hydrochloric acid, liberating nascent chlorine, which in turn combines with the platinum.

The reagent for the precipitation of potassium may be prepared as follows: 10 g. of dried, but not ignited, platinum black are covered with 50 cc. of concentrated hydrochloric acid, warmed to about 50° or 60° and 3% hydrogen peroxide slowly added, keeping just enough present to maintain a moderate evolution of chlorine, which will be seen to originate entirely on the platinum. When the platinum has been entirely dissolved, evaporate the solution to a volume of 100 cc., when it is ready for use. The use of peroxide as dilute as 3% may cause the volume to become too great during the operation. In this case it will be necessary to evaporate to a smaller bulk before the platinum has all been dissolved.

If "perhydrol" or concentrated hydrogen peroxide is available, it will be possible to keep the volume below 100 cc., thus shortening the time necessary to prepare the solution. The concentrated peroxide had best be added from a buret to avoid a large excess at one time, which might cause loss from frothing. We have found it convenient to prepare peroxide of 20% to 30% strength by distilling commercial hydrogen peroxide under a pressure of 4–5 cm. and at a temperature of 35–45°. On concentration to one-eighth of the original volume, 80% of the hydrogen peroxide remains in the residue and the loss from decomposition is negligible.

We take this opportunity of acknowledging the assistance rendered by Mr. W. C. Beaumont in the work described in this paper.

CHICAGO, ILL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

# THE EFFECT OF VARIOUS SUBSTANCES ON THE PHOTOCHEMICAL OXIDATION OF SOLUTIONS OF SODIUM SULFITE.

BY J. HOWARD MATHEWS AND MARY ELVIRA WEEKS.

Received February 14, 1917.

The phenomenon of "negative catalysis," *i. e.*, the inhibition of a reaction by the addition of a small amount of a foreign substance which appears unchanged in the end products of the reaction, is even more difficult of explanation than is the phenomenon of positive catalysis, for which science has as yet found no explanation which is generally accepted. While each of several individual explanations which have been offered for particular cases of catalytic action are satisfactory for those cases, none of the various explanations so far offered may be applied to all cases of catalysis. The intermediate compound theory, which is probably more widely accepted than any other, furnishes a satisfactory explanation for a considerable number of cases, but for many others it is entirely inadequate. By the postulation of the existence of certain ephemeral compounds having a transitory existence, one's imagination may perhaps supply what is very much lacking in the way of experimental evidence. But when we come to consider the phenomenon of "negative catalysis" the difficulties are still greater. Even admitting the validity of the Clément and Désormes theory attributing positive catalysis to the formation of an intermediate compound or compounds, the theory certainly does not explain "negative catalysis" for, as Ostwald[1] has shown, if the reaction proceeds more slowly by the formation of the intermediate compound than by the direct way, it proceeds by the direct route and the possibility of an intermediate compound has no effect on the reaction.

Luther[2] has advanced the idea that "negative catalysis" cannot occur in a reaction which is entirely free from positive catalyzers, and that the phenomenon is really due to the destruction or otherwise rendering latent of these positive catalyzers. Titoff,[3] as a result of his study of the combined effect of positive and negative catalyzers on the rate of oxidation of sodium sulfite, lends his support to Luther's theory.

The phenomenon of "negative catalysis" is very common in the case of photochemical reactions. In a study of the effect of added substances on the photolysis of hydrogen peroxide, Mathews and Curtis[4] found that of the sixteen substances whose effect was tried, four produced no appreciable effect, one increased the rate of decomposition, while the remaining eleven all inhibited the reaction to a greater or lesser degree. The chemical nature of the added substances furnished no criteria as to the effect produced.

In 1912 Mathews and Dewey[5] made a study of the effect of ultraviolet light on the oxidation of sodium sulfite in dilute solution. They found that for the light intensity employed, the oxidation of sodium sulfite solutions proceeded about twenty times as fast in ultraviolet light from the quartz mercury vapor lamp as in the ordinary light of the laboratory and also established the fact that this reaction is not a case of autoöxidation. They also found that uranium salts accelerate the photochemical oxidation of sodium sulfite, and in proportion to the amount of salt used.

The effect of "negative catalyzers" on the rate of oxidation of sodium sulfite was first studied by Bigelow,[6] who found that the oxidation of the salt in aqueous solution is greatly retarded by the presence of minute

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[1] "Grundriss der Allgemeine Chemie," p. 517.

[2] *Z. phys. Chem.*, **45**, 662 (1903).

[3] *Ibid.*, **45**, 641 (1903).

[4] *J. Phys. Chem.*, **18**, 166, 521 (1914).

[5] *Ibid.*, **17**, 211 (1913).

[6] *Z. phys. Chem.*, **26**, 493 (1898).

amounts of benzaldehyde, isobutyl alcohol, mannite, glycerol, phenol, potassium tartrate and certain other organic substances. Bigelow also demonstrated that the effect of the negative catalyzer is not on the rate of solution of oxygen, but on the rate of the reaction between the sulfite and oxygen. A few years later Titoff[1] substantiated Bigelow's results, and in addition studied the simultaneous effect produced upon the reaction by copper sulfate, a powerful accelerator, and mannitol, a strong inhibitor. He found that these two substances do not exert an additive effect, but influence each other.

