Conclusion.—An appraisal of the krypton adsorption method leads us to conclude that it may be used with a fair degree of accuracy on solids of specific surface area as small as 0.04 sq. m./g. (*e. g.*, quartz spheres). Further work is of course required to establish the limits of variation of σ_{Kr} for various adsorbents. Because in the case of the sample of anatase, the surface had been measured by independent methods including the absolute method of Harkins and Jura, we feel certain that the value 19.5 ± 0.4 sq. Å. for σ_{Kr} determined on anatase may be accepted with considerable confidence.

Summary

1. The method of Brunauer, Emmett and Teller has been applied with success to the measurement of specific surface areas in solids as low as 0.04 sq. m./g. using krypton vapor at liquid nitrogen temperatures.

2. The use of krypton offers the advantage of a low saturation pressure (approximately 2 mm.) at the conveniently obtainable liquid nitrogen temperature.

3. Making use of an anatase (TiO_2) sample the surface of which had been measured by the absolute method of Harkins and Jura, we have determined the value of σ_{Kr}, the area occupied by the krypton atom in the monolayer. This value is 19.5 ± 0.4 sq. Å. which is considerably higher than would be predicted on the assumption that the krypton atoms in the monolayer form a close-packed liquid monolayer.

4. To evaluate k for krypton in the equation of Harkins and Jura: $\Sigma = ks^{1/2}$, s has been determined from our adsorption data on anatase. Using the previously determined value of Σ, k is found to be 4.20 at the temperature of liquid nitrogen.

AMHERST, MASS. RECEIVED JUNE 2, 1945

[CONTRIBUTION FROM THE VENABLE LABORATORIES OF THE UNIVERSITY OF NORTH CAROLINA]

Indicator Constants in Solutions Containing Organic Solvents[1]

BY JOSEPH F. MASI AND SAMUEL B. KNIGHT

Numerous investigations have been concerned with the so-called "solvent effect" in the colorimetric determination of pH but, as yet, not enough data have been reported to draw theoretical conclusions as to the exact nature of the solvent error. Michaelis and Mizutani[2] have measured pK_I for a number of indicators in different alcohol concentrations, and Kolthoff[3,4] and co-workers have done work on the dissociation constants of indicators in alcohol and methanol.

The purpose of this paper is to show the effect of certain organic solvents on the constant of thymol blue (acid range) and brom thymol blue. To accomplish this purpose, hydrogen-ion activities have been determined in hydrochloric acid solutions in which the solvent is water, or water–ethanol, or water–ethylene glycol. Hydrogen-ion activities were also determined in citrate and phosphate buffers in the same solvents. These hydrogen-ion activity values were used along with spectrophotometric data to calculate the apparent indicator constants in each of the solvents.

Theoretical

In a solution containing a weak indicator acid, the constant of the indicator is related to the hydrogen-ion activity of the solution and the ratio of indicator in the "acid" and "basic" forms by the well-known indicator equation

$$pK_I = pa_{H^+} - \log \frac{x}{1 - x} \qquad (1)$$

where pK_I is the negative log of the apparent indicator constant, and x is the fraction of indicator transformed into the basic form.

The fraction, x, of equation (1) is determined most accurately from spectrophotometric data. Therefore, by combining spectrophotometric data with precise hydrogen-ion activity measurements, pK_I may be calculated directly.

From electromotive force measurements on the silver–silver chloride electrode combined with the hydrogen electrode, hydrogen-ion activities may be calculated at 25° by the equation

$$-\log a_{H^+} = \frac{E - E^0}{0.05915} + \log C_{Cl^-} - \frac{A\sqrt{\mu}}{1 + aB\sqrt{\mu}} + C'\mu + \log \frac{d_0}{d + 0.001\,(M_1 - M_2)C} \qquad (2)$$

where C_{Cl^-} is the molarity of the chloride ion, A and B are Debye–Hückel constants, a is the ion-size parameter, μ is the ionic strength, C' is the "salting-out" constant, d_0 and d are densities of the solvent and the solution, M_2 is the molecular weight of the chloride ion, and M_1 the mean molecular weight of the solvent.

The last term of equation (2) is added so that activities shall be expressed in moles per liter, and, since the electromotive force of the hydrogen–silver–silver chloride cell in its standard state depends on the units in which the activities are expressed, the proper value of E^0 must be used. At 25°, $E^0_c = E^0_m + 0.1183 \log d_0$, where d_0 is the density of the solvent. E^0 must be deter-

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[1] Original manuscript received December 16, 1944.

