## CORRECTION.

On page 174 of the February number read $k=k_0e^{\kappa C}$, instead of $k=k_0e^{C}$.

On page 176 (near the bottom): read $\ldots\ldots = \frac{k_0}{k_0'}. e^{(\kappa-\kappa')S} = K$, instead of $\ldots\ldots = \frac{k_0}{k_0'}\ \kappa-\kappa')S = K$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

# A RE-INVESTIGATION OF THE VELOCITY OF SUGAR HYDROLYSIS.

## SECOND COMMUNICATION: THE ROLE OF WATER.[1]

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In a former communication it was shown that sugar hydrolysis is strictly unimolecular with respect to the sugar itself. In the present communication an attempt will be made to show that water plays a double role in the reaction: on the one hand, it takes part in the reaction and contributes to its velocity according to the law of mass action; on the other hand, it acts as a negative catalyzer by its dissociating power. With respect to this retarding effect, the reaction will be shown to follow a catalysis principle which is also obeyed by several other reactions investigated here within the past few years.

### 1. The Anomaly of the Reaction.

In course of his classic researches on the strength of acids, Ostwald discovered a puzzling anomaly in the hydrolysis of cane sugar: contrary to the mass law for a unimolecular reaction, the velocity of hydrolysis was found to be a function of the initial concentration of the sugar.[2]

Shortly afterward Spohr advanced the idea that the cause of this phenomenon lies in the changing ratio of the concentrations of acid and water: the less sugar in the solution initially, the more water, therefore the "weaker" the acid and the slower the hydrolysis.[3] Three experiments reported by Spohr, in which different amounts of sugar were dissolved in equal amounts of tenth-normal hydrobromic acid, appeared to support this view, the three velocity coefficients being equal, or nearly so. But similar experiments with formic acid carried out in these laboratories have yielded velocity coefficients varying regularly with the initial amount of sugar. This shows that Spohr's observation was not of a general character and, hence, that his explanation of the anomaly is incorrect. Nor does the explanation appear plausible in the light of the dissociation theory: the more water in place of sugar, the greater must be the dissocia-

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[1] Presented before the New York Section of the Am. Chem. Soc. on October 11, 1912.

[2] Ostwald: *J. prakt. Chem.*, [2] 31, 316 (1885).

[3] Spohr: *Ibid.*, 33, 267 (1886).

tion of the acid, and hence the *greater* its catalytic power; while in Ostwald's experiments a decrease in the initial amount of sugar resulted in a decrease of the reaction velocity.

A new interpretation was proposed in 1897 by Ernst Cohen.[1] This investigator believes that in a more concentrated solution the reaction is faster because the available volume is smaller, the sugar molecules filling, and rendering unavailable, part of the volume. Accordingly, he introduces an impirical volume correction analogous to the quantity $b$ of the van der Waals equation and to the similar correction proposed by A. A. Noyes for van't Hoff's ideal law of osmotic pressure.[2] If, however, we consider that according to the mass law the velocity of hydrolysis should be the same whether the volume (or its reciprocal, the initial sugar concentration) is large or small, whether the whole of the apparent volume is available or not, Cohen's volume correction appears to emphasize the discrepancy between theory and fact, rather than account for it.

Still another idea, advanced by Arrhenius,[3] may be briefly stated as follows: The law of mass action, as deduced by van't Hoff thermodynamically, refers, not to concentrations, but to osmotic pressures. The customary employment of volume concentrations in place of osmotic pressures is admissible only at infinit dilution. At finite concentrations it is erroneous in principle and must lead to apparent discrepancies like that found by Ostwald. No discrepancy should appear if the mass law were applied to the osmotic pressures involved.

