~~DISPLAY~~ ~~REFERENCE~~
COPY NOT TO BE REMOVED FROM THE LIBRARY

TRITA - NA 7515

64

BIBLIOTHEQUE
20.04.76

CERN

THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM
SWEDEN

DEPARTMENT OF
INFORMATION PROCESSING
COMPUTER SCIENCE

CERN LIBRARIES, GENEVA

CM-P00069401

TRITA-NA-7515

Inst för Informationsbehandling
KTH
100 44 STOCKHOLM 70

Dept of Information Processing
The Royal Institute of Technology
S-100 44 STOCKHOLM 70, Sweden

NUMERICAL METHODS FOR
MASS ACTION KINETICS

by
Lennart Edsberg
TRITA-NA-7515

Presented at 80th National Meeting A.I.Ch.E., Boston September 1975.

NUMERICAL METHODS FOR MASS ACTION KINETICS.

Lennart Edsberg

Department of Information Processing Computer Science

The Royal Institute of Technology Stockholm Sweden

1. Introduction.

One of the simplest reactor models occurring in chemical technology is the isothermal batch reactor operating under constant volume. The simplicity is not only a consequence of the idealized conditions under which the reactor is supposed to be working but also that the mathematical description becomes simple at least formally.

The physical and chemical conditions under which this model is valid is that a number of reactions, say n , simultaneously take place between m species in a physical environment where the contributions from diffusion and convection are neglected, only the chemical kinetics contribute to the rate terms. Assume that the chemical species G_i , $i=1, 2, \dots, m$ react in n elementary reactions

where the matrices P and Q with entries p_{ij} and q_{ij} respectively are the reactant and product matrices respectively. Introduce the stoichiometric matrix

$$S = P - Q \quad (1.2)$$

and the concentrations c_i , $i=1, 2, \dots, m$ of the species and the kinetics of the system can be described by the following set of ordinary differential equations (ODE's), see e.g. (Gavalas 1968)

$$\dot{\bar{c}} = S \bar{r}(\bar{c}) \quad (1.3)$$

where $\bar{r}^T = (r_1, r_2, \dots, r_n)$ is a vector of rate functions r_i which depend on intensive thermodynamical variables of which temperature T and concentrations c_i (moles/unit volume) are the most important.

(1.3) is a simple consequence of mass conservation of the species G_i . The big problem is to obtain analytical expressions for the rate functions r_i . Several theories have developed for the prediction of the rates of elementary reactions. Collision theory in gases and transition state theory are examples, cf Banford, Tipper (1969). A rule which is used very often is the mass action law which states that the reaction rates are

$$r_j = K_j \prod_{k=1}^m c_k^{p_{kj}} \quad (1.4)$$

where K_j is some temperature dependent constant, the rate constant.

Although sometimes criticized (see e.g. Oster and Perelson (1974)) for its lack of consistency with thermodynamics the mass action law is one of the most frequently used "law" in practical engineering as well as in chemical mechanism models.

The very restrictive physical and chemical assumptions adhered to the model (1.3) imply that this model very seldom can be used in practise. However, with just a few additional modifications models are obtained which do occur frequently in practise.

A. If we allow continuous inlet and outflow of species (still under the assumption of constant reactor volume) the model is (see e.g. Aris 1965)

$$\dot{\bar{c}} = \frac{1}{\theta} (\bar{c}_f - \bar{c}) + S \bar{r}(\bar{c}) \quad (1.5)$$

which is the well-known CSTR (Continuousflow Stirred Tank Reactor). Here θ is the holding time and $\bar{c}_f^T = (c_{1f}, c_{2f}, \dots, c_{mf})$, c_{if} being the concentration of G_i in the inflow. Under certain circumstances the CSTR can be treated with the same formalism as the batch reactor, see Feinberg and Horn (1974).

B. If we cannot neglect the temperature variations due to the reactions taking place we must add an ODE for the energy balance

$$\dot{T} = \frac{1}{\theta} (T_f - T) + \Delta H \bar{r} + Q(T) \quad (1.6)$$

where T_f is the inlet temperature, ΔH_i is the heat of reaction i , $Q(T)$ is some function describing the cooling or heating of the reactor. The

temperature is coupled to (1.3) nonlinearly since K_j in (1.4) depends on T in a way which is often modelled by Arrhenius' law

$$K_j = k_j \exp(-E_j/RT) \quad (1.7)$$

where k_j is the so called frequency factor, E_j the activation energy and R the universal gas constant.

