in many sorption processes must involve activation energies frequently of a considerable magnitude. It was at first thought that the rate determining step was the approach of the gas molecule to the surface. That such could not universally be true was indicated by the work of Pace and Taylor[8] and by that of Kohlschuetter[9] demonstrating that, at a pressure of one atmosphere and within limited temperature ranges, hydrogen and deuterium were adsorbed with the same velocity on zinc chromite, nickel, and chromium oxide gel, and by the work of Burwell and Taylor[10] on the effect of pressure on the rate of the activated adsorption of hydrogen on chromium oxide gel.

Garner[6,11] has recently reiterated the contention that in general the slow process in activated adsorption is the "diffusion" of the gas down capillaries from an initial rapid adsorption, a view that derives initially from Ward.[12] The application of the term "diffusion" to the suggested mechanism is misleading since whereas true diffusion increases with the temperature as $\sqrt{T}$, the hypothesized "diffusion" of Ward and Garner increases very much more rapidly. Lennard-Jones[13] has shown that to account for the large temperature coefficient it is necessary to assume that before diffusion can take place, a molecule must be raised from its initially adsorbed state to a higher energy level. While the process proposed by Lennard-Jones may occur in some instances, it cannot be a general one. For this hypothesis requires that the amount of adsorption be initially proportional to the square root of the time, a relation which rarely fits time–adsorption data. Further, such a picture is unable to account for the identity of the rates of adsorption of hydrogen and deuterium on the catalysts mentioned previously.

Summary

Experiments are reported which indicate that: (1) carbon monoxide is decomposed in the sense of the equation, $2CO \longrightarrow C + CO_2$, on surfaces of zinc oxide at temperatures above 184°. (2) Carbon deposited on the catalyst is removed by hydrogen at temperatures of 184° and above, presumably as methane.

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[8] Pace and Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

[9] Kohlschuetter, *Z. physik. Chem.*, **A170**, 300 (1934).

[10] Burwell and Taylor, THIS JOURNAL, **58**, 697 (1936).

[11] Garner and Veal, *J. Chem. Soc.*, 1487 (1935).

[12] Ward, *Proc. Roy. Soc.* (London), **A133**, 522 (1931).

[13] Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Calculation of Second Order Reaction Velocity Constants

BY JULIAN M. STURTEVANT

Introduction.—In the application of physical methods to the determination of reaction velocities the observed quantity is usually a property of the reacting system which varies linearly with the concentrations of the reactants and products. To evaluate the two constants involved in this linear relation it is, in general, necessary to obtain the values of the observed property at the start and finish of the reaction. In many cases it is impossible to obtain these values reliably; for example, if the reaction is being followed by observation of the temperature changes resulting from the heat evolved in the system under adiabatic conditions, there would obviously be serious experimental difficulties in obtaining the temperature of the system at the completion of the reaction.

A method of calculation which eliminates these difficulties in certain cases has been described by Roseveare.[1] This method involves the analytical or graphical elimination of the "infinity reading." As pointed out by Roseveare, this method has the further advantage of not giving undue weight to the infinity reading in cases where it cannot be obtained with any greater accuracy than the other readings. Roseveare discussed the application of the method to first order reactions and to second order reactions in which the initial concentrations of the reactants are equal.

In extending the method to more complicated reactions one finds that the algebraic treatment becomes excessively cumbersome. In the present communication it will be shown that these difficulties are avoided by a simple application of the methods of projective geometry. In the course of this treatment there will be developed a very easily applied test as to whether a given set of

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[1] Roseveare, THIS JOURNAL, **53**, 1651 (1931).

experimental data follows a certain kinetic equation.

Kinetic Equation.—The general equations[2] for several types of reactions may be written in the form

$$kt = \ln c \frac{a - x}{b - x} \qquad (1)$$

where k is proportional to the velocity constant, $a \neq b$, c are constants, and x is the extent of the reaction at time t, or some quantity varying linearly with it. If $x = x_0$ at $t = 0$, $c = (b - x_0)/(a - x_0)$. Included among the types of reactions following this equation are bimolecular irreversible and reversible reactions (reverse reaction also bimolecular) in which the concentrations of the reactants are not equal, autocatalytic bimolecular irreversible reactions, and trimolecular irreversible reactions in which one reactant is a catalyst or its concentration is much greater than those of the other two reactants.

In equation (1) the constants a, b, c will in general involve the initial concentrations of the reactants, the equilibrium constant for the reaction if it is reversible, and x_0 and x_∞, the value of x at $t = \infty$. Our problem is to determine k from the observed values of x without using x_0, x_∞.

