

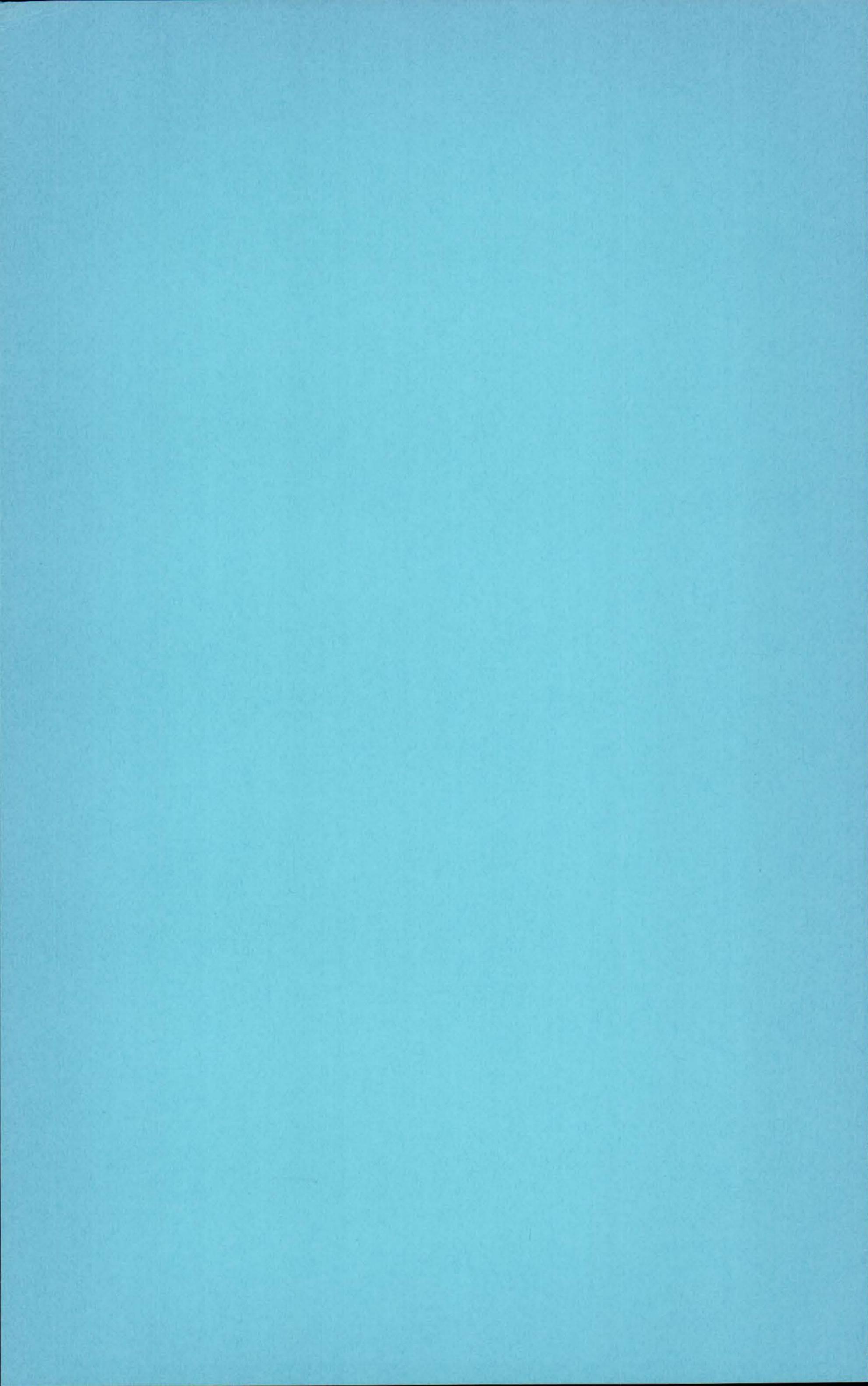
CHEMICAL ENGINEERING EDUCATION



CHEMICAL ENGINEERING DIVISION

THE AMERICAN SOCIETY FOR ENGINEERING EDUCATION

September 1963



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Chemical Engineering Division
American Society for Engineering Education

CONTENTS

On-Stream Computers, An Example and Some Generalities, by C. G. Laspe - - - - -	1
Optimization Theory in the Chemical Engineering Curriculum, by Douglass J. Wilde - - - - -	9
Fundamental Problems in Heterogeneous Catalysis, by Max Peters - - - - -	14
Planning Experiments for Engineering Kinetics Data, by H. M. Hulburt - - - - -	23

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CHEMICAL ENGINEERING EDUCATION (R), Journal of the Chemical Engineering Division, American Society for Engineering Education. Published Quarterly, in March, June, September and December, by Albert H. Cooper, Editor.

Publication Office; University of Connecticut
P.O. Box 445, Storrs, Connecticut

Subscription Price, \$2.00 per year.



ONSTREAM COMPUTERS -
AN EXAMPLE AND SOME GENERALITIES

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There are many excellent articles (1,2,3,4,5,6,8) giving the general reasons for and the philosophy behind the use of digital computers in the controlling of production processes. Some of the pioneering efforts by Stout and Laspe (1,2,3), as early as 1957, formed the basis for many of the digital control systems in use today. Subsequent papers by Roberts (6), Stout (6), Brandon (5), Madigan (12,13,14), Freilich (19), and Laspe (15) presenting the results of actual case studies have bolstered the technical literature on computer control systems. It is not the intent of the present paper to dwell heavily upon the objectives of computer systems, nor upon their design, for these aspects of the problem have received adequate attention in the afore-mentioned papers.

It is the purpose of this paper to present the broad aspects of on-stream computer control and especially as these aspects affect the curricula of chemical engineering. In attempting to accomplish this objective, I would like to present a few generalizations, followed by a survey of the extent to which computers are used in on-line control. Next, as an example, the computer control of an ammonia plant will be discussed to illustrate the various branches of engineering and science required in its design. Finally, the most important point, as touching upon this present session, will be a discussion of those fundamental things which a student in an engineering school should learn to understand the use of on-line control computers.

In order to orient our thinking along the lines of on-stream control computers, a few generalities should be considered. What are the ingredients that go into making up a computer controlled process? Once these individual ingredients are recognized, then we are in a better position to determine the engineering talents required for the design, construction and operation of such a system.

Let us briefly review a few fundamentals. All manufacturing processes are designed and intended to be operated to produce a profit. This profit results from the creation, by a combination of physical and chemical transformations, of a product or products whose value exceeds the cost of the raw materials and their processing. A major goal of management in plant operation is the maximization of this profit. This statement may be considered as the process objective. Therefore, the purpose of computer control is to provide the latest and the most efficient means of reaching this process objective. It is realized that, since physical and chemical transformation are involved, many variables influence the realization of the process objective. When one or more of these variables are beyond the control of the operator, such variables are classed as disturbance variables. Compensation for these disturbances is the prime justification for any control scheme. For without disturbances, control would not be required.

When there is but a single disturbance variable involved in the operation of a plant, then it is possible to derive a unique solution to the control problem. In other words, for any given value of the disturbance variable, there is only one set of control variables which will meet the desired objective. In this instance, simple relationships may be found which will relate the manipulated variables to the disturbance variables then in effect. On the other hand, when two or more variables are beyond the control of the operator an interesting situation arises. In this case there are generally two or more feasible solutions. Of these feasible solutions, one will probably yield the greatest economic return and, therefore, is the desired optimum solution. It is in these areas where computer control may be justified. Recently, an excellent article by Elliott and Longmire (21) gives the dollar incentives for computer control. The results of their studies on six different production processes is presented.

The March issue of Control Engineering presented a survey of on-stream control computers. At that time the score card showed 35 closed loop computing control installations, either on-line or scheduled to be on-line by early 1962. Of these 35 installations, nearly half were to be used in either chemical or petroleum processes. In September of 1961 Freilich (19) presented another survey of process control computers in use. Freilich shows a total of 63 process control computers, of which 20 are used in the chemical and petroleum industries. The latest figures available from the May 1962 issue of Control Engineering (20) show a total of 159 control computer sales, of which 43 are installed in the chemical and petroleum fields.

Although the preceding statistics are both encouraging and interesting, they do not tell the complete story. Table I summarizes the known installations of digital computers in process control or those units known to be on order. In the petroleum field, several installations have been reported on catalytic cracking plants and on crude distillation units. Single installations have been reported for catalytic polymerization, alkylation, and thermal cracking. In the chemical field ethylene and ammonia appear to be good candidates for computer control by reporting several installations on each. In addition other computer controlled chemical processes include vinyl chloride, styrene, acrylonitrile, acetaldehyde, ethylene oxide, and the exotic "alfol" plant of the Continental Oil Company. As can be seen from a study of this list, the gamut of applicable processes is limited only by economic necessity and the imagination of the system designer.

From the above list we have chosen as the working example to be discussed here today, the computer controlled ammonia plant of Monsanto Chemical Company at Luling, Louisiana. A fairly complete description of this particular installation has already been given by Eisenhardt and Williams (17) in the November 1960 issue of Control Engineering.

For purposes of description, the ammonia process can be conveniently divided into three separate operations. The first of these is concerned chiefly with the preparation of raw synthesis gas. The second section is concerned with purification and compression, and the third and final section is the synthesis unit itself. In the gas preparation area three chemical reaction stages are involved. The primary reformer, the secondary reformer, and the CO converter. The feed to the primary reformer consists of natural gas and steam which in the presence of a catalyst reacts to produce hydrogen, carbon monoxide, and some carbon dioxide. External heat is applied to this unit from a reformer furnace burning natural gas. Essentially 90% of the incoming gas is converted. Steam reforming is the principal reaction involved, although the water gas or CO conversion reaction accounts for some of the hydrogen produced. The variables over which control can be exercised are the flow rates of the natural gas, the fuel gas and the process steam.

The secondary reformer serves two specific functions. Firstly, to provide additional reaction volume for continuation of the reforming and CO conversion reactions initiated in the primary, secondarily, to serve as the injection point at which nitrogen is introduced into the system. Atmospheric air is used as the source of nitrogen. In the secondary reformer the oxygen from the air which has been introduced reacts with some of the methane and hydrogen in the feed to form water plus CO and CO₂. The only independent variable over which control can be exercised is the flow of process air. Note that at this particular point in the process, essentially all of the natural gas has been converted into product gases. The residual methane content is in the order of 0.3 of one percent. There is also an appreciable amount of carbon monoxide. The effluent from the secondary reformer flows directly to the CO converter.

The sole purpose of the CO converter is to produce additional hydrogen from the incoming carbon monoxide by means of the water gas reaction. Additional water is injected at this point in the form of low pressure steam. Because of fundamental thermodynamic and kinetic considerations, the carbon monoxide is not completely consumed. The exit concentration is in the order of three percent. At this point in the process the hydrogen to nitrogen ratio is fixed and remains constant throughout the remainder of the operations. At this particular point in the process, carbon dioxide represents approximately 15% of the entire raw synthesis gas. This along with the carbon monoxide must be removed before the synthesis gas can be charged to the final ammonia synthesis reaction stage.

Carbon dioxide is removed from this raw gas stream by passing it through a standard Girbotol unit. Mono-ethanol amine is used as the absorbent.

