to be adequate reason for believing that the communicative dance of bees represents a highly evolved form of primitive search pattern which is innate and stereotyped. There are many dances of bees, such as some of the transitional dances and dances signifying food close at hand [for example, the "pull dances" described by Hein (*6*) and the "sickle dances" described by Lindauer (*15*)], which are less stylized and uniform than the more widely publicized figure-of-eight waggle dances. Thus there appear to be all gradations between excited gyrations and organized dances in the Western honey bee, and from one species of bee to the next. It is not unreasonable to expect that these locomotory responses would be casually related to stimulation by food substances. Since taste threshold is clearly related to energy expended, taste stimulation offers a unique mechanism for a sensory measurement of expenditure.

Because the honey bee is a member of a complexly organized society there is frequently a tendency to regard it as a unit whose actions are subordinated to the needs of that society. Inherent in this view is the danger of considering the insect society as a superorganism (and indeed this view has at times been expressed in the classical literature) and, more dangerous still, of overlooking the physiology of the individuals which constitute the society. The point is well illustrated by the mode of thinking which treats the crop or honey sac of the honey bee as community property which the bee dutifully fills in the field and as dutifully empties in the hive. The fact of the matter is that the crop of the honey bee is as much its own as that of the blowfly is its own. In both insects it is a place of storage, since both insects gorge themselves to repletion upon finding food. Both species use the contents of the crop freely for their own requirements. As postingestion time lengthens, the contents of the crop are directed to the mid-gut for the individual's own metabolism, and as the insects fly the contents are used as fuel. In both species there is a tendency to regurgitate when the crop is full.

In many respects, if the physiology and behavior of the individual are considered, much of colonial life seems to have its basis in stereotyped aspects of behavior which are seen to be fully developed in solitary insects but which have been adapted for the special needs of colonial life and for cohesiveness of the colony. But the physiological requirements and behavior patterns of the individual are not thereby abrogated. The parallelism between the "dancing" of the fly and the dancing of the honey bee is a case in point. The fly and the bee alike are moved to dance by an innate response to a taste stimulus. In both insects the intensity of the taste stimulus is modified by the individual's nutritional state (*16*).

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Useful Application of Bronsted Catalysis Law

G. M. Steinberg, R. Swidler, S. Seltzer

In several studies on the reaction between isopropyl methyl phosphonofluoridate (Sarin) and nucleophilic agents where these agents have been the anions of families of weak acids such as the catechols (*1*), hydroxamic acids (*2*), and oximes (*3*), it has been observed that, within each family of weak acids, a linear free-energy relationship of the Bronsted type (*4, 4a*)

$$k = G_B K_B{}^{\beta} = G_B \left(\frac{K_w}{K_A}\right)^{\beta} \qquad (1)$$

exists between the rate of reaction and the ionization constant. In each case, the reaction was kinetically of the second order and was found to fit the following equation.

$$\frac{dx}{dt} = k\,[\text{Sarin}]\,[\text{anion}] \qquad (2)$$

In this reaction, 1 mole (or in some cases 2) of nucleophilic agent was consumed per mole of Sarin. However, if the nucleophile was maintained in large excess over the Sarin, the observed rate of the over-all reaction was first order, with the rate directly related to the concentration of anion. Under these conditions, the rate constant, $k_{\text{obs.}}$, is defined by

$$k_{\text{obs.}} = k\,[\text{anion}] \qquad (3)$$

Epstein, Rosenblatt, and Demek (*1*) have shown, in connection with their study of the rates of reaction between various catechols and Sarin, that, in aqueous solution under conditions of fixed *p*H and total concentration of reactant (anion plus free acid) for a series of compounds which exhibit a Bronsted relationship, there exists a very rapid reactant. The dissociation constant of this member of the series can be calculated by differentiating the observed rate constant with respect to the basic dissociation constant, K_B, of the reacting anion.