Young[2] discovered that small amounts of certain alkaloids greatly inhibit this oxidation, especially if the solution is alkaline, and the inhibitive effect of sucrose, invert sugar, aspartic acid, glutaric acid and potassium lactate have been noted by Saillard.[3]

The object of the present investigation was to study the oxidation of sodium sulfite solutions by the influence of ultraviolet light, and especially to determine the effect of various foreign substances on the rate of the reaction.

The sodium sulfite was prepared by passing a current of washed sulfur dioxide into a concentrated solution of pure sodium hydroxide, to neutrality. The precipitated salt was filtered and dried in a current of dry nitrogen, and kept in glass-stoppered bottles in the dark. The water used in making up all solutions was freshly distilled from potassium permanganate and sulfuric acid, and redistilled from barium hydroxide. After the second distillation, the water was preserved in a vessel of Jena glass, and was protected from carbon dioxide by means of a soda-lime tube.

The pyridine was allowed to stand over potassium hydroxide for several weeks, after which it was digested with barium oxide under a reflux condenser for ten hours and distilled. The methyl and ethyl acetates were purified by repeated treatments with a saturated solution of calcium chloride and subsequent distillation from phosphorus pentoxide. The copper sulfate, phenol, and hydroquinone were purified by recrystallization.

The source of ultraviolet light was a quartz mercury-vapor lamp run on direct current. To secure constant light intensity, the current was adjusted to 2.6 amperes with a potential drop across the terminals of 80 volts. In order to maintain the voltage at this constant value, a variable resistance was inserted in the circuit. As atmospheric oxygen enters into the reaction, it was necessary to provide for constant saturation of the solutions in the quartz reaction flasks. This was accomplished by

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[1] *Loc. cit.*

[2] THIS JOURNAL, **23**, 119 (1901); **24**, 297 (1902).

[3] *Z. Ver. Zuckerind.*, **63**, 1035, 1043 (1913).

means of small, hollow ⊥ shaped glass stirrers, run at high speed by an electric motor, which drew in air at the top and forced it into the solution at a lively rate.

Since considerable heat is developed by the lamp, it was necessary to provide suitable means for keeping the reaction flasks at a constant temperature, although the temperature coefficients for photochemical reactions are small. Dilute solutions of sodium sulfite oxidize even in the dark, though comparatively slowly, and what we measured was the summation of the two effects, the ordinary oxidation and the photochemical oxidation superimposed thereon. Hence it became essential to control the temperature more closely than we should have had to control it had we been dealing with a purely photochemical reaction. A thermostat of the usual type was used. It was electrically controlled and maintained a temperature of 26°, constant to less than 0.1°. The water from the thermostat was forced by means of a small centrifugal pump into a small reservoir above the lamp, from which it flowed down to and through hollow, perforated collars surrounding the necks of the quartz flasks, forming a film of water flowing evenly over the surface of the flasks. This film of water always flowing between the lamp and solution prevented the solution from being warmed appreciably by the lamp.

An approximately 0.2 *N* solution of the purified sodium sulfite was prepared for each determination. 200 cc. of this solution were introduced into each of the carefully cleaned quartz flasks, which were placed *equidistant* from the lamp, one on each side, and about three inches from it. While the lamp was attaining its equilibrium conditions of voltage, amperage and light intensity, it was screened by means of sheet asbestos. When the light intensity had become constant, as judged by constancy of voltage and amperage, the lamp was unscreened, the instant of unscreening being considered the starting point of the reaction. Since the oxidation proceeds slowly as soon as the solutions are made up it is obvious that the concentration would not necessarily always be the same at the moment of unscreening, as different lengths of time elapsed for the different experiments. However, the solutions were always somewhere near 0.2 *N*.

At intervals of about ten minutes, 10 cc. portions were withdrawn from the flasks by means of a pipet and were quickly run into an excess of a 0.03 *N* solution of resublimed iodine. The excess of iodine was then determined by titration with 0.03 *N* sodium thiosulfate.

Great care was taken to keep the voltage of the lamp constant throughout the determination, as fluctuations in the voltage would have caused irregularities in the course of the oxidation. Several preliminary determinations were made to make certain that the oxidation proceeded at the same rate in the two flasks, *i. e.*, that the light conditions were identical for the two portions of the same solution. Once the position of flasks and lamp necessary to bring about this result were obtained, care was taken always to keep them in the same position. Curve I, which shows the course of the oxidation of two identical solutions of sodium sulfite, shows that the oxidation proceeded at very nearly the same rate in the two flasks.

In order to determine the effect of the various foreign substances, the substance was introduced into the sulfite solution in one of the flasks, the other flask containing the sodium sulfite solution without the addition of the substance and serving as a "control reaction" for comparison. It was necessary to carry on this "control reaction," for it is not possible to duplicate either the concentrations of the sulfite solutions or the light intensity with sufficient exactness to make it safe to draw any conclusions from successive series of determinations of the rate of oxidation. This is apparent from an examination of the curves representing the "control reaction" for the determinations here reported, the curves often showing considerable difference in trend. However, this does not matter when "control reactions" are run, for the two solutions will be of the same original concentration and will be illuminated equally even though the light intensity may vary. Whenever a substance was added to the solution in one flask, an equal volume of distilled water was added to the other in order to keep the concentration of sulfite the same in the two flasks.

