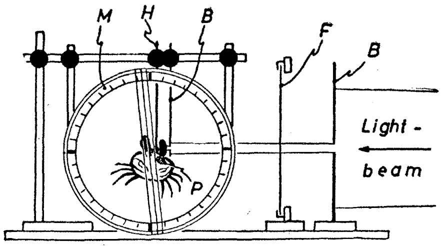

Fig. 1. Method of measuring the angle (α) between the right eyestalk axis and a horizontal plane when a small essentially parallel light beam stimulates the left eye laterally. *B*, diaphragm; *F*, linear polarizer; *H*, clamp; *M*, protractor; *P*, paraffin fixing the left eye.

hypothesis varied from .001 to .0001) with vertical polarization than with horizontal polarization of the same photometric intensity. On the average vertical polarization was more effective by 6°.

The intensity ratio ($I_1 : I_2$) of unpolarized light required to match approximately the differences in eyestalk deviations ($\alpha_v - \alpha_h$) evoked by the two polarization planes was found in a few experiments on one individual to be 3:1. For these results I_1 was about 800 lux, $\alpha_v - \alpha_h$ was 5.6° and $\alpha_{I_1} - \alpha_{I_2}$ was 5.2°. Variance of the readings was such that the differences in eyestalk deviations were significant in the two cases.

Because of the care taken to eliminate intensity artifacts, the observed difference in the effectiveness of the two planes of polarized light may be taken as evidence that the eye itself was acting as a polarized light analyzer. Earlier attempts to demonstrate polarized light sensitivity in decapod crustaceans have provided one somewhat doubtful report (*17*) or negative results (*5*); but since the present work was completed, extensive positive data have been obtained on orientation responses to polarized light by many kinds of decapods (*8, 18*). Also, previous efforts to demonstrate differential phototactic effects of vertically and horizontally polarized light failed with *Tenebrio* larvae, the beetle *Tetraopes*, and the terrestrial isopod *Cylisticus* (*19*).

At present neither the mechanism nor the biological significance of the polarized light responses reported here is known. Either a peripheral or central origin is possible for the observed lack of radial symmetry in sensitivity to plane of polarization (*5, 20*). In the insect *Notonecta*, a bilateral symmetry of the ommatidium is apparently involved since the amplitude of the electroretinogram in this plane of symmetry is about 22 percent greater than with the *e*-vector 90° away (*11*). The only hypothesis for the mechanism of polarized light sensitivity consistent with the known facts requires individual retinular cells to be differentially sensitive to *e*-vector positions (*3, 5, 10–12, 21*). In dipteran insects, intracellular electrodes have demonstrated the required type of photoreceptor element (presumably a single retinular cell) with response maxima and minima to plane polarized light 90° apart (*12, 21*). The intensity differences necessary to match these maxima and minima are rather similar to those found in the present data (*22*).

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9 March 1961

General Method of Plotting Kinetic Data for Reactions of Any Order

Abstract. A method is presented for obtaining from kinetic experiments both order of reaction and rate constant by means of a single straight-line graph, in contrast to previous methods, which require several steps including more than one graph or repeated trial-and-error calculations whenever there is no prior knowldege of the order of reaction.

Commonly used methods for evaluating reaction rate constants from experimental data either presuppose a knowledge of the reaction order or proceed by assuming an order in trial-and-error fashion. If, as frequently happens with complex and fractional-order reactions, the correct assumption is not made on the first trial, the computations can become tedious. This is true also of the direct determination of orders by the differential method of van't Hoff, which requires at least two separate plots as well as measurements of slopes often difficult to obtain with precision. Other direct methods, utilizing half-life periods or initial velocities for a series of reactant concentrations, are dependent on the availability of these additional experimental data for different initial concentrations.

All these procedures share the shortcoming of requiring a combination of several steps or plots before both order and rate constants can be evaluated. If the requisite number of trials is not made, the lack of sensitivity with respect to order inherent in some of these methods (for instance, the same set of data may give reasonably straight appearing lines if plotted according to the equations for more than one reaction order) can be the cause of inaccurate or misleading statements of the "order" of a reaction (see *1*).

These considerations make it desirable to find a way of obtaining both kinetic constants in a single step. Referring to the general differential equation for a simple reaction

$$dx/dt = k(a - x)^n \qquad (1)$$

(where a is the initial concentration; x is the amount reacted, in the same concentration units as a; t is the elapsed time; k is the rate constant; and n is the order of reaction), it does not appear unreasonable to search for a straight-line plot of some suitable simple functions of the reaction variables such that the two parameters of the line (slope and intercept) would uniquely determine the two constants

(n and k) of the differential equation.

