq 1$.

Obviously $f(0) = b > 0$, $f(1) = a < 0$ and $f'(x) = -\alpha ax^{\alpha-1} - b\beta(1-x)^{\beta} < 0$ for $0 < x < 1$.

Therefore f has exactly one zero in (0, 1). In particular the quadratic equation $-ax+b(1-x)^2 = bx^2-(2b+a)x+b = 0$ has one

root in (0, 1) and the other root in (1, ∞), since their product is 1. The equation $-ax^2 + b(1-x)^2 = (b-a)x^2 - 2bx+b = 0$, where the product of both roots is $\frac{b}{b-a}$, has one root in (0, 1) and the other root in ($-\infty$, 0) if $b < a$, and in (1, ∞) if $b > a$. We denote the roots with α and β such that $a < b$; then f can be written in the form $f(x) = b_0(x-\alpha)\ (x-\beta)$, where $b_0 = 4k_{-1}$ for 8.4, $b_0 = k_{-1}$ for 8.4' and $b_0 = mk_{-1} - k_1$ for 8.5.

1st case: $b_0 > 0$

The preceeding arguments have shown that $0 < \alpha < 1 < \beta$. Using the time scale $\tau = b_0 t$, each of the equations 8.4, 8.4' and 8.5 is transformed into the equation

$$x' = (x-\alpha)\ (x-\beta)$$

Since $c_1(0) = x(0) = 1$, we are concerned with the 2nd case of example 3 in sec. 3. The solution is given by 3.9 and satisfies $\lim_{t\to\infty} x(t) = \alpha$.

2nd case: $b_0 < 0$

We have seen that $\alpha < 0 < \beta < 1$. Using the time scale $\tau = -b_0 t$, equation 8.5 is transformed to

$$x' = -(x-\alpha)\ (x-\beta)$$

The initial condition $x(0) = 1 > \beta$ corresponds to the 3rd case of example 3' in sec. 3. The solution is given by 3.9' and satisfies $\lim_{t\to\infty} x(t) = \beta$.

In both cases the solution tends to that constant solution, that lies in (0, 1), in accordance with observation. So far we assumed that A_1 and A_2 had equal initial concentrations. Now we consider the irreversible reaction $A_1 + A_2 \longrightarrow B$ and suppose $\gamma := c_1(0) - c_2(0) \neq 0$, where γ is such that $c_2(0) = c_1(0) - \gamma \geq 0$. With 8.3a we get $c_2 = c_1 - \gamma$ and therefore the rate equation

$$c_1' = -kc_1c_2 = -kc_1(c_1-\gamma)$$

By the change of variable $\tau = kt$ it is reduced to

$$x' = -x(x-\gamma) \qquad (x=c_1)$$

Since the right member has the zeroes 0 and γ, the solution of this DE can be derived from 3.9', putting $\alpha=0$, $\beta=\gamma$ if $\gamma > 0$, and $\alpha=\gamma$, $\beta=0$ if $\gamma < 0$. For we assumed that $\gamma \leq c_1(0) = x(0)$, hence either $0 < \gamma = \beta \leq x(0)$ or $\gamma < 0 = \beta \leq x(0)$ holds. Thus, excluding the case $x(0) = \beta$ which leads to a constant solution, we have again the 3rd case of example 3' of sec. 3. From 3.9' we get

$$x(t) = \frac{\gamma}{1-c\,\exp(-\gamma t)} \qquad \text{if } \gamma > 0$$

$$x(t) = \frac{-c\gamma \exp \gamma t}{1-c \exp \gamma t} \qquad \text{if } \gamma < 0$$

The solution, that is c_1, tends to 0 if $\gamma < 0$, and to γ if $\gamma > 0$. Since $c_2 = c_1 - \gamma$, c_2 tends to $|\gamma|$ if $\gamma < 0$, and to 0 if $\gamma > 0$. That is, the reaction tends to a state, where one of the species A_1 or A_2 has disappeared and the other is remaining with concentration $|\gamma|$.

Now consider the consecutive reversible reactions

$$A \underset{a'}{\overset{a}{\rightleftharpoons}} B \underset{b'}{\overset{b}{\rightleftharpoons}} C$$

where the rate equations are

$$\begin{aligned} x_1' &= -ax_1 + a'x_2 \\ x_2' &= ax_1 - (b+a')x_2 + b'x_3 \\ x_3' &= bx_2 - b'x_3 \end{aligned} \tag{8.6}$$

We have $x_1' + x_2' + x_3' = 0$.