The results of the various experiments are shown in the accompanying tables and curves, the latter all being plotted to the same scale. The time at which samples were taken is plotted on the axis of abscissas while the corresponding concentrations are plotted along the axis of ordinates. In each case the broken curve drawn through the crossed circles represents the "control reaction," and the solid line curve represents the course of the reaction in the presence of the added substance.

The "control reaction" is a rapid one, a 0.2 $N$ solution of sodium sulfite being completely oxidized in the light in less than three hours. No positive catalysts for the reaction were found among the thirteen substances whose effects were tried. Copper sulfate, which Titoff found to be a powerful positive catalyzer in ordinary light, exerted no appreciable effect on the reaction in ultraviolet light (Curve II).

Of the organic substances, pyridine strongly inhibited the reaction when present in the proportion of five cubic centimeters to a liter of the solution (Curve III), while methyl (Curve IV) and ethyl acetate (Curve V) had a much weaker effect. Five drops of benzaldehyde to a liter of solution strongly inhibited the reaction (Curve VII), whereas the same amount of glycerol produced only a slight effect (Curve VI). It will be recalled that Bigelow found both of these to be powerful inhibitors for the ordinary oxidation. Urea, phenol, quinine sulfate, and hydroquinone were studied in 0.001 *N* solution. Urea exerted almost no effect whatever (Curve VIII), a slight inhibition appearing late in the course of the reaction. This would seem to indicate that the inhibition was due, not to the urea itself, but to some decomposition product formed under the influence of the light. The inhibitive effect of the hydroquinone, on the other hand, diminished as the reaction proceeded, indicating that the substance was probably changed under the influence of the light (Curve XI). Both hydroquinone and phenol (Curve IX) exerted a considerable inhibitive effect, but the effect of the quinine sulfate was still greater (Curve X). Sucrose, when present in about 0.025 *N* solution produced an inhibition which was slightly less than that produced by phenol in 0.001 *N* solution (Curve XII). Examination of the solution after the oxidation was complete, by means of the polariscope, showed no change in sucrose content.

In 1902 Young[1] made the prediction that all organic substances would be found to inhibit the oxidation of solutions of sodium sulfite. While this prediction was made with reference to the ordinary oxidation of sodium sulfite, the series of experiments here described seems to indicate that it applies here equally well. It appears, however, that the inhibiting effect is quite different in degree for the ordinary and for the photochemical oxidations.

In the presence of quinine sulfate or pyridine, the solution acquires a green color under the influence of the light, and with hydroquinone it becomes opalescent. The inhibition of the reaction in these cases may possibly be due, in part at least, to the increased opacity of the solution, since the photochemical effect is not limited wholly to the ultraviolet rays. However, the solution of copper sulfate was also green, and it did not inhibit the reaction. And, moreover, the inhibiting effect produced by hydroquinone fell off as the opalescence increased, though this may have been due to a destruction of the hydroquinone. The color probably has very little to do with the power of inhibition because the light which is chiefly responsible for the photochemical oxidation is the ultraviolet. A study of the relation between the effect produced and the absorption bands in the ultraviolet region is highly desirable. It may be found that the effect which we have called "negative catalysis" will be wholly explained by the changes produced in the absorption bands in the ultraviolet region. This study we hope to make.

The data from which the accompanying curves were plotted are given in the tables below:

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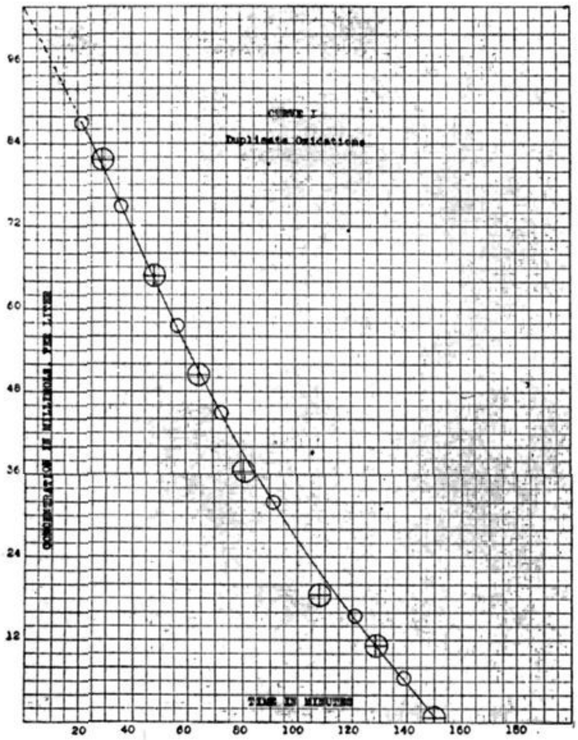
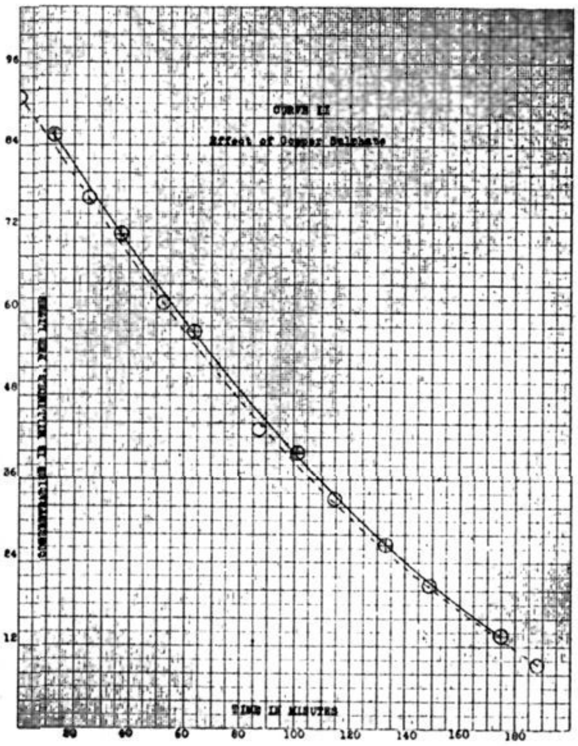
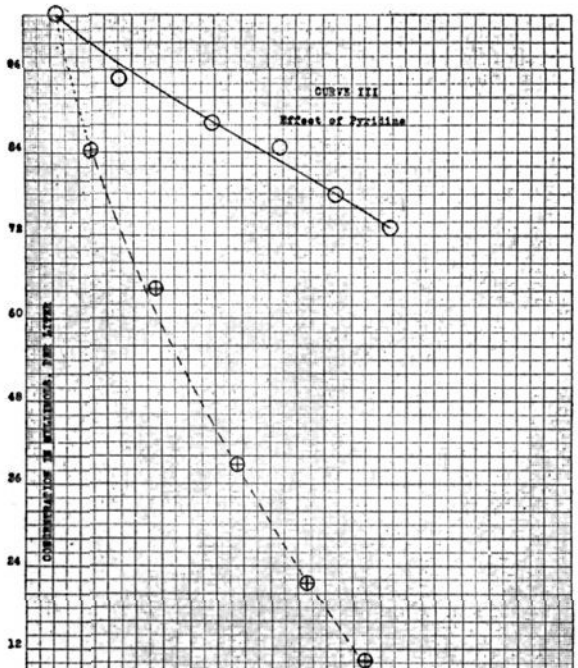
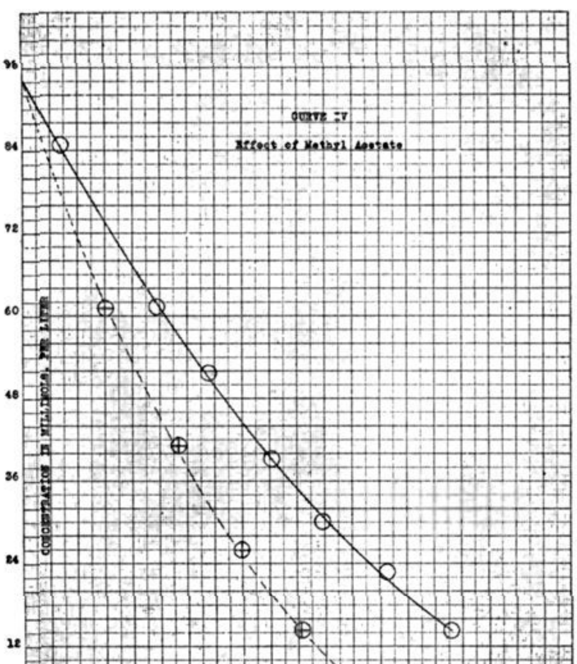
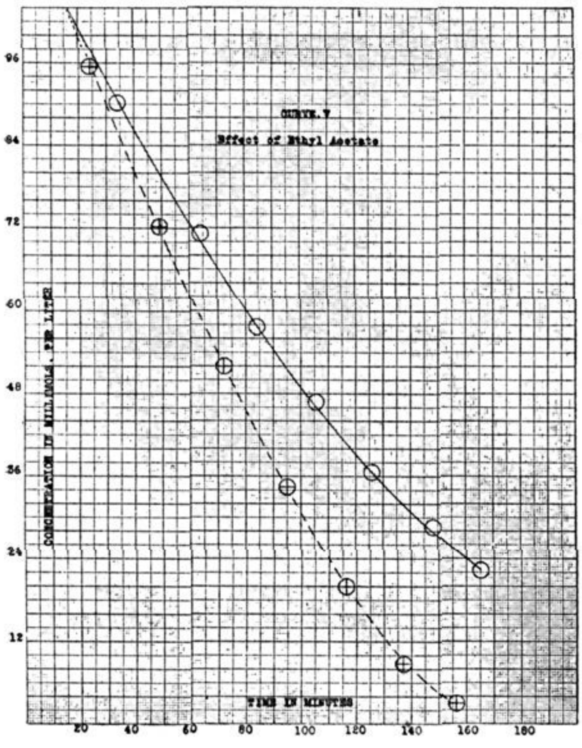
[1] *Loc. cit.*