C. The steady state of the PFTR (Plug Flow Tubular Reactor) can be modelled by ODE's very similar to (1.3). If F_i is the molar flux (moles/unit area and unit time) of component G_i the ODE's are

$$\bar{F}' = S \bar{r}(\bar{c}) \quad (1.8)$$

where ' denotes differentiation with respect to the length coordinate of the reactor. If the ideal gas law is assumed to be valid, we have the following coupling between c_i and F_i

$$\bar{c} = \frac{p}{RT} \frac{\bar{F}}{F} \quad \text{where } F = \sum F_i \quad (1.9)$$

see e.g. Aris (1965). For further references see Grover (1967) and Edsberg (1975).

If diffusion and/or convection cannot be neglected the models usually become much more difficult comprising nonlinear partial differential equations, see e.g. Himmelblau and Bischoff (1968).

From the models just described it is obvious that (1.3) plays a very important part in the mathematical treatment of chemical reactors. We will here treat the initial value problem, i.e.

$$\bar{c}(t_0) = \bar{c}_0 \quad (1.10)$$

is given together with (1.3).

In this paper we will treat the numerical solution of the initial value problem (1.3), (1.10). In many applications the corresponding ODE's will be stiff due to the wide spread in magnitude of the rate constants K_j . The reason for special investigation of these systems are twofold:

1. The right hand sides have a special structure which can be

utilized in the numerical implementation of a stiff method. Efficiency can then be gained compared to using a general purpose method.

2. Certain numerical difficulties have been observed on some practical examples; general purpose programs have failed on some test examples.

2. Some mathematical properties of mass action kinetics.

Assuming the validity of the mass action law the ODE's can be constructed once the elementary reactions are given. The matrices P and Q are uniquely determined from the reaction network. It is convenient to introduce a special notation for (1.3) when (1.4) is used.

Definition 1. Let $\bar{x}$ be $n \times 1$, $\bar{y}$ be $m \times 1$, A $m \times n$. Then $\bar{y} = \bar{x}^A$ means

$$y_i = \prod_k x_k^{a_{ik}}$$

Definition 2. $\text{dg}\bar{x} = X$, where X is diagonal and $X_{ii} = x_i$.

(1.3), (1.4) and (1.10) can now be written

$$\dot{\bar{c}} = S K \bar{c}^{-P^T}, \quad \bar{c}(0) = \bar{c}_0 \quad (2.1)$$

where $K = \text{dg}K_i$. (2.1) is in general a nonlinear set of ODE's. In the special case every column of P consists of only one element = 1, which we have in first order kinetics (see Wei and Prater 1962), we have a linear system with constant coefficients.

Example 1. The well-known enzyme-substrate model

is described by

$$\begin{aligned} \dot{x}_1 &= -k_1 x_1 x_2 + k_{-1} x_3 + k_2 x_3 \\ \dot{x}_2 &= -k_1 x_1 x_2 + k_{-1} x_3 \\ \dot{x}_3 &= k_1 x_1 x_2 - k_{-1} x_3 - k_2 x_3 \\ \dot{x}_4 &= k_2 x_3 \end{aligned} \quad (2.2)$$

where x_1, x_2, x_3, x_4 are the concentrations of E, S, C and P

respectively. For this system we thus have the matrices S and P as follows:

$$S = \begin{pmatrix} -1 & 1 & 1 \\ -1 & 1 & 0 \\ 1 & -1 & -1 \\ 0 & 0 & 1 \end{pmatrix} \quad P = \begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix}$$

For a closed system, which is assumed when (2.1) is valid, the total mass of the reacting system is preserved. This is expressed by

$$\frac{-T-}{m} \bar{c} = \frac{-T-}{m} \bar{c}_0 = k_0 \quad (2.3)$$

where $m_i > 0$ is the molecular weight of G_i and k_0 is a constant > 0 .

