[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

Potentiometric Methods for Following Reaction Rates

BY H. KWART[1,2] AND W. C. WILSON

RECEIVED AUGUST 17, 1953

A method is presented for obtaining solvolytic rate constants with high accuracy and precision using an automatic high-speed recording potentiometer in conjunction with a very stable high-impedance electronic detector. Two alternative procedures for calculation of the data are derived. A test application of the method is discussed, in which the glass electrode is used for following the solvolysis of *t*-butyl chloride.

Introduction

The problem of measuring the kinetics of rapid reactions has been approached in various ways. Among these the introduction by Swain and Ross[3] of the concentration cell is of particular value. Their method involves the addition of measured quantities of reagents to a reference cell containing a platinum electrode and determination of the progress of the reaction by observing the time required for the cell, containing the solution under study, to reach the same concentration of reactant as indicated by development of an equal potential across its platinum electrode. Such a process has rather large inherent errors. A particular disadvantage is the limited number of values which can be obtained during the first stages of a rapid reaction. Thus, although showing the ability of the potentiometric method to follow fast reactions, high precision was not obtained by these workers.

Edwards, Evans and Watson[4] have shown the glass electrode applicable to following the development of hydrogen ion concentration during slow reactions such as the hydrolysis of α-haloketones in aqueous solvents. Perley[5] has shown that the glass electrode can undergo a *p*H change from *p*H 6.86 to *p*H 4.01 and attain 99.5% of its equilibrium *p*H value in less than 2 seconds, including mixing time.

The response time in basic media was found to be somewhat slower. W. Love[6] using the stopped flow method has been able to record *p*H changes occurring about 0.06 second after mixing. The theoretical time constant (200 megohms and 40 micromicrofarads) of the glass electrode has not been approached. In acid media it would thus seem possible to follow the rapid development of hydrogen ion by use of the glass electrode with sufficient accuracy for kinetic studies of reactions having half-times of 10 to 30 seconds. An examination of the literature shows no such application to rapid reaction rates.

Other methods of following the rate of rapid reactions such as the intermittent titration method of Peters and Walker[7] and a polarographic method have been discussed by Swain and Ross[3] and are found to be of about equal precision to the concentration cell method.

In applying *p*H measurements to kinetic studies it must be borne in mind that the hydrogen ion concentration must change by a factor of ten in order that the *p*H change be equal to one *p*H unit. The *p*H change for the second half of the reaction is consequently 0.301. In order to obtain 1% precision in this region it is thus necessary that the *p*H be measured with an accuracy of at least ±0.003 *p*H unit. This is not possible since the absolute value of the *p*H cannot be determined with greater certainty than about 0.02 *p*H unit, due to the errors introduced by junction potentials.[8] The junction potential, though differing throughout a series of junctions, is constant for any given junction throughout the course of a reaction run. Consequently, if the kinetic equations can be related not to the absolute *p*H values but to voltage changes or *p*H changes, the accuracy necessary for kinetic studies can be obtained.

In the section on derivation of equations, it will be shown how such relations between cell voltage changes and reaction rate can be derived for the case of first-order and pseduo first-order reactions involving change in hydrogen ion concentration.

Derivation of Equations for Calculating Rate Constants

A first-order reaction yielding as one of its products hydrogen ion may be expressed by the general equation

$$A \longrightarrow B + H^+$$

For this reaction the rate constant is given by the integrated equation

$$k = \frac{2.303}{t_2 - t_1} \log \left[\frac{A_0 - H^+_1}{A_0 - H^+_2}\right] \qquad (1)$$

in which $[A_0]$ is the initial concentration of reactant A, $[H^+_1]$ and $[H^+_2]$ are the hydrogen ion concentrations at times t_1 and t_2, respectively. Substituting $e^{-2.303}\,p\text{H} = \text{H}^+$ into equation 1 yields

$$k = \frac{2.303}{t_2 - t_1} \log \left[\frac{A_0 - e^{-2.303}\,p\text{H}_1}{A_0 - e^{-2.303}\,p\text{H}_2}\right] \qquad (2)$$

The *p*H is related to the electrode voltage, v, by the equation

$$p\text{H} = a - bv \qquad (3)$$

where a is a constant giving the intercept of the voltage on the *p*H scale and b is the proportionality constant which relates the change in volts to the change in *p*H units. Equation (3) actually relates the voltage to the titrimetrically measurable con-

---

(1) This problem was initiated in 1951 under a grant by the Research Corporation of New York when this author was a member of the faculty of Bryn Mawr College.

