

tion and also the suggestion¹ that the Hofmeister series of the ions owes its nearly fixed order to the fact that the degree of hydration of the ions runs in the same order.

The peculiar behavior of the sulfates of sodium and ammonium in lowering the hydrogen-ion concentration of acid solutions, when one might have expected them to raise it very materially, may after all be found to be due to the same forces as bring about hydration. Their action can hardly be simply that of repressing the ionization of the acid because of their effect upon chrome liquors, whose resistance to precipitation by alkalies they increase very much more than chlorides do, and this in view of the fact that in some cases they lower the hydrogen-ion concentration to a point at which precipitation of basic chromic salts might be expected without any addition of alkali. The tendency of sulfates to form addition compounds may eventually afford an explanation.

The nearly quantitative agreement between hydration values of the alkali chlorides at infinite dilution given by Smith and those calculated in this paper from hydrogen-ion measurements seems to warrant a much more extensive pursuit of the subject and especially of the use of the electrometric method for studying hydration and its effect upon concentrated solutions.

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THE ACTIVATION OF HYDROGEN PEROXIDE BY LIGHT.

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Introduction.

In studying the photolysis of hydrogen peroxide at the University of Wisconsin several years ago, it was noted by the writer that the oxidizing power of dilute hydrogen peroxide is increased when the solution is exposed to the light from a mercury vapor quartz lamp. Later this activation of hydrogen peroxide was investigated further by the writer and one of his students, Mr. Benjamin D. Cornell, at the University of Colorado. The work was interrupted by the war before it had been carried to a logical conclusion, but it appears worth while to record the results obtained.

Method.

By working with a considerable number of dyes, a few were found which, under the conditions of the experiment, were not bleached to any great extent by either light alone or the peroxide alone, but which were bleached colorless after a few hours exposure to light in the presence of

¹ *J. Am. Leather Chem. Assoc.*, 13, 179 (1918).

hydrogen peroxide. Aniline green and fuchsine were finally chosen as suitable for the experiments in hand. Stock solutions of these dyes were made up with distilled water. The hydrogen peroxide solution was made by diluting 30% "Perhydrol" with distilled water to a concentration of about 3%, and was kept in paraffin-lined flasks. Reaction mixtures were made by diluting the stock dye solution with an equal volume of distilled water or with an equal volume of the 3% hydrogen peroxide. When the reaction mixture was to be exposed to light, it was placed in a quartz flask mounted along side the lamp. Water from a large thermostat was circulated over the flask and the reaction mixture was gently stirred during illumination¹. The rate of bleaching of the dye was followed by means of a Hellige-Leitz colorimeter. For dilute dye solutions, such as used, the readings of the instrument are inversely proportional to the amount of dye in solution.

Experimental Results.

A.—The effect of the light in hastening the bleaching of the dye (aniline green) in the presence of hydrogen peroxide is shown in the following table, and is represented graphically in Fig. 1.