We have
$$\frac{-T-}{m} \dot{\bar{c}} = 0 \quad (2.4)$$

Thus, $\dot{\bar{c}}$ belongs to a subspace L orthogonal to the vector $\bar{m}$. Since all components of $\bar{m}$ are positive the normal vector of L points out into the positive orthant. $\bar{c}$ belongs to a hyperplane L_0 parallel with L and intersecting the positive coordinate axes at intercepts $z_i > 0$.

It is consequently obvious that once $\bar{c}_0$ is chosen k_0 is determined and L_0 also. Less obvious is that for a system of ODE's of type (2.1) which has been constructed from the mass action law the solution $c_i(t) \geq 0$ if $c_{i0} \geq 0$. This, however, can be proved, see Edsberg (1975B) and as a consequence all solutions with nonnegative initial values belong to an invariant manifold Ω_0 , usually called the reaction simplex.

From numerical point of view it is convenient to have the dependent variables c_i scaled so that $0 \leq c_i \leq 1$ for all t. This can be achieved in the following way: Let

$$w_i = \frac{\min(m_i)}{\frac{-T-}{m} \bar{c}_0} c_i = \frac{\min(m_i)}{\frac{-T-}{m} \bar{c}} c_i \quad (2.5)$$

Then we have

$$w_i \leq \min(m_i)/m_i \leq 1 \quad (2.6)$$

Inserting (2.5) into (2.1) gives

$$\dot{\bar{w}} = S K' \bar{w}^{-P^T} ; \quad \bar{w}(t_0) = \bar{w}_0 \quad (2.7)$$

where $K' = q K (dg \bar{q}^{-P^T})^{-1}$, where $q = \min(m_i)/m^T c_0$ and $\bar{q} = (q, q, \dots, q)$.

Thus only K is affected by this scaling. However, if the components are scaled with different factors

$$\bar{w} = D \bar{c} \quad (2.8)$$

where D is a diagonal matrix of scaling factors, S will also be changed.

The existence and uniqueness of an equilibrium point $\bar{c}_\infty$ to (2.1) has attracted much interest recently. Very thorough treatment of these and related questions have been made by Horn and Jackson (1972A), Horn (1972B), Feinberg (1972) and Feinberg and Horn (1974). They introduce a concept they call complex balancing (closely related to the principle of detailed balancing or microscopic reversibility, cf Wei (1962) and Horn and Jackson (1972A)), CB, which can be established a priori for a system (2.1) by examining rather simple conditions on the structure of the chemical reaction system, thus no analysis of the ODE's is necessary. When CB is fulfilled they have shown that this is a sufficient condition for the existence of a unique equilibrium point $\bar{c}_\infty$ lying in the interior of Ω_0 . Thus for CB mass action systems all solutions starting in Ω_0 or on $\partial\Omega_0$ will eventually converge to $\bar{c}_\infty$. However, this is not true for all mass action kinetics; certain problems of type (2.1) may exhibit bistability (several equilibrium points) or sustained oscillations, a fact which is of great use in the modelling of certain biochemical systems, where this situation may occur in experiments.

3. Approximate methods for mass action kinetics.

In an earlier paper by Edsberg (1974) a brief survey of some methods which has been used in order to solve (2.1) approximately was made. References to other review articles on the area were also given. A rough classification of these methods can be made:

- A. Methods which treat (2.1) without any simplifying approximation like the steady-state approximation (see later). Since systems in chemical kinetics are very often stiff, explicit integration techniques are very

inefficient so implicit methods should be used in order to avoid the small stepsizes. Several program packages especially designed for chemical kinetics problems have been developed by e.g. Garfinkel (1968) (explicit technique), Curtis and Chance (1974) and Edsberg (1975A) (implicit techniques).

B. Methods which are based on some initial approximation of the system (2.1) with subsequent numerical treatment of the approximated system. One such method is the well-known steady-state approximation which assumes that the fast (stiff) components are at equilibrium while the slow (non-stiff) components generate a smooth solution. Hence we have

$$\begin{aligned}\dot{\bar{c}}_1 &= \bar{f}_1(\bar{c}_1, \bar{c}_2) \\ \dot{\bar{c}}_2 &= \bar{f}_2(\bar{c}_1, \bar{c}_2)\end{aligned}\tag{3.1}$$

where $\bar{c}^T = (\bar{c}_1^T, \bar{c}_2^T)$ and $\bar{c}_1$ corresponds to the fast variables and $\bar{c}_2$ to the slow ones. The stiff components are approximately at equilibrium due to heavy cancellations between large terms in the right hand side of (3.1) so we can write

