```
;                DOCUMENTATION AND SAMPLE RUN FILE
;                           for
;                      ACUCHEM/ACUPLOT
;                            a
;        Computer Program for Modeling Complex Reaction Systems
;
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;
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;
; I.  The Programs.
;There are two executable programs on this disk, Acuchem and Acuplot.
Acuchem
;models spacially homogeneous, isothermal, multicomponent chemical
reaction
;systems, prepares an output file which can be read using the program
;Acuplot.  There are two versions of Acuchem/Acuplot available. One
handles
;40 species and 80 reactions, the other 99 species and 200 reactions.
;The version on this disk is the 40 species/80 reactions one.
;
;  A.  Acuchem.
;This program reads an input file containing one or more reaction
mechanisms,
;processes this file, then solves the resulting system of differential
;equations.   Acuchem then generates an output file, containing species
con-
;centrations vs. reaction time for user chosen reaction times, or print-
times.
;
;  B.  Acuplot.
;The Acuchem output file can then be read by executing the program
Acuplot,
;which displays the file data, in either tabular or graphical form.
;
; II.  Hardware Requirements.
;These programs will run on IBM Personal Computer Family Models,  or PC
;compatible microcomputers which operate on MS-DOS or equivalent
operating
;systems.  At least 250k of memory and a math co-processor, either a 8087
or
;80287 is required.  The graphics routines within Acuplot require one of
the
;following display adapters:
;     a)  IBM Color Graphics Adapter (CGA)
;     b)  IBM Enhanced Graphics Adapter (EGA)
;     c)  IBM Professional Graphics Adapter (CGA emulation mode only)
;     d)  Hercules Monochrome Graphics Adapter (HMGC)
;     e)  Video-7 Enhanced Graphics Adapter (CGA, EGA, or HMGC mode)
;Hard-copy of a graphical display can be achieved by using any one of
many
;dot matrix printers. At least the following are supported:
;     a)  IBM Personal Computer Graphics Printer (Model 5152)
;     b)  IBM Propinter (Model 4201)
;     c)  Epson MX-80 Printer
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;     d)  Epson MX-100 Printer
;     e)  Epson MX-III Printer
;     f)  Epson FX-80 Printer
;     g)  Epson FX-100 Printer
;     h)  Epson FX-80+ Printer
;     j)  Epson FX-100+ Printer
;     k)  Epson RX-80 Printer
;     l)  Epson RX-100 Printer
;     m)  Epson JX-80 Printer
;
;
;  III:  Set-up of the Acuchem input file.
;
;The documentation in this section describes how to set up an Acuchem
input
;data file and how to execute the Acuchem/Acuplot programs.  Additional
;details, which may be helpful to the user, are also included.
;
;This documentation file is also an Acuchem input file.
;Up to this point all lines in this documentation contain leading
semicolons.
;The reason for this is that an Acuchem input file can contain comment or
;documentation lines, which are not read by the program, if prefaced by a
;semicolon.  The semicolon need not be left justified, but must be the
first
;non-(blank or horizontal tab) character on the line.
;
;  A:  Heading or Identification Line is the first line read by Acuchem.
;
Example.doc, an example mechanism file which can be run by Acuchem.
;
;Line above, without a leading semicolon, is the first line read by
Acuchem.
;It is reserved as an identification line and must appear even if it is
left
;blank!!  It is copied directly to the Acuchem output file and serves as
;a heading line on the final hard-copy.
;
;Additional comment lines, such as the present lines of text, can be
;interspersed within the file but must also contain a leading semicolon.
;Comments can also directly follow input data on the same line if also
;preceeded by a semicolon.
;
;In data lines which follow, in all cases, the data must be present in
the
;correct order, the correct number and the correct data type or else a
file
;read error will occur.
;
;No input line can be longer than 79 characters.
;
;  B:  Option Line is second line read by Acuchem.
;
;
;There are four consecutive single digit options which are either 0 or 1,
;(0=no, 1=yes), representing answers to the questions below.
;
;     computer        Printer         50 equi-             display
;     supports        supports        spaced print-        print-time
;     graphics?       graphics?       times to out-        to monitor
;                                     put file?            screen?
```

```
;
;     no              no              no                    yes
;
;
      0               0               0                     1
;
;The above option line, without a semicolon, is the second line read by
;Acuchem! A blank (space) or horizontal tab can be the only character
;separating these single digit numbers.  No space, however, is required.
;The above line could have been written as:
;0001
;omitting the leading semicolon.  Option explanations appear in sections
below.
;
