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Modelling of Chemical Reaction Systems

Editors:
K. H. Ebert P. Deuflhard W. Jäger

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K.H. Ebert, P. Deuflhard, and W. Jäger

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Preface

For rather a long time numerical results in chemical kinetics could only be obtained for very simple chemical reactions, most of which were of minor practical importance. The availability of fast computers has provided new opportunities for developments in chemical kinetics.

Chemical systems of practical interest are usually very complicated. They consist of a great number of different elementary chemical reactions, mostly with rate constants differing by many orders of magnitude, frequently with surface reaction steps and often with transport processes. The derivation of a 'true' chemical mechanism can be extremely cumbersome. Mostly this work is done by setting up 'reaction models' which are improved step by step in comparison with precise experimental data.

At this early stage mathematics is involved, which may already be rather complicated. Mathematical methods such as pertubation theory, graph theory, sensitivity analysis or numerical integration are necessary for the derivation and application of optimal chemical reaction models.

Most theoretical work aimed at improving the mathematical methods was done on chemical reactions which mostly were of little practical importance. Chemical engineers, who evidently know well how important the chemical models and their dynamics are for reactor design, have also to be convinced not only on the theoretical work but also on its practical applicability.

New methods, especially if they are of a multidisciplinary nature, usually take decades to develop.

It was the intention of the workshop to shorten this process by bringing together mathematicians, physical chemists and chemical engineers at an early stage. The organizers were aware of the fact that at this present stage there was not only little 'common language', but also a risk of confusion if different groups mean different things for the same term. On the other hand, there was the chance that groups of different disciplines, learning to understand each other's problems, might thereby be given new

ideas for their work. Experience within the research work of the 'Sonderforschungsbereich 123' has been encouraging, and it was hoped that a workshop on rather general subjects could help and that personal contacts between scientists working in this field would be appreciated by many and would stimulate more cooperation in the future.

The organizers of this workshop have the feeling that at least some of their intentions were accepted by the participants. Both large attendances and intense discussions alone justify the publication of the proceedings, which will make the contributions available to a wider audience.

Part I of the present volume covers the different types of mathematical treatment of chemical reaction systems. In Chap.1 (Othmer) and Chap.5 (Feinberg), the qualitative behavior of chemical systems is studied by graph theoretic means, looking at the associated network structure. From this point of view, these authors analyze the possible occurrence and stability of multiple steady states or the existence of temporal oscillations. Moreover, exotic dynamics are strictly ruled out. In Chap.2 (O'Malley) and Chap.3 (Hoppensteadt, Alfeld, Aiken) singular perturbation techniques (equivalent to QSSA) are discussed. This type of pre-processing is often successful in analysing chemical systems of moderate size. The analytic treatment leads to a differential-algebraic system, where the differential equations may be non-stiff. These techniques are based on the identification of some "small parameter", which may be assumed to vanish (in a first-order approximation) on the basis of insight into the chemical process. However, some types of systems may require different parametrizations in different phases of the reaction process - a feature, which is clearly pointed out in Chap.3. In more complex situations, the numerical integration of the full, usually stiff system of differential equations is certainly necessary. For this purpose, a new user-oriented simulation package for large chemical reaction systems is introduced in Chap.4 (Deuflhard, Bader, Nowak). The new package differs from comparable former packages in the choice of a new, rather efficient stiff integrator (of the extrapolation type) and in several facilities that make the code more flexible, convenient, and applicable to really large chemical reaction systems. In practice, simulation is often combined with some kind of sensitivity analysis. A survey of techniques for computing the sensivity matrices is presented in Chap.6 (Tilden, Costanza, McRay, Seinfeld). Chap.7 (Milstein) and Chap.8 (Bock) are devoted to the numerical treatment

of the so-called inverse problem, which means the actual identification of the rate constants from given experimental data. Chap.7 describes an iterative method based on random search directions (with some additional kind of memory), where the information from the sensitivity matrix is only used after the final iteration step (for the covariance analysis). Chap.8 proposes a different iterative method (a generalized Gauss-Newton method) that uses the information from the sensitivity matrix at each iterative step to generate a new search direction - thus producing a considerable speed-up of the computations, which is documented in several examples. Chap.9 (Keener) describes an analytic technique to study the entire periodic solution branch of a reaction system. The technique is exemplified in the simple reaction A B, but applies, in principle, to more complex situations, too. Chap.10 (Boissonade) presents a stochastic molecular dynamics technique for the investigation of fluctuations in non-equilibrium reaction-diffusion systems.