Unfortunately, the partial osmotic pressures of cane sugar in solutions undergoing inversion and containing both cane sugar and invert sugar, are unknown. Nevertheless, we were able to test Arrhenius' idea indirectly. If, namely, we assume, with Arrhenius, that active masses are to be measured by osmotic pressures, and denote by $\pi$ the pressure at the time $t$, we get:

$$d\pi/dt = -k\pi.$$

We must expect, then, that the relative change of $\pi$ per unit time will be constant during a single process and the same for different processes independently of the initial osmotic pressures involved. Denoting by $\pi_0$ the initial osmotic pressure and integrating:

$$\frac{1}{t}\log\frac{\pi_0}{\pi} = k.$$

For pure cane sugar solutions Arrhenius gives:[4]

$$G = 0.0541(p + 0.0132p^2),$$

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[1] Cohen: *Z. physik. Chem.*, 23, 442 (1897).

[2] A. A. Noyes: *Z. physik. Chem.*, 5, 53 (1890).

[3] Arrhenius, *Ibid.*, 28, 319 (1899).

[4] Arrhenius, *Ibid.*, 28, 320.

where G is the depression of the freezing point (which is very nearly proportional to the osmotic pressure) and $p$ is the number of grams of sugar per 100 cc. of solution. If this expression held true also in the presence of invert sugar, then, substituting[1] $0.5504\ (\alpha - \alpha_\infty)$ for $p$, we should have:

$$\frac{1}{t} \log_{10} \frac{(\alpha_0 - \alpha_\infty) + 0.00727\ (\alpha_0 - \alpha_\infty)^2}{(\alpha - \alpha_\infty) + 0.00727\ (\alpha - \alpha_\infty)^2} = k \text{ (constant)}.$$

As a matter of fact, owing to the presence of invert sugar, the osmotic pressures here taken into account are more or less different from the true partial osmotic pressures, and therefore the velocity coefficient $k$ calculated from the observed rotations cannot be expected to remain constant. But if the calculated coefficients are plotted against the time, extrapolation to $t = 0$ must give the *true* value of the coefficient $k$ for osmotic pressure; for in the beginning of the reaction no invert sugar is present, and as $t = 0$ is approached, the unknown partial osmotic pressures approach the known osmotic pressures of pure sugar solutions. (We neglect, with Arrhenius, the presence of acid.) Applying this process to Ostwald's four series of different initial osmotic pressures, we expect, then, the four extrapolated values of $k$ to be the same, if Arrhenius' view of the anomaly is correct and it is the relative variation of osmotic pressure, and not of volume concentration, that should be the same for the different solutions.

The results are shown in Tables I to IV below. Since Ostwald counted time from the arbitrary instant of the first reading, while our extrapolation requires knowledge of the time at which the reaction really began, we assumed the true $\alpha_0$ to have been 14.04° in the 10% solution (according to Ostwald, *loc. cit.*, p. 309) and proportional to the percentages (grams per 100 cc.) in the remaining solutions. It was then easy to calculate the initial times and change correspondingly the $t$'s recorded by Ostwald.

TABLE I.—SOLUTION CONTAINING 40 GRAMS OF SUGAR PER 100 CC.

| $t$ (min.). | $\alpha$. | $k \times 10^4$ (vol. concentrations). | $k \times 10^4$ (osmotic pressures). |
|---|---|---|---|
| 0 | 56.16° | ... | [38.6] |
| 11.9 | 50.46 | ... | .... |
| 71 | 28.30 | 28.84 | 37.5 |
| 127 | 13.60 | 29.25 | 36.9 |
| 178 | 4.44 | 29.21 | 36.0 |
| 226 | — 1.88 | 29.32 | 35.5 |
| 351 | —10.87 | 29.00 | 33.7 |
| ∞ | —17.98 | ... | .... |
| | | 29.12 | |

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[1] On the basis of Ostwald, *loc. cit.*, p. 309.

