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CACHE Standard Order Form

THE CACHE CORPORATION

WHAT IS CACHE?

CACHE is a not-for-profit organization whose purpose is to promote cooperation among universities, industry and government in the development and distribution of computer-related and/or technology-based educational aids for the chemical engineering profession.

CREATION OF THE CACHE CORPORATION

During the 1960s the rapid growth of computer technology challenged educators to develop new methods of meshing the computer with the teaching of chemical engineering. In spite of many significant contributions to program development, the transferability of computer codes, even those written in FORTRAN, was minimal. Because of the disorganized state of university-developed codes for chemical engineering, fourteen chemical engineering educators met in 1969 to form the CACHE (Computer Aids for Chemical Engineering) Committee. The CACHE Committee was initially sponsored by the Commission on Education of the National Academy of Engineering and funded by the National Science Foundation. In 1975, after several successful projects had been completed, CACHE was incorporated as a not-for-profit corporation in Massachusetts to serve as the administrative umbrella for the consortium activities.

CACHE ACTIVITIES

All CACHE activities are staffed by volunteers including both educators and industrial members and coordinated by the Board of Trustees through various Task Forces. CACHE actively solicits the participation of interested individuals in the work of its ongoing projects. Information on CACHE activities is regularly disseminated through CACHE News, published twice yearly.

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CACHE NEWS

The CACHE News is published twice a year and reports news of CACHE activities and other noteworthy developments of interest to chemical engineering educators. Persons who wish to be placed on the mailing list should notify CACHE at the aforementioned address. Contributions from CACHE representatives are welcome. This issue was edited by Christine Bailor with contributions from a number of CACHE members and representatives.

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Comments from the Editors

This is our third online issue of CACHE News. It is a pretty full issue, consisting of a Departments section, News from ChE Departments, seven Articles, a CACHE Standard Order Form, and these Comments from the Editors.

Unfortunately, we do not have a contribution for our Reflections section. We ask our faculty colleagues to please take advantage of this opportunity to communicate philosophical thoughts to more than one-hundred chemical engineering departments.

Adobe Acrobat, now in its version 5.0, has become the lingua franca of internet-based manuscript transfer, including **CACHE News**. If you only have Acrobat Reader 5.0, you should seriously consider going to the www.adobe.com web site and ordering a copy of the full version, which allows you to create PDF files from almost any software that has a Print command. Version 5.0, like version 4.0, also allows you to capture web pages from a website and convert them, with proper links, into a single PDF file.

While on the subject of **Acrobat PDF**, one of your co-editors recently came across the ACS Journals Manuscript Submission Site, http://pubs.acs.org/cgi-bin/submission_gen/index.pl?Journal=ancham, in this case, the site for the submission of articles to the journal, Analytical Chemistry. The site is rich with web pages that will assist you or your students with the creation of Acrobat PDF files. For example, there is a Macintosh and Windows "Templates" web page that permits you to download templates for (1) Microsoft Word 98 for Macintosh, (2) Microsoft Word 2000 for Windows, (3) Microsoft Word 97 for Windows, (4) Word Perfect 9 for Windows, and (5) Word Perfect 8 for Windows. In an educational environment, these templates are valuable for teaching students how to format laboratory reports.

Second, there is a "Check PDF" capability that allows you to type the complete filename of a PDF file on your hard disk in order to determine whether or not there are problems that will prevent you from successfully submitting the PDF file to Analytical Chemistry. This capability should be useful to you and your students. For example, we tested all of the articles in this issue. The chemical microengineering article had no errors (Acrobat 5.0 was used), but the others each had several errors (e.g., Font Times-... not embedded) and one caution (e.g., "Document is produced by Adobe PDFwriter"). **CACHE News** can live with such minor errors; we are not as finicky as is the ACS.

Third, three lists of supported file formats -- for what Analytical Chemistry calls "Option 1", "Option 2", and "Supporting Information" -- cover the complete list of files that Analytical Chemistry is willing to receive from authors.

Fourth, there is a "Frequently Asked Questions" web page that covers the topics of (1) Getting Started/General Questions, (2) Using the Template, (3) Saving ChemDraw Files, (4) Transmitting the Manuscript, (5) Supporting Information, (6) Reviewing the PDF, (7) Submitting the Manuscript, and (8) Revising the Manuscript. For ChE students, both undergraduate and graduate, this is useful information concerning manuscript creation, submission, and revision.

Your co-editor recalls the pioneering efforts, during the 1990s, of CACHE trustee and editor Brice Carnahan, who requested contributors to the FOCAP-X series of conference proceedings to utilize the templates that he created at a significant cost in time. Brice, through CACHE, was ahead of his time.

It comes as no surprise that the American Chemical Society is so progressive with its publication efforts. We hope that the AIChE is equally progressive with its own journals.

The Editors

Edward Rosen, Peter Rony, and Scott Fogler

IOWA STATE UNIVERSITY

A new Web site has been created that shows a collection of thermodynamic fundamental and state surfaces for generic one-, two-, and three-component, fluid-phase systems as modeled by the Peng-Robinson equation using common mixing rules. Kenneth Jolls (Iowa State University) and Daniel Coy (Nanophase Technologies Corporation) have used high-performance computer graphics to produce three-dimensional, parametric sections of the n-dimensional fundamental functions that result from various Legendre transformations. Selected equation-of-state surfaces resulting from differentiation of the fundamental forms are shown also and their connections with the parent functions are noted. Each surface covers a property range spanning a fluid-phase critical point, and color is used to partition the functions according to thermodynamic stability theory. The presentation offers excellent collateral reading for any advanced treatment of theoretical classical thermodynamics, such as in the books by Modell and Tester (Reid) or by Callen. The Web site has the title "Gibbs Models" and can be viewed at:

www.public.iastate.edu/~jolls/

IOWA STATE UNIVERSITY/RICE UNIVERSITY

A computer based tutorial for thermodynamic phase diagrams of binary, ternary, and quaternary systems has been developed at Iowa State University under the direction of Ken Jolls and at Rice University under the direction of Walter G. Chapman. The tutorial allows students to view, rotate, and slice 3-D phase diagrams interactively on a PC. The tutorial is a combination of powerpoint presentation and C++ visualization programs. For example, the student can view of P-T-xy diagram for a binary system and make constant temperature or constant pressure slices through the diagram. This enables the student more clearly see the form of the bubble and dew surfaces. The tutorial is available from Walter G. Chapman at Rice University by filling out the form on the web site:

www.owlnet.rice.edu/~wgchap.

The program uses the Open Inventor graphics library which was licensed from Silicon Graphics. Chapman has purchased a large number of licenses so that one copy is available to each university. Additional copies of the tutorial are available at the nominal cost of \$20 per copy. The tutorial provides an excellent introduction to thermodynamic phase diagrams for undergraduate and graduate students.

LEHIGH UNIVERSITY

We have recently released a set of ODE/DAE/PDE applications in the following areas:

1. Mass transfer and separations
2. Reactors and kinetics
3. Heat transfer
4. Fluid flow
5. Process control

Details for obtaining this set of applications are given in:

<http://www.lehigh.edu/~wes1/wes1.html>

MANHATTAN COLLEGE

1. Puri, Welsh and Chickos. Integrated computational and experimental investigation of the thermodynamic properties of polychlorinated biphenyls. University of Missouri.
2. Bamford. The prediction of Henry's law constants and its temperature dependence for polychlorinated biphenyls from computational and experimental data. Chesapeake Biological Laboratory, University of Maryland.
3. Totten, Liu, Braun and Assaf-Anid. Success of density functional theory in predicting enthalpy changes associated with two-electron reduction of polychlorinated biphenyls. Rutgers University, Columbia University and Manhattan College.
4. Fransisco. Atmospheric chemistry of alternative fuels. Purdue University
5. Tossell. Computing the properties of the Cu-thioarsenite complex. University of Maryland.

Please check our website:

<http://www.engineering.manhattan.edu/chemical/news/-events.html>

Chemical Engineering Faculty Openings on the Web

*Thomas F. Edgar
Executive Officer, CACHE Corporation*

This Fall the CACHE Corporation, in cooperation with the Chemical Engineering Education journal, has introduced a new service for faculty opening advertisements on its website, www.cache.org. As you know, there are many ways that chemical engineering departments seek faculty recruits, and classified ads are often used to inform and identify candidates for a faculty position. However, the classified ads for chemical engineering faculty are published in many different print journals, and a graduate student or existing faculty member who seeks a position is forced to consult many ad sources to get a complete picture of available openings. In addition, many of the ads have a short time frame (e.g., less than one month) because ads with longer durations are expensive.

The CACHE Corporation believes there is considerable value to the educational community by providing consolidated, low cost web pages for faculty openings. The CACHE ads are posted promptly on www.cache.org and run for a three month period. The site is completely open and not restricted to membership in a given professional organization, thus emphasizing the free, global flow of information. The price for one posting is not tied to number of words, but has a limit of 400 words. The price for the ad is \$100 if the Department is an annual supporter of CACHE (which is a \$200 per year fee), and \$200 for non supporting departments.

We will want to enlist the help of faculty in informing graduate students in your department about the existence of the site for the ads so they can take advantage of the timely information provided. Because this service is a new endeavor, we would welcome your suggestions on how to maximize the effectiveness of the faculty ad service. If you have any questions about the service, please contact edgar@che.utexas.edu. Thank you.

Chemical Microengineering. III. Multiphase Catalysis

By Peter R. Rony

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Introduction

This is the third in a CACHE News series [1,2] about a Virginia-Tech senior-elective course, entitled "chemical microengineering", that includes the study of the continuity-of-species equation for "small chemical systems". The first two articles are available as downloadable files at URLs

http://www.che.utexas.edu/cache/newsletters/fall2000_chemmicro.pdf (Fall 2000 issue) and

http://www.che.utexas.edu/cache/newsletters/spring2001_chemmicro.pdf (Spring 2001 issue).

Because of the similarities of the systems, the sections of this third article will be analogous to those for the second.

What is Multiphase Catalysis?

Multiphase catalysis is defined as a reactor technique that employs the distribution of reacting components between two or more different states -- one stationary and one mobile -- that permit the facile separation of products from the reaction state [3].

Example No. 1: Gas-Liquid Catalysis

As an example, consider gas-liquid catalysis, where a steady-state mixture of reacting components is input at the inlet of a long, hollow, stainless-steel or glass capillary column coated on the inside with a thin film of a non-volatile catalytic solution. A continuous, steady flow of gas passes through the column. After the input flow is started, a steady-state product stream appears at the exit of the column (Figure 1).

