

the back suction is relieved the hydrogen stream can be restored to its normal rate. This operation must be continued until all the burners are lighted and the temperature is full red. The angle piece of the tube, which should be as close to the furnace as possible, is now heated by a powerful Bunsen burner, and constantly struck with a piece of iron. The metallic cesium which has distilled into this part of the apparatus, will be liquefied, and will trickle down under the paraffin, collecting in silvery drops. The cesium comes out of the tube at the very end of the process and not before. If the foregoing directions are closely followed the whole operation can be accomplished in four hours without the slightest difficulty or danger. Explosions only occur when the tube is heated too rapidly and not sufficient attention paid to the pressure regulation. It is evident from the result of these experiments that Winkler was mistaken in stating that it is impossible to obtain cesium from its compounds by the aid of magnesium. We made cesium in quantity by our method and are now studying its physical properties.

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## THE OXIDATION OF FORMIC ALDEHYDE BY HYDROGEN PEROXIDE.<sup>1</sup>

BY J. H. KASTLE AND A. S. LOEVENHART.

Received October 24, 1898.

A FEW preliminary experiments seemed to indicate that the oxidation of formic aldehyde by hydrogen peroxide, could be easily and certainly followed by determining the quantities of formic acid produced as the result of the oxidation, by standard alkali, using phenolphthalein as the indicator. A study of this oxidation was therefore undertaken. A number of oxidations, involving hydrogen peroxide as the oxidizing agent, have been studied. The work of Magnanini<sup>2</sup> and that of Harcourt<sup>3</sup> and Essen on the effect of this substance on hydriodic acid, under different physical and chemical conditions, is important and interesting in this connection. A study of the oxidation of gaseous acetic aldehyde by oxygen gas was undertaken a short

<sup>1</sup> Read before the Boston meeting of the American Association for the Advancement of Science, August 25, 1898.

<sup>2</sup> *Gaz. chim. ital.*, 20, 377, 1890.

<sup>3</sup> *Phil. Trans.*, 1867, 157, 20, 460 and *Phil. Trans.*, 1895, 186, 817, 895.

time ago by van't Hoff<sup>1</sup> with the view of determining the relation of the pressure under which the oxygen acts to the rate of oxidation. He found the oxidation to proceed with convenient speed at 20° C. and observed that the action was affected by light. His results showed the velocity of the oxidation to be proportional to the pressure of the aldehyde vapor, and to the square root of the pressure of the oxygen. So far as we have been able to discover, this is the only case of the kind that has ever been investigated. It seemed to us, therefore, all the more important to undertake the study of the oxidation of formic aldehyde by hydrogen peroxide in aqueous solution. Marchand's hydrogen peroxide and Schering's formaldehyde were used in the investigation. The solution of formaldehyde was standardized by heating with potassium hydroxide, and the hydrogen peroxide by means of a standard solution of potassium permanganate. The peroxide was always standardized immediately before using, in order to correct any change in strength that it might have undergone. Normal solutions of formaldehyde and peroxide were employed in equivalent volumes, so that in all cases, not stated to the contrary, the reaction was studied at half-normal dilution.

The effect of temperature was first investigated. Our preliminary experiments indicated that the reaction proceeded with extreme slowness at ordinary temperatures, but with great velocity at the temperature of boiling water. It was therefore decided to conduct a series of experiments at each of the following temperatures; *viz.*, 20° C., 26° C., 40° C., 50° C., 60° C., 70° C., 80° C., 90° C., and 98° C. It should be said further that these several series were tried in dark, it having been observed that light exerted an accelerating influence on the progress of the reaction. In each of these experiments five cc. of normal formaldehyde was placed in a test-tube, together with five cc. of normal hydrogen peroxide; the tube was then sealed and placed in a water-bath, which was maintained constant at the temperature desired. The tube was then exposed to certain temperatures for different intervals of time, at the end of which they were plunged into cold water, opened and their contents titrated with fifth-normal potassium hydroxide. The coefficients of

<sup>1</sup> Etudes de Dynamique Chimique, 1895, p. 79.

velocity were then calculated from the results by the equation for bimolecular reactions:

$$\frac{1}{\theta} \left( \frac{x}{A-x} \right) \frac{1}{A} = K$$

where  $\theta$  represents time in minutes, A the initial amount of the substance present,  $x$  the amount of substances changed, and K is the constant which measures the velocity of the reaction.