$$\begin{aligned}\epsilon \dot{\bar{c}}_1 &= \bar{g}_1(\bar{c}_1, \bar{c}_2) \\ \dot{\bar{c}}_2 &= \bar{f}_2(\bar{c}_1, \bar{c}_2)\end{aligned}\tag{3.2}$$

where ϵ is a small parameter. The steady state approximation consists of letting $\epsilon = 0$. This zeroth order approximation of the singularly perturbed system (3.2) will give a very poor representation of the transient. More accurate techniques based on asymptotic expansion of the solution of (3.2) in powers of ϵ to the first term have been developed by Aiken and Lapidus (1974). Earlier program packages based on the steady-state approximation coupled with a Runge-Kutta technique were developed by e.g. Snow (1966) and Lawrendeau and Sawyer (1970). Another technique developed by Clark and Groner (1972) is applicable when all reactions involved are reversible, i.e. (1.1) has a forward as well as a backward rate constant (and can then be written as two irreversible reactions of type (1.1)). In their approach separation is made between the slow and the fast reactions instead of slow and fast components. The numerical technique consists of

an explicit method (of Runge-Kutta type) combined with a steepest descent and Newton technique to minimize the thermodynamic free energy function corresponding to the fast reactions in order to force them to equilibrium. Applied to the reaction system in example one (2.2) a steady state technique consists of letting $\dot{x}_3 = 0$ (usually known under the name Michaelis-Menten approximation) while a technique of the previously described type consists of letting the first reversible reaction to be in equilibrium the whole time (sometimes known as the Briggs-Haldane approximation, cf Aris (1969)).

The method to be described here is based on a stiff integration package as developed by Lindberg (1974). Utilizing certain characteristic features about mass action kinetics to be described later this method has been implemented as a program package for interactive simulation of systems of type (1.5), (1.6), i.e. the nonisothermal CSTR where the rate functions obey the mass action law, see Edsberg (1975A). The program is an extension of a previous version as described in Edsberg (1974). Lindberg's method is based on the implicit midpoint method with smoothing and extrapolation and it has turned out to be of an efficiency comparable to other good methods for stiff systems as e.g. Gear's method, cf the comparison of stiff methods by Enright, Hull and Lindberg (1975).

What will be discussed here is not the details of the program, but some special features and properties of mass action kinetics. These points of view are applicable to many other discretization methods, not only the implicit midpoint method.

3.1. The Jacobian evaluation.

In an earlier paper (Edsberg (1974)) it is shown that the Jacobian is simple to evaluate for mass action kinetics. The matrix S , which is in general rank deficient, can be represented in the following way. Let P be a permutation matrix which brings S on the form

$$P S = \begin{pmatrix} S_1 \\ S_2 \end{pmatrix}, \quad S_2 = L S_1 \quad (3.3)$$

Here S_1 has full rank r , so the rows of S_1 are linearly independent. Using (3.3)

(2.1) can (after permutation) be brought on the form

$$\dot{\bar{c}}_1 = S_1 K \bar{c}^{-P^T} \quad \bar{c}_1(0) = \bar{c}_{10} \quad (3.4)$$

and $\bar{c}_2$ which is needed in the evaluation of $\bar{c}$ is obtained from

$$\bar{c}_2 = \bar{c}_2(0) + L (\bar{c}_1 - \bar{c}_1(0)) \quad (3.5)$$

The rank deficiency depends on mass conservation described in chapter 2 and conservation of atomic species. The reduction of the number of equations from m to r is of importance for the efficiency since when using an implicit method at each step a set of nonlinear algebraic equations

$$\bar{\Phi}(\bar{x}) = \bar{x} - h\beta f(\bar{x}) + \bar{d} = 0 \quad (3.6)$$

where β is some constant characteristic of the method, must be solved by some Newton technique, i.e.

$$\bar{x}_{n+1} = \bar{x}_n - (I - h\beta f'(\bar{x}_n))^{-1} \bar{\Phi}(\bar{x}_n) \quad (3.7)$$

It can be shown that the Jacobian can be generated from the formula

$$\partial \bar{c}_1 / \partial \bar{c}_1 = S_1 K \text{dg } \bar{c}^{-P^T} P^T (\text{dg } \bar{c})^{-1} \begin{pmatrix} I \\ L \end{pmatrix} \quad (3.8)$$

as long as $c_i \neq 0$, which is usually the case as soon as the first step has been taken, see Edsberg (1975B). We see that the Jacobian is easily updated; $\bar{c}^{-P^T}$ is calculated when the right hand side is computed and $\bar{c}$ is the approximate values of the components themselves, all other matrices are constant.