Example No. 2: Supported Liquid-Phase Catalysis (SLPC)

As a second example, consider a typical, laboratory-scale, short, hollow, stainless-steel column packed with a porous solid that is filled approximately 30% with a catalyst solution based upon a soluble, transition-metal complex. A steady-state mixture of reacting components is input to the reactor, and products are obtained at the exit. A reactant diffuses into the pores of the porous solid, dissolves in the supported liquid, and reacts, with the products evaporating into the gas phase within the pores. It is important to have a balance of both gas and liquid phases within the pores. [4,5]

Example No. 3: Heterogeneous Catalysis (Gas-Solid Adsorption Catalysis)

As with Example No. 2, consider a typical, laboratory-scale, short, hollow, stainless-steel column packed with a porous solid that contains a dispersed metal such as, for example, platinum, palladium, or rhodium,

metal oxide, metal sulfide, metal carbide, or metal nitride. A steady-state mixture of reacting components is input to the reactor, and products are obtained at the exit. A reactant diffuses into the pores of the porous solid, adsorbs on the catalyst surface, and reacts to form product, which either desorb into the gas phase within the pores. [6]

What is the Gimmick Associated with Gas-Liquid Catalysis?

The basic "gimmick" behind ideal gas-liquid catalysis is the existence of two phases -- one stationary and one mobile -- between which the reacting components of an input mixture rapidly equilibrate. In the ideal case, the equilibration of each reacting component is ideal, in the sense that there exist no mass-transfer limitations to equilibration and the quantity of each component is sufficiently small such that linear partition coefficients apply. The reacting phase is stationary.

Just like ideal partition chromatography, ideal gas-liquid catalysis can be considered to be, in effect, an example of two-dimensional thermodynamics. The three vector directions in Example No. 1 include a single, axial coordinate direction (the length of the capillary tubing; see Figure 1) and two lateral coordinate directions (one being the radial direction) over which thermodynamic equilibrium exists at every point z within the steady-state gas-liquid catalytic column.

Typical Multiphase Catalysis Apparatus: A Tubular Flow System

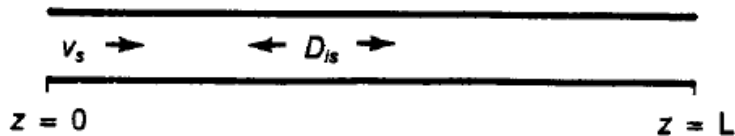


Figure 1. Steady-state reaction and convection in a tubular flow system. A mixture of components is fed continuously into the column at $z=0$ and the products appear at the exit, $z = L$.

Multiphase Catalysis as a Linear Multistate System

The teaching of the basic principles behind gas-solid and liquid-solid adsorption catalysis (typically called "heterogeneous" catalysis) has been a part of the chemical engineering curriculum for decades, specially in graduate school. However, the generality of multiphase catalysis has not been usually taught.

Consider the following linear partition coefficient between states 1 and 2 for an reacting component i ,

$$K_{i2} = \frac{C_{i2}}{C_{i1}} \tag{1}$$

which has units of concentration/concentration. The resulting conservation-of-species equation -- involving diffusion, convection, and irreversible first-order reaction along the axial coordinate direction z -- is,

$$\frac{\partial c_{is}}{\partial t} - D_{ieff} \frac{\partial^2 c_{is}}{\partial z^2} + v_{ieff} \frac{\partial c_{is}}{\partial z} + k_{ieff} c_{is} = 0 \quad (2)$$

In the absence of axial diffusion and the accumulation term, Equation (2) simplifies to,

$$v_{ieff} \frac{\partial c_{is}}{\partial z} + k_{ieff} c_{is} = 0 \quad (3)$$

For a boundary condition of

$$c_{is}(z=0) = c_{is}^0 \quad (4)$$

at the inlet to a column reactor, the concentration of the reactant at any point, z , within the reactor becomes,

$$\frac{c_{is}}{c_{is}^0} = e^{-\frac{k_{ieff} z}{v_{ieff}}} \quad (5)$$

The next step is to decide what are the specific forms for the effective rate constant and velocity.

What is a State?

Multiphase catalysis basically is the superposition of two-dimensional thermodynamics -- a non-reactive mobile phase and a reactive, stationary phase -- upon steady-state reaction and convection in a third dimension. The purpose of the mobile phase is to provide fresh reactants and to remove products. For simplicity, the two-dimensional equilibrium and third-dimension dynamics can be characterized by a pair of states for the rate-determining, reacting component in a catalytic column (see Figure 2).

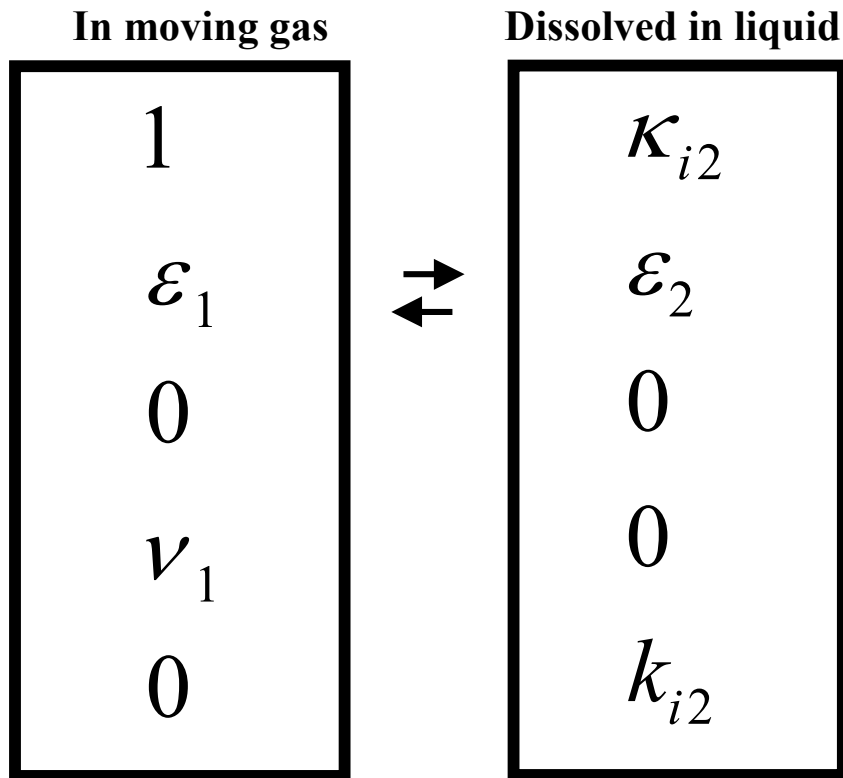


Figure 2. Box representation of the two states (for each reacting component i) in gas-liquid multiphase catalysis for a tubular column system.

In Figure 2, the subscript i represents a reacting component; the subscript numbers 1 and 2 represent the mobile and stationary phases, respectively; k is the first-order or pseudo-first-order rate constant in a phase; and v is the convective velocity of phase 1 . At the bottom of each state box, the value 0 indicates that diffusion is irrelevant to the multiphase catalysis model.

Description

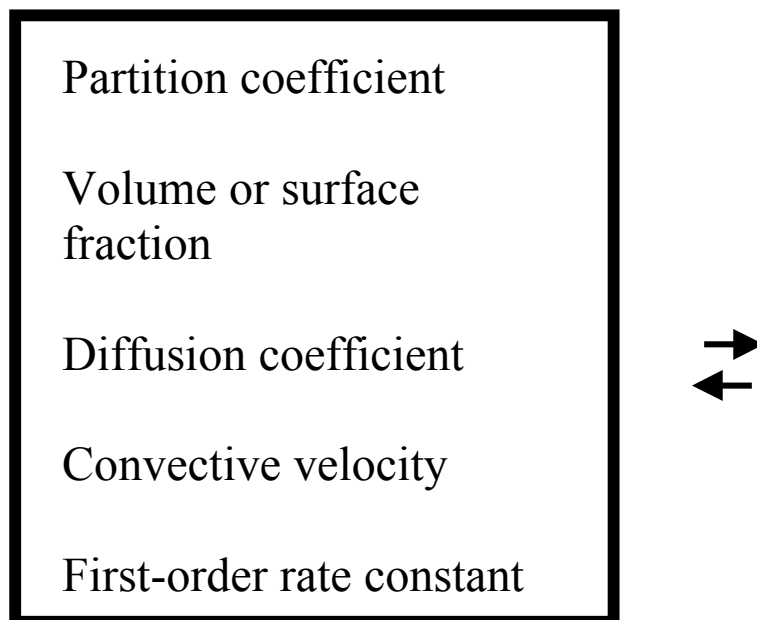


Figure 3. General box representation of a state in a linear multistate chemical system.

States in Gas-Liquid Catalysis

Figure 3 provides a general representation of a state box in any two-dimensional thermodynamic system in which reaction and mass transfer processes occur in the remaining coordinate direction. The quantity, k_{ieff} , is calculated as follows from Figure (2),

$$k_{ieff} = \frac{\varepsilon_2 \kappa_{i2} k_{i2}}{\varepsilon_1 + \varepsilon_2 \kappa_{i2}} \quad (6)$$

and the ratio of the effective rate constant to the effective velocity is,

$$\frac{k_{ieff}}{v_{ieff}} = \frac{\varepsilon_2 \kappa_{i2} k_{i2}}{\varepsilon_1 v_1} \quad (7)$$

The significance of Equation (7) can be understood by the following exponential ratio in Equation (5),

$$\frac{k_{ieff} L A_{\perp}}{v_{ieff} A_{\perp}} = \frac{\varepsilon_2 \kappa_{i2} k_{i2} A_{\perp}}{\varepsilon_1 v_1 A_{\perp}} \quad (8)$$

ε_1 and ε_2 are the volume fractions of the gas and liquid phases, respectively,

$$\varepsilon_s = \frac{\text{volume of phase } s \text{ in reactor}}{\text{total volume in reactor}} \quad (9)$$

Equation (8) therefore becomes,

$$\frac{k_{ieff} L A_{\perp}}{v_{ieff} A_{\perp}} = \frac{\varepsilon_2 \kappa_{i2} k_{i2} A_{\perp}}{\varepsilon_1 v_1 A_{\perp}} = \frac{V_2 \kappa_{i2} k_{i2}}{F_1} \quad (10)$$

Where A_{\perp} , V_2 is the total volume of liquid in a gas-liquid catalytic column, and F_1 is the gas flow rate at reactor conditions. Based upon Equations (5) and (10), it is possible to create a plot (Figure 3), the slope of which provides the product of thermodynamic and kinetic parameters,

