The Journal of the
American Chemical Society

VOL. 50 MAY, 1928 No. 5

[Contribution from Kent Chemical Laboratory, University of Chicago]

CATALYTIC ACTIVITY OF HYDROCHLORIC ACID AND OF POTASSIUM AND OF SODIUM HYDROXIDE IN AQUEOUS SOLUTION

By Ethel M. Terry

Received February 17, 1927 Published May 5, 1928

This paper reports a new formulation of the catalytic influence of hydrochloric acid in hydrolyses and related reactions. The new expression is made in terms of the so-called thermodynamic activity coefficients of the acid and the corresponding term for potassium hydroxide instead of that of potassium chloride as has been done heretofore.[1] Similar expressions are derived for the catalytic influence of potassium and sodium hydroxide. Presentation of this material seems worth while since for the first time the catalytic influence of these reagents in aqueous solution even in the presence of potassium or sodium chloride has been described in terms which are independent of measurements of the rates of the reaction. A tentative formulation of the new functions follows.

Two New Functions.—For each reaction carried out at constant temperature a so-called kinetic equation may be written which defines the rate of the reaction in terms of a characteristic coefficient and the molalities, respectively, of catalyst and reacting components. As is well known, the coefficient, $K_{\text{obs.}}$, is found not to be constant for all experiments as would be the case if all variables affecting the rate of reaction were defined in the equation. Changes in the molality of a non-electrolyte term seem to have but little to do with this effect. The principal cause of the variation of $K_{\text{obs.}}$ rests apparently in a failure to define the influence of the catalyst.

Pairs of solutions of hydrochloric acid and potassium hydroxide of like molality will now be considered since it may be assumed plausibly that the activities of the non-catalyst ions, chloride and potassium ions, are the same in the two solutions (assumption 1). Let γ be the activity coefficient[2]

---

[1] See, for example, Harned and Pfanstiel, This Journal, **44**, 2193 (1922).

[2] Except for the expression catalytic activity and catalytic activity coefficient which appear later, the terms activity and activity coefficient should be understood in the sense introduced by G. N. Lewis. See Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, pp. 255 and 328.

of the substance indicated by the subscript; let a bracketed formula represent the molality of the substance indicated by the formula. The terms which refer to the acid solution will be marked with a prime and those without the prime should be taken as belonging to the constituents of the alkaline solution. (All γ terms in the same expression refer to solutions of like molality of hydrochloric acid and potassium hydroxide unless otherwise stated.)

Since by definition, $\gamma'_{\mathrm{Cl}^-} \times \gamma'_{\mathrm{H}^+} = \gamma'^{2}_{\mathrm{HCl}}$ and $\gamma_{\mathrm{K}^+} \times \gamma_{\mathrm{OH}^-} = \gamma^{2}_{\mathrm{KOH}}$ if, as stated above, $\gamma_{\mathrm{K}^+} = \gamma'_{\mathrm{Cl}^-}$, then for each pair of solutions

$$\gamma'_{\mathrm{H}^+}/\gamma_{\mathrm{OH}^-} = \gamma'_{\mathrm{H}^+}\gamma_{\mathrm{Cl}^-}/\gamma_{\mathrm{K}^+}\gamma_{\mathrm{OH}^-} = \gamma'^{2}_{\mathrm{HCl}}/\gamma^{2}_{\mathrm{KOH}} \tag{1}$$

In every case of hydrochloric acid catalysis for which data are available if $K_{\mathrm{obs.}}$ (defined above) is divided by the activity coefficient characteristic of the acid under the conditions of the experiment for which $K_{\mathrm{obs.}}$ was determined, the quotient is found to increase with the molality of the catalyst in the reaction mixture. Therefore on the assumption (second assumption, basically that of Arrhenius) that the active agent of the acid is the hydrogen ion and therefore that variations of $K_{\mathrm{obs.}}$ are directly proportional to the activity coefficient of the catalyst ion, the activity coefficient of the catalyst ion must be considered greater than the activity coefficient of the catalyst. The latter, of course, is the geometrical mean of the activity coefficients of the two ions of each of the catalysts under consideration.