The following are the tabulated results of the series together with the calculated coefficients of velocity:

SERIES AT 40°.

Time. Minutes.	Fifth-normal potas- sium hydroxide neutralized. cc.	Decomposed. Per cent.	Coefficient of velocity.
30	0.29	1.16	0.0000157
60	0.63	2.52	0.0000172
90	0.97	3.88	0.0000179
120	1.32	5.28	0.0000185
150	1.71	6.84	0.0000196
180	2.00	8.00	0.0000193
222½	2.48	9.92	0.0000198
240	2.65	10.60	0.0000198
270	3.10	12.40	0.0000208
300	3.47	13.88	0.0000201

Average coefficient of velocity, 0.0000189

SERIES AT 50°.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
30	1.10	4.40	0.0000614
60	2.13	8.52	0.0000621
90	3.30	13.20	0.0000676
120	4.45	17.80	0.0000722
150	5.20	20.80	0.0000700
180	5.85	23.40	0.0000679
210	6.90	27.60	0.0000726
240	7.63	30.52	0.0000732
270	8.10	32.40	0.0000710
300	9.00	36.00	0.0000750

Average coefficient of velocity, 0.0000693

## SERIES AT 60°.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
75	7.75	31.00	0.000240
90	8.95	35.80	0.000248
105	9.75	39.00	0.000244
120	10.75	43.00	0.000251
135	11.45	45.80	0.000250
150	11.90	46.70	0.000244
165	12.55	50.20	0.000244
180	13.20	52.80	0.000249
195	14.15	56.60	0.000268
210	14.35	57.40	0.000257
225	14.70	58.80	0.000254
240	15.00	60.00	0.000250
255	15.5	62.00	0.000256
270	15.90	63.60	0.000259
285	16.15	64.60	0.000255
300	16.23	64.92	0.000247
Average coefficient of velocity,			0.000251

## SERIES AT 70°.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
15	5.15	20.60	0.000691
45	11.25	45.00	0.000727
60	13.20	52.80	0.000746
75	14.80	59.20	0.000774
90	15.65	62.60	0.000744
105	16.65	66.60	0.000760
120	17.45	69.80	0.000770
135	17.65	70.60	0.000711
150	17.75	71.00	0.000653
165	19.20	76.80	0.000802
180	19.55	78.20	0.000799
195	19.95	79.80	0.000772
210	20.65	82.60	0.000754
225	20.65	82.60	0.000704
240	20.65	82.60	0.000660
Average coefficient of velocity,			0.000711

## SERIES AT 80°.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
10	10.15	40.60	0.00273
20	13.85	59.40	0.00248
35	16.93	67.72	0.00240
50	19.05	76.20	0.00256
60	19.85	79.40	0.00257
80	20.60	82.40	0.00234
100	21.60	86.40	0.00254
120	21.95	87.80	0.00240
150	22.80	91.20	0.00276

Average coefficient of velocity, 0.00253

## SERIES AT 90°.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
5	12.10	48.40	0.00750
15	17.20	68.80	0.00590
20	18.54	74.16	0.00555
30	20.60	82.40	0.00625
50	21.70	86.80	0.00525
60	22.80	91.20	0.00690

Average coefficient of velocity, 0.00625

It was noted that considerable pressure was developed in the tubes up to this temperature, *viz.*, 90° C., owing to the fact that the hydrogen peroxide liberates its oxygen more rapidly than it is capable of acting on the formaldehyde; but at this temperature the pressure almost disappears indicating that the peroxide acts on the formic aldehyde at this temperature very nearly as rapidly as it is capable of liberating its oxygen.

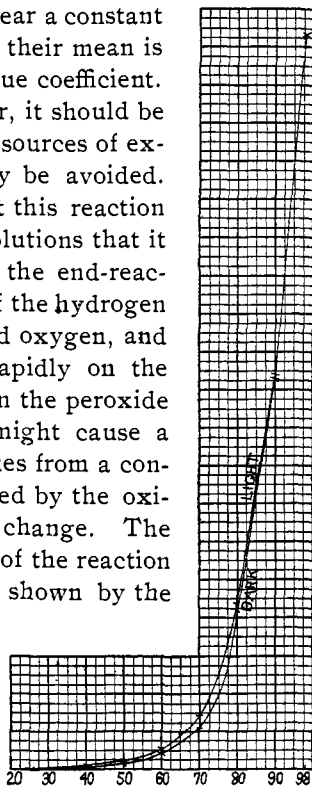
## SERIES AT 98°.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
10	18.90	75.60	0.0124
15	20.50	82.00	0.0122
20	21.60	86.40	0.0127
30	22.30	89.20	0.0110
45	23.06	92.24	0.0106
60	23.50	94.00	0.0105

Average coefficient of velocity, 0.0116

A few experiments were tried at lower temperatures; at 20° the coefficient of velocity was found to be approximately 0.00000855, and at 26°, 0.00000199.