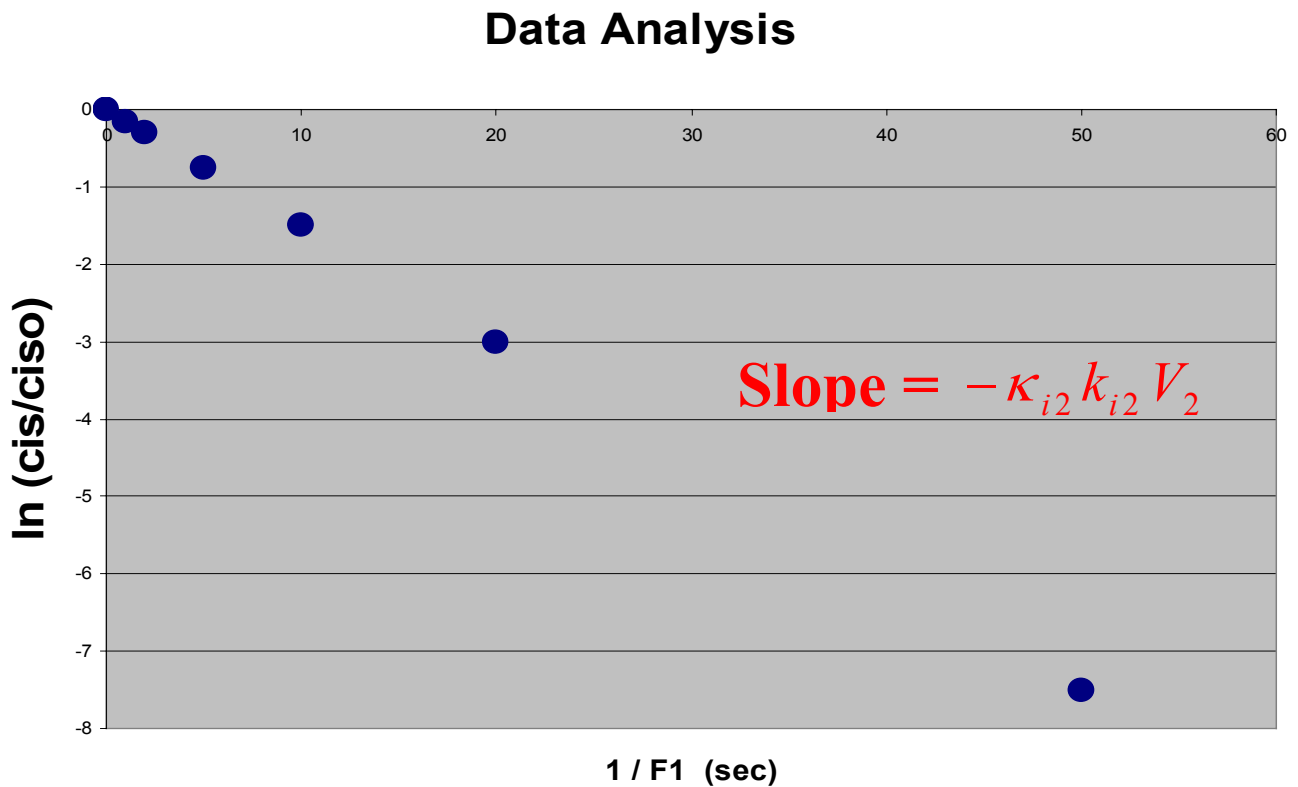


Figure 4. Plot of dimensionless conversion from a gas-liquid catalytic reactor versus the reciprocal gas flowrate at reactor conditions.

If we multiply the numerator and denominator of Equation (1) by the ratio of the volumes of phases 2 and 1, respectively, we obtain the distribution coefficient,

$$K_{i2} = \frac{c_{i2} V_2}{c_{i1} V_1} = \kappa_{i2} \frac{\varepsilon_2}{\varepsilon_1} \quad (11)$$

which has units of moles/moles.

States in Gas-Solid Adsorption Catalysis ("Heterogeneous Catalysis")

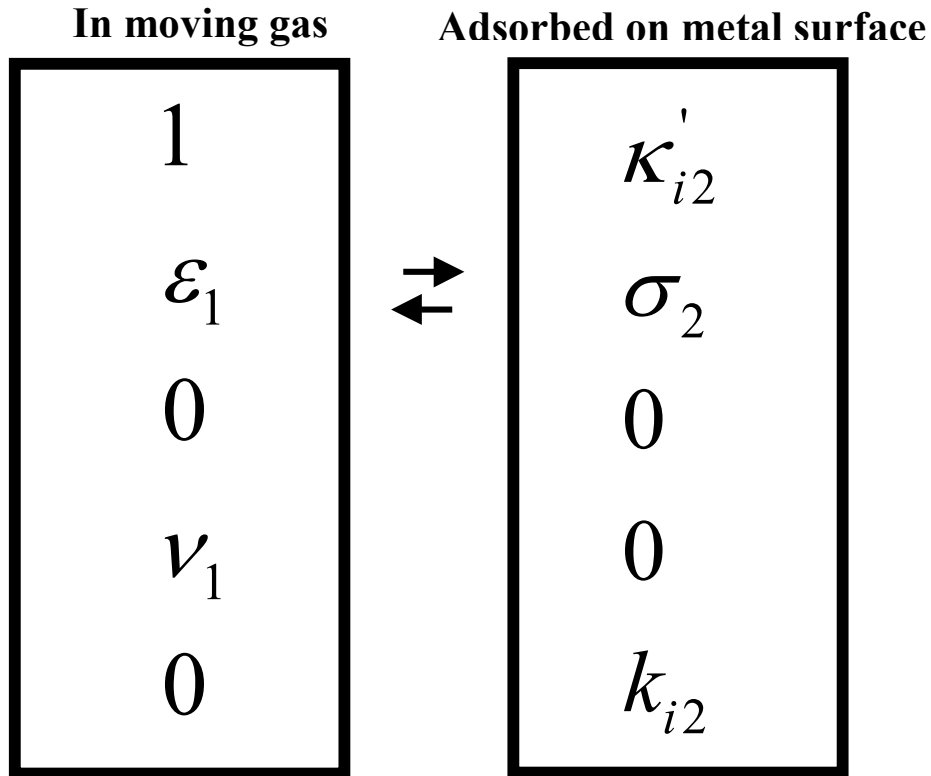


Figure 5. Box representation of the two states (for each reacting component i) in gas-solid adsorption catalysis for a packed tubular column system.

In the adsorbed state of Figure 5, σ_2 is a surface-to-volume ratio and κ'_{i2} is a surface partition coefficient, the ratio of the surface concentration of an adsorbed component divided by the concentration of the component within the gas phase. The distribution coefficient for a surface partition coefficient is,

$$K_{i2} = \frac{c_{i2} S_2}{c_{i1} V_1} = \kappa'_{i2} \frac{\sigma_2}{\varepsilon_1} \quad (12)$$

A gas-solid adsorption catalysis system experimental plot that corresponds to Figure 4 is shown in Figure 5.

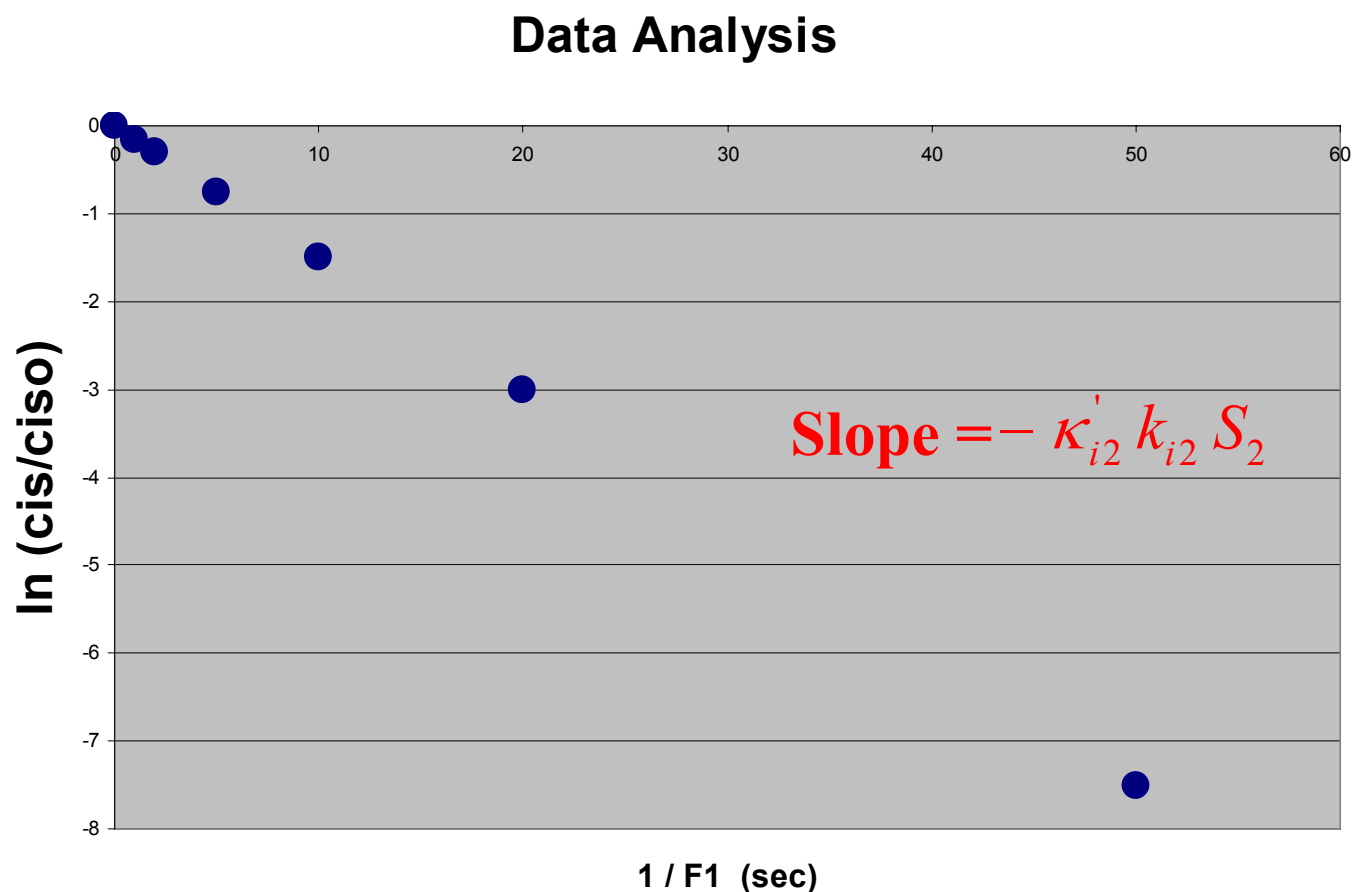


Figure 6. Plot of dimensionless conversion from a gas-solid adsorption catalytic (heterogeneous catalytic) reactor versus the reciprocal gas flowrate at reactor conditions.

In Figure 6, the slope product of the partition coefficient and the rate constant has units that seem to be cm/sec. Such units are incorrect, the correct answer being cubic centimeters gas volume divided by the product of square centimeters surface area and seconds.