TABLE II.—SOLUTION CONTAINING 20 GRAMS OF SUGAR PER 100 CC.

| $t$. | $\alpha$. | $k \times 10^4$ (vol. concentrations). | $k \times 10^4$ (osmotic pressures). |
|---|---|---|---|
| 0 | 28.08° | ... | [27.3] |
| 13.2 | 25.62 | ... | .... |
| 64 | 16.76 | 22.66 | .... |
| 127 | 10.30 | 22.85 | 26.6 |
| 177 | 6.00 | 22.82 | 26.2 |
| 225 | 2.74 | 22.91 | 26.0 |
| 350 | — 2.61 | 22.88 | 25.3 |
| ∞ | — 8.35 | ... | .... |
| | | 22.82 | |

TABLE III.—SOLUTION CONTAINING 10 GRAMS OF SUGAR PER 100 CC.

| $t$. | $\alpha$. | $k \times 10^4$ (vol. concentrations). | $k \times 10^4$ (osmotic pressures). |
|---|---|---|---|
| 0 | 14.04° | ... | [23.4] |
| 13.8 | 12.90 | ... | .... |
| 71 | 8.98 | 20.23 | 23.1 |
| 127 | 5.94 | 20.53 | 22.8 |
| 177 | 3.79 | 20.81 | 22.8 |
| 224 | 2.25 | 20.78 | 22.5 |
| 349 | — 0.46 | 20.52 | 21.9 |
| ∞ | — 3.91 | ... | .... |
| | | 20.57 | |

TABLE IV.—SOLUTION CONTAINING 4 GRAMS OF SUGAR PER 100 CC.

| $t$. | $\alpha$. | $k \times 10^4$ (vol. concentrations). | $k \times 10^4$ (osmotic pressures). |
|---|---|---|---|
| 0 | 5.62° | .... | [19.7] |
| 14.9 | 5.27 | .... | .... |
| 72 | 3.82 | 18.63 | .... |
| 127 | 2.63 | 19.46 | 19.6 |
| 176 | 1.88 | 19.12 | 19.3 |
| 223 | 1.29 | 18.88 | 19.2 |
| 348 | 0.09 | 19.40 | |
| ∞ | —1.42 | .... | |
| | | 19.10 | |

The bracketed figure in the fourth column of each table represents the velocity coefficient found by graphic extrapolation to $t = 0$. In the course of each series the coefficients based on volume concentrations remain constant, those based on osmotic pressures diminish regularly. The latter coefficients would come out constant if, owing to the appearance of invert sugar, the true osmotic pressures of cane sugar were proportional to the volume concentrations. In that case, however, there would be no advantage in introducing osmotic pressures in place of the usual volume concentrations.

But what concerns us most in the present connection is that the four extrapolated coefficients, 38.6, 27.3, 23.4, and 19.7, are unequal; *i. e.*, that the relative variation of osmotic pressure is by no means independent of the initial osmotic pressures of the solutions.[1] And so it is plain that whether osmotic pressures or volume concentrations are used in connection with the law of mass action, this law alone is incapable of fully describing the phenomena of sugar hydrolysis.

### 2. New Theory.

In a previous communication[2] it was shown that in the course of any single experiment sugar hydrolysis is strictly unimolecular with respect to the sugar itself, in accord with the stoichiometric equation:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

There is no doubt but the reaction follows the mass law also with respect to the reacting water; so that if S represents the initial concentration of the sugar, W the initial concentration of the water, and $x$ the amount of sugar inverted at the time $t$, the reaction proceeds as follows:

$$dx/dt = k(S - x)(W - x).$$

On account of the large molecular weight of cane sugar, the molar concentration of the water, W, is generally large compared with S and with $x$, and therefore the equation may be simplified into:

$$dx/dt = kW(S - x).$$

The "velocity coefficient" obtained, as usual, by the unimolecular equation is thus the *product* of the true velocity coefficient $k$ and the water concentration W.

