ChE classroom

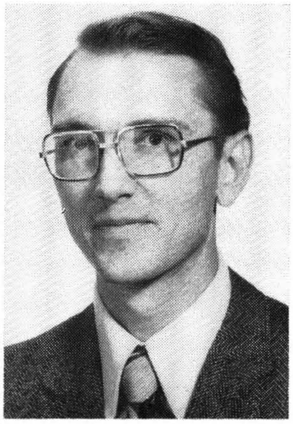
USE OF A CONTINUOUS SYSTEM SIMULATION LANGUAGE IN CHEMICAL REACTION ENGINEERING

R. D. WILLIAMS and D. WOLF*
University of Arizona
Tucson, Arizona 85721

MANY PROBLEMS IN ENGINEERING, and this is especially true in chemical kinetics and reaction engineering, are dynamic in nature and as such are described by differential equation. In the past, simulation of some of the more interesting of these problems for instructional purposes has been hampered by the lack of easy to use solution techniques. Often the student would become so embroiled in the method of solution that he would not obtain the desired experience with the physics of the problem. For example, setting up nonlinear or high ordered linear problems on an analog computer would involve considerable experience with the particular computer being used. If a digital solution was sought the student might be involved in a nontrivial exercise in numerical analysis. While these experiences are not in themselves bad they do tend to detract from the main point of the problem. The end result has been that often these more difficult problems have been avoided by the professor who feels he has a time constraint to cover some given amount of material.

User oriented Continuous System Simulation Languages (CSSL) have been developed to the point of practical use by undergraduate students in the study of such advanced dynamic systems. Experience with analog simulation and numerical techniques may be covered more specifically in other courses if desired, however, the availability of powerful CSSL will be such that they will be extensively used in industry, justifying their inclusion in the curriculum.

This paper is intended to briefly discuss the philosophy behind such software packages and to illustrate their successful implementation in teaching an undergraduate course in chemical kinetics and reactor engineering in the Department of Chemical Engineering at the University of Arizona. The specific simulation language used in this course is DARE IIIB (Differential Analyzer Replacement, Version IIIB) which was developed for CDC 6000 series computers by the Department of Electrical Engineering at the University of Arizona.



David Wolf is a graduate of the Technion-Israel Instittue of Technology, Haifa, Israel, where he received his BSc, MSc and DSc degrees in Chemical Engineering. In 1963 he spent a year doing postdoctoral work at Carnegie-Mellon University and from 1964 to 1966 he was Assistant Professor of Chemical Engineering at McGill University in Montreal. Since 1966 he has served as Associate Professor and Head of the Isotope Separation Plant at the Weizmann Institute of Science in Rehovot, Israel. He is also presently a Professor of Chemical Engineering at the Ben-Gurion University of the Negev in Beer Sheva, Israel. During the 1972-73 academic year, he spent a sabbatical leave at the University of Arizona. (LEFT)

Dick Williams received his undergraduate degree at Texas Tech University and his doctorate at Princeton University, all in Chemical Engineering. He has been at the University of Arizona since 1968 where his research has been involved primarily with chemical reaction engineering. Current research projects include the development of a hydrogen generator for automotive fuel applications and a study of the hydrometallurgical leach recovery of minerals from their ores with emphasis on characterization of the underlying mechanisms involved. (RIGHT)

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*Permanent address: Weizmann Institute of Science Rehovot, Israel and The University of the Negev Beer Sheva, Israel

CSSL PHILOSOPHY

A CSSL IS DESIGNED with one purpose in mind, to solve differential equations. It consists of one or several numerical integration algorithms conveniently programmed to allow the user to devote his attention to the problem physics rather than the solution technique. The development of such programs is a result of the logical extension of the concept of analog computer simulation. As digital computation speed and availability have increased they have been increasingly used to simulate the operation of analog computers but with much more accuracy and without the problems involved in scaling of analog computers.

Early digital simulation languages were developed with the analog computer user in mind in order to make his transition an easy one. Analog signal flow diagrams were prepared as usual. Each element of the analog computer program had an equivalent element in the digital program. The "connections" were then made by supplying to the digital computer, in tabular form, the inputs and outputs to the various elements of the model as well as the initial conditions and problem parameters. More modern simulation languages are statement oriented and users need not know anything of analog computers to use them, only a minimal knowledge of FORTRAN and differential equations is required.