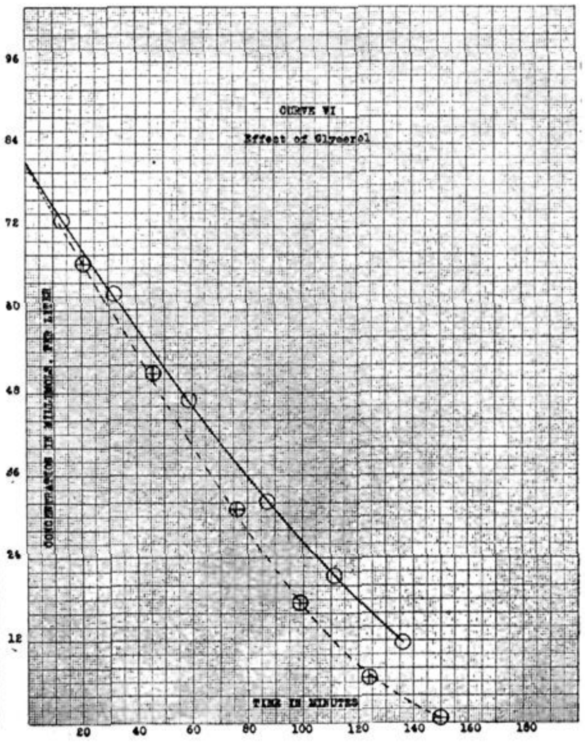

CURVE I
Duplicate Oxidations
CONCENTRATION IN MILLIMOLS. PER LITER
96
84
72
60
48
36
24
12
TIME IN MINUTES
20
40
60
80
100
120
140
160
180

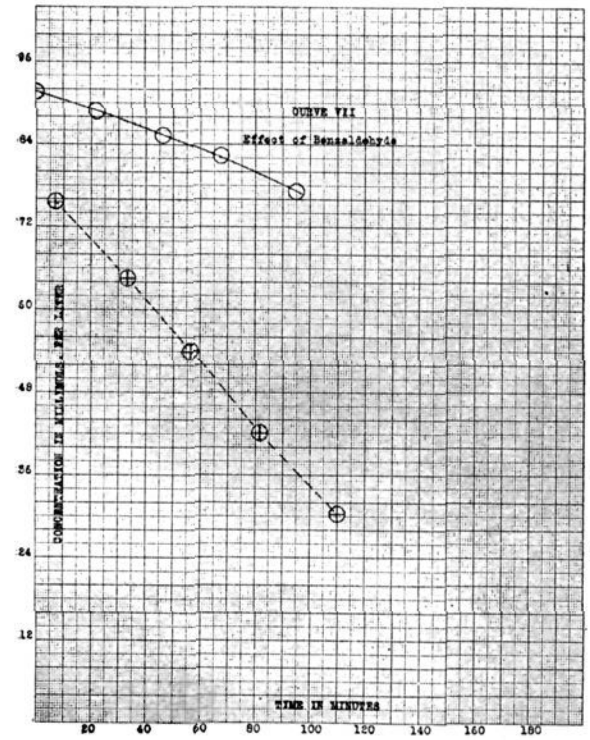

CURVE II
Effect of Copper Sulphate
CONCENTRATION IN MILLIMOLS. PER LITER
96
84
72
60
48
36
24
12
TIME IN MINUTES
20
40
60
80
100
120
140
160
180

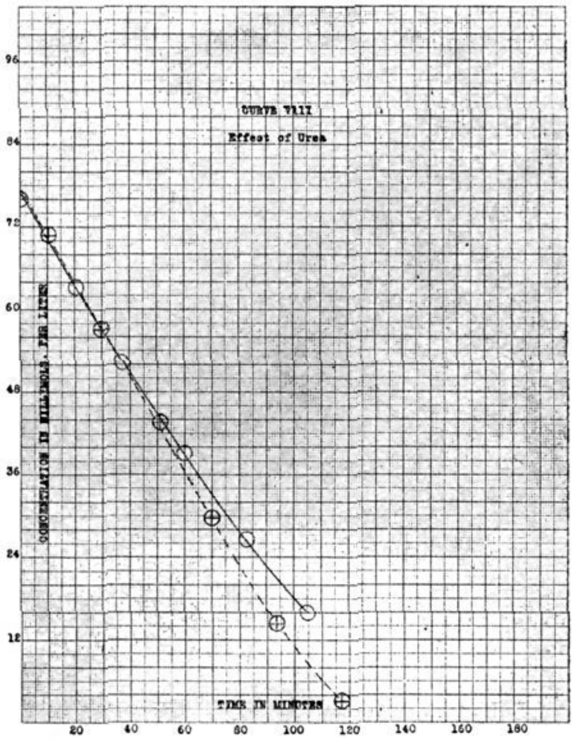

CURVE III
Effect of Pyridine
CONCENTRATION IN MILLIMOLS. PER LITER
96
84
72
60
48
36
24
12
TIME IN MINUTES
20
40
60
80
100
120
140
160
180