A compression plant consists of several parallel reciprocating compressors. Each compressor is equipped with five stages of compression. The gas pressure is boosted from approximately 20 pounds per square inch at the inlet to 5,500 pounds per square inch gage at the outlet. The entire gas stream, however, does not pass through all five stages. At the outlet of the fourth stage, the process gas is diverted to the high pressure purification unit. The main function of this unit is to remove carbon monoxide, plus any residual carbon dioxide. Copper formate is used as the absorbent for CO. The residual CO₂ is removed by a final caustic wash. After removal of impurities, the purified synthesis gas is then directed to the last stage of compression from whence the gas flows to the synthesis unit. An analysis of the exit gas shows an essentially pure hydrogen, nitrogen mixture in the ratio of approximately 3 to 1.

Table 1
SURVEY OF PROCESS COMPUTER APPLICATIONS

<u>Company-Location</u>	<u>Computer</u>	<u>Delivery</u>	<u>Process</u>
1. Allied Chemical Corp. South Point, Ohio	RW-300	1961	Ammonia
2. American Oil Company Whiting, Indiana	IBM-1710	1961	Crude distillation
3. B.A.S.F. Ludwigshafen, Germany	RW-300	1961	Chemical process
4. B.F. Goodrich Chemical Calvert City, Kentucky	RW-300	1959	Vinyl chloride and acrylonitrile
5. Celanese Corporation Bay City, Texas	H-290	1962	2-Ethly hexanol
Bishop, Texas	RW-300	1962	Vapor phase oxidation
6. Continental Oil Company Lake Charles, La.	RW-300	1961	Alfol process
7. Dow Chemical Company Midland, Michigan	GE-312		Styrene
8. Dupont Beaumont, Texas (2)	ISI-609	1960	Chemical process
Florence, S.C.	ISI-609	1960	Chemical process
Circleville, Ohio	ISI-609	1961	Chemical Process
Gibbstown, N.J.	IBM-1710	1961	Acrylonitrile pilot plant
9. DX-Sunray Tulsa, Oklahoma	RW-300	1961	Crude distillation
10. Gulf Oil Company Philadelphia, Pa.	RW-300	1961	Catalytic cracking
11. Imperial Chemical Ind. England	Ferranti		Soda Ash
12. Monsanto Chemical Co. Luling, Louisiana	RW-300	1959	Ammonia
Chocolate Bayou, Texas(4)	H-290	1962	Chemical process
13. Owens-Corning Fiberglass Aiken, S. Carolina	ISI-609	1960	Logger
14. Petroleum Chemicals, Inc. Lake Charles, La.	RW-330	1963	Ethylene
15. Phillips Chemical Co. Borger, Texas	Recomp II	1959	Portable Logger
Bartlesville, Oklahoma	TRW-330	1962	Portable logger
16. Shell Development Company Emeryville, Calif.	PB-250		Logger
17. Sun Oil Company Marcus Hook, Pa.	IBM-1710		Catalytic cracking logger
18. Standard Oil Co.(N.J.) Linden, N.J.	LGP-30		Pilot plant logger
Baton Rouge, La.	LGP-30		Catalytic cracking logger
19. Standard Oil Co.(Calif.) El Segundo, Calif.	IBM-1710	1961	Catalytic cracking
Richmond, Calif.	Recomp	1959	Product run calculations
20. Tennessee Eastman Kingsport, Tennessee	GE-312	1961	Chemical process
21. Texaco Port Arthur, Texas	RW-300	1959	Catalytic polymerization
22. Tidewater Oil Company Delaware City, Delaware	ISI-609		Naphthalene
23. Union Carbide Corp. Charleston, W. Va.	RW-300		Pilot plant logger
Seadrift, Texas	RW-300	1960	Chemical process
Seadrift, Texas	Daystrom	1961	Ethylene
24. Universal Oil Products Des Plaines, Illinois	Daystrom	1958	Pilot plant logger

Table II
CRITERIA FOR JUSTIFYING MONSANTO'S
COMPUTER CONTROL SYSTEM

1. Maintain maximum gas flow in spite of changing weather and process conditions.
2. Maintain an optimum hydrogen-to-nitrogen ratio.
3. Maintain an optimum methane concentration at the shift converter exit unless in conflict with 1 or 2.
4. Maintain maximum shift efficiency if not in conflict with objectives 1, 2, or 3.
5. Maintain objectives 2, 3, and 4 under reduced flow conditions.
6. Reduce raw materials flow immediately and safely to compensate for any loss of compression.
7. Log out all important process variables.
8. Provide the plant operator with messages in case of abnormal process or instrument conditions.
9. Provide failsafe features such that instrument or computer malfunctions are detected, alarmed, and prevented from affecting the process.
10. Control the fuel and air to the reformer furnace.
11. Maintain a specified steam-to-dry gas ratio at the exits of the secondary reformer and the CO converter.

The synthesis plant feed is combined with a recycle stream to form the feed to the synthesis reactors. Because of the low conversion per pass, (approximately 12%) a high recycle ratio is required. Ammonia is recovered in the reactor effluent gases by condensation. In order to prevent excessive build-up of inerts in the system, purging or venting is required.

Now let us turn our attention to some of the factors involved in making this particular plant a good candidate for computer control. As has been pointed out by Eisenhardt and Williams (17).

"While there may be a tendency to overdesign some plant equipment an engine-compressor system is usually conservatively sized because it represents a major fraction of the capital cost of an ammonia plant. The engine compressor system is thus likely to be one of the first units to bottleneck the plant as production increases. At Luling the highest possible production rate and therefore the maximum economic return is obtained by operating the compressor system at maximum possible capacity."

Due to the very definite influence of ambient conditions, particularly temperature, upon internal combustion engine compressor efficiencies, the allowable horsepower to be expended by the compressor is not a fixed or arbitrary constant. In fact the compressor capacity varies not only as the ambient temperature changes, but also as the mechanical condition of the compressors themselves are changed. In the case of a production limited plant, such as the one we are now discussing, it can readily be seen that the maximum plant throughput is never fixed, but varies in accordance with compression capacities. The purpose of the computer control system now becomes apparent. Its main function is to keep the plant running at maximum capacity by determining the maximum as limited by the capacity in the compression section. Once knowing the maximum allowable flow of purified synthesis gas, the computer can then go about its business of setting the many flow controllers in the reforming section. It is not enough that the compressors be fully loaded at all times. The synthesis gas must also have the proper quality as measured by the hydrogen and nitrogen ratio. Since each of the processes in the reforming area, namely, the primary reformer, the secondary reformer, and the shift converter involve chemical conversions, complicated kinetic and thermodynamic equations must be solved in arriving at the proper flow settings. To keep the plant properly balanced as well as keeping the compression section fully loaded then becomes the major job of the control computer. Table II lists the criteria for justifying Monsanto's computer control system. This table was taken directly from Eisenhardt's and Williams' article.

A question which immediately comes to mind is whether or not the predicted economic gains have been fully realized. Of course, basic economic figures are considered as proprietary information. However, in a qualitative way we can answer in the affirmative as Mr. Eisenhardt and Williams have said

"Immediately after placing the computer on control, the gains in control-ability became evident. When the process is not on computer control, the operator makes minor changes in controller setpoints trying to hold process temperatures within limits and maintain gas composition as required by the synthesis loop. Superimposed on top of these minor changes are larger step changes in throughput which are required to compensate for those uncontrolled variables affecting the plant capacity. At best these larger changes are made only several times a shift. Under computer control, however, the plant throughput is adjusted every eight minutes to obtain maximum possible production as uncontrolled variables changed. Qualitatively, one can observe from the computer log sheet the steadying of gas compositions and temperatures under computer control as compared with the irregular control obtained by even the best operator."

This now brings us to a consideration of the topic of engineering fundamentals as related to an understanding of computer control processes. The design of a computer controlled process requires the systems engineering approach. This means that the person in charge of the over-all project must view the project in its entirety. He should not be burdened with the many small details that go into the system design. But on the other hand, he should be fully aware of the many fundamental engineering sciences which are involved in such a project. In this sense the system engineering approach may be synonymous with the common core approach in chemical engineering education. In Table III are listed some of the fundamentals required of chemical engineering students for understanding of digital computer control processes.

Topping the list of required fundamentals is an understanding of economics. Since computer control is a tool to assist management in meeting the process objectives, which is normally the maximization of operating profit, the importance of a thorough understanding of economics can hardly be overemphasized. Methods for pricing intermediate products, an analysis of profit from incremental production, and a working knowledge of payout criteria for capital investment are especially important.

The basic curricula of chemical engineering will permit a reasonable understanding of the workings of most of chemical processes. However, in the computer control design area perhaps a little more emphasis should be placed upon chemical thermodynamics, chemical kinetics, and stoichiometry. For these are the basic sciences involved in deriving the predictive mathematical models used in the control computer.

Mechanical engineering enters into the design of computer control systems firstly, in the determination of the operating characteristics of the mechanical equipment involved. For example, in the ammonia plant system previously discussed, compressor capacity calculations were made. In addition to these, certain mechanical equipment limitations had to be evaluated. These limitations, which in computer parlance are called constraints, oftentimes determine or limit the area in which the process variables may be operated.

In the field of electrical engineering, as applied to the design of computer control systems, a main consideration is the communication between the computer proper and the process itself. A working knowledge of the basic AC/DC theory, transmission lines, impedance matching, and the filtering of electrical noise will go a long way in the understanding of the electrical requirements of computer control systems. It is not necessary to become too deeply involved in the computer circuitry itself. However, to deepen the appreciation for the entire control system, some instruction in this area would be profitable.

The ultimate success of any computer control system depends very heavily upon the ingenuity and mathematical ability of the process analysts. Most computer control systems operate on the basis of mathematical models which simulate or represent the operation of the existing plant. These models may be derived from fundamental theoretical considerations or possibly from regression analyses of plant data. In either event, considerable mathematical skill must be exercised in obtaining an accurate and representative set of equations. Once the mathematical model has been developed, the job is only half done. From here various optimizing techniques must be explored in order that the model may be used most efficiently in reaching the process objective.

Table III

FUNDAMENTALS REQUIRED OF CHEMICAL ENGINEERS FOR
UNDERSTANDING OF DIGITAL COMPUTER CONTROLLED PROCESSESI. Economics

- A. Process objectives
- B. Investment and payout criteria
- C. General knowledge of market prices
- D. Methods for pricing intermediate products
- E. Analysis of incremental profit
- F. General knowledge of utility costs, etc.