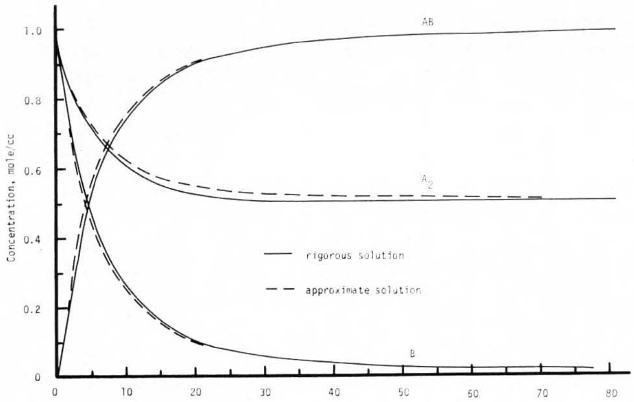

FIGURE 1: Concentration history for Example 1.

The user of DARE IIIB supplies the sequence of differential equations to be solved in FORTRAN form, in any order. In addition, initial conditions and problem parameters are specified as is the integration algorithm to be used (currently from a selection of eight) and the integration parameters (default values are automatically selected if the user does not specify these). Logic control may be exercised for iterative boundary valued problems, optimization problems and the like. Output options include lineprinter listings and plots, and Cal-Comp plotter displays. DARE IIIB can handle problems with 100 parameters, 200 state variables, and 350 output variables which is more than sufficient for most problems of interest in the instruction of undergraduates. More specific information on this simulation package is available elsewhere [1, 2, 3].*

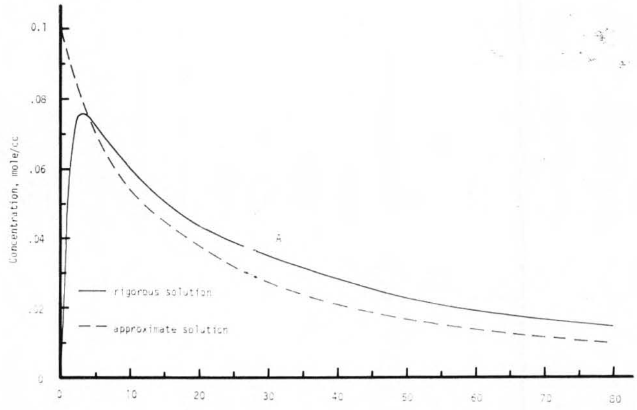

FIGURE 2: Concentration history for reactive intermediate for Example 1.

CSSL APPLICATIONS

THE APPLICATION EXAMPLES illustrated are taken from a course in chemical kinetics and reactor engineering and though specific to chemical engineering they are typical of the larger class of dynamic problems common to all engineering and scientific disciplines. These applications are (1) the use of the pseudo steady state hypothesis in formulating chemical reaction kinetic rate expressions and (2) the transient analysis of Continuous Stirred Tank Reactors (CSTR). Solution to problems of this type have been reported in the literature, often obtained with great effort. The purpose of this paper is to illustrate the ease with which they may be analyzed in detail by use of a CSSL such as DARE IIIB, making their detailed analysis in an undergraduate course more justifiable.

Example 1—Pseudo steady state hypothesis

When a sequence of chemical reactions occurs which involves a very reactive intermediate, the reaction rate expression may be considerably

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*For information on obtaining this simulation package write Dr. J. V. Wait, Dept. of Electrical Engineering, University of Arizona, Tucson, Az. 85721.

simplified by assuming that since the concentration of this reactive intermediate is very small as compared to the stable compounds, its time rate of change in the system will be negligible, except for a brief induction period. This assumption is termed the pseudo steady state hypothesis. Consider for example the following hypothetical chemical reaction sequence.

$$A_2 + B \underset{2}{\overset{1}{\rightleftarrows}} AB + A$$

$$B + A \overset{3}{\rightarrow} AB$$

In this sequence A_2, B, and AB are stable compounds and A is a reactive intermediate. If these reactions occur isothermally in a closed constant volume reactor, species continuity requires that Equations 1a-1d hold.