For the irreversible case, i.e. $a'=b'=0$, the general solution of the first two equations is given by 4.6. If $x_1(0)=1$, $x_2(0)=x_3(0)=0$. then

$$\begin{aligned} x_1 &= e^{-at} \\ x_2 &= \frac{a}{b-a}(e^{-at}-e^{-bt}) \\ x_3 &= 1-x_1-x_2 \end{aligned} \tag{8.7}$$

x_2 has a maximum at $t = \frac{\ln a - \ln b}{a-b}$, x_1 and x_3 are monotone.

If we suppose $x_1+x_2+x_3 = 1$, we can eliminate x_3 and get from 8.6 the reduced system

$$\begin{aligned} x_1' &= -ax_1 + a'x_2 \\ x_2' &= ax_1 - (b+a')x_2 + b'(1-x_1-x_2) \end{aligned} \tag{8.8}$$

We write $m_1=a+b+a'+b'$, $m_2=ab+ab'+a'+b'$. A particular solution of the inhomogeneous system 8.8 is the constant solution $\bar{x}_1 = \frac{a'b'}{m_2}$, $\bar{x}_2 = \frac{ab'}{m_2}$. The characteristic equation of the homogeneous system is $\lambda^2 + m_1\lambda + m_2 = 0$. Since $m_1 > 0$, $D_2 = m_1m_2 > 0$, the Routh-Hurwitz condition for asymptotic stability is satisfied. The general solution of the inhomogeneous system is obtained by adding $(\bar{x}_1,\bar{x}_2)$ to the general solution of the homogeneous system. The latter tends to zero, hence any solution of 8.8 tends to $(\bar{x}_1,\bar{x}_2)$, as t tends to ∞.

b) Stability

Suppose that the isothermal reactions

$$A_1 \xrightarrow{a_1} A_2 \xrightarrow{a_2} A_3 \longrightarrow \dots \xrightarrow{a_{n-1}} A_n \xrightarrow{a_n} A_{n+1} \tag{8.11}$$

are running in a closed reaction vessel, and let x_i denote the concentration of the chemical species A_i. This process is ruled by the system of linear equations

$$
\begin{aligned}
x_1' &= -a_1 x_1 \\
x_2' &= a_1 x_1 - a_2 x_2 \\
&\;\;\vdots \\
x_n' &= a_{n-1}\, x_{n-1} - a_n x_n \qquad (a_i > 0,\ i=1, \ldots, n)
\end{aligned}
\tag{8.11a}
$$

We could add the equation $x_{n+1} = a_n x_n$ to this system, but it is more convenient to determine x_{n+1} from the identity $x_1+x_2+ \ldots + x_{n+1} = \text{const}$. System 8.11a is a recursive system and therefore can be solved easily. We start with $x_1 = ce^{-a_1 t}$. Having computed x_i, we can solve $x_{i+1}' = a_i x_i - a_{i+1} x_{i+1}$ by means of formula 4.2. Alternatively, the method of eigenvalues can be applied. The eigenvalues of the coefficient matrix are the solutions of

$$
\begin{vmatrix}
-a_1-\lambda & 0 & \cdots & \cdots & 0 \\
a_1 & -a_2-\lambda & & & 0 \\
0 & a_2 & \ddots & & \vdots \\
\vdots & \ddots & \ddots & \ddots & \\
0 & \cdots & 0 & a_{n-1} & -a_n-\lambda
\end{vmatrix}
= (-1)^n(\lambda+a_1)(\lambda+a_2)\ldots(\lambda+a_n) = 0
$$

and are exactly the negative real numbers $-a_1, -a_2, \ldots, -a_n$.