Examples of Multiphase Catalysis Techniques

Table I. Standard multiphase catalysis techniques

Standard Multiphase Catalysis Technique	Mobile Phase	Stationary Phase
gas-liquid catalysis	gas	liquid contained in porous solid
gas-solid catalysis	gas	solid particles containing deposited catalyst
liquid-liquid catalysis	liquid	organic liquid contained in porous solid
solid-liquid catalysis	liquid	solid particles containing deposited catalyst
molecular-sieve chromatography	gas	molecular sieve contained deposited catalyst
ion-exchange catalysis	liquid	porous ion-exchange particles
gel-permeation catalysis	liquid	cross-linked solid particles

Table I and Table II summarize standard and non-standard multiphase catalysis techniques, respectively. Table III summarizes different categories of multiphase catalysis techniques. The techniques differ in the type of apparatus -- glass column, capillary column, stainless-steel, high-pressure column, paper, or glass plate; whether the technique employs one or two phases; and the possible existence of superimposed chemical equilibria within a liquid phase.

Table II. Non-standard multiphase catalysis techniques

Non-Standard Chromatographic Technique
aerosol catalysis
dust catalysis
solid-liquid fiber catalysis
gas-solid fiber catalysis
flotation catalysis
oxidation-reduction catalysis
electrode catalysis
membrane catalysis

Table III. Categories of multiphase catalysis techniques

Categories of Multiphase Catalysis Techniques	Special Characteristics
High-performance techniques	apparatus consists of column under high pressure
Column techniques	apparatus consists of a cylindrical column
Paper techniques	stationary phase is paper
Thin-layer techniques	stationary phase is thin layer of porous solids
Capillary techniques	apparatus consists of a capillary column
Micro-column techniques	column is very small

Summary

Multiphase catalysis is defined as a reactor technique that employs the distribution of reacting components between two or more different states -- one stationary and one mobile -- that permit the facile separation of products from the reaction state. The reaction *state* can be a dissolved component within a phase, an adsorbed component at an interface, or a reversibly complexed (to an ion or molecule) component within a liquid phase. The apparatus can consist of a vertical glass tube; a high-pressure stainless-steel column; a long glass or stainless-steel capillary tube; paper; an electrophoresis apparatus; or a plate with a thin-layer coating of porous solid.

Nomenclature

Arabic letters

c	Volume concentration of reacting component, used in Equation (1)
c'	Surface concentration of reacting component, used in Equation (12)
D	Diffusion coefficient, used in Equations (2) and (3)
k	First-order or pseudo-first-order rate constant, used in Equations (2) and (3)
K	Distribution coefficient, defined by Equation (11) or (12); units of moles/moles
t	time
v	velocity, used in Equations (2) and (3)
x	x axis
z	z axis

Greek letters

- ε Volume fraction, used in Figure (2), Figure (5), and Equations (6), (9), (11), and (12)
- κ Partition coefficient, a ratio of concentrations, used in Equation (1); units of concentration/concentration
- σ Surface-to-volume fraction, used in Figure (5) and Equation (12), units of volume concentration/surface concentration

Subscripts

- eff* Effective value index, defined in Equations (2), (3), and (4)
- i* Eluting component index
- s* Environment index
- i1* Component *i* in phase or environment **1**
- i2* Component *i* in phase or environment **2**
- i3* Component *i* in phase or environment **3**
- i4* Component *i* in phase or environment **4**

Superscripts

- ' Indicates a surface state

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Educating Undergraduate Chemical Engineers in Process Control Using a Real-time Approach

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Summary

This article describes the successful and revolutionary real-time approach to the education of undergraduate chemical engineers in the fundamentals of process control, i.e. teaching process control in the same way that process control is practised/implemented in the chemical and processing industries.

Introduction

The classical approach to process control education of chemical engineers has been to employ the frequency response methods of process control that were originally developed as pen and paper methods for the modeling of process systems. It has been evident for some time that the way process control is taught to chemical engineers needs to be updated.

There is an academic requirement that the fundamentals of process control be taught in a more practical and concrete way than afforded by the traditional classical approaches. It has been recognised for some time that chemical engineers trained in process control by a strict classical approach require almost complete re-education in process control when they are employed by industry. Brisk and Newell [1] recommended training students “in how to utilise process control systems with just enough theory that they can understand what they are using and maintaining”. And they went on to lament that “unfortunately most of our institutions are teaching too much theory, very little on utilisation and maintenance”. Doss [2] comments that “students tend not to retain the mathematical theory but to remember the experiences from control laboratory experiments and simulations”. Ramaker *et al.* [3], point out that “an undergraduate in a chemical engineering curriculum [studying] process control should be taught using concepts that fit with the rest of chemical engineering education ... maintaining the undergraduate curriculum as closely tied as possible to the time domain”.

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There is also an industrial imperative to teach material that is of use to the practising engineer. Downs and Doss [4] note that “what the [graduating engineer] needs is a base level understanding of differential equations, process dynamics, dynamic modelling of basic unit operations, basic control algorithms (such as PID), cascade structures and feed forward structures. With these basic tools and an understanding of how to apply them he can solve most of his control problems himself. What he does not need is the theory and mathematics that usually surround process control”. The industrial imperative is further reinforced by the comments such as the following that arise from practising Chemical Engineers working in process control or process operations [5]:

- “I never made use of Bode plots or root-locus when I was designing a control loop”
- “There are no transfer functions out there in the real plant”
- “The material I had been taught was of no use in commissioning a control loop”

Process control education clearly needs to do better.

The Classical Approach

Classical Control methods were developed between the 1940's and the 1960's in the mechanical and electromechanical engineering disciplines. Given the limitation of computer hardware and software at that time, it was impractical to solve large numbers of higher-order differential equations. Furthermore, since mechanical and electromechanical systems are typically linear and possess little dead time, they lend themselves to analytical and graphical techniques. Hence the development and popularization of analytical and graphical such techniques as:

- Transform methods (Laplace and Fourier Transforms)
- Graphical frequency domain methods (Bode, Nichols and Nyquist)
- Root locus analysis.

Given the fit to their purpose, classical control techniques still prevail and remain relevant in these engineering disciplines today.

Although these methods make up almost half the content of standard control texts, these methods all share a number of deleterious characteristics. They all require a substantial amount of applied mathematics. In spite of the high level of mathematics required, in order to apply the analysis,

the system must first be made linear and the methods have a transfer function basis, focus on individual units and are generally good only for single loops and PID control. Limited multivariable and no plant-wide controls are possible.

Beyond the engineering deficiencies of classical techniques, there are implications from a teaching and learning perspective. The abstraction of classical methods makes a difficult subject more difficult, and the methods lack physical meaning, obscuring the central problem of how to modify the system in order to achieve control [5]. These methods are also not suited to “what if” studies such as determining loop performance with parameter variation.

The ready availability of hardware and software now has called into question the relevance of these classical methods for a primary course on process control. A number of previous workers have also identified this need for change. Many workers in the past decade have incorporated simulation software into the syllabus and deleted previous graphical procedures, but retained the classical methods. However, Brauner *et al.* [6], and then Stillman [5], Bissell [7] and Ramaker *et al.* [3], almost simultaneously, all proposed the more radical solution of complete replacement of classical methods with computer simulation, i.e. not as an add on, but as an integral part of the teaching and learning of process control. Ramaker *et al.* [3], possibly say it best when they say “this doesn’t mean that the Laplace transform cannot be used as a tool to solve differential equations in the undergraduate course. Neither does it mean that frequency domain analysis and design are not useful in chemical engineering. It only means that we feel that frequency domain analysis and design should be taught at a graduate level, maintaining the undergraduate curriculum as closely tied as possible to the time domain”. In this article we outline and evaluate the actual implementation of such a complete real-time approach to process control education [8].

The Real-Time Approach

Unlike mechanical and electromechanical systems, chemical processes are characterized by high degrees of non-linearity, process interactions, and substantial dead time. Additionally, due to these non-idealities, chemical process control demands to be addressed with a multivariable and plant-wide view. As such, applying classical techniques to chemical process control is a bit like using a wrench to do a hammer’s work. In an ideal world, the chemical engineer would have a “virtual plant” on which to experiment. This plant would capture most of the important non-idealities the real world imposes, and would allow the engineer to readily test even the most outlandish of control structures with impunity.

Early attempts to realize this “ideal world” date back to the 1970’s and 1980’s when dynamic simulators such as DYFLO, DYN SYS or SPEEDUP first became available for the solution of

the non-linear differential equations describing process dynamics. However, the hardware was slow at this time, and the software was impractical for students to learn and implement in a reasonable time frame. There was effectively no user interface in that the graphics were poor and the programs were run batch-wise.

However, in today's "simulation-rich" environment, the right combination of hardware and software is available to implement a "real-time" approach to process control education. The hardware and software, such as HYSYS, Aspen Dynamics or MATLAB, is now fast and easy to use. Simple, complex and/or user defined process modules are available and it is now easy to do "what-if" studies, multi-loop and plant-wide control simulations. The software user interface is now graphical and interactive and the software can be painlessly run on a PC. In short, the "virtual plant" has arrived.

This real-time approach also quite naturally lends itself to active, "hands-on" or resource based learning. In our undergraduate course we use of a small number lectures at the beginning of the course to motivate students and provide a fundamental understanding rather than to transmit information and a majority of "hands-on" simulation tutorial sessions on case study projects facilitated by the instructors that we call workshops [8]. The syllabus covers the development of mathematical models to describe the transient real-time response characteristics of basic process elements, capacity and dead time; fundamentals of single input, single output systems; use of a dynamic process simulator; block flow diagram of a feedback control loop; process control hardware; basic control modes; tuning feedback controllers; cascade control; feedforward control; common control loops; distillation column control; design of multiple single loop controllers; plant-wide modelling and control.

We also note that while computer simulations provide generally favorable experiences, real experiments are still necessary and desirable for undergraduates. Therefore we employ in our undergraduate course a cascade of tanks and a heat exchanger in a pilot plant laboratory that allows students to perform process identification exercises on real plant and tune real controllers. So that the undergraduate student understands the underlying "physics" of process control, modeling exercises that require the student to write the describing differential equations and solve them numerically using MATLAB are associated with these laboratory plant experiences.

Student Evaluation

This real-time approach to process education was first developed in 1996 as a text and an associated set of workshops. This version was used at the University of Calgary during the 1997 academic year as a pilot course for nine students as their senior year controls course. Their comments were used and motivated a revised second version of the notes and workshops. This

second version was used as a basis for the classes of 1998, 1999 and 2000 at the University of Calgary, totaling forty-five, sixty and eighty students, respectively. A further revision has just been published [8] and was used for the 2001 class of 46 students.

As a means of generating feedback, the students were asked to complete a questionnaire. Overall, the overwhelming majority of undergraduate students preferred the “hands-on real-time approach” to learning process control. More than 80% of the undergraduate students said the approach was clear, concise, useful and applicable. The major complaints, but from a minority of undergraduate students, were that they did not like “hands-on” self directed learning, found the workshops too involved and time consuming and would have preferred a standard course consisting of standard lectures, assignments, quizzes and a written final exam. Our feedback from former students in industry is also overwhelming enthusiastic.