$$\frac{d[A_2]}{dt} = - k_1[A_2][B] + k_2[AB][A] \tag{1a}$$

$$\frac{d[B]}{dt} = - k_1[A_2][B] + k_2[AB][A] - k_3[B][A] \tag{1b}$$

$$\frac{d[A]}{dt} = k_1[A_2][B] - k_2[AB][A] - k_3[B][A] \tag{1c}$$

$$\frac{d[AB]}{dt} = k_1[A_2][B] - k_2[AB][A] + k_3[B][A] \tag{1d}$$

In these equations t is time, the k's are reaction rate constants and brakets symbolize molar concentrations of the species enclosed. Initial conditions are that $[A_2(0)] = [A_2]_0$, $[B(0)] = [B]_0$, $[A(0)] = [AB(0)] = 0$. This set of coupled equations may be simplified by making the pseudo steady state assumption [4] for reactive intermediate, A. This assumption requires that $d[A]/dt \simeq 0$ for all time. Equation 1c then reduces to Equation 2.

$$[A] \simeq \frac{k_1[A_2][B]}{k_2[AB] + k_3[B]} \tag{2}$$

Replacing Equation 1c with this result then gives a sequence of differential equations containing concentrations only of measurable chemical species, a desirable outcome, and the dimensionality is reduced by one.