In order to find the true coefficients corresponding to Ostwald's and Spohr's measurements, we were obliged to determin how much water was present in their solutions per unit volume. For this purpose we reprepared their solutions, weighing the several ingredients, including the water. Ostwald's four solutions were found to have contained, respectively, 39.28, 46.11, 49.48 and 51.43 mols of water per liter. His coefficients, $kW \times 10^4$, are respectively 29.16, 22.87, 20.63, and 19.14. Dividing these by the values of W just given we obtain, as the true velocity coefficients: 0.0000742, 0.0000496, 0.0000417, and 0.0000372. While, then, the unimolecular coefficients change in the ratio of about 3 to 2, the corrected coefficients change in the greater ratio of 2 to 1, so that the

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[1] Arrhenius' own calculations show that in Ostwald's four series the initial change of *volume concentration* $[dx/dt]_{t=0}$ is proportional to the initial *osmotic pressure* $\pi_0$. But such a *mixed* system of active masses is scarcely justifiable theoretically. As a matter of fact, the proportionality found by Arrhenius does not appear at all when the mixed system is applied to the results reported in Tables VII to XIII of the present communication.

[2] Rosanoff, Clark and Sibley, THIS JOURNAL, 33, 1917 and 1921 (1911).

anomaly is even greater than it appears when the mass action of the water is not taken into account.

Let us now apply to the reaction the views of homogeneous catalysis recently formulated by one of us.[1] According to these, chemical reactions, in general, would be fully described by the mass law only if the influence of medium were reduced to nothing, as in the gaseous state at infinit dilution. Under real working conditions, and when the concentrations of the substances forming the medium suffer changes, the mass law must lead to changing velocity coefficients. Such changes, which are outside the scope of the mass law itself, must be subject to a special catalysis law. In connection with a number of reactions, a general catalysis equation, of which the following is the simplest form, has been found to represent the experimental data with precision:

$$k = k_0 e^{\kappa C}.$$

Here $k$ is the velocity coefficient of the mass law, C the concentration of the principal substance determining the nature of the medium, and $\kappa$ the catalysis coefficient of that substance.

In Ostwald's experiments the medium consisted principally of water, but the concentration W of the water was quite different in the four series. From the above point of view, therefore, variation of the velocity coefficient $k$ from series to series must be *expected*; and since increasing dilution (*i. e.*, increasing concentration of the water) causes great diminutions of the velocity coefficient, water must be recognized as a powerful negative catalyzer of sugar hydrolysis. Its coefficient $\kappa$ in the above equation should, accordingly, be a negativ constant. Tables V, VI and XIV show this to be the case.

Tables V and VI are based on Ostwald's and Spohr's measurements, respectively. Table XIV is based on seven new series of measurements. While Ostwald and Spohr used respectively hydrochloric and hydrobromic acids, we used formic acid to make sure that the anomaly of sugar hydrolysis is not somehow connected with the abnormal properties of strong electrolytes, and also for the purpose of testing the catalysis equation on a more extensive series of experiments than those of Ostwald and of Spohr. Our measurements are reported in Tables VII to XIII.

TABLE V.—APPLICATION OF THE CATALYSIS EQUATION TO OSTWALD'S MEASUREMENTS.

| Grams sugar per liter. | W (mols. water per liter). | $k$W. | $k$ observed. | $k$ calculated. |
|---|---|---|---|---|
| 400 | 39.28 | 0.002916 | 0.0000742 | 0.0000742 |
| 200 | 46.11 | 0.002287 | 0.0000496 | 0.0000504 |
| 100 | 49.48 | 0.002063 | 0.0000417 | 0.0000416 |
| 40 | 51.43 | 0.001914 | 0.0000372 | 0.0000373 |

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[1] Rosanoff, THIS JOURNAL, 35, 173 (1913).

