RISØ

DK9900033

CHEMSIMUL: A Simulator for Chemical Kinetics

Peter Kirkegaard and Erling Bjergbakke

30 - 07

CHEMSIMUL: A Simulator for Chemical Kinetics

Peter Kirkegaard and Erling Bjergbakke

Abstract   CHEMSIMUL is a computer program system for numerical simulation of chemical reaction systems. It can be used for modeling complex kinetics in many contexts, in particular radiolytic processes. It contains a translator module and a module for solving the resulting coupled nonlinear ordinary differential equations. An overview of the program system is given, and its use is illustrated by examples. A number of special features are described, in particular a method for verifying the mass balance. Moreover, the document contains a complete User's Guide for running CHEMSIMUL on a PC or another computer. Finally, the mathematical implementation is discussed.

Contents

Preface

The CHEMSIMUL program system was created several decades ago by the pioneering work of Ole Lang Rasmussen at Risø National Laboratory in Denmark. Since then the program has evolved and expanded alongside with its practical use by chemists in Denmark and elsewhere.

Recently, Risø National Laboratory and chemists at CEA Saclay in France have initiated a collaboration with the aim of updating CHEMSIMUL with a set of new features, and consolidating some of the old ones.

For fruitful inspiration in the development of the present version of the program we thank Dr. P. Bouniol, Dr. C. Corbel, and Dr. B. Hickel, all at CEA Saclay. Moreover, Dr. Frank Markert, Risø, has contributed with valuable comments to the report.

Peter Kirkegaard, e-mail peter.kirkegaard@risoe.dk
Erling Bjergbakke, e-mail erling.bjergbakke@risoe.dk

1   Introduction

Chemical transformations taking place in the natural environment as well as in industrial processes are in general very complex. Even in well designed laboratory experiments it is often difficult to study elementary chemical reactions without interference from simultaneous side reactions. Therefore computer simulation has become a powerful tool for the analysis of complex reactions, which are fundamental for understanding atmospheric chemistry, combustion chemistry and air pollution problems, and for the development of new technologies.

1.1   Overview

The program system CHEMSIMUL was developed at Risø National Laboratory as the result of a close co-operation between chemists and applied mathematicians. CHEMSIMUL is a computerized simulator of chemical kinetics with the following main components:

- Module for input of reaction equations in chemical notation

- Automatic translator from chemical equations to differential equations

- Solution of system of ordinary differential equations

- Output routines

- Miscellaneous facilities

The simulation results will be concentrations of the chemical species in the reaction system as functions of time. These can be given in tabular and graphical form.

CHEMSIMUL is tailor-made to simulation of radiation chemistry, where bursts of electron beams or γ-rays are modeled by rectangular source pulses of finite time duration. Heat generation from the reactions may also be taken into account. There are a number of other special features to be described in the following, notably a method for checking the mass balance.

1.2   CHEMSIMUL development and related work

Chemists at Risø and elsewhere have used CHEMSIMUL and its predecessors for many years as a simulation tool supporting their experimental work. Rasmussen and Bjergbakke [1] give a historical account of the development of software for kinetics simulation at Risø over several decades, right from the beginning in 1966 when analogue methods were still prevailing. They point out the close connection with establishment of numerical techniques for fast and accurate integration of "stiff" non-linear differential equations. In the chemists' language stiffness means that the kinetic system has a wide range of relaxation times for perturbations. Stiff methods for Ordinary Differential Equations (ODE) were introduced at Risø shortly after 1971 when Gear [2] published his DIFSUB code. They replaced the classical fifth-order Runge-Kutta methods. Eventually, the ODE software in CHEMSIMUL was again replaced, first by a revised DIFSUB, then by EPISODE (Hindmarsh and Byrne [3]), and still later by the LSODA program (Hindmarsh [3], Petzold [4]), which is the solver used today.

It was early realized that the construction of the ODEs from the reaction equations, which was originally done manually, should be automated, and this led to the development of the translation module in CHEMSIMUL. It was a design criterion for the system that the chemist could express the reaction processes to be studied in familiar chemical nomenclature.

The early versions of CHEMSIMUL were written in ALGOL. The old documentation by Rasmussen and Bjergbakke [1] relates to this language. Since 1986 PASCAL and MODULA-2 were in use as programming languages for mainframe versions, but from 1992 CHEMSIMUL has been entirely FORTRAN based. In 1997 it was converted to FORTRAN 90

with the result that most of the restrictions on problem size were alleviated. An overview of the updates since the previous version in 1993 is given in Section 8. The PC is now the most important computer platform for running CHEMSIMUL at Risø and elsewhere; however, the program may also run under Digital VMS and under several Unix systems.

Other computer programs are available with application fields more or less overlapping with CHEMSIMUL. Curtis and Sweetenham [5] have constructed the Harwell simulator FACSIMILE (= Flow and Chemistry Simulator). It has broader scope than CHEMSIMUL, being a general system for time evolution problems. It also solves partial differential equations and mixed algebraic-differential systems. Braun et al. [6] have developed the simulator program ACUCHEM, Deuflhard et al. [7] the program LARKIN, and Kee et al. [8] the Sandia program CHEMKIN. These programs are alike CHEMSIMUL in some respects, apart from CHEMSIMUL's facilities for radiation chemistry and thermodynamics.

1.3 Chemical kinetics with pulse radiolysis

CHEMSIMUL is constructed to simulate homogeneous kinetics in monophase. Only zero-, first-, and second-order reactions are allowed. Reactions of higher order must be emulated by suitable first- and second-order reactions.

When preparing input data for CHEMSIMUL, the reactions are written in normal chemical notation, e.g.

$$A = B + C; \quad k_1 \tag{1}$$

for a first-order reaction, and

$$A + D = E + F; \quad k_2 \tag{2}$$

for a second-order reaction; k_1 and k_2 are the rate constants for these reactions.

An important facility in CHEMSIMUL is its ability to simulate radiolytic processes. These are zero-order reactions, whereby a species A is produced by radiation, say from electron beams or γ-rays. The rate of production is proportional to the dose rate $D(t)$:

$$\frac{d[A]}{dt} = c\,G(A)D(t). \tag{3}$$

Here, $G(A)$ is the so-called G-value for radiolytic production of the given species A with concentration [A], and c is the conversion constant whose value will be given in Section 1.4, where units are discussed.

G-values can be negative as well as positive. In case of radiation produced species with positive G-values a corresponding negative value for $G(H_2O)$ should be included in order to preserve the mass balance.

Though the concept of G-values is primarily designed for calculation of irradiation yields, it can be used for zero-order reactions in general. In this way other types of reactions can be simulated.

CHEMSIMUL normally assumes that the dose rate $D(t)$ is a rectangular pulse:

$$D(t) = \left\{ \begin{array}{ll} D_0 & 0 < t < t_r \\ 0 & \text{otherwise,} \end{array} \right. \tag{4}$$

where t_r is the time of radiation. However, it is also possible to handle cases with a sum of exponentially decaying dose rates. This is described in Section 4.7.

1.4 Units

CHEMSIMUL allows a free choice of units in the computations, although the program originally was designed for kinetics in condensed phase with the traditional units: concentration in $mol \times dm^{-3}$, rate constants in s^{-1} and $s^{-1} \times mol^{-1} \times dm^3$ for first and second order reactions, respectively, activation energy in $kcal \times mol^{-1} \times dm^3$, heat formation in $kcal \times mol^{-1} \times dm^3$, and specific heat capacity in $K^{-1} \times mol^{-1} \times dm^3 \times kcal$, cf. Sections 4.3 and 4.4. Now CHEMSIMUL can be used with other units as well, for example

the standard gas kinetics units: concentration in $molecules \times cm^{-3}$ and rate constant in $s^{-1} \times molecules^{-1} \times cm^3$ for second order reactions. Please observe that all units must be changed. The term G-value was introduced in (3) in Section 1.3. Its definition is *molecules per* $100\,eV$.

The conversion constant c in (3) depends on the units for concentration and dose. Choosing these as $mol \times dm^{-3}$ and $krad$, respectively, we find c by computing $d[A]/dt$ for $D(t) = 1\,krad \times s^{-1} = 10^5\,erg \times g^{-1} \times s^{-1} = 10^{17}/1.60207\,eV \times g^{-1} \times s^{-1}$:

$$\frac{d[A]}{dt} = G(A) \times \frac{10^{15}}{1.60207}\,molecules \times g^{-1}s^{-1} =$$

$$G(A) \times \frac{10^{15}\rho}{1.60207}\,molecules \times cm^{-3}s^{-1} = G(A) \times \frac{10^{18}\rho}{1.60207 \times 6.02322 \cdot 10^{23}}\,mol \times dm^{-3}s^{-1}. \quad (5)$$

In irradiation of water where $\rho = 1\,g \times cm^{-3}$ we thus obtain

$$c = 1.036 \cdot 10^{-6}, \quad (6)$$

which is the default setting in CHEMSIMUL. If the unit for absorbed dose is changed to *Gray*, then c must be changed to $1.036 \cdot 10^{-7}$, and if ρ is different from $1\,g \times cm^{-3}$, c should likewise be changed. Such changes of the conversion constant are easily accommodated for in CHEMSIMUL by the command CONVERT, see Section C of the User's Guide.

In Section 4.3 it is mentioned that CHEMSIMUL accepts rate constants in the modified Arrhenius form (14). If you use this facility, you should note that the gas constant must be entered in the input file either as $R = 1.9869 \cdot 10^{-3}\,kcal \times mol^{-1} \times dm^3 \times K^{-1}$ if the activation energy E_a is entered in unit $kcal \times mol^{-1} \times dm^3$, or as $R = 8.317\,Joule \times mol^{-1} \times dm^3 \times K^{-1}$ if E_a is entered in unit $Joule \times mol^{-1} \times dm^3$. See also Section C of the User's Guide.

We have collected the relevant CHEMSIMUL units in Table 1 below, where each line represents a consistent set of units.

