

Chemical Kinetics in Laboratory and Classroom

Chemical kinetics is a subject of such importance to chemistry that the teaching of it must of necessity permeate the entire curriculum. The student is introduced to rates of reaction in freshman chemistry (or better yet, in high school chemistry). The framework of kinetics is set forth in the usual physical chemistry course. Examples and more elaborate developments are presented in advanced courses on inorganic and organic chemistry. In spite of the ubiquitous nature of this subject, many institutions have found it advisable to supplement the above fare with a further more-or-less intensive helping of kinetics for the undergraduate. In the following I will present the experience at Berkeley in teaching selected aspects of kinetics in an undergraduate laboratory course on inorganic chemistry. Although the examples are chosen from inorganic systems, the methods are generally applicable.

The course consists of a one hour lecture once a week and two laboratory periods of 3 hours each. By no means is the course devoted entirely to kinetics: perhaps 75% of the lectures deal with kinetic problems but only about one-third of the laboratory work, the remainder being concerned with equilibria, stoichiometry, etc. The chief architect of this course was Professor William C. Bray to whom must go the major credit for its successes. Others who have participated in making substantial modifications are Professors Rollefson, Powell, and myself. Professor Powell particularly has influenced the lecture treatment.

The course content concerned with kinetics has practical objectives. The aim is to give the student a working knowledge which will enable him to plan, carry out, and interpret measurements on rates of reaction. It is hoped that the student will develop a clear understanding of kinetics and will learn to apply his knowledge readily whenever he deals with a rate of reaction.

The lectures start with various stratagems for finding the rate law from experimental data. Important in this connection is the proper planning of experiments so that the data can be readily and reliably applied to establishing the rate law. The technique of "flooding" is emphasized because of the simplification it ordinarily produces by reducing the rate equation to a power dependence on a single concentration. The student is shown how the complete rate law may be obtained even though the concentration of the same

substance is always kept small in the flooding procedure—a point which invariably gives some difficulty.

For cases where flooding is possible, concentration dependences and rate constants may be obtained readily by (a) substitution into the integrated rate law, (b) plotting in such a fashion as to yield a straight line (e.g., $\log(\text{conc.})$ versus time for a first order reaction), or (c) by a Powell plot.¹ Except for refined calculations, it is advantageous to use a plotting method so that all the data are displayed simultaneously. The importance of having an estimate of the experimental uncertainty of the data is stressed, particularly where one plots logarithms or reciprocals of measured quantities.

When flooding is not convenient experimentally, the rate equation is not so readily integrated and the correct rate law can usually be found more easily by use of the differential form. The student is given practice in this procedure by plotting concentration-versus-time data, taking the slopes at intervals, and substituting these values into various assumed rate equations in the differential form until the correct one is found.

Laboratory Experiments

The planning and interpretation discussed in the lectures is put into practice in the laboratory when the student determines the rate law for the following net reaction:



The reaction takes place in a few minutes at room temperature with reasonable concentrations and is accompanied by a readily observable color change. The student is instructed to carry out the measurements by preparing in a test tube a standard triiodide solution corresponding to a small fraction reaction of the peroxide, say 10%. He then observes by eye the time for the reaction to proceed this far in another test tube of the same size. By varying the concentrations of the reactants one by one he can find the order with respect to each and thus the form of the rate law.

It is obvious that the method of measurement used here is crude, yet it is intentionally so. The time for a certain per cent reaction may be obtained much more precisely by adding the appropriate amount of thiosulfate at the start of the experiment and observing the sudden appearance of the triiodide color when the $\text{H}_2\text{O}_2\text{-I}^-$ reaction has produced just sufficient triiodide to consume all of the thiosulfate. Our experience in using this latter procedure, however, was that the student centered his attention on the method of detection rather than the rate of reaction under study.

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¹ FROST, A. A., AND PEARSON, R. G., "Kinetics and Mechanism," John Wiley and Son, New York, 1961, p. 14.

The visual detection of a certain extent of reaction has additional advantages. The student learns that simple observations and particularly visual observations are important and can lead to useful conclusions. In the present case, after a few trials, he has little difficulty in obtaining times for reaction within $\pm 15\%$ of the correct values.

In interpreting the data the differential form of the rate law is used. A doubling of the iodide concentration leads to a halving of the reaction time for the same standard. It is desirable to give the student experience in handling the differential form since he is not apt to get it in the physical chemistry laboratory and because the physical meaning of the mathematical expression is more easily grasped with the differential than with the integrated form of the rate law. The student must think clearly about what to expect when he doubles his initial peroxide concentration but also doubles his blank to correspond to the same fraction reacted.