In harmony with the theory of bimolecular reactions the coefficients of velocity of this reaction, for any particular temperature, approach a constant value. This is especially true of the values obtained for 50° C., 60° C., and 70° C., and in all cases they are probably sufficiently near a constant value to justify one in assuming that their mean is a very close approximation to the true coefficient. In considering these results, however, it should be borne in mind that there are several sources of experimental error which can scarcely be avoided. One of these is due to the fact that this reaction takes place so rapidly in alkaline solutions that it is difficult oftentimes to make sure of the end-reaction. Then, again, a small amount of the hydrogen peroxide decomposes into water and oxygen, and this liberated oxygen acts far less rapidly on the formaldehyde than that contained in the peroxide molecule. A third factor which might cause a slight departure of the observed values from a constant is that the formic acid produced by the oxidation very slightly accelerates the change. The effect of temperature on the course of the reaction under consideration is very clearly shown by the curve. On this, temperatures have been laid off on the axis of abscissas, the ordinates being the average coefficients of velocity of the reaction, multiplied, for convenience, by 3333 $\frac{1}{8}$ . The enormous but regular effect of temperature on the velocity of this reaction is clearly shown by this curve. From 20° to 40° C. it will be observed that the curve is nearly coincident with the axis of  $x$ ; then, very slowly at first, but very rapidly later on, it begins to diverge from it, until at 50° to 98° C. it is almost perpendicular to it, indicating that we would not have to raise the temperature



Ordinates = Average  
Coefficients of velocity  $\times$  3333 $\frac{1}{8}$ .

Temperature (°C)	Average Coefficient of Velocity $\times$ 3333 $\frac{1}{8}$
20	0.00000855
26	0.00000199
50	0.00000199
60	0.00000199
70	0.00000199
98	0.00000199

of the system any very great deal in order to make the change practically instantaneous.

The effect of light on the progress of reaction has also been investigated. The fact that hydrogen peroxide is more unstable in the light than in the dark would naturally lead to the supposition that light would probably accelerate the oxidation under discussion. A few preliminary experiments indicated that such was really the case. Two tubes, each containing ten cc. normal formic aldehyde and ten cc. normal hydrogen peroxide, were kept at 20° C., one in the sunlight and one in the dark, for five and one-half hours. The tube in the dark showed a decomposition of seven-tenths per cent., whereas that in the light gave four per cent. decomposition. It was therefore decided to carry through several series in the direct sunlight at the same temperature as those which were tried in the dark, and under conditions as nearly identical as possible. The extremely variable character of even bright sunlight is capable of causing variations in the velocity of the reaction in the same series, so that for the several series in the sunlight the values of K show greater deviation from a constant value than those obtained for the same series in the dark. In light at 20° the coefficient of velocity was found to be 0.00000505 and at 26°, 0.00000629.

SERIES IN DIRECT SUNLIGHT AT 40° C.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
45	0.75	3.00	0.0000275
60	1.00	4.00	0.0000278
90	1.85	7.40	0.0000355
120	2.85	11.40	0.0000429
150	3.30	13.20	0.0000401
180	4.40	17.60	0.0000475
240	5.10	20.40	0.0000427

Average coefficient of velocity 0.0000378, thus showing an increase of 100 per cent. over the average coefficient of velocity in the dark at the same temperature.

