

A Course in Chemical Reaction Engineering

REACTOR DESIGN

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At the University of California, Davis (UCD) two quarter-length (3 lectures/week) graduate courses are available in chemical reaction engineering. The first course, which is required, is a general treatment. The second is an optional offering the contents of which are more specialized and may vary from time to time. The goal of the first course is to complete the outline shown in Table I. However, even though most students have had an undergraduate kinetics course, our experience has been that a semester-length offering would be desirable to cover the subjects listed.

Following each major topic in the outline are references to appropriate books and papers. Together the book references include all the major texts in the field. At UCD several of these (3, 24, 27, 29) have been used as the textbook for the course. On other occasions, the complete list has been assigned as a set of references. We find that even graduate students benefit from thorough familiarity with one reasonably general book.

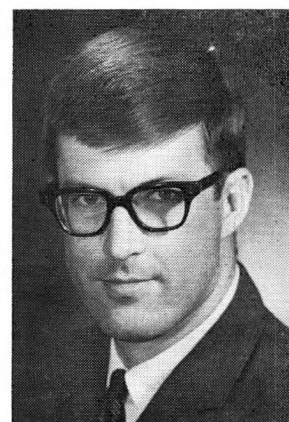
The course starts out with a review of chemical reaction equilibria to ensure that the student understands how to evaluate equilibrium product distributions. At this time it is also convenient to introduce the interrelations between kinetics and thermodynamics.

The differential conservation equations (Section II) provide the basis for subsequent design of whatever degree of complexity. The equations of motion are generally omitted, to be picked up in context as needed. The energy equation is ordinarily simplified to neglect kinetic and potential energies and shaft work. It is developed carefully in terms of both partial molar enthalpies and temperature, since this seems frequently a source of confusion.

The point material-balance equations also serve to introduce the reaction source term or rate expression. At this point the continuity equation



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for homogeneous reaction is integrated for constant-volume and variable-volume uniform batch reactors, to stress the nature of the source term in the material balance as a function of instantaneous local properties, independent of the type of constraints on the reacting volume.

The discussion of chemical kinetics (Section III of Table I) is necessarily brief. Students will have had an introduction at least to formal kinetics in undergraduate physical chemistry and chemical engineering kinetics courses. We acknowledge that chemical kinetics in its present state of development is only rarely predictive but often permits more reliable interpolation and limited extrapolation.

The steady-state approximation is discussed fairly thoroughly (2), and its mathematically very valuable consequence—that it reduces a stoichiometrically complex reaction sequence to a stoichiometrically simple reaction—is stressed.

With the information presented the student should be able to follow most of the chemical engineering literature insofar as it attempts to discern reaction mechanisms. On the other hand,