[2] L. Michaelis and M. Mizutani, *Biochem. Z.*, **174**, 7 (1924).

[3] I. M. Kolthoff, *J. Phys. Chem.*, **35**, 2732–2748 (1931).

[4] I. M. Kolthoff and L. S. Guss, THIS JOURNAL, **60**, 2516 (1938); **61**, 16 (1939).

mined for each solvent, and activities as calculated by equation (2) are referred to the standard state of unit activity in the solvent used.

pK_I values calculated from hydrogen-ion activities obtained from cells without liquid junction are more directly comparable in the different solvents since there is no uncertain liquid junction potential contributing a different amount to E and E^0 as dielectric constant changes with different solvents. It should be remembered, however, that the hydrogen-ion activity as calculated by equation (2) is really a mean activity, and is equal to the H^+ activity only if it is assumed that the activity coefficient of the chloride ion can be calculated exactly in the various solvents by the Debye–Hückel expression.

Experimental

Potential measurements were made of the cell

$$\text{Pt, } H_2 \mid \text{Solution} \mid \text{AgCl, Ag}$$

at 25° in solutions of hydrochloric acid in water, in 10 and 20% by weight ethanol–water mixtures, and in 20 and 40% by weight ethylene glycol–water mixtures. Potential measurements were also made on hydrochloric acid-citrate buffers and on phosphate buffers in the above five solvents. A constant amount of potassium chloride was added to each phosphate buffer.

After electromotive force measurements had been made on a solution, thymol blue or brom thymol blue was added and the fraction of indicator in the basic form was determined spectrophotometrically.

Materials

Water.—Distilled water was slowly re-distilled in an all-Pyrex apparatus. Tank nitrogen was purified and used to displace the air from the still. The water so prepared had a specific conductance of the order of 10^{-7} mhos, and was used to prepare all solutions.

Ethanol.—Absolute ethyl alcohol supplied by U. S. Industrial Chemicals, Inc., was distilled successively from concd. sulfuric acid, silver oxide, and aluminum amalgam.

Ethylene Glycol.—Ethylene glycol obtained from Carbide and Carbon Chemical Co. was fractionated at 5 mm. pressure in a slow stream of purified nitrogen. The density of the final product agreed with that recorded by Taylor and Rinkenback[5] for pure ethylene glycol.

Hydrochloric Acid.—Constant boiling acid was used to make stock solutions. A gravimetric analysis for chlorides was made as a final check on acid concentration.

Monopotassium Citrate.—The anhydrous salt was prepared according to directions given by Kolthoff.[6] Stock solutions were made by weight, and the molarity (0.250) checked by titration against standard alkali.

Monopotassium Phosphate.—Merck reagent grade monopotassium phosphate was dried at 110°. Stock solutions were made by weight and the molarity (0.500) was checked by titration with standard alkali.

Potassium Chloride.—Baker C. P. potassium chloride was recrystallized once and dried at 120°. Solutions were prepared by weight, approximately 0.1000 molar, and analysed gravimetrically for chlorides.

Sodium Hydroxide Solution.—A 0.2620 molar solution at 25° of carbonate-free sodium hydroxide was preserved in a four-liter Pyrex bottle which had been coated thinly with paraffin. The molarity was checked from time to time by titration against potassium acid phthalate.

Indicator Solutions.—Thymolsulfonphthalein from Coleman and Bell Co. and dibromothymolsulfonphthalein from Eastman Kodak Co. were used without further purification. One-tenth per cent. solutions were prepared by the directions of Clark.[7]

Hydrogen Gas.—Electrolytic hydrogen delivered from a tank was passed successively through a tube containing soda-lime, a bubble counter containing concd. sulfuric acid, and into a Pyrex furnace containing platinized asbestos. The furnace was heated electrically to 500° by means of a Nichrome wire inside of the furnace. The gas was finally dried by allowing it to pass through a long tube containing "Drierite." Only glass and copper-sealed-to-glass connections were used on the exit side of the furnace.