In Part II the first two papers (Chap.11 by Golden and Chap.12 by Warnatz) point to limitations, which have to be considered in setting up reaction models for kinetic calculations. Besides stoichiometric and thermodynamic constraints there is always a certain inaccuracy in the empirical measurements for estimating rate constants. Furthermore, even in 'simple-looking' reactions as e.g. in flames the behavior of the system, complicated as it is, changes in respect to time (ignition, propagation) and space (even if stabilized) and can only be sufficiently described if there are models for flow, diffusion and heat conduction. In a number of papers methods of setting up reacting models of rather complicated chemical processes are described. The nature of the chemical systems vary widely. Polymer degradation (Chap.13 by Ederer, Basedow and Ebert) and hydrocarbon pyrolysis (Chap.16 by Isbarn, Ederer and Ebert) are treated as examples for huge systems and the need for early application of mathematical methods to sensitivity studies becomes evident. A more special approach was proposed in Chap.14 (Koch). Combustion processes are treated from different aspects (Chap.15 by Peters and Chap.17 by Vidóczy, Botár, Lukás, Nemes and Gál) and attempts to model heterogeneous reactions are reported (Chap.18 by Morton and Goodman and Chap.19 by Comincioli, Faucitano A., Faucitano Martinotti F., and Cesca). In a workshop like this, further work on the famous Belousov-Zhabotinskii reaction could not possibly be absent (Chap.20 by Geiseler and Bar-Eli, and Chap.21 by Noszticzius and Farkas).

A general survey of the present status of application of models in industry has been presented in the first paper of Part III (Chap.22 by Eigenberger). The behavior of chemical reactors in respect of multiple steady states (Chap.23 by D. Luss) and travelling wave fronts (Chap.24 by Gilles) is discussed in a more theoretical way. These problems are applied to polymer synthesis for different kinetic mechanisms and with dependence of heat and mass transfer within a reactor (Chap.25 by H. Ray). In Chap.26 (Kahlert et al.), a theoretical study is presented to show how complex the dynamics, even of a rather simple reaction, may be and what conditions are responsible for a behavior which would be a nightmare for chemical engineers. In conclusion a study is presented (Chap.27 by Petrich) of a simulation of the behaviour of a single extraction apparatus (mixer-settler) for the uranium-plutonium separation within the purex process. This work points to a promising procedure for industrial problems, introducing methods to single reaction steps rather than to a whole chemical process.

We are indebted to Prof. Richard N. Noyes who presented an excellent summing up in conclusion of the workshop (Part IV), naturally of course from the point of view of a physical chemist.

We are grateful to the 'Deutsche Forschungsgemeinschaft' who made possible the establishment of the 'Sonderforschungsbereich 123' at the University of Heidelberg, thereby facilitating interdisciplinary cooperation. BASF, Ludwigshafen, have supported the workshop most generously, although they are aware that it will be some time before results of practical use to industry could be developed.

It is our fond hope that the workshop and the proceedings will contribute to the future development of this fascinating field in which mathematics and chemistry are closely interacting with the object of a better understanding of the dynamic behavior of chemical reactions with special reference to industrial application.

Heidelberg, July 1981 *K.H. Ebert, P. Deuflhard, W. Jäger*

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Part I

Mathematical Treatment

1. The Interaction of Structure and Dynamics in Chemical Reaction Networks

H. G. Othmer

1.1 Introduction

Chemical reaction dynamics or chemical kinetics is concerned with the problem of predicting the temporal evolution of the composition of a reacting mixture, given its composition at an initial instant of time. To do this, one must know the mechanism and the rate constants of the various elementary steps, and one aspect of the problem concerns the *a priori* prediction of rate constants from bond energies and other properties of the reacting molecules. This aspect is covered in Golden's contribution to this volume (Chap. 10). Another aspect concerns the question of how the topological structure of the reaction network, by which we mean the pattern of connections between species or groups of species imposed by the reactions between them, affects the dynamical behavior of the system. More precisely, one would like to know when such phenomena as multiple steady states, temporal oscillations, and chaotic dynamics can be ruled out solely on the basis of network structure, or on the basis of network structure and some general properties of the rate laws, both for well-mixed systems and for systems in which transport occurs on the same time scale as does reaction.

The latter aspect of chemical kinetics is the subject of Feinberg's paper (Chap.5) and of this one. In closed systems, the dissipation hypothesis precludes periodic solutions and chaotic dynamics, but multiple steady states may exist in nonideal mixtures. An example of this is given in the following section. In the third section we present a graph-theoretic framework within which the foregoing questions can be dealt with for open systems. The last section deals with the problem of diffusive instabilities of a spatially uniform solution in an open system, both when the uniform solution is time-invariant and when it is time-periodic.