II. Chemical Engineering

- A. Unit operations
- B. Chemical thermodynamics
- C. Chemical Kinetics
- D. Stoichiometry

III. Mechanical Engineering

- A. Operating characteristics of mechanical equipment
- B. Constraints imposed thereupon

IV. Electrical Engineering

- A. Basic AC & DC theory
- B. Transmission lines
- C. Impedance matching
- D. Filtering of noise

V. Mathematics

- A. Methods of correlation analysis
 - 1. Regression techniques
 - 2. Curve fitting
- B. Optimizing techniques
 - 1. Maximization by calculus
 - 2. Gradient methods
 - 3. Linear programming
 - 4. Nonlinear programming
 - 5. Dynamic programming
 - 6. Calculus of variations

VI. Control System Theory

- A. Linear Feedback systems
- B. Nonlinear feedback systems
- C. Sampled data systems
- D. Laplace transforms
- E. Z- transforms

VII. Instrumentation

- A. Hardware
 - 1. Types
 - a. Pneumatic
 - b. Electric
 - c. Hydraulic
 - d. Other
 - 2. Measurement equipment
 - a. Temperature
 - b. Pressure
 - c. Flow
 - d. etc.
 - 3. Analytical instruments
 - a. Chromatographs
 - b. Infrared
 - c. Physical properties
 - d. etc.
 - 4. Controllers
 - a. Proportional
 - b. Derivative
 - c. Integral
 - d. Other
- B. Methods of interconnection
- C. Reliability and accuracy

VIII Computer Fundamentals

- A. Types and characteristics
 - 1. Digital
 - 2. Analog
 - 3. DDA
- B. Applicability of computers
- C. Basic understanding theory of operation
- D. Programming
 - a. Flow charting
 - b. Coding
 - c. Machine language
 - d. Instructions
 - e. Routines and sub-routines

As a part of the applied mathematics curricula, considerable attention should be paid to control system theory. Here such subjects as linear feedback systems, nonlinear feedback systems, sampled data systems, Laplace transforms, and Z transforms should be studied. Since the on-stream computer is connected, as it were, to a live process, attention must be paid to the process dynamics. All computer systems must recognize these dynamics. Obviously, control actions must not be taken too frequently that the plant is always in a state of jitters, nor must they be taken too infrequently or else the full benefit of computer control will not be realized.

The study of instrumentation is essential for a complete understanding of the computer control process. By instrumentation we think of the hardware involved - the sensing elements, the transducers, and the control equipment. It is these items that allows the computer to recognize or sense the state of the process. It is also these items that allows the computer to take corrective action upon the process. In a sense the primary measuring elements represent the sensors of a living organism. The transmission lines are the nerves. The control valves and controllers are the muscles, while the computer controlled systems possess the same attribute via the local feedback control loops.

Finally, some instruction should be given in computer fundamentals. The differences between the characteristics of digital, analog and the DDA computers should be carefully noted. A basic understanding of the theory of operation of these computers is profitable, though not essential. Some programming instruction should also be given with exercises in flow charting, coding, and in the use of routines and sub-routines.

In closing I might say that it is impossible for any single man to understand completely all the workings of a digital computer control system. The design of such a system is the work of a team of experts. And yet, this complexity does not preclude its use as an effective and efficient production tool. Let me give you an example. There are not many people that completely understand the entire working of a television set or even, for that matter, of the automobile in which we drive to and from work. And yet, there are millions of these machines in everyday use. By the same token the digital computer controlled process, though its design is complex, its operation can be made simple enough for a single operator to comprehend. The efficiency of this production tool, this man-machine-process combination will be increased in the future through continued research efforts in all the areas that have gone into its design.

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OPTIMIZATION THEORY IN THE CHEMICAL ENGINEERING CURRICULUM

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Introduction

This article is intended to acquaint teachers of chemical engineering with the theory of optimization, which has developed so rapidly in eleven years that it is now finding its way into the practice, literature, and curricula of our profession. Optimization theory is composed of technical methods for computing the greatest (or least) value of some criterion of value or effectiveness measuring the performance of a system being studied. Since optimization involves, roughly speaking, finding the best way to do things, it has obvious applications in the chemical industry, where small changes in efficiency can spell the difference between success and failure. Today as always many important decisions can be made simply by choosing some measure of effectiveness and then optimizing it.

To justify the inclusion of this new material into the already crowded curriculum we cannot be content with describing the technical content of optimization theory. We must also show why the profession needs it and how it might be fit into existing graduate and undergraduate programs. Moreover, we must assess the pedagogical value of optimization theory in developing engineering judgment, scientific objectivity, and intellectual creativity in our students.

To begin we shall advance two arguments suggesting the chemical engineers' need for optimization theory. The first of these will be speculative, analyzing the role of optimization in engineering decision-making. The second will be historical, showing how our very lack of attention to optimization theory has created demands for operations analysts and management scientists to solve problems which could well be handled by engineers.

In the heart of the article we shall combine a review of optimization theory with description of a three-hour, one semester course already given to chemical engineering seniors having no special preparation. This resume will include references to recent developments of pedagogical interest. As each phase of the theory is discussed, its most important industrial applications will be mentioned so that the "why" may be unfolded at the same time as the "what" and "how". It is quite possible that a professor may not wish to offer an entire course in optimization theory, preferring instead to incorporate parts of the theory into various existing courses. Indeed, one would hope that eventually optimization theory would be absorbed into the curriculum in this way. To facilitate such gradual integration we shall indicate where each of the three main parts of optimization theory may be pertinent to such existing courses as plant design, kinetics, control, economics, and mathematics. Thus optimization theory may be introduced suddenly or gradually depending on local circumstances.

Finally we shall show how study of optimization theory gives a student a set of rules potentially valuable to him in making complex decisions. The rules and procedures are of course worthwhile in themselves, but equally important is the fact that their study reinforces the student's confidence in the rational scientific approach to problems. Optimization theory gives good training in the analysis of functions of many variables (via multidimensional geometry) and in the use of precise, logical reasoning. Moreover, the very novelty of the mathematics and the newness of the theory are great stimulants to the creativity and imagination of the students.

The Need For Optimization Theory

Let us examine two arguments tending to justify the need of the chemical engineering profession for optimization theory. First consider the typical engineering project. Theoretical principles are combined with experimental data to describe the system under study. It is rare that such a study is made for the sake of knowledge alone; ultimately the information is to be used for making some sort of decision -- build a new plant, replace a heater, or change a catalyst. Without optimization theory, such decisions must often be made impetuously, or at best, after laborious case studies, despite the good engineering that went into the study itself. Such a situation is intellectually (and often economically) unsatisfying.

Secondly, consider the rapid growth of the new profession of "operations research" or "management science", defined by most of their practitioners as "the scientific preparation of decisions". This sounds suspiciously like engineering, and on examination of their methods for making decisions, we find three steps: (1) rational (preferably mathematical) description of the system, (2) choice of a measure of effectiveness, and (3) optimization of that measure. Now in most industrial problems, rational description is precisely the job of the engineer, while the choice of a measure of effectiveness is either obvious or impossible. Thus the only difference between industrial operations research and engineering is usually that the former profession has better optimization techniques. We submit then that the rise of operations research has been due not only to the ability and imagination of its own pioneers, who contributed much to the theory of optimization, but also to the failure of the engineers to study optimization problems. Our loss has been their gain.

Optimization Theory

Before 1951, optimization had hardly been studied at all since the development of the calculus of variations two centuries earlier and today most engineers know only one method for finding an optimum -- the differential calculus. By this method one expresses the criterion of effectiveness as a function of the independent variables, equates the first derivations to zero and then solves the resulting equations. But in industrial problems it is rarely possible to perform all these steps, and even when it is, the "solution" is often unattainable because of physical restrictions on the process. We shall distinguish three branches of optimization theory here, classifying them according to the very obstacles preventing their solution by the differential calculus. The three types of problems are: (1) experimental problems in which the measure of effectiveness is unknown and must be determined by direct experiment, (2) feasibility problems in which the apparent optimum lies outside the physical constraints on the system, and (3) interaction problems in which there are so many variables that the problem must be decomposed and solved in pieces.

Each type of problem can be covered in one semester-hour of undergraduate work, either all at once in a single three hour course or as parts of other existing courses. There are optimization problems which do not fit into these three categories, but we are limiting ourselves here to material that can be taught to a senior engineering student in one semester and be of use to him when he graduates.

After each type of problem is described, its historical development will be traced and references of either research or pedagogical interest cited. Then applications will be mentioned and finally, possible locations in the curriculum will be suggested.

Experimental problems

In an experimental problem one knows almost nothing about the dependence of the measure of effectiveness on the independent variables, and the only way to obtain information about this dependence is to take measurements. Kiefer (1.) has described a highly efficient way to carry out the search when there is but one independent variable and no experimental error, as for example in the calculation of the optimal number of stages in a distillation column or evaporator. A description of this Fibonacci search procedure in engineering terms is given in (2.) It is interesting perhaps that with this technique one could find the best case out of a possible twenty after only seven case studies.

Unfortunately the elegant Fibonacci technique cannot be extended to situations with more than one independent variable, and in 1951, the year of revival of interest in optimization, Box and Wilson (3.) suggested their method of steepest ascent for multivariable problems. Recently newer approaches to this problem have been advanced -- the geometric techniques of Buehler, Shah, and Kempthorne (4.) and the author (5.), as well as the logical methods of Hooke and Jeeves (6.) and Mugele (7.).

The presence of experimental error requires different methods, known in general as stochastic approximation procedures. Dvoretzky (8.) has generalized the early methods of Robbins and Munro (9.) and Kiefer and Wolfowitz (10.), an acceleration technique has been proposed by Kesten (11.), and multivariable extensions have been developed by Blum (12.). Some of these procedures have been reviewed from the chemical engineers' point of view by Lapidus et. al. (13.).

These methods are applicable to design and operating problems involving either complicated computations or significant measurement error. The Fibonacci technique could conceivably fit into a plant design or economics course, or even into the exposition of staged unit operations. Multivariable procedures are more appropriate in plant design courses, and the insight they give into multidimensional geometry could well suit them for inclusion in an advanced mathematics course. Stochastic approximation, since it depends on some probability theory, would be appropriate in an engineering statistics or probability course. In our experience the theory of experimental search for an optimum has been extremely stimulating to students, who seem to be inspired by it to surprisingly original contributions.

The author is presently completing a monograph on experimental optimization, reviewing and explaining all these developments, hopefully in language that an engineering senior can understand. Engineering professors can obtain a free preliminary draft of this material by writing the author, who would be grateful for suggestions and corrections.

Feasibility Problems

When, as is often the case in the industrial world, the ranges of variation of the independent variables are limited, it is sometimes physically impossible to attain the conditions where the first derivatives of the efficiency criterion all vanish. Such restrictions give rise to feasibility problems because only feasible conditions, those respecting all the constraints, can be considered. The technical term "mathematical programming" (not to be confused with the "programming" of computers) is often applied to such problems. The year 1951 also marks the beginning of the theory of mathematical programming. In that year Dantzig published his "simplex method" for solving the linear case. Since that time literally hundreds of articles have appeared on applications of the simplex method, and many petroleum companies have justified the installation of large electronic computers on the improvements in refinery scheduling and product blending made possible by mathematical programming.

It is traditional in operations research curricula to spend a great deal of time on mathematical programming, especially the linear case, which is the simplest. Much of this time is consumed in introducing the student to matrix algebra. While matrix algebra is interesting in its own right, we have found that one can profitably develop mathematical programming without it and save considerable time. This is achieved by treating feasibility problems as simple extensions of the classical optimization problem solvable by the differential calculus. Since engineering students are more adept at manipulating derivatives than matrices, this approach has proven quite successful, and it has been possible to take a class through linear and quadratic programming, as well as the decomposition principle to be discussed later, in only six weeks. This differential approach, which we think has great pedagogical value, is illustrated in (2.) and justified theoretically in (14.)

Discussion of feasibility problems is appropriate in any economics or design course. The subject may also be used in applied mathematics courses as an application of matrix theory; Lapidus has used this approach in his new book (15.) With the differential approach, mathematical programming can be covered in any engineering calculus course, almost as an exercise in partial differentiation.