This proves, that the zero solution of 8.11a is asymptotically stable. Now we pass to the nonlinear case. Let A_k in 8.11 be replaced by $\nu_{1k}A_{1k} + \ldots + \nu_{r_k k} A_{r_k k}$ $(\nu_{ik} > 0)$. c_{ik}, the concentration of the species A_{ik}, is related to c_{1k} by equation 8.3a, where c_i and c_1 are to be replaced by c_{ik} and c_{1k} resp. We write

$$\varepsilon_i = \frac{\nu_{i1}}{\nu_{11}} \qquad \gamma_i = c_{i1}(0) - \varepsilon_i C_{11}(0) \qquad i=2, \ldots, r_1$$

$$A_k = \sum_{i=1}^{r_k} \nu_{ik} \qquad x_k = c_{1k} \qquad k=1, \ldots, n$$

and suppose $c_{i1}(0) > 0$ $\qquad i=1, \ldots, r_1$

$$\gamma_i \geq 0 \qquad i=2, \ldots, r_1$$

$$c_{ik}(0) = 0 \qquad i=1, \ldots, r_k;\ k=2, \ldots, n+1$$

With these conventions the rate equations for the sequence of reactions

$$\nu_{11} A_{11} + \ldots + \nu_{r_1 1} A_{r_1 1} \longrightarrow \nu_{12} A_{12} + \ldots + \nu_{r_2 2} A_{r_2 2} \longrightarrow \ldots$$

take the form

(8.12)

$$\begin{aligned} x_1' &= -\nu_{11} g_1(x_1) &&= f_1 \\ x_2' &= \nu_{12} g_1(x_1) - \nu_{12} g_2(x_2) &&= f_2 \\ &\vdots &&\vdots \\ x_n' &= \nu_{1n} g_{n-1}(x_{n-1}) - \nu_{1n} g_n(x_n) &&= f_n \end{aligned}$$

where

$$g_1 = k_1 x_1^{\nu_{11}} \prod_{i=2}^{r_1} (\varepsilon_i x_1 + \gamma_i)^{\nu_{i1}} \qquad (k_1 > 0)$$

$$g_j = k_j x_j^{\alpha_j} \qquad (k_j > 0) \qquad j = 2, \ldots, n$$

Theorem 8.1

Any solution of 8.12, which satisfies $X(0) \geq 0$, exists and is nonnegative for all $t \geq 0$. It tends to the zero solution as t tends to ∞.

Proof: Obviously f_i satisfies condition (i) of theorem 2.1. Now

$$\sum_{i=1}^{n} \frac{f_i}{\nu_{1i}} = -g_1 + (g_1 - g_2) + \ldots + (g_{n-1} - g_n) = -g_n, \text{ and } -g_n(x_n) \leq 0$$

for $x_n \geq 0$. Therefore condition (ii) is satisfied, too. Furthermore, the functions f_i are lipschitzian. Hence for any $X_o \geq 0$ there exists a unique solution that satisfies $X(0) = X_o$ and is defined and nonnegative for all $t \geq 0$. Now we will construct a Liapunov function and show that the zero solution of 8.12 is asymptotically stable, the invariant set being $\Omega = \{X \in R^n: X \geq 0\}$. Choose positive numbers $p_1, \ldots, p_n$ such that $p_n = 1$ and

$$\eta_k := \nu_{1k} p_k - \nu_{1,k+1}\, p_{k+1} > 0 \qquad k=1, \ldots, n-1$$

We define $V(X) = \sum_{k=1}^{n} p_k\, x_k$. V is positive definite in Ω, and for $X \in \Omega$ we have

$$\sum_{k=1}^{n} \frac{\partial V}{\partial x_k} f_k = \sum_{k=1}^{n} p_k\, f_k(X) = (-p_1\nu_{11}+p_2\nu_{12})g_1(x_1) + \ldots\ldots$$

$$\ldots + (-p_{n-1}\, \nu_{1,n-1} + p_n\, \nu_{1n})\, g_{n-1}\, (x_{n-1}) - \nu_{1n}\, g_n(x_n)$$

$$= -\sum_{k=1}^{n} \eta_k\, g_k\, (x_k)$$

where we have put $\eta_n = \nu_{1n}$. Therefore $\sum \frac{\partial V}{\partial x_k} f_k$ is negative definite and the assertion now follows by theorem 6.4.

