

A Kinetics Course*

INFLUENTIAL PAPERS IN CHEMICAL REACTION ENGINEERING

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THIS PAPER DESCRIBES the genesis, development, implementation, and evaluation of a graduate level kinetics course based upon selected influential papers in chemical reaction engineering. The starting point was the following letter of January 1976.

This spring I will be teaching a graduate course in Chemical Reaction Engineering. My thought is to select ten to fifteen of the most influential research papers in this area and to build the course around them. Just to pick a couple of examples, consider "Hougen, O. A., and Watson, K. M., "Solid Catalysts and Reaction Rates," *Ind. Eng. Chem.* 35, 529-541 (1943) and Danckwerts, P. V., "Continuous Flow Systems, Distribution of Residence Times," *Chem. Eng. Sci.* 2, 1-13 (1953).

No doubt you have your own favorites. So I am asking you along with a number of our colleagues to send me the references to a few papers that you consider to be of special importance.

One should not conduct a survey without sharing the results with the respondents. Also you may be interested in the cumulative opinion of your peers. So I will send a tabulation of the responses to everyone who contributes. Thank you for your help.

Twenty-two such letters were sent to individuals prominent in chemical reaction engineering. Sixteen responses were received including four from the researchers surveyed outside of the United States. All responses came from academic researchers although one industrial person was solicited. The list, shown in Table I, comprises the suggestions of fourteen of the respondents. Two respondents referred only to chapter bibliographies in their books. These responses, while useful, would produce an even longer list. Papers are listed first by frequency of mention and second by date of publication.

*Presented at the Summer School for Chemical Engineering Faculty held at Snowmass, Colorado, 1977.

TABLE I
List of Suggested Influential Papers

5 MENTIONS

Thiele, E. W., "Relation Between Catalytic Activity and Size of Particle," *Ind. Eng. Chem.* 31, 916-920 (1939).

3 MENTIONS

Denbigh, K. G., "Velocity and Yield in Continuous Reaction Systems," *Trans. Faraday Soc.* 40, 352-373 (1944).

Wheeler, A., "Reaction Rates and Selectivity in Catalyst Pores," *Advances in Catalysis* 3, 249-327 (1951).

Aris, R., and Amundson, N. R., "An Analysis of Chemical Reactor Stability and Control I," *Chem. Eng. Sci.* 7, 121-131 (1958). See also parts II and III, pp. 132-155.

Weisz, P. B., and Hicks, J. S., "The Behaviour of Porous Catalyst Particles in View of Internal Mass and Heat Diffusion Effects," *Chem. Eng. Sci.* 17, 265-275 (1962).

2 MENTIONS

Hougen, O. A., and Watson, K. M., "Solid Catalysts and Reaction Rates," *Ind. Eng. Chem.* 35, 529-541 (1943).

Van Krevelen, D. W., and Hoftijzer, P. J., "Kinetics of Gas-Liquid Reactions Part I. General Theory," *Rec. Trav. Chim. Pays-Bas* 67, 563-586 (1948). See also Part II pp. 587-599.

Yang, K. H., and Hougen, O. A., "Determination of Mechanism of Catalyzed Gaseous Reactions," *Chem. Eng. Progr.* 46, 146-157 (1950).

Danckwerts, P. V., "Continuous Flow Systems—Distribution of Residence Times," *Chem. Eng. Sci.* 2, 1-13 (1953).

Weisz, P. B., and Prater, C. D., "Interpretation of Measurements in Experimental Catalysis," *Advances in Catalysis* 6, 143-196 (1954).

Wheeler, A., "Reaction Rates and Selectivity in Catalyst Pores," in *Catalysis*, Vol. II, Emmett (ed.), 105-165 (1955).

Van Heerden, C., "The Character of the Stationary State of Exothermic Processes," *Chem. Eng. Sci.* 8, 133-145 (1958).

Uppal, A., Ray, W. H., and Poore, A. B., "On the Dynamic Behavior of Continuous Stirred Tank Reactors," *Chem. Eng. Sci.* 29, 967-985 (1974). Also "The Classification of the Dynamic Behavior of Continuous Stirred Tank Reactors—Influence of Reactor Residence Time," *Chem. Eng. Sci.* 31, 205-214 (1976).