## SERIES IN DIRECT SUNLIGHT AT 50° C.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
60	3.35	13.40	0.000104
75	4.05	16.20	0.000103
90	4.85	19.40	0.000107
105	5.45	21.80	0.000106
120	6.95	27.80	0.000128
135	7.15	28.60	0.000119
150	7.70	30.80	0.000119
165	8.65	34.60	0.000128
180	10.35	41.40	0.000156
195	11.05	44.20	0.000162
215	11.78	47.12	0.000168
233	11.78	47.12	0.000153
Average coefficient of velocity,			0.000129

## SERIES IN DIRECT SUNLIGHT AT 60° C.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
30	3.85	15.40	0.000243
45	5.30	21.20	0.000239
60	6.65	26.60	0.000242
75	8.05	32.20	0.000253
90	8.85	39.40	0.000288
105	10.75	43.00	0.000287
120	11.53	46.12	0.000285
135	12.35	49.40	0.000290
150	13.39	53.56	0.000308
165	13.63	54.52	0.000291
180	15.01	60.04	0.000336
195	15.85	63.40	0.000356
216	16.35	65.40	0.000350
225	16.40	65.60	0.000339
270	18.20	72.80	0.000397
300	19.05	76.20	0.000427
Average coefficient of velocity,			0.000308

## SERIES IN DIRECT SUNLIGHT AT 70° C.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
45	5.95	47.60	0.000805
90	7.95	63.60	0.000777
135	9.45	75.60	0.000918
180	10.15	81.20	0.000959
Average coefficient of velocity,			0.000865



## SERIES IN DIRECT SUNLIGHT AT 80° C.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
20	13.85	55.40	0.00248
35	17.10	68.40	0.00247
50	18.90	75.60	0.00248
60	20.00	80.00	0.00267
80	21.31	85.20	0.00288
100	21.95	87.80	0.00288
120	21.95	87.80	0.00240
150	23.00	92.00	0.00307
225	23.20	92.80	0.00228
Average coefficient of velocity,			0.00262

## SERIES IN DIRECT SUNLIGHT AT 90° C.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
15	17.30	69.20	0.00595
20	19.30	77.20	0.00675
30	20.40	81.60	0.00590
55	22.10	88.40	0.00555
75	23.20	92.80	0.00690
Average coefficient of velocity,			0.00621

The results, like those obtained in the dark, can best be represented graphically by the curve, the abscissas of which represent the temperatures and the ordinates the average coefficients of velocity multiplied by  $3333\frac{1}{3}$ . From this it will be seen, at a glance that for certain temperatures, at least, light exerts an accelerating influence on the progress of the reaction. The point of chief interest, however, is that the effect of light is different for different temperatures. What it is at 0° C. we have not yet had an opportunity to determine, in consequence of the extreme slowness of the change. Generally, however, it will be seen that the accelerating effect of light is greatest for low temperatures, gradually diminishing with increasing temperature until at a temperature just a little below 90° C., the curves intersect and become identical for light and dark. When we compare the velocity of this reaction at 20° C. and 40° C. and observe the great falling off in the rate of change it can be fairly surmised that somewhere, probably not very far removed from 0° C. on either side, the reaction would cease altogether, both in light

and dark. It would seem then that the accelerating influence of light is possible only between certain rather narrow limits of temperature. That such is the case seems to have been proved also, for reactions other than the one under discussion. Amato<sup>1</sup> has shown, for example, that if a mixture of hydrogen and chlorine be cooled to  $-12^{\circ}$  C. it could be exposed to direct sunlight for hours without any combination taking place. It is further conceivable with reference to this particular reaction that at very high temperatures it would take place so rapidly that light would be without effect on the change. In the same way Beatty<sup>2</sup> and one of us have shown that while light cannot cause the combination of hydrogen and bromine at ordinary temperatures, it greatly accelerates their combination at  $197^{\circ}$  C.; at still higher temperatures it is quite possible that its effect on this system would be lost. The chemical action of light is at best so little understood that considerable interest attaches to these results which would seem to support the view that a certain amount of the energy of the light actually enters into, and becomes a part of, the system undergoing change. Below a certain temperature the heat and light energy together might be insufficient to cause the change. At temperatures at which the given reaction becomes possible, however, light would accelerate, for the reason that the increment of energy furnished by it would be a measurable amount of the entire quantity of energy present. At very high temperatures this increment of light energy would become so small, as compared with the increased heat energy of the system, as to cause the effect of the light to disappear altogether.

#### ON THE EFFECT OF ACIDS AND BASES ON THE OXIDATION.

It has been announced as a general proposition that "all oxidation and reduction processes are accelerated by the presence of free acids, in proportion to their coefficients of affinity."<sup>3</sup> It was therefore deemed desirable to try the effect of acids on this particular case. In order to do this, three series of experiments were carried through at  $50^{\circ}$  C.: one with hydrochloric

<sup>1</sup> *Gazz. chim. ital.*, 14, 57.