Determination of ***k, a, b, c.***—Proceeding in a manner analogous to that recommended by Roseveare[1] for first order reactions we suppose readings x_1, x_2, x_3, x_4 are taken at t, $t + \Delta t$, $t + 2\Delta t$, $t + 3\Delta t$, readings x_1', x_2', x_3', x_4' at t', $t' + \Delta t$, $t' + 2\Delta t$, $t' + 3\Delta t$, and so on. Substitution of these values in equation (1) and subtraction gives a series of simultaneous equations

$$\frac{(a - x_2)(b - x_1)}{(a - x_1)(b - x_2)} = \frac{(a - x_3)(b - x_2)}{(a - x_2)(b - x_3)} = \frac{(a - x_4)(b - x_3)}{(a - x_3)(b - x_4)} = \frac{(a - x_2')(b - x_1')}{(a - x_1')(b - x_2')} = \ldots \equiv \alpha = \text{constant} \qquad (2)$$

from which a, b may be determined in terms of x_1, x_2, . . . Substitution of these values in any of the equations

$$k\Delta t = \ln \frac{(a - x_2)(b - x_1)}{(a - x_1)(b - x_2)} = \ldots = \ln \alpha \qquad (3)$$

would enable us to obtain k. However, treatment of equations (2) by the usual algebraic methods leads immediately to cumbersome equations the simplification of which is difficult.

The observation[3] that the quantity $\frac{a - x_2}{b - x_2} \Big/ \frac{a - x_1}{b - x_1}$ is the so-called anharmonic ratio[4] or cross-ratio of the range of points a, b, x_2, x_1 suggests that the methods of projective geometry may find application here.

The anharmonic ratio of a range of four collinear points, P_1, P_2, P_3, P_4 may be defined as

$$[P_1P_2P_3P_4] = \frac{P_1 - P_3}{P_2 - P_3} \times \frac{P_2 - P_4}{P_1 - P_4} \qquad (4)$$

In this notation equations (2) become

$$[abx_2x_1] = [abx_3x_2] = [abx_4x_3] = [abx_2'x_1'] = \ldots = \alpha \qquad (5)$$

If we consider a, b as fixed points on a line the position of any other point P_i on the line is fixed by the ratio

$$\alpha_i = (a - P_i)/(b - P_i) \qquad (6)$$

It is easily shown that $[abP_iP_j] = \alpha_i/\alpha_j$, so that equations (5) become

$$\alpha = \frac{\alpha_2}{\alpha_1} = \frac{\alpha_3}{\alpha_2} = \frac{\alpha_4}{\alpha_3} = \frac{\alpha_2'}{\alpha_1'} = \ldots \qquad (7)$$

Using equations (6) and (7) and the definition of the anharmonic ratio we readily find that

$$[ax_1x_2x_3] = [ax_2x_3x_4] = [ax_1'x'x_3'] = \ldots = 1 + \alpha^{-1} \qquad (8)$$

$$[bx_1x_2x_3] = [bx_2x_3x_4] = [bx_1'x_2'x_3'] = \ldots = 1 + \alpha \qquad (9)$$

and

$$-[x_3x_1x_2x_4] = -[x_3'x_1'x_2'x_4'] = \ldots = \alpha + 1 + \alpha^{-1} = \text{constant} \equiv A \qquad (10)$$

Equation (10) gives us a simple method for calculating k and a criterion as to whether experimental data follow equation (1). Evidently

$$\alpha = \frac{A - 1}{2} \pm \sqrt{\left(\frac{A - 1}{2}\right)^2 - 1} \qquad (11)$$

where

$$A = \frac{(x_3 - x_2)(x_4 - x_1)}{(x_2 - x_1)(x_4 - x_3)} = \frac{(x_3' - x_2')(x_4' - x_1')}{(x_2' - x_1')(x_4' - x_3')} = \ldots > 3 \qquad (12)$$

so that

$$k\Delta t = \ln \alpha = \cosh^{-1}((A - 1)/2) \qquad (13)$$

According to equation (12) data which conform to equation (1) should give a constant value of $A > 3$. This test of the conformity of the data requires no knowledge of the concentrations of the reactants and, as stated before, x may be any quantity varying linearly with the concentrations.

From the value of A the constant k may be calculated. The determination of the sign of the radical in equation (11) offers no difficulty, since

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[2] See the summary of equations, Vol. II, in "*Treatise on Physical Chemistry*," edited by H. S. Taylor, D. Van Nostrand Company, New York, 1931, p. 960.

[3] The author is indebted to Professor H. T. Engstrom of the Department of Mathematics for suggesting the use of projective geometry in this problem.