1 MENTION

1900-1949

- Bodenstein, M., and Wolgast, K., "Reaktionsgeschwindigkeit in Strömenden Gasen," *Z. Physik. Chem.* 61, 422-436 (1903).
- Liljenroth, F. G., "Starting and Stability Phenomena of Ammonia-Oxidation and Similar Reactions," *Chem. Metal. Eng.* 19, 287-293 (1922).
- Hatta, S., *Techn. Repts. Tohōku Imperial Univ.* 8, 1 (1928); 10, 119 (1932).*
- Damkoehler, G., *Chem. Eng.* 46, 430 (1937).*
- Frank-Kamenetskii, D. A., *Zhur. Fiz. Khim.* 13, 756 (1939).*
- Voorhies, A., "Carbon Formation in Catalytic Cracking," *Ind. Eng. Chem.* 37, 318-322 (1945).
- Denbigh, K. G., "Continuous Reactions Part II. The Kinetics of Steady State Polymerization," *Trans. Faraday Soc.* 43, 648-660 (1947).

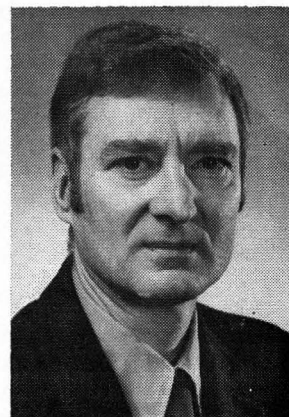
1950-1959

- Bernard, R. A., and Wilhelm, R. H., "Turbulent Diffusion in Fixed Beds of Packed Solids," *Chem. Eng. Progr.* 46, 233-244, (1950).
- Eldridge, J. W., and Piret, E. L., "Continuous Flow Stirred-Tank Reactor Systems," *Chem. Eng. Progr.* 46, 290-299 (1950).
- Singer, E., and Wilhelm, R. H., "Heat Transfer in Packed Beds," *Chem. Eng. Progr.* 46, 343-357 (1950).
- Danckwerts, P. V., "Gas Absorption Accompanied by Chemical Reaction," *AIChE Journal* 1, 456-463 (1955).
- Weller, S., "Analysis of Kinetic Data for Heterogeneous Reactions," *AIChE Journal* 2, 59-62 (1956).
- Boudart, M., "Kinetics on Ideal and Real Surfaces," *AIChE Journal* 2, 62-64 (1956).
- Bilous, O., and Amundson, N. R., "Chemical Reactor Stability and Sensitivity," *AIChE Journal* 2, 117-126 (1956).
- Yagi, S., and Kunii, D., "Studies on Effective Thermal Conductivities in Packed Beds," *AIChE Journal* 3, 373-381 (1957).
- Danckwerts, P. V., "The Effect of Incomplete Mixing on Homogeneous Reactions," *Chem. Eng. Sci.* 8, 93-102 (1958).
- Zwietering, T. N., "The Degree of Mixing in Continuous Flow Systems," *Chem. Eng. Sci.* 11, 1-15 (1959).
- Barkelew, C. H., "Stability of Chemical Reactors," *Chem. Eng. Progr. Symposium Series* 55, 37-46 (1959).

1960-1969

- Van Deemter, J. J., "Mixing and Contacting in Gas-Solid Fluidized Beds," *Chem. Eng. Sci.* 13, 143-154 (1961).
- Chu, C., and Hougen, O. A., "Optimum Design of a Catalytic Nitric Oxide Reactor," *Chem. Eng. Progr.* 57, 51-58 (1961).
- Bischoff, K. B., "A Note on Boundary Conditions for Flow Reactors," *Chem. Eng. Sci.* 16, 131-133 (1961).

This paper describes the genesis, implementation, and evaluation of a graduate level kinetics course based upon selected influential papers in chemical reaction engineering.



Robert L. Kabel received his B.S. degree from The University of Illinois in 1955 and his Ph.D. from The University of Washington in 1961. From 1961-1963 he served in the U.S. Air Force Space Systems Division receiving the Commendation Medal for Meritorious Achievement. Since 1963 he has been at The Pennsylvania State University where he is Professor of ChE. He was at The Technical University of Norway (1971-72) and Pahlavi University in Iran (1978) as visiting professor and lecturer, respectively. He has served recently as Chairman of the AIChE's Chemical Engineering Education Projects Committee (1976-77) and the Central Pennsylvania section of the American Chemical Society (1970). His research centers around catalytic kinetics and air pollution meteorology. He is active in industrial consulting, flying, and squash.

