activity of the agents in question even when they function in the presence of neutral salts (potassium and sodium chlorides) in acid and alkaline hydrolysis of esters, and in the decomposition of diacetone alcohol in the presence of potassium hydroxide.

Alternative interpretations of the new expressions are discussed.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE EFFECT OF NEUTRAL SALTS ON THE VELOCITY OF SAPONIFICATION OF ETHYL ACETATE BY SODIUM HYDROXIDE. I

BY STANLEY DAVIS WILSON AND ETHEL M. TERRY

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The following report[1] contains new data on the effect of sodium chloride, sodium acetate and sodium nitrate respectively on the velocity of saponification of ethyl acetate by sodium hydroxide in water solution at 25.00°.

The technique already reported[2] was used in the measurements except that in part of this work a more convenient apparatus[3] was employed. Important details of the experiments will be found in the second part of this paper.

From the results a coefficient, K_1, was calculated by means of the equation for the rate of a bimolecular change:

$$dX/dt = K_1\,[B - X][E - X] \qquad (1)$$

In this expression and elsewhere in this paper, K represents a coefficient defined by the equation, the number of which is indicated by the subscript. The terms B and E are the initial molalities (gram molecular weights per 1000 g. of water) of the sodium hydroxide and ester, respectively. The molality of ester or of sodium hydroxide transformed up to the time, t, is represented by X. The values found for K_1, though constant for any stage of a given reaction, decreased as the molality of salt present at the beginning of the experiment was increased, as shown in Table I. The rate of this decrease proved to be characteristic of the salt used, as was of course expected. The coefficients are reproducible to within a quarter of one per cent. and are accurate to three-fourths of one per cent., as is explained in the preceding paper.[2]

Fundamental Equation for the Reaction.—Elsewhere[4] it has been

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[1] The experimental work of this paper was completed in 1916 and was presented by S. D. Wilson as part of a thesis submitted in fulfilment of part of the requirements for the degree of Doctor of Philosophy at the University of Chicago. See also note of Terry and Stieglitz, Ref. 2.

[2] Terry and Stieglitz, THIS JOURNAL, 49, 2216 (1927).

[3] This will be described in a later paper by Gooch and Terry.

[4] Terry, THIS JOURNAL, 50, 1239 (1928).

TABLE I

SAPONIFICATION OF ETHYL ACETATE BY SODIUM HYDROXIDE IN AQUEOUS SALT SOLUTION

Ester = 0.0080 Molal. NaOH = 0.010 Molal

Experiments on NaCl solutions			Experiments on $NaC_2H_3O_2$ solutions		Experiments on $NaNO_3$ solutions	
Molality of NaCl	K_1	Average K_1	Molality of sodium acetate at start	K_1	Molality of $NaNO_3$	K_1
0.0000		6.76	0.00	6.76	0.00	6.76
.0208	6.68					
.0208	6.70	6.68	0.021	6.71	0.014	6.68
.0209	6.67					
.0200	6.67					
.0350	6.67	6.67	.048	6.65	.049	6.57
.103	6.57	6.57	.093	6.66	.099	6.41
.104	6.57					
.511	6.13	6.13	.505	6.61	.355	5.87
.511	6.13				.502	5.66

shown that the catalytic activity coefficient of potassium hydroxide present in solution with no other electrolyte or in solutions of potassium chloride is the ratio of two terms. The first term is the activity coefficient of potassium hydroxide determined by electromotive force, etc., measurements on solutions of potassium hydroxide or potassium hydroxide and potassium chloride each at the molality present in the reaction mixture. The second term is the activity coefficient of hydrochloric acid at like molality to that of the potassium hydroxide in the reaction mixture and present in a solution of potassium chloride equal in molality to that in the reaction mixture. If A represents the catalytic activity of potassium hydroxide, then it may be represented in the form of an equation, as follows

$$A_{\text{KOH}} = (\gamma_{\text{KOH}}/\gamma_{\text{HCl}})(\text{KOH}) \qquad (2)$$

The gamma terms here, as elsewhere in this paper, represent the activity coefficients of the substances indicated in the subscripts. Gamma terms which appear in the same equation always refer to like molalities of the substances named and are determined under corresponding conditions as stated above. The term (KOH) is the molality of potassium hydroxide in the experiment in question.