(2) We wish to acknowledge, with gratitude, the generous support of part of this work by the U. S. Army Chemical Center at Edgewood, Md., under contract with the University of Delaware.

(3) C. G. Swain and S. D. Ross, THIS JOURNAL, **68**, 658 (1946).

(4) E. G. Edwards, D. P. Evans and H. B. Watson, *J. Chem. Soc.*, 1942 (1937).

(5) G. A. Perley, *Anal. Chem.*, **21**, 559 (1949).

(6) In "Technique of Organic Chemistry," by Arnold Weissberger, Interscience Publishers, Inc., New York, N. Y., 1953, Vol. VIII, p. 733.

(7) R. A. Peters and E. Walker, *Biochem. J.*, **17**, 260 (1923).

(8) R. Bates, *Chem. Revs.*, **42**, 1 (1948).

centration of hydrogen ions since the proportionality constant b is obtained by direct calibration at the acid concentrations to be encountered in the experiment. It is not to be supposed that the symbol pH as used here is a measure of hydrogen ion activity. Substituting into equation 2 from equation 3 gives

$$k = \frac{2.303}{t_2 - t_1} \log \left[\frac{\mathrm{A}_0 - e^{-2.303a_e + 2.303bv_1}}{\mathrm{A}_0 - e^{-2.303a_e + 2.303bv_2}}\right] \qquad (4)$$

If now a constant increment $t_2 - t_1$ is taken, the following equation may be written

$$K = \frac{\mathrm{A}_0 - e^{-2.303a_e + 2.303bv_1}}{\mathrm{A}_0 - e^{-2.303a_e + 2.303bv_2}} \qquad (5)$$

where K is a new constant.

On rearrangement of terms this is transformed into the linear relation

$$e^{2.303bv_1} = Ke^{2.303bv_2} + A_0e^{2.303a}(1 - K) \qquad (6)$$

wherein a plot of $e^{2.303bv_1}$ values *vs.* $e^{2.303bv_2}$ values will yield a straight line of slope K. It is therefore useful to express equation 4 in the form of

$$k = \frac{2.303}{t_2 - t_1} \log K^{9} \qquad (7)$$

In order to calculate k it is necessary only to select a series of voltage readings separated by a constant time increment from some second series of readings. By plotting the readings in the first set against their complementary readings from the second set a straight line is obtained, the slope of which is K. This method of calculating k depends upon the three quantities t, v and b. If the voltage is measured by some recording device such as the L. I. & N. Speedomax which has a very accurate time scale, then the error in t becomes small in comparison to the error in v. By the nature of the equation the effect of b on the accuracy is an inverse function of the time increment. Thus the effect of this term can be made small by using a sufficiently large time increment. For all cases in this paper the error in k due to b is less than 10% of the error in b, *i.e.*, if the error in b is 1% the corresponding error in k will be 0.1%, or less. It will be seen from the calibration curve, Fig. 3, that the uncertainty in b is less than 1% and so its effect on k may be considered negligible. The only error which affects the value of k is thus the error in v. By using a least squares solution to solve for K, the error due to an average uncertainty of 0.1 millivolt in the electrode potential results in an error in k of about 1%.

An alternative method of calculating the rate constant, which in certain instances would be found very useful, may be obtained through the following derivation. Where $[\mathrm{H^+}_0]$ is the initial concentration of hydrogen ion, $[\mathrm{H^+}]$ the instantaneous concentration, and $\mathrm{A} = [\mathrm{A}_0 - \mathrm{H}^+ + \mathrm{H^+}_0]$, the rate equation may be expressed in the form

$$\mathrm{d}[\mathrm{H}^+]/\mathrm{d}t = k[\mathrm{A}_0 - \mathrm{H}^+ + \mathrm{H^+}_0] \qquad (8)$$