- Hougen, O. A., "Engineering Aspects of Solid Catalysts," *Ind. Eng. Chem.* 53, 509-528 (1961).
- Yagi, S., and Kunii, D., "Fluidized-Solids Reactors with Continuous Solids Feed—I. Residence Time of Particles in Fluidized Beds; II. Conversion for Overflow and Carryover Particles; III. Conversion in Experimental Fluidized-Solids Reactors," *Chem. Eng. Sci.* 16, 364-371, 372-379, 380-391 (1961).
- Yoshida, F., Ramaswami, D., and Hougen, O. A., "Temperatures and Partial Pressures at the Surfaces of Catalyst Particles," *AIChE Journal* 8, 5-11 (1962).
- Wakao, N., and Smith, J. M., "Diffusion in Catalyst Pellets," *Chem. Eng. Sci.* 17, 825-834 (1962).
- Wei, J., and Prater, C. D., "The Structure and Analysis of Complex Reaction Systems," *Advances in Catalysis* 13, 203-392 (1962).
- Liu, S-L., Aris, R., and Amundson, N. R., "Stability of Nonadiabatic Packed Bed Reactors," *IEC Fundam.* 2, 12-20 (1963).
- Liu, S-L., and Amundson, N. R., "Stability of Adiabatic Packed-Bed Reactors," *IEC Fundam.* 2, 183-189 (1963).
- Weisz, P. B., and Goodwin, R. B., "Combustion of Carbonaceous Deposits within Porous Catalyst Particles I. Diffusion-Controlled Kinetics," *J. Catal.* 2, 397-404 (1963).
- Levenspiel, O., and Bischoff, K. B., "Patterns of Flow in Chemical Process Vessels," *Advances in Chem. Eng.* 4, 95-198 (1963).
- Johnson, M. F. L., and Stewart, W. E., "Pore Structure and Gaseous Diffusion in Solid Catalysts," *J. Catal.* 4, 248-252 (1965).
- Karplus, M., Porter, R. N., and Sharma, R. D., "Exchange Reactions with Activation Energy," *J. Chem. Phys.* 43, 3259-3287 (1965).

- Weisz, P. B., and Goodwin, R. B., "Combustion of Carbonaceous Deposits within Porous Catalyst Particles II. Intrinsic Burning Rate," *J. Catal.* 6, 227-236 (1966).
- Weisz, P. B., "Combustion of Carbonaceous Deposits within Porous Catalyst Particles III. The CO₂/CO Product Ratio," *J. Catal.* 6, 425-430 (1966).
- Masamune, S., and Smith, J. M., "Performance of Fouled Catalyst Pellets," *AIChE Journal* 12, 384-394 (1966).
- Carberry, J. J., "Yield in Chemical Reactor Engineering," *Ind. Eng. Chem.* 58, 40-53 (1966).
- Thiele, E. W., "The Effect of Grain Size on Catalyst Performance," *Amer. Scientist* 55, 176-184 (1967).
- Satterfield, C. N., and Cadle, J., "Gaseous Diffusion and Flow in Commercial Catalysts at Pressure Levels above Atmospheric," *IEC Fundam.* 7, 202-210 (1968).
- Kunii, D., and Levenspiel, O., "Bubbling Bed Model," *IEC Fundam.* 7, 446-452 (1968); "Bubbling Bed Model for Kinetic Processes in Fluidized Beds," *IEC Proc. Des. Devel.* 7, 481-492 (1968).
- Villadsen, J. V., and Stewart, W. E., "Solution of Boundary-Value Problems by Orthogonal Collocation," *Chem. Eng. Sci.* 22, 1483-1501 (1967). See also 23, 1515 (1968).

1970-1975

- Hutchinson, P., and Luss, D., "Lumping of Mixtures with Many Parallel First Order Reactions," *Chem. Eng. Journal* 1, 129-136 (1970).
- Szekely, J., and Evans, J. W., "A Structural Model for Gas-Solid Reactions with a Moving Boundary," *Chem. Eng. Sci.* 25, 1091-1107 (1970).
- Mears, D. E., "Diagnostic Criteria for Heat Transport Limitations in Fixed Bed Reactors," *J. Catal.* 20, 127-131 (1971). See also "Tests for Transport Limitations in Experimental Catalytic Reactors," *IEC Proc. Des. Devel.* 10, 541-547 (1971) and "On the Relative Importance of Intraparticle and Interphase Transport Effects in Gas-Solid Catalysis," *J. Catal.* 30, 283-287 (1973).
- Weekman, V. W., Jr., "Laboratory Reactors and Their Limitations," *AIChE Journal* 20, 833-840 (1974).
- Finlayson, B. A., "Orthogonal Collocation in Chemical Reaction Engineering," *Catal. Rev.* 10, 69-138 (1974).
- Cordova, W. A., and Harriott, P., "Mass Transfer Resistances in the Palladium-Catalyzed Hydrogenation of Methyl Linoleate," *Chem. Eng. Sci.* 30, 1201-1206 (1975).
- Weller, S., "Kinetic Models in Heterogeneous Catalysis," *Adv. in Chem. Series No. 148*, 26-49 (1975).

*These references were not located.