Interaction Problems

Sometimes the criterion of effectiveness depends on so many factors that it is impractical or impossible to find the optimum by classical methods. Often such problems are generated by the interaction of smaller systems with each other. In such cases it is occasionally possible to decompose the large problem into smaller ones, solve the sub-problems, and recombine these sub-optimal systems in such a way that the interactions are properly taken into account. This exploitation of the structure of a system is advantageous because the number of calculations tends to increase as the cube of the number of variables. Thus doubling the number of variables will ordinarily increase the computation load by a factor of eight. If the problem can be split in two, however, the number of calculations will only double or triple.

Bellman (16.) has shown how to decompose a series of decisions, each depending on the one preceding, by the method he calls "dynamic programming." This technique, which might also be called "serial optimization", has many applications to such long range planning problems as capital investment, production scheduling, and maintenance planning. Application of dynamic programming to the design of chemical reactors has been described in Aris' recent monograph (17.) Nemmhauser has given a very clear example of design of a straight-line chemical plant by dynamic programming (18.) The conventional exposition of this subject using functional equations is often confusing to students, and we have found the block diagram approach of reference (2.) to be helpful in the classroom.

The solar system-satellite structure of many multiplant scheduling problems lends itself to analysis by Dantzig and Wolfe's decomposition principle when all the equations are linear (19.) A numerical example of the application of this principle to centralized planning is available (20.) This example illustrates the power and clarity of the differential approach mentioned earlier, and senior students have had little difficulty absorbing this material, considered quite abstruse by many operations analysts.

References (2), (16), and (17) give many applications of dynamic programming, whose ability to handle time-dependent problems makes the process dynamics and control course an attractive place for its introduction. Aris' work suggests that the kinetics and reactor design course would also be suitable. Again, plant design and economics offerings can be used to introduce serial optimization techniques. Related to dynamic programming is Pontryagin's maximum principle (21). The decomposition principle should be discussed as an extension of linear programming rather than as a separate topic for the differential formulation makes this extension relatively painless.

Pedagogical Values

In describing the outline of a course in optimization theory we have indicated how it is a good vehicle for developing mathematical maturity and respect for the scientific method on engineering students. But aside from the technical material, the decision rules themselves can build sound engineering judgment in the student that will help him make up his mind intelligently even when there is no time for detailed and rigorous analysis. Study of the one-variable experimental optimization problem gives insight into the important minimax concept and the somewhat startling concept of randomization. Analysis of multivariable problems unearths some rather disturbing facts about graphical reasoning and the paradoxes that can arise from failing to realize that engineers often work in non-Euclidean space (2.) Linear programming shows that it is sometimes economical to give a customer higher quality than he asks for at no increase in price. The classic "law of diminishing returns" is illustrated quite clearly in the study of quadratic programming. Anyone's point of view is affected by insight into the far-sighted philosophy of dynamic programming, which begins by analyzing the last rather than the first decision in a sequence. Perhaps the most surprising decision rule of all comes from study of the decomposition principle, which shows that a central planning board should ask branch managers for non-optimal production plans. This is particularly significant because few organizations presently operate this way, at least intentionally.

Concluding Summary

In this review we hope we have given information upon which chemical engineering professors can decide why and how they might introduce optimization theory, or parts of it, to their students. The demands of industry have made this necessary; research has made it possible; and pedagogical advances have made it practical. The rest is up to the profession itself.

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FUNDAMENTAL PROBLEMS IN HETEROGENEOUS CATALYSIS

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At the Chemical Engineering Teachers Summer School in 1939, K.M. Watson presented a paper in which he discussed chemical reaction kinetics for engineers and made an appeal for including more of this type of training in the undergraduate chemical engineering program. At the next Chemical Engineering Teachers School, held in 1948, Watson once again talked on the subject, but this time his emphasis on necessary training was in the area of kinetics of catalytic reactions (25, 26). Since that time, kinetics courses have been included in most of the undergraduate and graduate chemical engineering curricula in the United States. With the increased emphasis on the chemical aspects of chemical engineering, teaching and academic research in the area of chemical engineering kinetics will become even more essential as a component of any adequate undergraduate and graduate program.

The area of heterogeneous catalysis presents one of the most challenging opportunities for new approaches from the viewpoints of both research and teaching. The teaching of heterogeneous catalysis for undergraduate or graduate engineers offers an ideal opportunity to impress on the students the importance of recognizing the practical limits of purely theoretical analyses while simultaneously emphasizing the necessity for understanding the fundamental theoretical concepts. The literature is full of examples of controversial claims in catalytic kinetics based on putting too much emphasis on a given theory without adequate evaluation of other possible interpretations. One example is the critical article by Weller on the engineers' use of the Langmuir-Hinshelwood approach when a power series of the Freundlich type would be equally applicable (29). A rebuttal to the Weller article based on an analysis of real and ideal surfaces is presented by Boudart (3). Another example is the critical analysis of least-squares determinations of rate constants presented by Chow (10).

The controversial nature of many of the currently applied techniques of interpretation in heterogeneous catalysis illustrates vividly the need for more research. The teacher of the subject is dealing with a field which cannot be presented as ancient history with all problems solved. Instead, the teaching can be made extremely interesting by bringing out the fact that many of the past engineering techniques in heterogeneous catalysis are questionable. If the course is taught correctly, perhaps the students can catch some of the excitement of being part of an important engineering area which is ripe for the development of new ideas and new approaches. The recent survey by Hougen on Engineering Aspects of Catalysis emphasizes these points (15).

In the past, there has been some tendency to teach chemical engineering kinetics strictly from the viewpoint of design techniques, leaving the fundamentals to the area of chemical kinetics. This approach is completely inadequate for heterogeneous catalysis because of the many assumptions required for normal design applications. Consequently, to give the engineer a background for intelligent understanding of the design aspects of heterogeneous catalysis, it is essential to discuss the basic considerations and, from these, go through the assumptions necessary to give a workable final design equation. In this paper some of the basic considerations in heterogeneous catalysis normally passed over in undergraduate engineering courses will be discussed.

Surface Characteristics

An obvious starting point for the teaching of heterogeneous catalysis is to present an analysis of surface characteristics for solids with an initial approach through discussion of physical adsorption and chemisorption. Because the energy of activation for physical adsorption is small, the activation energies for reactions involving physically adsorbed molecules cannot be far different than for the homogeneous reaction. Consequently, physical adsorption does not play an important direct role in catalysis, but it does become important in considering fractions of surface area available on a solid catalyst.

Conventionally, the engineering approach to teaching about physical adsorption and chemisorption is to immediately develop the Langmuir adsorption isotherm for a unimolecular adsorbed layer in a form such as

$$\theta = \frac{hp}{1 + hp} \quad (1)$$

where θ represents the fraction of the surface covered by an adsorbed monomolecular layer at equilibrium, h is the adsorption equilibrium constant, and p represents the partial pressure of the gas adsorbed. From this point, with a few brief comments about multilayer adsorption, the Brunauer, Emmett, and Teller equation for estimation surface area is normally presented in the following form (7):

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{(c-1)p}{cV_m p_0} \quad (2)$$

where c is a constant for the system and temperature, p_0 is the saturation vapor pressure for the gas at the temperature used, and v_m is the volume of the gas adsorbed to cover the surface completely with a monomolecular layer

Here is represented the type of engineering approach many educators find objectionable. If it is worth presenting Equation 2 at all, then it certainly is necessary to present the limitations on this Equation. This starting point would be a good spot to impress the students with the need for understanding any equations they may use, and, despite the time it might take, a relatively complete derivation of Equation 2 could get an engineering course in heterogeneous catalysis off to a good start.

The development of Equation 2 is based on the existence of multimolecular layers of physically adsorbed molecules with a derivation similar to that of the Langmuir isotherm for unimolecular layers. At equilibrium, the rate of condensation on the bare surface must equal the rate of evaporation of molecules in the first layer. Similarly, for each succeeding layer, the rate of evaporation must equal the rate of condensation on the preceding layer. Therefore,

$$a_1 p s_0 = b_1 s_1 e^{-E_1/RT} \quad (3)$$

$$a_2 p s_1 = b_2 s_2 e^{-E_2/RT} \quad (4)$$

$$a_i p s_{i-1} = b_i s_i e^{-E_i/RT} \quad (5)$$

where a and b are constants, s represents the surface area covered only by the subscript-indicated layers of molecules, and E represents the heat of adsorption for the indicated layer. Thus, the total surface area of the catalyst and the total volume adsorbed are, respectively:

$$A = \sum_{i=0}^n s_i \quad (6)$$

$$V = \frac{V_n}{A} \sum_{i=0}^n i s_i \quad (7)$$

where n represents the number of layers.

As indicated in Equations 3, 4, and 5, the heat of adsorption is involved exponentially in each of the equilibrium expressions for the rate. The assumption is made that, for all layers except the first, the heat of adsorption is constant and equal to the heat of evaporation. It is further assumed that the ratio of b/a is constant for all layers except the first. In other words, the Van der Waals forces of physical adsorption are involved only in the first layer of molecules on the surface.

With these assumptions the summation expressions can be developed directly to give a value of V/V_m as follows:

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \frac{b_i}{a_i} = g \quad (8)$$

$$E_2 = E_3 = E_i = E_v \quad (9)$$

From Equations 3, 4, and 5

$$s_i = \frac{p}{J} s_{i-1} = \left(\frac{p}{J}\right)^2 s_{i-2} = \left(\frac{p}{J}\right)^{i-1} s_1 = c \left(\frac{p}{J}\right)^i s_0 \quad (10)$$

where $J = g e^{-E_v/RT}$ and $c = \frac{g a_1 e^{(E_1 - E_v)/RT}}{b_1}$

Therefore,

$$\frac{V}{V_m} = \frac{c s_0 \sum_{i=1}^n i \left(\frac{p}{J}\right)^i}{s_0 - c s_0 \sum_{i=1}^n \left(\frac{p}{J}\right)^i} \quad (11)$$

Because $\sum_{i=1}^{\infty} \left(\frac{p}{J}\right)^i$ converges to $\frac{p/J}{(1-p/J)^2}$ and $\sum_{i=1}^{\infty} \left(\frac{p}{J}\right)^i$ converges to $\frac{p/J}{1-p/J}$, the summations represented in Equation 11 are such that the equation reduces to

$$\frac{V}{V_m} = \frac{cp/J}{1-p/J} \frac{1 - (n-1)(p/J)^n - n(p/J)^{n-1}}{1 - (c-1)(p/J) - c(p/J)^{n-1}} \quad (12)$$

When p equals the saturation pressure of the gas, p_0 , complete condensation can occur and V must approach infinity. This can only occur if J is equal to p_0 . For the case where $p < p_0$ or for the case where n is a large number, Equation 12 can be rearranged to give Equation 2, and a complete derivation of Equation 2 showing all assumptions has been presented.

The question immediately arises as to the desirability of presenting this much detail in an undergraduate chemical engineering course on heterogeneous catalysis. Actually, the derivation as presented here is relatively simple and the insight it gives the students into the limitations of the final equation plus the added understanding of the types of forces involved in condensation and adsorption make the time spent on such a derivation worth while. With this background, students making the standard plots of $p/V(p_0-p)$ versus p/p_0 to determine catalyst surface area will have a real understanding of what they are doing. The value of the constant c now has physical significance and could be used to give an approximation of E_1-E_v since ga_1/b_1 is normally close to unity.

Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm, as presented in Equation 1, can be developed directly from Equation 3 as follows to give a physical meaning to the constant h :

$$\frac{s_1}{s_0 - s_1} = \theta = \frac{s_0 a_1 e^{E_1/RT} p}{b_1} = \frac{hp}{1 - hp} \quad (13)$$

$$\text{where } h = \frac{a_1}{b_1} e^{E_1/RT} \frac{s_0 - s_0}{b_1} \frac{a_1 e^{E_1/RT} p}{p}$$

In catalytic studies, use is regularly made of this relationship to develop a model for the reaction. An ideal surface is assumed so that h , and consequently the heat of adsorption E_1 , remain constant. For any real surface, there is no valid reason to assume E_1 will remain constant independent of the amount adsorbed. This explains one reason why experimental values of h obtained from reaction rate data often do not agree with theoretically equivalent adsorption constants obtained from direct adsorption measurements.

Despite these limitations, chemical engineers have been highly successful in using the Langmuir adsorption isotherm as an approach for correlation of rate data. Because of this success, some novices are convinced that the relationships are completely sound theoretically and attempt to develop detailed mechanisms on this basis. This approach has been attacked by Weller who proposed that real and ideal surfaces were so different that the practical engineer was wasting his time in attempting to use the Langmuir-Hinshelwood approach (29). He proposed instead the far simpler Freundlich type of expression for expressing reaction rate. For example, for the gas reaction $A + B \rightleftharpoons C$ catalyzed by a solid, the Freundlich power-series type of rate equation would be

$$\text{rate} = k(p_A)^j (p_B)^m (p_C)^0 \dots \quad (14)$$

while the Langmuir-Hinshelwood result might be in the form of

$$\text{rate} = \frac{k p_A p_B}{(1 - K_A p_A - K_B p_B - K_C p_C)^2} \quad (15)$$

The mathematics of handling Equation 14 is far simpler than for Equation 15; however, a specific reaction mechanism can be applied for Equation 15 while no mechanism can be given for Equation 14. Weller opposes the use of the Langmuir-Hinshelwood approach on the grounds that real and ideal surfaces are not similar and the results obtained tend to be misleading. Boudart has responded to this by proposing that discrepancies in the constancy of the adsorption energy can be accounted for by approximating a temperature dependence of this energy as

$$E_1 = E_{01} + zT \quad (16)$$

where E_{01} and z are constants (3).

The type of approximation represented by Equation (14) would be an excellent method to use for initial analysis of reaction rate data. However, for any general application of kinetic results, a mechanism must be satisfied. Accordingly, the information obtained by a preliminary analysis of the Equation 14 type should be used to attempt to predict a mechanism, and this should then be confirmed by a detailed analysis of the type represented by Equation 15 plus recognition of the factors introduced by surface non-ideality.

The over-zealous ambition of chemical engineers to prove a mechanism on the basis of an incompletely understood theory has caused many ridiculous claims to be made in the literature. This illustrates the need for careful development of the theory combined with discussion of its limitation in the teaching of heterogeneous catalysis.

The preceding analysis has been concerned almost completely with the thermodynamics of adsorption as affected by the heat of adsorption with no attention being given to the concept of entropy relationships. Because gas molecules are free to move in three dimensions and adsorbed molecules are restricted to no more than two dimensions of motion, a reduction of entropy must occur on adsorption as pointed out by Brunauer (6). Entropy calculations can give information on whether the adsorbed molecule is free to move about the surface or is localized with no free rotation. Such information is important in considerations of catalytic kinetics, and variation in entropies of adsorption can be used, at least partially, to explain changes in heats of adsorption. The concept of entropy has only recently been given serious consideration as being important in supplementing the heat of adsorption type of analysis for thermodynamics of surface processes (5, 19)

Active-Site Theory

Despite the limitations of the simple adsorption theory with its assumption of ideal surfaces, this concept has been extended by chemical engineers to include models whereby catalytic surface reactions take place by means of molecules or atoms adsorbed on so-called "active sites" on the surface. Thus, the reaction could occur between an adsorbed reactant molecule and a gas-phase molecule or between two adjacently adsorbed molecules. In presenting this simple model, authors have recognized the limitations of the theory and have consequently tended to present derivations that include incorrect statements which are eventually corrected by the empirical nature of the results. For teaching purposes, errors of this type, even though not important in the final analysis, should be avoided.

One example of an error is presented in a classic pioneer publication by Hougen and Watson (16) which was corrected in their later work. This was the statement that the dual-site surface concentration of vacant sites adjacent to sites containing adsorbed material A is

$$C_{AV} = 1/2 S C_A \frac{C_V}{C_T} \quad (17)$$

where S represents the number of equidistant active sites adjacent to an average active site and the subscripts A, V, and T stand for materials A, vacant sites, and total sites. The error in Equation 17 lies in the $1/2$ which should be unity. A similar error was made by Smith (21) who said it would be more accurate to use $C_T - C_V$ in place of C_T .

Any argument that these two errors are valid can be eliminated by an extremely simple mathematical analysis in which a summation is made of the total possible dual sites on an ideal surface containing only vacant sites (C_V) and adsorbed sites (C_A). For adjacent similar sites, the dual-site concentration must be one-half of the total number of possible adjacent sites times the fraction of total sites occupied by the material. In this case, the one-half is necessary because each pair of adjacent molecules

counted twice. If the adjacent sites are not occupied by similar materials, the one-half should not be included. For this case, therefore,

$$\text{Total dual sites} = \frac{SC_T}{2} = \text{Sites V-V} - \text{Sites A-V} - \text{Sites A-A} \quad (18)$$

$$\frac{SC_T}{2} = \frac{SC_V C_V}{2C_T} - \frac{SC_A C_V}{C_T} - \frac{SC_A C_A}{2C_T} \quad (19)$$

$$\frac{SC_T}{2} = \frac{S(C_V - C_A)^2}{2C_T} = \frac{SC_T^2}{2C_T} \quad (20)$$

The identity in Equation 20 can only occur if Equation 17 is incorrect and if C_T is used in the denominator. Obviously, these two errors as discussed are not important but, for teaching purposes, analysis of this situation and discussion of past errors of this type serve to stimulate class interest and give the students more insight into the type of problems involved in trying to specify surface characteristics.

Solid State Analysis and Electrochemical Potential

In recent years, hope has been raised that catalytic activity might be explained by a new and quantitative approach involving electronic chemical potential and based on the principles of solid-state physics. Unfortunately, this approach has not yet produced any significant results, and it is doubtful if it should have more than passing mention in an undergraduate course on chemical engineering kinetics.

In this approach, the assumption is made that chemisorption is accompanied by a transfer of electrons between the adsorbing solid surface and the adsorbent. The adsorbent acts either as a donor or acceptor depending upon the direction of electron transfer. Because of the high density of electrons on a metal surface, exact quantitative analysis of the charge-transfer process is difficult. However, the surfaces of semiconductors have a far lower concentration of electrons or free carriers than metals and, consequently, are much more satisfactory for theoretical analyses of the charge-transfer process and the resulting energy-level changes (4, 23).

The Fermi level has been proposed as one means for explaining catalytic activity. At equilibrium conditions, there is a probability (designated as the Fermi-Dirac function) that a given quantum state of energy will be occupied by an electron. The energy at which this probability is one-half is designated as the Fermi level (20). The Fermi level of a semiconductor may increase or decrease depending on the concentration of impurities and the temperature. Semiconductors are characterized by densities of electrons (n) and of so-called holes (p). Thus an n-type semiconductor has a conductivity due to excess electrons and is a donor while a p-type semiconductor is an acceptor.

In applying the electrochemical potential theories to catalytic kinetics, one can consider that a gas molecule can be adsorbed on a surface in different forms. For example, isopropyl alcohol might be adsorbed on chromium oxide catalyst as a donor through a hydrogen atom, as an acceptor through a hydroxyl group, or with no net charge transfer. If the most reactive group were the form adsorbed with no net charge transfer, then a maximum would be expected in the reaction rate if the catalyst were changed gradually from a p- to an n-type semiconductor. If the catalyst is initially a p-type material it might be changed to an n-type by increasing the pressure of hydrogen in the gas since the hydrogen would release electrons to the solid catalyst. In other words, there would be a shift in the Fermi level and a maximum catalyst activity would be expected at one Fermi level.

Figure 1 presents results on the rate of dehydrogenation of isopropyl alcohol catalyzed by chromium oxide from experiments carried out at the Institute of Physical Chemistry of Madrid (13, 14). Under normal conditions a regular decrease in rate with increase in hydrogen partial pressure would be expected as indicated by the dashed line in Figure 1. The experimental results are indicated by the solid line. One possible explanation for this apparent discrepancy could be based on the analysis presented in the preceding paragraph wherein there is a Fermi level shift through the level corresponding to maximum activity as the solid catalyst changes from a p-type to n-type semiconductor.

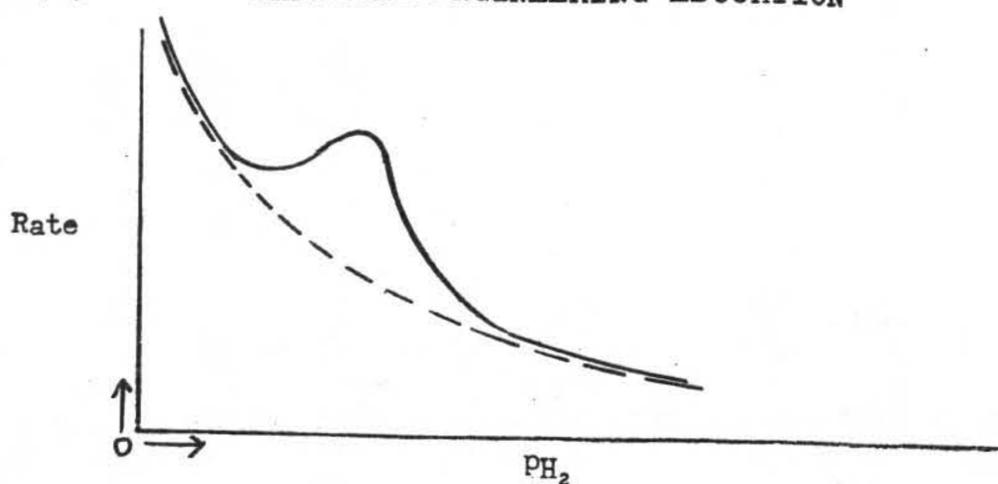


Figure 1. Rate of Dehydrogenation of Isopropanol Catalyzed by Chromium Oxide at Constant Total Pressure with Varying Partial Pressures of Hydrogen in Isopropanol (13).

Heat and Mass Transfer

For the design of catalytic reactors, basically three relationships are needed as follows:

- (a) The design equation.
- (b) The rate expression.
- (c) An energy balance.

In the simplest possible case of a plug-flow reactor operated adiabatically the design can be accomplished with:

- (a) The Design Equation: $Fdx = rdW$ (21)
- (b) The Rate Expression: $r = \phi(x, T)$ (22)
- (c) The Energy Balance: $(-H) Fdx = F_i c_{pi} dT$ (23)

where x represents the fraction of reactant converted, F is the feed rate of reactant, r is the reaction rate based on an amount of catalyst W , ΔH is the heat of reaction, c_{pi} is the heat capacity, and subscript i indicates the individual components.