Conclusions

The need for change to conventional process control education was identified. The change that is required is from a classical frequency domain methodology to instruction using concepts that fit with the rest of chemical engineering education, i.e. a real-time approach.

A real-time simulation approach to undergraduate process control education in chemical engineering with the aid of realistic “hands-on” workshops involving real-time simulation of chemical processes was outlined. The workshops are based on fundamental process models of industrial unit operations using educationally affordable and readily available commercial process simulation software.

Student feedback from four years of implementation at the undergraduate level in the University of Calgary evaluated the new “hands-on” real-time simulation workshop approach as effective, useful and applicable.

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On Testing C++ DLLs

by

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Introduction

It is generally recommended that C++ DLLs be tested in the C++ environment before being made available for calling from VBA (Visual Basic for Applications). The procedures used for preparing and calling C++ DLLs from VBA have been described by Rosen (1). The C++ environment is Visual C++ (6.0).

The procedures for developing the C++ DLLs and testing them in the IDE (Integrated Development Environment) using the Wizard differ from those used in preparing and calling the DLLs from VBA.

Preparing C++ DLLs for Use in C++

1. After invoking Visual C++ select “File” and “New”
2. In the project window, give the project a name. Here we have chosen “zzz” and chosen to place it in c:\ctest\
3. Select a “Win32 Dynamic-Link Library”
4. Select “A DLL that exports some symbols”

The Wizard then informs you that the following programs and headers have been prepared:

```
DllMain  
zzz.cpp  
zzz.h  
Stdafx.h  
Stdafx.cpp
```

5. Figure 1 is a listing of the file zzz.cpp after the function Vari has been added. The “Rebuild All” command is invoked and the compiler informs you that the files zzz.dll and zzz.lib have been created. The zzz.dll file is in c:\ctest\zzz\debug\
Note the differences between Figure 1 and Figures 1a and 1b of Reference (1).

6. After the `zzz.cpp` compiles successfully, under “Build” invoke the “Set Active Configuration” to “Win32 Release” and then “Rebuild All”.
7. Copy the `zzz.dll` in `c:\ctest\zzz\release\` and place it in `Windows\System` folder so it can be found by other programs.

Visual C++ Test Program

The general testing procedures are described in by McMahon (2) and Horton (3) though they differ somewhat in that detailed here.

1. Invoke Visual C++ 6.0 and select “File and “New”. Here we have chosen the `testzzz` for the project name and `c:\ctest` as the location.
2. Select a “Win32 Console Application”
3. Select “A simple application”

The Wizard will inform you that the following have been prepared:

Main: `testzzz.cpp`
Stdafx.h
Stdafx.cpp

4. Figure 2 is a listing of the file `testzzz.cpp`, the test program that calls the `Vari` function.

It is important that locations of the `zzz.dll` and the `zzz.lib` be specified during the “Rebuild All”.

Note that we have placed the `zzz.dll` file into the `Windows/System` folder. We must also add the `zzz.lib`, in `c:\ctest\zzz\release\zzz.lib`, in the libraries searched under Project Settings – Link.

5. After the `testzzz` program has been successfully compiled and linked, reset the Active Configuration to “Win32 Release” and the “Rebuild All”.

When the execute `testzzz.exe` item is invoked, a DOS window appears and the result of the calculations are indicated. Figure 3 is the output.

Summary

The procedures for utilizing C++ DLLs in a C++ program and in VBA differ both in the preparation of the DLLs and their use.

Procedures other than those described here and in Reference (1) may exist. It is noted that the DUMPBIN utility (see the Internet for a description) may be useful in solving linker problems.

References

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```

// zzz.cpp : Defines the entry point for the DLL application.

#include "stdafx.h"
#include "zzz.h"

BOOL APIENTRY DllMain( HANDLE hModule,
                      DWORD ul_reason_for_call,
                      LPVOID lpReserved
                      )
{
    switch (ul_reason_for_call)
    {
        case DLL_PROCESS_ATTACH:
        case DLL_THREAD_ATTACH:
        case DLL_THREAD_DETACH:
        case DLL_PROCESS_DETACH:
            break;
    }
    return TRUE;
}

// This is an example of an exported function.
ZZZ_API double Vari( double in_data[], long NumItems)
{
    //Function : Vari
    //Description : Returns the variance for array in_data

    long j;
    double sumx=0, sumsqared=0;
    double vari=0;

    for (j=0; j< NumItems; j++)
    {
        sumx += in_data[j];
        sumsqared += in_data[j]*in_data[j];
    }

    vari =(sumsqared - (sumx*sumx/(double)NumItems))/((double)NumItems -1.0);

    return(vari);
}

```

Figure 1. The zzz.cpp File

```

// testzzz.cpp : Defines the entry point for the console application.
#include <stdafx.h>
#include <iostream>
using namespace std;

extern double Vari(double in_data[] , long NumItems);

int main(int argc, char* argv[])
{
    long NumItems1;
    long NumItems2;
    long NumItems3;

    double data1[] = {5.,6.,8.,9.,12.,33.,19.,22.};
    double data2[] = {8.,9.,20.,33.,56.};
    double data3[] = {1345.,1301.,1368.,1322.,1310.,1370.,1318.,1350.,1303.,1299.};
    double var;

    NumItems1 = (sizeof data1)/(sizeof data1 [0]);
    NumItems2 = (sizeof data2)/(sizeof data2 [0]);
    NumItems3 = (sizeof data3)/(sizeof data3 [0]);

    cout <<endl;
    cout <<"\nNumItems1 = " <<NumItems1;
    cout <<endl;

    cout <<endl;
    cout <<"\nNumItems2 = " <<NumItems2;
    cout <<endl;

    cout <<endl;
    cout <<"\nNumItems3 = " <<NumItems3;
    cout <<endl;

    var = Vari(data1, NumItems1);

    cout <<endl;
    cout <<"\nvar = " <<var;
    cout <<endl;

    var = Vari(data2, NumItems2);

    cout <<endl;
    cout <<"\nvar = " <<var;
    cout <<endl;

    var = Vari(data3, NumItems3);

    cout <<endl;
    cout <<"\nvar = " <<var;
    cout <<endl;