Solutions for Measurement.—A total of a hundred and fifteen solutions were prepared for measurement, and were classified into five series according to the composition of the solvent by weight: series I, water; series II, 10% ethanol–water; series III, 20% ethanol–water; series IV, 20% ethylene glycol–water; series V, 40% ethylene glycol–water. The solutions in each series were sub-classified into an A series, which contained hydrochloric acid or hydrochloric acid–monopotassium citrate mixtures for use with thymol blue, and a B series which contained sodium hydroxide–monopotassium phosphate mixtures for use with brom thymol blue.

In making the hydrochloric acid solutions, weighed quantities of stock acid (±0.1 mg.) were diluted to a liter with water or organic solvent and water after adjusting the temperature to 25°.

In making the phosphate buffer solutions, conductivity water, sodium hydroxide stock solution, 50.00 ml. of 0.500 molar monopotassium phosphate, 50.15 ml. of stock potassium chloride, and the proper amount of organic solvent were mixed in a volumetric flask. After standing for twenty to thirty minutes in a water-bath, the flasks were filled to the mark. The percentage of organic solvent for all solutions is correct to ±0.05%. All volumetric glassware was calibrated.

Electromotive Force Measurements.—The cell vessels were a slight modification of those employed by Harned and Morrison.[8]

Silver–silver chloride electrodes were prepared by caking silver oxide paste on platinum spirals and heating in a furnace at 450°, for half an hour according to the directions of Harned.[9] Finally they were chloridized according to the directions of Owen,[10] employing 0.5 N HCl, a 3-volt D. C. source, and a current of 12 ma. for two hours. The electrodes were reproducible and had little tendency to flake.

Hydrogen electrodes were prepared in the usual manner by plating a film of platinum black from a 3% solution of chloroplatinic acid.

A type K-1 potentiometer and high sensitivity galvanometer were employed for electromotive force measurements. Readings were begun an hour after starting the hydrogen and continued at twenty to thirty minute intervals until several successive readings were the same (±0.02 mv.) and agreement was obtained among all cells containing the same solution. The final reading on each cell was corrected to that at 1 atm. of hydrogen making use of the observed barometric pressure, the calculated vapor pressure, and the height of the solution above the electrodes.

Spectrophotometric Measurements.—The Coleman Model 10 S Double Monochromator Spectrophotometer equipped with a 5 mμ slit was used for the colorimetric comparison of the indicator solutions. Transmittance measurements were made on solutions containing thymol blue at a wave length setting of 540 mμ, and on brom thymol blue at 615 mμ, the points of minimum transmittance.

For thymol blue (acid range) it was found that the presence of ethanol or ethylene glycol had no effect on

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(5) C. A. Taylor and W. H. Rinkenback, *Ind. Eng. Chem.*, **18**, 676 (1926).

(6) I. M. Kolthoff, "Acid-Base Indicators," The Macmillan Co., New York, N. Y., 1937, p. 253.

(7) W. M. Clark, "The Determination of Hydrogen Ions," 3rd ed., Williams and Wilkins Co., Baltimore, Md., 1928, p. 91.

(8) H. S. Harned and J. O. Morrison, *Am. J. Sci.*, **33**, 161 (1937).

(9) H. S. Harned, THIS JOURNAL, **51**, 416 (1929).

(10) B. B. Owen, *ibid.*, **60**, 2229 (1938).

either the per cent. transmittance or wave length of minimum transmittance. Furthermore, the completely acid color is obtained only in rather concentrated acid in agreement with Holmes.[11]

For brom thymol blue, the presence of ethanol or ethylene glycol affects the % transmittance and, consequently, cognizance of this effect was taken in making spectrophotometric comparisons to determine the fraction of indicator in the "basic" form.

Three hundredths of a milliliter (± 0.002) of thymol blue or 0.500 ml. (± 0.002) of brom thymol blue was added to 50 ml. of a solution on which an electromotive force measurement had been made. The ratio of the extinction value for the solution under examination to the extinction value of completely acid thymol blue or completely basic brom thymol blue is equal to x of equation (1). pK_I for the indicator was then calculated from equation (1).