SELECTION OF PAPERS

THE RESULTS OF THE survey led to a very nice course structure with very little artificial juggling. The papers selected for the course included all multiply mentioned ones except those which overlapped other selected papers. For practical reasons, extremely long papers were omitted. With one exception [Flory, P. J., "The Mechanism of Vinyl Polymerization," *J. Am. Chem. Soc.* 59, 241-253 (1937)] all papers selected came from the list of Table I. Table II presents the selected topics

The students were asked to "Choose a chemical reaction of commercial importance and, utilizing the decision process suggested by Weekman, discuss the type of reactor best suited to study the reaction." Toward the end of the course, commercial reactors were considered.

and source papers in the order in which they were taken up in the course. It can be seen that the selected papers yield a reasonably coherent and comprehensive course according to subject matter. The most obvious omission is in the area of fluidized beds where none of the papers appeared to be quite suitable. Thermodynamics also is not mentioned in Table II, but it does play a role in a number of papers. Comments follow on the individual papers selected and their roles in the course.

Hougen and Watson (1943) was treated first for several reasons. Its emphasis on catalytic kinetics was a good starting point. As a very comprehensive paper, it gave a good introduction to

TABLE II
Course Organization by Subject

TOPIC	REFERENCE
Catalytic Kinetics and Reactors	Hougen and Watson (1943)
Laboratory Reactors	Weekman (1974)
Flow Reactors (esp. CSTR's)	Denbigh (1944)
Residence Time Distribution	Dankwerts (1953)
Mass Transfere with Chemical Reaction	van Krevelen and Hoftijzer (1948)
Polymerization	Flory (1937)
Multiple Steady States and Stability	van Heerden (1958)
Stability and Control	Aris and Amundson (1958)
Pore Diffusion	Thiele (1939)
Effectiveness Factors	Weisz and Hicks (1962)
Heat Transfer in Packed Beds	Singer and Wilhelm (1950)
Coke Formation on Catalysts	Voorhies (1945)
Selectivity and Yield	Carberry (1966)
Commercial Reactors	—
Optimization	Chu and Hougen (1961)

much of what was to follow. Their original derivation of the plug flow reactor mass balance could well have appeared later in the course sequence. Nevertheless, it was desirable for me to present this paper first to set an example for the students and to allow them time to prepare their material (see Class Organization).

Weekman (1974) discussed selection of laboratory reactors. This paper is perhaps not a classic but it served well to introduce the various kinds of reactors. The students were asked to "Choose a chemical reaction of commercial importance and, utilizing the decision process suggested by Weekman, discuss the type of reactor best suited to study the reaction." Toward the end of the course commercial reactors were considered.

Denbigh (1944) is surely a landmark paper in the quantitative treatment of flow reactors. We used it especially in relation to continuous flow stirred tank reactors; however, its treatment of plug flow was compared to Hougen and Watson's. Denbigh also analyzed by-passing effects, selectivity and yield, and temperature programming of reactors. These subjects all arose again in subsequent papers.

Danckwerts' (1953) paper on residence time distribution followed naturally after Denbigh's. An important and unique class of heterogeneous reactions, gas-liquid, was powerfully influenced by van Krevelen and Hoftijzer (1948). To bring in more kinetics and the important subject of polymerization, we selected the 1937 paper by Flory on the mechanism of vinyl polymerization. Van Heerden's work on multiple steady states is so well known that no further comment is required to demonstrate its influence. No one in the class discovered that 35-40 years earlier Liljenroth, F. G., "Starting and Stability Phenomena of Ammonia-Oxidation and Similar Reactions," *Chem. Met. Eng.* 19, 287-293 (1918) had made many of the same points. Aris and Amundson (1958) provided a culmination of the treatment of homogeneous reaction systems with a seminal paper in the area of reactor control.

The most mentioned paper was Thiele (1939) on pore diffusion. This served as a basis for much

TABLE III
Some General Characteristics of
Chemical Reaction Engineering

I. Types of Technical Activity	
A. Determination of Effect of Process Variables on Reactor Performance	
1. Variables	2. Performance
Temperature	Conversion
Pressure	Yield
Composition	3. Analysis
Reactor Type	Input + Process → ?
B. Characterization of Reactions and Reactor Specifications	
1. Synthesis (Design)	
Input + ? → Output	
C. Experimentation and Data Interpretation	
1. Data Interpretation	
?? + Process → Output	
II. Some Related Subject Areas	III. Other Important Aspects
A. Thermodynamics	A. Uniqueness
B. Thermostatics	B. Quality Specifications
C. Stoichiometry	C. Optimization
D. Chemical Kinetics	D. Scale Up
E. Economics	E. Communication
F. Statistics and Distribution	F. Integration

of the work on the ubiquitous effectiveness factor and its ramifications, of which the paper of Weisz and Hicks (1962) is a foremost example. Way ahead of their time were Singer and Wilhelm (1950) on heat transfer in packed beds. This paper was chosen for the course but a sister paper [Bernard, R. A., and Wilhelm, R. H., "Turbulent Diffusion in Fixed Beds of Packed Solids," *Chem. Eng. Progr.* 46, 233-244 (1950)] should be acknowledged. Voorhies (1945) was so successful in correlating coke formation on catalysts that very few papers appeared on this subject for twenty years. You might call its influence adverse.