;
;  C:  Beginning of Reaction Mechanism, the third line read by Acuchem.
;
       1,a+b=c,1
;The line above, without a semicolon, is the third line read by Acuchem.
;
;Leading number is for user's convenience in numbering reactions. It can
be a
;number or characters or both.  Only 4 alphanumeric characters are
allowed.
;This identification sequence is not actually used by the program.  If
;it is used it must be followed by a comma; if it is not used, a comma
must
;still preceed the reaction mechanism.
;
;The comma following species, c, is also required!  The number
;following the comma is the reaction rate constant and can be an integer,
;a decimal,  or in E format.
;
;also note that the use of blanks is allowed within the line, and the
line
;need not be left justified provided that there are only leading blanks
or
;horizontal tabs.  For example reaction 1, can also be written as:
;               1, a + b = c , 1.0E00
;without the leading semicolon.
;
;Species names can be 12 characters long, not counting embedded spaces.
;
;only zero order, first order and second order reactions are allowed!
;
;An example of a first order reaction is:
;               77,sam=aBb,7.0e-14
;which is interpreted as aBb is formed from sam at a rate 7.0e-14 in
;units of per time. Species sam is lost at the same rate.  The mechanism
;equations need not be stoichiometric but a species balance is always
;maintained, e.g. the loss of 1 molecule of Sam results in the gain of
;one molecule of aBb.
;
;Note that species characters are ordered and cased e.g. aBb is distinct
;from AbB  and AB is distinct from BA etc.
;
;An example of a zero order rate equation is:
;               78,=aBb,8.0e-12
;which is interpreted as aBb is formed from (nothing) at the constant
rate
;of 8.0e-12 in units of concentration/time.
```

```
;
;An example of a second order rate equation is:
;              79,CH3+C2H5=CH4+C2H4,7.0E-12
;This line is interpreted as,  CH3 reacts with C2H5 to yield one CH4 and
one
;C2H4 with a rate constant of 7.0E-12 in units of 1/(concentration*time).
;
;Reactions are interpreted as proceeding only in the forward direction,
;left to right.  In order to represent a reversible reaction, such as
; a + b = c + d, it must be entered as two separate (forward) rate
processes,
;for example:
;              80,a+b=c+d,3.4e-14
;              81,c+d=a+b,6.25678e-15
;replacing 81,with
;              82,a+b=c+d,-6.2567e-15
;will not give the same result as 81 and should be avoided!!
;
;Termolecular rates, with rate constants in units of
;1/(time*concentration*concentration) cannot be explicitely handled by
;this program (that is, not in one reaction step).
;Such a rate process as, for example,
;              83,a+b+c=ab+c,4.5e-37
;can be treated in one of two possible ways:
;The first way is quite simple; it is the preferred method, if it can be
;used.  If one of the species concentrations is quasi-constant it can be
;incorporated into the rate constant.  Assume that the species c has a
;concentration of 1.0e17 which is at least two orders of magnitude larger
;than that of either a or b.  We can then write reaction 83 as:
;              84,a+b=ab,4.5e-20
;that is, the rate constant for reaction 83, 4.5e-37 is multiplied by
1.0e17
;and the product, 4.5e-20 is used as an effective second order rate
constant.
;It is very usual, in termolecular reactions, that one species is in
large
;excess and can legitimately be taken as quasi-constant!
;
;The second method (which is the way most termolecular reactions actually
;proceed) involves the use of the reversible reaction represented
;by 85 and 86 below, followed by the second order reaction, 87:
;              85,a+b=ab*,k(85)
;              86,ab*=a+b,k(86)
;              87,ab*+c=ab+c,k(87)
;where,
;              k(83)=k(85)*k(87)/(k(86)+k(87)*c).
;If k(86) is chosen much larger than k(87)*c(0), where c(0) is the
initial
;concentration of species c, then the following expression applies:
;                k(83)=k(85)*k(87)/k(86).
;Having chosen the ratio of k(86) to k(87) so that the latter
approximation
;is valid, the ratio of k(85) to k(86) should be chosen so that the con-
;centration of ab* is always much less than a, b, or c.
;
;If two species react to form three, such as:
;              88,a+b=c+d+e,5.345e-14
;This should be entered into the file as,
;              88a,a+b=c+dummy,5.34e-14
;              88b,dummy=e,1.0e14
;The first order rate constant for the decay of dummy should be fast
```

```
;enough that its concentration is small compared with the other major
species.
;
;More complex schemes can be composed of simpler reversible bimolecular
;and unimolecular reactions involving hypothetical intermediates. Complex
;reactions always proceed by simpler steps so that such an excercise,
while
;necessary to the use of the program, is usually also instructive.
;An example of a complex reaction is the equilibrium reaction between NO2
;and water to yield nitric acid and NO:
;
;              992, 3NO2  + H2O = 2 HNO3 + NO , K(992)