Heat and mass transfer considerations must be taken into account when the plug-flow assumption is not valid. The same general approach is used for both heat and mass transfer; so this discussion will be limited to mass transfer and development of the appropriate design equations. The conventional approach is to correct for radial and longitudinal diffusivity by using an effective diffusivity for each representing the actual packed bed as being replaced by a fictitious homogeneous material with the appropriate diffusivity. Radial bulk flow is neglected. With these assumptions, the following equations can be developed by material balances:

- (a) For the case of radial diffusion only with constant De/u ,

$$-J \frac{(uC)}{JZ} - \frac{De}{u} \frac{1}{r} \frac{J(uC)}{Jr} - J^2 \frac{(uC)}{Jr^2} - r_B = \frac{JC}{J\theta} \quad (24)$$

- (b) For the case of longitudinal diffusion only with constant D_L/u ,

$$- \frac{D_L}{u} \frac{J^2(uC)}{JZ^2} - \frac{J(uC)}{JZ} - r_C = \frac{JC}{J\theta} \quad (25)$$

- (c) For the case of both longitudinal diffusion and radial diffusion,

$$- \frac{J(uC)}{JZ} - \frac{De}{u} \frac{1}{r} \frac{J(uC)}{Jr} - \frac{J^2(uC)}{Jr^2} - \frac{D_L}{u} \frac{J^2(uC)}{JZ^2} - r_B = \frac{JC}{J\theta} \quad (26)$$

In vector notation, the preceding equation reduces to

$$\text{div}(uC) - \text{div} \left(\frac{D}{u} \text{Grad}(uC) \right) - r_B = - \frac{JC}{J\theta} \quad (27)$$

where u is velocity, C is concentration, r is radius, Z is reactor length, ρ_B is bulk catalyst density, θ is time, and the D 's represent diffusivity.

Development of the preceding design equations along with the corresponding energy balances are straightforward and should be presented in undergraduate courses on heterogeneous catalysis. However, the important engineering function comes in applying these equations, and the solution of the equations can become quite involved. An example of the problems involved in selecting boundary conditions along with the need for clear thinking is presented in the following for the case of Equation 25.

For a first-order irreversible reaction, $r = kC$, and steady state, Equation 25 becomes a second-order, linear, ordinary differential equation with a solution in the form of $C = (\text{Const}) e^{mZ}$ where m is a constant. Smith presents limits as follows to give a very simple solution (22):

Boundary conditions proposed by Smith: $C = C_0$ at $Z = 0$
 $C = 0$ at $Z = \infty$

$$\text{Solution is } \frac{C}{C_0} = e^{-Z} \text{ where } Z = \frac{u}{2D_L} \left(1 - \frac{1 - 4k_1 B D_L}{u^2} \right) \quad (28)$$

Danckwerts and others (11, 27) have proposed much more reasonable limits based on a concentration gradient existing at the entrance to the reactor. The resulting solution is far more complex and more realistic than that shown by Equation 28.

Boundary conditions proposed by Danckwerts and Damkohler:

$$C = C_0 - \frac{D_L}{u} \frac{dC}{dZ} \text{ at } Z = 0$$

$$\frac{dC}{dZ} = 0 \text{ at } Z = L$$

The resulting solution is

$$\frac{C}{C_0} = e^{-\frac{uZ}{D_L}} \frac{2(1 - a') e^{\frac{ua'}{2D_L}(L-Z)} - Z(1-a') e^{\frac{ua'}{2D_L}(Z-L)}}{(1 - a')^2 e^{\frac{ua'L}{2D_L}} - (1-a')^2 e^{-\frac{ua'L}{2D_L}}} \quad (29)$$

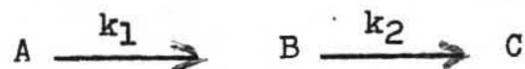
$$\text{where } a' = 1 - \frac{4kD_L B}{u^2}$$

A rather detailed discussion of the disadvantages of oversimplifying, as illustrated by Smith's boundary conditions, can stir up much interest among the students and will simultaneously serve to illustrate the need for the students to think on their own rather than merely blindly accept anything they see in print. The fact that both Equations 28 and 29 reduce to the basic plug-flow expression as D_L approaches zero can be used to illustrate the fact that one proof of a given theory is not always sufficient to establish its validity.

Computer Solutions

We have now reached the point where use of computers for problem solution should be completely acceptable for undergraduates in Chemical Engineering. The kinetics course is an ideal place for including outside problems for solution on the computer, and at least one problem of this type should be part of the course. A simple example is given in the following of a typical problem in kinetics which can readily be solved on a small analog computer of a type similar to the Pace TR-10.

For the case of the following consecutive reactions carried out isothermally



the rate equations for a constant-volume reactor are

$$\frac{dC_A}{d\theta} = -k_1 C_A \quad (30)$$

$$\frac{dC_B}{d\theta} = -k_1 C_A - k_2 C_B \quad (31)$$

Analytical solutions of the first order linear differential equations are

$$C_A = C_{A0} e^{-k_1 \theta} \tag{32}$$

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} (e^{-k_1 \theta} - e^{-k_2 \theta}) \tag{33}$$

$$C_C = C_{A0} - C_A - C_B \tag{34}$$

where C's represent concentration and subscript o represents initial concentration of pure A at zero time.

From Equations 30, 31, 34, plots of either C_A , C_B , or C_C versus θ could be obtained directly with a small analog computer by use of the unscaled diagram shown in Figure 2. A typical concentration-time plot that would result on the x-y plotter from the computer is also shown in Figure 2.

This simple example can be used effectively with undergraduates to familiarize them with the use of the analog computer. It is particularly appropriate because the students can easily calculate analytically from Equations 32, 33, 34 the concentration-time values for direct comparison to the computer results.

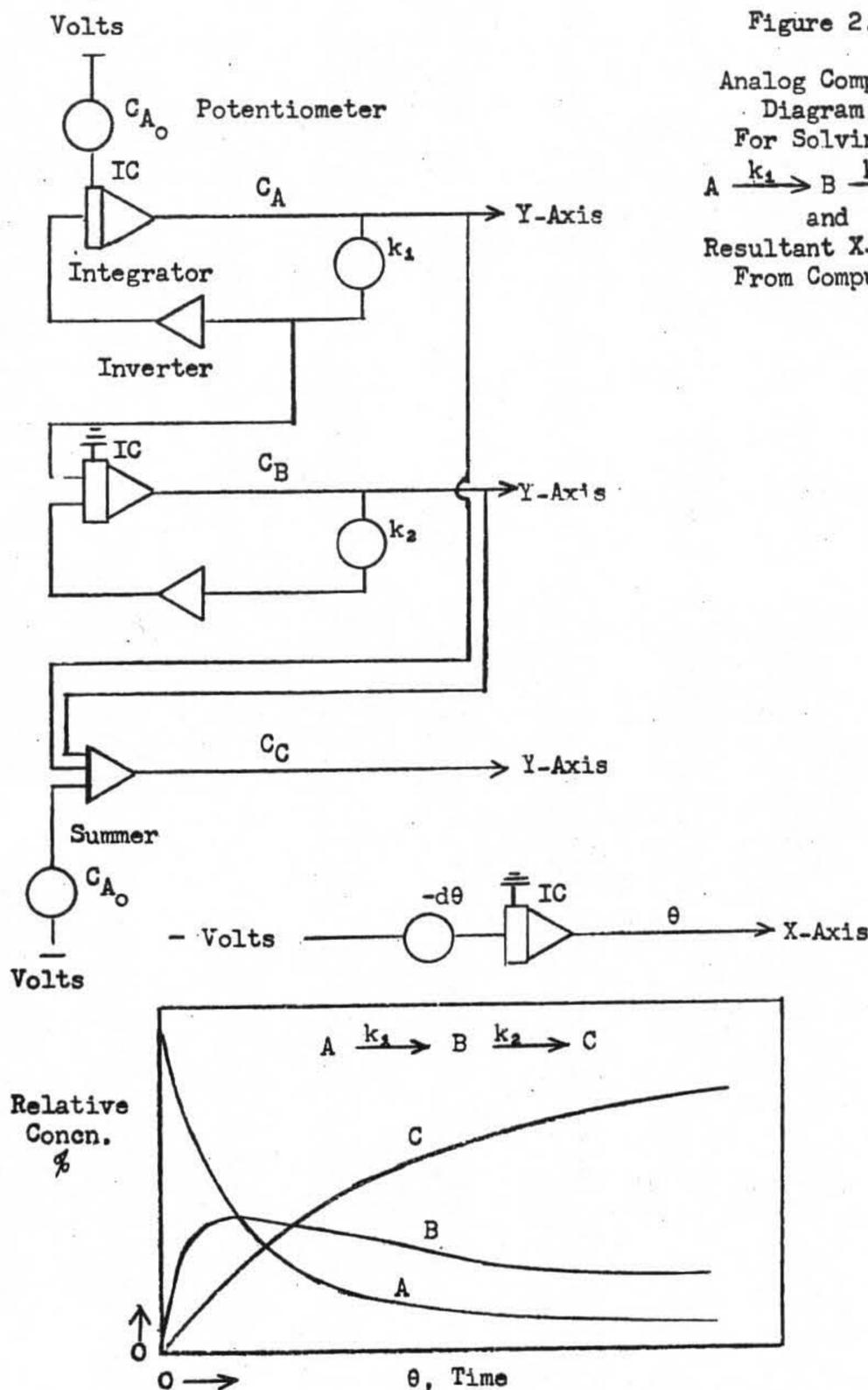


Figure 2.
Analog Computer Diagram For Solving $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ and Resultant X-Y Plot From Computer

If the students have the background and facilities for solving problems on the digital computer, programs are available for solution of Langmuir-Hinshelwood types of rate expressions as presented in Equation 15 (12, 18). Other programs are available for the digital computer which could be used for problems relating to operational characteristics of isothermal tubular flow reactors (2), isothermal batch chemical reactors (17), or solution of the Brunauer, Emmett, and Teller Equation 2 (8).

Conclusion

The subjects discussed in this paper represent some of the special problems in heterogeneous catalysis that would be appropriate for presentation in an undergraduate course. Obviously, there are many standard subjects, all of which also involve fundamental problems, which should be included. Among these would be analyses of the various resistances involved in the catalytic kinetic processes, experimental techniques, interpretation of experimental results, types of reactors including special problems of construction and operation, optimization techniques, poisoning effects, and many others.

Intraparticle transport is another fundamental problem which has received inadequate attention in many chemical engineering courses on kinetics. Pore diffusion and catalytic effectiveness are often completely neglected even though these are important factors in as much as perhaps eighty per cent of all catalytic processes. The work of Thiele (24), Wheeler (30), Aris (1), Weisz (28), and Hougen (15) are significant in showing the advances being made in this area, and an excellent summary of the current situation on this fundamental problem is presented by Carberry (9).

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PLANNING EXPERIMENTS FOR ENGINEERING KINETIC DATA

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Since chemical kinetics is not as yet a predictive science, one of the tasks commonly faced by the engineer in process development is the accumulation of rate data to be used in reactor design. This paper will discuss some of the principles and techniques which can be used to establish useful design data for complex reactions of obscure mechanism which occur under ill-defined conditions and yield incompletely characterized products -- in other words, the usual case of practical interest.