Therefore, according to assumption 2, $\gamma_{\mathrm{H}^+} > \gamma_{\mathrm{HCl}}$ and by similar logic $\gamma_{\mathrm{OH}^-} < \gamma_{\mathrm{KOH}}$.

The terms of the right-hand side of Equation 1 are rearranged in Equation 2 in order that it may be expressed as the ratio of two terms, the one in the numerator being greater than γ_{HCl} and the one in the denominator being less than γ_{KOH} (except, of course, at infinite dilution when these terms are all equal to one).

$$\gamma'_{\mathrm{H}^+}/\gamma_{\mathrm{OH}} = (\gamma'_{\mathrm{HCl}}/\gamma_{\mathrm{KOH}})/(\gamma_{\mathrm{KOH}}/\gamma'_{\mathrm{HCl}}) \tag{2}$$

Therefore,

$$\gamma'_{\mathrm{H}^+}/(\gamma'_{\mathrm{HCl}}/\gamma_{\mathrm{KOH}}) = \gamma_{\mathrm{OH}}/(\gamma_{\mathrm{KOH}}/\gamma'_{\mathrm{HCl}}) = d \tag{3}$$

and d is a value defined by Equation 3.

Then for any molality of hydrochloric acid

$$\gamma'_{\mathrm{H}^+} = d\gamma'_{\mathrm{HCl}}/\gamma_{\mathrm{KOH}} \tag{4}$$

and for any molality of potassium hydroxide

$$\gamma_{\mathrm{OH}^-} = d\gamma_{\mathrm{KOH}}/\gamma'_{\mathrm{HCl}} \tag{5}$$

If K_0' is the coefficient of the reaction when the influence of the catalyst is proportional to its molality, then for reactions catalyzed by the hydrogen ion of hydrochloric acid

$$K_{\mathrm{obs.}} = K_0'\gamma_{\mathrm{H}^+} = K_0'd\gamma'_{\mathrm{HCl}}/\gamma_{\mathrm{KOH}} \tag{6}$$

then

$$K_{\mathrm{obs.}}\,(\gamma_{\mathrm{KOH}}/\gamma'_{\mathrm{HCl}}) = K_0'd \tag{7}$$

Similarly for reactions catalyzed by the hydroxide ion of potassium hydroxide

$$K_{\text{obs.}}\ \gamma'_{\text{HCl}}/\gamma_{\text{KOH}} = K_0 d \qquad (8)$$

and K_0 is the coefficient of the reaction when the influence of the base is proportional to its molality.

Before discussing the truth of the two tentative assumptions and the possible nature of the term d, demonstration will be made of the peculiar fact that $K_0'd$ and K_0d are constant values in the cases of ester hydrolyses and similar reactions.

Hydrolysis of Ethyl Acetate in Hydrochloric Acid Solution.—It will be remembered that if the hydrolysis of ethyl acetate is carried out in dilute aqueous solution, the reaction proceeds to an equilibrium state representing about 95% transformation of the initial ester as indicated by the chemical equation

$$H_2O + C_2H_5\text{—}O\text{—}CO\text{—}CH_3 \longrightarrow C_2H_5OH + HO\text{—}CO\text{—}CH_3$$

The catalyst acid is unchanged by the reaction and affects both the rate of the forward reaction (hydrolysis) and the backward reaction (esterification).

The best data available are those of Harned and Pfanstiel,[1] who report the coefficients of the rate of reaction calculated as follows: t is the time in minutes elapsed since the beginning of the reaction; E is the initial molality of the ester and A the initial molality of water; X is the molality of ester transformed at the time, t; K_9 is the coefficient of the rate of hydrolysis and K_9' is the coefficient of esterification; (HCl) is the molality of the catalyst acid.