;
;The following four reversible reactions, added together will result
;in the overall stoichiometry of reaction 992:
;
;              993,   NO2 + NO  = N2O3 ,        K(993)
;              994,  N2O3 + H2O = HONO + HONO , K(994)
;              995,  HONO + NO2 = HNO3 + NO ,   K(995)
;              996,  HONO + NO2 = HNO3 + NO ,   K(996)
;
;Here the K's are not rate constants, but equilibrium constants.  The
;equilibrium constant, K(992) can be calculated from tabulated Free
;Energies, since all of the reactants are stable molecules.  The Free
;Energies of some of the intermediates in the reaction sequence 993-
;996 have been estimated, and thus even for these, the equilibrium
constants
;can be determined.  The following relationship must be adhered to:
;               K(992)=K(993)*K(994)*K(995)*K(996).
;Further, each of the reversible reactions 993-996 must be presented
;as two separate reactions, as expained above; and as well, rate
constants,
;not equilibrium constants should be used.  That poses no particullar
problem
;once it is understood that the Equilibrium constant is equal to the
ratio of
;the forward rate constant divided by the reverse rate constant.  As an
;example reaction 993 is written as 993a, and 993b:
;
;              993a, NO2 + NO = N2O3 ,     k(993a)
;              993b, N2O3     = NO2 + NO , k(993b)
;
;and K(993)=k(993a)/k(993b), where the small k's are rate constants in
;correct units.  If the individual rate constants for steps 994,995 and
;996 are chosen much larger than those for reaction 993, these steps will
;always be in equilibrium and reaction 993 will be the rate controlling
step.
;Under these conditions K(992)=k(993a)*k(994a)*k(995a)*k(996a)/(k(993b)*
;k(994b)*k(995b)*k(996b)).  This relationship must be strictly adhered to
;even if the ratios of the individual rate constants are arbitrarily
chosen
;(because the equilibrium constants for the reactions 993-996 are either
not
;known or the decision not to use them has been made).
;
;Duplicate reaction mechanisms can be run simultaneously.  For example,
;              100,a1+b1=c1+d1,k(1,1)
;              101,a2+b2=c2+d2,k(2,1)
;              102,a1+c1=e1,k(1,2)
;              103,a2+c2=e2,k(2,2)
```

```
;essentially duplicates a mechanism and allows a change in one or more
rate
;constants or concentrations.  The effects of the changes in the
mechanism
;parameters can thus be probed in the same run file.  Of course the
duplicate
;species names must be identified differently.  The use of matrix
notation,
;for example A(1), A(2), B(1), B(2) is an alternative notation.
;
;Entering the same reaction line twice, for example,
;              87,h+i=j+k,4.0e-12
;              97,h+i=j+k,4.0e-12
;has the effect of doubling the rate constant.  The net effect is:
;              98,h+i=j+k,8.0e-12
;
;Also note that the main use of the comment (semicolon) option is to
;allow the user to remove certain mechanism lines and later re-activate
them
;by simply placing and removing a semicolon.  This saves typing time and
;provides the user with a record of previous iterations.
;
;The user can use any choice of concentration units, either molecular or
;molar.  The Acuchem program actually scales the concentrations and rate
;constants and runs identically irrespective of the units.  Outputs are
then
;re-scalled to the user's units. Rate constants must be in units
consistent
;with the concentration and time units.
;
;
;the remainder of this mechanism file continues
;
2, c=a+b,.001; a comment can be added here if the user desires!!
3,a+b=d,1.
4,d=a+b,1.0E-03
;
;  D:  End of Reaction Mechanism Statement:
;
end; This line is required!
;It is essential that the end statement be added to close the mechanism
;sequence.  Upper case END is also allowed.  Blanks between the E and the
N
;and the N and the D and the use of leading blanks is allowed.
;
;  E:  Species Identification and Concentration:
;
;the following line(s) specify the species and their concentrations.  If
a
;species and its concentration is not listed the program will assume that
;it is 0.0000.
;
a,1.0
b,2.10789
;
;This information must be entered in in the order:  species name, a
comma,
;the concentration, then a blank or a semicolon.
;Only one species and its concentration per line!!
;
;  F:  End of Species, Concentration Sequence:
```

```
;
end; This line is required!
;
;An end statement specifies that all non-zero concentrations have been
;logged in.  This also must be present or else a file read error will
;be generated!!
;
;  G:  Integration Tolerance:
;
0.001
;
;The above line specifies the integration tolerance.  It must be
positive.
;Small values cause the program to run longer, larger values can result
in
;inaccurate results.  The usual range for this parameter is from about
0.0001
;to 0.1 but values outside of this range are possible.
;
;
;  H:  Print-times, for which Reaction time & Concentrations are
;      Written to the Acuchem Output File.
;
1.E-4,1.E-3,1.E-2,1.E-1,1.,
2.,3.0,4.0,10.
```