The first derivative with respect to time of equation 3, *viz.*

$$\mathrm{d}[\mathrm{H}^+]/\mathrm{d}t = [\mathrm{H}^+](2.303b)\mathrm{d}v/\mathrm{d}t \qquad (9)$$

may now be equated to 8 and the resulting expression rearranged to give

$$[\mathrm{H}^+] = \frac{k[\mathrm{A}_0 + \mathrm{H^+}_0]}{k + (2.303\mathrm{b})\mathrm{d}v/\mathrm{d}t} \qquad (10)$$

On differentiating again with respect to time and making appropriate substitutions in the resulting relation one obtains

$$[\mathrm{H}^+] = \frac{k[\mathrm{A}_0 + \mathrm{H^+}_0]z}{\mathrm{d}z/\mathrm{d}t} \qquad (11)$$

where $z = \mathrm{d}v/\mathrm{d}t$. The difference between equations 10 and 11 can be rearranged into the form

$$\mathrm{d}z/\mathrm{d}t = -z(k + 2.303bz) \qquad (12)$$

which gives on integration

$$t = \frac{1}{k} \ln \left[\frac{k + 2.303bz}{z}\right] + C_1 \qquad (13)$$

where C_1 is the constant of integration. Substitution for z to obtain the relation in terms of v and subsequent integration yields

$$v = \frac{1}{2.303b} \ln (1 - 2.303be^{-kC_1}e^{-kt}) + C_2 \qquad (14)$$

where C_2 is a constant of integration. Applying the boundary conditions that at $t = \infty$, $v_\infty = C_2$ and at $t = 0$, $v_0 = (1/2.303b) \ln (1-2.303be^{-kC_1})$ equation 14 may be converted to

$$(v - v_\infty) = \frac{1}{2.303b} \ln \{1 - e^{-kt}[1 - e^{-2.303b(v_\infty - v_0)}]\} \qquad (15)$$

which can be rearranged further into

$$k = \frac{2.303}{t} \log \left[\frac{1 - e^{-2.303b(v_\infty - v_0)}}{1 - e^{-2.303b(v_\infty - v)}}\right] \qquad (16)$$

The solution for v_∞ is obtained from the following considerations For two times t_1 and t_2 where $t_2 = 2t_1$ equation 16 reduces first to

$$\frac{1}{t_1} \log \left[\frac{1 - e^{-2.303b(v_\infty - v_0)}}{1 - e^{-2.303b(v_\infty - v_1)}}\right] = \frac{1}{t_2} \log \left[\frac{1 - e^{-2.303b(v_\infty - v_0)}}{1 - e^{-2.303b(v_\infty - v_2)}}\right] \qquad (17)$$

then to

$$\frac{1 - e^{-2.303b(v_\infty - v_0)}}{[1 - e^{-2.303b(v_\infty - v_1)}]^2} = \frac{1}{1 - e^{-2.303b(v_\infty - v_2)}} \qquad (18)$$

and finally to

$$v_\infty = \frac{1}{b} \log \left[\frac{e^{2.303b(v_0 + v_2)} - e^{2.303b(2v_1)}}{e^{2.303bv_0} - 2e^{2.303bv_1} + e^{2.303bv_2}}\right] \qquad (19)$$

At t_∞, $e^{2.303bv_1} = e^{2.303bv_2} = e^{2.303bv_\infty}$. From equation 6 by proper substitution and rearrangement of terms the following equation can be obtained

$$v_\infty = \frac{1}{b} \log \left(\frac{B}{1 - K}\right) \qquad (20)$$

where B is the intercept in the linear equation. This affords us a second method for determining the ultimate value of the electrode voltage.

Of these alternative methods of computation, the one applying equation 6 and the other equations 19 and 16, the former has, in general, proved to be the simpler and more accurate. It has the virtue of being amenable to machine calculation

---

(9) Although this is a Tau method it should not be confused with the method of Guggenheim (as referred to in A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 48–49) which requires that the experimental measurement be a linear function of the concentration of the varying factor in the rate equation. In the method derived above, clearly, the hydrogen ion concentration is an antilogarithmic function of the experimentally measurable quantity (v), and consequently cannot be fitted into the Guggenheim treatment.

and through use of the least squares solution all values of the varying voltage are weighted equally in the determination of k. The latter method permits calculation of k values for each point on the graph and so is better adapted for determining the constancy of k throughout a particular set of data. It is, however, more cumbersome and less accurate in that all the values of k are somewhat dependent on the three values of the voltage chosen in calculating v_∞. A further limitation to the use of this method is apparent from an examination of equation 17. It is seen that for values taken near the end of the reaction the difference $(v_\infty - v)$ becomes small. For points taken from near the beginning of the curve the ratio $1 - e^{-2.303(v_\infty - v_0)}/1 - e^{-2.303(v_\infty - v)}$ approaches unity and the log approaches zero. These two effects can result in considerable loss in accuracy and limit the useful range of the method to values of voltage which differ from both v_0 and v_∞ by at least 1.00 unit.