The values under "$k$ calculated" are given by the equation:

$$k = 0.0006883e^{-0.05669\mathrm{W}},$$

or,

$$\log_{10} k = \bar{4}.83778 - 0.024621\mathrm{W}.$$

Table VI.—Application of the Catalysis Equation to Spohr's Measurements.

| Grams sugar per liter. | W. | $k$W. | $k$ observed. | $k$ calculated. |
|---|---|---|---|---|
| 300 | 42.71 | 0.002721 | 0.0000637 | 0.0000633 |
| 200 | 45.55 | 0.002421 | 0.0000531 | 0.0000536 |
| 100 | 48.12 | 0.002100(?) | 0.0000436(?) | 0.0000461 |
| 20 | 50.32 | 0.002047 | 0.0000407 | 0.0000406 |

The values under "$k$ calculated" are given by the equation:

$$k = 0.0007711e^{-0.05853\mathrm{W}},$$

or,

$$\log_{10} k = 4.88712 - 0.02542\mathrm{W}.$$

Table VII.—Hydrolysis at 27.00° ± 0.015°, the Solution Containing per Liter 57.50 Grams Formic Acid, 400.0 Grams Sugar, and 705.4 Grams Water.

| $t$ (hours). | $\alpha$. | $k$W. |
|---|---|---|
| 0 | [74.73°] | ..... |
| 17.50 | 53.51 | 0.00595 |
| 20.75 | 50.64 | 0.00580 |
| 24.39 | 47.76 | 0.00563 |
| 27.38 | 44.30 | 0.00579 |
| 30.58 | 41.46 | 0.00579 |
| 40.83 | 32.75 | 0.00583 |
| 44.87 | 29.92 | 0.00576 |
| 48.17 | 27.74 | 0.00576 |
| 52.58 | 24.72 | 0.00576 |
| 65.45 | 16.85 | 0.00578 |
| 69.75 | 14.30 | 0.00582 |
| 74.66 | 11.80 | 0.00582 |
| 78.50 | 10.13 | 0.00579 |
| 89.50 | 4.90 | 0.00587 |
| 93.92 | 3.50 | 0.00581 |
| 98.50 | 1.36 | 0.00589 |
| 102.58 | 0.05 | 0.00587 |
| 113.35 | — 3.45 | 0.00590 |
| ∞ | —24.82 | ..... |

Mean $k$W = 0.00581
W = 39.15
$k$ = 0.0001484

TABLE VIII.—HYDROLYSIS AT 27.00 ± 0.015°, THE SOLUTION CONTAINING PER LITER 57.50 GRAMS FORMIC ACID, 300 GRAMS SUGAR, AND 768.52 GRAMS WATER.

| $t$. | $\alpha$. | $k$W. |
|---|---|---|
| 0 | [55.32°] | ..... |
| 17.43 | 40.36 | 0.00566 |
| 20.66 | 37.78 | 0.00572 |
| 24.28 | 35.29 | 0.00568 |
| 27.27 | 33.00 | 0.00575 |
| 30.66 | 31.00 | 0.00568 |
| 40.75 | 24.70 | 0.00573 |
| 44.70 | 22.63 | 0.00570 |
| 48.08 | 20.60 | 0.00576 |
| 52.45 | 18.50 | 0.00574 |
| 65.32 | 12.84 | 0.00572 |
| 69.77 | 11.15 | 0.00570 |
| 74.77 | 9.45 | 0.00567 |
| 78.54 | 7.70 | 0.00576 |
| 89.50 | 4.15 | 0.00576 |
| 93.92 | 2.65 | 0.00581 |
| 98.66 | 1.49 | 0.00578 |
| 102.58 | 0.50 | 0.00578 |
| ∞ | —18.30 | ..... |

Mean $k$W = 0.00570
W = 42.65
$k$ = 0.0001337

TABLE IX.—HYDROLYSIS AT 27.00 ± 0.015°, THE SOLUTION CONTAINING PER LITER 57.50 GRAMS FORMIC ACID, 200 GRAMS SUGAR, AND 829.60 GRAMS WATER.