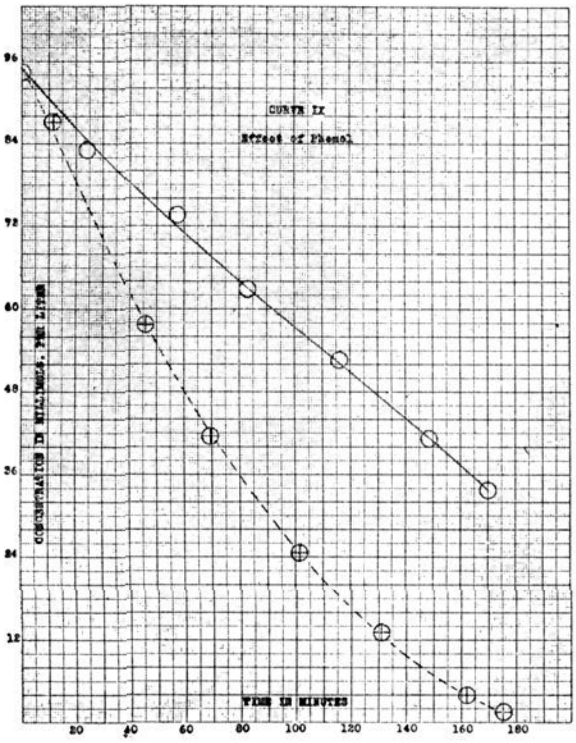

CURVE IV
Effect of Methyl Acetate
CONCENTRATION IN MILLIMOLS. PER LITER
96
84
72
60
48
36
24
12
TIME IN MINUTES
20
40
60
80
100
120
140
160
180

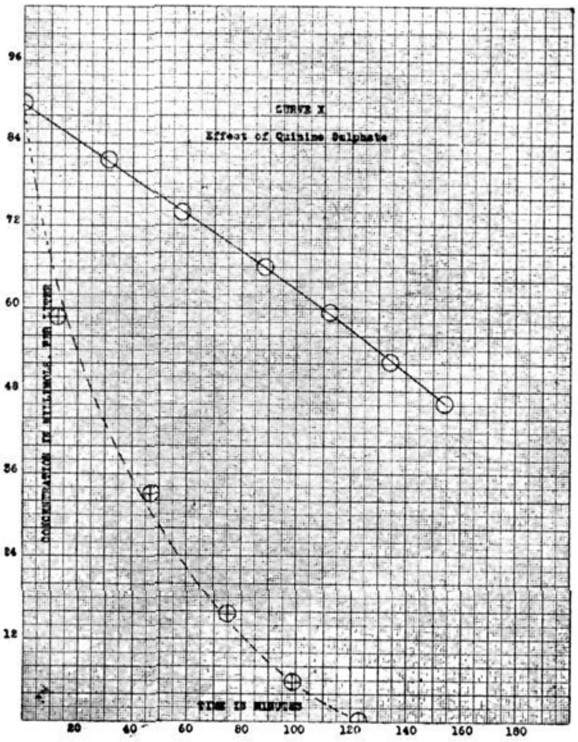

CURVE V
Effect of Ethyl Acetate
CONCENTRATION IN MILLIMOLS. PER LITER
96
84
72
60
48
36
24
12
TIME IN MINUTES
20
40
60
80
100
120
140
160
180

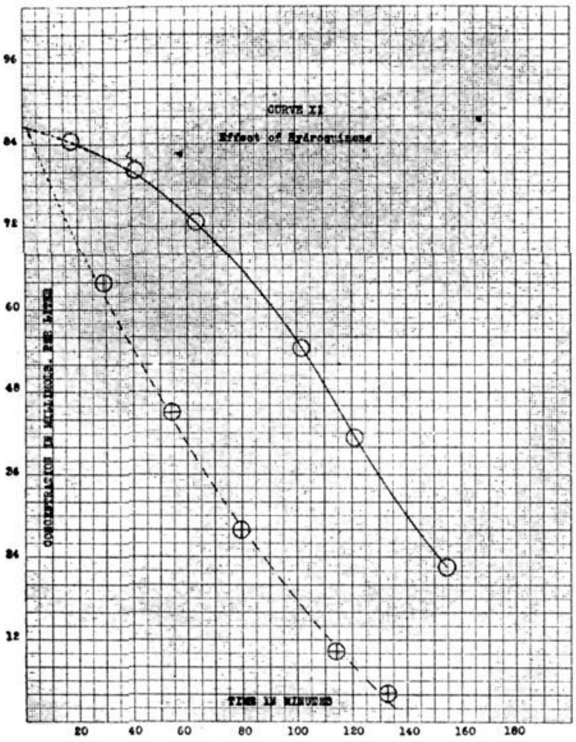

CURVE VI
Effect of Glycerol
CONCENTRATION IN MILLIMOLS. PER LITER
96
84
72
60
48
36
24
12
TIME IN MINUTES
20
40
60
80
100
120
140
160
180

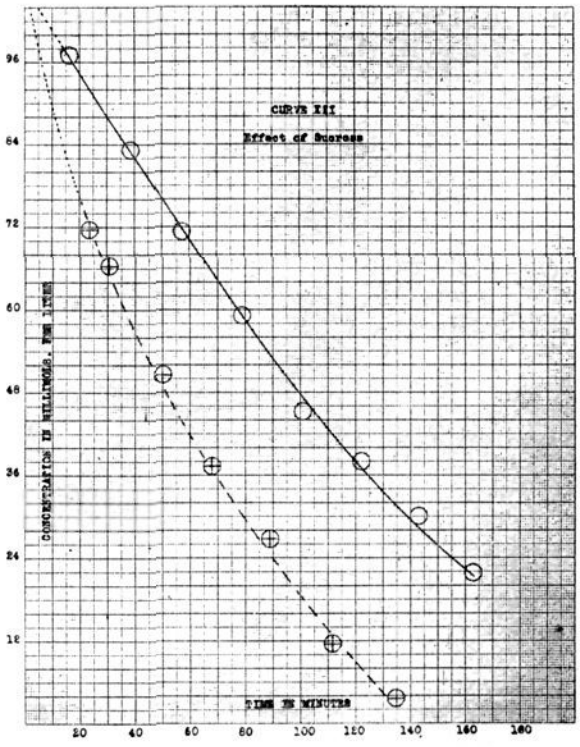

CURVE VII
Effect of Benzaldehyde
CONCENTRATION IN MILLIMOLS. PER LITER
96
84
72
60
48
36
24
12
TIME IN MINUTES
20
40
60
80
100
120
140
160
180