Concentration	Rate Constants		Gas Constant	Activation Energy	Heat of Reaction	Specific Heat Capacity
CON	1.order	2.order	R	EA	Q	HCV
$mol \times dm^{-3}$	s^{-1}	$mol^{-1} \times dm^3 \times s^{-1}$	$kcal \times mol^{-1} \times dm^3 \times K^{-1}$	$kcal \times mol^{-1} \times dm^3$	$kcal \times mol^{-1} \times dm^3$	$K^{-1} \times mol^{-1} \times dm^3 \times kcal$
$mol \times dm^{-3}$	s^{-1}	$mol^{-1} \times dm^3 \times s^{-1}$	$Joule \times mol^{-1} \times dm^3 \times K^{-1}$	$Joule \times mol^{-1} \times dm^3$	$Joule \times mol^{-1} \times dm^3$	$K^{-1} \times mol^{-1} \times dm^3 \times Joule$
$molecules \times cm^{-3}$	s^{-1}	$molecules^{-1} \times cm^3 \times s^{-1}$	$kcal \times mol^{-1} \times dm^3 \times K^{-1}$	$kcal \times mol^{-1} \times dm^3$	$kcal \times molecules^{-1} \times cm^3$	$K^{-1} \times molecules^{-1} \times cm^3 \times kcal$
$molecules \times cm^{-3}$	s^{-1}	$molecules^{-1} \times cm^3 \times s^{-1}$	$Joule \times mol^{-1} \times dm^3 \times K^{-1}$	$Joule \times mol^{-1} \times dm^3$	$Joule \times molecules^{-1} \times cm^3$	$K^{-1} \times molecules^{-1} \times cm^3 \times Joule$

Table 1. Consistent sets of units for CHEMSIMUL

2 Translating reactions to differential equations

When explaining the translation in CHEMSIMUL from chemical reactions to differential equations we shall first use a very simple reaction scheme with only one reaction, and then a more realistic sample case from combustion.

2.1 Simple example with one reaction

Consider the reaction

$$R1 + R2 \rightarrow R3 + R4 \quad (7)$$

with 4 *species* (2 *reactants* and 2 *products*). We assume that the reaction proceeds according to the law of mass action with the rate constant k. Suppose also that the chemical medium is irradiated either by an electronic beam or by γ-rays, such that the species R2 and R3 are produced by this radiation with yields determined by $G(R2)$ and $G(R3)$, respectively, cf. Sections 1.3 and 1.4. Then the resulting differential equations for the concentrations are

$$\frac{d[R1]}{dt} = -k[R1][R2]$$

$$\frac{d[R2]}{dt} = -k[R1][R2] + c\,G(R2)D(t)$$

$$\frac{d[R3]}{dt} = k[R1][R2] + c\,G(R3)D(t)$$

$$\frac{d[R4]}{dt} = k[R1][R2]$$

(8)

Here $[\cdot]$ denotes concentration, $D(t)$ is the dose rate at time t (normally a rectangular pulse), and c is the conversion constant.

The reaction between R1 and R2 is a second-order reaction, while the radiolytic production of R2 and R3 are zero-order reactions. (CHEMSIMUL does not treat third-order reactions or higher directly, so these must be emulated by lower-order reactions, cf. Section 4.5.) We see that a single chemical reaction equation is described by a system of Ordinary Differential Equations (ODE), which are non-linear in the concentrations. Starting with the time $t = 0$ and the initial values of the reactant concentrations $[R1]_0$, $[R2]_0$, $[R3]_0$ and $[R4]_0$ we can integrate the system up to some final time $t = t_{end}$.

Very small chemical systems such as (7) can be simulated by making a direct write-up of the ODE system, but for larger systems this would be tedious and error-prone. Therefore CHEMSIMUL has a module for automatic translation of the chemical reactions to differential equations.

2.2 Sample case from combustion

Let us now consider a more realistic reaction system discussed in [9] for modeling a H_2–O_2 combustion process. This example will be used repeatedly as a sample case:

(R1)	$H + H$	$\rightarrow$	H_2
(R2)	$H + O_2$	$\rightarrow$	HO_2
(R3)	$H + HO_2$	$\rightarrow$	$OH + OH$
(R4)	$HO_2 + HO_2$	$\rightarrow$	$H_2O_2 + O_2$
(R5)	$OH + OH$	$\rightarrow$	H_2O_2
(R6)	$H + OH$	$\rightarrow$	H_2O
(R7)	$OH + HO_2$	$\rightarrow$	$H_2O + O_2$
(R8)	$OH + H_2$	$\rightarrow$	$H_2O + H$

(9)
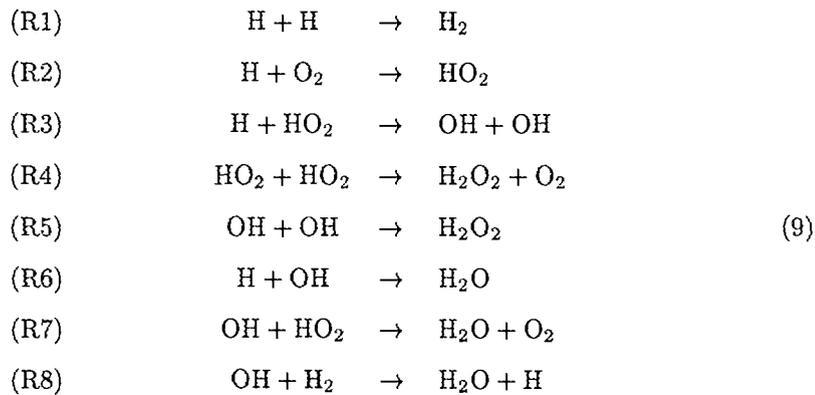
The corresponding part of the CHEMSIMUL input file, with rate constants, reads:

```
RE1: H+H=H2; A=4.0E7
RE2: H+O2=HO2; A=4.5E8
RE3: H+HO2=OH+OH; A=6.5E10
RE4: HO2+HO2=H2O2+O2; A=2.0E9
RE5: OH+OH=H2O2; A=4.0E9
RE6: H+OH=H2O; A=1.0E10
RE7: OH+HO2=H2O+O2; A=6.0E10
RE8: OH+H2=H2O+H; A=4.0E3
```

We note the similarity with the chemical notation in (9). When processing a reaction system as this, CHEMSIMUL scans and "digests" all the kinetic equations, symbol by symbol. On encounter it tabulates every new species and includes its name in the current set of symbols. It also stores the reaction rates. After the scan phase an assembly phase is invoked. The technical details are discussed in Section 7.1. Here we shall only show the outcome of the translation process, where we for illustration use CHEMSIMUL's ODE printout feature (Section 3.3):

```
D[H]/DT    = - 2*K1*H*H - K2*H*O2 - K3*H*HO2 - K6*H*OH + K8*OH*H2
             + G(H)*CONST*DOSE
D[H2]/DT   =   K1*H*H - K8*OH*H2                                        (11)
D[O2]/DT   = - K2*H*O2 + K4*HO2*HO2 + K7*OH*HO2
D[HO2]/DT  =   K2*H*O2 - K3*H*HO2 - 2*K4*HO2*HO2 - K7*OH*HO2
D[OH]/DT   =   K3*H*HO2 + K3*H*HO2 - 2*K5*OH*OH - K6*H*OH - K7*OH*HO2
             - K8*OH*H2
D[H2O2]/DT=    K4*HO2*HO2 + K5*OH*OH
D[H2O]/DT  =   K6*H*OH + K7*OH*HO2 + K8*OH*H2
```

The complete CHEMSIMUL input data file for the sample case is shown in Section F of the User's Guide.

3   Output possibilities

When running CHEMSIMUL, the program will produce a result file. Moreover, it has facilities for presenting the output in graphical form. We shall give a short description of each of these features, illustrating with the sample data set in Section F of the User's Guide.

3.1   Result file

The name of the result file will be the name of the input file with the extension replaced by .res. The first part of the file is an echo of the CHEMSIMUL input data as prepared according to the User's Guide, Section 5. Then follows the integration results in tabular form. These comprise the concentrations of all reacting species as functions of time (possibly supplemented by heat production and temperature for adiabatic processes, cf. Section 4.4).

By and large the CHEMSIMUL output is self-explanatory. We show below the result file for our H_2–O_2 combustion case in Section 2.2:

```
###################################
CHEMSIMUL COMPILED:    DEC 1998
###################################

INPUT DATA FILE: h2-o2
DATE OF COMPUTATION: 22-DEC-1998 14:06
-------------------------------------------
CASE: 5 mbar O2 + 100 mbar H2 + Ar to 1 atm. k8=4000

NO. OF REACTION EQUATIONS =   8
NO. OF G-VALUES           =   1
NO. OF CONCENTRATIONS     =   2

REACTION EQUATION SYSTEM
```

```
----------------------------
RE1:H+H=H2;A=4.0E7
RE2:H+O2=HO2;A=4.5E8
RE3:H+HO2=OH+OH;A=6.5E10
RE4:HO2+HO2=H2O2+O2;A=2.0E9
RE5:OH+OH=H2O2;A=4.0E9
RE6:H+OH=H2O;A=1.0E10
RE7:OH+HO2=H2O+O2;A=6.0E10
RE8:OH+H2=H2O+H;A=4.0E3
```

PLOT EXPRESSIONS

PE1:HO2

G - VALUES

G(H)=1.0

START CONCENTRATIONS

CON(O2)=2.0E-4
CON(H2)=4.0E-3

```
NO. OF TERMS IN DIFFERENTIAL SYSTEM =  25
NO. OF SPECIES                      =   7
NO. OF REACTION EQUATIONS           =   8
```

START VALUES FOR THE SPECIES

```
G(H)   = 1.00E+00   CON(H)   = 0.00E+00
G(H2)  = 0.00E+00   CON(H2)  = 4.00E-03
G(O2)  = 0.00E+00   CON(O2)  = 2.00E-04
G(HO2) = 0.00E+00   CON(HO2) = 0.00E+00
G(OH)  = 0.00E+00   CON(OH)  = 0.00E+00
G(H2O2)= 0.00E+00   CON(H2O2)= 0.00E+00
G(H2O) = 0.00E+00   CON(H2O) = 0.00E+00
```

```
TOTAL DOSE.....................= 9.00E-01
RADIATION TIME.................= 5.00E-09
FIRST INTEGRATION STEP ATTEMPTED.= 1.00E-09
MAXIMUM INTEGRATION STEP ALLOWED.= 1.00E-05
NO. OF RESULTS DURING RADIATION..=  2
TOTAL NO. OF RESULTS.............= 12
MAXIMUM INTEGRATION TIME.........= 1.00E-03
RELATIVE TOLERANCE IN LSODA......= 1.00E-02
```