The lines above specify the reaction times for which each species concentration is written to the Acuchem output file.

If a line in this section ends with a comma, Acuchem expects additional Print-time lines. If a line in this section ends with a blank or semicolon,
Acuchem does not expect any additional information and assumes that the input file is complete. For that reason, all of the lines of text following
the entry 10., above are written without leading semicolons!

Note that there are 9 print-times specified above. These will determine the print-time entries that will be written to the Acuchem out-put file unless the third option in the option line is set to 1. In that case there
will be 50 equispaced print-times written to the Acuchem output file up to the largest time value in the print-time sequence above,
which is 10. in the present case. There is no need to log in print-times in
the order of increasing time since the program sorts (and then orders) them.

IV. How to Run Acuchem/Acuplot.

This documentation represents an unusual input file, but it will run and the
user can try this file as a trial run. Execute Acuchem by typing Acuchem.
Acuchem then requests the name of the input file and this file, called EXAMPLE.DOC, should be entered. Acuchem further requests the name of an output file and some suitably chosen name such as EXAMPLE.OUT should be entered. Alternatively, all or part of this file information can be included
directly on the command line, and the file information will not be requested

by the program, unless a file duplication condition is detected.

Standard MS-DOS file specifiers can be used. For example the following command lines are illustrative:

```
Acuchem  A:\kin\example.doc  B:\results\example.out
```

also,

```
Acuplot  B:\results\example.out
```

That is, the input and output file names, here included on the command line, can be entered in the form, disk:\directory\filename.ext. In general, results should be kept separate from the Acuchem/acuplot programs since space limitations, if a floppy disk is used, will eventually require such action.

Acuchem will take several seconds to run this file. Note, when running much more complex mechanism files, the user can terminate execution by typing in a control c at any time. If option 4 on the option line is set to 1, the print-times are writted to the monitor which shows the number of time-concentration entries that have been written to the Acuchem output file. On premature termination of Acuchem, these data entries exist on the output file and can be scanned. That is, an acuchem output file will be produced which has fewer print-times than the number specified in the Acuchem input file.

After running Acuchem the user should type Acuplot, with or without the Acuchem output file specified. If it is not specified, Acuplot will request the output file name which must then be entered. Acuplot will display the results to either the monitor screen or to the printer with the further option of graphically displaying the results (if option 1 on line 2 is set to 1). Also, if option 2 on file line 2 is set to 1 the program will assume that the user has a printer which is supported by the graphics package and the option of generating a hard-copy on the printer is requested by the program.

Acuplot reads the Acuchem output file and if requested, the user can scan the the reaction time, species concentrations in the Acuchem output file in a convenient way, either to the monitor screen or to a printer. The display to the monitor occurs one page at a time. Using the z or Z key, scans the file forward; using the a or A key scans the file backwards (towards the beginning). Once the end of the data file is reached, the user is notified, and another chance of scanning the file towards the beginning is possible by typing in the a or A key. At this point typing in z or Z will exit this file display mode.

The graphics routines, within Acuplot, can display the Acuchem results on the monitor screen-up to 5 species at a time. If a graphics printer is attached, a hard-copy of the screen display can be obtained. A heading line can also be included. Concentrations are automatically scaled. The species are distinguished on the graph using different plotting symbols and further identified in the figure legend by name and symbol with the appropriate concentration scale factors. To convert species concentrations to their real (unscaled) values the value on the graph must be multiplied by the displayed scale factor. This can be done virtually by inspection to an accuracy of better than 2% (at the ordinate midscale). Scale factors are integer and result in sensible displays. The abscissa, time, is not scaled and a maximum time value should be chosen which is divisible by 2 or 5 to allow for a sensible time axis display.

V. Run time Errors.

Certain safety features are included in Acuchem: 1) If a specified input file is not found a message to that effect is written to the monitor and the program is terminated. 2) The same is true if an output file is designated as an Acuchem input file. 3) If an output file is specified which already exists Acuchem will flag this condition and allow the option of overwriting the file or substituting another file name. 4) Certain input file errors are detected as such and are flagged with a relatively friendly message followed by program termination. However, out of sequence numeric input data will generally result in a compiler generated error message as will insufficient disk space for the output file. These will also result in run termination. 5) The differential equation solver flags certain errors which are displayed to the monitor screen such as an unreasonable integration tolerance or too many internal integration steps.