| $t$. | $\alpha$. | $k$W. |
|---|---|---|
| 0 | [34.71°] | ..... |
| 4.08 | 32.40 | 0.00541 |
| 5.10 | 31.80 | 0.00549 |
| 7.75 | 30.45 | 0.00538 |
| 16.75 | 25.95 | 0.00540 |
| 19.50 | 24.60 | 0.00545 |
| 20.80 | 23.95 | 0.00548 |
| 21.70 | 23.65 | 0.00543 |
| 30.50 | 19.93 | 0.00544 |
| 30.75 | 19.80 | 0.00545 |
| 43.08 | 15.15 | 0.00549 |
| 48.08 | 13.73 | 0.00541 |
| 65.08 | 8.93 | 0.00538 |
| 68.08 | 7.98 | 0.00544 |
| 75.33 | 6.28 | 0.00544 |
| 80.00 | 5.45 | 0.00537 |
| 91.00 | 2.89 | 0.00549 |
| 93.15 | 2.69 | 0.00543 |
| 95.15 | 2.26 | 0.00545 |
| ∞ → | —11.85 | ..... |

Mean $k$W = 0.00544
W = 46.04
$k$ = 0.0001182

TABLE X.—HYDROLYSIS AT 27.00 ± 0.015°, THE SOLUTION CONTAINING PER LITER 57.50 GRAMS FORMIC ACID, 160 GRAMS SUGAR, AND 855.52 GRAMS WATER.

| $t$. | $\alpha$. | $k$W. |
|---|---|---|
| 0 | [29.21°] | ..... |
| 2.83 | 27.89 | 0.00549 |
| 3.83 | 27.44 | 0.00531 |
| 10.83 | 24.49 | 0.00522 |
| 20.83 | 20.41 | 0.00538 |
| 24.42 | 18.82 | 0.00556 |
| 31.66 | 16.51 | 0.00546 |
| 34.75 | 15.54 | 0.00545 |
| 45.52 | 11.91 | 0.00566 |
| 49.00 | 11.53 | 0.00553 |
| 51.17 | 10.84 | 0.00547 |
| 54.75 | 9.76 | 0.00554 |
| 58.90 | 9.17 | 0.00538 |
| 69.90 | 6.69 | 0.00542 |
| 74.50 | 5.59 | 0.00550 |
| 78.75 | 4.76 | 0.00544 |

TABLE XI.—HYDROLYSIS AT 27.00 ± 0.015°, THE SOLUTION CONTAINING PER LITER 57.50 GRAMS FORMIC ACID, 140 GRAMS SUGAR, AND 867.60 GRAMS WATER.

| $t$. | $\alpha$. | $k$W. |
|---|---|---|
| 0 | [50.47°] | ..... |
| 7.33 | 44.79 | 0.00530 |
| 17.83 | 37.35 | 0.00535 |
| 20.53 | 35.40 | 0.00543 |
| 27.33 | 31.17 | 0.00544 |
| 31.33 | 29.20 | 0.00533 |
| 42.66 | 23.34 | 0.00532 |
| 46.90 | 21.00 | 0.00541 |
| 51.42 | 19.26 | 0.00534 |
| 55.25 | 17.71 | 0.00532 |
| 66.05 | 13.29 | 0.00537 |
| 69.57 | 13.02 | 0.00537 |
| 73.57 | 10.38 | 0.00543 |
| 78.90 | 8.97 | 0.00536 |
| 90.17 | 5.35 | 0.00544 |
| 96.52 | 3.65 | 0.00546 |

TABLE X (*continued*).

| *t*. | α. | *k*W. |
|---|---|---|
| 82.50 | 4.21 | 0.00547 |
| 93.16 | 2.36 | 0.00552 |
| 97.25 | 1.66 | 0.00556 |
| 100.90 | 1.35 | 0.00548 |
| 106.50 | 0.64 | 0.00547 |
| 115.45 | —0.89 | 0.00566 |
| ∞ | —9.47 | ..... |

Mean *k*W = 0.00548
W = 47.48
*k* = 0.0001156

TABLE XI (*continued*).

| *t*. | α. | *k*W. |
|---|---|---|
| 103.90 | 1.86 | 0.00546 |
| ∞ | —16.60 | ..... |

Mean *k*W = 0.00538
W = 48.15
*k* = 0.0001117

TABLE XII.—HYDROLYSIS AT 27.00 ± 0.015°, THE SOLUTION CONTAINING PER LITER 57.50 GRAMS FORMIC ACID, 100 GRAMS SUGAR, AND 892.82 GRAMS WATER.