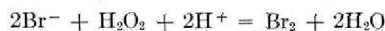
The student is instructed to determine the hydrogen ion dependence from *ca.* 10^{-5} to *ca.* $0.5M$ H^+ . Since the rate law is²

$$+ \frac{d[I_3^-]}{dt} = k_1[H_2O_2][I^-] + k_2[H_2O_2][I^-][H^+]$$

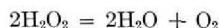
he undergoes the rewarding experience of interpreting an apparent non-integral concentration dependence.

As an extra experiment the student may elect to measure a heat and entropy of activation.

In another laboratory experiment the student learns something of the nature of steady states through the study of the catalytic decomposition of hydrogen peroxide by the Br^- - Br_2 couple.³ The two reactions bringing about the steady state are



The net reaction at the steady state, where the above two rates of reaction are equal, is the sum, i.e.



In qualitative experiments the student first demonstrates that a steady state is approached from either side, i.e., by starting with peroxide and bromide or with peroxide and bromine, both in acidic solution. In quantitative experiments he determines the value of the steady state quotient R which has the form

$$R = \frac{[Br_2]}{[H^+]^2[Br^-]^2}$$

as a consequence of the rate laws for the two reactions. The distinctions between a steady state and an equilibrium are discussed.

In many minor experiments in the laboratory the student encounters reactions which do not occur in a reasonable length of time. He is faced with the two possibilities: the reaction is slow or the equilibrium is unfavorable. In most cases he can decide about the position of the equilibrium through available data on equilibrium constants, free energies, emf's, or heats and entropies.

² See for example LIEBHAFSKY, M. A. AND MOHAMMAD, A., *J. Am. Chem. Soc.*, **55**, 3977 (1933).

³ BRAY, W. C. AND LIVINGSTON, R. S., *J. Am. Chem. Soc.*, **50**, 1654 (1928); **45**, 1251, 2048 (1923). LIVINGSTON, R. S., *J. Am. Chem. Soc.*, **48**, 53 (1926).

Topics Discussed in Lectures

A substantial section of the lecture material considers what can be deduced about mechanisms from rate laws—and what cannot be deduced. For a simple, single-term rate law the formula of the activated complex corresponds to the stoichiometry of the rate law, plus or minus solvent, provided only a single activated complex controls the rate.⁴ From the form alone of such a rate law the existence of equilibria before the rate determining step can be concluded only if one or more of the concentrations has a negative or fractional exponent. Generally the conclusion that there is an equilibrium before the rate determining step does not lead to an unambiguous identification of that equilibrium. The above statements depend on the assumption that a single activated complex controls the rate. When more than one activated complex is involved the interpretation is more complicated.

Basically two complex forms of rate law exist: the multiple term numerator and the multiple term denominator. When concentrations are expressed in terms of actual species present, these two forms have the simple physical interpretations of parallel reactions for the first and non-productive step(s) competing with a productive step for the second. The student is given practice in postulating mechanisms for such cases. The idea of the steady state approximation enters here. Stress is laid on the exact nature of the approximation and the fact that it does not lead to a constant concentration of intermediate.

Chain reactions are considered briefly. Rate laws are derived from mechanisms but the more difficult task of finding mechanisms from rate laws is only mentioned.

At this point the student is assigned a paper in the literature and is required to write a brief criticism of it. The paper chosen contains an unusual number of errors, both fundamental and trivial. For the good students this is a valuable experience in pitting their intellect against that of the authors. For all of the students it serves as an invaluable demonstration of the care which one must exercise in accepting conclusions even though they are in printed form.

The deduction of the reverse rate law from a combination of the forward rate law with the equilibrium expression is carried out along with a discussion of the principle of microscopic reversibility. The ambiguity in the derived rate law is considered and it is shown how the experimental determination of a single parameter for the reverse reaction, such as the exponent of one concentration or the ΔH^\ddagger for the reverse reaction, suffices to remove the ambiguity. It is also pointed out that the removal of this ambiguity gives additional mechanistic information, i.e., the number of reactant molecules disappearing for each activated complex.

Electrolyte effects are considered briefly in terms of the Brønsted equation derived from activated complex theory. Reference is made to useful approximations for estimating activity coefficients of ions outside of the Debye-Hückel region and attention is paid to the uncertainty in such estimates.

⁴ There is an unimportant exception to this rule which may occur when two or more intermediates have concentrations proportional to each other or to some power of each other.

A discussion is given of the maximum rate possible for a bimolecular reaction in a solvent such as water. The available experimental results are shown to be in substantial agreement with these expectations. The concept of a limiting rate is useful in proving that certain mechanisms cannot possibly account for observed rates, and examples are considered.

It is shown how the rates of dissociation of acids and

bases may be estimated. It is now well established that hydrogen and hydroxide ions ordinarily react with bases and acids at approximately diffusion-controlled rates. Combining these estimated rates with the equilibrium constant for dissociation one has an estimate of the rate constant for dissociation. It is instructive to the student to learn how slowly water dissociates.

