

CORRECTION.

On page 174 of the February number read $k = k_0 e^{\kappa C}$, instead of $k = k_0 e^C$.

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

[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.

I. 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-

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).