NOTES

Needle-Shaped Crystals of Sodium Chloride Obtained by Percrystallization

By Henry Tauber and Israel S. Kleiner

In 1917 the observation was made by Kober,[1] that if a collodion container, filled with a saturated ammonium sulfate or a saturated sodium chloride solution, and with the open end closed tightly with a cord, was suspended in the air and fanned in a warm room, crystals of these salts "crystallized on the outside and blew off like snow." He called this phenomenon "percrystallization." To our knowledge no use has been made since that time of this method of crystallization. While working on the purification of enzyme material, we thought that this method would afford a practical way of getting rid of the inorganic diffusible salts and at
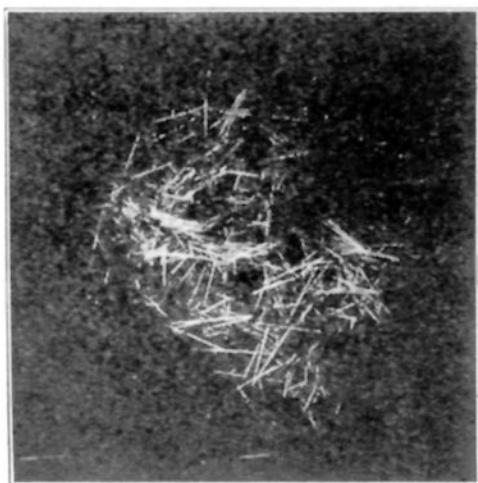

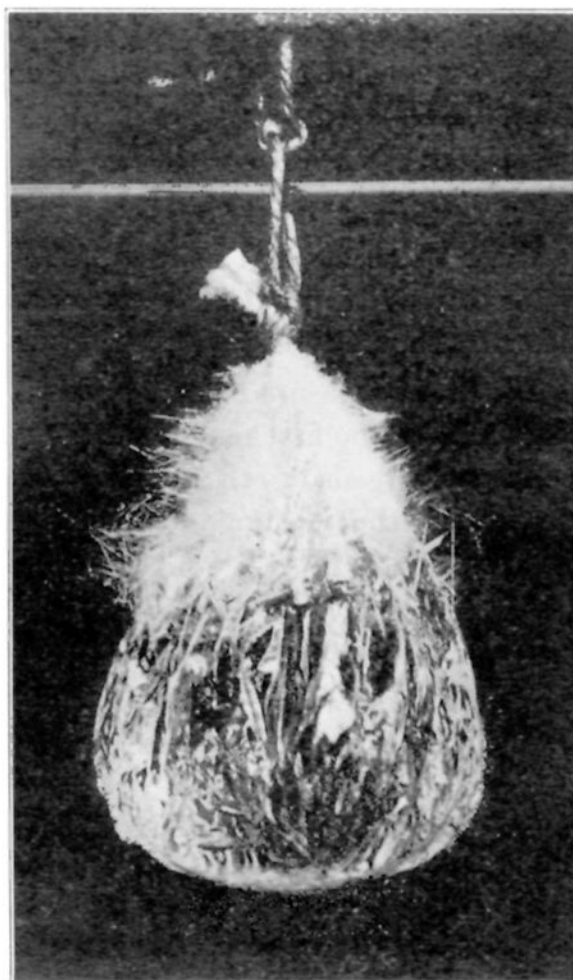Fig. 1.—Crystals of sodium chloride obtained by percrystallization, natural size.

Fig. 2.—Collodion bag with sodium chloride needles forming by percrystallization.

the same time of concentrating the enzyme. We found that the sodium chloride, which was present in the enzyme-salt mixture, crystallized outside the collodion bag, but instead of the usual cubic habit, the sodium chloride crystallized in beautiful needles about 1 cm. long (see Fig. 1).

The procedure (without fanning), repeated with c. p. sodium chloride (Baker's), yielded the same needles. One hundred fifty cc. of a half-satu-

[1] Kober, This Journal, **39**, 944 (1917).

rated solution was placed in a 250-cc. collodion bag at 20°. Within one hour the needles (see Fig. 2) crystallized outside on the upper part of the bag, above the level of solution.

Drs. W. J. McCaughey of Ohio State University and J. B. Niederl of New York University examined these crystals and found that they belong to the regular cubic system.

The fact that the crystals mainly develop in one direction seemed to be worthy of note.

We are greatly indebted to Professors W. J. McCaughey and J. B. Niederl for examining the crystals.

The Generalized Theory of Acid and Base Catalysis Applied to the Rate of Ionic Reactions

BY ROBERT LIVINGSTON

The rate of the catalytic decomposition of hydrogen peroxide in an acid bromine–bromide solution has been measured both in solutions of hydrobromic acid and in solutions containing sulfuric acid and potassium bromide.[1]

The corrected rate constant, χ in the equation

$$v = \chi(H_2O_2)(H^+)(Br^-)\gamma^2{}_{HBr}$$

is about 10% higher for the solutions containing sulfuric acid. While it is not impossible that this difference is due to experimental error,[3] it seems more probable that it is a real effect, probably due to the specific catalytic action of the acid molecule $HSO_4{}^-$.[4] Although the generalized theory of acid (and base) catalysis has never been demonstrated for reactions between ions, there is no *a priori* reason why this type of reaction should not occur. On the assumption that $HSO_4{}^-$ acts similarly to and simultaneously with H_3O^+, the total rate equation would be

$$v = (H_2O_2)(H^+)(Br^-)\left[\chi_{H_3O}\gamma^2{}_{HBr} + \chi_{HSO_4} \frac{(HSO_4{}^-)}{(H^+)} \frac{\gamma_{HSO_4-}\gamma_{Br-}}{\gamma_x} \right]$$

While this is qualitatively in agreement with the experimental facts, a quantitative test is impossible, owing to uncertainties in the computation

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[1] (a) Bray and Livingston, THIS JOURNAL, 45, 1251 (1923); (b) Livingston and Bray, *ibid.*, 45, 2048 (1923).

[2] Livingston, *ibid.*, 48, 53 (1926).

[3] It might be due to "promoter action" or to negative catalysis, caused by a trace of some unknown impurity, or else to a systematic error in the determination of the activity coefficients.

[4] Brönsted. *Chem. Rev.*, 5, 231 (1928).