| *t*. | α | *k*W |
|---|---|---|
| 0 | [17.47°] | ..... |
| 23.25 | 11.69 | 0.00530 |
| 26.25 | 10.91 | 0.00535 |
| 29.00 | 10.31 | 0.00537 |
| 33.08 | 9.45 | 0.00540 |
| 43.75 | 7.56 | 0.00535 |
| 47.25 | 6.71 | 0.00548 |
| 50.75 | 6.58 | 0.00544 |
| 53.08 | 6.06 | 0.00535 |
| 56.58 | 5.71 | 0.00524 |
| 67.08 | 4.00 | 0.00542 |
| 71.33 | 3.39 | 0.00546 |
| 74.50 | 2.99 | 0.00548 |
| 77.16 | 2.83 | 0.00539 |
| 81.16 | 2.26 | 0.00547 |
| 98.33 | 0.53 | 0.00550 |
| 104.75 | 0.08 | 0.00545 |
| 116.16 | —0.56 | 0.00531 |
| ∞ | —6.30 | ..... |

Mean *k*W = 0.00539
W = 49.54
*k* = 0.0001088

TABLE XIII.—HYDROLYSIS AT 27.00 ± 0.015°, THE SOLUTION CONTAINING PER LITER 57.50 GRAMS FORMIC ACID, 60 GRAMS SUGAR, AND 916.86 GRAMS WATER.

| *t*. | α. | *k*W. |
|---|---|---|
| 0 | [9.78°] | ..... |
| 21.66 | 6.59 | 0.00523 |
| 44.25 | 3.81 | 0.00551 |
| 47.17 | 3.60 | 0.00542 |
| 51.17 | 3.24 | 0.00540 |
| 55.50 | 3.00 | 0.00523 |
| 65.75 | 2.25 | 0.00515 |
| 70.17 | 2.08 | 0.00500 |
| 75.66 | 1.37 | 0.00533 |
| 79.66 | 1.23 | 0.00521 |
| 89.45 | 0.42 | 0.00543 |
| 94.11 | 0.18 | 0.00542 |
| 99.20 | —0.02 | 0.00534 |
| 103.45 | —0.37 | 0.00550 |
| 113.45 | —0.52 | 0.00517 |
| ∞ | —4.12 | ..... |

Mean *k*W = 0.00531
W = 50.88
*k* = 0.0001044

TABLE XIV.—APPLICATION OF THE CATALYSIS EQUATION TO THE MEASUREMENTS REPORTED IN TABLES VII TO XIII.

| W. | *k* observed. | *k* calculated. |
|---|---|---|
| 39.15 | 0.0001484 | 0.0001485 |
| 42.65 | 0.0001337 | 0.0001335 |
| 46.04 | 0.0001182(?) | 0.0001203 |
| 47.48 | 0.0001156 | 0.0001152 |
| 48.15 | 0.0001117 | 0.0001128 |
| 49.54 | 0.0001088 | 0.0001081 |
| 50.88 | 0.0001044 | 0.0001039 |

The values under "$k$ calculated" are given by the equation:

$$k = 0.000490e^{-0.03049\text{W}},$$

or,

$$\log_{10} k = \bar{4}.6900 - 0.01324\text{W}.$$

In Tables V, VI and XIV the changes of medium, which we regard as the sole cause of the changing velocity coefficients, are expressed in terms of the water concentration W, and then water appears as a negative catalyzer. But the changes of medium might equally well be described in terms of the concentration of the sugar. Then, since the reaction velocity increases with increasing sugar concentration, sugar would appear as a positive catalyzer. Exactly speaking, then, water is a negative medium-catalyzer as compared with sugar, or, what is the same thing, sugar is a positive medium-catalyzer as compared with water. To eliminate from the velocity coefficient the medium-effects of both sugar and water, the catalysis equation would have to be employed in the form:

$$k = k_0 e^{\kappa_1\text{S} + \kappa_2\text{W}}.$$

However, in connection with the above data, this equation would yield the same results as the simpler equation actually used, for the reason that the sugar concentration[1] S is very closely a linear function of the water concentration W. Other experiments would be necessary to bring out the catalysis coefficients of sugar, water and acid separately, and thus to find the reaction velocity $k_0$ altogether freed from medium-influence. But this is beyond the needs of the present discussion.