A relationship of this type, when applicable, can be of considerable practical value in the development of "best" reagents where rapidity of reaction is important, as for example in decontamination, detection, certain chemotherapeutic applications, and in analytic procedures. Thus, once the Bronsted relationship has been found to apply on the basis of a limited sampling (as indicated by a linear relationship between log k and pK_A), it is possible to predict which

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member of the series will give maximum rate and also to predict the actual rate that will be observed. It provides a means of pointing out the occasional exception that may provide leads to more rapid reactants. Also, in comparing compounds of different chemical types, one can make rough estimates of relative activity with available samples, even if pK_A is not near the optimum, since in most cases the values of β have been observed to vary between 0.3 and 0.9 (*4*).

The following discussion represents an evaluation of the relationship over a wide range of values of β (*5*) and its expression in convenient graphic form. Furthermore, the potential application of a relationship of this type in studies of biological assessment is indicated.

Evaluation of the Bronsted Relationship

For purposes of comparison of the specific rate constants of the members of a series of weak acids (or bases) at constant *p*H under conditions where they are incompletely neutralized, and where only one member of the acid-base equilibrium relationship is active, we define a constant *total* concentration of acid and anion C

$$C = [HA] + [\text{anion}] \qquad (4)$$

where the relative concentrations of acid and anion are defined by the acidic dissociation constant, K_A,

$$K_A = \frac{[H^+]\,[\text{anion}]}{[HA]} \qquad (5)$$

Under conditions where the reaction is observed to be kinetically of the first order (for example, the reagent is a catalyst, or if it is a reactant it is present in large excess) the rate will be defined by Eq. 3. By substituting Eq. 1, 4, and 5 into Eq. 3, we obtain

$$k_{\text{obs.}} = \frac{K_A C G_B}{[H^+] + K_A}\left(\frac{K_w}{K_A}\right)^{\beta} \qquad (6)$$

which describes the rate relationship among the members of any one series, with G_B and β the fixed constants for the particular series under the defined reaction conditions. The logarithmic form of this relationship is

$$\log_{10} k_{\text{obs.}} = \log_{10} K_A C G_B - \log_{10} ([H^+] + K_A) + \beta \log_{10}\left(\frac{K_w}{K_A}\right) \qquad (7)$$

For general application of the relationship, it is most convenient to use the family of curves which are obtained by variation of the factors β, K_A, and $[H^+]$ in Eq. 7; the latter two variables are most conveniently handled in terms of the expression ($pK_A - p$H). Figure 1 represents a plot of $\log_{10} k_{\text{obs.}}$ versus ($pK_A - p$H) for several values of β; for purposes of convenience in calculation of the values of $k_{\text{obs.}}$, the product CG_B has been arbitrarily assigned the value of 10^{12} so that the values of $k_{\text{obs.}}$ are comparative.

Having previously ascertained the value of β from rate data on a few members of the series (it is the slope of the straight line that is obtained in a plot of $\log_{10} k$ versus pK_A), we may compare the relative values of the specific rate constants $k_{\text{obs.}}$ for the entire series (at a constant value of C; Eq. 4) from the particular curve in Fig. 1 that has the nearest value of β.

The maximum rate at a defined *p*H may be described by the expression

$$\frac{d\,k_{\text{obs.}}}{d\,K_A} = 0.$$

After appropriate operation on Eq. 6, we find that at maximum $k_{\text{obs.}}$

$$pK_A - p\text{H} = \log \frac{\beta}{1 - \beta}$$

The broken line in Fig. 1 passes through the maximum in each of the curves.

Equation 6 applies to the specific case of a second-order reaction between substrate and the unprotonated (basic) member of a reagent which is in acid-base equilibrium, under conditions of constant *p*H and constant concentration of the reagent. The basic reactant may be either the anion of a protonic acid or a free base—for example, an organic amine. In the parallel case where reaction occurs between substrate and the protonated form of a reactant that is in acid-base equilibrium—for example, free acid or salt of a base—the resulting relationship under the conditions specified may be derived from the form of the Bronsted equation relating to acid catalysis,

$$k = G_A K_A{}^{\alpha} \qquad (8)$$

and is given by

$$k_{\text{obs.}} = \frac{C G_A [H^+] K_A{}^{\alpha}}{[H^+] + K_A} \qquad (9)$$

where G_A and α are constants which are fixed for a given reaction under defined reaction conditions, and the other symbols are as previously defined.