    return 0;
}

```

Figure 2. testzzz.cpp File

NumItems1 = 8

NumItems2 = 5

NumItems3 = 10

var = 94.2143

var = 398.7

var = 754.267

Figure 3. Output from testzzz

Determination of Heterogeneous and Homogeneous Reaction Rate Constants Using Non-linear Optimization.

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Abstract

Experimental reaction data must be fitted into a useful reaction rate equation in order to use in the simulation of reactor design and sizing. While optimization techniques of experimental data of homogeneous reaction are well established, many challenges are encountered when experimental data are of catalytic reactions. A computer simulation tool has been developed to accept experimental reaction data and fit the data into a nonlinear reaction rate equation. More than 180 of the L-H reaction rate equations are built into the program. The program will estimate catalytic adsorption constants and other reaction rate constants, and recommend the best reaction rate equation. The non-linear optimization methods available in GAMS are used via a Visual Basic user-friendly interface.

Introduction

In the industrial applications of kinetics, knowledge of chemical rate equation is essential in establishing the optimum conditions of pressure, temperature, feed composition, space velocity, extent of conversion and recycling. (Yang and Hougen, 1950) The algorithm for collecting information for catalytic reactor design is shown in Figure 1. The objective of the

research is to develop a computer optimization tool to determine the best catalytic and non-catalytic reaction rate equation and reaction rate constants based on available experimental data.

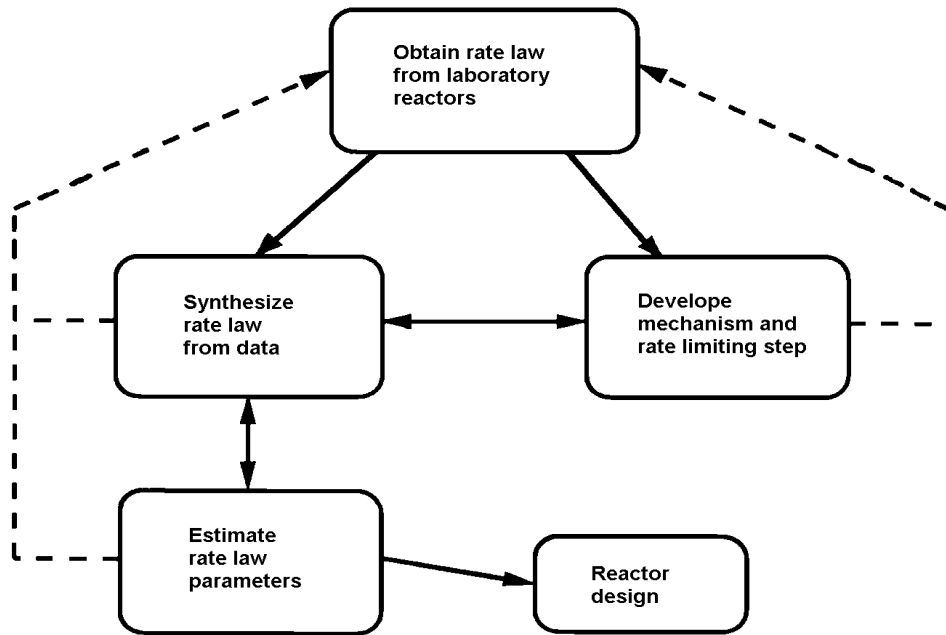


Figure 1. Collecting Information for Catalytic Reactor Design

Source: Fogler, H. Scott. (1994). Elements of Chemical Reaction Engineering (2nd ed.). Englewood Cliffs, NJ: Prentice Hall.

Experimental data of a homogeneous or heterogeneous reaction may be fitted into a theoretical, semi-theoretical, or empirical rate equation. The rate equation is used to predict the reaction rate within the ranges of the variables studied and in some cases to allow cautious extrapolation. This is most frequently done with a set of Langmuir-Hinshelwood (L-H) rate equations. The L-H rate equation of heterogeneous catalysis is widely used by chemical engineers in the correlation of experimental catalytic reaction rate data. (Kabel and Johanson, 1962) L-H rate equations are used to represent heterogeneous reactions where adsorption effects are important. With the knowledge of kinetic constants these rate equations are screened to reject those that are inadequate in the light of the data. (Kittrell, Hunter and Watson, 1965)

The optimization problem can be quite difficult for L-H rate equations because of many factors. First, these rate equations are frequently nonlinear with respect to the rate constants within these rate equations. Second, the number of rate constants contained in each rate equation

can be too many for the range of the experimental data. (Mezaki and Kittrell, 1967) Rate constants in L-H rate equation are optimized using the principle of minimization of sum of squares of residuals.

The present work can be used to find out possible rate equations for homogeneous and heterogeneous reactions. After testing corresponding rate equations versus available experimental data, the most suitable mechanism representing the reaction and the corresponding rate equation and constants can be selected on the basis of sum squares of residuals and sign of kinetic constant. NLP solver of GAMS is used to optimize the rate constants in Langmuir-Hinshelwood equations. NLP solver is used to minimize the sum of square of residuals.

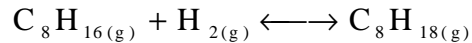
Literature Survey

Heterogeneous Reactions

Langmuir-Hinshelwood rate equations have provided a pragmatic approach to the correlation of experimental data for heterogeneous catalytic reactions. Hougen and Watson

pioneered in this approach and showed the significant features of the method. (Lapidus and Peterson, 1965)

Hougen and Watson (1959) studied the case of vapor phase catalytic hydrogenation of mixed iso-octenes. Mixed iso-octenes are commercially known as codimer. The reaction is as follows.



Hougen and Watson suggested 18 different mechanisms were possible and the final equation they suggested was:

$$r = \frac{kK_B K_A p_B p_A}{(1 + K_A p_A + K_B p_B + K_R p_R)^2}$$

Where, A refers to hydrogen, B to unsaturated component, R to saturated component.

This is the classic case later studied by many more kinetists using different mathematical methods to estimate the rate constants.

Yang and Hougen (1950) have described mathematical expression for heterogeneous rate equation as combination of three terms, the kinetic term, the potential term, and the adsorption term, arranged thus

$$r = \frac{(\text{kinetic term})(\text{potential term})}{(\text{adsorption term})^N}$$

Langmuir-Hinshelwood Approach

The approach in determining catalytic and heterogeneous mechanisms is usually termed as the Langmuir-Hinshelwood approach. It was derived from ideas proposed by Hinshelwood based on Langmuir's principles for adsorption. It is based on the following hypotheses:

1. Uniformly energetic adsorption sites.
2. Monolayer coverage.
3. No interaction between adsorbed molecules. (Froment and Bischoff, 1979)

Once the reactant has been adsorbed onto the surface, it is capable of reacting in number of ways to form the reaction product. Three of these ways are:

1. Single site mechanism
2. Similar or dissimilar dual site mechanism
3. Eley-Rideal Mechanism

Algorithm for Rate Constant Optimization

There are broadly two types of estimation procedures, namely linear least square method and nonlinear least square method. The objective of both methods is to arrive at the most probable or “best” relationship, which will represent all of the experimental data with minimum average error or deviation.

Linear Least Square Method

The method of linear least squares may be used to determine the best constants in a given form of equation and also for establishing the best form of equation for a given set of data. The best constants are first evaluated for each form of equation under consideration. The best form of equation is then that for which the average of the squares of the deviations is the least. (Hougen and Watson, 1959)

Unfortunately this method has a number of defects. (Seinfeld and Lapidus, 1974) Foremost among these is the fact that few rate equations of any complexity occur in the desired linear form. As a result the rate equation must be linearized or rearranged to be handled by this method. Thus the original distribution of errors are not preserved.

Nonlinear Least Squares Method

In a broad-gauged description of this method, one attempts to minimize sum of squares of residuals, SSR, in an iterative fashion rather than in a single step.

Difficulties faced on linear least square method are eliminated in nonlinear least square method. The algebraic rate equation is used in the original form without imposing arbitrary transformations. Thus the minimization of the sum of squares of the errors is appropriate in terms of untransformed variables.

The nonlinear least square method has been extensively used to solve the problem of rate constant optimization in heterogeneous catalytic reaction rate equation.

Application of GAMS for Rate Constant Optimization

Langmuir-Hinshelwood catalytic rate equations are essentially nonlinear. GAMS (General Algebraic Modeling System; GAMS Release 2.25 © GAMS Development Corporation) is used for formulating, solving, and analyzing optimization problems. The design of GAMS has incorporated ideas drawn from relational database theory and mathematical programming. (Brooke, Kendrick 1997) GAMS provides a solver called NLP to solve nonlinear programming problems. NLP solver can be used to minimize the sum of squares of residuals. Lower bounds of rate constants to be estimated are needed to initialize the program. NLP solver in GAMS returns the optimized rate constants if the lower bounds are lower than optimum value. GAMS also returns the sum of squares of residuals along with the optimized rate constants.

Criterion for Rate equation Selection

It is the requirement of the theory upon which L-H equations are based that all rate constants must have positive or zero values. (Hougen and Watson, 1959) Rate constants actually are adsorption equilibrium constants. Adsorption equilibrium constant can either be positive or zero that is no adsorption is taking place. But it cannot be negative. All the rate equations are rejected which give negative rate constants. The rate equation with all positive rate constants and with lowest sum of squares of residuals is considered as the suitable rate equation.

GAMS has facility to enter lower bounds for rate constants. So the rate constant will never take the negative value even if the rate equation is not suitable. To solve this problem one can try different lower bounds. For the best fitting rate equation all lower bounds will converge to the same values of rate constants, while for unsuitable rate equations the final values of rate constants will be different. After selecting the rate equations with positive rate constants one can compare the sum of squares of residuals to select the best rate equation.

Optimization of Kinetic Constant for Homogeneous Reactions

The principle of minimization of sum of squares of residuals is used for optimization of kinetic constants in homogeneous reactions (Himmelblau, Jones and Bischoff, 1967). The program is having a subroutine to optimize kinetic constants in homogeneous reactions. The necessary data is number of reactions, number of components, stoichiometry of reactions and guess values of forward and backward reaction constants along with experimental data of concentration and time. The program can produce tabular and graphical output along with optimized rate constants.

Program Features

The program developed in this study is a useful tool in determining the kinetic rate equation and optimizing the rate constants of homogeneous and heterogeneous reactions. The interface is user friendly and very easy to understand.

Heterogeneous Catalytic Reactions

Heterogeneous catalytic reactions can be divided into four basic reactions. Each reaction could be reversible or irreversible. The program displays various L-H equations for each reaction type, depending upon whether the reaction is reversible or irreversible. L-H equation is determined by species that are adsorbed and rate controlling reaction step. Combinations of adsorbed species and rate controlling steps are given on “Mechanism” tab (see Figure 2).

Table 1 gives the number of mechanisms available for each reaction including reversible and irreversible reactions.

Table 1.

Number of Mechanisms Available for Each Reaction

Type of Reaction	Number of Mechanisms Available
$A \longleftrightarrow R$	24
$A \longleftrightarrow R + S$	36
$A + B \longleftrightarrow R$	54
$A + B \longleftrightarrow R + S$	74

Lower bounds of rate constants are entered as starting point for GAMS. If lower bounds of rate constants remain unchanged in GAMS, then still lower values of rate constants need to be entered. This way one can optimize the rate constants. Lowest values one can enter are zero.

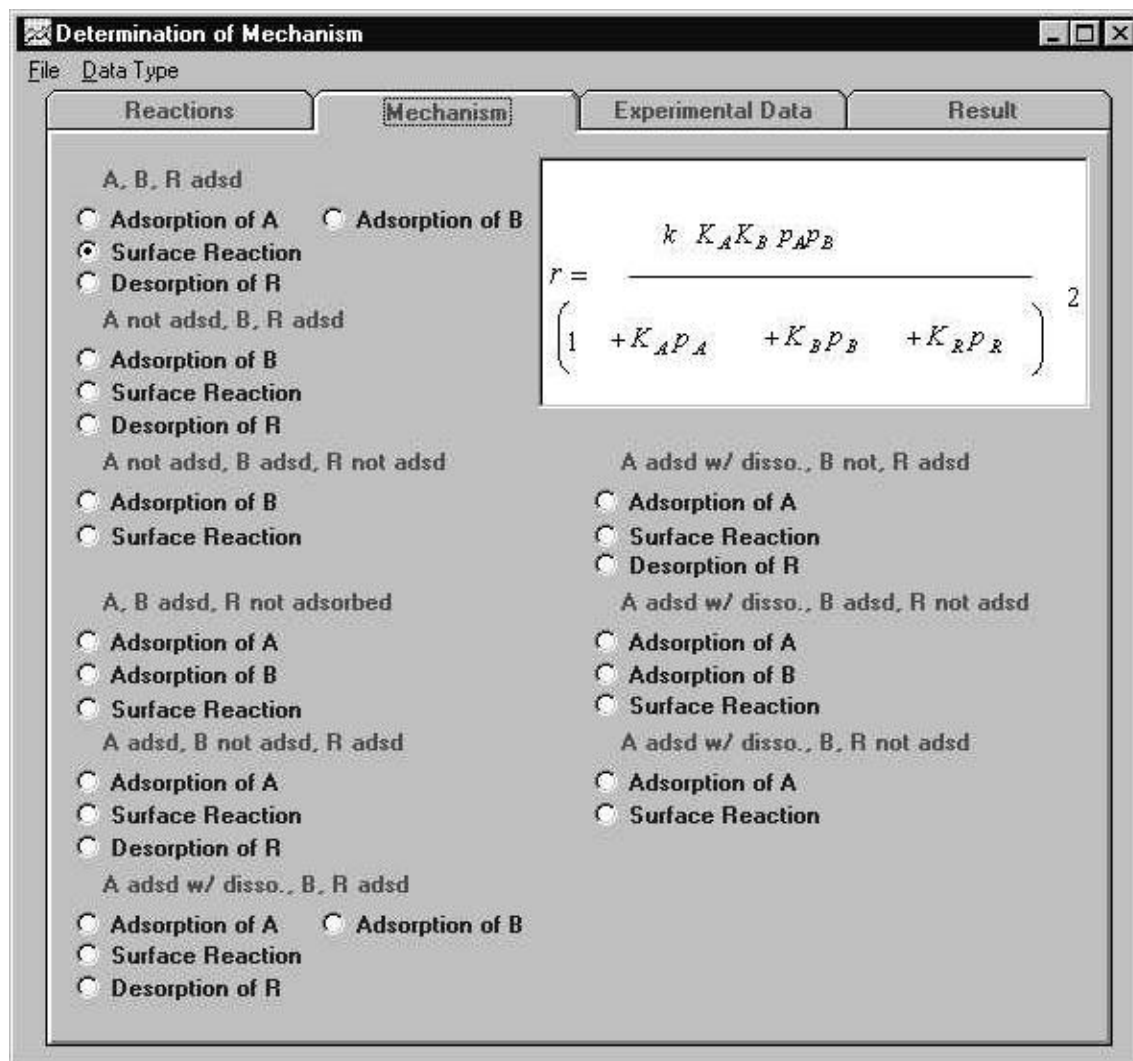


Figure 2. Heterogeneous Reactions: Mechanism Tab

The rate constants are changed in such a way that calculated data is as close to the experimental data as possible. When the difference between calculated data and experimental data is the minimum then rate constants are optimized. Usually the equation, which gives the minimum sum of squares of residuals and all positive rate constants, is the suitable one.

The result tab displays the sum of squares of residuals and optimized rate constants along with the rate equation. If the result is not satisfactory then user can select other mechanism or he can enter new guessed rate constants and run the program again.

Homogeneous Catalytic Reactions

Homogeneous catalytic reactions are those reactions in which a catalyst is in solution with at least one of the reactants. An example of homogeneous catalysis is the industrial Oxo process for manufacturing normal isobutylaldehyde. There are three basic types of homogeneous reactions: series, parallel and independent. (Fogler, 1994)

In parallel reactions (also called competing reactions) the reactant is consumed by two different reactions to form different products. For example,

$$\begin{array}{l} A \xrightarrow{k_1} B \\ A \xrightarrow{k_2} C \end{array}$$

