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REACTION SPEED OF H_2O_2 AND SO_2 BY CONDUCTIVITY

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An attempt was made to measure the rate of reaction of H_2O_2 and SO_2 forming H_2SO_4 by the accompanying change in conductivity, after a literature study was made to see if such a reaction was known. Evidence was found in Jacobson, *Encyclopedia of Chemical Reactions*, vol. III, p. 641, III-2263, Reinhold (1949), that the reaction which had been studied by J. H. Kastle and A. S. Loevenhart had been published in Am. Chem. J., 29, 569 (1903).

It was recorded that the H_2O_2 added directly onto the H_2SO_3 forming H_4SO_5, and that this in turn broke down into H_2SO_4 and H_2O. This change of sulfurous to sulfuric acid produced the change in conductivity which was measured in this experiment.

Preliminary Experiments

Three percent H_2O_2 and a saturated water solution of SO_2 (H_2SO_3) were used as starting reagents. The 3 percent H_2O_2 and saturated SO_2 were poured into the electrolytic cell (cell constant=approximately 86.3) and a conductivity reading was immediately taken on the Thiessen Wheatstone Bridge.[1] This was found to be .0017 mhos, but after setting for a considerable length of time, no change was observed.

Next SO_2 alone was tested, with a result of .00027 mhos; this indicated there had been a change which had been too rapid to measure.

The test with H_2O_2 and SO_2 was repeated using solutions diluted approximately 1:4 before mixing. This time the conductivity was .00032 mhos. Still no change was observed. No change was again observed when 3 drops of each reagent were used in enough H_2O to fill the cell (14 ml.).

A different cell was now used (cell constant = approximately .238) in order to measure smaller conductivities. It had a shorter distance between electrodes with a much larger cross-sectional area. Using this new cell, the reagents were each diluted 1 drop to 10 ml. of H_2O. Two drops of each of these were used with enough H_2O to fill the cell (20 ml.). A definite change was noticed.

Main Experiment

Now the reaction was carried out more accurately in a thermostatically controlled cabinet (26.5° C.), using the same dilutions outlined above. A smoothly progressing list of 22 readings was obtained over a period of 94 minutes. The observed change in conductivity was from .00015 mhos to .00070 mhos. These readings are listed below.

Time	*Conductivity*
0.0	.00015
1.0	.00020
2.0	.00022

[1] Thiessen, G. W., and Wertz, J., 1949, A direct-reading, inexpensive conductivity bridge: Chemist Analyst, vol. 42, no. 4, p. 91.

Time	*Conductivity*
3.0	.00062
4.0	.00065
6.0	.00067
7.5	.00070
8.5	.00025
9.5	.00027
11.5	.00030
13.5	.00032
15.5	.00035
18.0	.00037
23.0	.00040
25.5	.00042
30.0	.00045
34.5	.00047
48.5	.00050
51.5	.00052
58.0	.00055
66.0	.00057
94.0	.00060

Next the possible kinetics of the reaction were studied. With a moles of SO_2 and b moles of H_2O_2 and x moles of H_2SO_4 formed in v liters after t time and x = O when t =O, the equation for the first order reaction is:

$$\frac{-1}{v}\frac{dx}{dt} = k\frac{a - x}{v}$$

which integrates thus:

$$\int\frac{-dx}{a - x} = k\int dt$$

$$kt = \ln(a - x) + C$$

If t = O and x = O, then —ln a = C

$$kt = \ln(a - x) - \ln a$$
$$= \ln\frac{a - x}{a}$$

$$kt = 2.30 \log\frac{a - x}{a}$$

$$\underbrace{t}_{Y} = \underbrace{\frac{2.30}{k}}_{m}\underbrace{\log(a - x)}_{X} - \underbrace{\frac{2.30 \log a}{k}}_{+\ b}$$

Y = m X + b (straight line plot)

This formula was used in plotting a graph of t vs. log (a — x). The change in conductivity from zero time was used for (a — x). Instead of a straight line, what seemed to be an equilateral hyperbola was obtained. If this had been true, using the reciprocal of either of the components should have yielded a straight line. On the contrary, this method gave a curve which seemed to be broken into two parts, each a straight line.

In a further attempt to interpret the results, a different arrangement of the formula was used, letting L ∞ be the conductivity at infinite time and Lt the conductivity at time t. Starting with the formula listed above,

$$t = \frac{2.30}{k} \log (a - x) - \frac{2.30 \log a}{k}$$

$$\begin{aligned} \log (a - x) &= X \\ t &= Y \\ a &= L\infty \\ x &= Lt \end{aligned}$$

$$t = -\frac{2.30}{k} \log (CL\infty - CLt) + b$$

$$t = \frac{2.30}{k} \log C (L\infty - Lt) + b$$

$$\underbrace{t}_{Y} = \underbrace{\frac{2.30}{k}}_{m} \underbrace{\log (L\infty - Lt)}_{X} + \underbrace{\log C + b}_{b}$$

$$Y = m \qquad X \quad + \quad b$$

This new idea was used in plotting a graph yielding another curve, which seemed to be broken into two shorter straight lines.

The best interpretation obtained thus far is that this verifies the fact found in the literature—the action proceeds in two steps, first yielding H_4SO_5, which in turn breaks down into H_2SO_4 and H_2O.

At the beginning, the concentration of the H_2SO_3 was high enough to cause the reaction to begin quite rapidly. Of course the H_2O_2 was in excess enough that the change in its concentration was negligible. As the concentration of the H_2SO_3 decreased this first step of the reaction slowed down to a point where its change in conductivity could be observed. By this time the concentration of H_4SO_5 was high enough to cause it to decompose quite rapidly as the first step of the reaction was slowing down. By the time the H_2SO_3 was nearly all gone and the first step had practically ceased, the concentration of the H_4SO_5 had become low enough and its decomposition slow enough so that its change in conductivity could be observed.