As a typical example, we may examine the reaction between hydroxamic acids and Sarin at *p*H 7.6. It has been determined that the β value for this reaction is 0.8 (*2*). Hence it can be predicted that maximum rate will be observed with a hydroxamic acid of $pK_A = 8.2$ and that the observed rate will fall off much more rapidly by decreasing pK_A than by increasing it. Thus, a hydroxamic acid with a pK_A of 5.6 would react only 1/23 as rapidly as one with a pK_A of 8.2. Also, if for practical application, we would be satisfied with a rate that was, for instance, as little as one-half of the maximum, we observe that we can use any hydroxamic acid in the pK_A range 7.2 to 10.0 ($\log_{10} k_{\text{obs.}}$ at max. = 6.18; therefore at $k_{\text{obs.}}/2$, $\log_{10} k_{\text{obs.}} = 5.9$). However, it should be noted that if maximum reaction rate is desired, and if there are no limitations placed upon the *p*H of the reaction system, the most rapid reaction will occur with the member of the series having the highest pK_A at a *p*H at which it is "completely" dissociated—that is, at $p\text{H} = pK_A + 2$.

Possible Application to Biological Assessment

Studies at constant *p*H are of prime importance to the physiological chemist. It was of interest to determine whether a similar relationship could be observed between ionization constant and physiological activity within a series of weak acids or bases. Others have noted correlations between physiological activity and ionization constant (*6*, chapter 4). However, the type of relationship described by Eq. 2 or 8 represents a potential improvement over simpler correlations because it defines a wide range of permissible relationships. These may vary between the limits β (or α) = 0 (zero correlation between functions—for example, all members of the series are

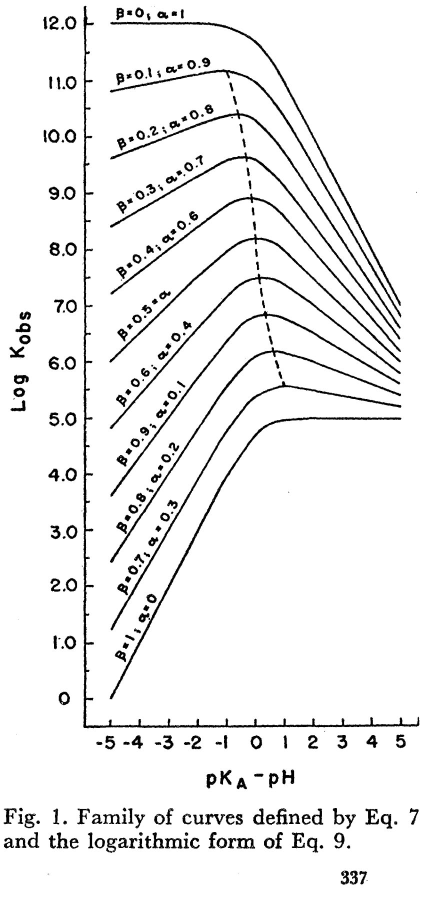

Fig. 1. Family of curves defined by Eq. 7 and the logarithmic form of Eq. 9.

equally active) to β (or α) = 1 (where the correlation is 1 to 1).

Detailed examination was made of two systems: the bacteriostatic effectiveness of a series of acridines (*6*, p. 84 and Appendix I) at pH 7.2 to 7.4 and the similar activity of a series of sulfonamides (*7*) at pH 7. In the first system, it was observed by Albert (*6*, p. 84 and Appendix I) that the active principle is the acridinium cation and that structural modifications are of minor importance in determining activity compared with that of pK_A. We plotted log activity (*8*) versus $(pK_A - pH)$ and, in agreement with Albert, we observed an α value of near 0. With the sulfonamides, activity is believed to reside primarily in the anion.

Bell and Roblin (*9*) obtained a nearly symmetrical, bell-shaped curve when they plotted log activity versus pK_A; but they were unable to develop a completely satisfactory mathematical relationship to fit their data. Their curve corresponds to those in Fig. 1 with a β value of 0.5 or 0.6 in that the maximum is correctly located; however, the slopes of both limbs of their observed curve are far too great to be accommodated by either of those from Fig. 1 or their own mathematical relationship. An attempted correction by Bell and Roblin for activity that might be due to the free acid gave only slight improvement. We examined the possibility that the free acid also was active and that its activity was related to pK_A by the exponential relationship (Eq. 8) and found that a very satisfactory fit could be obtained if one assumed a β value of 0.6 for the anion and an α value of 0.4 for the free acid.