<sup>2</sup> *Am. Chem. J.*, 20, 159.

<sup>3</sup> Schlundt and Warder: *Am. Chem. J.*, 18, p. 31.

acid, one with formic acid, and one with water alone. In each experiment five cc. normal formaldehyde, five cc. normal hydrogen peroxide, and five cc. of water or the acid were mixed, placed in sealed tubes and kept at 50° C. for the several desired intervals of time. The following series were carried through:

- (1) With hydrochloric acid ..... 0.0000754  
 (2) With formic acid ..... 0.0000705  
 (3) With water ..... 0.0000670

#### HYDROCHLORIC ACID SERIES.

Mixture: Five cc. normal hydrogen peroxide, five cc. normal formaldehyde, and five cc. normal hydrochloric acid.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
60	2.25	9.00	0.0000659
90	3.53	14.12	0.0000737
120	4.33	17.32	0.0000698
180	6.55	26.20	0.0000789
210	7.45	29.80	0.0000809
240	8.00	32.00	0.0000784
270	8.75	35.00	0.0000799

Average coefficient of velocity, 0.0000754

#### FORMIC ACID SERIES.

Mixture: Five cc. normal hydrogen peroxide, five cc. normal formaldehyde, and five cc. normal formic acid.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
60	2.10	8.40	0.0000611
90	3.15	12.60	0.0000641
120	4.40	17.60	0.0000745
150	5.08	20.32	0.0000680
180	6.20	24.80	0.0000733
210	6.95	27.80	0.0000733
240	7.80	31.20	0.0000756
270	8.40	33.60	0.0000750

Average coefficient of velocity, 0.0000705

## SERIES WITH WATER.

Mixture : Five cc. normal hydrogen peroxide, five cc. normal formaldehyde, and five cc. water.

Time. Minutes.	Fifth-normal potas- sium hydroxide. cc.	Decomposed. Per cent.	K.
60	2.10	8.4	0.0000611
90	3.20	12.8	0.0000652
120	4.07	16.28	0.0000648
150	4.90	19.60	0.0000650
180	5.88	23.52	0.0000680
210	6.92	27.68	0.0000730
240	7.30	29.20	0.0000690
270	8.12	32.48	0.0000712

Average coefficient of velocity, 0.0000670

It will be observed that the acids caused some acceleration in the rate of change, and that hydrochloric acid caused a greater acceleration than formic. It is not by any means so marked as it is in certain other oxidations that have been studied, a fact that can doubtless best be explained by assuming that the accelerative tendency of the acid is counterbalanced to some extent by an increased stability in the hydrogen peroxide, which latter is also brought about in some way by the acid. The acceleration produced by formic acid, however, is probably sufficiently great to account for the increase in velocity usually observed at the end of a long series. The formic acid produced during the oxidation would cause the reaction to proceed more rapidly towards the end. The effect of bases on the rapidity of the oxidation is certainly most remarkable. In consequence of the rapidity of the oxidation, all of our experiments with bases have been conducted at ordinary temperatures. In each experiment five cc. normal formaldehyde and five cc. normal hydrogen peroxide were placed in a flask, and a quantity of half-normal base then added—equivalent to the amount of formic acid produced by the oxidation, and from the time of adding the solution of the base the duration of the experiment was counted. At the end of a given time an amount of normal hydrochloric acid was added—equivalent to the original amount of base present—and the solution was then titrated back with standard caustic potash, using phenolphthalein as an indicator. During the progress of the reaction with bases, considerable effervescence occurred, due to escaping oxygen. The reaction is affected by

light, and slight changes in temperatures also produced quite a noticeable effect on the rate of change.

Caustic potash, caustic soda, and ammonia were first compared as to their effect on the reaction, each active substance reacting in fourth-normal solution. The results obtained are given in the following table.

TABLE I.