3.2. Instability outside the reaction simplex.

In the previous chapter it was stated that (2.1) under certain circumstances (which in fact are fulfilled for most examples in practise) has a unique equilibrium point in Ω_0 . When (2.1) is a linear system this point will eventually be reached from any starting point in L_0 , i.e. even points where some c_{i0} are negative. Hence the equilibrium point is asymptotically stable in the whole of L_0 not only Ω_0 .

This, however, is not true for nonlinear systems of type (2.1). Horn and Jackson (1972A) have shown that for a CB system the equilibrium point is

globally asymptotically stable with respect to Ω_0 , but not with respect to L_0 . This is visualized with the simple irreversible reaction

the dynamics of which is described by

$$\dot{x} = -2kx^2; \quad x(0) = x_0 \quad (3.10)$$

which has the solution

$$x = x_0 / (1 + 2x_0 kt) \quad (3.11)$$

From this simple example we see that

1. The equilibrium point ($x_\infty = 0$) is stable only for positive perturbations of x .
 2. Once x becomes negative for some reason the solution becomes unstable.
- This 'semistability' character has turned out to be a problem for certain testexamples. For chemical problems the stiff variables often are small and as soon as they are negative due to some perturbation (e.g. rounding errors) the solution leaves Ω_0 and becomes unstable.

Example 2. The following problem occurred in practise in a model describing propane production. The reaction system

and the corresponding ODE's are after application of the mass action law

$$\dot{x}_1 = -k_1 x_1 - k_2 x_1 x_2$$

$$\dot{x}_2 = k_1 x_1 + k_3 x_3 - k_4 x_2 x_4 - 2k_5 x_2^2$$

$$\dot{x}_3 = k_2 x_1 x_2 - k_3 x_3$$

$$\dot{x}_4 = -k_4 x_2 x_4$$

$$\dot{x}_5 = k_4 x_2 x_4 + 2k_5 x_2^2$$

In the special application we had the following values of the

rate constants: $k_1 = 10^{-4}$, $k_2 = 2.9 \cdot 10^4$, $k_3 = 5 \cdot 10^3$, $k_4 = 10^4$ and $k_5 = 6.7 \cdot 10^{10}$. The initial values were $x_{10} = 0.6$, $x_{20} = 0$, $x_{30} = 0$, $x_{40} = 0.4$, $x_{50} = 0$. The general behaviour is that x_1 and x_4 slowly decrease monotonically, x_5 increases while x_2 and x_3 both reach a maximum at $t = 5.6 \cdot 10^{-3}$, with values 10^{-7} and $3.6 \cdot 10^{-7}$ respectively.

Before we continue to present the results of different runs of example 2 it is convenient to say something about the scaling problem in general for stiff systems. The following types of scaling are possible for an implicit method.

1. Scaling of the variables in the ODE's, i.e. transformation of the ODE's after application of (2.8).
2. Use of a scaled norm in the computation of the local error estimate.
3. Use of a scaled norm to measure the accuracy of the iterates obtained from the Newton-Raphson procedure.

In Lindberg's program it is possible to give scaling factors for the local error and the Newton iterations. When the problem was run without any scaling, i.e. all scaling factors were set to 1 the program immediately slipped off the solution with positive values to an unstable solution. When the local error and the errors in the Newton iterates were scaled by the factors $1, 10^7, 10^7, 1, 1$ the correct trajectory was followed but the stepsize increased very slowly. However, when the ODE's were scaled by factors so that the maximum value of each component were of the same order ($= 1$) the program behaved 'normally'. The same type of behaviour turned out to be present when a version of Gear's package was used. In both cases the problems were run on an IBM 360/75 in double precision. It is still an open question which type of scaling is the best in general, but numerical experiments on a lot of other test examples have shown that scaling of type 1 seems to be the safest at present, which, however, demands a priori knowledge of the magnitude of the components.