Carberry's (1966) article induced a good look back over our earlier papers in addressing the important and complex topic of selectivity and yield. This moved the class closer to the consideration of the details of commercial reactors. Finally the paper of Chu and Hougen (1961), though not very influential, served as a comprehensive example of design and intuitive optimization.

In addition to the source material, another uncommon aspect to this course was the designation of each student as a specialist with regard to one of the central papers. The student was responsible for advance study of the assigned article including references to earlier work.

TABLE IV
Quantitative Structure of
Chemical Reaction Engineering

- I. Some preliminary considerations
 - A. Reaction stoichiometry
 - B. Determine thermodynamic feasibility
 - C. Heat effects
 - D. Physical and chemical properties
 - E. Analytical techniques
 - F. Mass balances
 - G. Energy balance
- II. Kinetics
 - A. Reaction mechanism
 - B. Find rate equation
 - C. Effect of temperature and pressure
 - D. Experimentation
 - E. Data handling and error analysis
 - F. Flow ramifications
 - G. Selectivity
- III. Engineering aspects
 - A. Catalyst selection
 - B. Select reactor(s) type (simple or combination)
 - C. Heat and mass transfer in heterogeneous and homogeneous systems
 - D. Effectiveness factors
 - E. Residence time distribution
 - F. Process dynamics
 - G. Optimization
- IV. Other aspects
 - A. Safety
 - B. Pollution control
 - C. Preprocessing and subsequent operations
 - D. Further recommendations
 - E. Admission of inadequacies

For each article there was an introductory lecture of about 15 minutes and assignment of homework. At the next class, the specialist gave his main lecture, discussed the homework, and made new assignments.

CLASS ORGANIZATION

THE EARLY CLASSES were spent organizing the course and discussing the nature of chemical reaction engineering. Two results of these discussions are shown in Tables III and IV. It can be seen that most of these aspects could be expected to come up in the study of the central papers and their literary kin.

In addition to the source material, another uncommon aspect to this course was the designation of each student as a specialist with regard to one of the central papers. The student was responsible for advance study of the assigned article including references to earlier work. In this way he would

The most mentioned paper was Thiele (1939) on pore diffusion. This served as a basis for much of the work on the ubiquitous effectiveness factor and its ramifications . . .

understand the circumstances in which the article appeared. Further by checking the citation index and recent textbooks he could discover the influence of the assigned article on subsequent work. With consultation with the instructor, the specialist prepared lectures and homework assignments for the class.

For each article there was an introductory lecture of about 15 minutes and assignment of homework. At the next class, the specialist gave his main lecture, discussed the homework, and made new assignments. In the following class period about 30 minutes were devoted to wrapping up all aspects of a given topic. The student also reviewed (as did the instructor) the homework, providing constructive criticism. Sometimes the specialist would assign required or optional supplementary reading. In this course structure each student served as a specialist in one area, studied all of the primary source papers and occasional supplements, worked homework assignments, lectured and reviewed homework papers, and took two written exams prepared and graded by the instructor.

One final activity of the specialist was the preparation of a summary of his area with special attention to the documentation of key references. These summaries were reviewed by the instructor, typed, and distributed to the class. To give a more concrete picture of the course; the assignments, exam question, and summary relating to Hougen and Watson (1943) are given as an appendix to this article.

EVALUATION

At the end of the term, class members were asked to evaluate the course. Of the twelve respondents, eight were enthusiastic about the course structure (i.e. the use of student specialists), two preferred that the instructor handle it in a conventional manner, and two were neutral. Several students suggested that early in the term (but after the specialty topics have been assigned) instruction should be given in effective teaching.

The students were asked to indicate which two
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INFLUENTIAL PAPERS

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articles they liked best and which two they liked least. The results are given in Table V. Perhaps there is a message here, perhaps not.