RESULT TABLE

TIME	H	H2	O2	HO2	OH	H2O2
0.00E+00	0.00E+00	4.00E-03	2.00E-04	0.00E+00	0.00E+00	0.00E+00
2.50E-09	4.66E-07	4.00E-03	2.00E-04	5.24E-11	2.93E-15	4.89E-21
5.00E-09	9.32E-07	4.00E-03	2.00E-04	2.10E-10	3.43E-14	9.84E-20
1.00E-04	1.68E-11	4.00E-03	2.00E-04	2.80E-07	4.40E-08	3.29E-08
2.00E-04	1.74E-12	4.00E-03	2.00E-04	2.22E-07	9.87E-09	4.53E-08
3.00E-04	4.93E-13	4.00E-03	2.00E-04	1.98E-07	2.80E-09	5.40E-08
4.00E-04	1.58E-13	4.00E-03	2.00E-04	1.82E-07	8.96E-10	6.12E-08
5.00E-04	5.52E-14	4.00E-03	2.00E-04	1.69E-07	3.13E-10	6.73E-08
6.00E-04	2.07E-14	4.00E-03	2.00E-04	1.58E-07	1.17E-10	7.27E-08
7.00E-04	8.26E-15	4.00E-03	2.00E-04	1.48E-07	4.68E-11	7.74E-08
8.00E-04	3.48E-15	4.00E-03	2.00E-04	1.40E-07	1.97E-11	8.15E-08
9.00E-04	1.53E-15	4.00E-03	2.00E-04	1.33E-07	8.67E-12	8.52E-08
1.00E-03	7.05E-16	4.00E-03	2.00E-04	1.26E-07	3.99E-12	8.86E-08

RESULT TABLE

TIME	H2O
0.00E+00	0.00E+00
2.50E-09	1.22E-20
5.00E-09	3.25E-19
1.00E-04	2.71E-07
2.00E-04	3.05E-07
3.00E-04	3.12E-07

```
4.00E-04  3.14E-07
5.00E-04  3.14E-07
6.00E-04  3.15E-07
7.00E-04  3.15E-07
8.00E-04  3.15E-07
9.00E-04  3.15E-07
1.00E-03  3.15E-07

EXECUTION TIMES FOR CHEMSIMUL (SECS)
  INPUT     SETUP   INTEGRATION   OUTPUT        TOTAL
  0.05      0.00       0.11        0.11         0.27
```

3.2   Graphical output and plot expressions

CHEMSIMUL also produces a plot table file whose name will be the name of the input file, with the extension replaced by .tbl.

The plot table file has one column for time, and one column for each of the "plot expressions" that are specified in the input file.

Plot expressions (PE...) are discussed in Section C of the User's Guide, and in Section 7.5. A plot expression may be just a single species concentration, as PE1:HO2 in our sample case. However, the concept is much more versatile, as it supports all the 5 operations +, −, ×, /, and ^ (exponentiation). This is a useful facility, when a researcher wants to plot a curve which is directly comparable with certain experimental results. An example is the measurement of extinction

$$E = (\varepsilon_A[\text{A}] + \varepsilon_B[\text{B}])\ell \tag{12}$$

where ε_A and ε_B are the extinction coefficients for species A and B, respectively, ℓ is the optical path length, and [·] denotes concentration.

CHEMSIMUL has an interface to the public-domain program GNUPLOT [10], which is in widespread use on many different computers. For each run, CHEMSIMUL generates a command file gnu.cmd, which you may execute by the following GNUPLOT command:

gnuplot gnu.cmd

GNUPLOT will then plot the simulation results from the CHEMSIMUL plot table file. Hardcopies can be produced by the set terminal facility in GNUPLOT [10].

As the plot table file is just a normal text file, you may of course use it in connection with other graphics programs as well.

Two examples of plots produced by CHEMSIMUL/GNUPLOT are shown in Section 6.4.

3.3   Formal printout of differential equations

The program can give a formal print-out of the differential equation system to be solved. This may be a useful tutorial facility for understanding reaction kinetics. An example of this was shown at the end of Section 2.2. The reaction rates are labelled Kn corresponding to reaction REn. The ODE print-out is activated by the command DIFFEQ, cf. Section C of the User's Guide.

4   Miscellaneous features

In the following a number of additional CHEMSIMUL features will be described.

4.1   The stoichiometric mass balance

The accurate solution of the differential equation system describing the chemical reactions requires an overall conservation of the chemical mass balance. The numerical integration

scheme itself preserves the mass balance, cf. Section 7.2, so there is no need to check for mass balance continually. We use instead a static consistency check. If the check fails, the simulation is halted before integration; this practice has proved useful for detecting input errors in the write-up of the reaction equations. CHEMSIMUL recognizes each species as an entity with a name. This means that a formal stoichiometric balance does not imply an atom-to-atom balance. But it is possible to perform a *partial* consistency check based on the *stoichiometric matrix* **A**. This matrix is defined formally in Section 7.1, but its meaning is clear from the following example, where the reactions of the H_2–O_2 combustion case (9) are written in matrix form as a balance equation:

$$
\begin{pmatrix}
-2 & 1 & 0 & 0 & 0 & 0 & 0 \\
-1 & 0 & -1 & 1 & 0 & 0 & 0 \\
-1 & 0 & 0 & -1 & 2 & 0 & 0 \\
0 & 0 & 1 & -2 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & -2 & 1 & 0 \\
-1 & 0 & 0 & 0 & -1 & 0 & 1 \\
0 & 0 & 1 & -1 & -1 & 0 & 1 \\
1 & -1 & 0 & 0 & -1 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
H \\ H2 \\ O2 \\ HO2 \\ OH \\ H2O2 \\ H2O
\end{pmatrix}
= 0
\tag{13}
$$

It must be possible to satisfy this equation by a set of strictly positive values for the masses of all the elements of the species vector.

The mathematical implementation of the balance check is discussed in Section 7.2.

4.2   Check of electro neutrality

As explained in Section B of the User's Guide, CHEMSIMUL admits species names with charge designators as e.g. FE[+++] or OH^{-}. Such a convention enables the program to check the electro neutrality both in the individual reactions and for the totality of G-values. Like the mass balance check, this feature may be useful in catching errors in the input data file.

4.3   Variation of rate constant with temperature

CHEMSIMUL accepts rate constants in the modified Arrhenius form

$$
k = AT^\beta \exp(-E_a/(RT))
\tag{14}
$$

where T is the absolute temperature, E_a the activation energy, R the gas constant, and β an empirical exponent. The factor T^β is included for gas phase kinetics.

The components A, β, and E_a are entered as A, B, and EA, respectively, in the record description of the reaction in the input file. See also Section B of the User's Guide. For proper choice of units, see Section 1.4.

4.4   Adiabatic processes

It is possible to simulate an adiabatic reaction at constant volume. In particular this means that the total heat formation Q_{tot} and the temperature T can be simulated by two extra equations. The specific heat capacity, $c_v(R_s)$, must be known for each species R_s, and the specific heat of reaction, q_r, must be known for each reaction r. In this context q_r is defined as $-\Delta H$ (H = enthalpy), which means that q_r is positive for an exothermic reaction. The proper units are $K^{-1} \times mol^{-1} \times dm^3 \times kcal$ or $K^{-1} \times mol^{-1} \times dm^3 \times Joule$ for c_v and $kcal \times mol^{-1} \times dm^3$ or $Joule \times mol^{-1} \times dm^3$ for q_r. The differential equations governing Q_{tot} and T are

$$
\frac{dQ_{tot}}{dt} = \sum_{r=1}^{M} k_r[R_j][R_k] \, q_r
\tag{15}
$$

and

$$\frac{dT}{dt} = \frac{dQ_{tot}/dt}{\sum_{s=1}^{N} c_v(R_s)[R_s]} = \frac{\sum_{r=1}^{M} k_r[R_j][R_k] q_r}{\sum_{s=1}^{N} c_v(R_s)[R_s]},$$ (16)

respectively, where M is the number of reactions and N the number of species in the system. In (15) R_j and R_k are the second-order reactants attached to the reaction r with rate constant k_r. For a first-order reaction we should set $[R_k] = 1$. Zero-order reactions are not envisaged to contribute to Q_{tot}.

If some of the reaction rates k_r assume the modified form (14), then there will be a coupling between (15), (16), and the kinetic differential equations. If, on the other hand, all the k_r are constant, then (15) and (16) will be completely decoupled from the kinetic equations.

The specific heats q_r are entered in the input records for the corresponding reactions r as Q = ..., see Section B of the User's Guide. The specific heat capacities $c_v(R_s)$ are given for each species by the command HCV = ..., see Section B of the User's Guide.

4.5 Third body reactions

Reactions of higher order than 2 should not be considered in condensed phase, and the present version of CHEMSIMUL does not accept reactions of higher order.

However, in gas phase many reaction rates are dependent on a "third body" to absorb surplus reaction energy, as in the reactions

$$A + B + M \rightarrow P + M$$ (17)

and

$$A + M \rightarrow C + D + M$$ (18)
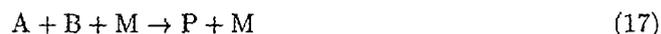
These reactions are formally third and second order reactions, but actually they are pseudo-second and pseudo-first order, respectively, because the concentration [M] does not change during the reaction. This mean that the differential equation of third-order reaction type

$$\frac{d[P]}{dt} = k[A][B][M]$$ (19)

can be reduced to

$$\frac{d[P]}{dt} = k_M[A][B]$$ (20)

where

$$k_M = k[M].$$ (21)

The substitution (21) will be done automatically for all reactions containing M (both pseudo-first and pseudo-second order) by using the input command THIRD(M) = [M], see Section C of the User's Guide.

4.6 Maximum values and half-lives for species

From the computed simulation curves CHEMSIMUL may estimate maximum-values and half-lives for all the species. The latter are stated as period of formation as well as period of decay, both related to the maximum, if there is such a maximum.

4.7 Mixed particle irradiation

The simulation of the radiation chemistry with storage of radioactive waste includes variation with time of dose rate as well as radiation yields.

The present version of CHEMSIMUL is able to simulate a mixture of exponentially decaying dose rates.