TABLE I. APPLIED KINETICS AND REACTOR DESIGN SUBJECT OUTLINE

	References		
I. Review of chemical reaction eq.	7, 26, 29	7. Effect of intrapellet transport on selectivity	34
II. Conservation equations for systems with chemical reaction	10	C. External transport	27-29
A. Continuity equations with homogeneous reaction		1. Mass and energy transfer coefficients	
B. Continuity equations with heterogeneous reaction		2. Effect of external transport upon global rate	
C. Energy equation		a. Single reactions	
III. Reaction rate expressions	11, 20	b. Selectivity effects	
A. Material balances with reaction		3. Multiple steady states (stability)	1
B. Stoichiometrically simple reactions		V. Reactor design	
C. Stoichiometrically complex reactions	3, 27	A. Uniform batch reactor	
1. Determination of an independent set		B. Continuous stirred-tank reactor	
2. Analysis of extents of complex reactions		1. Steady-state design	
D. Kinetic treatment of reaction mechanisms	6, 17, 23	2. Multiple steady states and stability	1, 8, 15
1. Molecular reactions		C. CSTR sequences	
2. Steady-state approximation for reactive intermediates		D. Tubular reactor	
a. Open sequences		1. Plug-flow reactor	
b. Closed sequences		2. Tubular reactor with homogeneous reaction	12, 13, 31, 32
(1) Initiation-termination processes		3. PFR with axial dispersion	24
(2) Constancy of number of reactive intermediates		4. Three-dimensional design for packed beds	5
E. Empirical rate expressions		5. Stability and parametric sensitivity	4, 9, 16, 21
F. Pseudohomogeneous rate expr.	27	6. Autothermal operation	15, 18, 19
IV. Physical transport and reaction in heterogeneous systems		VI. Transport parameters for packed-bed reactors	5, 27-29
A. Pseudohomogeneous rate equations—global rate		A. Velocity profiles	
B. Intrapellet transport		B. Pressure drop	
1. Isothermal effectiveness factors	27, 29, 34	C. Radial mass and heat transfer parameters	
a. Pellet geometry		1. Effective diffusivities and thermal conductivities	
b. Reaction order		2. Wall heat-transfer coefficients	16
c. Criteria for absence of diff. retardation of rate	27	D. Axial mass and heat transfer parameters	
2. Non-isothermal effectiveness factors	27, 28	VII. Design of fluidized-bed reactors	22, 29, 30
3. Physical properties of porous catalysts	29	A. Mixing phenomena	
a. Surface area		B. Models of reactor behavior	
b. Pore volume, porosity		VIII. Miscellaneous reactor types	
c. Pore volume distribution		A. Gas-solid non-catalytic reactions	22, 24
4. Diffusion in porous media	27-29, 34	1. Global rate equations	
a. Bulk and Knudsen diffusion		2. Reactor design	
b. Surface migration		a. Well-mixed fluid phase	
c. Effective diffusivities		b. Moving fluid, stationary solid phase	
5. Heat transfer in porous media	27-29,	c. Moving fluid and solid phases	
a. Free molecule and normal conduction		B. Slurry reactors	28, 29
b. Effective thermal conductivity		1. Global rate equations	
6. Effect of poisoning on the global rate	34	2. Reactor design	
		IX. Non-ideal homogeneous reactors	15, 24, 25
		A. Nature of deviations from ideal flow	
		B. Measurement of residence-time distribution functions (RTD)	
		C. Modeling actual reactors with PFR and CSTR assemblies	
		D. Effect on conversion	

Teaching, understanding, and applying the principles of reactor design will long remain a major challenge . . . students benefit from thorough familiarity with one reasonably general book.

a discussion follows in which the wholly empirical nature of much practical rate data is noted, dealing as it so often does with complex and unanalyzed mixtures, empirical parameters such as research octane number, catalyst deactivation, trace poisons, etc.

Finally, a brief discussion of rate data for heterogeneous reactors, usually treated altogether by homogeneous transport models on a global scale, leads naturally into physical transport questions, that is, Section IV of Table I.

In Section IV effectiveness-factor concepts are first developed, and then their numerical evaluation is investigated. This approach leads conveniently to a discussion of physical properties of porous catalysts, followed by study of diffusion and heat transfer with the effective diffusivity and thermal conductivity the goal. External transport resistances complete this Section. Here care is taken to emphasize the relative importance of heat and mass transport effects for various types of heterogenous environments such as packed-bed, fluidized-bed, and slurry reactors.

The integral reactor design equations (Section V) are developed rather quickly and little attention is given to their application to isothermal examples. The students are assumed to have had prior experience with this in an undergraduate course. Somewhat more attention is given to non-isothermal cases, since time frequently prohibits adequate consideration of these at the undergraduate level. Particular emphasis is placed on reactor thermal stability. Stirred-tank reactor sequences are discussed briefly, and their use in modeling tubular reactors [e.g., ref. (14)] is noted.

Primary emphasis in Section V is placed on the phenomena which occur in packed-bed reactors. Again, particular attention is given to thermal effects, which Denbigh (15) has emphasized as "undoubtedly the biggest factor of uncertainty in the design of fixed-bed reactors at the present time." Quantitative analysis of these effects requires numerical values for radial and axial Peclet numbers for heat and mass transfer. Empirical correlations and theories for these quantities are discussed in Section VI.