In series reactions, also called consecutive reactions, the reactant forms an independent product, which reacts further to form another product. For example, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

Homogeneous reactions involve a combination of both series and parallel reactions, such as

$$\begin{array}{l} A + B \longrightarrow C + D \\ A + C \longrightarrow E \end{array}$$

Complex Reactions:

A system of complex chemical reaction in which there is coupling between all species is shown in Figure 3. There are three chemical species, A_1 , A_2 , and A_3 , where these symbols stand for the species as well as concentration and they are connected by reaction scheme (Amundson, 1966)

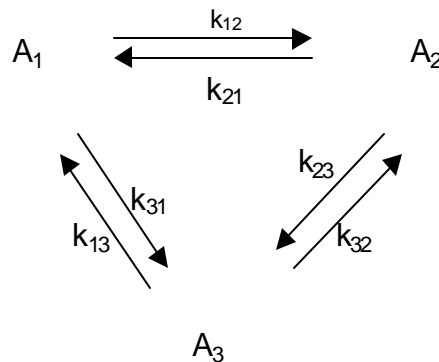


Figure 3. System of Complex Reaction

Source: Amundson, N.R. (1966). *Mathematical Methods in Chemical Engineering*. Englewood Cliffs, New Jersey: Prentice Hall

Where, k_{ij} is the absolute rate constant and $k_{ij}A_j$ is the rate of formation of A_i from A_j in moles per unit volume per unit of time. For the above reaction scheme, the rate equations are

$$\begin{aligned}\frac{dA_1}{dt} &= -(k_{12} + k_{31})A_1 + k_{21}A_2 + k_{31}A_3 \\ \frac{dA_2}{dt} &= k_{21}A_1 - (k_{12} + k_{32})A_2 + k_{23}A_3 \\ \frac{dA_3}{dt} &= k_{31}A_1 + k_{32}A_2 - (k_{13} + k_{31})A_3\end{aligned}$$

Such system may be generalized to n chemical species, each of which is coupled to every other species by chemical reaction to give ($k_{jj} = 0$ for all j)

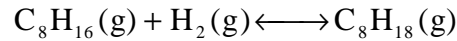
$$\begin{aligned}\frac{dA_1}{dt} &= -\sum_{j=1}^n k_{1j}A_j + k_{21}A_2 + k_{31}A_3 + \dots + k_{n1}A_n \\ \frac{dA_2}{dt} &= k_{21}A_1 - \sum_{j=1}^n k_{2j}A_j + k_{23}A_3 + \dots + k_{n2}A_n \\ &\vdots \\ \frac{dA_n}{dt} &= k_{n1}A_1 + k_{n2}A_2 + \dots + k_{n,n-1}A_{n-1} - \sum_{j=1}^n k_{nj}A_n\end{aligned}$$

This system of equations is solved using nonlinear least square method to obtain unknown k_{ij} , provided concentration-time data is given.

Case Study

Various cases were selected from the literature, and solved using the NLP solver in GAMS.

The vapor phase hydrogenation reaction of mixed iso-octenes to the corresponding iso-octanes (Hougen and Watson, 1959) is:



Authors suggested reaction between molecularly adsorbed hydrogen and adsorbed codimer with surface reaction controlling mechanism be the most suitable for given experimental data. The equation is:

$$r = \frac{kK_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B + K_R P_R)^2}$$

Results from literature and REACAT are given in from Table 2 to Table 4. k in $\text{gmol}/(\text{g catalyst hr})$, K_A , K_B , K_R in atm^{-1} .

Table 2

Result obtained by Hougen and Watson (1959) (Linear least square method)

Rate Constant	200°C	275°C	325°C
k	0.644	0.830	0.954
K _A	0.383	0.246	0.190
K _B	0.580	0.503	0.469
K _R	0.489	0.0646	0.0222
SSR	7.315E-5	2.427E-4	1.347E-4

Table 3

Result obtained by Blakemore and Hoerl (1963) (Nonlinear least square method)

Rate Constant	200°C	275°C	325°C
k	0.65	0.94	0.99
K _A	0.38	0.24	0.18
K _B	0.55	0.58	0.40
K _R	0.54	0.23	1E-5
SSR	1.1E-5	1.4E-5	1.4E-5

Table 4

Result using REACAT (GAMS)

Rate Constant	200°C	275°C	325°C
k	0.709964	1.036669	0.890046
K _A	0.331107	0.220122	0.188581
K _B	0.481635	0.587166	0.413597
K _R	0.417908	0.341022	0
SSR	6.239E-5	8.064E-5	3.433E-5

GAMS program predicted zero value for K_R because GAMS provides syntax to enter the lower bound of a rate constant. Result obtained from REACAT for rate constant k, K_B and K_A varies ±10% from result given by Blakemore and Hoerl. Rate constant K_R varies more widely from 22% for 200°C to 48% for 275°C. For 325°C, Blakemore and Hoerl calculated value of K_R

as 1E-5, which is almost zero. The result for 200°C, which contains optimized rate constants, sum of squares of residuals (SSR) and rate equation is shown in Figure 4.

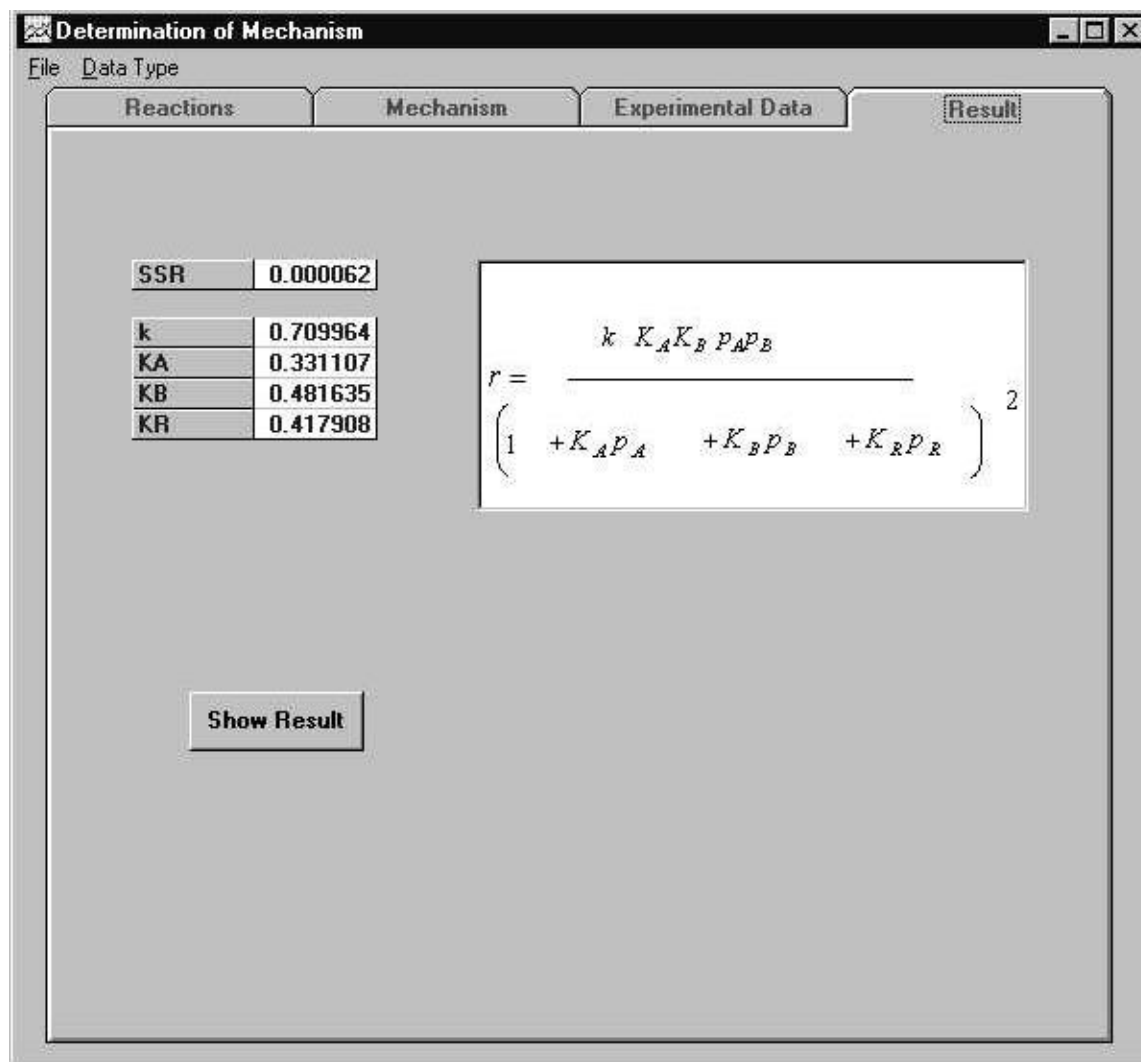


Figure 4. Result Tab

Conclusion

A program for the optimization of kinetic rate constants for homogeneous and heterogeneous reactions was developed in this work. The NLP solver of GAMS was used for optimization of rate constants in heterogeneous reactions. Visual Basic 5 was used as visual interface for input and output. The study covered various types of mechanisms and rate controlling steps in heterogeneous reactions. The total number of L-H rate equations included for all four types of reactions and for reversible-irreversible reactions is 188. Also simple and complex homogeneous reactions were studied to optimize the rate constants.

The results generated by the program include the sum of squares of residuals and the values of kinetic constants. In case of homogeneous reactions, the graph of concentration as function of time is displayed. These results can be stored in data files and further used for reactor design. It is possible to change the guess values of kinetic constants and see the effect on sum of squares of residuals. Also it is possible to check the fit of experimental data into various mechanisms and rate controlling steps.

GAMS proved to be a powerful tool to solve the optimization problem in heterogeneous catalysis. NLP solver in GAMS converges the program even if initial guesses are far away from global optimum.

Acknowledgment

Support from the Gulf Coast Hazardous Substance Research center and the Environmental protection Agency is gratefully acknowledged

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Computer Programming in the Chemical Engineering Curriculum: Some Empirical Observations

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In 1996 Kantor and Edgar [1] opined that computer programming (in languages such as FORTRAN, C or PASCAL) is not a vital skill for chemical engineers in industry. Surveys of industrial engineers indicated that many companies explicitly tell their engineers not to write software because of the difficulty of maintaining such programs written by individuals. On the other hand, formal courses on computer programming appear to remain a required element of many undergraduate chemical engineering programs. A more recent survey by Dahm et al. [2] shows that 83% of programs (84/160 departments responding) require a computer-programming course (taught by either computer science or engineering faculty) and 45% require programming in “several” subsequent courses; see Tables 1 and 2. Dahm et al. believe that there has been a shift away from teaching traditional computer programming. 16% of respondents indicated that their curriculum no longer contains computer programming at all, a fairly recent development. Other respondents indicated that the programming present in their curriculum does not employ traditional languages such as C or FORTRAN, but higher-level programming environments such as Maple or MATLAB. Swinnea [3] recently surveyed 160 Chemical Engineering departments and received 43 replies. Many of the respondents indicated that they were examining their computing curriculum and were interested in the survey results. Of the 43 respondents, all but five indicated that they have some sort of programming course requirement. Many of them indicated that they teach more than one programming “language”. The distribution is as follows: (see Table 3).

C/C++	17
FORTRAN	10
MATLAB	16
Excel	13
V. Basic	7
MathCAD	6
Other	4

Swinnea also inquired about coverage of numerical methods: 21 teach a separate course, but 17 teach no specific course, although several departments stated that numerical techniques are introduced throughout the curriculum. Five indicated that numerical methods are included in the programming course.

The results of Swinnea’s survey are intriguing in that there seems to be a wide range of approaches to addressing instruction in numerical methods and instruction. There are many factors that contribute to this lack of consensus: resistance to change (how many years has this requirement been in place?), lack of qualified instructors, teaching loads, overall engineering curriculum requirements (e.g., freshmen core course

requirements), a need to retain computer science credit hours in the university, etc. I believe that this aspect of the curriculum has not received as much scrutiny as has the integration of computer software into design, control, thermodynamics, and unit operations. This is somewhat surprising given the continuing pressure on the number of required hours in the B.S. curriculum. The purpose of this article is to present empirical evidence of the many different approaches used in U.S. chemical engineering departments, without reaching specific conclusions. Hopefully this will initiate discussions in different venues on how to most effectively incorporate instruction of programming and numerical methods. Please send comments to Tom Edgar (edgar@che.utexas.edu).

Table 1: Response to “Which of the following best describes your department’s use of computer programming languages?” (84 responses) [2]

Response	% Yes
One required course taught by computer science and no programming required in subsequent chemical engineering courses	13%
One required course taught by chemical engineering and no programming required in subsequent chemical engineering courses	11%
After students take the required programming course, they are required to program in one subsequent ChE course.	7%
After students take required programming course, they are required to program in several subsequent ChE courses.	45%
Students are required to program in upper level chemical engineering courses without having taken a formal programming courses.	8%
None of the above selected	16%

Table 2: Response to “Indicate the mathematical applications software required of chemical engineering undergraduates” (84 responses) [2]

Response	% Yes
POLYMATH ³⁹	37%
MATLAB	65%
Maple	24%
MathCAD	37%
EZ-Solve	5%
Spreadsheets	82%
Mathematica	13%
Other	15%

Table 3: Department Responses on Numerical Methods and Programming Instruction [3]

Institution	Numerical Methods Course	Programming Course
Arizona	3hrs Soph, 3hrs Junior	3hrs C++
Clarkson University	No	2hrs Excel, Maple, MATLAB
Colorado	3hrs MATLAB, Excel	3hrs VBA, Mathcad, Excel, MATLAB
Colorado School of Mines	2hrs	2hrs Visual Basic
Colorado State University	MATLAB	3hrs C++
Connecticut	3hrs Mathcad, MATLAB	No
Cornell University	80% Take Engineering Calculations elective (MATLAB)	4hrs MATLAB, Java
Delaware	3hrs MATLAB	No
Iowa	3hrs MATLAB	3hrs C, Fortran
Iowa State Science and Tech.	3hrs Fortran, MATLAB	3hrs Fortran Excel, Visual Basic
Kansas	No	3hr Fortran, Excel, Powerpoint
Kansas State University	Included in programming course	2hrs Fortran
Kentucky	No	2hrs C++ Maple, MATLAB, Aspen
Lehigh University	No	No
Maine	None indicated	3hrs Mathcad
Massachusetts Inst of Tech.	Included in Programming course	6hrs C MATLAB, 3hrs Visual Basic, MATLAB
Michigan State University	No	3hrs Fortran, Visual Basic, Mathcad, Excel
Minnesota at Duluth	3hrs	3hr C++ or Fortran
Missouri-Rolla	No	No
Nevada, Reno	3hrs Mathcad, MATLAB, Excel, Polymath, Maple, ChemCad	4hrs C
New Hampshire	Applied Math Course using C, Excel, Mathcad introduced in other courses	No
North Dakota	No	2hr Excel, MATLAB, 4hr C++
Northeastern University	No	3hrs MATLAB
Notre Dame	3hrs MATLAB	3hrs MATLAB, Excel
Ohio University	3hrs MATLAB	1hr Mathcad, Excel
Oklahoma	3hr Mathcad, Fortran, Excel	2hrs Fortran
Oklahoma State University	No	4hrs C Excel, MATLAB
Purdue University	No	3hrs Unix, MATLAB, Maple, Fortran (self paced)
Rice University	3hrs Fortran, MATLAB	2hrs C++
Rose-Hulman Inst. of Tech.	No	4hrs C++
Rowan Univ.	No	3hrs MATLAB, Excel
San Jose State Univ.	3hrs MATLAB Excel	Visual Basic, Excel, Mathcad, Aspen
South Alabama	No	3hrs C++
State New York at Buffalo	No	3hrs C
Syracuse Univ.	Adding Excel/MATLAB course	3hrs Fortran
Tennessee Tech Univ.	3hrs	3hrs Fortran or C
Texas	4 hrs MATLAB, some programming	No
Texas A&M Univ.-Kingsville	No	3hrs C or Visual Basic
Tri-State Univ.	2hrs Mathcad, Excel	3hrs MATLAB
Vanderbilt Univ.	No, teach Aspen to sophmores	3hrs Excel Mathcad , MATLAB, Pro/II, HYSYS
Washington State Univ.	Included in programming course	3hrs C++, MATLAB, Excel
West Virginia Univ.	3hrs Polymath, Excel, Mathcad	3hrs Fortran or C
Wyoming	Same course	No

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GAMS Newsletter – Number 5

Bruce McCarl

CPLEX 7 and Dual - Update

Thanks to John Gregory and others at CPLEX I was able to resolve problems I was having with CPLEX 7. I found out that big performance declines can be caused by the existence of artificially large upper bounds particularly on the objective function and the new CPLEX feature that on restarts it automatically goes to the dual simplex algorithm. Namely to find unboundedness at some point I put in the bound profit.up = 10000000; If you find restarts (second and subsequent solves) to be very slow then remove such bounds (removal causes a reduction in solution time from hours to seconds). You also could use the CPLEX option file options:

```
lpmethod 1
pdswitch 1
startalg 1
```

GAMSWORLD

GAMS corporation has worked with others to create a new web site called <http://www.gamsworld.org/>. This web site contains quite a lot of material on Mixed Integer Nonlinear Programming (MINLP) but also has material on conversion to other languages such as AMPL and MPS format. A link to NEOS through the converter section (GAMS2XX) also allows one to submit jobs for solution on the NEOS computers.

Presentations and Papers

GAMS has recently introduced a presentations and contributed documentation web page on <http://www.gams.com/presentations/>. Look there for papers on GAMS use and some instructional materials including some of the things I generated for past newsletters. Also see the Erwin Kalvelagen report on solving large MIP's with CPLEX on http://www.optimization-online.org/DB_HTML/2001/06/352.html.

Basic Learning Material

Basic material appears, among other places, in the Rosenthal section in the GAMS manual or on <http://www.gams.com/docs/gams/Tutorial.pdf>; in the primer by Rob Delink and Judit Sznyi on http://www.sls.wau.nl/me/education/scenariostudies_and_the_environment/gams/default.htm; in McCarl and Spreen Chapter <http://ageco.tamu.edu/faculty/mccarl/mccspr/new05.pdf>; in basic materials by me on <http://www.gams.com/mccarl/aggamint.pdf>; or Rardin's <http://gilbreth.ecn.purdue.edu/~rardin/gams/notes.html>. CGE materials are on Rutherford's <http://robles.colorado.edu/~tomruth/mpsge.htm>, on the GAMS presentations web page within documents by Loftgren, Delink and Sznyi; on the MPSGE page <http://www.gams.com/solvers/mpsge/>. Other materials are on <http://www.gams.com/presentations/> including ones in Russian and Spanish.

Courses Offered

I teach Basic GAMS in College Station, Texas November 5-8, 2001 (note this is a change from the earlier announced time) and Advanced GAMS in Texas in January 7-10, 2002. Further information and other courses are listed on <http://www.gams.com/courses.htm>.

Links to Other Programs - Spreadsheets, Databases

A topic of interest to many is the link between GAMS and other programs. I will be covering such topics here and in subsequent newsletters. For now I provide a document on how to develop an EXCEL spreadsheet that runs GAMS in the background. The document is on <http://www.gams.com/mccarl/excelgams.pdf> and the associated spreadsheet and GAMS file are on <http://www.gams.com/mccarl/excelgams.zip>. Later look for material on links when GAMS is in charge, Delphi, databases, graphics programs and put files. Also see the general treatment covering spreadsheets, databases in <http://www.gams.com/interface/interface.html>, Tom Rutherford's graphics and spreadsheet tools on <http://debreu.colorado.edu/~tomruth/inclib/tools.htm> or Uwe Schneider's graphics tools on <http://ageco.tamu.edu/faculty/mccarl/gnuplot/gnuplot.html>.

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A View to the Future Integration of R&D Manufacturing and the Global Supply Chain

Over the last decade the scope of the area of process operations has expanded from operational issues in manufacturing plants to the management and optimization of entire supply chains. Furthermore, its scope has also been expanded towards R&D activities on the one hand, and on the other hand towards distribution and logistics of products. The new expanded scope of process operations offers exciting possibilities at the practical and at the research level. At the practical level it has promoted the integration of computer and information technologies with large-scale modeling and optimization tools that are being translated into large economic savings by improved coordination of operations, decreased inventories and higher levels of service. At the research level process operations has given rise to a number of modeling, algorithmic, and integration challenges in order to effectively tackle large and complex systems that are characterized by frequent dynamic changes and uncertainties.

In an efficient Sunday-Wednesday format, FOCAPO 2003, will be convening a group of international experts from industry, academia, vendors, and consulting companies to discuss the new directions and challenges in process operations. Participants will discuss needs for process oriented industries such as chemicals, energy, food and beverage, pharmaceutical, and metals.

A preliminary announcement can be found in:

<http://www.cheme.cmu.edu/focapo>

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