Calculations

The value of the ionic strength in equation (2) for each solution containing hydrochloric acid alone was the same as the molarity of the acid. The ionic strength of each citrate buffer solution was obtained from the molarities of the constituent ions, each ion concentration being calculated as follows

$$c_{\mathrm{Cl^-}} = c_{\mathrm{HCl}};\ c_{\mathrm{K^+}} = c_{\mathrm{KH_2\,citrate}} = 0.0250;\ c_{\mathrm{H^+}} = x;$$

$$c_{\mathrm{H_2\,citrate^-}} = x + (0.0250 - c_{\mathrm{HCl}});\ \text{and, } K = \frac{(c_{\mathrm{H^+}})(c_{\mathrm{H_2\,citrate^-}})}{(c_{\mathrm{HCl}} - c_{\mathrm{H^+}})}$$

Several values of the first ionization constant, K, of citric acid are given in the literature. Kolthoff's value of 8.7×10^{-4} at 25°[6] was chosen for the calculations and, since constants for citric acid in ethanol–water and glycol–water mixtures have not been reported, this same value of K was used for these solvents also.

The ionic strengths of the phosphate buffer solutions were calculated on the assumption that the reaction, $H_2PO_4^- + OH^- \rightarrow HPO_4^= + H_2O$, is complete. The concentration of potassium chloride was 0.005 molar in all of these solutions, and the initial concentration of monopotassium phosphate was 0.0250 molar. Therefore

$$\mu = \frac{2(0.005 + 0.0250) - C_{\mathrm{NaOH}} + 4C_{\mathrm{NaOH}} + C_{\mathrm{NaOH}}}{2} = 0.00300 + 2C_{\mathrm{NaOH}}$$

Density values for equation (2) were measured directly or read from large plots of density *versus* molarity. Data for aqueous hydrogen chloride were taken from "International Critical Tables," and for 10 and 20% alcohol solutions of hydrogen chloride from the data of Harned and Calmon.[12]

The experimental values of electromotive force and concentration, and the density, were substituted in equation (2) to obtain $pa_{\mathrm{H^+}}$ values. It was necessary to evaluate carefully the constants to be used in this equation. The final values for each series of solutions are listed in Table I. A and B were calculated from the latest values of the universal constants, and dielectric constants were obtained from Akerlof.[13] Harned and Owen[14] tabulate values of E_c^0 for water and for 10 and 20% ethanol–water solutions. To check these values and find the best value of a for these three solvent mixtures, E_c^0 was calculated from the extended Debye–Hückel equation for these solvents using various values of a until one was found which gave a constant value for E_c^0 in dilute solutions.

E_c^0 values for hydrochloric acid in 20 and 40% glycol were calculated from the equation, $E_c^0 = E_m^0 + 0.1183 \log d_0$. Values of E_m^0 were obtained from work in this laboratory to be published in the near future. The corresponding a values were estimated from preliminary extrapolations to be 4×10^{-8} cm. in both the glycol–water solvents. This same value of a and various values of the constant C' were used for all the phosphate buffer solutions. These C' values were taken from the work of Cohn[15] on aqueous phosphate solutions who found that the value of C' varied with the ratio of secondary phosphate to total phosphate concentration. In recent very careful work on aqueous phosphate–chloride solutions, Bates and Acree[16] also found it necessary to assign various values of C' for different buffer ratios. The latter use 3.8 Å. for a.

The values of C' for hydrochloric acid–water solutions were those of Harned and Ehlers,[17] and for ethanol–water solutions of hydrochloric acid, the values of Harned and Calmon[12] were used. Since 20% glycol has the same dielectric constant as 10% ethanol, and 40% glycol the same as 20% ethanol, the C' values given by Harned and Calmon for ethanol solutions were used also for the glycol solutions.

Results

Tables II and III show the experimental results of the 20% glycol series. These values for concentration, ionic strength, electromotive force, $pa_{\mathrm{H^+}}$ and pK_I are typical for all of the five solvents.

Table II shows values for hydrochloric acid solutions which were used with thymol blue. Citrate buffers were used in the last four solutions of the series.

Table III shows values for the phosphate buffer solutions which were used with brom thymol blue.

The mean values of the apparent indicator constants of thymol blue and brom thymol blue together with the average deviation from the mean are recorded in Table IV for the five solvents.

A plot of $pa_{\mathrm{H^+}}$ *vs.* fraction of indicator in the "basic" form is given for brom thymol blue in Fig. 1.

From these tables it is seen that the constant of thymol blue is definitely, but not greatly, affected by the change in solvents. However, the constant

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[11] W. C. Holmes, THIS JOURNAL, **46**, 629 (1924).

[12] H. S. Harned and C. Calmon, *ibid.*, **61**, 1491 (1939).

[13] G. Akerlof, *ibid.*, **54**, 4125 (1932).