Two principal advantages inherent in both methods are that exact knowledge of the initial concentration of substrate is not essential and t_0 may be arbitrarily chosen. Thus, in a very rapid reaction, with the usual methods of measurement of rate, mixing time can extend over an appreciable fraction of reaction time, such as can occur, for example, when delivery and drainage of a pipet are involved. The present procedure permits the introduction of an approximate amount of reagent into the rapidly stirring solvent in a very rapid jet, thereby reducing mixing time to a minimum, and by arbitrarily choosing t_0 at some time after mixing is complete the exact mixing time need not be determined.

Description of Apparatus

The apparatus shown in Fig. 1 consisted of the electrodes, amplifier, voltage divider, recorder and biasing voltage source.

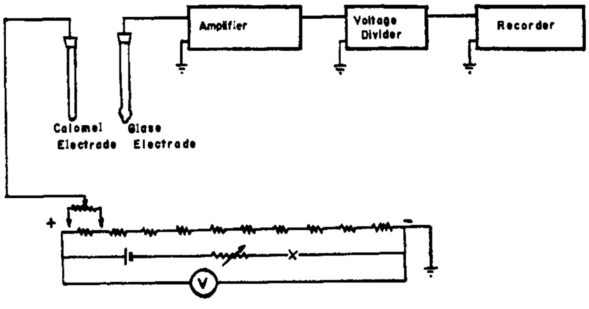

Fig. 1.

The detector was a special design rapid response chopper-type d.c. amplifier having a high impedance input and equipped with amplifications of 10, 25 and 50.[10] The bias source consisted of ten matched 25-ohm resistors in series, across which was impressed one volt from a wet-cell storage battery. The negative end of the series of resistors was grounded. Fine adjustment of the bias voltage was obtained by means of a 20,000 ohm precision helical potentiometer, in series with the calomel electrode, which could be shunted across any one of the series resistors by means of a multi-pole switch. This arrangement provided for the application of a biasing voltage of 0 to 1 v. in continuous gradations of 0.0001 v. The bleeder consisted of a resistor with a variable tap for division of the voltage by 1, 10, 100 and 1000. The recorder was a 10-millivolt L. & N. Speedomax type G with a full scale deflection time of less than one second and a chart speed of nearly six inches per minute. All electrical components were in well grounded shielded cases, and all connections between units were made with shielded cable.

The glass cell, shown in Fig. 2, was provided with an inner vessel of about 125-ml. capacity surrounded by a water jacket for the thermostating. The cell cover fitted to the cell by means of a ground glass joint contained a ground-in glass stirrer, holes for the electrodes and an opening fitted with a ground glass plug for admission of the sample. The cell was enclosed in a heavy iron container which was well grounded to protect against stray fields. The electrode system consisted of a Beckman glass electrode no. 4990-83 and a L. & N. calomel electrode no. 1100-31.

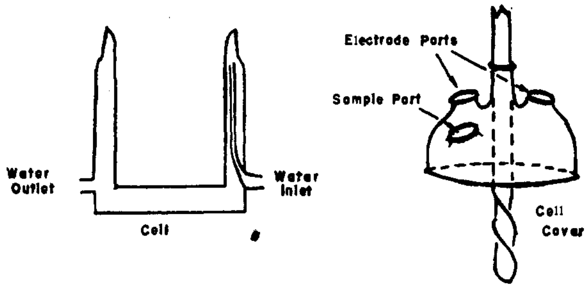

Fig. 2.

With the amplifier set for amplification 10 and the bleeder setting at 1/100, a sensitivity approximately equal to ±0.002 pH unit was obtained. This was the setting used for all the runs reported in this paper. With this setting one pH unit corresponded to a change of approximately 6 millivolts deflection on the recorder scale.