For general reversible reactions Shear ([14]) has proven asymtotic stability of the steady state. He assumes that rate equations derived from the law of mass action describe the behaviour of the reaction system at constant temperature, pressure and volume. The system may be open to matter and energy fluxes so long as the species that are free to move in and out of the system do not explicitly appear in the rate expressions. It is further assumed that there is exactly one stationary solution $(\bar{c}_1, \bar{c}_2, \ldots, \bar{c}_n)$ of the rate equations. Then the function

$$V(c_1, c_2, \ldots, c_n) = \sum_{k=1}^{n} \{c_k \ln \frac{c_k}{\bar{c}_k} - c_k + \bar{c}_k\}$$

is considered. With $x_k = \frac{c_k - \bar{c}_k}{\bar{c}_k}$ we can write

$$V(c_1, c_2, \ldots, c_n) = \tilde{V}(x_1, \ldots, x_n) = \sum_{k=1}^{n} \bar{c}_k [(1+x_k) \ln(1+x_k) - x_k]$$

It is shown that $\tilde{V}$ is positive and $\sum \frac{\partial V}{\partial x_k} f_k$ negative definite. Hence the steady state $(\bar{c}_1, \bar{c}_2, \ldots, \bar{c}_n)$ that corresponds to X=0 is asymptotically stable.

A different approach is used by Gavalas [5] in his analysis of the number and stability of steady states. If $\bar{X}$ is a stationary solution of 6.4, i.e. $F(\bar{X}) = 0$, and if F is twice differentiable, then

$$f_k(X) = \sum_{i=1}^{n} (x_i - \bar{x}_i) \frac{\partial f_i(\bar{X})}{\partial x_k} + \text{higher order terms}$$

and $\bar{X}$ is asymptotically stable, if all the eigenvalues of the matrix $F = [\frac{\partial f_i(\bar{X})}{\partial x_k}]$ have negative real part. He assumes, that there exists a region $\Omega \subset R^n$ such that the vector F(X) points to the interior of Ω for all X on the boundary of Ω (this condition is satisfied e.g., if conditions (i) and (ii) of theorem 2.1 hold with m=M=0). Using the topological index he shows, that the number of steady states is odd, 2m+1, among which m at least are unstable. In the case of one reaction, exactly m of the steady states are unstable and the remaining m+1 are stable. In particular, if the steady state is unique, it is also stable.

The laws of thermodynamics give rise to some special Liapunov functions. J. Wei [19] has indicated, that excess entropy and Gibbs free energy are Liapunov functions for adiabatic and isothermal reacting systems, respectively.

c) Oscillations

A function of one variable is called oscillating, if it has infinitely many maxima and minima. Oscillations of a system governed by an autonomous equation (see sec. 7) are called free oscillations, while oscillations caused by a time-dependent periodic forcing term are called forced oscillations. If an oscillating system admits a sort of energy or potential function that is constant along the solutions, then it performs conservative oscillations, and limit cycle oscillations (see sec. 7) else. Oscillations with decreasing (constant) amplitudes are called damped (sustained) oscillations.

Oscillations in chemical reaction systems are very rare. Prigogine [13] has proved that sustained oscillation is not possible in a closed system, regardless of the order of the reactions taking place.

Hearon [7] showed, that neither damped nor sustained oscillations are possible in a closed isothermal system of first-order reactions, when the principle of detailed balancing

holds. Gray [6], also using detailed balancing, proved that the steady state of a system of reactions of arbitrary order is approached without oscillation. There may be several maxima and minima (so-called undershoot-overshoot), but their number is limited by the number of reactants. We will prove a stronger result for the case of consecutive irreversible reactions.

Theorem 8.2

The component x_k of any solution of 8.12 has at most k-1 relative maxima and minima.

Proof: First we'll prove by induction that $x_k(t) > 0 \; \forall t > 0$, $k = 1, \ldots, n$. For convenience we put $\nu_{1k} = 1$. Since zero is a solution of $x_1' = -g_1(x_1)$, and $x_1(0) > 0$, it follows by the uniqueness theorem that $x_1(t) > 0 \; \forall t \geq 0$. Now suppose that $x_k(t) > 0 \; \forall t > 0$. If $x_{k+1} \equiv 0$ in $[0, \delta]$ for some $\delta > 0$, then $x_{k+1}' = g_k(x_k) > 0$ in $[0, \delta]$ and $x_{k+1}' \geq h > 0$ in $[\frac{\delta}{2}, \delta]$, hence $x_{k+1}(\delta) \geq \frac{1}{2} h\delta > 0$, a contradiction. Therefore a $\delta' > 0$ exists, such that $x_{k+1}(t) > 0$ for $0 < t \leq \delta'$. Since $x_k > 0$, $g_k(x_k) > 0$, we have $x_{k+1}' > -g_{k+1}(x_{k+1})$ for $t \geq \delta'$ and $x_{k+1}(\delta') > 0$. Therefore, applying the comparison theorem to x_{k+1} and the zero solution of $u' = -g_{k+1}(u)$, we obtain $x_{k+1}(t) > 0$ for $t \geq \delta'$, hence for all $t > 0$. In the final step we'll use the property that $g_j'(u) > 0$ and $g_j(u) > 0$ for $u > 0$ $(j=1,\ldots,n)$ and the fact, that between two maxima there is at least one minimum, and vice versa. We'll prove that x_k has at most k-1 relative extrema and that $x_k'' \neq 0$ in each extremal point.