$$dX/dt = (\text{HCl})\ K_9\ (E - X)\ (A - X) - K_9'\ (\text{HCl})\ X^2$$

The ratio of K_9'/K_9 was taken as 4, the value determined by Berthollet for the ratio $(E - X)(A - X)/X^2$ at equilibrium. Therefore, this equation was simplified by substitution of $4K_9$ for K_9', as follows

$$dX/dt = K_9\ (\text{HCl})\ [(E - X)\ (A - X) - 4X^2] \qquad (9)$$

In the data to be discussed, the variations in the term $(A - X)$ are within the apparent error of experiment (1%), so that the success of Equation 9 in describing the results of a given experiment is no indication that this term represents a real factor as has been pointed out by Worley.[3] It seems best to omit it[3a] until positive evidence for its adoption is found. The equation for the reaction is therefore

$$dX/dt = K_{10}\ (\text{HCl})\ [(E - X) - K_{10}'\ X^2]$$

---

[3] Worley, *Proc. Roy. Soc. (London)*, **87**, 885 (1912). (a) Obviously, although the ions of water are ultimately consumed in the reaction, it does not follow that water is an active agent of the slowest stage which is the stage measured. See Scatchard, THIS JOURNAL, **43**, 2406 (1921), for an important effort to correlate the activity of water with variations of $K_{\text{obs.}}$ in sucrose hydrolysis.

From the data of Harned and Pfanstiel K_{10}' is found to equal 0.068 K_{10}. Therefore the equation may be rewritten as follows

$$dX/dt = K_{10}\,(\mathrm{HCl})\,[(E - X) - 0.068\,X^2] \qquad (10)$$

In this expression K_{10} is the coefficient of the hydrolysis calculated on the assumption that water is not an active agent of the reaction measured. The other terms have the meaning already assigned.

Equation 10 may be integrated after substitution as follows

Let $f = 0.068$ and $g = \sqrt{4Ef + 1}$: then

$$(\mathrm{HCl})K_{10} = (2.303/gt)\,\log_{10}\,(g + 2fX + 1)\,(g - 1)/(g - 2fX - 1)\,(g + 1)$$

In Table I are given the details of an experiment reported by Harned and Pfanstiel.[1] The column headings are self explanatory. It will be seen that since $(\mathrm{HCl})K_{10}$ has the same order of constancy as $(\mathrm{HCl})K_9$, Equation 10 describes the rate of reaction in question just as satisfactorily as Equation 9.

TABLE I

HYDROLYSIS OF ETHYL ACETATE IN 0.20 MOLAL AQUEOUS HYDROCHLORIC ACID SOLUTION AT 25°

Data of Harned and Pfanstiel[1]

$E = 0.4724$ Molal $g = 1.0623$ $f = 0.068$ (HCl) = 0.20 Molal

X	Time, minutes	$(\mathrm{HCl})\ K_9 \times 10^5$	$(\mathrm{HCl})\ K_{10} \times 10^3$
0.000	0	...	...
.06433	119	2.345	1.232
.1058	206	2.345	1.231
.1486	307	2.337	1.231
.1895	419	2.347	1.226
.2283	539	2.335	1.227
.2676	686	2.335	1.227
.3102	885	2.338	1.223
.3406	1058	2.353	1.230
	Average	2.341	1.228

The difference between the lowest and the highest values of coefficients in either series is 0.5%.

In Cols. 1 and 2, Table II, are given the data of an extended series of experiments of Harned and Pfanstiel. From these data, for each experiment represented, the values of X for selected intervals of time were calculated and to these data Equation 10 was applied. The values of K_{10} found appear in Col. 3 of Table II.[4]

Cols. 4 and 5 contain γ'_{HCl} and γ_{KOH} taken from the data of Scatchard[5] and of Harned,[6] respectively.

---

[4] Reference should be made to the Harned and Pfanstiel paper (ref. 1) for the equation for calculation of the values of X. In brief, the equation used was

$$K_9\,(\mathrm{HCl}) = \frac{0.04117}{t}\log\frac{(-2.738 - 0.1506X)}{(-2.738 + 6X)}$$

[5] Scatchard, THIS JOURNAL, 47, 641 (1925).

[6] Harned, *ibid.*, 47, 682 (1925).