My opinion is that the course was less efficient than a conventional textbook course in teaching facts, concepts, methods, etc. Still it was much more effective in conveying a comprehensive view of chemical reaction engineering than anticipated. The dynamics of history are not so easily and dramatically conveyed via technical texts. Also, with this course format, it was natural to bring each topic right up to date. With one or two exceptions only, these "influential papers" were excellently written. The students enjoyed a realistic teaching experience. Because of the nature of

TABLE V
Article Preference

	(most - least = net)
Hougen & Watson	(6 - 0 = 6)
Thiele	(3 - 0 = 3)
Carberry	(3 - 1 = 2)
Danckwerts	(3 - 1 = 2)
Denbigh	(2 - 0 = 2)
Weisz & Hicks	(2 - 0 = 2)
van Krevelen & Hoftijzer	(2 - 0 = 2)
van Heerden	(1 - 0 = 1)
Weekman	(1 - 1 = 0)
Voorhies	(1 - 2 = -1)
Flory	(1 - 2 = -1)
Singer & Wilhelm	(1 - 4 = -3)
Aris & Amundson	(0 - 6 = -6)
Chu & Hougen	(0 - 9 = -9)

their involvement, they were surely provided with a strong feeling for the flow of research and technology.

There is much more to be said about the central and related papers than can be accommodated by this article. At the suggestion of one respondent, Michel Boudart, it is my intention to prepare an annotated collection of "Influential Papers in Chemical Reaction Engineering." Your suggestions on papers to be included will be appreciated.

ACKNOWLEDGMENTS

I would like to acknowledge the contributions of the respondents to the original survey and the students in the course. Special thanks go to Mr. Deepak Perti for his assistance in the large

amount of library work necessary to develop this course and for his service as a specialist in an area where he had unique expertise. □

APPENDIX

CHEMICAL ENGINEERING 535

Assignments

Monday 28 March 1977

Read Hougen and Watson (1943)

Work #1 and 2 below.

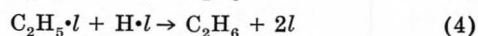
Wednesday 30 March 1977

Read Weller (1956) and Boudart (1956). Photocopies of these two articles are available in the ChE Reading Room and on reserve in the Physical Sciences Library. In addition the *AIChE Journal* is available in both of these locations.

Optional reading—Weller (1975) gives excellent up-to-date perspective on the topic of catalytic kinetics. Copies of this article are also located in the reading room and the library.

Work #3 and 4 below.

- The vapor phase hydrogenation of ethylene ($C_2H_4 + H_2 \rightarrow C_2H_6$) on a well dispersed platinum catalyst (0.05% Pt on SiO_2) is described by Sinfelt, *J. Phys. Chem.*, 68, 856 (1964). The overall reaction is virtually irreversible and is considered to occur according to the following mechanism.



Reaction (4) is very rapid. Reaction (3) is the rate determining step.

- Use the methods of Hougen and Watson (1943) to derive an equation for the rate of reaction of ethylene. The equation should contain only rate and equilibrium constants and partial pressures of the reaction components.
 - It is known that hydrogen adsorption, although significant (K_H is finite) and necessary, is slight. Use this information to simplify your rate equation.
 - At rather low temperatures the rate of reaction at constant ethylene partial pressure will be directly proportional to the square root of the hydrogen partial pressure and at constant hydrogen partial pressure will be inversely proportional to the ethylene partial pressure. Explain why these experimental observations are consistent with your rate equation from part (b).
- Write a three dimensional, unsteady state mass balance on a differential element of a fixed bed catalytic reactor. Show how to reduce this equation to the one dimensional, steady state form for a plug flow reactor, given by equation (56) in Hougen and Watson (1943).
 - Refer back to the system of problem #1. For experiments conducted at constant P_{H_2} but over a wide range of $P_{C_2H_4}$, sketch a graph of $\log r$ vs $\log P_{C_2H_4}$. Indicate quantitative features on the graph where you can.

4. Akers and White, *Chem. Eng. Progr.* 44, 553 (1948) reported the following data for the synthesis of methane from CO and H₂ over a nickel-kieselguhr catalyst at 1 atm and approximately 300°C with a feed gas containing 44.5% CO, 53.9% H₂, 0.4% CO₂ and 1.2% inert.

lb catalyst-hr/mol feed	mol CH ₄ in product/mol feed
7.13	0.187
2.97	0.154
1.68	0.120
0.38	0.045

Determine the specific rate and tabulate as a function of the mol CH₄/mol feed.

Examination #1 (Take home)

1. In Hougen and Watson (1943)* equation (12) gives the rate of a catalytic reaction in terms of adsorbed phase concentrations and the concentration of vacant sites, c_v . In equation (14) the adsorbed phase concentrations are gone and fluid phase concentrations appear. During our study of this paper, one student asserted that there was an error in equation (14). Show in complete detail how equation (14) is obtained from equation (12). If there is an error in equation (14), give the correct result and compare it to equation (14).