It is a truism so obvious it is usually not taught in physical chemistry courses that one should first establish the stoichiometry of the reaction he is studying. Yet in process development this is often difficult. Analytical methods for the mixtures being produced may be time-consuming or unavailable and expensive to develop. There is a strong temptation to determine the principal product and most troublesome byproduct and ignore the rest. Gross material balances can often be made on the basis of elemental analyses without detailed knowledge of molecular composition. Yet these incomplete analyses often fail to give adequate kinetic data. When reactions are not well understood, it is not unusual to discover the appearance of a new product when conditions are changed. If the design has been based on data taken in ignorance of this product and operation extrapolated beyond the pilot plant range, serious trouble can ensue.

The first step, therefore, is a qualitative survey of the reaction stoichiometry over as wide a range of conditions as possible. The objective of this survey is to establish the main features of the reaction mechanism. For design purposes, the molecular mechanism will never need to be known in detail, but enough of its properties must be determined to formulate a kinetic model of the reaction for the range of conditions of design interest. The more nearly this model reflects the actual mechanism, the more confidently can it be applied over a wide range of conditions. Nevertheless, at some stage, the engineer must be satisfied to work with the data he has, recognizing that he has not established a mechanism fully.

Is the principal reaction product the ultimate product of reaction; or does it disappear in side or subsequent reactions under some conditions? Are the byproducts formed as or from intermediates en route to the main products, or are they formed by independent reaction routes? Do some or all of the products reach equilibrium or steady-state concentrations which are insensitive to residence time? Is there a phase separation in the course of the reaction? Not every autoclave that is loaded with a homogeneous solution and delivers a homogeneous product solution has had homogeneous contents throughout the course of the run. Are mass or heat transfer rates comparable to or slower than the chemical reaction rates? These are all questions that can receive qualitative answers by comparing the results of a few well-planned runs.

Consider a hypothetical example in which Q-acid is made by catalytic conversion of electamine and carbon dioxide in a fluid bed. Under reaction conditions, Q-acid is volatile in an atmosphere of carbon dioxide but it is found that organic matter accumulates on the catalyst to a degree depending on the temperature and feed ratio of electamine to CO₂. Some undesirable electaminic acid is found both in the product vapor and in the organic residue on the catalyst, which, however, is largely unidentified material. The acid could be formed by carboxylation of the amine, but there is no evidence for the actual mechanism.

First experiments might be to vary the gas residence time in the converter, determining the space-time yield and purity of the electamine product. For experimental convenience in these survey runs, the process is not run in continuous steady-state. Instead, electamine is added to the catalyst to a predetermined loading at a temperature below that at which Q-acid is formed. The temperature is then raised and Q-acid stripped off in a stream of CO₂ sufficient to fluidize the bed. The concentration of Q-acid in the product stream is followed during the stripping process. It was found that the pounds per hour of product recovered is directly proportional to the CO₂ flow rate, other conditions being fixed, but is nearly independent of the electamine remaining on the catalyst. This was established by a set of runs at two temperatures in which CO₂ rate and initial electamine loading were varied.

At each temperature, the partial pressure of Q-acid in the off-gas was nearly constant throughout each run. However, with high initial loading of electamine, this partial pressure was less than with low initial loading. With other conditions comparable, the partial pressure of Q-acid was higher at higher temperature. Because of initial transients during the stripping runs as the temperature was being raised, the earliest steady data could be obtained only after 20% to 40% of the Q-acid had been stripped off. These results give a strong presumption that Q-acid is being formed in vapor-solid equilibrium with the organic matter on the catalyst, since as much conversion was obtained in a run as in runs with twice the residence time. However, runs which differ in initial loading gave somewhat different apparent vapor pressures. Hence, we must conclude that there is additional complexity in the mechanism. An additional complication in a fluid bed is the possibility of poor contacting of vapor reactant with catalyst when large "bubbles" can form. Since this bypassing increases with gas velocity, a lower yield at high gas velocity would be expected from this cause alone if it were operative, even though the dense phase reaches equilibrium.

Four more runs under strictly continuous steady operation should settle the qualitative nature of the mechanism. In these, temperature and feed composition are fixed but feed rate and bed height are varied as follows:

Run	1	2	3	4
V (cu.ft./hr.)	Q	2Q	2Q	4Q
H (ft.)	L	L	2L	2L
τ (hr.)	AL/Q	AL/2Q	AL/Q	AL/2Q

Conversion of electamine to Q-acid product is the measured response. The following logic ensues:

Sequence Compare	If	Then
A 1. Runs 1 and 2	Same conversion	Equilibrium is attained
B 1. Runs 1 and 2	Different conversion	Either kinetic control or by-passing
B 2. Runs 1 and 3	{ Same conversion { Different conversion	{ No bypassing { Bypassing occurs

From this logic, Run 4 appears superfluous. However, adding it gives a 2 x 2 factorial experiment in bed-height and residence time.

H τ	L	2L
AL/2Q	2	4
AL/Q	1	3

In this balanced design the following effects are measurable.

$$\text{Kinetics: } K = Y_1 - Y_2 + Y_3 - Y_4$$

$$\text{Bed Height: } H = Y_4 - Y_2 + Y_3 - Y_1$$

$$\text{Bypassing: } B = Y_1 - Y_2 - Y_3 + Y_4$$

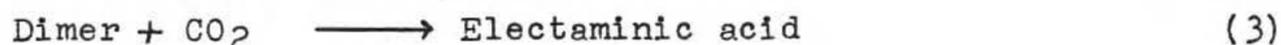
The bypassing effect appears as an interaction between the two main effects and the techniques of statistical analysis can be used to get the most out of the data. At the cost of an extra run, considerable additional confidence can be obtained in the conclusions.

In this example, we see the diagnostic value of a few well-chosen runs. Even more insight can be gained by abandoning the pilot reactor and studying the reaction in an altogether different configuration. Electamine and carbon dioxide might be loaded into a pressure cell adapted to an ultraviolet spectrometer. The product Q-acid vapor as well as the byproduct, electaminic acid could be followed readily by its UV absorption. In this small batch reactor,

the approach to steady vapor pressure of Q-acid could be followed conveniently at times close to the onset of reaction and at a series of temperatures. By interrupting the run at a given time and analyzing the catalyst and its organic contents, it is possible to associate the composition of organic solids with the progress of the main reaction.

In this way, the puzzling dependence of rate on feed composition can be resolved. In the case on which this hypothetical example is based, it was found that a non-volatile dimeric product of electamine forms rapidly on the catalyst with evolution of CO_2 . In a second step, dimer reacts with CO_2 and forms a solid, "pre-Q", which rapidly develops a steady vapor pressure of Q-acid. At the same time dimer reacts slowly with CO_2 to form the byproduct electaminic acid. Thus in the initial runs in which the loading of electamine was low, little dimer was formed and the conversion to Q-acid proceeded rapidly, being governed by the rate of evaporation of pre-Q. In the runs in which the loading of electamine was high, dimer formed rapidly and the conversion of dimer to Q-acid was slower, being governed by the rate of conversion of dimer to pre-Q.

Thus a kinetic model might be written:



Reaction 1 is supposed reversible but not instantaneous. Reaction 2 is irreversible and comparable in speed to reaction 1. Reaction 3 is irreversible and slow. Reaction 4 is reversible and very rapid.

Thus far, although rates have been measured, no use has been made of their quantitative magnitudes. The arguments have depended upon relative values, the shapes of time-concentration curves and similar qualitative data. As a result, however, a reaction model has been reached in terms of which rate data can be quantitatively analyzed.

In many cases, such a model is previously known or is sufficiently probable that one can proceed to the quantitative phase with few preliminaries. In such a case, however, the experimental design should permit testing the fit of the data to the model as well as evaluation of the rate constants and activation energies.

When a model has been proposed as the basis for further kinetic study, the methods of statistical experimental design can greatly reduce the number of runs required to determine the rate constants and reaction orders. These methods are now quite readily available in the literature³ and it is not proposed to discuss them in detail here. They must be used with insight, however, and are no substitute for thought. Some examples will illustrate the power and some of the precautions necessary in this approach.

Srini Vasan and the writer⁴ studied the kinetics of the water-gas shift reaction over a commercial iron oxide catalyst. The literature and previous experience suggested a kinetic model, due to Temkin:⁷

$$R = - \frac{dp_{\text{CO}}}{dt} = k p_{\text{CO}}^a \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^b \quad (5)$$

Although the reaction is reversible, conditions were chosen to minimize the extent of back-reaction. Taking logarithms,

$$\log R = \log A - \frac{E}{RT} + a \log p_{\text{CO}} + b \log p_{\text{H}_2\text{O}} - b \log p_{\text{H}_2} \quad (6)$$

This is a linear form in $1/T$ and the $\log p_i$. Standard methods for the design and analysis of experiments permit the determination of best values for the parameters E/R , $\log A$, a , and b as well as a test of the goodness-of-fit of Equation (6) if fairly general conditions on the errors of measurement are satisfied. At no increased labor, the model could be generalized to include all of the possible components with arbitrary exponents:

$$R = k p_{\text{CO}}^a p_{\text{H}_2\text{O}}^b p_{\text{H}_2}^c p_{\text{CO}_2}^d$$

The geometrical interpretation of the experimental design is quite helpful. We may think of R as a function of $1/T$ and the $\log p_i$ which can be plotted in n -dimensional Euclidean space with the independent variables as coordinate axes. We seek a mathematical representation of the hypersurface $\log R(1/T, \log p_i)$. If Equation (6) is such a representation, $\log R$ will be a plane parallel to the axis of $\log p_{CO_2}$. Furthermore, its intercepts on the $\log p_{H_2O}$ and $\log p_{H_2}$ axis will be equal but opposite in sign. If Equation (7) holds, the $\log R$ surface will still be planar, but there will be no a priori constraints on its orientation. The experimental design problem is now to test whether $\log R$ is indeed a plane, and, if so, to find its equation. With five factors, a 5-plane in six-dimensional space is determined by five points. By determining $\log R$ at additional points, the deviation from planarity can be tested. In the example cited, sixteen points were determined and it was decisively shown that Equation (6) could not represent the data within the reproducibility of experiments.

If the $\log R$ surface is not planar, what shape is it? Standard methods now exist to determine the best quadratic approximation to $\log R$. It is tempting to use this approximation, since the experiments already done to test the planar hypothesis are the core of the design which determines the quadratic approximation. Before succumbing to temptation, however, one should consider his objectives carefully. Equation (6) or (7) has a theoretical interpretation in that a molecular mechanism can be formulated which leads to it. Of course, the possibility of deriving a kinetic equation from a mechanism does not necessarily make it valid. However, the general quadratic form is not derivable from any mechanism and hence cannot possibly be valid except as an empirical interpolation formula. If the design studies which are contemplated will never go outside the range of the data taken, then an interpolation formula may be a sufficient representation of the kinetics. However, if extrapolation is necessary, much greater confidence can be had in kinetic models based on the best mechanism which can be proposed.