TABLE II

COEFFICIENTS OF THE RATE OF HYDROLYSIS OF ETHYL ACETATE IN SOLUTIONS OF VARYING HYDROCHLORIC ACID MOLALITY AT 25°[1]

Molality of ester, 0.47

HCl, molality	$K_9 \times 10^6$ (ref. 1)	$K_{10} \times 10^3$ or $K_{\text{obs.}} \times 10^3$	γ'_{HCl} (ref. 5)	γ_{KOH} (ref. 6)	$K_0'd \times 10^3$ (see Equation 7)
0.010	1.167	6.19	0.910	0.920	6.26
.030	1.147	6.03	.860	.857	6.01
.050	1.146	6.02	.836	.820	5.96
.070	1.139	5.99	.817	.800	6.03
.100	1.146	6.01	.801	.789	5.92
.150	1.157	6.09	.787	.774	5.99
.200	1.164	6.15	.774	.763	6.06
.300	1.178	6.20	.763	.746	6.06
.500	1.201	6.30	.763	.732	6.04
.700	1.229	6.47	.778	.737	6.13
1.000	1.252	6.58	.817	.760	6.12
1.500	1.307	6.87	.905	.819	6.20

Average of all = 6.06
Average of 1st 6 values of $K_0'd$ = 6.02
Average of 2nd 6 values of $K_0'd$ = 6.10
Difference between 1st and 2nd 6 values of $K_0'd$ = 1.3%

In Col. 6 is the product $K_{10}\gamma_{\text{KOH}}/\gamma'_{\text{HCl}}$, or $K_{\text{obs.}}\gamma_{\text{KOH}}/\gamma'_{\text{HCl}} = K_0'd$ of Equation 7. The constancy of the product over a variation of acid molality from 0.01 to 1.50 is remarkable. The average of the first six values differs from the average of the last six by only 1.3%.

Hydrolysis of Ethyl Acetate by Hydrochloric Acid in the Presence of Either Potassium or Sodium Chloride.—Harned[7] reports a summary of his own and Taylor's data[8] on the effect of potassium and sodium chlorides on the rate of hydrolysis of ethyl acetate when catalyzed by hydrochloric acid in aqueous solution at 25°. These data are given in Table III.

Both Taylor and Harned calculated the rate of hydrolysis on the assumption that the reaction was complete. The integrated equation used by them in calculating the coefficient, K_{11}(HCl), of the reaction follows

$$(\text{HCl})K_{11} = [1/(t_2 - t_1)] \log_{10} [(E - X_1)/(E - X_2)] \qquad (11)$$

In this expression the symbols are used in the sense already defined except that formula weights per liter are implied instead of molality.

The data for sodium chloride solutions have been included since it seemed probable that at least over a moderate range the activity of the chloride ion in a solution of hydrochloric acid and sodium chloride might be taken as close to that of sodium ion in a solution of sodium hydroxide of like molality to the hydrochloric acid and of like molality of sodium chloride to that of the sodium chloride in the hydrochloric acid solution. Thus

---

[7] Harned, THIS JOURNAL, **40**, 1461 (1918).

[8] Taylor, *Medd. Vetenskapsakad. Nobelinst.*, **2**, No. 34 (1913); also THIS JOURNAL, **37**, 551 (1915).

$K_0'd$ should be equal to $K_{\mathrm{obs.}} \times \gamma_{\mathrm{NaOH}}/\gamma'_{\mathrm{HCl}}$ if the latter terms are determined in solutions of the same molality of sodium chloride as that used in the catalysis experiments.

The electrolyte composition of the solutions was put in terms of molality on the basis of calculations made from the density data of Ruby and Kawai.[9] No account could be taken in these calculations of the ester in the mixture, as suitable data were not given by the authors. It will be assumed that this error appears consistently in all the results of Table III.

Since the molality of hydrochloric acid was found to have changed slightly from one experiment to the other, a proportionate correction was applied to K_{11} in order to have the results refer to a solution of 0.1005 molality. These coefficients appear as (HCl)K_{11}' in Col. 5, Table III. In this table values of γ'_{HCl}[10] and of γ_{KOH}[11a] and of γ_{NaOH}[11b] are taken from the work of Harned. Col. 8 gives the product $K_{11}'\gamma_{\mathrm{KOH}}/\gamma'_{\mathrm{HCl}}$, which is the same as $K_{\mathrm{obs.}}\gamma_{\mathrm{KOH}}/\gamma'_{\mathrm{HCl}} = K_0'd$ of Equation 7. The absolute value of K_0d ($288 \times 10^{-5} \times 2.303 = 6.67 \times 10^{-3}$) is not the same as that of Table II, which is 5.92×10^{-3}. A small part of the difference may be accounted for by the neglect of the presence of the ester already referred to. However, the main part of the difference must be due to some consistent difference of experimental conditions. The slight irregularity of the values is within the probable limits of experimental error. For concentrations up to 1 *N*, the agreement is close. For greater concentrations a slight increase is found in the potassium chloride experiments and a slight decrease in the sodium chloride series.