1.2 Closed, Spatially-Uniform Systems

Suppose that there are n reacting species M_i and $r \leq n - 1$ independent reactions amongst them, written as

$$\sum_{i=1}^{n} \nu_{ij} M_i = 0 \quad j = 1, \ldots r \quad . \tag{1.1}$$

The ν_{ij} are stoichiometric coefficients that represent the relative molar proportions of the species in a reaction. For the present we assume that they are integers and that $\nu_{ij} > 0$ (<0) according as species i is a product (reactant) in the jth reaction. Throughout we assume that the temperature and pressure are constant and that volume changes due to reaction are negligible. Therefore, the state of the mixture is specified by the concentration vector $c = (c_1, \ldots, c_n)^T$, and this must lie in $\bar{R}_n^+$, the nonnegative 'orthant' of an n-dimensional real vector space.

Associated with each reaction, all of which are assumed to be reversible, is a rate $R_i(c)$, and the temporal evolution of the mixture is given by the solution c(t) of the differential equation

$$\frac{dc}{dt} = \nu R(c) \quad c(0) = c_0 \quad . \tag{1.2}$$

The $n \times r$ matrix ν is the stoichiometric matrix and since the r reactions are independent, $\text{rank}(\nu) \equiv \rho(\nu) = r$. The components $R_i(c)$ of R(c) are polynomials in ideal systems that follow mass action kinetics and in general are assumed to be smooth enough that the solution of (1.2) exists locally in t and is unique and nonnegative for any nonnegative c_0.

In a closed system, the total mass and perhaps other quantities are conserved, and any such invariant combination of concentrations has the form

$$\langle \Omega_j, c(t) \rangle = \langle \Omega_j, c_0 \rangle \quad j = 1, \ldots s \quad , \tag{1.3}$$

where $\nu^T \Omega_j = 0$, i.e., $\Omega_j \in N(\nu^T)$.[1] Since dim $R(\nu) < n$, the semiflow defined by (1.2) is confined to the coset of $R(\nu)$ defined by (1.3). The intersection of this linear manifold with $\bar{R}_n^+$ is called the reaction simplex and is denoted $\Omega(c_0)$. Because the total mass is conserved, one of the Ω_j's has strictly positive components, and as a result $\Omega(c_0)$ is compact. It follows from

1 Unless specified otherwise, <,> denotes the Euclidean inner product and $\|\cdot\|$ the associated norm. $N(A)$ and $R(A)$ are the null space and range, respectively, of the linear transformation A.

Brouwer's fixed point theorem that (1.2) always has at least one time-invariant solution, any of which we call a kinetic equilibrium point. Since $\rho(\nu) = r$, all kinetic equilibria are solutions of the system

$$R_i(c) = 0 \quad i = 1, \ldots r \quad . \tag{1.4}$$

If we introduce intrinsic coordinates $\{\xi_i\}$ in $\Omega(c_0)$ via

$$c - c_0 = \nu\xi \quad ,$$

then (1.2) can be written

$$\frac{d\xi}{dt} = R(c_0 + \nu\xi) \equiv \tilde{R}(\xi) \quad . \tag{1.5}$$

The thermodynamic properties of the mixture are fixed, at constant T and P, once the composition dependence of the Gibbs free energy G is prescribed. G is homogeneous of first degree in the concentrations c_i and thus can be written

$$G = \langle\mu,c\rangle \quad , \tag{1.6}$$

where

$$\mu_i = \partial G/\partial c_i \tag{1.7}$$

is the chemical potential of species i. It can be written in the form

$$\mu_i = \mu_i^0(T,P) + RT \ln \tilde{\gamma}_i(c)x_i \quad , \tag{1.8}$$

where $\tilde{\gamma}_i(c)$ is the activity coefficient of species i and x_i is its mole fraction. The solution is ideal with respect to species i if $\tilde{\gamma}_i = 1$. In any case, we require that $\tilde{\gamma}_i x_i \to 0$ as $x_i \to 0$. For convenience, we set $\gamma_i(c) = \bar{c}\tilde{\gamma}_i(c)$ and rewrite (1.8) as

$$\mu_i = \mu_i^0(T,P) + RT \ln \gamma_i(c)c_i \quad . \tag{1.9}$$

Since the composition is restricted to lie in $\Omega(c_0)$, we restrict G(c) to $\Omega(c_0)$ by setting

$$\tilde{G}(\xi) \equiv G(c_0 + \nu\xi) \quad . \tag{1.10}$$

According to the classical definition [1.1], the thermodynamic equilibrium points occur at the compositions corresponding to critical points of $\tilde{G}(\xi)$, i.e., points at which the affinity