Confusion in the use of this approximation arises not from the mathematical mechanics but from the justification for its use, i.e., it is not intuitively obvious to the student that the approximation is a good one or under which conditions it may be. This is where DARE IIIB comes in. Solutions to Equations 1 for various values of the reaction rate constants may be easily obtained and compared to solutions of the equations when the approximation is made. In doing this, values of rate constants or rate constant ratios may be obtained for which the approximation is appropriate. Table 1 gives the lineprinter concentration history for the rigorous case when $[A_2(0)] = [B(0)] = 1$ and $k_1 = 0.1$, $k_2 = 0.05$, and $k_3 = 1.0$. Lineprinter plots of the state variables are given in Figures 1 and 2. In Figure 1 concentrations of stable compounds are plotted against time for the rigorous case (solid lines) and with the steady state approximation (dashed line). It may be seen that the approximate concentration histories for these compounds are in good agreement with the exact values. Figure 2 gives the same comparison for unstable intermediate, A. The descrepancy in this case results from the non-zero initial value of [A(0)] as given by Equation 2 when the approximation is used.

```
LFN = INPUT
  $D1
       A2. = —C11*A2*B + C12*AB*AST
       AST = C11*A2*B/(C12*AB + C21*B)
       B. = —C11*A2*B + C12*AB*AST — C21*AST*B
       AB. = C11*A2*B — C12*AB*AST + C21*AST*B
       TOTA = 2.*A2 + AST + AB
       TOTB = B + AB
       A21. = —C11*A21*B1 + C12*AB1*AST1
       AST1. = C11*A21*B1 — C12*AB1*AST1 — C21*AST1*B1
       B1. = —C11*A21*B1+C12*AB1*ASTI—C21*AST1*B1
       AB1. = C11*A21*B1—C12*AB1*AST1+C21*AST1*B1
       TOTAL = 2.*A21+AST1+AB1
       TOTB1 = B1+AB1
  7/8/9
  7/8/9
     $SYSTEM TMAX = 100.0,NPOINT = 51$
     $ST1 A2 = 1.0,B = 1.0, AB=0.0, A21=1.0,B1=1.0,AST1=0.0,
       AB1=0.0$
     $UND C11 = 0.1,C12 = .05,C21=1.0$
  7/8/9
  LIST,A2,B,AST,AB,TOTA,TOTB
  LIST,A21,B1,AST1,AB1, TOTAL,TOTB1
  PLOT, A2,A21,B,B1,AB,AB1
  PLOT,AST,AST1
  7/8/9
  7/8/9
  7/8/9
  6/7/8/9
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FIGURE 3: Program used in solving Example 1.

This exercise provides a better understanding of the implications of making the pseudo steady state assumption, but without the agony of a complicated analysis. Figure 3 gives the entire program supplied in obtaining these results.

Example 2—Unsteady state CSTR and steady state multiplicity

An important area of chemical reactor engineering is the transient response of continuous stirred tank reactors, especially when multiple steady states are possible for a given set of operating conditions. The possibility of multiple steady states and stability is a new concept to students in the reactor engineering course, but lend themselves readily to student investigation using a CSSL. The differential equations to be solved in this case, with the usual assumptions [5], are:

$$q\rho C_p(T_F-T) + US(T_c-T) + \frac{r_i(-\Delta H_r)V}{a_i} = V\rho C_p \frac{dT}{dt} \tag{3a}$$

$$q\,(C_{iF}-C_i) + r_iV = V\,\frac{dC_i}{dt} \tag{3b}$$

The kinetic rate expression, r_i, is left implicit in these equations and is specified in a separate algebraic statement for ease in adapting the program to investigate the effect of various types of kinetics. For simplicity a first order irreversible rate expression may be used with Arrhenius temperature dependence.

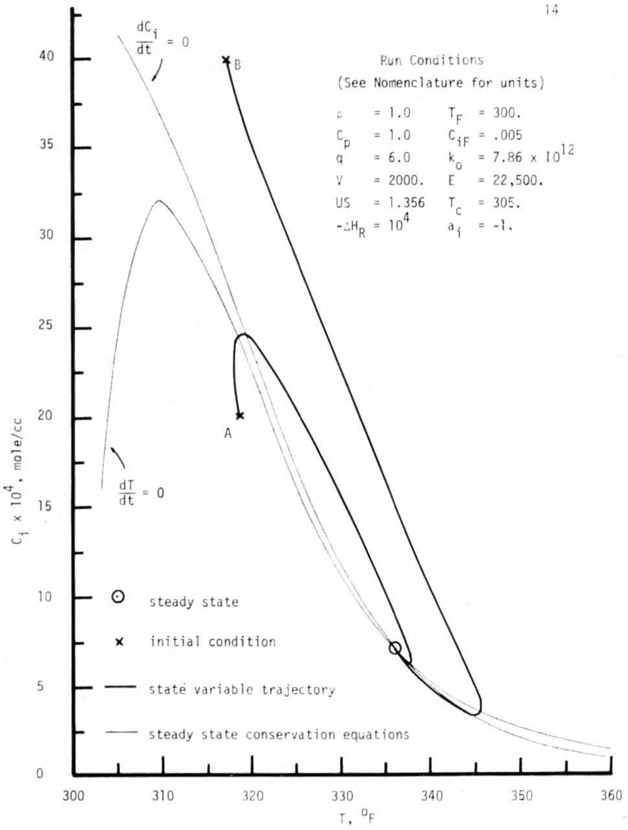

FIGURE 4: Phase plane plot for CSTR with a single steady state.

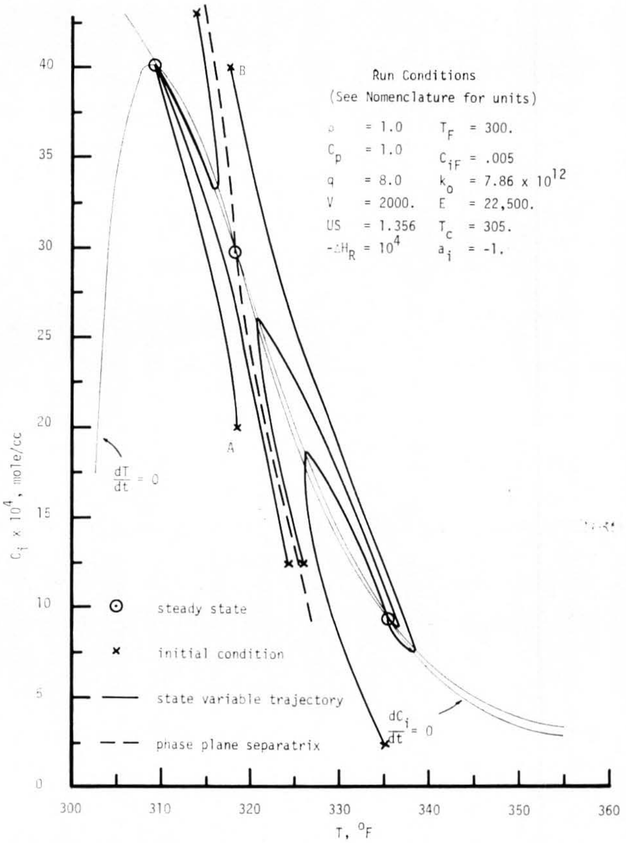

FIGURE 5: Phase plane plot for CSTR with multiple steady states.

$$r_i = -k\,C_i \tag{4a}$$

$$k = k_o \exp(-E/RT) \tag{4b}$$

The differential equations may now be solved subject to an appropriate set of initial conditions, $C_i(0)$ and $T(0)$.

Reactor conditions (adapted from Bilous and Amundson [6]) which will give single and multiple steady states are given in Figures 6 and 7.

Steady state values of reactant concentration and temperature in the reactor are found by setting their derivatives equal to zero in Equations 3 and solving the two resulting algebraic equations. A lineprinter plot of these equations for conditions resulting in multiple steady states is given in Figure 4. The three intersection points correspond to the possible steady states for the conditions imposed.

A typical lineprinter phase plane trajectory is given in Figure 5. The existence of multiple steady states is readily confirmed for the second set of reactor conditions. Reactor sensitivity to variables other than flow rate may also be easily investigated.

CONCLUSION

OBVIOUSLY MANY OTHER applications of CSSL may be envisioned, not only in kinetics and reactor engineering, but in other areas of chemical engineering and other engineering and scientific disciplines as well. These languages should be used as instructional aids in the investigation of advanced dynamic systems on the undergraduate level. They allow considerable ease of analysis such that the student may devote his attention to a detailed study of system mechanics. This does not constitute much of a compromise in the education process since the details of numerical analysis are normally covered in other, more basic, applied math courses. Digital simulation is fast replacing analog simulation and the modern CSSL represents an exteremely high level, user oriented simulation package. ☐