Experimental Procedure

All runs reported here were done either in 95–5 or 90–10 water–acetone (by volume) solution. The application of the instrument, however, is not limited to use with these solvents. The following description of a typical experiment should only serve to illustrate the procedure for obtaining the data discussed in this report. It will be obvious that a large number of procedural variations are possible.

The motor stirrer was started and the required amount of distilled water and acetone were added to the cell and allowed to come to temperature. The recorder was then started and 1 ml. of acetone containing approximately 0.01 mole of t-butyl chloride was rapidly injected. The reaction was followed for from two to three minutes depending upon its speed. After each run the cell and electrodes were immediately rinsed thoroughly with distilled water. It was found that temperature increase upon adding the stock solution was 0.1 to 0.2°. By precooling the stock solution the error due to the heat of mixing can be eliminated. Precooling is not essential, however, since the temperature raise is so small and the rate of heat exchange of the cell with the coolant sufficiently slow that the temperature did not fall by more than 0.05° during the course of a run.

Calibration of the Instrument to Obtain b.—The procedure for obtaining the change in millivolts with pH was as follows. One hundred milliliters of distilled water was added to the cell, the stirrer started and temperature equilibrium at-

---

[10] This instrument is manufactured by Process and Instruments of 60 Greenpoint Avenue, Brooklyn 22, New York.

tained. Then 0.1 ml. of a solution of approximately 0.1 *N* HCl was added from a calibrated pipet. The reading obtained for this solution was taken as zero. Nine successive 0.1-ml. portions were then added and the reading noted after each addition. A plot was then made of log (1/ml.) *vs.* millivolts. From the slope of this curve the value (d mv.)/(d *p*H) was obtained. It is not necessary that the exact normality of the HCl solution be known for this calibration since the concentration change in going from an addition of 0.1 to 1.0 ml. of acid represents a tenfold increase in the concentration of hydrogen ion which is equivalent to one *p*H unit. It is only necessary that the first 0.1 ml. of acid raise the *p*H of the distilled water by more than 2 *p*H units. In this particular calibration it was found that the initial *p*H change corresponded to about 2.5 *p*H units. It is not possible to compare the values obtained with those given in tables for this electrode combination since the amplification and voltage division factors are not perfectly exact, although they are constant and reproducible. The results of a sample calibration on distilled water are plotted in Fig. 3.

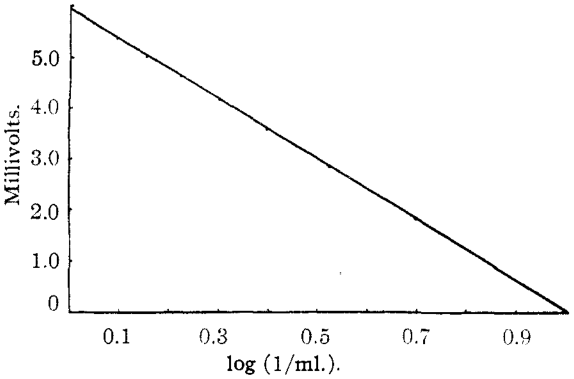

Fig. 3.—Calibration curve distilled water at 26.3°, b = (5.93 mv./*p*H)$^{-1}$.

A Study of the Solvolysis of *t*-Butyl Chloride.—In order to evaluate the operating characteristics of the instrument and test the general applicability of the method, it was thought desirable to apply it to a study of the solvolysis of *t*-butyl chloride, a reaction of known mechanism. The results of four such runs are summarized in Table I.

TABLE I

SOLVOLYSIS OF *t*-BUTYL CHLORIDE AT 26.3°

Run no.	Solvent	$k \times 10^2$, sec.$^{-1}$ Eq. 7[a]	Eq. 16	Average $t_{1/2}$ (sec.)	v_∞, millivolts Obsd.	Eq. 19	Eq. 20
1	5% aq.[b]	2.59	2.57 ± 0.03	26.7 ± 0.2	6.73	6.67	6.80
2	acetone	2.63	2.61 ± .01		6.40	6.36	6.42
3	10% aq.[c]	2.26	2.19 ± .02	31.0 ± 0.3	7.47	7.43	7.51
4	acetone	2.29	2.22 ± .01		7.53	7.63	7.59

[a] By least squares solution for slope K. [b] b = 5.53^{-1}. [c] b = 5.21^{-1}.