Time. Minutes.	Potassium hydroxide. Per cent.	Sodium hydroxide. Per cent.	Ammonium hydroxide. Per cent.
2	48.4	46.0	15.0
4	62.5	61.0	24.0
6	70.0	69.0	31.0
8	76.5	74.0	37.0
10	78.0	77.0	40.0
15	87.0	88.0	44.0
20	99.5	99.0	49.0
25	....	....	54.4
35	....	....	56.0
83	....	....	69.0
1350	....	....	86.4

These results are of interest, first, as showing the remarkable acceleration produced by alkalis on the progress of this reaction. Few, if any, attempts have been made to follow any reaction occurring with such rapidity. It will be seen, further, that caustic potash and soda are practically the same in their effect, and that both act much more vigorously than ammonia. This is in harmony with our present knowledge respecting the activity of these bases. The action of barium hydroxide on this oxidation was also tried. Owing to lack of solubility, it could not be compared with these bases at the dilution at which the above comparisons were made. As concentrated a solution as possible of this base was made (which happened to be nearly third-normal), 14.5 cc. being equivalent to five cc. normal hydrochloric acid. This was compared with caustic potash of exactly the same strength, so that in these experiments the active substances were present in about fifth-normal solution. In each experiment five cc. normal formic aldehyde, five cc. hydrogen peroxide, and 14.5 cc. of the given base were employed. The following results were obtained :

TABLE II.

Time. Minutes.	Potassium hydroxide. Per cent.	Barium hydroxide. Per cent.
2	43.0	53.4
4	57.0	67.4
6	63.0	68.0
8	66.4	71.0
10	72.0	74.0
15	74.4	78.0
20	82.4	81.0
25	84.4	82.4
30	85.0	86.0

In the last five experiments of this series it will be observed that caustic potash and barium hydroxide are exerting practically the same effect on the rate of oxidation. At first, however, the barium hydroxide acts more rapidly. In the experiments with barium hydroxide at this dilution we always obtained a white precipitate, probably barium dioxide, and this may have altered the conditions to such an extent as to cause this difference in the effect of these two bases. It is our intention to study the effect of bases at greater dilutions, so as to include lime and strontium hydroxide in the comparison. The great acceleration produced by bases on this oxidation has suggested another important line of work, in which only the merest beginning has as yet been made. This is with reference to the hydrolysis of salts. It was thought that this reaction might furnish us with a very delicate method for the measurement of the hydrolysis of alkaline salts. It has been found, for example, that while common salt is without influence on rate of change at 50° C., it is greatly accelerated by sodium acetate. We have not yet had an opportunity to make any thorough study of this phase of the reaction, but the following comparisons of the action of hundredth-normal potassium hydroxide and normal sodium acetate is interesting, as showing the possibilities of this method in measuring the hydrolysis of salts.

Two series of experiments were tried, in the dark, at 60° C. In series No. 1, one cc. normal formaldehyde was mixed with one cc. normal hydrogen peroxide, one cc. hundredth-normal caustic potash, and seven cc. of water in each experiment. In series No. 2, exactly the same quantities of substances were used, except that instead of hundredth-normal caustic potash, one

cc. normal sodium acetate was employed. The coefficients of velocity obtained in the two series are given in Table III.

Time. Minutes.	Series No. 1, potas- sium hydroxide.	Series No. 2, normal sodium acetate.
68	0.000141	0.000218
90	0.000141	0.000209
120	0.000156	0.000231
Average	0.000146	0.000219

These results would indicate that at this temperature and dilution, sodium acetate is hydrolyzed to the extent of over one per cent. This number is probably not far from the truth. A more thorough study especially of this last phase of the reaction will soon be undertaken.

STATE COLLEGE OF KENTUCKY,  
LEXINGTON, July, 1898.

## UPON THE ACTION OF SULPHURIC ACID ON THYMOL.<sup>1</sup>

[THIRD PAPER.]

BY JAMES H. STEBBINS.

Received December 15, 1898.

**M**Y motive in taking up this subject again, is for the purpose of clearing up certain doubts which had arisen in my mind, in connection with my previous experiments.<sup>2</sup>

Photomicrographic examinations of the products previously obtained showed so many different forms of crystallization, that I was led to believe that by the treatment of thymol with 66° sulphuric acid, at steam-bath temperature, possibly several isomeric acids are formed.

To gain more light upon this question, therefore the following experiments were made :

Sixty grams of powdered thymol were heated in a beaker on the water-bath, under constant stirring, with fifty grams of 66° sulphuric acid, until the mixture solidified to a crystalline mass, which occurs after nine to ten minutes' heating.

As previously noted, a small quantity of a clear, oily-looking liquid separates, on pressing, from the crystalline cake. This, on being poured off into a beaker, solidifies on cooling to a mass of minute white needles.

<sup>1</sup> Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

<sup>2</sup> This Journal, 3, 103, 110, (1881).