TABLE III

EFFECT OF NEUTRAL SALTS ON HYDROLYSIS OF ETHYL ACETATE IN *M*/10 HCL AT 25°

Normality of salt (KCl)	$K_{11} \times$ (HCl) $\times 10^5$ Harned,[7] Taylor[8]	Molality of salt (KCl)	Molality of acid	K_{11}' $\times 10^5$ ($K_{\mathrm{obs.}}$)	γ_{HCl}[10]	γ_{KOH}[11a]	$K_0'd$ $\times 10^5$	Difference from 288 $\times 10^5$, %
0.00	28.8	0.00	0.1005	288	0.79	0.789	288	. . .
.50	31.45	.51	.1020	309.8	.716	.666	288	0.0
1.00	34.3	1.04	.1040	331.4	.725	.645	295	2.5
1.50	36.6	1.58	.1050	350.1	.750	.644	301	4.5
2.00	39.2	2.12	.1060	371.6	.793	.645	302	5.0
(NaCl)		(NaCl)				γ_{NaOH}[11b]		
0.50	31.75	0.50	0.1005	318	0.741	0.660	283	−2.0
1.00	35.9	1.02	.1020	354	.783	.636	288	0.0
1.50	39.3	1.56	.1040	379	.855	.625	279	−3.0
2.00	42.85	2.09	.1045	411	.944	.620	270	−6.6

Since Taylor[8] has shown that the change in reaction coefficient which is brought about on the addition of salt to a hydrochloric acid solution

---

[9] Ruby and Kawai, THIS JOURNAL, **48,** 1119 (1926).

[10] Harned, *ibid.*, **48,** 326 (1926).

[11] (a) Harned, *ibid.*, **47,** 689 (1925); (b) *ibid.*, p. 684.

of an ester is the same for a variety of esters, the fact that $K_0'd$ is virtually a constant value is proof that the correlation of the influence of the acid as a catalyst with its activity as an acid given in Equation 7 may be considered representative of all hydrolyses of all esters in aqueous hydrochloric acid solution, provided, of course, the ester molality is small so that no material change in the dielectric of the medium is brought about.[12]

Hydrolysis of Sucrose in Hydrochloric Acid Solution.—If $K_0'd$ is calculated for hydrolysis of sucrose on the basis of the data of Fales and Morrell,[13] it is found to be far from constant. Thus for experiments in which the molality of hydrochloric acid is 1.2 $K_0'd$ is 46% greater than that for 0.1 M hydrochloric acid experiments.

Palmaer,[14] years ago, showed that whereas the influence of hydrochloric acid on ester hydrolysis is nearly proportional to its concentration up to tenth normal value, the same is true of sucrose hydrolysis only up to one hundredth normality. This apparently greater catalytic influence of hydrochloric acid in the case of sucrose has been ascribed to an increase in thermodynamic activity of hydrochloric acid brought about by the presence of the sugar.[15]

However, Coppadoro[16] and Griffith, Lamble and Lewis[17] have reported that ester hydrolysis catalyzed by hydrochloric acid takes place at the same rate whether sucrose is present or not, provided that the molalities of the acid and ester are the same in each experiment. Furthermore, Caldwell[18] has shown that for solutions of sucrose varying in molality from 0.25 to 1 and catalyzed by 1 M hydrochloric acid, the coefficient $K_{\text{obs.}}$ is constant within 3%. This could hardly be true if sucrose increases the influence of hydrochloric acid as catalyst.