That the pronounced retarding effect of water is connected with its great dissociating power is indicated by the fact that when sugar is partly replaced by substances similar to it in dissociating power (dielectric constant??), the physico-chemical character of the medium remains unchanged and then the reaction velocity, too, remains unchanged.[2] Thus, in a certain solution containing 150.452 grams of sugar per liter the velocity coefficient was found to be *0.0147;* in a solution similar to this in acid and water content, but containing 57 grams of sugar and 88 grams of mannite (the latter occupying the volume filled in the first solution by 93.452 grams of sugar), the velocity coefficient was found to be *0.0146.* It may be confidently expected that neutral substances of smaller dissociating (greater associating) power than sugar, if introduced in place of part of the sugar, will *increase* the velocity of hydrolysis, *i. e.*, will act as positiv catalyzers.

From this point of view the mechanism of sugar hydrolysis appears to depend on the existence of a molecular complex whose concentration de-

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[1] We mean the initial sugar concentration. Inverted sugar has practically the same medium effect as cane sugar.

[2] See Rosanoff, Clark and Sibley, THIS JOURNAL, 33, 1914–1916 (1911).

termins the velocity of the reaction. Water retards the reaction simply by dissociating this complex, as it dissociates salts electrolytically and as it breaks up associated molecular species generally. It is important to observe that the existence in sugar solutions undergoing inversion of a special compound, an "active sugar," has been inferred from entirely different phenomena by Arrhenius.[1] The nature of this hydrolyzable complex is being studied here in connection with the role of the acid.

In conclusion, it is a pleasure to acknowledge our indebtedness to the Bache Fund of the National Academy of Sciences for a pecuniary grant in aid of these investigations. Pending the construction for us of a large instrument by Schmidt and Haensch, we used a saccharimeter placed at our disposal by Professor Alfred M. Peter, of the Agricultural Experiment Station of the University of Kentucky. We again thank Dr. Peter for his courtesy and generosity.

WORCESTER, MASS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WYOMING EXPERIMENT STATION.]

# ZYGADENINE. THE CRYSTALLIN ALKALOID OF ZYGADENUS INTERMEDIUS.[2]

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The poisonous properties of the genus *Zygadenus* have for some time been correctly ascribed to the alkaloidal substances present, but no satisfactory description of a chemically pure substance has been offered. In general, the crude alkaloidal mixture has been extracted, and to this various color reactions have been applied.

Slade[3] obtained evidence by means of such color tests which led him to conclude that the alkaloids were identical with sabadine, sabadinine, and veratralbine. Reid Hunt,[4] by similar methods, showed reason for believing that the crude alkaloidal mixture resembles veratrine. Georg Heyl,[5] working with the product of an alkaloidal assay of a California species of *Zygadenus*, ascribes a definit melting point, 134–135°, but does not go further than this statement.

It has been shown in a previous communication from this laboratory[6] that the leaves of *Zygadenus intermedius*, when assayed by gravimetrical methods, will yield between 0.3% and 0.4% of a crude alkaloidal mixture.

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[1] Arrhenius: *Z. physik. Chem.*, 4, 233 (1889).

[2] The expenses of this investigation were defrayed from the Adams fund.

[3] *Am. J. Pharm.*, 77, 262 (1905).

[4] *Am. J. Physiol.*, 6, 19 (1901).

[5] *Süddeut. Apoth. Zeit.*, 43, No. 29.

[6] THIS JOURNAL, 33, No. 2, Feb., 1911.