Again we proceed by induction. For k=1 the statement is true, since $x_1 > 0$ and $x_1' = -g_1(x_1) < 0 \forall t \geq 0$. It is impossible, that $x_k' \equiv 0$ in some interval, because this would imply that $0 \equiv x_k'' = x_{k-1}' g_{k-1}'(x_{k-1})$ and thus $x_{k-1}' \equiv 0$ in the same interval, etc. But this leads to a contradiction, since $x_1' < 0 \forall t \geq 0$. Now suppose, that x_k has at most k-1 extrema and that $x_k'' \neq 0$ in the extremal points. Then there exist at most k open intervals, such that x_k' is zero only at the endpoints and has constant sign in each interval and opposite sign in subsequent intervals. Now, if x_{k+1} has an exremum in $t_o > 0$, then $x_{k+1}'(t_o) = 0$ and $x_{k+1}''(t_o) = x_k'(t_o)\, g_k'(x_k(t_o))$, hence

$$\text{sign } x_{k+1}''(t_o) = \text{sign } x_k'(t_o) \tag{8.14}$$

Therefore, each of the above mentioned intervals, k in number contains either only maxima or only minima, and consequently contains at most one maximum or minimum. Can there be extrema at the endpoints of those intervals? This would imply for some $t_1 > 0$, $x_k'(t_1) = x_{k+1}'(t_1) = x_{k+1}''(t_1) = 0$, hence $x'''_{k+1}(t_1) = x_k''(t_1)\, g_k''(x(t_1)) \neq 0$. But then t_1 is not extremum of x_{k+1} but an inflection point. Therefore x_{k+1} has not more than k extrema $\tau_1, \ldots, \tau_k$; we have $x_k'(\tau_i) \neq 0$ and, according to 8.14, $x_{k+1}''(\tau_i) \neq 0$ (i=1, ..., k).

Oscillation is possible, however, in open systems and in autocatalytic reactions. Recently much work has been done in this

field, because it is believed, that the rise of oscillations in chemically reacting systems is a decisive step in the development of life (see [15], [16]). A survey by Noyes and Field [12] with a large bibliography has appeared in 1974.

As early as 1920 A. Lotka [10] considered the hypothetic autocatalytic reaction

(8.15)
$$A + X \xrightarrow{1} 2X$$
$$X + Y \xrightarrow{2} 2Y$$
$$Y \xrightarrow{3}$$

where a, the concentration of A, is assumed to be constant. The rate equations are

(8.15a)
$$x' = k_1 ax - k_2 xy$$
$$y' = -k_3 y + k_2 xy$$

which gives the system 7.6, if we write $a_1 = k_1 a$, $a_2 = k_3$, $b_1 = b_2 = k_2$. We define $V(x,y) = -a_2 \ln x + b_2 x - a_1 \ln y + b_1 y$. It is easy to prove that V has a minimum in $(\frac{a_2}{b_2}, \frac{a_1}{b_1})$ and that $\frac{dV}{dt} = 0$. We can add a constant to V such that $V(0, 0) = 0$, then V will be a Liapunov function for 8.15a. The steady state $(\frac{a_2}{b_2}, \frac{a_1}{b_1})$ is therefore stable, but not asymptotically stable. The solution paths in the phase plane are the curves $V(x,y) = \text{const}$. These curves are closed lines around the point

$(\frac{a_2}{b_2}, \frac{a_1}{b_1})$, where V has its minimum.