Through a heuristic approach guided by somewhat analogous relationships in other branches of physical science, a graphical treatment of data has been devised which essentially accomplishes this end (*2*). It is convenient here to follow the reaction in terms of the fractional extent of reaction, $f = x/a$, and to introduce a new variable termed "unit reaction time," defined as the ratio t/f. By appropriate algebraic manipulation of the integrated form of Eq. 1, using series expansions, one can express unit reaction time as a series in t,

$$\frac{t}{f} = \frac{1}{a^{n-1}k} + \frac{n}{2}\,t + \frac{n(2-n)}{12}a^{n-1}kt^2 + \ldots \quad (2)$$

It is seen that for $n = 2$ a plot of unit reaction time versus elapsed time is a straight line; for $n \neq 2$, the plot is found not to deviate greatly from a straight line at moderate values of f (for example, $f = 0.25$). Extrapolation toward $t = 0$ usually is a sufficient approximation to the tangent at the ordinate intercept and yields the information of interest: the reaction order is obtained directly from

$$\text{Initial slope} = n/2, \quad (3)$$

and k (with n and a known) is obtained from

$$\text{Ordinate intercept} = 1/(ka^{n-1}). \quad (4)$$

A longer paper containing the derivation of these relationships, together with a discussion of the limitations to which this treatment is subject, is in preparation. It may be mentioned here that, by its nature, the method is particularly sensitive to the early points of the reaction. Thus it is relatively little affected by the occurrence of consecutive or opposing reactions; however, timing errors due to uncertainty of the start of the reaction may introduce considerable curvature into the beginning of the plot. With suitable modifications the method is then still usable provided the curve straightens out sufficiently before the reaction is affected appreciably by other complicating factors, such as side reactions. In unfavorable cases, additional kinetic data for different initial concentrations may be needed for an unambiguous determination of the order. Such eventualities are no reflection on the method, inasmuch as defects in the data would affect any other method also, though without always giving as clear an indication of their presence.

The method can be made applicable also to certain complex reactions and to reactions between reactants at unequal initial concentrations.

Plots (*A*) and (*B*) of Fig. 1 provide an example of the treatment of an identical set of data by a conventional method and by the present method, respectively (*3*). In plot (*A*), $n = 2$ has been *assumed* in plotting $1/(a - x)$ against t, to obtain a value of $k = 11.74$ lit.·mole^{-1}·min^{-1}. (*B*), the plot of t/f against t, has a slope of 0.994, indicating $n = 2$, by Eq. 3; from the intercept, 8.64 min, and $a = 0.100$ mole/lit., k is then found to be 11.58 lit.·mole^{-1}·min^{-1}, by Eq. 4. Because different ways of plotting are mathematically equivalent to differing weighting of the experimental points, results in other cases may be in less close agreement, but at least a fair approximation for k can usually be expected from this simple and rapid method.

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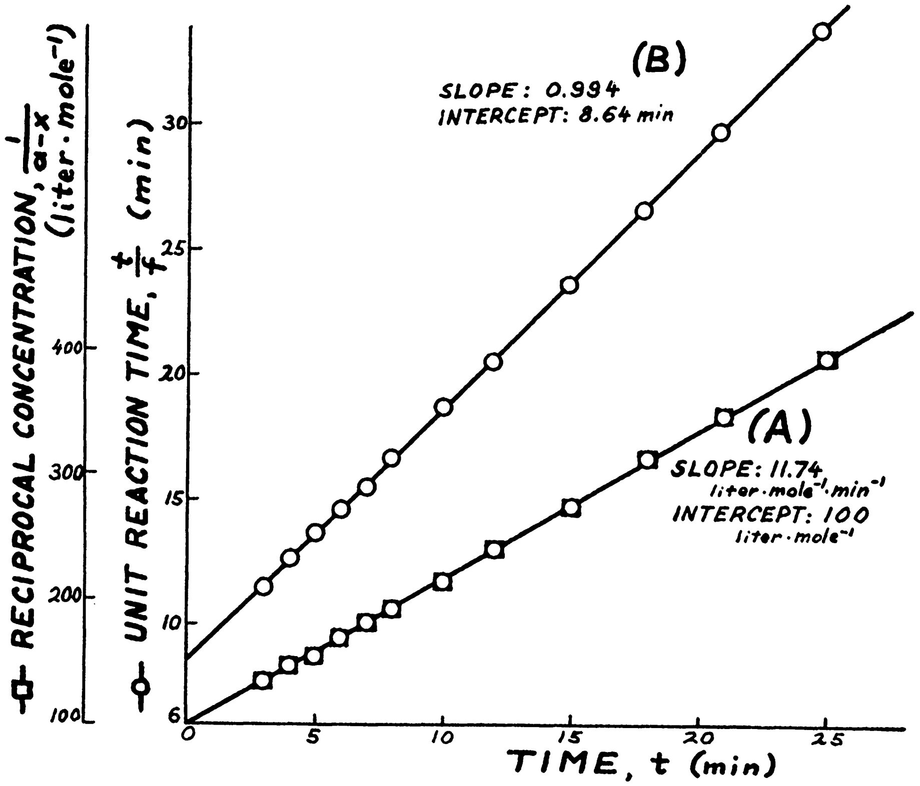

Fig. 1. Kinetics of saponification of methyl iodide by sodium hydroxide, at equal initial concentrations of 0.0100 mole/lit. Plot (*A*), conventional method, according to integrated form of second-order equation. Plot (*B*), "unit reaction time" method, without prior knowledge of order.

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2. In investigating this subject, I have become indebted to Robert Blum and to Gail L. Miller for valuable comments, to Warren Watanabe for communicating an independent and somewhat divergent development of substantially the same topic, and to Serge Gratch for a generous contribution of helpful discussion. The topic first came up for attention in late 1951 and was made the subject of a seminar presentation by me at Temple University on 14 May 1952. Mimeographed abstract copies were distributed at the time and have been on record since then at the chemistry department library. Journal publication, however, was delayed, because it was felt that it should await a thorough exploration of the limitations and modifications referred to, for which time and opportunity were then lacking. Recent revival of interest in the method on the part of a number of workers in these laboratories has prompted the conviction that in view of its potential utility publication should be delayed no longer.
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