[14] "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, N. Y., 1943, p. 336.

[15] E. J. Cohn, THIS JOURNAL, **49**, 173 (1927).

[16] R. G. Bates and S. F. Acree, *J. Research Nat. Bur. Standards*, **30**, 129 (1943).

[17] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **55**, 2179 (1933).

TABLE I

CONSTANTS OF EQUATION (2)

Series	I	II	III	IV	V
E^0_c, volts	0.22154	0.21343	0.20560	0.21057	0.1993
A	.5089	.5701	.6457	.5701	.6515
$B \times 10^{-7}$	.3286	.3413	.3558	.3413	.3568
D	78.54	72.8	67.0	72.8	66.6
d_0	0.99707	0.98038	0.96640	1.0230	1.049
M_1	18.0	19.2	20.5	21.0	25.1
$0.001\ (M_1 - M_2)$	−0.0175	−0.0163	−0.0150	−0.0145	−0.0104
Series	I A	II A	III A	IV A	V A
$a \times 10^8$	4.3	5.8	5.6	4.0	4.0
C'	0.13	0.135	0.14	0.135	0.14
Series	I B	II B	III B	IV B	V B
$a \times 10^8$	4.5	4.5	4.5	4.5	4.5
C'	varying				

TABLE II

THE INDICATOR CONSTANT OF THYMOL BLUE IN 20% GLYCOL SOLUTION

No.	C_{Cl^-}	μ	E	pa_{H^+}	Fraction in "basic" form	pK_I
1	0.00163	0.00163	0.54306	2.812	0.075	1.72
2	.00385	.00385	.50115	2.465	.137	1.67
3	.00658	.00658	.47409	2.232	.238	1.73
4	.00871	.00871	.46062	2.120	.252	1.65
5	.01601	.01601	.43078	1.867	.381	1.66
6	.02204	.02204	.41561	1.741	.482	1.71
7	.02553	.02553	.40844	1.680	.506	1.69
8	.04037	.04037	.38596	1.486	.600	1.66
9	.05949	.05949	.36774	1.334	.696	1.69
10	.08534	.08534	.35008	1.180	.780	1.73
11[a]	.0179	.0266	.49438	2.977	.073	1.86
12	.0281	.0312	.44522	2.337	.189	1.70
13	.0291	.0319	.44123	2.284	.209	1.71
14	.0341	.0359	.42459	2.069	.284	1.68
					Mean =	1.70 ± 0.02

[a] Out of range, not averaged.

TABLE III

THE INDICATOR CONSTANT OF BROM THYMOL BLUE IN 20% GLYCOL SOLUTION

No.	C_{NaOH}	μ	E	pa_{H^+}	Fraction in "basic" form	pK_I
1	0.0043	0.0387	0.73551	6.479	0.103	7.42
2	.0065	.0429	.74858	6.699	.163	7.41
3	.0090	.0481	.76069	6.902	.220	7.45
4	.0131	.0562	.77763	7.187	.379	7.40
5	.0152	.0604	.78640	7.333	.456	7.41
6	.0177	.0654	.79790	7.527	.568	7.41
7	.0194	.0688	.80711	7.682	.664	7.39
					Mean =	7.42 ± 0.02

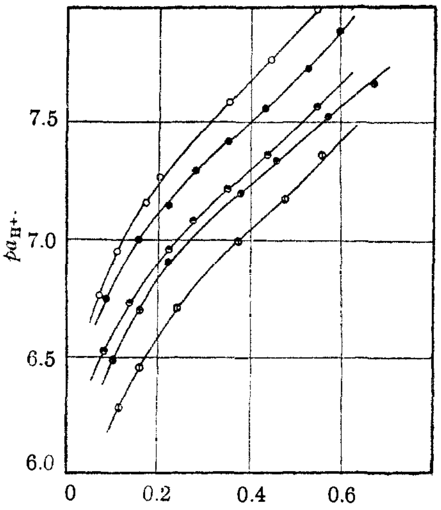
TABLE IV

INDICATOR CONSTANTS IN FIVE SOLVENTS

Solvent	pK_I Thymol blue	pK_I Brom thymol blue
Water	1.60 ± 0.04	7.21 ± 0.02
10% Ethanol	1.63 ± .03	7.49 ± .02
20% Ethanol	1.68 ± .06	7.85 ± .01
20% Glycol	1.70 ± .02	7.42 ± .02
40% Glycol	1.80 ± .01	7.69 ± .02

for brom thymol blue changes rapidly with change in solvent. The effect is determined mainly by the dielectric constant of the solvent, and the extent of the influence which organic solvents exert upon the color of an indicator depends upon the nature of the indicator and the kind of acid–base system in the solution. It is to be expected that dissociation of thymol blue, a strong acid, should not be much altered by the presence of the organic solvents but that the constant of brom thymol blue should be altered more radically. This accords with experimental results.

