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

THE COEFFICIENT OF SAPONIFICATION OF ETHYL ACETATE BY SODIUM HYDROXIDE

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An accurate determination of the coefficient of saponification of ethyl acetate by sodium hydroxide in mixtures of about one-hundredth molar concentration was undertaken as a part of the studies of catalysis carried out in this Laboratory under the direction of one of us.

The general method of work was not new. However, each detail of operation was carried out with greater precision than had been attempted before. Accurately measured volumes of reaction mixture were discharged at noted times into measured quantities of acid, calculated to be slightly in excess of that needed to neutralize the sodium hydroxide in the samples taken. The excess acid was then titrated and the concentration of sodium hydroxide calculated from the data thus obtained. The critical points in the success of the work were, first, the establishment of a suitable technique for handling the solutions without contamination with carbon dioxide of the air, and, second, the design of an apparatus which permitted very rapid discharge of accurately measured volumes of reaction mixture without exposure of the main solution to air. Details of the method and the preparation of materials will be found in Part II of this paper.

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[1] The work herewith presented was completed in 1913 and embodied in the dissertation of one of us in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.

[2] The present investigation was designed to lay the foundation for a critical study by exact methods of catalysis by alkalies as affected by ionization, by the presence of salts and by other factors. The further development of the study was carried out under the direction of Dr. Terry, acting at first as my research assistant but later acting independently. The results of these later investigations will be published by Dr. Terry and her collaborators as follows:

Influence of Added Salts on the Velocity of Saponification of Ethyl Acetate by Sodium Hydroxide. I, by S. D. Wilson (1916); II, by Ralph E. Nelson (1918).

The Coefficient of Saponification of Methyl Acetate by Sodium Hydroxide, by W. T. Gooch (1918).

Influence of Light on the Saponification of Ethyl and Methyl Acetate by Sodium Hydroxide, by W. T. Gooch (1918).

The Saponification of Ethyl Formate by Ammonium Hydroxide in the Presence of Ammonium Salts, by E. N. Roberts.

The delay in publication has been altogether due to pressure of work on the present writer. Dr. Terry kindly consented finally to undertake the critical study of the results as a whole in the light of more recent knowledge of the nature of solutions and has developed a theory covering the data obtained under a wide range of experimental conditions.

This theory will be presented by Dr. Terry in another paper.—Julius Stieglitz.

The coefficient of the reaction was calculated by the well-known bimolecular reaction equation, $dx/dt = K(A-X)(E-X)$. K is the coefficient; A represents the initial concentration (moles per liter of solution) of sodium hydroxide; E, the initial concentration of ester; X is the concentration or moles per liter of solution of alkali or ester used in the reaction at the moment considered; t is the time in minutes. The integrated form for the interval between two observed times, t_1 and t_2, is

$$K = \frac{2.303}{(A - E)(t_2 - t_1)} \log \frac{(E - X_1)(A - X_1)}{(A - X_2)(E - X_2)}$$

TABLE I

A REPRESENTATIVE EXPERIMENT

Initial concentration of sodium hydroxide = 0.01001 *N;* initial concentration of ester = 0.008072 *N.*

Time, min.	Temp., °C.	Concn. of NaOH	K, if $t_1 = 2.27$	K, if $t_1 = 3.01$
2.27	24.915	0.008934	..	..
3.01	24.920	.008630	..	..
5.85	....	.007669	6.71	6.71
6.83	24.915	.007392	6.72	6.71
8.02	24.920	.007085	6.72	6.71
8.92	24.920	.006872	6.70	6.69
10.05	24.920	.006632	6.68	6.67
10.96	24.920	.006441	6.71	6.70
11.93	24.920	.006258	6.71	6.70

Average temperature of this experiment, 24.92°.

Average = 6.70 for 24.91°, the temperature of series of experiments.

TABLE II

SUMMARY OF EXPERIMENTS

Exp.	NaOH, moles per liter	Ethyl acetate, moles per liter	K Temp. = 24.91°	K Temp. = 25.11°
1	0.009984	0.008023	6.71	...
2	.009984	.007964	6.70	...
3	.009984	.007983	6.68	...
4	.009984	.008168	6.71	...
5	.009984	.008073	6.70	...
6	.009984	.008064	6.695	...
7	.009984	.007940	6.715	...
8	.009986	.008014	6.705	...
9	.009986	.008117	6.71	...
10	.009983	.007990	6.70	...
11	.009986	.007989	6.70	...
			Average 6.70	
12	.009984	.008055	..	6.805
13	.009984	.008106	..	6.780
14	.009984	.008055	..	6.790
15	.009986	.008112	..	6.820
17	.009986	.008165	..	6.790
				Average 6.79

Change in reaction coefficient for rise of 0.20° = 0.09.
Therefore, coefficient for 25.00° = 6.75.