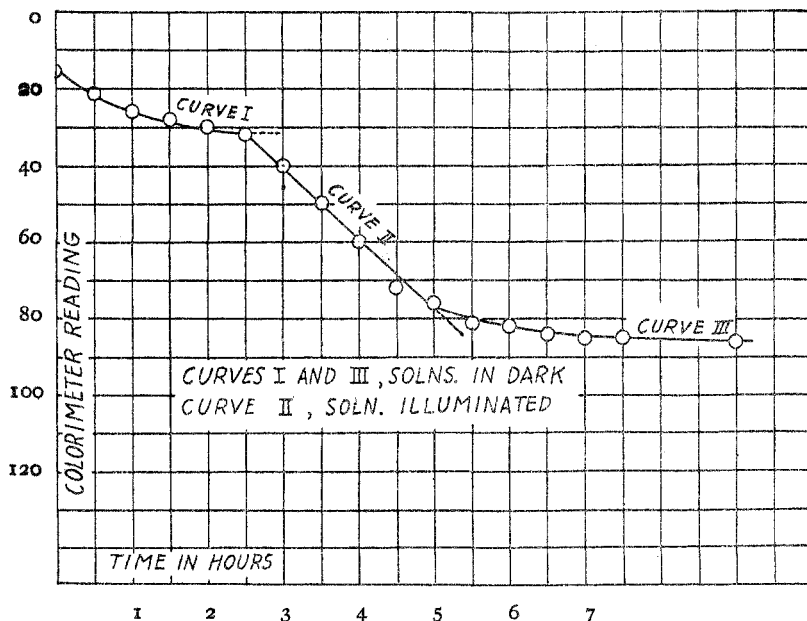


Fig. 1.

¹ For a diagram of this apparatus see Mathews and Curtis, *J. Phys. Chem.*, 18, 521 (1914).

TABLE I.—EFFECT OF LIGHT ON BLEACHING.

Time. a.m.	Colorimetric readings. Reaction mixture in the dark.	Time. p.m.	Colorimetric readings. Light cut off at 12.30 p.m.
8.00	15	1.00	76
8.30	21	1.30	81
9.00	26	2.00	82
9.30	28	2.30	84
10.00	30	3.00	85
10.30	32	3.30	85
		5.00	86

Reaction mixture exposed to light at 10.30 a.m.

11	40
11.30	50
12.00	60
p. m.	
12.30	72

B.—Three reaction mixtures were made, one of them containing the dye solution diluted with an equal volume of distilled water, the other 2 containing both the dye and the peroxide. The dye solution and one of the dye-peroxide solutions were exposed to the light, the other dye-peroxide solution being kept in the dark. Results tabulated below are shown graphically in Fig. 2.

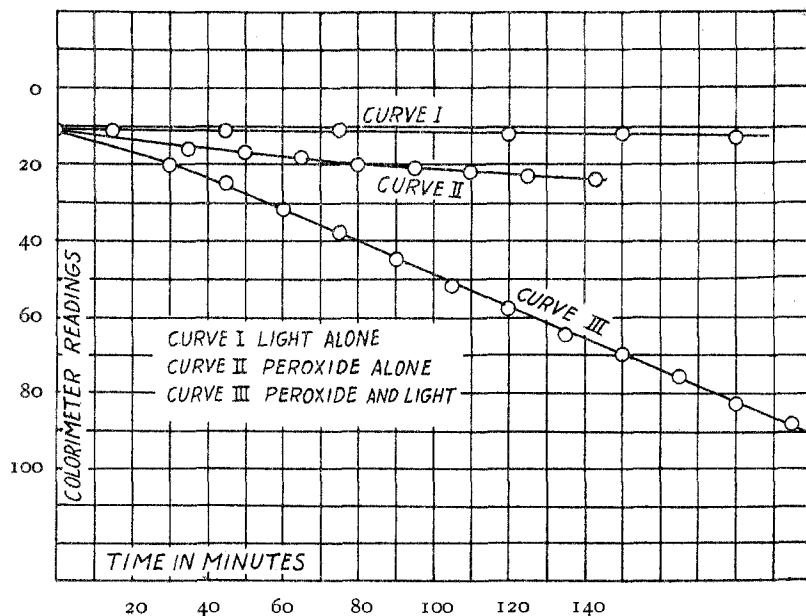


Fig. 2.

TABLE II.—EFFECT OF PEROXIDE AND LIGHT ON BLEACHING.

Action of light alone.		Action of peroxide alone.		Action of peroxide and light.	
Time, minutes.	Reading.	Time, minutes.	Reading.	Time, minutes.	Reading.
0	11	0	11	0	11
15	11	35	16	30	20
45	11	50	17	45	25
75	11	65	18	60	32
120	12	80	20	75	38
150	12	95	21	90	45
180	13	110	22	105	52
		125	23	120	58
		143	24	135	65
				150	70
				165	76
				180	83
				195	88

C.—Since ozone is produced by exposing oxygen to light of short wave lengths it might be thought that the effect when both light and peroxide were used resulted from an ozonizing of the oxygen liberated from the peroxide. Such is apparently not the case, for if oxygen be bubbled in a fine stream through the dye solution under exposure to light the following results are obtained.