It seemed probable that the corresponding expression

$$A_{\text{NaOH}} = (\gamma_{\text{NaOH}}/\gamma_{\text{HCl}})(\text{NaOH}) \qquad (3)$$

would be found to describe the catalytic activity of sodium hydroxide in the saponification of an ester in the dilute solutions used in the present work.

The equation for the reaction, therefore, should be

$$dX/dt = K_4\,(\gamma_{\text{NaOH}}/\gamma_{\text{HCl}})(B - X)(E - X) \qquad (4)$$

K_4 is the coefficient of the reaction. The other terms are used in the sense already defined. By comparison of Equation 1 with Equation 4, it is found that

$$K_4 = K_1\,\gamma_{\text{HCl}}/\gamma_{\text{NaOH}} \qquad (5)$$

Since in the reaction in question sodium acetate replaces sodium hydroxide as the reaction progresses, it is proper to consider the activity coefficient of sodium hydroxide constant and equal to that of the initial sodium hydroxide. Since the solutions are dilute[5] this assumption is a close approximation to the truth so that the uncertainty of the activity coefficients is not greater than 1%.

The activity coefficients of sodium hydroxide and hydrochloric acid in solutions of one one-hundredth molality and varying molality of sodium chloride have been supplied by Harned.[6]

These are given in the unbracketed values of columns in Table II.

TABLE II

APPLICATION OF EQUATIONS 4 AND 5 TO THE DATA FOR SODIUM CHLORIDE (TABLE I)

(Bracketed data are extrapolated)

Molality of NaCl	K_1	γ_{HCl} (0.01 Molal)[6b,7]	γ_{NaOH} (0.01 Molal)[6a]	K_4
0.00	6.76	0.91	0.92	6.69
.021	6.68	[.86]	.847	6.78
.035	6.67	[.84]	.817	6.85
.104	6.57	.784	.758	6.81
.511	6.13	.729	.661	6.81
			Average,	6.79

The bracketed values of γ_{HCl} are taken from the data of Scatchard[7] and are the activity coefficients of hydrochloric acid at molalities equal to that of the sodium chloride plus one one-hundredth. This interpolation of the activity coefficients of the reagents in these dilute solutions is correct to within 1%, since a comparison of the interpolated and observed values for tenth molal solutions of salt and 0.01 molal acid or base gives agreement to 1%.

The constancy of the values of K_4 is apparent from an inspection of Col. 5, Table II. The average value is 6.79 and the widest deviation from the mean is 1.5%.

Therefore, Equation 4 describes correctly the rate of saponification of ethyl acetate in dilute sodium hydroxide and chloride solution. Possible interpretations of this equation are discussed elsewhere.[4]

Suitable activity coefficients are lacking for an interpretation of the data for reactions in which sodium acetate and sodium nitrate are present.

Part II. Details of Experiments

As has been stated, the general method of procedure was much the same as that employed by Terry and Stieglitz.[2] In addition, the following points should be mentioned.

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[5] See Lewis and Randall's discussion of this subject, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 367.

[6] (a) Harned, THIS JOURNAL, **47**, 684 (1925); (b) **48**, 326 (1926).

[7] Scatchard, *ibid.*, **47**, 645 (1925).

The ester used was prepared exclusively by the Wade and Merriman[8] method, as this was found to be the most efficient.

Soda lime used in purifying air for solution containers was prepared by the method of Atwater and Benedict.[9] It always contained traces of iron from the vessels used in its preparation and it is interesting that Guareschi[10] reports that such a product is more efficient than soda lime made from pure materials.

Sodium chloride and sodium nitrate solutions were made from dried samples of the c. p. salts. The sodium acetate solution was made from pure acetic acid and sodium hydroxide. Special precautions were taken to be sure that these solutions were carbon dioxide free. A known amount of the corresponding acid was added to each salt solution and the mixture was aerated with carbon dioxide free air. The salt solutions were then brought to the point of equivalent acid and base by suitable addition of the latter.

In all cases the concentration of salt in the reaction mixture was calculated on the assumption that the total volume of solution equaled the sum of the volumes of water and reagent solutions which had been combined. This involved an error of less than 0.5% in the estimation of the concentration of the salt and was a negligible matter.