Specific, but practically important, types of heterogeneous reactors are considered in Sections VII and VIII, with fluidized-bed systems singled out for particular emphasis. While gas-solid non-

catalytic and slurry reactors are the only ones listed in Section VIII, it is at this point that other specialized forms can be introduced.

The final subject is non-ideal flow in homogeneous reactors. The time spent here is dependent upon the background of the class. Practical situations where non-ideal flow has a significant effect upon conversion are stressed; for example, the CSTR with one or more internal cooling coils.

RESEARCH IN REACTOR DESIGN

A state-of-the-art graduate course will naturally bare the limitations of our present knowledge, as well as a variety of bypassed problems. A discussion of fluid-solid processes reveals many such areas, both for global rates and reactor design. The role of surface migration, inhomogeneity of catalysts, and heat and mass transfer in real solids are examples, for global rates, of research problems of chemical engineering interest. Work in this area often encounters unusual practical consequences. An interesting recent example is the report of Weisz (33) that catalyst attrition rates in a fluidized catalytic cracking unit can be greatly affected by intraparticle diffusion limitations in the cyclic formation and burnoff of coke deposits. In the design of non-adiabatic packed-bed reactors, uncertainties in the calculation of temperature profiles remain a major source of concern. The scale-up of non-catalytic fluid-solid reactors such as carbon black reactors and lime kilns is hindered because of lack of research on mixing patterns. Many computational difficulties remain in the design of integral reactors because of the complexity of boundary conditions in heterogeneous systems.

Research on the design and operation of reactors for treating both municipal and industrial waste water is of literally vital significance. Improvement in the operation of biological reactors for treating primary effluents is an urgent need. New schemes are needed for the treatment of secondary effluents, and the chemical-reaction route offers many advantages. The design of photochemical reactors, which offer a new kind of nonuniformity, that of the light intensity, is an area of active research.

Though by no means exhaustive, these research areas are illustrative of both the work basic to reactor design yet to be done and the demanding

practical needs of society which application of our knowledge of reactor design offers hope of meeting. Teaching, understanding, and applying the principles of reactor design will long remain a major challenge to chemical engineers.

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PROBLEMS (Cont'd from p. 217.)

$$\Delta G_{\text{products}} = \Delta G_{\text{azeo}} + \Delta G_{\text{acetone}} - \Delta G_{\text{azeo}}$$

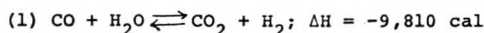
$$\Delta G_{\text{azeo}} = (1.99)(561) \left[\frac{(10)(39)}{61} \right] \ln(0.39)(1.9) + 10 \ln(0.61)(1.258) \\ = -5,050 \text{ Btu}$$

$$-W_r = \Delta G = \Delta G_{\text{products}} - \Delta G_{\text{feed}}$$

$$= -5050 + 18140 = 13090 \text{ Btu/100 moles feed}$$

No. 5. Badische Anilin and Soda-Fabrik AG of Ludwigshafen am Rhein give this data.

"Water-Gas Shift Reaction--Conversion of the carbon monoxide proceeds according to the expression:

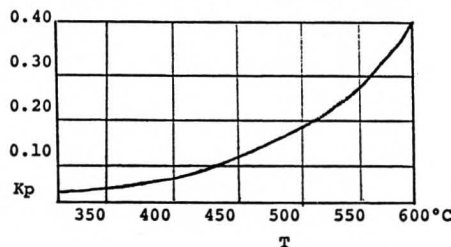


It is an equilibrium reaction with a temperature-dependent equilibrium constant,

$$(2) K_p = \frac{(\text{CO})(\text{H}_2\text{O})}{(\text{CO}_2)(\text{H}_2)}$$

The location of the equilibrium for a given gas composition is independent of the total pressure of the system." Also presented with the above statements is a graph which is reproduced below. Please study this information and demonstrate (a) by numerical calculations whether their data are concordant, and determine (b) the free energy change of the reaction at 500°C.

Temperature dependence of the equilibrium constant K_p



(Continued on page 226.)