CURVE VIII
Effect of Urea
CONCENTRATION IN MILLIMOLS. PER LITER
96
84
72
60
48
36
24
12
TIME IN MINUTES
20
40
60
80
100
120
140
160
180


CURVE IX
Effect of Phenol
CONCENTRATION IN MILLIMOLS. PER LITER
TIME IN MINUTES
96
84
72
60
48
36
24
12
20
40
60
80
100
120
140
160
180


CURVE X
Effect of Quinine Sulphate
CONCENTRATION IN MILLIMOLS. PER LITER
TIME IN MINUTES
96
84
72
60
48
36
24
12
20
40
60
80
100
120
140
160
180


CURVE XI
Effect of Hydroquinone
CONCENTRATION IN MILLIMOLS. PER LITER
TIME IN MINUTES
96
84
72
60
48
36
24
12
20
40
60
80
100
120
140
160
180


CURVE XII
Effect of Sucrose
CONCENTRATION IN MILLIMOLS. PER LITER
TIME IN MINUTES
96
84
72
60
48
36
24
12
20
40
60
80
100
120
140
160
180

### DATA FOR CURVE I.

Duplicate Reactions.

| Reaction in Flask A. | | Reaction in Flask B. | |
|---|---|---|---|
| Time in min. | Conc. of $Na_2SO_3$ in millimols per liter. | Time in min. | Conc. of $Na_2SO_3$ in millimols per liter. |
| 21.5 | 87.4 | 29.5 | 81.5 |
| 35.75 | 74.9 | 48.5 | 64.8 |
| 57.0 | 57.6 | 65.0 | 50.6 |
| 73.0 | 45.0 | 81.25 | 36.6 |
| 91.25 | 32.0 | 108.0 | 18.6 |
| 120.75 | 15.5 | 128.0 | 11.3 |
| 139.5 | 6.7 | 149.75 | 0.8 |

### DATA FOR CURVE II.

| "Control Reaction." | | 0.0001 $N$ $CuSO_4$. | |
|---|---|---|---|
| 0 | 91.3 | 12.5 | 85.7 |
| 25.5 | 76.3 | 38.0 | 71.1 |
| 52.5 | 61.4 | 64.0 | 57.3 |
| 87.5 | 43.3 | 101.5 | 39.8 |
| 114.5 | 33.3 | 133.0 | 26.6 |
| 149.0 | 20.7 | 175.0 | 13.6 |
| 188.0 | 9.4 | | |

### DATA FOR CURVE III.

| "Control Reaction." | | 5 cc. Pyridine per Liter. | |
|---|---|---|---|
| 24.25 | 84.4 | 12.5 | 100.5 |
| 48.5 | 64.4 | 35.25 | 94.7 |
| 77.75 | 38.8 | 69.0 | 88.3 |
| 103.25 | 21.7 | 94.0 | 84.9 |
| 124.25 | 10.3 | 113.75 | 78.0 |
| 140.25 | 4.9 | 133.75 | 73.2 |

### DATA FOR CURVE IV.

| "Control Reaction." | | 5 cc. Methyl Acetate per Liter. | |
|---|---|---|---|
| 30.5 | 61.3 | 14.0 | 84.9 |
| 57.0 | 41.1 | 48.75 | 61.4 |
| 80.0 | 25.9 | 68.0 | 51.8 |
| 101.5 | 14.4 | 91.25 | 39.2 |
| 121.0 | 6.4 | 109.5 | 30.2 |
| 142.0 | 0.7 | 132.75 | 22.9 |
| | | 156.25 | 14.5 |

### DATA FOR CURVE V.

| "Control Reaction." | | 5 cc. Ethyl Acetate per Liter. | |
|---|---|---|---|
| 24.0 | 95.5 | 11.25 | 106.9 |
| 49.5 | 72.2 | 34.0 | 90.2 |
| 72.25 | 51.9 | 64.0 | 69.1 |
| 95.0 | 34.5 | 84.25 | 57.4 |
| 116.25 | 20.0 | 105.5 | 46.7 |
| 137.5 | 8.9 | 125.75 | 36.7 |
| 156.5 | 3.0 | 148.5 | 28.6 |
| | | 165.25 | 22.4 |

### Data for Curve VI.

| "Control Reaction." | | 5 Drops Glycerol per Liter. | |
|---|---|---|---|
| Time in min. | Conc. of $Na_2SO_3$ in millimols per liter. | Time in min. | Conc. of $Na_2SO_3$ in millimols per liter. |
| 21.25 | 66.7 | 13.0 | 73.0 |
| 46.0 | 50.8 | 32.0 | 62.4 |
| 76.25 | 31.2 | 59.0 | 47.0 |
| 98.75 | 17.6 | 87.0 | 32.2 |
| 124.0 | 6.6 | 110.75 | 21.4 |
| 150.0 | 0.7 | 136.25 | 11.8 |