The average temperature (approximately 25°) per minute during the measurement of the reaction was computed and called the temperature of reaction. Then measurements were made at two-tenths of a degree higher temperature and the coefficient determined. From this it was estimated that the coefficient increased by 0.0045 for a rise of 0.01°. The results of each experiment were then corrected for difference in temperature from 24.91 in the first series or 25.11 in the second series. Data from a typical experiment are given in Table I. A summary of experiments appears in Table II.

When further studies were made on the saponification of ethyl acetate, these measurements were repeated from time to time as a means of ascertaining that experimental conditions were being kept constant. A summary of the data of various workers is given in Table III, together with a statement of the number of experiments represented, and the average and the maximum deviation of values from the average for the coefficient at 25.00° by each worker.

TABLE III

SUMMARY OF VALUES FOUND BY DIFFERENT WORKERS IN THIS LABORATORY (REF. 1)

Observer	No. of expts.	Av. coeff.	Av. dev. from mean, %	Max. dev., %
Terry (1913)	17	6.75	0.06	0.4
Wilson (1916)	8	6.76	.04	.3
Gooch (1918)	8	6.77	.2	.6

From Table III it will be seen that the results were reproducible to within one-third of one per cent. However, the error in the evaluation of the coefficient was three-quarters of one per cent. because of limitations of accuracy of measurement of time and of volume of solutions as will be explained in Part II.

TABLE IV

SUMMARY OF OLDER WORK

Experimenter	NaOH	Ethyl acetate	Temp.	Coeff., K	Coeff., at 25°
Warder[3]	0.02	0.02	25	6.4	6.4
Ostwald[4]	.025	.025	25	6.48	6.48
Arrhenius[5]	.025	.025	24.7	6.59	6.77
	.0125	.0125	24.7	6.48	6.66
	.00625	.00625	24.7	6.58	6.77
Cohen[6]	.025	.025	25	6.86	6.86
Reicher[7]	0.02–03	.016–024	24.22	6.15	6.36
Crichton[8]	.01	.01	24.85	6.47	6.84

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[3] Warder, *Ber.*, **14**, 1361–65 (1881). Coefficient at 25° is calculated from his temperature coefficient.

[4] Ostwald, *J. prakt. Chem.*, **35**, 112 (1887); also Ref. 5, note 4.

[5] Arrhenius, *Z. physik. Chem.*, **1**, 110 (1887).

[6] Cohen, *Proc. Acad. Sci. Amsterdam*, **2**, 618 (1900).

[7] Reicher, *Ann.*, **228**, 257 (1885).

[8] Crichton, *Proc. Roy. Soc.* (London), **78**, 157 (1907).

The value 6.76 may, therefore, be taken for the coefficient at 25° with the certainty that the error is less than three-fourths of one per cent.

The necessity of the above work will become apparent from Table IV, which contains a summary of the results of previous workers. Except where otherwise indicated, the temperature coefficient of 0.0045 for 0.01° change was used in estimating the reaction coefficient at 25°. A divergence of 7.5 per cent. will be observed between the highest and lowest results.

Part II. Experimental Detail

All vessels were filled with carbon dioxide-free air before they were used. When a transfer of solution was made, the opening of the flask which received the liquid was plugged lightly with cotton in the free space between buret tip or discharge tip and neck, etc. Only pure (carbon dioxide-free) air was allowed to enter the vessel from which the discharge was made.

Solutions were made with water of not greater than 1×10^{-6} mho conductance. All solutions, whether acid or alkaline, were handled as described above.

Sodium hydroxide was made by plunging freshly cut pieces of sodium under water at 0°. Each piece was held in a copper gauze basket, which was withdrawn as soon as the reaction was over. An atmosphere of carbon dioxide-free nitrogen was maintained over the water during the operation. Tests showed that no contamination of the solution by the copper basket took place.

Hydrochloric acid used in the titrations was standardized by the silver chloride method.

Ethyl acetate was made in four different ways: action of (1) acetyl chloride on alcohol; (2) acetic acid on alcohol, catalyzed by hydrochloric acid; (3) acetic anhydride on alcohol; and (4) alcohol, sulfuric acid and acetic acid, as described by Wade and Merriman.[9] In each case the final purity of the product was tested by saponifying a weighed sample of ester and titrating the unused alkali. A fifth sample was obtained from Kahlbaum and purified by fractional distillation.

The indicator used in the titrations was phenolphthalein. It was purified by the method of McCoy[10] and dissolved in carbon dioxide-free alcohol.