There is an infinite family of conservative oscillations, each corresponding to a particular constant value of V. It should be noted, that this doesn't contradict the stability theorem of Shear (sec. 8b), since the species Y, that moves out of the system, appears in the rate equations.

In [15] the autocatalytic reaction

(8.16)
$$\begin{aligned} A &\longrightarrow X \\ B + X &\longrightarrow Y + D \\ 2X + Y &\longrightarrow 3X \\ X &\longrightarrow E \end{aligned}$$

is considered, where the concentrations of A,B,D and E are held constant. With methods of nonlinear mechanics (see e.g. Minorsky, Nonlinear Oscillations) the existence of a limit cycle is proved. Reactions of the type 8.15 and 8.16 have not yet been really observed. But they are "realistic" in the sense, that they don't violate any laws of chemistry or physics. Moreover, it is shown in [15], that 8.16 is the simplest chemically realistic example of limit cycle oscillations. Tyson [16] has tried to show that chemical reactions "can exhibit all of the interesting and well known behaviour of nonlinear oscillators". Zhabotinski and others have observed

oscillations in actual chemical reactions, but the corresponding rate equations are rather complicated and have not yet been investigated (see [15]).

Bibliography

[1] R. Aris and N.R. Amundson,
An analysis of chemical reactor stability and control I,
Chem. Eng. Science 7 Nr. 3, 121-131 (1958).

[2] R. Becker,
Theorie der Wärme, Heidelberg 1975.

[3] J.R. Bowen, A. Acrivos and A.K. Oppenheim,
Singular perturbation refinement to quasi-steady state approximation in chemical kinetics, Chem. Eng. Science 18, 177-188 (1963).

[4] K. Dialer und A. Löwe,
Chemische Reaktionstechnik, Carl Hanser Verlag, München Wien 1975.

[5] G.R. Gavalas,
Nonlinear differential equations of chemically reacting systems, Springer Tracts in Natural Philosophy vol. 17, Springer Verlag 1968.

[6] F. Gray,
Oscillatory approach to equilibrium in closed chemical systems, Trans. Faraday Soc. 66, 363-371 (1970).

[7] J.Z. Hearon,
Bull. Math. Biophys. 15, 121- (1953).

[8] F.G. Heiniken, H.M. Tsuchiya and R. Aris,
On the mathematical status of the pseudo-steady state hypothesis of biochemical kinetics, Math. Biosciences 1, 95-113 (1967).

[9] S.L. Liu and N.R. Amundson,
Polymerization reactor stability, Z. Elektrochemie 65, 276-282 (1961).

[10] A. Lotka,
Undamped oscillations derived from the law of mass action, J. Am. Chem. Soc. 42, 1595-1599 (1920).

[11] R. Luus and L. Lapidus,
An averaging technique for stability analysis, Chem. Eng. Science 21, 159-181 (1966).

[12] R. M. Noyes and R.J. Field,
Oscillatory chemical reactions, Ann. Rev. Phys. Chem. 25, 95-119 (1974).

[13] I. Prigogine,
Thermodynamic of irreversible processes, Interscience 1967.

[14] D. Shear,
An analog of the Boltzmann H-Theorem (a Liapunov function) for systems of coupled chemical reactions, J. Theoret. Biol. 16, 212-228 (1967).

[15] J.J. Tyson and J.C. Light,
Properties of two-component bimolecular and trimolecular chemical reaction systems, J. Chem. Phys. 59, 4164-4173 (1973).

[16] J.J. Tyson,
Some further studies of nonlinear oscillations in chemical systems, J. Chem. Phys. 58, 3919-3930.

[17] R.B. Warden, R. Aris and N.R. Amundson,
An analysis of chemical reactor stability and control - VIII, Chem. Eng. Science 19, 149-172, -IX-, Chem. Eng. Science 19, 173-190 (1964).

[18] A.B. Vasiljeva,
Russian Math. Surveys 18, 13- (1963).

[19] J. Wei,
Axiomatic treatment of chemical reaction systems, J. Chem. Phys. 36, 1578- (1962).

[20] W. Hurewicz,
Lectures on ordinary differential equations, M.I.T. Press, 1958.

[21] S. Lefschetz,
Differential equations: geometric theory, Interscience 1957.

[22] R.D. Driver,
Ordinary and delay differential equations, Springer Verlag 1977, Applied mathematical sciences, vol. 20.