A Course in

KINETICS OF CHEMICAL PROCESSES

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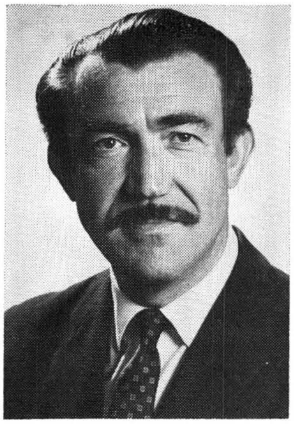

THE RATE OF CHEMICAL processes can be studied at four different levels. In practice, the chemistry of the process is most frequently disguised under transport phenomena. The study of the interaction between physical and chemical variables in the chemical reactor is the province of chemical engineering kinetics or chemical reaction engineering. This discipline emerged in the late thirties and blossomed up after the war. It is normally taught to chemical engineers at both undergraduate and graduate levels.

The success of this first approach, especially in the design of reactors, depends largely on knowledge that is obtained at subsequent levels dissection of the chemical processes. A second level of knowledge is that of the process unfettered from gradients of temperature and concentrations. Usually the process then consists of a network of single reactions in parallel and in series. To understand the network, it is necessary to understand its component single reactions and the kinetic study of single reactions constitutes the third level of endeavor.

Indeed, each single reaction takes place normally through a sequence of elementary steps and the dissection of the single reaction into its component steps is a formidable task in the study of all catalytic and chain reactions.

Finally, kinetic information on the isolated elementary steps themselves must be obtained for a complete knowledge of the entire process. The study of elementary steps is the domain of pure chemical kinetics dominated by the theory of the transition state or activated complex. However, with the rapid development of molecular beams and computational techniques, the classical aspects of chemical kinetics are replaced more and more by a complete description which is the object of the new molecular dynamics. Both classical chemical kinetics and molecular dynamics constitute the fourth and ultimate level of kinetic knowledge and these topics are normally taught in advanced physical chemistry courses.

CLEARLY THEN, there is a gap between the first and the fourth levels of kinetic knowledge that must be filled, especially for the education of chemical engineers. This gap I have attempted to fill by means of a textbook published in 1968 by Prentice Hall. This book can be followed closely in undergraduate courses. At the graduate level, it can be supplemented by reading assignments from the current literature in Journal of Catalysis, Transactions of the Faraday Society and Kinetics and Catalysis.

The purpose of the course is to provide the student with the judgment required to obtain, evaluate and improve rate equations that must be used in the design, operation and optimization of chemical reactors. With a proposed rate equation, the important question is not so much: "how well does it fit the data?" but rather: "what does it mean physically?".

To answer the latter question, it is necessary to scrutinize the numerical values of the parameters of the rate equation. Of even greater importance than activation energies and enthalpies of individual steps, are standard entropies of activation and reaction. The advanced student must become able to pass judgment on possible rate equations from such a physical standpoint. He must recognize the frailty of numerical analysis in deciding between alternative mechanisms. He must free himself from routine application of a limited number of types of sequences of elementary steps. A lot can be done in this field with a bare minimum of chemistry.

The general tools available to the student who wishes to gain confidence in kinetics rather than become an expert are few, but they are powerful if they are well understood. They are: the theory of the transition state, the steady state approximation, the concept of rate determining step, the

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concept of most abundant intermediate and the idea of interaction between single reactions in parallel or in series.

Transition state theory remains the workhorse of pure chemical kinetics in spite of the exciting but limited forays at the new frontier of molecular dynamics. The important realization here is first that calculations of activation energies are ruled out for some time to come but that very simple and reliable estimates of entropies of activation can be made for many elementary steps. Theory does not provide numbers that can be used for design. These numbers must, alas, always come from the experimental reactor. But theory provides a useful guide that permits us to accept or reject possible rate equations.

The steady state approximation is the second general tool and it is so good as a rule that the further qualifications of "quasi" as in quasi steady state approximation seems to be unnecessarily cautious. Nevertheless, interesting exceptions are known and their discussion in a graduate course is apt to stimulate the more mathematically gifted student.

OF GREAT VALUE but much more limited applicability is the concept of rate determining step. While this concept is not foreign to the chemical engineering student, it is usually misunderstood and it is of great importance to stress its meaning. Thus, it may come as a surprise to some students that it is still perfectly legitimate to talk about a rate determining step of a single reaction that has reached chemical equilibrium. Possible methods to assign a rate determining step are among the topics that are of interest to the more serious graduate students.

Another key idea which I have found particularly useful in the kinetic treatment of chain and catalytic reactions, is that of the most abundant intermediate. It is found frequently that among all the free radicals or adsorbed intermediates that take part in the sequence of steps, only one is "kinetically significant" because of its much larger concentration. Ways to predict such a situation and to take advantage of it, deserve proper attention and provide many useful illustrations.

FINALLY, WHENEVER a reaction network must be treated, it is essential to keep in mind that the rates of single reactions in the network may be different from the rates of these same reactions measured individually. This is due to the interaction between single reactions as a result of competition of reactants for the intermediates appearing in the various sequences. Many fascinating cases of such interactions are known among chain and catalytic reactions. With mixed feeds, as for instance in steam cracking, these effects can be very striking.

Besides these five key concepts, a graduate course in chemical kinetics for chemical engineers should also cover the following topics: branched chain reactions, nucleation and growth especially in reactions involving solids, wall effects, proper measurement of catalytic rates, the principle of microscopic reversibility, thermal ignition, inhibition and the kinetic use of tracers. All of these are likely to be encountered by the chemical engineer engaged in process research and development. If the student becomes imbued with the power and generality of these kinetic principles, a course in the Kinetics of Chemical Processes can be very rewarding. Indeed, I feel rather strongly that a course of this type is a bread and butter course for all graduate students of chemical engineering. It has been my experience over the past nine years, first at Berkeley where I originated it and then at Stanford, that the material is well received even by students who have little affinity for chemistry.