[4] See, for example, "*The Principles of Projective Geometry*," by J. L. S. Hatton, Cambridge University Press, 1913.

the quantity with the plus sign is the reciprocal of that with the minus sign, and one can readily tell whether $k\Delta t$ should be positive or negative. Unfortunately there will be a serious magnification of errors in cases where A is not much larger than 3, since α varies rapidly with A in this vicinity. Means of avoiding this difficulty are described below. In passing it may be pointed out that expansion of the inverse hyperbolic cosine gives the expression

$$k^2\Delta t^2 = (A - 3)\ [1 - (A - 3)/12 + \ldots] \quad (14)$$

In cases where α may be calculated accurately by this method we may evaluate a, b from equations (8) and (9)

$$a = \frac{\alpha x_1(x_3 - x_2) - x_3(x_2 - x_1)}{\alpha(x_3 - x_2) - (x_2 - x_1)}, \qquad b = \frac{x_1(x_3 - x_2) - \alpha x_3(x_2 - x_1)}{(x_3 - x_2) - \alpha(x_2 - x_1)} \quad (15)$$

and similar equations involving the other x's. Also c is readily obtained from equation (1)

$$c = \frac{\alpha(x_3 - x_2) - (x_2 - x_1)}{(x_2 - x_2) - \alpha(x_2 - x_1)}\ \alpha^{(t + \Delta t)/\Delta t} \quad (16)$$

In such cases it would thus be possible in general to evaluate one of the initial concentrations or the equilibrium constant from the observed data, in addition to x_0 and x_∞.

The magnification of errors involved in equation (11) in many cases may be avoided by using the experimentally determined values for the initial concentrations (and the equilibrium constant if the reaction is reversible). In general it will be possible to calculate one of the quantities a, b, c (or some combination of them) accurately from the known initial concentrations. Then one merely has to calculate α from the appropriate one of equations (15) and (16) (or the appropriate combination of them). If c is the constant whose value is considered as being accurately known, α will have to be calculated by successive approximations, the first of which may be obtained from equation (11).

In connection with this method of calculation two things may be pointed out. It is only necessary to have three readings x_1, x_2, x_3 in each set so that the time interval Δt may be taken larger. Also, in cases where α is very sensitive to the value of A, there will be a corresponding sensitivity of c and either a or b to α, so that the value of α may be obtained accurately.

It may be emphasized again that this extension of Roseveare's method of calculation will be of greatest importance in cases where it is physically impossible to obtain initial or final values of x. For example, in the determination of reaction velocities by following the rate of heat evolution[5] it will evidently be out of the question to observe directly either the value of x_0 because of the heat of mixing, or of x_∞ because of calorimetric difficulties. On the other hand, the concentrations of the reactants at $t = 0$ will be known from the make-up of the reacting solution with an accuracy great enough to warrant their use in the manner described above. As a matter of fact, if it is possible to make the original observations at uniform time intervals, the present method of calculation may result in a considerable saving of time even in cases where initial and final values of x can be obtained with good accuracy, both in enabling one to cease observations before the reaction is finished and in simplifying the calculations.

Example.—The data of Harned and Pfanstiel[6] for the bimolecular reversible hydrolysis of ethyl acetate catalyzed by acids have been treated by the above method. These data follow equation (1) very closely when calculated in the usual way.

In this particular case of a bimolecular reversible reaction the constants k and c are given by

$$k = K\sqrt{(A - B)^2 + 4ABC} \quad (17)$$

$$c = \frac{A + B + \sqrt{(A - B)^2 + 4ABC}}{A + B - \sqrt{(A - B)^2 + 4ABC}} \quad (18)$$

where A, B are the initial concentrations of water and ester, K is the velocity constant (natural logarithms) and C is the equilibrium constant. Naturally k and c have different values with reactions of other types. The quantity x in this case is the titer of the reacting solution, and may be observed in terms of alkali of unknown strength. Since there is acid present as catalyst $x_0 > 0$.

The experimental data[7] given by Harned and Pfanstiel for one run were plotted on a large scale, and four sets of values of x were read off the plot, with $\Delta t = 300$ minutes. These sets gave the values $A = 3.153$, 3.144, 3.142, 3.110. The trend observed here is possibly somewhat outside the experimental error, though it should be observed that the quantity $x_4 - x_3$ (≈ 13) is the difference of considerably larger quantities (≈ 60). At any rate, it is obvious that a satisfactory value of K could not be otained from these readings. The

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(5) This method of determination will be the subject of a future communication.

(6) Harned and Pfanstiel, THIS JOURNAL, **44**, 2194 (1922).

