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

[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).

of (HSO_4^-) and the impossibility of determining $\gamma_{HSO_4^-} \cdot \gamma_{Br^-}/\gamma_x$. In sufficiently dilute solutions these quantities might be computed from the Debye–Hückel limiting law; unfortunately, accurate rate measurements would be practically impossible in this region. The occurrence of generalized acid catalysis in this reaction might be tested by using solutions containing small concentrations of potassium bromide and a moderately weak, chemically inert acid in the presence of a high constant concentration of an inert salt, e. g., sodium perchlorate.

Other ionic reactions might be expected to show a similar effect; for example, the oxidation of hydriodic acid by chloric acid,[5] or the basic hydrolysis of the nitrourethan ion.[6]

[5] Bray, J. Phys. Chem., 7, 92 (1903).

[6] Brönsted and Delbanco, Z. anorg. allgem. Chem., 144, 248 (1925).

The Entropy of Bromine from Spectroscopic Data

BY WELDON G. BROWN*

A recent fine structure analysis of the visible absorption bands of bromine by the writer[1] has provided data from which accurate values of the thermodynamic constants of bromine may be calculated. These calculations involve nothing essentially new, although certain consequences of a rather unique isotope situation become emphasized. In this note the entropy calculated from band spectrum data is to be compared with a less accurate value obtained from experimental measurements of the specific heat.

There are two isotopes of bromine, 78.92 and 80.92, which, according to Aston's measurements,[2] are equally abundant. These give rise to three kinds of molecules, Br_2^{79}, $Br_2^{79,81}$ and Br_2^{81}, in the proportions $1:2:1$, respectively. A slight difference in the molecular constants of the Br_2^{79} and Br_2^{81} molecules leads to slightly different entropies, but because of their equal abundance this becomes smoothed out when, in calculations of thermodynamic constants, one uses the data for the $Br_2^{79,81}$ molecule. There is an additional effect due to the lack of symmetry which results in the entropy of $Br_2^{79,81}$ being greater than the entropy of either of the symmetrical species by $R \ln 2$ per mole, or $1/_2 R \ln 2$ per mole of the actual mixture since this species constitutes one-half of ordinary bromine.

The moment of inertia of bromine is sufficiently large and the centrifugal

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[1] Brown, Phys. Rev., 39, 777 (1932).

[2] Aston, Proc. Roy. Soc. (London), 115, 487 (1927); 132, 489 (1931).