SUMMARY OF STUDY ON HOUGEN AND WATSON (1943)

This excellent paper was a remarkably comprehensive, trendsetting, and futuristic paper. It dealt effectively with many of the topics which have proved to be important in the more than thirty years since its appearance. Among these are catalytic kinetics, catalyst deactivation, effectiveness factors, external mass transfer, and fixed bed reactor analysis and design. One can see that many of the topics now considered crucial in research, teaching, and practice of chemical reaction engineering were anticipated by Hougen and Watson. This review chooses those two items in which the impact of this 1943 paper has been greatest: catalytic kinetics and the tubular reactor mass balance,

$$r \rho_B dV = F dx_A.$$

The above equation provided a quantitative basis for rational tubular reactor design. Before its appearance semi-quantitative scale up procedures were used. A rather sophisticated illustration of this earlier mode of thought can be provided by reference to an article by Emmett and Kummer (1943). There they give 9 graphs of % NH₃ in the exit gas versus space velocity for three temperatures, three pressures, and three N₂:H₂ feed ratios. From such graphs (which might come from the laboratory or pilot plant) encompassing the processing conditions of interest, one can find the space velocity to achieve a specified conversion. With the assumed analogy between tubular and batch reactors, the intuitive argument that the space veloc-

*Some errata in Hougen and Watson (1943) are as follows:

Eqn (9), C_A should be C_A'

p. 531, left side, line 1, C_{Al} should be C_{A'l}

Eqn (14), K_A C_{Al} C_l should be K_A a_{Al} C_l

p. 533, left side, line 3, 25 should be 27

p. 533, left side, line 10, unadsorbed should be unadsorbed

p. 538, right side, line 4b, absorption should be adsorption

My opinion is that the course was less effective than a conventional textbook course in teaching facts, concepts, methods, etc. Still it was much more effective in conveying a comprehensive view of chemical reaction engineering than anticipated.

ity is inversely proportional to the contact time (imperfect for reactions like ammonia synthesis in which there is a change in the total moles), and the hypothesis that only contact time determines the conversion, the pilot plant could be scaled up directly by calculating the commercial reactor volume from the space velocity and the specified commercial feed rate. It would remain to determine the reactor shape (usually characterized by the length to diameter ratio) from previous experience with similar systems. Major factors in this determination would be catalyst characteristics and heat transfer. Among other things, it was the physical processes like heat and mass transfer and mechanical characteristics of catalysts and reactors that made scale up from small to large reactors so uncertain.

Apart from its design application, the tubular flow reactor mass balance enabled the isolation of reaction kinetics from reactor characteristics. This in turn allowed much better reaction rate data to be obtained in catalytic reactions and led ultimately to improved characterizations (rate equations) of catalytic kinetics.

Probably the earliest attempts to write rate equations for heterogeneous catalytic reactions followed the equation forms which had proved satisfactory in homogeneous reaction rate studies. Empirical use of such equations continues today with a vigorous endorsement in a prominent textbook (Levenspiel, 1972). At the same time the approach of Hougen and Watson finds wide application among academic and (more significantly) industrial practitioners.

The catalytic rate equations of Hougen and Watson stem directly from a classical paper by Langmuir (1922) in which he proposed a number of catalytic mechanisms based upon his monolayer theory of chemisorption. Hinshelwood (1940) applied Langmuir's treatment to a large number of reactions. This approach has become known as the Langmuir-Hinshelwood model of heterogeneous catalysis. Hougen and Watson (1943) rather independently developed, extended, and popularized this model for chemical engineering use. Yang and Hougen (1950) systematized the previous work bringing together the rate equations for many situations and putting them into a generalized form. So influential were these works that the model became known as "Hougen and Watson rate equations" and its use and abuse exploded. In 1956, back-to-back articles by Weller and Boudart appeared. Weller suggested that the Langmuir-Hinshelwood, Hougen-Watson approach does not have the theoretical validity commonly attributed to it and that, lacking theoretical validity, it is unnecessarily complex for use as an empirical equation when compared for simplicity to the common power function (homogeneous) type of equation. Boudart supported the rational use of the L-H, H-W approach with his discussion of the limitations and strengths of that theory. Kabel and Johanson (1962) made an experimental attempt to reconcile the argument using the ion exchange resin catalyzed dehydration of ethanol. They found that the Langmuir equilibrium adsorption constants de-

rived from a Hougen and Watson kinetic analysis of the rate data agreed quite well with the corresponding constants obtained directly from independent adsorption experiments. Their results generated other papers by Lapidus and Peterson (1965), Kabel (1968), and Mezaki and Kittrell (1968).

