

3. Germanium dioxide gel was found to possess an adsorptive power for the vapors of benzene, ethyl ether and carbon tetrachloride comparable with that of silica gel.

4. Germanium dioxide gel adsorbs water vapor but upon the removal of the adsorbed water the adsorptive power of the gel for benzene vapor was found to have decreased.

ITHACA, NEW YORK

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES,  
AND THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

## THE EFFICIENCY OF THE REACTION $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$ AND ITS BEARING ON THE REACTION BETWEEN HYDROGEN AND OXYGEN<sup>1</sup>

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RECEIVED SEPTEMBER 30, 1931

PUBLISHED FEBRUARY 5, 1932

The experiments by von Elbe on the photochemical reaction between hydrogen peroxide and hydrogen or carbon monoxide described elsewhere,<sup>4</sup> and a careful estimate, from earlier measurements,<sup>5</sup> of the intensity of incident radiation from the zinc spark, allow one to estimate a limit of the efficiency and the heat of activation of the reaction



The total number of quanta entering the reaction vessel per second was  $2 \times 10^{15}$ . Assuming that the absorption of hydrogen peroxide for the spectral lines used is 30%, calculated from the absorption measurements of Urey, Dawsey and Rice,<sup>6</sup> and a quantum efficiency of  $1\text{H}_2\text{O}_2$  decomposed per quantum absorbed yielding  $2\text{OH}$ , the number of OH radicals formed (volume of vessel 86 cc.) was  $1.4 \times 10^{13}$  per sec. per cc.

The experimental data show that  $5.6 \times 10^{13}$  molecules of hydrogen reacted per second per cc. Thus, practically as many hydrogen molecules disappear per second as hydroxyl radicals are formed per second. The difference between the values  $5.6 \times 10^{13}$  and  $1.4 \times 10^{13}$  is apparently due primarily to the inaccuracy of the estimated light intensity. We note that the stationary concentration of OH must therefore be smaller or equal to about  $5.6 \times 10^{13}$  radicals per cc. In the latter case, the collision frequency between OH and  $\text{H}_2$  at  $40^\circ$  is  $3.9 \times 10^{23}$  per sec. per cc. From these data we can conclude that at least 1 out of  $7 \times 10^9$  collisions between OH and  $\text{H}_2$

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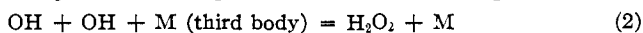
<sup>4</sup> G. von Elbe, *THIS JOURNAL*, **54**, 821 (1932).

<sup>5</sup> Bernard Lewis, *J. Phys. Chem.*, **32**, 270 (1928).

<sup>6</sup> Urey, Dawsey and Rice, *THIS JOURNAL*, **51**, 1376 (1929).

succeeds in reacting according to (1). This provides an upper limit for the heat of activation—namely, 14,100 calories. Frankenburger and Klinkhardt<sup>7</sup> calculate a lower limit of 13,500 calories from experiments on the reaction between hydrogen and oxygen under the influence of photochemically produced hydrogen atoms. The true heat of activation must therefore lie about these values, or in other words the collision efficiency must be about  $10^{-10}$  at  $40^\circ$ .

It will now be shown that all experimental data published thus far regarding reactions of OH radicals which have a bearing on the present considerations are consistent with the above conclusion. Let us consider the other probable ways of removing OH radicals in these experiments.



Reaction 4 can be eliminated since its activation energy is too high.<sup>8</sup> The number of triple collisions occurring by Reaction 2 is between  $10^{11}$  and  $10^{12}$  per second per cc. (The third body is hydrogen at a pressure of about one atmosphere.) Since the OH concentration is  $10^{13}$ , then only about  $1/100$  to  $1/10$  of these OH radicals can disappear per second per cc. by triple collisions, assuming that each triple collision forms hydrogen peroxide.