A second consideration is often important, however. Complex mechanisms involve many parameters. The general Langmuir mechanism ⁵ for the catalytic irreversible reaction $A + B \longrightarrow \text{Products}$ has the form

$$R = \frac{kp_A^a p_B^b}{[1 + K_A p_A + K_B p_B]^n} \quad (8)$$

Each of the parameters k , K_A , and K_B is exponentially temperature dependent:

$$k_j = A_j e^{-E_j/RT} \quad (9)$$

There are thus nine parameters to determine. Usually they will differ widely in magnitude, but theory will not predict in advance which ones may turn out to be negligible.

It is a fact of the imperfect world that the more parameters that must be determined, the more difficult it usually is to estimate them. When the models are linear in the parameters, experimental designs may be found which will, in theory, allow good estimates to be obtained. The upper limit on precision is determined largely by the magnitude of the experimental error, the number of runs to be made and the experimental range of the variables. In practice, however, the operable region may be such that balanced designs are made impossible by interdependence of the supposedly independent variables. That is, the process may not remain operable unless a change in one variable is compensated for in part by a change in another. In this way correlations tend to creep in to reduce the precision of the estimates as the number of parameters and variables increase. The only partial counter measures are (a) the difficult course of attempting to reduce the magnitude of the experimental errors or (b) an increase in the range of the variables. Chemical processes, however, always have finite restrictions on the operable range of the design variables. The workable temperature range is finite; permissible feed compositions may be limited by phase changes or explosion limits.

When models are non linear in the parameters, the same difficulties exist except that correlations between estimated parameters are more apt to exist. First the optimum theoretical designs in an unhampered experimental region which would maximize the precision of the estimates are usually extremely difficult to find mathematically and secondly, the nature of the function itself may make a high dependence of the estimates unavoidable. Hence in any actual case, there will be a maximum number of kinetic parameters which can be determined with precision from experimental data. The more careful and precise the data, the larger this number becomes, but it rarely exceeds five or six. One must, therefore, scrutinize complex theoretical mechanisms to discover which of the many parameters are likely to be buried in the experimental error.

The quadratic empirical surface can be of great help in this process. Thus, if Equation (8) is rewritten and expanded into the form of Equation (7), it will be discovered that K_A and K_B occur only in quadratic terms involving $1/T$ and the $\log p_A$ and $\log p_B$, respectively. Hence, if the empirical quadratic surface lacks terms in $1/T \times \log p_A$ and $\log p_A \times \log p_B$, one can be confident that p_A can be omitted from the denominator of Equation (8) without worsening the fit. In fact, K_A could not be determined with precision from the data that fixed the quadratic surface. In this way, complex mechanisms can be rationally simplified without overstepping the limits of reliability of the data.

One may find, of course, that the data can be more simply represented by a new choice of coordinates. Thus Equation (8) is more naturally represented in the form

$$(1/R)^{1/n} = \frac{1}{k_1 p_A^{a/n} p_B^{b/n}} \frac{K_A}{k_1 p_A^{a/n-1} p_B^{b/n}} \frac{K_B}{k_1 p_A^{a/n} p_B^{b/n-1}} \quad (10)$$

This suggests $1/p_A$ and $1/p_B$ as better variables than $\log p_A$ and $\log p_B$ for testing this mechanism. In this space, the original experimental points which are well-spaced in $\log p_i$ may be poorly placed to give the best determination of the $R^{-1/n}$ surface. New data may be required to determine the parameters of Equation (10) with precision.

The availability of high-speed computing capacity modifies some of these possibilities. It may no longer be necessary to linearize the rate expression for computational reasons. Techniques for non-linear estimation² permit working directly with the proposed model. However, the number of parameters which can be determined simultaneously is limited as before and most theoretical mechanisms must be simplified to make non-linear estimation feasible.

In some cases the ultimate design problem may be able to accommodate an integral kinetic form rather than a differential one. If, for instance, it is clear that a batch reactor will be used with no internal concentration gradients, only the total volume or residence time will be required for the design basis. Rather than design a differential reactor or differentiate integral data, one may then propose a kinetic model in which time is an explicit factor. Our previous remarks about the maximum complexity of a useful model are especially pertinent.

These points are illustrated in the case of a study undertaken recently in connection with the purification steps of a commercial process. A minor impurity is removed by precipitation with aqueous ammonia. Complication arises out of the base catalyzed hydrolysis of the principal product, which represents a loss. The kinetic study was designed to locate the conditions under which yield at required purity could be maximized. However, since in design it might become necessary to modify some of the conditions, a kinetic model valid over a range of conditions was required. The change in concentration of the impurity is small and small hydrolysis of the principal product is expected, even though a large single stage integral converter is ultimately envisioned.

As is often the case, some older data were available for which the experimental precision was only moderate. New data in both small and large reactors were obtained to test the assumed independence of yields on reactor size. In all, four sets of data were available:

1. New small reactor data
2. Old small reactor data
3. New large reactor data
4. Old large reactor data

Four independent variables had been studied:

1. Temperature (T)
2. Weight per cent product initially in the impure mixture (P)
3. Weight per cent ammonia initially (N)
4. Reaction time (θ)

The response in each run was the precipitate produced, measured as y, per cent of the initial product P.

Since it was desired to make use of the unplanned older data, an orthogonal factorial design or central composite second order design was not possible. As a preliminary survey, a full quadratic model in four variables was fitted by least squares to four groups of data:

- a. Sets 1 and 2
- b. Sets 1, 2 and 3
- c. Sets 1, 3 and 4
- d. Sets 1, 2, 3, and 4

An additional block variable was added for data in sets 3 and 4 to test the effect of reactor size. This effect proved to be non-significant and comparison of residual mean squares of each group of data showed no significant difference between groups. Hence all of the data was used in the final analysis.

A full quadratic model in four variables has fifteen coefficients, four of which only serve to locate the origin with respect to which linear terms vanish. By rotating axes about this origin, the six cross-terms can be eliminated, leaving only the four squared terms and the constant. This reduction to canonical form is done by proper choice of four new independent linear combinations of the independent variables. The results of this analysis are:

$$y = .65362 + .49854 z_1^2 - .09111 z_2^2 - .02671 z_3^2 - .00083 z_4^2 \quad (11)$$

where

$$z_1 = .95990 T' - .27634 P' + .02143 N' + .04214 \theta' \quad (12)$$

$$z_2 = .08732 T' + .37390 P' + .92333 N' - .00672 \theta' \quad (13)$$

$$z_3 = .26183 T' + .88518 P' - .38296 N' + .03520 \theta' \quad (14)$$

$$z_4 = .04916 T' + .01703 P' - .01892 N' - .99847 \theta' \quad (15)$$

Here the primes refer to scaled values of the independent variables.

For example,

$$T' = (T(^\circ\text{C.}) - 141.85)/27 \quad (16)$$

From Equation (11) we see that z_1 is by far the most important term. By Equation (12), z_1 is nearly independent of N and θ and measures T and P most strongly. Reaction time, θ , is almost identical with z_4 . Hence we feel justified in treating its small effect independently of the other variables. Since many of the twenty-one coefficients are small and probably non-significant, one suspects that there are many alternatives to the quadratic form which fit the data as well.

Therefore, a reasonable mechanism was postulated as a guide to a simpler kinetic expression. Suppose the hydrolysis to be catalyzed by hydroxyl ion. Then one might have



$$\frac{d[\text{POH}^-]}{d\theta} = k_1 \frac{[P][\text{OH}^-]}{[\text{OH}^-]} \quad (19)$$

$$\frac{[\text{OH}^-]}{[\text{NH}_4^+]} = K_2 \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = K_2 \frac{N_0 - [\text{OH}^-] - [\text{POH}^-]}{[\text{OH}^-] [\text{POH}^-]} \quad (20)$$

$$[P] = P_0 - [\text{POH}^-] \quad (21)$$

$$y = [\text{POH}^-] / P_0 \quad (22)$$

whence

$$\frac{dy}{d\theta} = \frac{1}{P_0} \frac{d[\text{POH}^-]}{d\theta} = k_1 k_2 \frac{1 - ([\text{OH}^-]/N_0) - (y P_0/N_0)}{[\text{OH}^-]/N_0 + (y P_0/N_0)} (1-y) \quad (23)$$

since y remains much less than unity throughout all the tests, and initially

$$[\text{OH}^-]_0/N_0 = K_2^{1/2} / N_0^{1/2} \quad (24)$$

which is also small, Equation (23) can be simplified to

$$\frac{dy}{d\theta} = \frac{k_1 K_2 N_0 (1-y P_0/N_0)}{P_0 y} \quad (25)$$

$$= \frac{k_1 K_2 N_0}{P_0 y} - k_1 K_2 \quad (26)$$

When y is very small, the first term dominates and the initial conversion should be given approximately by

$$y = (k_1 K_2 N_0 / P_0)^{1/2} \theta \quad (27)$$

This suggests a slightly generalized empirical kinetic expression

$$\log (y - C) = \log A - \frac{\theta}{T} p \log P + n \log N + \alpha \log \theta \quad (28)$$

A preliminary estimate of the coefficients with their confidence limits gave the data in Case I of Table I. This confirms our earlier conclusion that θ could be treated independently as shown in Equation (27). The data were then refitted fixing $\alpha = -p = n = 0.5$, their theoretical values in Equation (27). This gave Case II in Table I.

Table I

	Case I		Case II	
	Coefficient	95% Conf. Limits	Coefficient	95% Conf. Limits
ln A	+ 16.64	± 4.75	+ 16.16	± 4.46
θ	+ 8257.87	± 1889.65	+ 7648.17	± 1928.25
p	- 0.562	± 0.344	(-0.50)	± 0
n	+ 0.261	± 0.567	(+0.50)	± 0
α	+ 0.978	± 0.279	(+0.50)	± 0

There is no significant difference in the fit between Equation 28 with four constants (Case I) and Equation 11 with fifteen.

Note that while n and p are not significantly different from their theoretical values, α is significantly larger than 0.5. Nevertheless, the fit forced with $\alpha = 0.5$ (Case II) is not tremendously worse.

Examination of the residuals shows that the fit is poorest at low N_0 . In fact, some hydrolysis occurs even in the absence of added ammonia. The hypothetical mechanism does not allow for this. The empirical models based on it force the fit by averaging up the reaction order with respect to ammonia. A more realistic model might arise by adding a term to Equation (26) which is proportional to $1-y$. This, when integrated, leads to

$$y = c_1 \theta + \frac{c_2 N_0}{P_0} \ln \left(1 + \frac{N_0 y}{c_2 P_0} \right) \quad (29)$$

where c_1 , c_2 and c_3 might each have exponential temperature dependence. The difficulty of fitting Equation (29) is much increased by its non-linear form. For small y , Equation (29) reduces to Equation (28). Hence it will be essential to use the non-linear form if any improvement is to be expected.

In this example, an empirical quadratic form has again given insight into what mechanistic terms should be retained in formulating a kinetic model with fewer constants to determine. It should be clear that there are a large number of kinetic models that will represent a given set of data. Unless these data are of very high precision, the fact that the engineer has found one such set lends very little support to the corresponding mechanistic interpretation. However, qualitative features can be discerned and more sensitive experiments are suggested by the analysis which may test the mechanistic assumptions in a less equivocal way. Nevertheless, the mechanistically inspired empirical kinetic form will usually be simpler and reliable over a wider range of variables than a pure linear or quadratic form in the original experimental variables. Thus the requirements of engineering data for design purposes can be met without sacrificing the best theoretical knowledge available.

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