It seems improbable, therefore, that the difference in result in the two reactions is due primarily, at least, to a change in behavior of acid but rather to some other variable not yet defined. The greater complexity of the sucrose molecule suggests that more than one catalyst group may be active.[19] The point important to this discussion is that from the failure

---

[12] See Harned and Fleysher, THIS JOURNAL, **47**, 82 (1925); Scatchard, *ibid.*, **47**, 2098 (1925); Lucasse, *ibid.*, **48**, 626 (1926), for examples of the effect of non-electrolytes on the activity of hydrochloric acid in aqueous solution.

[13] Fales and Morrell, *ibid.*, **44**, 2021 (1922).

[14] Palmaer, *Z. physik. Chem.*, **22**, 492 (1897).

[15] Jones and W. C. McC. Lewis, *J. Chem. Soc.*, **117**, 1123 (1920). See also ref. 13 and Scatchard, THIS JOURNAL, **48**, 2026 (1926).

[16] Coppadoro, *Gazz. chim. ital.*, **31**, I, 425 (1901).

[17] Griffith, Lamble and Lewis, *J. Chem. Soc.*, **111**, 389 (1917).

[18] Caldwell, *Proc. Roy. Soc. (London)*, **78A**, 272 (1906).

[19] In a forthcoming paper it will be demonstrated that

$$K_{\text{obs.}} = A(\gamma_{\text{HCl}}/\gamma_{\text{KOH}}) + B(\gamma_{\text{HCl}}^2)\,[\text{HCl} + \text{KCl}]$$

In this expression A and B are constants characteristic of the temperature at which measurements are made. (E. M. T., February, 1928.)

of Equation 7 to describe the results of sucrose hydrolysis we may not yet conclude that the success of this equation with other reactions is purely an empirical matter.

Summary of Results on Catalysis by Hydrochloric Acid.—The constancy of $K_0'd$ calculated by means of Equation 7 has been established for the hydrolysis of esters in the presence of hydrochloric acid and potassium or sodium chloride over a very considerable variation of molality. It is of interest that Taylor and Close[20] report the variation of catalytic power of hydrochloric acid with changing molality or with the addition of neutral salts in the case of the formation of valerolactone from hydroxyvaleric acid is parallel to the variation of activity of hydrochloric acid under the same conditions in the case of ester hydrolysis. It is true that there is much similarity between ester hydrolysis and lactone formation in that it is probable that both depend on the formation of intermediate oxonium compounds.[21] However, they represent the simplest cases of catalysis and should be taken as the basis of study of this obscure subject.

Equation 7 does not describe the results of sucrose hydrolysis. However, this reaction is more complex than the above type and it is to be anticipated that it may be interpreted in the light of the success gained with the simpler cases.

The Catalytic Activity of Potassium Hydroxide and of Sodium Hydroxide.—The most extensive data on the catalytic influence of potassium hydroxide and sodium hydroxide are those of Åkerlöf[22] on the decomposition of diacetone alcohol to form acetone

$$CH_3—CO—CH_2—CHOH—(CH_3) \longrightarrow 2CH_3—CO—CH_3$$

In aqueous solution the change may be considered complete and for a given molality of catalyst a coefficient of the reaction may be calculated by application of the well known equation for a monomolecular change to the variation of the volume of the solution. Neither initial nor final material binds an appreciable part of the catalyst.

Table IV presents the data of Åkerlöf on the rate of this reaction in the presence of tenth molal potassium hydroxide in potassium chloride of varying molality up to 2. The final column gives K_0d and it is seen to be a truly constant term.[23]

[20] Taylor and Close, THIS JOURNAL, **39**, 422 (1917); Taylor and Wilberforce, *J. Phys. Chem.*, **29**, 1085 (1922).

$K_0'd$ calculated for their data is constant to 2+% for molalities of KCl up to 0.5. They report one other value and this is for unit molality of KCl from which a value of K_0d is found which is 7% higher than the average of others.

[21] (a) Stieglitz, *Int. Comg. Arts Sci.*, **4**, 276 (1904); (b) *Am. Chem. J.*, **39**, 181 (1907); (c) Kendall and Booge, THIS JOURNAL, **38**, 1713 (1916).

[22] Åkerlöf, THIS JOURNAL, **48**, 3046 (1926); see also ref. 23.

