1 Modelling of Complex Chemical Reactions

Introduction

For complex reaction schemes analytical solutions of the rate equations are extremely difficult or non-existent; for this reason other approaches have been developed based on the numerical solution (in practice this means by computer) of the coupled rate equations.

There are a number of computer applications which can be used to model the reactions of chemical, biological, nuclear and atmospheric processes; here you will use KINTECUS.

Application Kintecus

Overview

KINTECUS is essentially a DOS based application and does not have the user-friendliness of Windows programs but it is very powerful and fast. It can be run under Windows 95/98/NT but it does so in a separate window.

How to run

The simplest way to run KINTECUS is to set up a batch file, that is, a set of commands which not only run the program but also instruct it to read the input data from three named files and write the output to a file. For example, the batch file below, 'JMS.BAT', reads three files 'MODjs.dat', 'SPECjs.dat' and 'PARMjs.dat', and, writes the output to the file 'output.dat'.

```
@ECHO OFF
CD\
cd Progra~1\Kintecus\
echo .
echo [ Running Kintecus ... ]
echo .
KINTECUS -MOD:MODjs.dat -SPEC:SPECjs.dat -PARM:PARMjs.dat -OUT:output.dat -d044
```

The batch file must be given a legal name of the form '*.BAT' where * can be most any combination of up to eight keyboard characters. Use the Windows application EXPLORER to run the batch file by double-clicking on it.

Preparing input

Use an editor such as NOTEPAD or PFE to write simple text or data files (as opposed to complicated wordprocessing documents) which will contain all the input data that KINTECUS needs to run. There are three input files needed, one to specify the chemical reactions ('model'), one to set the initial concentrations ('species') and one to set the initial conditions of temperature, pressure, *etc* ('parameters').

Model description

The model description input file has the following structure; there are three fields (normally separated by commas), the first is the value of the rate constant, the second is the reaction and the third an optional comment. Any line that begins with a # sign is *ignored* by the application and is used for comments.

```
# Input filename: 'MODjs.dat'
# Rate constant , reaction , optional comment
1.14E-02 , C2H6 ==> 2CH3
1.19E+06 , CH3 + C2H6 ==> CH4 + C2H5
1.57E+03 , C2H5 ==> C2H4 + H
6.99E+13 , 2H ==> H2
END
```

Species description

The species involved are named in a separate file, 'SPECjs.dat', with the following layout shown below; note that the most important columns are 1 and 3 where the species are named and their initial concentrations are set.

```
# Input filename: 'SPECjs.dat'
# Species Residence time Initial   Display  External SSA ? Constant Comment
#  Name     in CSTR (s)   Conc.     Y/N     Conc. (Y/N)   File/#/N
   C2H6 ,           0., 5.95E-6,    Yes,      0.,  No,        No,
    CH3 ,           0., 0.0    ,    Yes,      0.,  No,        No,
    CH4 ,           0., 0.0    ,    Yes,      0.,  No,        No,
   C2H5 ,           0., 0.0    ,    Yes,      0.,  No,        No,
      H ,           0., 0.0    ,    Yes,      0.,  No,        No,
     H2 ,           0., 0.0    ,    Yes,      0.,  No,        No,
END
```

Parameter description

The parameter description input file, 'PARjs.dat', sets out a number of different parameters but the only ones that we shall focus on here are the 'simulation length', that is, how long we want the simulation to run for. Here it is set at 1.0×10^6 or 1,000,000 seconds. The temperature, T, and pressure, P, need to be specified here as well. The units used to express the concentrations can be set here either in mol dm^3, or molecules cm^{-3} or in ppm.

```
#  Input filename: 'PARjs.dat'
#Minimum Integration Maximum Integration X23   Units  Turbo
#     Time (s)             Time(s)             (0/1/2) (0/1)
     1.00E-3     ,          1     ,       0 ,    1   , 0
# T (K)  P (kPa)  L  X0    X0
  220  ,   101  , 1 , 1 ,  0
#Simulation Length:
#Days  Hours  Minutes Seconds PicoSeconds
  0  ,  0   ,   0   , 1.0E06 ,   0
#   hv    Sampling  Percent Accuracy  X9
# (file)  interval    (%)
  None1 ,    1    ,   0. , 1.00E05 , 0
# X10  X78  X12  X13  X0
   0 ,  0 ,  0 ,  0 , 0
END
# Units code is: 0--mol/l, 1--molecules/cm3, 2--ppm
```

Example

Edit all the files to reflect the problem that you want to simulate; save copies to your own floppy disk.

Viewing the output

You can view the output onscreen by editing it with NOTEPAD or PFE or you can print the output file directly or you can import it into a spreadsheet such as Excel or a plotting program such as Origin.

Bromine in the stratosphere

Bromine atoms play an important role in the depletion of stratospheric ozone, as of course do chlorine atoms. The largest man-made (anthropogenic) source of bromine is the agricultural

fumigant methyl bromide which diffuses up through the atmosphere and is photolysed by sunlight to yield bromine atoms:

$$H_3CBr + h\nu \rightarrow H_3C^\bullet + Br^\bullet$$
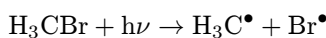
The reactions in Table 1 comprise a *simple model* for the interaction of bromine and ozone [taken from "Chemical Kinetics and Dynamics", J. I. Steinfeld, J. S. Francisco & W. L. Hase, Prentice–Hall, 1999].

#	Reaction	Rate constant, k	$k(220\ \mathrm{K})$
1	$Br + O_3 \rightarrow BrO + O_2$	$1.7 \times 10^{-11} \exp\left(-800/T\right)$	
2	$BrO + HO_2 \rightarrow HOBr + O_2$	$2.5 \times 10^{-12} \exp\left(+521/T\right)$	
3	$HOBr + h\nu \rightarrow OH + Br$	1.0×10^{-3}	1.0×10^{-3}
4	$OH + O_3 \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} \exp\left(-940/T\right)$	

Table 1: Reactions and rate constants (units: cm^3, molecule, s)

The concentrations of the relevant species at an altitude of 25 km above the Earth's surface where the temperature is 220 K are given in Table 2.

Species	[X]
O_3	4.4E+12
OH	3.0E+06
HO_2	1.0E+07
O_2	2.0E+17
Br	3.2E+05
BrO	6.4E+06
HOBr	3.2E+06

Table 2: Concentrations, molecules cm^{-3}, at 25 km altitude

Calculate the rate constants at 220 K (the values missing in Table 1) and then simulate these reactions using the application KINTECUS and attempt the following questions:

1. What is the *net* reaction if you add up reactions 1–4?

2. Do reactions 1–4 lead to *catalytic ozone depletion*? Explain using the results of your simulation which you should run for 1.0×10^6 seconds. (In other words, how many ozone molecules are destroyed *per* bromine lost?)

3. What percent ozone loss occurred over 1.0×10^6 seconds? Using this value, estimate the percent loss in 1 year and in 10 years.

4. The US government is considering whether to ban or phase out methyl bromide. By how much would it be necessary to reduce the concentrations of all the bromine species to cut ozone depletion in half?

5. Is the model an important source for ozone depletion *at night*? (Run the simulation over a much shorter timescale of 20 seconds to tackle this question).

6. Most reactions speed up at higher temperatures. Run the simulation at 298 K for 1.0×10^6 seconds and determine the ozone loss. Is *more* or *less* ozone depleted than at 220 K?