The change in ionization constant of a weak acid with change in dielectric constant of solvent is



Fraction in "Basic" Form (x of eq. 1).

Fig. 1.—Brom thymol blue: ⦶, water; ⊕, 20% glycol; ⊖, 10% ethanol; ●, 40% glycol; ○, 20% ethanol.

discussed by Harned and Owen,[14] but no satisfactory general theory has yet been advanced to explain all of the observed facts. A regular, though non-linear, increase in the ionization constants of several aliphatic acids has been observed with change in $1/D$ when an organic solvent is mixed with water in increasing proportions.

Our work shows the specific effect of the organic solvent. Ten per cent. ethanol and 20% glycol have the same dielectric constant, but thymol blue shows pK values of 1.63 and 1.70 in the two solvents, while brom thymol blue has pK values of 7.49 and 7.42. Thus, 10% ethanol has less effect on thymol blue than 20% glycol, and more effect on brom thymol blue than 20% glycol. Exactly the same effect is seen by comparing values in 20% ethanol and 40% glycol, solvents of equal dielectric constant. Therefore, no general conclusions can be drawn until more data are accumulated with the same indicators in other hydroxy solvents and with other indicators.

The results may be briefly compared with some previous values. Kolthoff[6] has evaluated the various reported values of indicator constants in aqueous solutions and gives as best, values of 1.65 for thymol blue and 7.15 for brom thymol blue at an ionic strength of 0.05. The same author has calculated from experimental data the ethanol correction factor which must be applied in the colorimetric determination of pH. At 10–20° he gives an alcohol correction of 0.00 and +0.02 for thymol blue in 10 and 20% alcohol by volume. No work has been reported in glycol.

Summary

1. Electromotive force measurements have been made at 25° on the cell Pt | H_2 | Solution | AgCl | Ag in five solvents, water, 10% by weight ethanol, 20% by weight ethanol–water, 20% by weight ethylene glycol–water, and 40% by weight ethylene glycol–water.

2. Hydrogen ion activities have been calculated from the electromotive force measurements and used, along with spectrometric measurements, to determine the apparent indicator constants of thymol blue (acid range) and brom thymol blue in the above five solvents.

Chapel Hill, N. C. Received June 11, 1945

[Contribution from the Department of Chemistry, Yale University]

Exchange Reactions between p-Nitrobenzyl Halides and Halide Ions[1]

By Tom A. Bither,[2] Julian M. Sturtevant[3] and Henry C. Thomas

The mechanisms of several simple types of organic reactions have been studied through the aliphatic halides. Displacement reactions of these compounds have been the subjects of numerous investigations, as, for example, in the work of Conant, Kirner and Hussey,[4] Young and Olson,[5] Koskoski, Dodson and Fowler,[6] Elliot and Sugden,[7] Seelig and Hull,[8] and many others.[9] The study of the kinetics of such reactions has produced significant information on reaction mechanism, for example, the well-known proof that the Walden inversion proceeds by a substitution mechanism.

With the hope of uncovering regularities in a limited but inclusive field, a study has been made of the kinetics in acetone–water solutions of the four possible displacement reactions between p-nitrobenzyl chloride and bromide and the chloride and bromide ions

[1] This paper is based on the dissertation presented in 1942 to the Faculty of the Graduate School of Yale University by Tom A. Bither in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[4] Conant, Kirner, and Hussey, This Journal, **47**, 488 (1925).

[5] Young and Olson, *ibid.*, **58**, 1157 (1936).

[6] Koskoski, Dodson and Fowler, *ibid.*, **63**, 2149 (1941).

[7] Elliot and Sugden, *J. Chem. Soc.*, 1836 (1939).

[8] Seelig and Hull, This Journal, **64**, 940 (1942).

[9] A rather complete bibliography of work on the kinetics of displacement reactions is to be found in Tom A. Bither, Dissertation, Yale University, 1942.