Let m isotopes be given. Each of them is a potential emitter of α-, β-, γ-, and neutron-radiation. With isotope i we assign the following parameters:

$$\tau_i \quad = \quad \text{period (half-life) in } s. \text{ May be } \infty \text{ (default).} \tag{22}$$

$$\lambda_i \quad = \quad \text{decay rate} = \ln 2/\tau_i \text{ in } s^{-1}. \text{ May be } 0 \text{ (default).} \tag{23}$$

$$D_i^\alpha \quad = \quad \alpha \text{ dose rate} \tag{24}$$

$$D_i^\beta \quad = \quad \beta \text{ dose rate} \tag{25}$$

$$D_i^\gamma \quad = \quad \gamma \text{ dose rate} \tag{26}$$

$$D_i^n \quad = \quad \text{neutron dose rate} \tag{27}$$

where the above dose rates are initial values; the units for the α-, β-, γ-, and neutron dose rates are $krad \times s^{-1}$ or $Gray \times s^{-1}$. Moreover, we shall define G-values for the four types of radiation for each species R_s ($s = 1, \ldots, N$): G_s^α, G_s^β, G_s^γ, G_s^n. We are now able to compute the production rate for R_s from all these radiation types at time t:

$$\frac{d[R_s]}{dt} = \sum_{i=1}^{m} e^{-\lambda_i t}(G_s^\alpha D_i^\alpha + G_s^\beta D_i^\beta + G_s^\gamma D_i^\gamma + G_s^n D_i^n) \times c, \tag{28}$$

where c is the conversion constant introduced in Sections 1.3 and 1.4. When setting up the differential equations, the sum in (28) should be added to the right-hand side (cf. (8), (11), and (56)).

For input prescriptions concerning mixed particle irradiation you should consult Section E of the User's Guide.

5 User's Guide for CHEMSIMUL Version Dec 1998

The present User's Guide is written as an almost self-contained manual within the frames of the complete CHEMSIMUL document.

A Running the program

CHEMSIMUL runs on PC, VMS, UNIX, and other systems, cf. Section 9. You may run CHEMSIMUL directly by just typing:

```
chem
```

Then the program answers with the text:

```
ENTER NAME OF INPUT FILE:
```

You now type the input file name, including its extension (normally .dat), e.g. mycase.dat (when the extension is .dat it may be omitted); the output file will then be named mycase.res. If the input file is not available in your current directory, or is corrupted, the program aborts with a message like:

```
INPUT FILE COULD NOT BE OPENED (ERROR CODE =    16534)
*** THIS CASE IS DELETED ***
```

(the actual error code may be system dependent), and the program must be restarted. CHEMSIMUL checks all the input data, and if errors are found the program is discontinued with an error message in plain text on the computer screen. The error messages should be sufficient for identifying the kind of errors and correcting them in the input file. When the input file is accepted, the program types:

```
REACTION SYSTEM IS BALANCED - PROGRAM CONTINUES -
WAIT UNTIL STATUS BAR BELOW IS FILLED WITH ASTERISKS ...
```

The status bar reflects the current fraction of the simulation that is already completed. It is useful for estimating the progress of the integration procedure for long simulations. A snapshot of the status bar may look as follows:

```
**************************  .      .      .      .      .      .      .      .
end{verbatim}
After the status bar is completely filled with asterisks, the
program continues:

\begin{verbatim}
EXPERIMENTAL FILE CAN BE PLOTTED TOGETHER WITH THE PLOT EXPRESSION(S):
PE1:(expression)
PE2:(expression)
ENTER FILE NAME (RETURN FOR NO EXPERIMENTAL FILE):
```

If you wish to compare the simulation with experimental data you now type the name of the file. If you have no experimental file you start the computation with a (RETURN).

After the CHEMSIMUL run you may plot the results by GNUPLOT or by other means. You invoke GNUPLOT by the following command:

```
gnuplot gnu.cmd
```

Here gnu.cmd is a file created by CHEMSIMUL that causes GNUPLOT to read and display the data file mycase.plt, also created by CHEMSIMUL, where mycase was the name of your problem. (Other graphics programs may of course be substituted for GNUPLOT to display the data in mycase.plt.)

Some CHEMSIMUL installations for PC are equipped with a menu driver. The user interface for this driver is a set of DOS batch files 1.BAT, 2.BAT, 3.BAT, 4.BAT, 5.BAT, and 6.BAT. Thus by giving a numeric command you may e.g. run the CHEMSIMUL code and then automatically GNUPLOT, if a plot was requested. You may also browse through the result file. CHEMSIMUL drivers are available for Windows 95, too.

B Description of general part of input file

Preliminaries

All input data are identified by well-defined character strings. The reaction equations always begin with RE, the start concentration of reactants always with CON, etc.. The order of the input data can be chosen freely according to the user's taste. The program is case insensitive for command typing, but case sensitive for typing the species names in the reaction equations.

Only plain ASCII text characters are applied, so you may just use your favorite editor to edit the CHEMSIMUL input files.

Reaction equations

Each reaction equation is prefixed with an identification REn:, where RE means Reaction Equation and n is the equation identification number. The reaction equation terminates with a semicolon (;) followed by the thermodynamics constants A, EA, B (Section 4.3), and Q(Section 4.4), separated by a comma (,). Interspersed blanks for enhancing readability are allowed. Example:

```
RE3: H[+]+OH[-]=H2O; A=2.35E13, EA=3
RE2: H+HO2=OH+OH; A=2.5E11, EA=1.9, Q=38.3
RE64: 2*OH=H2O2; A=6.0E9
```

The stoichiometric constants are integers, while the rate constants are real numbers; their values can be entered in free format. CHEMSIMUL supports "scientific notation" for exponents, using the symbol E (or D) for the exponent, i.e. 1.4E11 means $1.4 \cdot 10^{11}$. The maximum order of a chemical reaction to be simulated is limited to 2, i.e. up to 2 reactants can be written on the left hand side of the reaction equations, but there are virtually no restrictions on the number of products on the right hand side. The maximum number of characters in a species (i.e. reactant or product) is 16. The are no bounds on the number of reactions or species.

The terms A, EA and B are related to the modified Arrhenius expression for the rate constant given in Section 4.3, $k = AT^\beta \exp(-E_a/(RT))$, where T is the temperature in Kelvin: $A = A$, EA $= E_a$, and B $= \beta$. The factor T^β is included for gas phase kinetics, with β being an empirical exponent. A is the so-called frequency factor, and E_a the activation energy.

If only A is included in a reaction then its value will be just the rate constant.

The term Q corresponds to the specific heat formation q_r for reaction r, as described in Section 4.4.

Default values for EA, B, and Q are zero, while the input of A is mandatory for all reactions.

Names of species

Names of species may be chosen freely, apart from certain restrictions. The main rule is that they should be alphanumeric and begin with a letter; they may contain small and

capital letters and are interpreted in a case-sensitive way. However, species names may also be qualified by square brackets containing strings of + or -, like FE[+++] or OH^{-}. This feature enables CHEMSIMUL to check the electro neutrality. It is also allowed to use square brackets as numerical markers of species names, like A[2]. The two modes may be combined, but not within a single pair. Thus A[2][+] would be legal but not A[2+].

Concentration values

The command CON(S) = ... gives the numerical value of the start concentration for the reactant S. Example:

con(OH^{-}) = 1.0E-7

Default values of the concentrations are 0, i.e. those chemical species in the reaction equations for which no start concentrations are given, are automatically assigned the initial concentration zero. The concentration unit is $mol \times dm^{-3}$ or $molecules \times cm^{-3}$.

G values

If the reaction system is irradiated e.g. by high-energetic electrons or by gamma rays, then the G-values must be specified. G-values were discussed in Sections 1.3 and 1.4. They are in units of $molecules$ per $100\,eV$. If say the reactant OH is produced by an irradiation given by the total dose D $krad$ during the radiation time t_r, then the rate of change of [OH] measured in $mol \times dm^{-3}$ is given by:

$$\frac{d(\text{OH})}{dt} = c \times G(\text{OH}) \times D \,/\, t_r, \tag{29}$$

where $c = 1.036 \cdot 10^{-6}$ is the conversion constant. (The numerical value of c depends on density and units (Section 1.4) and may be reset by the command CONVERT (Section C); if e.g. $Gray$ is used, then you should set $c = 1.036 \cdot 10^{-7}$.) The G-values default to 0 in CHEMSIMUL. Example:

G(OH) = 2.7

Heat capacity values

In Section 4.4 it was discussed how CHEMSIMUL can deal with adiabatic processes. When simulating such a system, the specific heat capacity HCV = $c_v(R_s)$ should be entered for the species involved as well as the reaction heat, Q = q_r, for all reactions. The proper units are $K^{-1} \times mol^{-1} \times dm^3 \times kcal$ or $K^{-1} \times mol^{-1} \times dm^3 \times Joule$ for HCV and $kcal \times mol^{-1} \times dm^3$ or $Joule \times mol^{-1} \times dm^3$ for Q. By default the specific heat capacity values are set to zero. Example:

hcv(H2O) = 0.018

Hint: In diluted aqueous solutions it is sufficient to enter HCV for water.

C Simulation commands

In the following we have collected all the various commands in CHEMSIMUL that in some sense are related to the simulation process. They are ordered alphabetically. Note that some of them are obligatory and are marked accordingly. Also note that an asterisk (*) in front of a command makes the command inoperative. For example:

*rstart

CASE

This begins an identifying text for the case to be simulated. Example:

```
case: SIMULATION OF NOX.
```

It is possible to continue the case text over a second line. In that case the first character on the second line must be an asterisk (*).

CONVERT

Sets the conversion constant c (Sections 1.3 and 1.4), if you need another value than the default value $c = 1.036 \cdot 10^{-6}$. Example:

```
convert = 1.036E-7
```

Recall that the conversion constant depends on the unit for dose:

Irradiation dose	Conversion constant
TOTALDOSE	CONVERT
krad	1.036E-6 (default)
Gray	1.036E-7

Table 2: Value of the conversion constant c

DIG

This command defines the number of significant digits in the result table of CHEMSIMUL. By default DIG = 3. Example:

```
dig = 5
```

DIFFEQ

If this command is written in the input file, then the differential equation system will be printed. By default the system is not printed. See also Sections 3.3 and Sections 2.2.

ENDDATA

* Obligatory.
This command ends the data for a simulation, and commands after ENDDATA are ignored.

EPS

* Obligatory.
The command EPS = ε_{rel} gives the relative accuracy ε_{rel} in the integration routine (LSODA). Example:

```
eps = 0.01
```

Hint: The normal range for EPS is between 0.1 and 0.001. EPS = 0.01 can be used in most cases.