Subsequent to the report of Bell and Roblin, several attempts were made to develop mathematical expressions to fit the data based on postulated mechanistic sequences of action. The most successful was that of Northey (*7*), who developed a satisfactory equation based upon the assumptions that activity within the cell was due to the anionic species and that the protonated form was essential to penetration through the cell wall.

Thus, it would seem that the relationships discussed in this paper are also of potential value in correlating physiological activity with dissociation constant and may be worthy of further examination in the field of biological assessment.

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4a. In Eq. 1, k is the second-order rate constant as defined in Eq. 2, G_B and β are constants which are fixed for a given reaction under defined reaction conditions (temperature, solvent), K_B and K_A are the basic and acidic dissociation constants of the anion and its conjugate acid, and K_w is the ionization constant of water.

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E. L. DeGolyer, Father of Applied Geophysics

Everette Lee DeGolyer, renowned as the world's foremost geologist and the father of applied geophysics, died 14 December at the age of 70, in Dallas, Texas, ending a half-century of brilliant service to the industry and the nation.

DeGolyer was born 9 October 1886, of homesteader parents, near Greensburg, Kansas. He attended the Joplin, Missouri, high school and entered the University of Oklahoma in 1906. There he studied geology and worked during the summers for the U.S. Geological Survey in the Rocky Mountain area. He left the University of Oklahoma as a senior, in 1908, to work for the Oklahoma Geological Survey and in the fall of 1909 accepted a job as field geologist for Mexican Eagle Oil Company, Ltd. While he was with Mexican Eagle, he staked the discovery well of the Tierra Amarilla field.

When DeGolyer staked the location for the prolific Potrero del Llano No. 4, he attained his first geologic fame. The well ultimately produced more than 100 million barrels.

DeGolyer returned to the University of Oklahoma in 1911 for his A.B. degree in geology. During this period he married Nell Goodrich, daughter of an Oklahoma City dentist.

In 1914 DeGolyer left Mexican Eagle and set up a consulting practice at Norman, Oklahoma. He made a geologic reconnaissance of western Cuba in 1915 and in 1916 opened a consulting office in New York. In 1918 he went to work for the U.S. Treasury, and his resulting study of Gulf Coast production-decline curves was incorporated in the Treasury's *Manual for the Oil and Gas Industry under the Revenue Act of 1918.* In 1919 he organized Amerada Petroleum Corporation for Sir Weetman Pearson and built the company into one of this country's most successful independent oil firms. Amerada's success was due largely to DeGolyer's pioneering efforts in oil geophysics, and it was during this period that he successfully directed the first geophysical survey of an oil field in the United States—a torsion-balance survey of prolific Spindletop field. The first salt dome and oil structure discovered in the United States by any geophysical method was the Nash Dome in Brazoria County, Texas, found early in 1924 by a torsion-balance survey made by the Rycade Oil Corporation, of which DeGolyer was president. DeGolyer also introduced the refraction and reflection seismic method of exploration and was well known for organization work throughout the industry.

In addition to organizing Amerada, he established the Geophysical Research Corporation and Geophysical Service, Inc., and was instrumental in the organization of Core Laboratories, Inc. In 1936, together with Lewis W. MacNaughton, he formed an association which resulted in the oil appraisal concern of DeGolyer and MacNaughton. The most recent product of his organizational genius was the founding of Isotopes, Inc., in 1955.

The oil and gas industry bestowed upon DeGolyer its most prized awards for his outstanding service. In addition to a host of honorary degrees and memberships, these include the Texas Mid-Continent Oil and Gas Association's distinguished service award, in 1939; the Anthony F. Lucas medal of the AIME, in 1941; the John Fritz medal of the Founder Societies (ASCE, AIME, ASME, and AIEE), in 1942; and the AAPG's Sidney Powers memorial award in 1950.

At his death, DeGolyer was senior chairman of the board of DeGolyer and MacNaughton and an active member of many other boards, including Louisian Land and Exploration Company, Repub lic Natural Gas Company, Southern Pa cific Company, General Minerals, an