[23] Since the presentation of this paper, February, 1927, Dr. Åkerlöf has published

The data for sodium hydroxide catalysis of the reaction in question are not so regular; values of K_0d calculated for 0.0, 0.5, 1.0, 1.5 and 2 molal sodium chloride, respectively, with tenth molal sodium hydroxide are 0.202, 0.189, 0.186, 0.186, 0.186. The variation of K_0d is a matter of 8%.

TABLE IV

APPLICATION OF EQUATION 8 TO DATA OF ÅKERLÖF ON THE DECOMPOSITION OF ACETONE ALCOHOL[1] AT 25° IN SOLUTIONS OF 0.1 M POTASSIUM HYDROXIDE AND VARYING POTASSIUM CHLORIDE MOLALITY

KCl molality	γ_{KOH}[13]	γ'_{HCl}[12]	$K_{obs.}$	K_0d
0.00	0.789	0.79	0.204	0.204
.50	.666	.74	.183	.204
1.00	.643	.78	.166	.201
1.50	.644	.845	.153	.201
2.00	.645	.93	.142	.205
			Average	.203

Widest deviation from the average, 1%.

Elsewhere[24] it is shown that Equation 8 applies accurately to the data of hydrolysis of ethyl acetate in hundredth molal sodium hydroxide in the presence of sodium chloride up to half molality (the extent of the measurement).

The alkaline hydrolysis of sucrose is not being considered in this paper as it is still more complex than the acid hydrolysis. For example, Cohen[25] has shown that sucrose binds no small portion of the catalyst base. The decomposition of nitrosotri-acetone-amine to form phorone and nitrogen is also not considered since Francis and co-workers,[26] who have made the measurements on this reaction, report it complex and the true nature of all the products unknown.

Summary of Results on the Catalytic Activity of Potassium Hydroxide and Sodium Hydroxide.—In dilute solutions of sodium or potassium hydroxide, hundredth to tenth molal for example, it is usually found[27] that the coefficient of the catalyzed reaction $K_{obs.}$ is constant. During this interval the ratio $\gamma_{KOH}/\gamma'_{HCl}$ is very nearly equal to 1 so that the application of Equation 8 to the data is successful. A severe test is made, however, when Equation 8 is applied to the data of Åkerlöf in which

---

further results of measurements on this reaction in more concentrated potassium hydroxide solutions. Since he does not assure us that the products are the same as in the dilute solution reactions, the interpretation of the results is in doubt. Nevertheless, it is of interest that K_0d proves to be constant for molalities of KOH up to 1.0. See THIS JOURNAL, **49,** 2955 (1927).

[24] Wilson and Terry, THIS JOURNAL, **50,** 1250 (1928).

[25] Cohen, *Z. physik. Chem.*, **37,** 68 (1901).

[26] Francis and Clibbens, *J. Chem. Soc.*, **101,** 2358 (1912); Francis and Geake, *ibid.*, **103,** 1722 (1913).

[27] See for example ref. 24; also the work of Koelichin, *Z. physik. Chem.*, **33,** 129 (1900), on the decomposition of acetone alcohol in dilute aqueous alkali.

the molality of the salt, potassium chloride, varied from 0 to 2.0 and the two γ terms change in a quite different manner. The data of Wilson and Terry also furnish a convincing test that Equation 8 does formulate the real variables of experiment.

The Catalytic Activity Coefficients of Hydrochloric Acid, Potassium Hydroxide and Sodium Hydroxide.—Since each of the terms $\gamma'_{HCl}/\gamma_{KOH}$, $\gamma_{KOH}/\gamma'_{HCl}$ and $\gamma_{NaOH}/\gamma'_{HCl}$ multiplied by the molality of the catalyst to which they respectively refer describes the activity of that catalyst as measured by its influence on the rate of the reaction in question, these terms may be properly called the catalytic activity coefficients of hydrochloric acid, potassium hydroxide and sodium hydroxide. The formulation of these coefficients in terms of experimental data secured from measurements other than those of the rate of the reactions catalyzed is new and their correctness is an experimental fact.

Discussion of Results.—The very considerable breadth of application of Equations 7 and 8 warrants a brief discussion of the possible validity of their derivations and an expression of opinion as to the nature of the *d* term.