Discussion of Results

From the results as shown in Table I and in Fig. 5 it can be seen that either equation 7 or 16 gives comparable values of good precision. A comparison of the rate constant obtained in runs 1 and 2 may be made with the published data of Swain and Ross.[3] They obtained the value 27 ± 3 seconds for the half-time of the solvolysis of *t*-butyl chloride in 95% water–5% acetone at 25°. The average value obtained in this investigation at 26.3° is 26.7 ± 0.2 seconds. The small temperature difference will result in half-time difference of slightly more than one second, assuming an activation energy of about 22,000 to 23,000 cal./mole.[11] The two values therefore appear to be in agreement.

Figure 4 shows the raw data as it comes from the recorder. It will be noted that the zero time reading is chosen at approximately 12 seconds after injection of the sample. In certain cases readings can be obtained at times closer to the injection time by adding a small amount of acid to the solvent before the sample is introduced in order to lower the initial *p*H. This has the effect of reducing the magnitude of the *p*H change in the first stages of the reaction and permits recording of the entire reaction on the graph without changing the bias voltage. By utilizing this procedure the time lapse between injection of the sample and the first reading can be considerably reduced and since the method of calculation is independent of the initial *p*H no loss in accuracy is encountered, providing the reaction being studied is not subject to hydrogen ion catalysis.

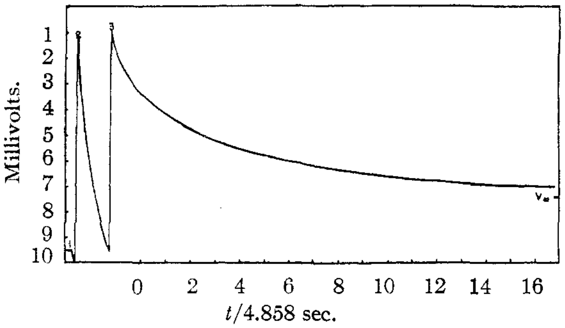

Fig. 4.—Raw data: 1, bias 0.600 v.; 2, bias 0.700 v.; 3, bias 0.800 v.

In this work readings used for calculation were restricted to the first 75% of the reaction or less. Of these at least 40% of the readings are from the first half-time. This is to be contrasted with the methods discussed by Swain and Ross[1] which yield almost exclusively readings after the first half-time of the reaction.

Factors Determining the Range of Application.—In the runs reported herein, a time increment ($t_2 - t_1$) of 20 seconds was found to give the best results. Smaller time increments, *e.g.*, 5 seconds, were tried but the reproducibility was found to decrease to an error of approximately 5% in *k*. Ordinarily, it is a simple matter to establish the optimum interval to be used in the calculations.

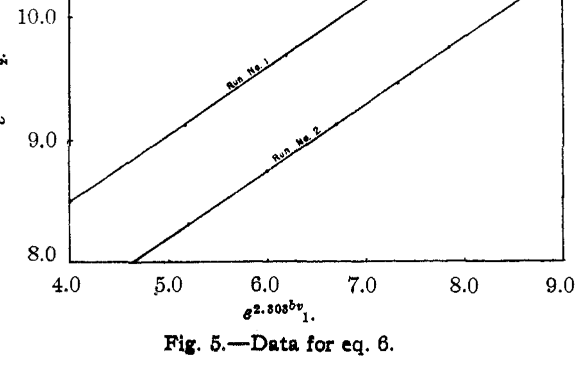

Fig. 5.—Data for eq. 6.

---

[11] E. D. Hughes, *J. Chem. Soc.*, 255 (1935).

Obviously, the smallest magnitude of this quantity which can be used is determined by the precision with which the corresponding smallest increment of voltage change throughout the course of the run can be recorded.

The limiting factors in the measurement of fast reactions with the present apparatus are the response times of the electrode system, the amplifier and the recorder. The electrode and recorder characteristics have been discussed above. The frequency response of the amplifier is flat to ten kilocycles, *i.e.*, the amplifier time constant is less than one-tenth of a millisecond. Thus the recorder we used was the factor determining the upper limit of reaction rate that could be measured. The use of oscilloscopic or photographic-galvanometer recorders represents a possible extension of our method for achieving the rates of faster reactions.