(7) The quantity recorded by Harned and Pfanstiel is $x - x_0$, but since only differences in x appear in the calculations we may use $x - x_0$ in place of x.

mean value of A leads to $K = 2.20 \times 10^{-5}$, while Harned and Pfanstiel found $K = 2.342 \times 10^{-5}$. It is thus necessary to calculate K from the known value of c. The constants a, b involve x_0, x_∞ and therefore cannot be used.

Four sets of three readings each were interpolated with $\Delta t = 400$ minutes. From these sets, together with the value $c = -39.86$ calculated from the initial concentrations and equilibrium constant, the values $\alpha = 1.701$, 1.700, 1.698, 1.691 were calculated by successive approximations. The trend here, amounting to a total of 0.6%, may be partially due to inaccuracies introduced by the graphical interpolation. From the mean value of α one obtains $K = 2.365 \times 10^{-5}$, which is 1% higher than the value of Harned and Pfanstiel. This method of calculation eliminates the necessity of calculating the initial and final values of the titer as done by Harned and Pfanstiel. It should be emphasized that the value of α would be changed by less than 0.1% by a change of 5% in c.

Summary

An application of the methods of projective geometry to a series of measurements of a property x (of a system reacting in accord with the kinetic equation $kt = \ln c\ (a - x)/(b - x)$) which varies linearly with the progress of the reaction, taken at uniform time intervals, Δt, gives the result

$$A \equiv \frac{x_3 - x_2}{x_2 - x_1} \times \frac{x_4 - x_1}{x_4 - x_3} = 1 + 2 \cosh (k\,\Delta t)$$

By means of this result the necessity of obtaining initial and final values of x is eliminated.

The method is illustrated using the data of Harned and Pfanstiel on the hydrolysis of ethyl acetate.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY, HARVARD UNIVERSITY]

The Atomic Weights of Some Radiogenic Leads

BY G. P. BAXTER, J. H. FAULL, JR.,[1] AND F. D. TUEMMLER

In connection with the programs of the Committee on Geophysical Research of Harvard University and the Committee on Determination of Geologic Time of the National Research Council the atomic weights of some new specimens of radiogenic leads have been determined.

Samarskite from Glastonbury, Connecticut, U. S. A.—The original ground sample, weighing 1130 g., had been cleaned by gravity and magnetic methods by Mr. Harry Berman of the Harvard Mineralogical Laboratory. A preliminary analysis of a part of this material by R. C. Wells[2] shows 6.91% uranium, 3.05% thorium, 0.311% lead.

Treatment with redistilled hydrofluoric acid in platinum followed by repeated evaporation with nitric acid to remove the hydrofluoric acid and extraction of the insoluble residue with nitric acid, all in platinum, was carried out by Dr. C. M. Alter. The nitric acid solution on standing for several months deposited much columbic acid (40 g.). The dried insoluble residue weighed 970 g. This residue was found spectroscopically to contain most of the lead.

Lead was separated from the nitric acid solution by double precipitation of basic acetates and treating the filtrates with hydrogen sulfide. The original insoluble residue and that which separated from the nitric acid solution were digested for long periods with redistilled hydrochloric acid and the lead precipitated from the extract after neutralization with ammonium acetate. About 0.1 g. of lead was obtained from the extract, 1.6 g. from the insoluble residues, together representing about half the lead content of the original mineral.

Purification included the following processes: conversion of sulfide to sulfate through the chloride, solution of the sulfate in ammonium acetate and reprecipitation with hydrogen sulfide, solution of the sulfide in hydrochloric acid and conversion of the chloride to nitrate by repeated evaporation with nitric acid, four recrystallizations of the nitrate from nitric acid in quartz, conversion of nitrate to chloride with hydrochloric acid in quartz, four recrystallizations of chloride in quartz, and distillation of the chloride in dry hydrogen chloride in a quartz tube. All the product was used in one analysis. Lead was recovered from the solution of lead nitrate resulting from the first analysis and from the mother liquors remaining from the purification by precipitation as sulfide, and after conversion to the nitrate through the chloride it was re-purified as above.

Beaverlodge Lake Pitchblende.—This specimen was collected and contributed by Dr. Fred Joliffe from a quartz vein near Beaverlodge Lake, Northwest Territories, Canada, about one hundred miles south of Great Bear Lake. The mineral consists chiefly of an intimate mixture of pitchblende and specularite. Weighted averages from analyses of five lots of similar material, representing 3000

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(1) Research Associate in Geology in Harvard University, 1935. The present work is Paper No. 33 published under the auspices of the Committee on Geophysical Research and of the Division of Geological Sciences at Harvard University.

(2) R. C. Wells, Reports of the Committee on Determination of Geologic Time, of the National Research Council, April, 1935, and Sept., 1936.