FSTSTP

* Obligatory.
The command FSTSTP = h_0 gives the initial integration step h_0, measured in seconds. (The program has automatic step size control.) Example:

```
fststp = 1.0E-8
```

Hint: The integration time increases if FSTSTP *is too large or too small. The optimum* FSTSTP *depends on the chemical kinetics.*

HMAX

* Obligatory.
The command HMAX = h_{max} gives the maximum length h_{max} of an integration step in *s*. HMAX should be small enough to preserve the important features, but large enough to admit a reasonable integration time. Example:

```
hmax = 0.001
```

Hint: Use a HMAX *equal to, say,* TEND/10 *in the first attempt of a simulation.*

MATHINFO

When this command is present, an additional file message.ode will be created that contains statistical information about the numerical integration.

MAXCON

To find the maximum concentration value $[S]_{max}$, together with the formation and decay half-lives (in *s*) for a species S (Section 4.6), you should type the command MAXCON(S). Example:

```
maxcon(H[+])
```


NORMALIZE

With this command CHEMSIMUL will normalize the plot by setting the maximum value of the calculated plot expressions equal to 1.0. Experimental files cannot be plotted when NORMALIZE is used.

OUTTYPE

Defines scaling type of the plot. There are four different types. By default OUTTYPE = 1.
OUTTYPE = 1, linear time and concentration scales.
OUTTYPE = 2, linear time, logarithmic concentration scales.
OUTTYPE = 3, logarithmic time, linear concentration scales.
OUTTYPE = 4, logarithmic time and concentration scales.

Example:

```
outtype = 3
```


PE

CHEMSIMUL supports the so-called *plot expressions*. These admit general arithmetic expressions in the species concentrations and/or heat (HEAT) and temperature (TEMP) to be plotted as functions of time. Allowed operators are sum (+), difference (−), product (*), and exponentiation (^) (cf. Section 7.5). Functions are not included in the present version. Plot expressions are initiated by PE followed by a number (in sequence), and a colon. Example:

```
PE1: OH
PE2: TEMP-273
PE3: 210*H2O2+1800*O2[-]-FE[+++]^1.5/220
```

When an invalid operation occurs during evaluation of a plot expression, e.g. a zero division, a warning will be printed on first instance only and the result cleared to zero. Problems with zero initial concentrations in denominators may sometimes be circumvented by restarting from the trailing edge of the rectangular radiation pulse, cf. the command RSTART.

PLONPA

Defines the maximum number of curves (plot expressions) on each plot. The command is also used to seperate plots with corresponding experimental data. By default PLONPA = *number of plot expressions*. Example:

plonpa = 2

GNUPLOT generates automatically the maximum value on the y-axis according to the highest calculated value of any plot expression in a plot. If, however, an experimental file is included, then the maximum value on the y-axis will be chosen according to the highest experimental value.

PRINTS

* Obligatory.
The command PRINTS = n defines the total number n of output lines in the result table after time-zero. Must be positive. Each line contains the value of the time followed by the values of concentrations belonging to that time. Example:

prints = 25

R

* Obligatory if you use activation energy expressions in the reactions (Section 4.3).
The gas constant in the the units you chose. Example:

r = 1.9869E-3

RADPRS

* Obligatory in case of irradiation.
The command RADPRS $= n_r$ defines the number n_r of output lines in the result table during irradiation after time-zero. Note: RADPRS must satisfy the condition 0 < RADPRS < PRINTS. See also PRINTS. Example:

radprs = 5

RADTIME

The command RADTIME = t_r gives the irradiation time t_r in seconds for the rectangular pulse. Default value is zero. Example:

radtime = 1E-8

RSTART

With this command CHEMSIMUL will produce a restart file holding the concentration of all species at TEND. This file contains the concentration value for a continuation of the simulation. The continuation is made by using the same .dat file, with the data in the restart file inserted at the end, just before the end command ENDDATA. When the program

reads the .dat file, then the input of the concentration values are overwritten by the values from the restart file. The restart file has the name of the input file with the extension .sav. Example:

```
rstart
```

If this command is used e.g. in the input file nox.dat, then the restart file gets the name nox.sav. The continuation is made by pasting the .sav file at the end (just before ENDDATA) of the .dat file that you want to use for the simulation.

The restart facility may e.g. be used in the simulation of circulating cooling water in reactors where the different stages in the cooling cycle present different reaction conditions like dose rate and temperature. The results from the simulation of the first stage is used as start concentrations in the input file for the second stage, the results from the second stage as input in the third stage, and so on, until the cycle is completed.

TEMP

The command TEMP $= T$ defines the temperature T of the reaction system in degree Kelvin (K). By default $T = 300$. Example:

```
temp = 455
```

TEND

* Obligatory.
The command TEND $= t_{end}$ gives the end time t_{end} in s for the simulation. Example:

```
tend = 12
```

THIRD

The command THIRD(M) $=$ [M] includes a third-body species M in the rate constant for its reaction as explained in Section 4.5. Example:

```
third(M) = 0.013
```

TOTALDOSE

The command TOTALDOSE $= D$ gives the total irradiation dose D in *krad* during the irradiation time for the rectangular pulse. Example:

```
totaldose = 3.7
```

If TOTALDOSE is entered in *Gray*, the the conversion constant c must be set to $1.036 \cdot 10^{-7}$ by the command CONVERT.

Use of the command TOTALDOSE precludes the use of the ISOTOPES block decribed in Section E.

D Description of the experimental file

The name of the experimental file can be chosen freely. The file contains pairs of experimental data in two columns separated by an optional comma and at least one space. The time is in the first column and the measured value (corresponding to a plot expression PE) in the second. Example:

```
        0 0
        2E-6 2.4E-4
        4E-6 3.2E-4
        6E-6 3.6E-4
```

E Isotope input

We shall here give the format of input data for the mixed-particle irradiation facility described in Section 4.7. All isotope data must be confined to a single block in the data file. This block begins with the command ISOTOPES $= m$, where m is the total number of isotopes, and it ends with the command END ISOTOPES. The isotope block may be positioned freely in the data file before ENDDATA, and its data may come in arbitrary order. With reference to Section 4.7 we write PERIOD(i), DA(i), DB(i), DG(i), DN(i) for τ_i, D_i^α, D_i^β, D_i^γ, D_i^n, respectively, and we write GA(R), GB(R), GG(R), GN(R) for the G-values G_s^α, G_s^β, G_s^γ, G_s^n, for a given species R $=$ R$_s$. By default all periods τ_i are ∞. Thus if half life is not entered in the input data there will be no decay, and mixed-particle irradiation in reactors can be simulated. An example is sketched below:

```
ISOTOPES = 2
PERIOD(1) = ...
DA(1) = ...
DB(1) = ...
DN(1) = ...
     .
     .
     .
GA(OH[-]) = ...
GB(OH[-]) = ...
GG(OH[-]) = ...
GN(OH[-]) = ...
END ISOTOPES
```

Use of the ISOTOPES block precludes the use of the command TOTALDOSE in Section C.

F Sample data set

The complete input data file for the sample combustion test that produced the output in Section 3.1 is listed below:

```
RE1: H+H=H2; A=4.0E7
RE2: H+O2=HO2; A=4.5E8
RE3: H+HO2=OH+OH; A=6.5E10
RE4: HO2+HO2=H2O2+O2; A=2.0E9
RE5: OH+OH=H2O2; A=4.0E9
RE6: H+OH=H2O; A=1.0E10
RE7: OH+HO2=H2O+O2; A=6.0E10
RE8: OH+H2=H2O+H; A=4.0E3
G(H)=1.0
TOTALDOSE=0.9
CON(O2)=2.0E-4
CON(H2)=4.0E-3
RADTIME=5.0E-9
FSTSTP=1.0E-9
PRINTS=12
RADPRS=2
TEND=1.0E-3
EPS=1.0E-2
HMAX=1.0E-5
PE1:HO2
*DIFFEQ
CASE: 5 mbar O2 + 100 mbar H2 + Ar to 1 atm. k8=4000
ENDDATA
```
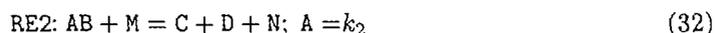
6 Hints for solving special problems

6.1 How to mark a reaction

If you want to know how much material is passing through a single reaction you can mark the reaction without sacrificing the material balance: The reaction

$$\text{RE1: A} + \text{B} = \text{C} + \text{D}; \quad \text{A} = k_1 \tag{30}$$

is marked like this:

$$\text{RE1: A} + \text{B} = \text{AB}; \quad \text{A} = k_1 \tag{31}$$

$$\text{RE2: AB} + \text{M} = \text{C} + \text{D} + \text{N}; \quad \text{A} = k_2 \tag{32}$$

$$\text{CON(M)} = [M] \tag{33}$$

To ensure that RE1 is rate determining during the whole simulation you must choose high values for [M] and k_2:

$$[\text{M}] \times [\text{AB}] \times k_2 \gg [\text{A}] \times [\text{B}] \times k_1 \tag{34}$$

The simulated concentration [N] represents the yield of this reaction.

6.2 Maintaining a constant concentration of a solute

The program is designed to preserve the mass balance unconditionally, so if you want to maintain a constant concentration for solute S you may use either of two possible methods:

6.2.1 The equilibrium method

You must assign a high DUMMY concentration in equilibrium with S:

$$\text{CON(DUMMY)} = M \tag{35}$$

$$\text{RE1: DUMMY} = \text{S}; \quad \text{A} = a \tag{36}$$

$$\text{RE2: S} = \text{DUMMY}; \quad \text{A} = b \tag{37}$$

Choose a value for the rate constant a (e.g. 100) and calculate b from the equation:
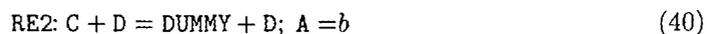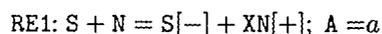
$$[\text{DUMMY}] \times a = [\text{S}] \times b \tag{38}$$

The concentration CON(DUMMY) $= M$ must be so high that the change in concentration during the simulation is insignificant.
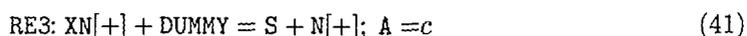
6.2.2 The conservation method

This method recreates S whenever S is consumed in a reaction, and removes S whenever S is produced in a reaction. Consider the reactions:

$$\text{RE1: S} + \text{N} = \text{S}[-] + \text{N}[+]; \quad \text{A} = a$$

$$\text{RE2: C} + \text{B} = \text{S} + \text{D}; \quad \text{A} = b \tag{39}$$
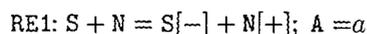
Assign a high DUMMY concentration as in (35). Change the equations as follows:

$$\text{RE1: S} + \text{N} = \text{S}[-] + \text{XN}[+]; \quad \text{A} = a$$

$$\text{RE2: C} + \text{D} = \text{DUMMY} + \text{D}; \quad \text{A} = b \tag{40}$$

and add the reaction

$$\text{RE3: XN}[+] + \text{DUMMY} = \text{S} + \text{N}[+]; \quad \text{A} = c \tag{41}$$

Choose the rate constant c so high that S is produced much faster in RE3 than it is consumed in RE1.