As a preliminary to the measurements for sodium hydroxide and ester concentration, it was first necessary to show that a given quantity of hydrochloric acid or acetic acid (such as was used in our samples) would require the same quantity of standard base in the presence of the excess salt (sodium chloride, nitrate or acetate) as in the absence of salt, that is, that the sensitiveness of the indicator, phenolphthalein, was not materially altered by the presence of high concentrations (0.5 N) of salt. No salt effect was found provided titrations were carried out at 0°.

In the case of the acetate solutions, it was necessary to consider whether the results of titration represented correctly the concentration of free base in the reaction mixture. As long as excess sodium hydroxide was present, the salt could be considered non-hydrolyzed. However, as the end-point was approached in titrations, this condition did not hold. In other words, a small quantity of the salt was used up in titration to an end-point of $[H^+] = 10^{-8}$, so that the results of these measurements were a little too high. Corrections were calculated from the usual equation for the hydrolysis of sodium acetate, $K_{\text{hydrolysis}}$ being taken as $0.11 \times 10^{-14}/1.77 \times 10^{-5}$.[11] The correction for half molar sodium acetate mixtures proved to be 0.09 cc. of $M/100$ HCl reagent for each titration value (125 cc. volume), and for tenth molar sodium acetate the correction was 0.02 cc.

Summary

Report is made of determinations of the effect of sodium chloride, sodium acetate and sodium nitrate, respectively, on the rate of saponifi-

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[8] Wade and Merriman, *J. Chem. Soc.*, **101**, 2429 (1912).

[9] Atwater and Benedict, *Carnegie Inst. Washington Pub.*, **42**, p. 29.

[10] Guareschi, *C. A.*, **10**, 25 (1916).

[11] 0.10×10^{-14}, the ion product of water at 0°, is an average value taken from data given by Landolt-Börnstein, Julius Springer, **1923**, p. 1164.

cation of ethyl acetate by sodium hydroxide in aqueous solution. The initial molalities of ester and alkali were 0.008 and 0.01, respectively. The molality of the salt solutions varied from 0.02 to 0.5.

Only in the case of solutions of sodium chloride are suitable activity coefficients available for the interpretation of the results. In these instances it was demonstrated that the rate of the reaction is dependent on the molality of the ester and the catalytic activity of sodium hydroxide calculated by means of the expression corresponding to that which has elsewhere been shown to represent correctly the catalytic activity of potassium hydroxide.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE SOILS RESEARCH LABORATORY, ALABAMA AGRICULTURAL EXPERIMENT STATION]

THE ADJUSTMENT OF THE REACTION OF INDICATOR SOLUTIONS AND ITS IMPORTANCE IN DETERMINING THE HYDROGEN ION CONCENTRATION OF SLIGHTLY BUFFERED SOLUTIONS

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Introduction

The determination of the hydrogen ion concentration of slightly buffered solutions has been known to be subject to various sources of errors. It has long been recognized that the hydrogen electrode, as ordinarily used, is unsatisfactory for such solutions. Lately, Beans and Hammett[1] have shown that by taking certain precautions the hydrogen ion concentration of slightly buffered solutions can be determined by the hydrogen electrode, but their electrodes become inactive quickly and the method is not adapted to routine work. Kolthoff and Bosch[2] studied the use of the quinhydrone electrode for such solutions. They found that it can be used with certain modifications for slightly buffered solutions but that it is best suited for use with solutions of moderate buffer capacity. The most generally used method for the determination of the reaction of slightly buffered solutions, however, is the indicator or colorimetric method. It, too, is open to certain objections. The one error most commonly overlooked is probably the reaction of the indicator solutions used. This has recently been emphasized by the work of Stern[3] and of Schlegel and Stueber.[4] During the last few years the writers have observed the importance of this point in working with slightly buffered soil extracts.

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[1] Beans and Hammett, THIS JOURNAL, **47**, 1215 (1925).

[2] Kolthoff and Bosch, *Chem. Weekblad*, **24**, 78–80 (1927); *C. A.*, **21**, 1586 (1927).

[3] Stern, *J. Biol. Chem.*, **65**, 677 (1925).

[4] Schlegel and Stueber, *Ind. Eng. Chem.*, **19**, 631 (1927).