For reactions of half-life greater than one hour the glass electrode drift (approximately 0.01 *p*H unit per hour) may become significant. In such cases, however, it is still possible to measure reaction rates during the first few per cent. of reaction providing a sufficient voltage change is obtainable.

Both equations 19 and 20 allow calculation of the v_∞. It should be possible, by utilizing these equations in conjunction with points obtained during the early stages of the reaction before the rate can be appreciably affected by any side or reverse reactions, to calculate equilibrium constants through the v_∞ observed and the v_∞ calculated. For this purpose the following equation can be readily derived. Proceeding on the findings of Hughes[9] that at equilibrium the olefin content is negligible the solvolysis reaction may be written

$$t\text{-BuCl} + H_2O \rightleftarrows t\text{-BuOH} + H_3O^+ + Cl^-$$

The equilibrium constant for this reaction is then

$$K_{\text{eq}} = \frac{[H^+]^2}{[A_0 - H^+]} \tag{21}$$

Substituting $[H^+] = e^{-2.303a}(e^{2.303bv_\infty} - e^{2.303bV})$ and $[A_0] = e^{-2.303a}(e^{2.303bv_\infty} - e^{2.303bv_0})$, gives

$$K_{\text{eq}} = \frac{e^{-2.303a}(e^{2.303bv_\infty} - e^{2.303bv})^2}{(e^{2.303bv} - e^{2.303bv_0})} \tag{22}$$

where v is the observed voltage at infinite time, v_∞ is the calculated voltage for infinite time and v_0 is the voltage at the arbitrarily chosen time t_0. The value of the constant a is determined by measuring the *p*H of the solution and applying the equation 3.

The close agreement of the v_∞ observed and the v_∞ calculated indicates that the solvolysis of *t*-butyl chloride, under the conditions of this study and to the limit of experimental accuracy is complete.

We are now engaged in extending this method to other electrode systems especially to applications involving halogen ions and oxidation–reduction systems.

NEWARK, DELAWARE

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

Detection of Anionic Complexes by *p*H Measurements. I. Polymeric Borates

BY JOHN O. EDWARDS

RECEIVED MAY 18, 1953

On the basis of acidity data obtained with the glass electrode, it is concluded that concentrated aqueous solutions of boric acid contain two polyborate ions. Calculated values based on the assumption of a singly-dissociated trimer and a singly-dissociated hexamer are in good agreement with the observed acidities. It was found that equilibrium is attained in the time of mixing.

Stetten[1] recently demonstrated by *p*H measurements that polymeric borates must be present in concentrated boric acid solutions, as these solutions are more acidic than can be explained on the basis of monomeric H_3BO_3 alone. He reported that the average degree of polymerization is 3.2, but he made no attempt to determine the exact constitution of the polymer(s).

Previously, Thygesen,[2] on the basis of conductivity measurements, and Owen,[3] on the basis of cell potentials, concluded that polyborates exist in aqueous solutions. Thus, it seems to be reasonably well established from these physical measurements that polyborates do exist in solution.

Studies on the colligative properties of aqueous H_3BO_3 solutions have failed to show the existence of polyborates[4,5]; therefore these polyborates must be present in comparatively minor amounts.

The purpose of this study is to determine the exact degrees of polymerization of the polymer acids in concentrated H_3BO_3 solutions. The results, which are of importance to the aqueous chemistry of boron, are needed as a foundation for the next study which involves similar *p*H measurements designed to detect peroxyboric acids.

Experimental

The *p*H measurements were made with a Beckman model G *p*H meter; the electrodes were checked with commercial standard buffers. All measurements were made at 25.0 ± 0.2°.

The H_3BO_3 employed was reagent grade. It was recrystallized from distilled water three times, as small amounts

---

(1) D. Stetten, *Anal. Chem.*, **23**, 1177 (1951).

(2) J. E. Thygesen, *Z. anorg. u. allgem. Chem.*, **237**, 101 (1938).

(3) B. B. Owen, THIS JOURNAL, **56**, 1695 (1934).

(4) L. Kahlenberg and O. Schreiner, *Z. physik. Chem.*, **20**, 547 (1896).

(5) H. Menzel, *Z. anorg. u. allgem. Chem.*, **164**, 1 (1927).