$$A_j \equiv -(\nu\tilde{G})_j = -\sum_{i=1}^{n} \nu_{ij}\mu_i \tag{1.11}$$

vanishes for every reaction. Under the assumption that $\gamma_i(c)c_i \to 0$ as $c_i \to 0$ for every i, it can be shown that there is at least one thermodynamic equilibrium point in the interior of $\Omega(c_0)$ and that $\tilde{G}$ has a minimum there. Furthermore, if the solution is ideal, the thermodynamic equilibrium point in the interior of $\Omega(c_0)$ is unique. If it is also assumed that every species participates in at least one reaction, then there are no thermodynamic equilibrium points on the boundary of $\Omega(c_0)$. There is no loss of generality in making this assumption, because when inert species are present, one can simply work in a lower-dimensional space. Of course, the dependence of the chemical potential on inert species must still be taken into account.

We have defined two different types of equilibria and the question arises as to when they coincide. Let us define a dissipation function Φ as

$$\Phi = \frac{-d\tilde{G}}{dt} = \langle\tilde{A},\tilde{R}\rangle \tag{1.12}$$

and postulate that $\Phi \geq 0$ along orbits or (1.5), with equality if and only if $\tilde{R} = 0$. This 'dissipation hypothesis' is the nonequilibrium generalization of the second law of thermodynamics, and under it every thermodynamic equilibrium point is a kinetic equilibrium point ($\tilde{A} = 0 \Rightarrow \tilde{R} = 0$). Furthermore, it can be shown that when this hypothesis holds,

a) $\tilde{A} = 0$ at any kinetic equilibrium point that is positively or negatively stable (i.e., is a sink or source, respectively)
b) $\tilde{A} = 0$ at any kinetic equilibrium point that is a saddle point if Φ is differentiable and $\partial\tilde{R}/\partial\xi$ is nonsingular there.

Complete equivalence between thermodynamic and kinetic equilibria cannot be hoped for, because under reasonable assumptions there are no thermodynamic equilibria on the boundary of $\Omega(c_0)$, but there may be kinetic equilibria there. For instance, if the reaction is

$$M_1 + M_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2M_1$$

and

$$R = k_1c_1c_2 - k_{-1}c_1^2 \quad ,$$

then it is easily shown that $\Phi \geq 0$ if $k_1/k_{-1} = K_{eq}$, where K_{eq} is the usual equilibrium constant. Clearly there is a kinetic equilibrium point on the boundary of the simplex, and one finds that $d\Phi/d\xi \to +\infty$ as $c_1 \to 0^+$ and that $\partial\tilde{R}/\partial\xi \neq 0$ there. In the terminology used by PRIGOGINE and DEFAY [1.1], points at which $\tilde{R} = 0$, but $\tilde{A} \neq 0$, are called false equilibria, and thus all boundary equilibria are false equilibria.

When the mixture is not ideal, $\tilde{G}$ need not be globally convex and there may be more than one thermodynamic equilibrium point. Several different models of solution behavior that can lead to this phenomenon have been analyzed [1.2] and several real systems in which it might occur have been suggested [1.3]. We shall not go into details here, but will give one elementary example. Consider the reaction

$$-M_1 + M_2 = 0 \tag{1.13}$$

in a binary regular solution for which

$$\gamma_1 = \exp[\omega(1 - x_1)^2] \quad \gamma_2 = \exp(\omega x_1^2) \quad .$$

The reaction simplex is given by $x_1 + x_2 = 1$, and there is no need to introduce ξ coordinates here. Suppose that

$$\tilde{R} = k_1\gamma_1 x_1 - k_{-1}\gamma_2(1 - x_1) \quad , \tag{1.13}$$

where k_1 and k_{-1} are positive constants. The affinity for (1.13) is

$$\tilde{A} = -(\mu_2 - \mu_1) = -\Delta\mu = -\Delta\mu^0 + RT \ln \frac{\gamma_1 x_1}{\gamma_2(1 - x_1)} \quad ,$$

and $\tilde{A} = 0$ implies that

$$\frac{\gamma_1 x_1}{\gamma_2(1 - x_1)} = \exp(\Delta\mu^0/RT) \quad .$$

Similarly, $\tilde{R} = 0$ implies that

$$\frac{\gamma_1 x_1}{\gamma_2(1 - x_1)} = \frac{k_{-1}}{k_1} \quad ,$$

and therefore, $\tilde{A} = 0$ if and only if $\tilde{R} = 0$, provided that

$$\frac{k_{-1}}{k_1} = \exp(\Delta\mu^0/RT) \quad . \tag{1.14}$$

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