At the outset it must be remembered that we have no insight into the mechanism of the reactions in question other than that given by the successful formulation of equations describing the rate of change. That an equation should be broadly successful argues that it gives at least a graphic representation of the variables affecting the slowest stage of the reaction. The case of the hydrolysis of sucrose, to which the equation does not apply, makes us aware of a new variable which may have existed in the cases of successful operation of the equation but may have been hidden by other unknown and compensating effects. Therefore, until we have an expression which describes the catalytic activity of hydrochloric acid in sucrose hydrolysis both with and without the presence of salts, there is no certainty that the correctness of the simple assumptions used in the derivation of Equations 7 and 8 is confirmed by the latters' success.

We may, however, weigh the possible meaning of the evidence at present available. Assumptions 1 and 2 have been generally used[28,29] and at present there is no evidence against them. The *d* term is the obvious basis of speculation. The reciprocal value, $1/d$, is that factor which multiplied by the thermodynamic activity coefficient of the catalyst ion gives the coefficient characteristic of its catalytic behavior (calculated in terms of molality of ion present). The present currently used conception of the independent

---

[28] Assumption 1 was first used by MacInnes, THIS JOURNAL, **41**, 1086 (1919). He assumed that the activities of potassium and chloride ion at like molalities are the same in neutral and non-neutral solutions. This is not done in the present work.

[29] For an excellent bibliography of recent efforts, see Note 1, p. 3046, of ref. 22.

activities of ions leads to the conclusion that $1/d$ is not a constant. Nevertheless, it should be remembered that this theory of ionic behavior has no direct experimental basis.[30]

The fact that the catalytic activity coefficients of hydrochloric acid and potassium hydroxide are reciprocal values so that their product is unity may seem critical evidence against the idea that d is a constant; for in solutions of potassium chloride (and sodium chloride), the (geometric) average of the activity of coefficients of hydrogen and hydroxide ion have been proved by Harned[31] to vary with the molality of salt present in solution. Obviously either the indicated relation of the activity coefficients of hydrogen and hydroxide ions does not hold completely to zero molality of acid and base or else the new functions are not the thermodynamic activity coefficients of the catalyst ions. The correct choice of these alternatives may not yet be made.

It may therefore be concluded that it is not impossible that d is a constant term, and that the activity of the catalyst is defined by the thermodynamic activity of the catalyst ion. However, not until more extensive evidence is available will this interpretation seem probable.

A totally different interpretation of Equations 7 and 8 would be that of the Brönsted theory[32] which calls for equations of just such form. However, the fact that in many reactions the catalytic activity coefficient of hydrochloric acid is independent of the substance undergoing change is in conflict with this theory.

Summary

Expressions are reported which represent the influence of aqueous hydrochloric acid, potassium hydroxide and sodium hydroxide, respectively, as catalysts at varying molalities. The terms of these expressions are the thermodynamic activity coefficients of the substances named.

It is demonstrated that these expressions describe correctly the catalytic

---

[30] This principle has been adopted as the simplest explanation of the experimental fact pointed out by Lewis and Randall, THIS JOURNAL, **43**, 1141 (1921), that in dilute solution (about up to 0.02 ionic strength) the activity coefficient of a given electrolyte is determined by (its valence type and) the ionic strength of the solution and is not dependent on the nature of the other ions present in solution. However, as Lewis and Randall point out (ref. 2, p. 380) the deduction from this fact, that the activity coefficient of an *ion* is likewise independent of the nature of its neighbors, is not a necessary one since "some peculiar compensation" may operate so that though in dilute solution the geometric mean of the activity coefficients of the ions of a given electrolyte is independent of the nature of other ions present in solution, still the activity coefficients of the ions themselves vary. It should be added that these authors believe the second explanation improbable.

[31] Harned, THIS JOURNAL, **47**, 930 (1925). Harned's activity coefficient of water is the activity coefficient of ionized water, not the activity coefficient of water calculated from vapor pressure measurements.

[32] Brönsted, *Z. Physik*, **102**, 169 (1922); **115**, 337 (1925).

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.

Chicago, Illinois

[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

Received July 5, 1927 Published May 5, 1928

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

---

[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).