6.3 Maintenance of gas/liquid equilibrium

If you have a gas phase (volume $= g$) in equilibrium with a liquid phase (volume $= \ell$) and you want to maintain the equilibrium of for example oxygen during the simulation, this can be accomplished in the following way:

First determine the equilibrium concentration ratio of liquid oxygen O_2 and gas phase oxygen $O_{2,gas}$:

$$\frac{[O_2]}{[O_{2,gas}]} = r \tag{42}$$

Then calculate [DUMMY] as the oxygen concentration if the gas phase has the same volume as the liquid phase:

$$[DUMMY] = [O_2] \times \frac{g}{\ell} \tag{43}$$

Finally determine the rate constants a and b in the equilibrium reactions

$$RE1: DUMMY = O2; \ A =a \tag{44}$$

$$RE2: O2 = DUMMY; \ A =b \tag{45}$$

Choose the value for a (e.g. 100) and calculate b from the equations:

$$[DUMMY] \times a = [O_2] \times b \tag{46}$$

and

$$\frac{[O_2]}{[DUMMY]} = r \tag{47}$$

6.4 Transport, dissolution and diffusion.

Problems with transport, dissolution, and diffusion, can be solved by using a first or zero order reaction. In case of diffusion in or out of the solution a first order reaction should be used:

$$RE1: H2 = DUMMY; \ A =f(D) \tag{48}$$

where $f(D)$ is a function of the diffusion constant D.

This method can also be used to modify adiabatic systems with transport of heat in or out of the system by using a first order reaction with a Q value:

$$RE1: S = DUMMY; \ A =c; \ Q =q \tag{49}$$

If CON(S) = [M], the heat transport will be determined by:

$$\frac{dQ}{dt} = a \times [M] \times q \tag{50}$$

In case of dissolution or precipitation two zero order reactions can be used:

$$G(solute) = a \tag{51}$$

and

$$G(solid) = -a \tag{52}$$

If you use a total dose D_{tot} $krad$, the irradiation time t_r s and G(solute) = 1, then

$$\frac{d[solute]}{dt} = c \frac{D_{tot}}{t_r} \ mol \times dm^{-3} \times s^{-1} \tag{53}$$

where $c = 1.036 \cdot 10^{-6}$ is the conversion constant.

A saturated solution in equilibrium with solid matter is treated as the gas equilibrium. Transport in form of addition into the system must be solved according to the actual method of addition. In case of a continuous addition during the the whole computation time either a zero order reaction (G-value) or a first-order reaction can be used. If the addition is instantaneous at time t you can simulate the reactions until time t using the RSTART command. Then add the concentration of the new solute to the .SAV file and enter the .SAV concentrations into your .DAT file as new start concentrations for the continued simulation.

Rasmussen and Bjergbakke [1] give several examples of simulations using an earlier version of CHEMSIMUL. Their examples span from dosimetry and NO_x processes in the atmosphere to the study of radiolysis of ground water from spent nuclear fuel. They also simulate classical processes, notably the Belusov-Zhabotinskij oscillating reaction, which has gained renewed interest as a chemical example of a dynamic system with the typical nonlinear features of limit cycles, period doubling, and eventually chaos.

Here we shall only illustrate two of these test runs with graphical output obtained with CHEMSIMUL plot expressions and GNUPLOT. Details for these examples are found in Rasmussen and Bjergbakke [1].

6.5 Fricke dosimeter

CASE: Fricke dosimeter

6.6 Oregonator

CASE: OREGON Belusov-Zhabotinskii
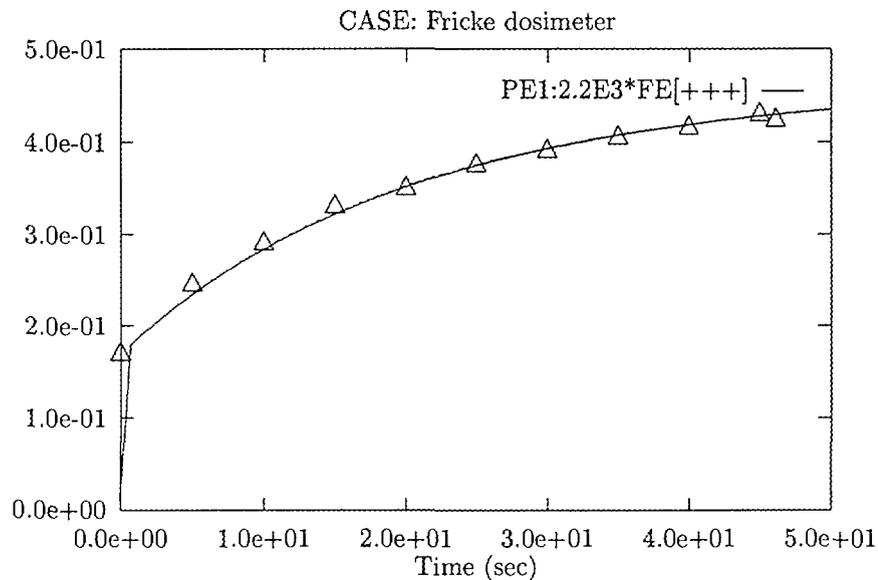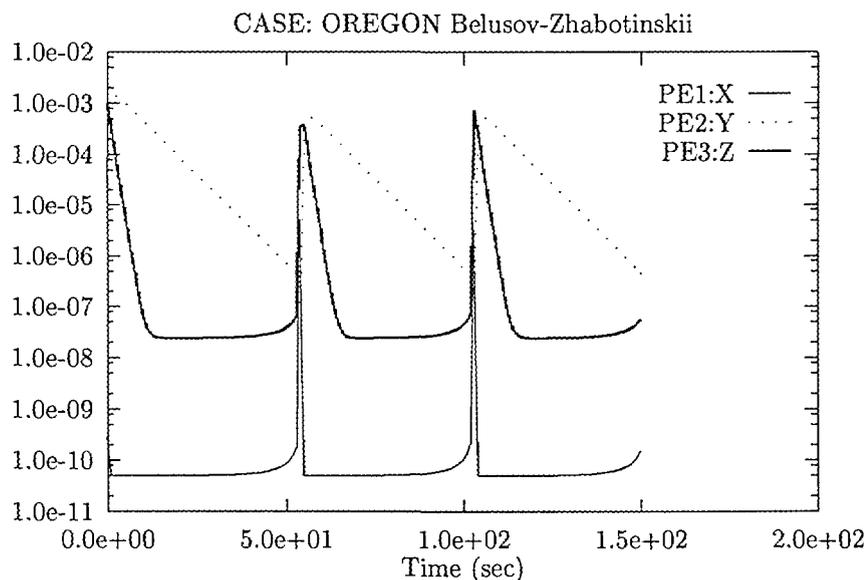
## 6.7 Further references to works using CHEMSIMUL

Moreover, CHEMSIMUL was used in numerous research projects through the last decades. To give a few references to relevant publications, we mention the papers by Christensen and Bjergbakke [11, 12, 13], by Hart *et al.* [14], and by Bjergbakke *et al.* [15, 16].

7 Mathematical implementation

In the following we shall discuss the principal features in the mathematical implementation of the CHEMSIMUL program. Readers without special interest for the CHEMSIMUL mathematics may skip this chapter.

7.1 Translation principle for reactions

To explain the mechanism of the CHEMSIMUL translator, let us assume a general chemical system being specified with M reactions involving altogether N species. We write the reaction system in the following way:

$$\text{Re}(r): \quad \alpha_j \times R_j + \alpha_k \times R_k \to \sum \alpha_\ell \times R_\ell, \quad r = 1, \ldots, M, \quad (54)$$
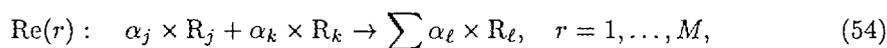
where R_s is the chemical symbol for species s, $s = 1, \ldots, N$. The left-hand side is empty for a zero-order reaction. Otherwise α_j, α_k, α_ℓ are non-negative integers satisfying $1 \leq \alpha_j + \alpha_k \leq 2$. For a second-order reaction we may have $j \neq k$ or $j = k$; in both cases $\alpha_j + \alpha_k = 2$. Each reaction $\text{Re}(r)$ is assigned a rate constant k_r. Moving the reactant terms in (54) to the right-hand side, we may assign with every species s in reaction r a *stoichiometric coefficient* a_{rs}, which is positive for a product and negative for a reactant. Setting unassigned entries $a_{rs} = 0$, we obtain the *stoichiometric matrix* $\mathbf{A} = \{a_{rs}\} \in \mathbb{Z}^{M \times N}$. This enables us to express the reaction system in compact vector-matrix notation as

$$\mathbf{A}\mathbf{v} = \mathbf{0}, \quad (55)$$

where the N-dimensional *species vector* $\mathbf{v}$ contains the distinct species names R_s, $s = 1, \ldots, N$. The resulting general ODE system for the species concentrations has the form

$$\frac{d[R_s]}{dt} = \sum_{j,k} n_{jks} M_{jks} [R_j][R_k] + \sum_j n_{js} M_{js} [R_j] + c\, G_s D(t), \quad s = 1, \ldots, N. \quad (56)$$

The right-hand side of (56) is the sum of a quadratic form coming from the second-order reactions, a linear form from the first-order reactions, and a term coming from the radiolytic zero-order reactions. The 3-dimensional tensors n_{jks} and M_{jks} contain the stoichiometric coefficients a_{rs} and the reaction rates k_r, respectively. For a given s, the sum is taken over pairs (j, k) for which (R_j, R_k) is a reacting pair in some reaction $r = r(j, k)$ involving R_s on either side, with $n_{jks} = a_{rs}$ and $M_{jks} = k_r$. A similar interpretation holds for the linear form. For simplicity we here assume that the zero-order term has the form $c\, G_s D(t)$, where c is the conversion constant, G_s the G-value for species s, and $D(t)$ the dose rate at time t. (In case of mixed-particle irradiation the zero-order term is given by the right-hand side of (28).)