The end-point of the alkalimetric titrations was taken as the first faint color of the indicator. This is reported to represent a hydrogen-ion concentration close to 10^{-8}.[11] The accurate observation of this color required white light and a true white background. A so-called daylight lamp was found to be a great help in securing the correct conditions.

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

[10] McCoy, *Am. Chem. J.*, **31**, 507 (1904).

[11] Clark, "The Determination of the Concentration of Hydrogen Ion," Williams and Wilkins, Baltimore, **1922**, p. 301.

Air for filling containers for samples to be titrated was purified by filtration through moist soda lime about one meter in length. That used for the larger containers was stored over molar sodium hydroxide usually about 24 hours prior to use. Test of the purity of the air was made by titrating 50 cc. of water which had been shaken with a 500cc. sample of the air. One drop of 0.01 *N* baryta was sufficient to bring the color change of the indicator, phenolphthalein, if the air was of acceptable purity.

Apparatus.—The apparatus was simply an improvement of Reicher's device.[7] It can best be described by reference to Fig. 1. A is a container for the reaction mixture. B is a removable head. It consists of a rubber stopper, backed with a monel metal plate fitted with lugs which permitted rapid clamping into place. Through the stopper passed a Beckmann thermometer, an air outlet tube with the stopcock 1 and the discharge tube C. A mercury pipet D was connected to A through stopcock 2. Mercury was fed into the pipet through the stopcock 3 from a reservoir under pressure from water from the hydrant. The flow of mercury to A from D was controlled by stopcock 3. The mercury pipet had two graduated scales at n and m, as indicated, and the volumes between the various graduations were known. At the start of the experiment the connections from C to A were filled with mercury as shown. All rubber-to-glass or glass-to-metal joints were made with de Khotinsky cement.

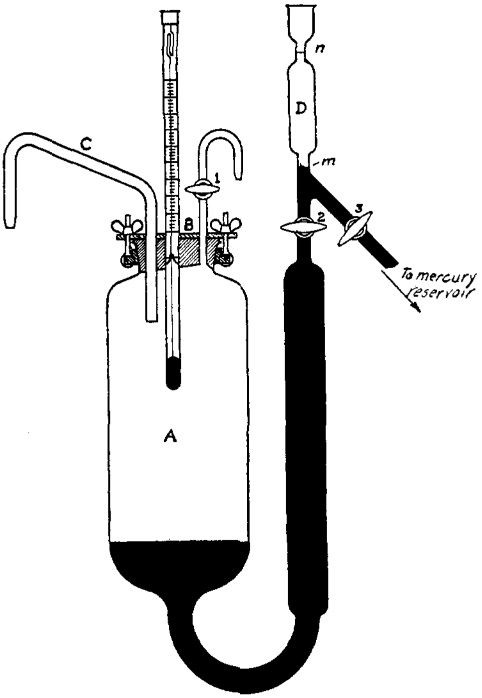

Fig. 1.

The apparatus was contained in a de Khotinsky thermostat, regulated with a constancy of 0.01°. The thermometers used were standardized by comparison with two Baudin thermometers.

Manipulation of Apparatus.—When a mixture of sodium hydroxide and ethyl acetate solution had been made in A, the top was clamped into place and mercury was forced into A to displace the air. The operator closed the discharge tube with the left hand and finally closed the air tube after the exclusion of air had been completed. A container holding the necessary acid was then put in place before the tube C and mercury discharged from the pipet into A, thus displacing a sample of the same volume from A into the receiver. The discharge occupied about five seconds and it was usually possible to collect the first sample two minutes after the original mixture had been made. The volume of the discharge, about 100 cc., was known from the levels of the mercury in m at the start and in n at the end of the discharge. The time of half discharge was observed and also the temperature of the mixture.

Analysis of Samples.—As has been stated, samples were discharged into a known quantity of acid. Before titrating the excess acid the mixture was frozen and allowed to thaw during the titration at such a rate that the last of the ice melted just before the titration was completed. From the data of titration, the concentration of sodium hydroxide at the time of discharge was calculated. The alkali was always greater in concentration than the ester. Hence, the final concentration of alkali gave the difference in concentration of alkali and ester, and thus the calculation of the concentration of ester at the time of each discharge was made possible.