Almost 20 years after his original article Weller (1975) has written a very comprehensive analysis of the state of catalytic kinetics. It is recommended reading for those wishing an up-to-date perspective.

REFERENCES

- Hougen, O. A., and Watson, K. M., "Solid Catalysts and Reaction Rates," *Ind. Eng. Chem.*, **35**, 529-541 (1943).
- Emmett, P. H., and Kummer, J. T., "Kinetics of Ammonia Synthesis," *Ind. Eng. Chem.*, **35**, 677-683 (1943).
- Levenspiel, O., "Chemical Reaction Engineering," 2nd ed., John Wiley & Sons, Inc., New York, 1972.
- Langmuir, I., "The Mechanism of the Catalytic Action of Platinum in the Reactions $2CO + O_2 = 2CO_2$ and $2H_2 + O_2 = 2H_2O$," *Trans Faraday Soc.*, **17**, 621 (1922).
- Hinshelwood, C. N., "The Kinetics of Chemical Change," Oxford University Press, New York, 1940.
- Yang, K. H., and Hougen, O. A., "Determination of Mechanism of Catalyzed Gaseous Reactions," *Chem. Eng. Prog.*, **46**, 146 (1950).
- Weller, S., "Analysis of Kinetic Data for Heterogeneous Reactions," *AIChE Journal*, **2**, 59 (1956).
- Boudart, M., "Kinetics on Ideal and Real Surfaces," *AIChE Journal*, **2**, 62 (1956).
- Kabel, R. L., and Johanson, L. N., "Reaction Kinetics and Adsorption Equilibria in the Vapor Phase Dehydration of Ethanol," *AIChE Journal*, **8**, 621-628 (1962).
- Lapidus, L., and Peterson, T. I., "Analysis of Heterogeneous Catalytic Reactions by Nonlinear Estimation," *AIChE Journal*, **11**, 891 (1965).
- Kabel, R. L., "Homogeneous versus Heterogeneous Rate Equations for Catalytic Reactions," *AIChE Journal*, **14**, 358 (1968).
- Mezaki, R. and Kittrell, J. R., "Nonlinear Least Squares for Model Screening," *AIChE Journal*, **14**, 513 (1968).
- Weller, S., "Kinetic Models in Heterogeneous Catalysis," *Adv. in Chem. Series, No. 148*, 26-49 (1975).

ChE book reviews

SI UNITS IN CHEMICAL ENGINEERING AND TECHNOLOGY

By K. D. Chandrasekaran and D. Venkateswarlu
*Indian Institute of Technology
Madras, India. June 1974.*

Reviewed by G. R. Youngquist
Clarkson College of Technology

This paperbound four-chapter handbook presents a summary of the SI system of units, conversion factors, and tables of numerical data in SI for physical and thermal properties. The first chapter briefly but adequately introduces the SI system along with conventions for its use and

provides an extensive list of derived units which are of interest to chemical engineers. The second chapter is devoted to SI units for quantities commonly used in chemical engineering practice. Fifty-five tables listing the preferred SI unit, recommended multiples, and conversion factors for quantities such as mass transfer coefficients, heat flux, viscosity, thermal conductivity and the like are given. The third chapter consists of 88 tables of physical constants, physical properties of solids, liquids, and gases, and thermochemical and thermodynamic properties of selected substances. These are more extensive than found in a typical textbook, but quite naturally less complete than other handbook sources. The final chapter provides 20 example problems.

The background information presented is concise and should be sufficient for most users of SI. The conversion tables are convenient, and the tables of data serve a useful purpose in the absence of other sources which use SI. The book is suitable for desk reference or as a textbook supplement. An annoying feature of the book was the poor quality of the binding. Even the brief use encountered in the course of this review caused several pages to detach. □

FUEL CELLS

By Angus McDougall, Halstead Press, a division of John Wiley & Sons, New York, N.Y. 1976.

Reviewed by Robert D. Walker, University of Florida

This small book of thirteen chapters presents a reasonably adequate discussion of the major aspects of fuel cells at a quite elementary level. It will be useful, therefore, for introducing new students or casual readers to the subject without confusing them with unnecessary details. In spite of this advantage, however, it appears to this reviewer that the book suffers from a number of shortcomings. In the first place, the author includes no references to sources of the data used; indeed, there are no references to any other publications. The reader is, therefore, left with no suggestions as to more advanced literature. Secondly, the case for fuel cells as energy sources is consistently presented too optimistically; the efficiency and performance described are substantially in excess of those achieved practically. Finally, the usefulness of the book for the American reader is diminished by the author's discussion of British fuel cells alone; no American (or other) fuel cells are described. □