Most errors are the result of typograhical errors in the input file, missing end statements, data entered out of proper sequence or insufficient disk space for the output file.

VI. Additional Comments.

We suggest that the user make backup copies of the Acuchem/Acuplot programs. At that time the user can use the standard MS-DOS Rename command and change the names of these programs to AC.exe and AP.exe to simplify typing.

The present executable programs, Acuchem and Acuplot were compiled using the F77L Fortran77 Compiler, Ver 2.0, written by Lahey Computer Systems, Inc., 31244 Palos Verdes Drive West, Suite #243, Rancho Palos Verdes, Ca 90274.

VII. Description of Acuchem Output File.

The following details will only be of interest to users who are interested in programming and wish to interact with the current programs through their own routines.

The following describes the format in which the Acuchem output file is written. The user can write individualized programs to read this output file, to use other graphics, to insert laboratory data into the Acuchem output file to compare calculated and experimental results.
A possible algorithm to do this is the following:
1) read the Acuchem output file,
2) add additional species entries to accomodate actual laboratory data,
3) add laboratory data entries,
4) finally, generate a merged file.
This new file can then by read by Acuplot and the calculated and experimental results can be compared directly through the graphics mode.

The Reaction Mechanism matrix is used to write the output reaction mechanism in shorthand form. It is not necessary for the user to know this is done, but for the sake of completeness the following describes how the Reaction Matrix is defined.

The Reaction Matrix, defined as JS(A,B), is a shorthand way of describing the reaction mechanism, where A is the species position index within the the mechanism line and B is the reaction number.

Each mechanism line is of the form, one equal sign with 0, 1 or 2 species entries on either side of it. The JS( ) matrix notation always assumes that there are exactly 4 species entries per reaction mechanism line, two to the left of the equal sign, two to the right, whether they are present or not.
If a species entry is missing, the JS( ) index for that entry is set to zero.
Acuchem numbers species consecutively as it scans the reaction mechanism sequence and then generates the JS( ) shorthand for each mechanism line.
An example best shows how this is done. Consider the following three line mechanism,

```
001, A+B=C,k(001)
002,   C=D+E,k(002)
003,    =F,k(003)
etc.
```

The JS( ) matrix is:

	JS(i=1,k)	+	JS(i=2,k)	=	JS(i=3,k)	+	JS(i=4,k)
JS((i=1,4),k=1) :	1	+	2	=	0	+	3
JS((i=1,4),k=2) :	0	+	3	=	4	+	5
JS((i=1,4),k=3) :	0	+	0	=	0	+	6

etc.

Note the indexing and that the value of JS( ) = 0 when an entry does not appear on the reaction mechanism line. Once a species is identified by a number e.g. C is number 3, every time species C appears in the reaction
mechanism it is specified as number 3, and that number must appear in the JS( ) matrix for that line with i=1 or 2 if it is on the left side of equal sign or i=3 or 4 if it appears to the right of the equal sign. There
is no significance to the particullar ordering of i=1 and i=2 nor to the ordering, of i=3 and i=4. That is, JS(i=1,k)=0 and JS(i=2,k)=3 is entirely
equivalent to JS(i=2,k)=0 and JS(i=1,k)=3.

Format of Acuchem output file follows:

Line1: format(79A1), contains the entry O*TPUT, identifying this as
an output file.
Line2: format(79A1), line copied directly from Acuchem input file, contains
identification line information.
Line3: format(5I1), contains 5 options, without leading or imbedded blanks.
line4: format(E10.4), contains the Integration Tolerance parameter in the
specified format.
line5: format(2(1x,I4)), contains total number of species, N; and total number
of mechanism lines, L, in the format specified.
line6
thru
line(6+L/9):
format(8(1x,4I2), contains 4*L, JS( ) matrix entries, up to 32/line.

line(6+L/9+1)
thru
line(6+L/9+1+N/7):
format(6(1x,A12)), contains N species names up to 6/line.

line(6+L/9+N/7+2)
thru
line(6+L/9+N/7+2+L/7):
format(6(1x,E12.6)), contains L rate constants, up to 6/line.

line(6+L/9+L/7+N/7+3)
to
end of file:
format(1x,I3,2x,E12.6), contains print #, 1 for first, 2 for second,
etc., and print-time, on one line,
followed by,
format(6(1x,E12.6)), a total of N concentrations, as many as 6/line.
then, this sequence is repeated for each successive print-time.
e.g.
next print #, and print-time, if it is there!
again followed by a total of N concentrations, etc.