In Frankenburger and Klinkhardt's experiments the dominant reaction was Reaction 2. Indeed they show that in order to explain their results the triple collision must occur more frequently than the reaction



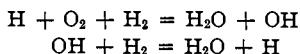
In our case the reverse is true due to our lower OH concentration. Frankenburger and Klinkhardt's results also show that the number of triple collisions is in excess of the number of successful collisions between two OH radicals. It follows that Reaction 3 is successful less than once in  $10^4$  collisions between two OH radicals. On the other hand, Bonhoeffer and Pearson's data indicate that Reaction 3 is successful at least once in  $10^4$  collisions between two OH radicals. Since their gases were heated somewhat by the discharge, their limiting efficiency may be less than this value at the temperature of Frankenburger and Klinkhardt's experiments (about  $60^\circ$ ). Therefore, it is evident that the two results are consistent.

From the latter result it can be shown that in the experiments under consideration, less than  $1/100$  of the OH radicals can be removed by Reaction 3 since the number of such successful collisions is somewhat less than  $10^{11}$  per second per cc. This disposes of all reactions of OH radicals except Reaction 1 with hydrogen.

Frankenburger and Klinkhardt's estimate of the length of the chains in the hydrogen-oxygen reaction at  $400^\circ$  by the Bonhoeffer and Haber mechanism

<sup>7</sup> Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, **123**, 431 (1931).

<sup>8</sup> Bonhoeffer and Pearson, *Z. physik. Chem.*, **14B**, 1 (1931).



puts up a strong case for this mechanism. However, some experiments recently published by Pease<sup>9</sup> are very difficult to explain if hydrogen peroxide can be formed only through Reaction 2.

Pease found a considerable yield of hydrogen peroxide on passing a mixture of hydrogen and oxygen through a Pyrex tube at 550°, amounting in some experiments to as much as one molecule of hydrogen peroxide for four molecules of water formed. Reaction 2 cannot be held responsible for this result for the following reason. Reaction 1 has a collision yield of  $1.8 \times 10^{-4}$  at 550°. In order for Reaction 2 to be the source of hydrogen peroxide, one of these should take place for every *ca.*  $10^4$  collisions of OH with H<sub>2</sub>, which means that the concentration of OH would have to be of the order of the H<sub>2</sub> concentration, namely, *ca.*  $10^{19}$  per cc. This is obviously impossible. We are compelled for these reasons to assume with Pease, who experimented in the non-explosive region, that some other mechanism for the formation of hydrogen peroxide must be in operation.

<sup>9</sup> Pease, *THIS JOURNAL*, **52**, 5106 (1930); **53**, 3188 (1931).

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY,  
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## ACTIVITY COEFFICIENTS OF SALTS IN ACETIC ACID SOLUTIONS FROM SOLUBILITY MEASUREMENTS

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RECEIVED SEPTEMBER 30, 1931

PUBLISHED FEBRUARY 5, 1932

Measurement of the solubility of salts in the presence of other salts, although complicated by the introduction of a third component, offers the most exact method of measuring changes in the activity coefficients of salts at low concentration in non-aqueous solutions. Previous research in this field includes the work of Williams<sup>1</sup> on methyl alcohol solutions, Hansen and Williams<sup>2</sup> on ethyl alcohol-water mixtures, Kraus and Seward<sup>3</sup> on isopropyl alcohol and acetone, Robinson<sup>4</sup> on acetone and Seward and Schumb<sup>5</sup> on ethyl alcohol. The results of these investigations have been compared in each case with those predicted by the interionic attraction theory of Debye and Hückel.<sup>6</sup> If the observed activity coefficient changes are

<sup>1</sup> Williams, *THIS JOURNAL*, **51**, 1112 (1929).

<sup>2</sup> Hansen and Williams, *ibid.*, **52**, 2759 (1930).

<sup>3</sup> Kraus and Seward, *J. Phys. Chem.*, **32**, 1294 (1928).

<sup>4</sup> Robinson, *ibid.*, **32**, 1089 (1928).

<sup>5</sup> Seward and Schumb, *THIS JOURNAL*, **52**, 3962 (1930).

<sup>6</sup> Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).