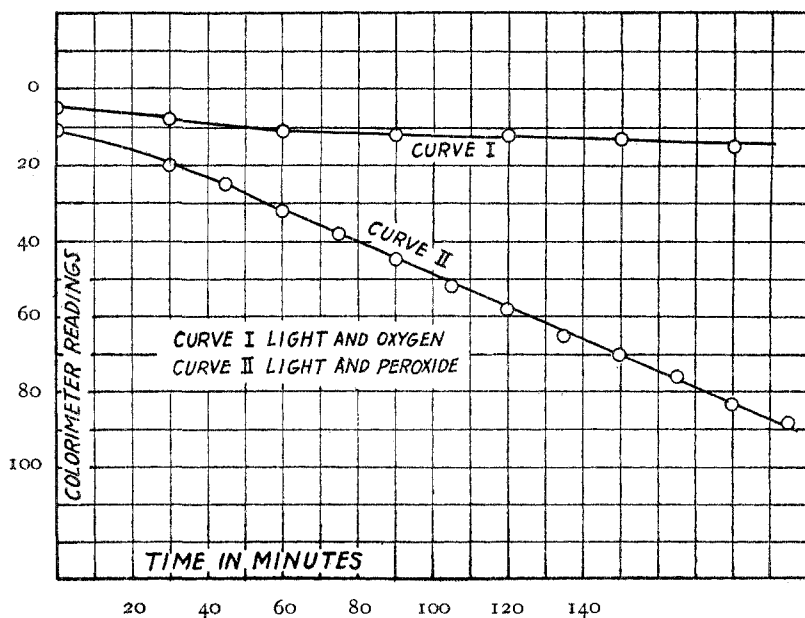


Fig. 3.

TABLE III.—EFFECT OF OZONE AND LIGHT ON BLEACHING.

Time, minutes.	Reading.	Time, minutes.	Reading.
0	5	120	12
30	8	150	13
60	11	180	15
90	12

In Fig. 3 the above data are plotted together with those for the combined light and peroxide from the earlier table.

Summary.

It has been shown that the oxidizing power of hydrogen peroxide, as manifested in the bleaching of dyes, is increased by exposing the reaction mixture to light of short wave lengths.

This effect cannot be duplicated by substituting oxygen for hydrogen peroxide in the reaction mixture, indicating that the result is not due to formation of ozone.

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[CONTRIBUTION FROM THE LABORATORY OF GRINNELL COLLEGE.]

FURTHER WORK ON POTASSIUM HYDROGEN PHTHALATE AS A STANDARD IN VOLUMETRIC ANALYSIS.

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Several years ago the writer showed that potassium hydrogen phthalate and sodium hydrogen phthalate may be used with advantage as standard in volumetric analysis.¹ They can be prepared easily in a state of great purity, they have large molecular weights, 204.14 and 188.04, respectively, and only one hydrogen ion. The potassium salt has the great advantage of absence of water of crystallization. So little work has been done on these salts and so little is known of their properties that it seemed desirable to study further the potassium salt, which is to be preferred as a standard. The objects were: (1) to determine the practicability of the preparation and use of the salt as a standard, by others; (2) to determine the necessary degree of purification for ordinary purposes, and the yield on the basis of the phthalic anhydride used; (3) to determine the hygroscopic character of the salt and the means necessary to dry it.

The laboratory work on potassium hydrogen phthalate here described was done by Mr. Sereno Norton, then a senior in Grinnell College, now a chemist with the Hercules Powder Company.

The potassium hydrogen phthalate was prepared by the method described in the paper already cited. Several preparations were made and titrated. There is one chance of error in its preparation, which might easily be made by comparatively inexperienced hands, and which should

¹ THIS JOURNAL, 37, 2352 (1915).