3.3. Some results concerning the Newton-iterations.

One of the heavy computational parts when solving stiff problems with implicit methods is the solution of the set of nonlinear algebraic equations (3.6) in each step. To increase the efficiency in most program packages one uses the same LU-decomposed matrix

$$(I - h\beta\bar{f}/\partial\bar{x})^{-1} \quad (3.12)$$

for several steps before it is updated at steplength changes or if the rate of convergence is not satisfactory. The reason why Newton iterations are used when solving (3.6) is that a direct iteration scheme

$$\bar{x}_{n+1} = h\beta\bar{f}(\bar{x}_n) - \bar{d} \quad (3.13)$$

will not converge. Only in the initial phase of the integration, where h is so small that

$$||h\beta\bar{f}/\partial\bar{x}|| < 1 \quad (3.14)$$

such a method converges. However, if it is possible to make a partitioning of the set of ODE's into fast and slow components, i.e. the partitioning (3.1) we can use a mixed iterative scheme of the type

$$\begin{aligned} \bar{c}_{1n+1} &= \bar{c}_{1n} - (I - h\beta\bar{f}_1/\partial\bar{c}_1)^{-1}\bar{\phi}_1(\bar{c}_{1n}, \bar{c}_{2n}) \\ \bar{c}_{2n+1} &= h\bar{f}_2(\bar{c}_{1n+1}, \bar{c}_{2n}) + \bar{d}_2 \end{aligned} \quad (3.15)$$

thus the stiff components are solved by Newton-iterations while the non-stiff are solved with direct iterations. The method was suggested by Dahlquist (1974), where also some discussion of the convergence properties are discussed. Recently Robertson (1975) has suggested a similar technique.

A good behaviour of such a method when implemented in a method would be that in the initial phase all equations are solved with the direct technique, while in the asymptotic phase, where large steps can be taken, Newton-iterations are used on the whole system. In the intermediate phase the components are investigated with respect to stiffness and the partitioning (3.1) is modified succesively. At present this automatic partitioning has not been implemented but in the program package by Edsberg (1975A) this par-

tioning has recently been implemented in such a way that the user can give it interactively. This partitioning is then kept fixed during the whole range of integration.

We report here the experiences of this method on two test-examples, example 2 given in chapter 3.2 and the famous example by Robertson

$$\begin{aligned} \dot{x}_1 &= -k_1 x_1 + k_2 x_2 x_3 & x_{10} &= 1 \\ \dot{x}_2 &= k_1 x_1 - k_2 x_2 x_3 - k_3 x_2^2 & x_{20} &= 0 \\ \dot{x}_3 &= k_3 x_2^2 & x_{30} &= 0 \end{aligned} \quad (3.16)$$

In example 2 x_2 and x_3 are the stiff components and in Robertson's example x_2 is stiff ($k_1 = 0.04$, $k_2 = 10^4$, $k_3 = 3 \cdot 10^7$). Some of the results obtained are given below. In the table A means accuracy, B the number of LU-decompositions, C the maximum number of iterations needed in a step, D the number of steps to t_e = end of integration interval and E the partitioning used.

Example	A	B	C	D	E
Robertson	10^{-5}	12	4	20 $t_e=0.05$	x_2 stiff
	10^{-5}	13	2	20 $t_e=0.05$	whole system
Example 2	10^{-4}	14	2	14 $t_e=0.01$	x_2, x_3 stiff
	10^{-4}	16	2	14 $t_e=0.01$	whole system

We see from this that this mixed iterative scheme may be quite efficient compared to using Newton-iterations on the whole system. In example 2 this mixed method needed to invert only a 2×2 matrix instead of a 5×5 matrix and yet the number of iterations were not increased. Test runs with this method in the asymptotic region, however, showed that the condition (3.14) was violated by the stepsize regulation; too large steps were taken with respect to this condition so it would have been advantageous to switch to Newton-iterations on the whole system somewhere in the intermediate phase. Work on this is made at present.