Accuracy of Results.—Rigid adherence to an established technique permitted the reproduction of results to within one-third of one per cent. There were, however, certain limitations of the absolute accuracy of the results. When carbon dioxide is rigorously excluded from titrations of 0.01 N sodium hydroxide solutions, they may be completed with an accuracy limited only by the correct choice of indicator and the reading error of the buret. If allowance is made for the error in measurement in volumes not only of samples of reaction mixture, but also of the acid used to neutralize the sample and of the alkali used in completing the titration, then an error of 0.10 cc. will be seen to be the maximum probable. If the measurements had not been carried out with a strict observance of the conditions of calibration of the apparatus used, so great an accuracy could not be claimed. An error of 0.10 cc. was of no importance in the measurements made during the progress of the reaction. However, at the end of the reaction the titration results were equivalent to only 20–30 cc. of reagent, so that this error could then cause an error of one-half of one per cent. in the evaluation of $(A-E)$ and, therefore, of the coefficient.

Another source of error was the determination of the time of half discharge. This was observed by coöperation of two persons, one watching the descent of the mercury and the other watching the stopwatch in the usual way. The error could not have been greater than two-fifths of a second and the net effect on the accuracy of the determination of the coefficient was not over one-fourth of one per cent. Since the accuracy of the stopwatch was checked by comparison with a standard timepiece with which it agreed within five seconds over a period of 24 hours, no other error was introduced.

Therefore, the absolute accuracy of the value of the coefficient of the saponification may be taken to be better than three-fourths of one per cent.

Summary

Measurements were made of the velocity of saponification of ethyl acetate by sodium hydroxide in aqueous solution in mixtures of approximately one-hundredth normal concentration. The coefficient of the reaction calculated on the basis of the bimolecular equation is 6.76 for 25.00° and is accurate to three-fourths of one per cent. A change of 0.10° in temperature alters the coefficient by 0.045. The technique established

has been the basis of forthcoming studies on different aspects of the problem of catalysis of ester saponification in water solution.

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[CONTRIBUTION FROM THE EPPLEY LABORATORY]

CELLS OF THE STANDARD CELL TYPE WITH LOW ELECTROMOTIVE FORCES

BY WARREN C. VOSBURGH

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A standard cell with a low electromotive force would have some advantages over the ordinary standard cell in the measurement of small electromotive forces. Obata[1] has investigated the possibility of using for this purpose the cells

$$\mathrm{Cd(Hg)} \mid \mathrm{CdCl_2.2.5H_2O,\ sat.} \mid \mathrm{CdCl_2.2.5H_2O + PbCl_2,\ sat.} \mid \mathrm{Pb(Hg)} \qquad (1)$$

$$\mathrm{Cd(Hg)} \mid \mathrm{CdI_2,\ sat.} \mid \mathrm{CdI_2 + PbI_2,\ sat.} \mid \mathrm{Pb(Hg)} \qquad (2)$$

Taylor and Perrott[2] set up and measured some cells similar to Cells 1 and 2, the only difference being that they used an unsaturated lead amalgam, 0.72% lead. By combining the electromotive forces of their cells with the electromotive force of the cell

$$\mathrm{Pb} \mid \mathrm{Pb^{++}} \mid \mathrm{Pb\ amalgam,\ 0.72\%};\ E_{25} = 0.0109 \qquad (3)$$

which was measured by Brönsted,[3] and that of the cell

$$\mathrm{Pb} \mid \mathrm{Pb^{++}} \mid \mathrm{Pb(Hg),\ sat.};\ E = 0.0057 + 0.000016\ (t-25) \qquad (4)$$

which was measured by Gerke[4] the electromotive forces of Cells 1 and 2 can be calculated. For Cell 1 at 25° the value 0.1432 volt is obtained from the results of Taylor and Perrott, while Obata found 0.1408 volt. Similarly for Cell 2 at 25° the value 0.1020 volt is obtained from the results of Taylor and Perrott, while Obata found 0.0996 volt. Thus, there is a difference of about 2.2 mv. between the results of Taylor and Perrott and those of Obata for both cells.

Van Ginneken and Kruyt[5] have given as the requirement for a standard cell that, with temperature and pressure constant, both electrode systems must be invariant systems of the same components. The cells of Taylor and Perrott did not conform to this specification because the lead amalgam was not a two phase amalgam. One electrode system, therefore, was not an invariant system. Also, the other electrode system contained no lead. The cells of Obata were not true standard cells because the cadmium-amalgam electrode system contained no lead.

[1] Obata, *Proc. Phys. Math. Soc. Japan* [3], **3**, 64, 136 (1921).

[2] Taylor and Perrott, THIS JOURNAL, **43**, 486 (1921).

[3] Brönsted, *Z. physik. Chem.*, **56**, 668 (1906).

[4] Gerke, THIS JOURNAL, **44**, 1697 (1922).

[5] Van Ginneken and Kruyt, *Z. physik. Chem.*, **77**, 744 (1911).