Given a computerized write-up like (10) of the reactions (54), CHEMSIMUL is now able to assemble the ODE system (11) or (56) from all the individual pieces in the reactions. On encounter it tabulates every new species and includes its name in the symbol set S. It also stores the rate constants k_r. After the scan phase an assembly phase is invoked. Here CHEMSIMUL constructs a table with a line for each term on the right-hand side of the total ODE system. Entry 2 in the line contains the stoichiometric coefficients n_{jks}, while the other entries contain address pointers to 1) the species s, 3) the reaction r, 4) $[R_j]$, and 5) $[R_k]$ (for first-order processes we may set $[R_k] = 1$). This pointer table gives a complete description of the ODE system and permits the evaluation of its Jacobian.

7.2 Stoichiometric balance check by linear programming

The accurate solution of the ODE system in chemical kinetics requires an overall conservation of the mass balance, as pointed out by Ridler et al. [17]. This balance may be affected by two main factors, the reaction mechanism and the integration process. Being a linear multistep method, the numerical integration scheme in CHEMSIMUL has the implicit property of mass preservation, as shown by Rosenbaum [18, 19]. Hence it is sufficient to make a static consistency check, and as stated in Section 4.1, such a check should be based on the demand of existence of strictly positive solutions to the balance equation (13) or (55) where A is the stoichiometric matrix and v the species vector.

Ridler et al. [17] proposed a heuristic checking method based on Gaussian elimination in integer arithmetic on A, and that method was adopted by Rasmussen and Bjergbakke in [1]. Later we have replaced it by a mathematically more stringent method: By the homogeneity of (55) we can replace the demand of positive values by a demand of all values be ≥ 1. Thus, if $A = \{a_{ij}\}$, it must be possible to find solutions $y_j \geq 1$ to the equations

$$\sum_{j=1}^{N} a_{ij} y_j = 0, \quad i = 1, \dots, M. \tag{57}$$

On writing $y_j = x_j + 1$ we may replace (57) by the system

$$Ax = b, \quad x \geq 0, \tag{58}$$

where $x = \{x_j\}$ and $b = \{b_i\}$ with $b_i = -\sum_{j=1}^{N} a_{ij}$. To decide the feasibility of (58) is a standard linear-programming problem. It can be solved efficiently by the simplex method.

7.3 Solution of the ODE system

The ODE systems in chemical kinetics are non-linear and often autonomous. As mentioned in Section 1.2 the corresponding initial-value problems may be of the stiff type. After many years of experience we are still in favor of using the LSODA solver from Hindmarsh' ODE-PACK collection, written by Petzold [4] and Hindmarsh [20]. This code switches automatically between stiff and nonstiff methods, starting with a nonstiff (Adams) method.

When the stiff (BDF) procedure is invoked, the Jacobian df/dy will be needed. Experience shows that it is more efficient to supply an analytical Jacobian than to let LSODA compute it internally by difference approximations. For kinetics problems df/dy is normally simple and cheap to calculate. There might, however, be a concern about space, if we want to solve really big problems, because the Jacobian is treated as a full matrix.

LSODA admits a combined relative and absolute error control: It controls the vector $e = \{e_i\}$ of estimated local errors in the solution $y = \{y_i\}$ by the restriction $\|r\|_\infty \leq 1$, where $r = \{r_i\}$ is given by $r_i = e_i/w_i$ with $w_i = \varepsilon_i^{\text{rel}}|y_i| + \varepsilon_i^{\text{abs}}$. Normally CHEMSIMUL will not need this flexibility; usually fixed relative and absolute tolerances $\varepsilon_i^{\text{rel}} = \varepsilon_{\text{rel}}$ and $\varepsilon_i^{\text{abs}} = \varepsilon_{\text{abs}}, \forall i$, give good results in practice.

Simulations over very long time spans may exploit the restart facility provided by LSODA.

In radiolytic simulations, where the radiation burst induces a constant source term in the finite time slot $[0, t_r]$ and then disappears, we found that the best way of using the solver was to select the one-step mode in combination with a critical time barrier $t = t_r$ (ITASK = 5 in LSODA). Integration beyond t_r proceeds ab initio from $t = t_r$.

Other useful options in LSODA are specification of a minimum step length h_{min}, a maximum step length h_{max}, and an initial step length h_0 to be attempted instead of the internally computed default value. On combining these possibilities judiciously we can solve quite hard kinetics problems efficiently. In rare cases, where a species approaches zero concentration very rapidly, we have seen traces of instability with negative concentrations. The best cure here is to restrict h_{max}; we could also decrease the tolerance ε_{rel}, but this has an adverse effect on computing time.

7.4 The Jacobian

When LSODA switches to its stiff integration procedure, it will need the Jacobian $d\mathbf{f}/d\mathbf{y}$ of the right hand side of the ODE system

$$\frac{d\mathbf{y}}{dt} = \mathbf{f}(\mathbf{y}, t) \tag{59}$$

This is a square matrix whose order m equals the dimension of $\mathbf{y}$. As mentioned in Section 7.3 it is better to supply an analytical Jacobian than to rely on an internal numerical estimation within LSODA. Let us first consider the case where the vector $\mathbf{y}$ contains concentrations only. In that case $m = N$, i.e. the number of species, and it is easy to compute $d\mathbf{f}/d\mathbf{y}$ from (56); see also the ODE system (11) for our sample case. We find for the (s, k)-element:

$$\left(\frac{d\mathbf{f}}{d\mathbf{y}}\right)_{sk} = \sum_j (n_{jks} M_{jks} + n_{kjs} M_{kjs})[\mathrm{R}_j] + n_{ks} M_{ks}. \tag{60}$$

For the interpretation of the j-sum, see similar comments in Section 7.1.

Incorporation of the adiabatic process descibed in Section 4.4 induces an augmentation of the Jacobian with two extra rows and columns, such that now $m = N + 2$. Row and column $m - 1$ refer to the total heat formation Q_{tot}, while row and column m refer to the temperature T. The entire column $m - 1$ becomes zero. The first N entries of row $m - 1$ are computed from (15):

$$\left(\frac{d\mathbf{f}}{d\mathbf{y}}\right)_{m-1,\ell} = \sum_{r=1}^{M} k_r q_r (\delta_{j\ell}[\mathrm{R}_k] + \delta_{k\ell}[\mathrm{R}_j]), \quad \ell = 1, \dots, N, \tag{61}$$

where the species indices $j = j(r)$ and $k = k(r)$ depend on the reaction r, and where δ_{ij} is the Kronecker delta. For first-order reactions r the corresponding summand in (61) should read $k_r q_r \delta_{j\ell}$. If the reaction rates k_r are independent of the temperature T, then the $(m - 1, m)$-entry is zero. If, on the other hand, there is a T-dependence through (14), then

$$\left(\frac{d\mathbf{f}}{d\mathbf{y}}\right)_{m-1,m} = \sum_{r=1}^{M} \frac{\partial k_r}{\partial T}[\mathrm{R}_j][\mathrm{R}_k] q_r, \tag{62}$$

where the temperature derivative of $k_r = k$ is found from (14):

$$\frac{\partial k}{\partial T} = AT^\beta \exp(-E_a/(RT)) \left(\frac{\beta}{T} + \frac{E_a}{RT^2}\right). \tag{63}$$

For the last row we find from (16):

$$\left(\frac{d\mathbf{f}}{d\mathbf{y}}\right)_{m\ell} = \frac{1}{S_{\text{cap}}^2} \left(\left(\frac{d\mathbf{f}}{d\mathbf{y}}\right)_{m-1,\ell} S_{\text{cap}} - S_{\text{heat}} c_v(\mathrm{R}_\ell)\right), \quad \ell = 1, \dots, N, \tag{64}$$

where S_{heat} and S_{cap} are the numerator and denominator, respectively, in (16). Moreover

$$\left(\frac{d\mathbf{f}}{d\mathbf{y}}\right)_{mm} = \frac{1}{S_{\text{cap}}} \left(\frac{d\mathbf{f}}{d\mathbf{y}}\right)_{m-1,m}. \tag{65}$$

Finally, the first N entries of the last column are computed from (56):

$$\left(\frac{d\mathbf{f}}{d\mathbf{y}}\right)_{sm} = \sum_{j,k} n_{jks} \frac{\partial M_{jks}}{\partial T}[\mathrm{R}_j][\mathrm{R}_k] + \sum_j n_{js} \frac{\partial M_{js}}{\partial T}[\mathrm{R}_j], \quad s = 1, \dots, N, \tag{66}$$

where the temperature derivative of the reaction rates are evaluated as in (63).

The dose terms in (56) or (28) bear no influence on the Jacobian.

7.5 Implementation of plot expressions

When describing the implementation of plot expressions (cf. PE in Section C of the User's Guide) we use an example:

```
PE1: 4711.77 + (5.4*OH[-]/7.45) - H2O2^1.5
```

The interpretation of such an expression has two phases, a lexicographical analysis and a successive processing. The lexicographical analysis decomposes the plot expression into a list of *atoms*. Each atom is a constant, a species name, or an operator. The 7 possible operators are those of elementary algebra: *, /, +, −, ^, (, and), where ^ stands for exponentiation; depending on context + and − can be infix or unary. The string of atoms is ended with an "empty atom", which is considered as an extra operator. In the above example we get the following table of atoms, where species are supposed to be assigned definite concentration values:

Atom#	Atom	Type
1	4711.77	Constant
2	+	Operator
3	(	Operator
4	5.4	Constant
5	*	Operator
6	OH^{-}	Species
7	/	Operator
8	7.45	Constant
9	)	Operator
10	−	Operator
11	H2O2	Species
12	^	Operator
13	1.5	Constant
14	empty	Operator

We process this table atom by atom using common techniques from computer science: We create and maintain two stacks V and O, the first for values (operands) and the second for operators.

An operand may be a constant, a concentration value, or a computation result. A fresh operand always pushes V and enters its top.