```
LFN = INPUT
  $D1
      C1 = Q/V
      C2 = —DHRXN/(RO*AA*CP)
      C3 = US/(V*RO*CP)
      RA = —RKO*EXP (—E/(R*TEMP))*CA
      CA. = C1* (CAO-CA) +RA
      CB = CAO-CA
      TEMP. = C1*(TF-TEMP) + C2*RA+C3* (TC-TEMP)
  7/8/9
  7/8/9
    $SYSTEM TMAX = 5000., DT = 0.01, DIMIN=0.01, NPOINT =
      51$
    $ST1 CA = 0.002, TEMP = 318.5$
    $UND RO=1., CP=1., Q=8.0, V=2000., US = 1.356, DHRXN
      = —10000., TF = 300., CAO = 0.005, RKO=7.86E+12, R=
      1.9872, TC=305., AA=—1.$, E=22500.$
  7/8/9
  LIST, CA, CB, TEMP
  PLOTXY, TEMP, CA
  PLOT, CA, CB
  PLOT, TEMP
  7/8/9
  6/7/8/9
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FIGURE 6: Program used in solving Example 2.

REFERENCES

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NOMENCLATURE

a_i	Stoichiometric coefficient, dimensionless.
C_i, C_{iF}	Reactant concentration in reactor and reactor feed respectively, moles/cc.
C_p	Reacting fluid heat capacity, cal./(gm.)(°C.).
E	Activation energy, cal./mole.
ΔH_R	Energy of reaction, cal./mole.
k, k_o	First order reaction rate constant and pre-exponential factor respectively, sec^{-1}.
k_1, k_2, k_3	Second order reaction rate constants, liter/(mole)(sec.).
q	Volumetric flow rate, cc./sec.
r_i	Reaction rate, mole/(cc.) (sec.).
R	Gas law constant, cal./(mole)(°K).
S	Heat exchange surface area, cm.^{2}.
t	Time, sec.
T, T_F, T_c	Temperature in reactor, reactor feed, and to heat exchange coil respectively, °C.
U	Overall heat transfer coefficient, cal./(cm.^{2})(°C.)(sec.).
V	Reactor volume, cc.
ρ	Reacting fluid density, gm./cc.
[ ]	Denote molar concentration of enclosed species.

THERMOMOMETRY: Levenspiel

Continued from page 105.

factor from our lives (all thermo students would cheer this), that miserable gas constant. Thus, for a mole of ideal gas

$$pV = RT \text{ would become } pV = T$$

$$C_p - C_v = R \text{ would become } C_p - C_v = 1,$$

for one mole of any substance

$$C_p \text{ and } S \text{ would be dimensionless}$$

and the gas constant R, the Boltzman constant *k*, and Avogadro's number A would be related as follows:

$$R = \frac{k}{A} = 1 \quad \text{or} \quad k = \frac{1}{A}$$

Imagine, the letter R would be free forever more to play new roles. In fact so would the Boltzman constant *k*. With all the new concepts of science crying for symbols what a boon this would be.

I wonder whether a change to so pure and rational a temperature scale could receive serious consideration today, or is science too big, with too much inertia? We'll see. ☐