4. Conclusions

The problem class of mass action kinetics contains examples of problems which can be very stiff and also exhibit other numerical difficulties which must be taken into consideration in the implementation of a method. But there are also certain short-cuts to be taken. Often the poser of a chemical kinetics problem has some a priori knowledge about which components are fast and which are slow. In such a case a special type of iterative scheme seems to be worth trying since the amount of work to be expected is much smaller than if a general purpose program is used.

5. Acknowledgements.

This work was supported by the Swedish Institute of Applied Mathematics. The author wishes to thank Prof. G. Dahlquist for many stimulating discussions.

References

- Aiken R.C., Lapidus L. "An effective numerical integration method for typical stiff systems", A.I.Ch.E. 20 no 2,368 (1974)
- Aris R. "Introduction to the analysis of chemical reactors", Prentice Hall (1965)
- Aris R. "Mathematical aspects of chemical reaction", Ind. Engn. Chem. Fund: 61, 17 (1969)
- Banford C.H., Tipper C.F.H. "Comprehensive chemical kinetics" Banford, Tipper eds, vol. 2 "theory of kinetics" Elsevier (1969)
- Clark R.L., Groner G.F. "A CSMP/360 precompiler for kinetic chemical equations", Simulation, 127, oct (1972)
- Curtis A.R., Chance E.M. "Chek and Chekmat; two chemical reaction kinetics programs", A.E.R.E. Rep 7345, Harwell England (1974)
- Dahlquist G. "Problems related to the numerical treatment of stiff differential systems", in "ACM Proc. of Int. Comp. Symp.", North Holland (1974)
- Edsberg L. "Integration package for chemical kinetics" in "Stiff differential systems (Willoughby R ed) Plenum Press (1974)
- Edsberg L. "Some mathematical properties of mass action kinetics" Rep TRITA-NA-7505, Dep. of Inf. Proc. Computer Science, The Royal Inst of Techn Stockholm Sweden (1975^BA).
- Edsberg L. "KEMPEX II, A program package for interactive simulation of some chemical reactors", Rep TRITA-NA-7504, Dep. of Inf. Proc. Computer Science, The Royal Inst of Techn Stockholm Sweden (1975^AB)
- Enright W., Hull T., Lindberg B. "Comparing numerical methods for stiff ODE's" BIT 15 10-48 (1975)
- Feinberg M. "On chemical kinetics of a certain class", Arch.Rat.Mech.Anal. 46,1 (1972)
- Feinberg M., Horn F.J.M. "Dynamics of open chemical systems and the algebraic structure of the underlying reaction network", Chem. Engng. Sci. 29, 775 (1974)
- Garfinkel D. "A machine-independent language for simulation of complex chemical and biochemical systems", Comp. and Biom. Res. 2, 31 (1968)

- Gavalas G.R. "Nonlinear differential equations of chemically reacting systems", Springer (1968)
- Grover S.S. "Application of computers in chemical reaction systems", Cat. Rev. 1, 153 (1967)
- Himmelblau D.M., Bischoff K. "Process analysis and simulation: deterministic systems", Wiley (1968)
- Horn F. "Necessary and sufficient conditions for complex balancing in chemical kinetics", Arch. Rat. Mech. Anal. 49, 172 (1972B)
- Horn F., Jackson R. "General mass action kinetics", Arch. Rat. Mech. Anal. 47, 81 (1972A)
- Laurendeau N., Sawyer R.F. "General reaction rate problems: combined integration and steady state analysis", Rep. no TS-70-14. Thermal Systems division, Dep. of Mech. Engr., University of California (1970)
- Lindberg B. "Package based on the implicit midpoint method" in "Stiff differential Systems" (Willoughby R. ed) Plenum Press (1974)
- Oster G.F., Perelson A.S. "Chemical reaction dynamics" Arch. Rat. Mech. Anal. 55, 230 (1974)
- Robertson H.H. "Numerical integration of systems of stiff ordinary differential equations with special structure", Numerical Analysis rep no 8 march 1975, Dep. of Mathematics, Univ. of Manchester England (1975)
- Snow R.H. "A chemical kinetics computer program for homogeneous and free radical systems of reactions", J. of Phys. Chem: 70, 9, 2780 (1966)
- Wei J. "An axiomatic treatment of chemical reaction systems", J. Chem. Phys. 36, 1578 (1962)
- Wei J., Prater C.D. "The structure and analysis of complex reaction systems", Adv. Catalysis 13, 203 (1962)