Let N be a new operator and T the current top-of-stack operator. If $N = $ "(", it pushes O and enters its top. If $|O| = 0$ the same happens: N pushes O and goes to its top. If $|O| > 0$ we observe if $T = $ "(" $\wedge N = $ ")". If so, T is devoured, O is popped, and a new atom enters. Otherwise N is compared with T according to priorities π. If $\pi(N) \leq \pi(T)$, a unary or binary operation takes place on the current top value(s) and O is popped, while the top value is updated with the current result. If the operation was binary, V is popped, too. After popping O we go back in the algorithm to the point where we checked if $|O| = 0$. If, on the other hand, $\pi(N) > \pi(T)$, then O is pushed and N stored on its top.

After storing the operator N, a new atom will be processed. The algorithm terminates when the empty operator enters the top of O. When this happen we must have $|V| = 1$.

We use the following priority list (from low to high):

$$\{empty\}, \quad \{(,)\} \quad \{infix+, infix-\}, \quad \{*, /\}, \quad ^\wedge, \quad \{unary+, unary-\}. \qquad (68)$$

The rules given above are fairly standard for processing expressions in programming languages and calculators. Quite general formulas can be treated in this way, like for instance

$$(+A + 0.19 * B * (B − 3) * C * Q − J/40) * (−E/F * 0.2 + 1/G^3) \qquad (69)$$

Note that functions are not supported in the present version of CHEMSIMUL.

8 Updates since previous version

CHEMSIMUL has undergone a number of revisions and enlargements since the original 1984 edition, documented by Rasmussen and Bjergbakke [1].

The previous CHEMSIMUL version dates back to 1993. By and large, this was a FORTRAN translation of the 1984 ALGOL code, with few new facilities, notably the modified Arrhenius rate constants (Section 4.3) and inclusion of adiabatic processes (Section 4.4).

The present 1998 edition, written in FORTRAN 90, has many new and improved features compared to the 1993 version, and some minor errors were corrected:

- The program is now independent of specific units (Section 1.4).

- The mass balance check is now made mathematically correct by linear programming technique (Section 7.2).

- The diagnostics for input errors are improved and made more precise.

- There is no limit on the number of reactions.

- There is no limit on the number of species.

- There is no limit on the number of terms in differential equations.

- Decaying mixed-particle radiation can be handled (Section 4.7).

- There is a test for electro neutrality for each reaction (Section 4.2).

- There is a test for electro neutrality for the totality of G values (Section 4.2).

- Gas constant R entered in input file when needed (Section C of the User's Guide).

- Conversion constant c may be modified in the input (Section C of the User's Guide).

- Default value of conversion constant c corrected from $1.038 \cdot 10^{-6}$ to $1.036 \cdot 10^{-6}$.

- An erroneous evaluation of the analytical Jacobian for adiabatic processes was corrected.

- Exponentiation operator is allowed in plot expressions (Section C of the User's Guide).

- Problem case text may be continued on a second line (Section C of the User's Guide).

- Case-sensitive interpretation of species names.

- Status bar on screen showing progress of simulation.

- Year 2000 protection.

- Miscellaneous minor improvements.

9 Computer requirements

CHEMSIMUL is written in Standard FORTRAN 90 and should therefore be able to run on many different computer systems. If you are interested in acquiring CHEMSIMUL, you should contact the authors. A PC demo version MINICHEM is freely available on request (Section 9.2).

9.1 Computer platforms

The main platform for running CHEMSIMUL is the PC (any 386, 486, Pentium or newer). It is also running on an Alpha platform under Digital VMS, and under several UNIX systems, e.g. HP and SGI.

A graphical interface is made to the bannerware program GNUPLOT [10], which is in widespread use. However, the CHEMSIMUL plot tables should allow you to use any other graphics system you might prefer.

The standard version of CHEMSIMUL has, in principle, no limits on the number reactions, species, etc.. Nevertheless, the specific hardware you are using might put its own restriction on problem size by limiting the total amount of allocatable data storage.

9.2 MINICHEM

MINICHEM is a limited PC version of CHEMSIMUL for demonstration purpose. It is freely available on request from the authors. MINICHEM has the same features as CHEMSIMUL, but problem size parameters are restricted in the following way:

Maximum number of reactions	10
Maximum number of species	20
Maximum number of isotopes	1

Otherwise MINICHEM runs precisely as CHEMSIMUL does, and the present manual therefore applies to MINICHEM, too.

References

[1] O. L. Rasmussen and E. Bjergbakke, "CHEMSIMUL — a program package for numerical simulation of chemical reaction systems," Tech. Rep. Risø-R-395(EN), Risø National Laboratory, DK-4000 Roskilde, Denmark, 1984.

[2] C. W. Gear, "Algorithm 407, DIFSUB for solution of ordinary differential equations," *Commun. ACM*, vol. 14, p. 185, 1971.

[3] A. C. Hindmarsh and G. D. Byrne, "EPISODE: An experimental package for the integration of systems of ordinary differential equations," Tech. Rep. UCID-30112, Livermore, 1975.

[4] L. R. Petzold, "Automatic selection of methods for solving stiff and nonstiff systems of ordinary differential equations," Tech. Rep. SAND80-8230, Sandia, 1980.

[5] A. R. Curtis and W. P. Sweetenham, "FACSIMILE release H user's manual," Tech. Rep. AERE R 11771, Harwell, 1985.

[6] W. Braun, J. T. Herron, and D. Kahaner, *ACUCHEM/ACUPLOT - A computer program for modelling complex reaction systems.* Gaithersburg, Maryland: National Bureau of Standards, 1986.

[7] P. Deuflhard, G. Bader, and U. Nowak, "LARKIN — a software package for the numerical simulation of LARge systems arising in chemical reaction KINetics," in *Modelling of chemical reaction systems* (K. H. Ebert, P. Deuflhard, and W. Jäger, eds.), (Berlin, Heidelberg, NY), Springer-Verlag, 1981.

[8] R. J. Kee, J. A. Miller, and T. H. Jefferson, "CHEMKIN: A general-purpose, problem-independent, transportable, FORTRAN chemical kinetics code package," Tech. Rep. SAND80-8003, Sandia, 1980.

[9] O. L. Rasmussen, E. Bjergbakke, P. Pagsberg, and P. Kirkegaard, "CHEMSIMUL — software and methods for numerical simulation of chemical reaction systems," in *Industrial Mathematics Week*, (Trondheim), pp. 174–181, Norwegian Institute of Technology (NTH), 1992. Paper presented by P. Kirkegaard.

[10] T. Williams and C. Kelley, *GNUPLOT — An Interactive Plotting Program*, 1993. Manual for Version 3.5.

[11] H. Christensen and E. Bjergbakke, "Alfa-radiolysis of aqueous solutions," in *Mat. Res. Soc. Symp. Proc.*, vol. 50, p. 401, Materials Research Society, 1986.

[12] H. Christensen and E. Bjergbakke, "Application of CHEMSIMUL for groundwater radiolysis," *Nuclear and Chemical Waste Management*, vol. 6, p. 265, 1986.

[13] H. Christensen and E. Bjergbakke, "Radiation induced dissolution of UO2," in *Mat. Res. Soc. Symp. Proc.*, vol. 84, (Boston), Materials Research Society, 1987.

[14] E. J. Hart, K. Sehested, E. Bjergbakke, and J. Holcman, "Gamma-ray initiated chain decomposition of aqeuous ozone solutions," *Radiat. Phys. Chem.*, vol. 29-5, p. 399, 1987.

[15] E. Bjergbakke, Z. D. Draganic, K. Sehested, and I. G. Draganic, "Radiolytic products in waters. Part I: Computer simulation of some radiolytic processes in the laboratory," *Radiochimica Acta*, vol. 48, p. 65, 1989.

[16] E. Bjergbakke, Z. D. Draganic, K. Sehested, and I. G. Draganic, "Radiolytic products in waters. Part II: Computer simulation of some radiolytic processes in nature," *Radiochimica Acta*, vol. 48, p. 73, 1989.

[17] G. M. Ridler, P. F. Ridler, and J. G. Sheppard, "A systematic method of checking of systems of chemical equations for mass balance," *J. Phys. Chem.*, vol. 81, p. 2435, 1977.

[18] J. S. Rosenbaum, "Conservation properties of numerical integration methods for systems of ordinary differential equations," *J. Comp. Phys.*, vol. 20, p. 259, 1976.

[19] J. S. Rosenbaum, "Conservation properties of numerical integration methods for systems of ordinary differential equations. 2.," *J. Phys. Chem.*, vol. 81, p. 2362, 1977.

[20] A. C. Hindmarsh, "LSODE and LSODI, two new initial value ordinary differential equation solvers," *ACM-SIGNUM Newsletter*, vol. 15, no. 4, pp. 10–11, 1980.

Bibliographic Data Sheet   Risø-R-1085(EN)

Abstract (Max. 2000 char.)

CHEMSIMUL is a computer program system for numerical simulation of chemical reaction systems. It can be used for modeling complex kinetics in many contexts, in particular radiolytic processes. It contains a translator module and a module for solving the resulting coupled nonlinear ordinary differential equations. An overview of the program system is given, and its use is illustrated by examples. A number of special features are described, in particular a method for verifying the mass balance. Moreover, the document contains a complete User's Guide for running CHEMSIMUL on a PC or another computer. Finally, the mathematical implementation is discussed.

Descriptors INIS/EDB

RADIOLYSIS; CHEMICAL REACTION KINETICS; COMPUTERIZED SIMULATION; COMPUTER PROGRAM DOCUMENTATION; PULSE TECHNIQUES; DIFFERENTIAL EQUATIONS

RISØ

Risø National Laboratory carries out research within science and technology, providing Danish society with new opportunities for technological development. The research aims at strengthening Danish industry and reducing the adverse impact on the environment of the industrial, energy and agricultural sectors.

Risø advises government bodies on nuclear affairs.

This research is part of a range of Danish and international research programmes and similar collaborative ventures. The main emphasis is on basic research and participation in strategic collaborative research ventures and market driven tasks.

Research is carried out within the following programme areas:

- Industrial materials
- New functional materials
- Optics and sensor systems
- Plant production and circulation of matter
- Systems analysis
- Wind energy and atmospheric processes
- Nuclear safety

Universities, research institutes, institutes of technology and businesses are important research partners to Risø.

A strong emphasis is placed on the education of young researchers through Ph.D. and post-doctoral programmes.

Copies of this publication
are available from

Risø National Laboratory
Information Service Department
P.O. Boks 49
DK-4000 Roskilde
Denmark
Telephone +45 4677 4004
risoe@risoe.dk
Fax 4677 4013
Website www.risoe.dk