### Data for Curve VII.

| "Control Reaction." | | 5 Drops Benzaldehyde per Liter. | |
|---|---|---|---|
| 7.0 | 75.7 | 0 | 91.5 |
| 33.5 | 64.6 | 22.0 | 88.8 |
| 56.5 | 54.0 | 46.0 | 85.4 |
| 81.5 | 42.2 | 67.5 | 82.5 |
| 110.0 | 30.4 | 95.0 | 77.2 |

### Data for Curve VIII.

| "Control Reaction." | | 0.001 *N* Urea. | |
|---|---|---|---|
| 10.5 | 70.7 | 0 | 76.0 |
| 30.0 | 57.1 | 20.5 | 63.4 |
| 51.0 | 43.5 | 37.0 | 52.5 |
| 70.0 | 29.8 | 60.0 | 39.1 |
| 93.5 | 14.4 | 83.0 | 26.6 |
| 117.0 | 3.2 | 105.0 | 15.9 |

### Data for Curve IX.

| "Control Reaction." | | 0.001 *N* Phenol. | |
|---|---|---|---|
| 11.5 | 80.9 | 0 | 94.5 |
| 46.5 | 57.8 | 24.0 | 83.2 |
| 69.5 | 41.5 | 57.5 | 73.6 |
| 101.5 | 24.6 | 83.0 | 63.0 |
| 131.0 | 13.2 | 116.0 | 52.6 |
| 162.0 | 4.1 | 148.5 | 41.1 |
| 175.5 | 1.5 | 170.0 | 33.8 |

### Data for Curve X.

| "Control Reaction." | | 0.001 *N* Quinine Sulfate. | |
|---|---|---|---|
| 12.5 | 58.7 | 0 | 89.9 |
| 46.75 | 33.1 | 31.0 | 81.7 |
| 75.0 | 15.6 | 58.0 | 74.1 |
| 98.75 | 5.8 | 88.5 | 66.1 |
| 122.75 | 0.2 | 111.5 | 59.6 |
| | | 133.75 | 52.5 |
| | | 153.75 | 46.4 |

### Data for Curve XI.

| "Control Reaction." | | 0.001 *N* Hydroquinone. | |
|---|---|---|---|
| 29.25 | 63.9 | 18.0 | 84.6 |
| 54.5 | 45.0 | 41.5 | 80.2 |
| 79.75 | 28.1 | 64.0 | 72.7 |
| 114.5 | 10.4 | 101.75 | 54.5 |
| 133.0 | 4.2 | 121.0 | 41.4 |
| | | 154.5 | 22.6 |

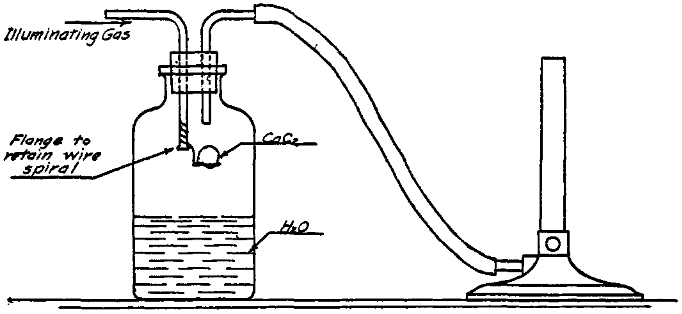
Data for Curve XII.

| "Control Reaction." | | 0.0243 $N$ Sucrose. | |
|---|---|---|---|
| Time in min. | Conc. of $Na_2SO_3$ in millimols per liter. | Time in min. | Conc. of $Na_2SO_3$ in millimols per liter. |
| 23.75 | 71.7 | 16.25 | 97.0 |
| 30.5 | 66.3 | 38.5 | 83.2 |
| 50.25 | 50.6 | 57.5 | 71.4 |
| 68.0 | 37.4 | 79.0 | 59.2 |
| 89.0 | 26.9 | 100.75 | 45.3 |
| 111.5 | 11.6 | 122.0 | 38.1 |
| 135.0 | 3.6 | 143.25 | 29.9 |
| | | 154.0 | 25.5 |
| | | 163.25 | 21.8 |

Madison, Wisconsin.

## NOTES.

**Laboratory Experiment—The Enrichment of Illuminating Gas.**—A trap, consisting of a wide-mouth bottle, is introduced between the gas outlet and an ordinary Bunsen burner. A copper wire is wrapped around one of the tubes which project through the stopper and serves to support a piece of calcium carbide.



O. r. d. Luft.

While the carbide is in position the gas is lighted and the air vents of the burner adjusted so the flame is barely non-luminous. The carbide is then shaken off into the water where acetylene is produced. The flame becomes quite luminous and remains so for a convenient length of time.

The apparatus may be easily and quickly cleaned for a repetition of the experiment.

Ross Allen Baker.

University of Minnesota,
Minneapolis.

**A New Form of Conductivity Cell for Electro-titration.**—The increasingly frequent use of the electro-titrametric process for determining the end points of reactions makes a special apparatus for this operation desirable.