of the general equation to Usher's data for decomposition[13] to 57%, showed that the velocity constant falls steadily as the reaction proceeds, as if due to reverse reaction. The results of Lind and Bardwell,[12] in which decomposition proceeded to 73%, show a similar and more far-reaching drop with some indication that the yield in synthesis is somewhat nearer 0.3 than 0.2 molecule per ion pair.

Summary

Using a method of flowing a stoichiometric mixture of hydrogen and nitrogen past an α-ray bulb, the rate of ammonia synthesis found by chemical titration is estimated to be 0.2 to 0.3 molecule per ion pair produced in the mixture, a yield higher than previously found in stagnant gases for this reaction but low in comparison with the majority of gas reactions under α-radiation. This yield in synthesis is in general accord with the observed fall of velocity constant in decomposition of ammonia by α-rays as a function of the ammonia concentration.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 43]

AN INVESTIGATION OF THE REACTION OF SODIUM ALIZARIN MONO-SULFONATE WITH ALUMINUM UNDER DIFFERENT EXPERIMENTAL CONDITIONS WITH REFERENCE TO ITS USE IN COLORIMETRY

BY JOHN H. YOE AND WILLIAM L. HILL

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A method for the colorimetric determination of aluminum has been reported by Atack,[1] in which the principal reagent is sodium alizarin mono-sulfonate (Alizarin Red S). With aluminum in alkaline solution this dye forms a red lake which is fairly stable in the presence of a considerable excess of acetic acid.

> "The original solution (5 to 20 cc.) is acidified with hydrochloric acid or sulfuric acid, as acetic acid would form the highly dissociated aluminum acetate, and this has been found to give a somewhat more intense coloration than the inorganic salts; nitric acid in considerable amounts leads to the partial destruction of the coloration. Ten cc. of glycerine and 5 cc. of a 1% solution of Alizarin S are added, the solution made up to about 40 cc. with water, and then rendered slightly ammoniacal. After standing for five minutes it is acidified with dilute acetic acid, the Alizarin S acting as an indicator, acetic acid being added until no further change in the coloration occurs. The liquid is then made up to 50 cc. and compared with a standard."

Commenting upon this procedure, Atack states in substance:

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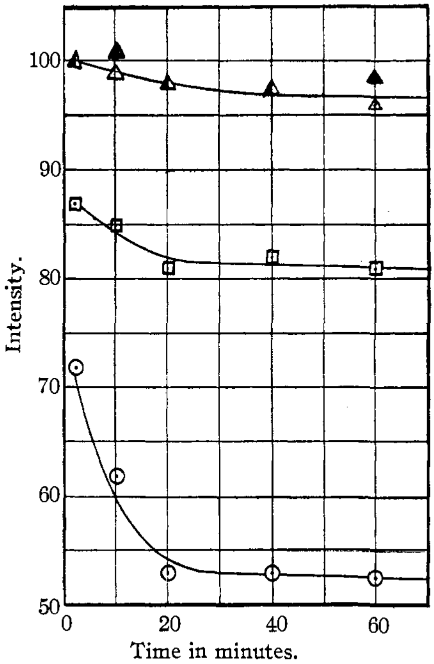
[13] Lind, *J. Phys. Chem.*, **16**, 595 (1912).

[1] Atack, *J. Soc. Chem. Ind.*, **34**, 936 (1915).

(1) A very large excess of the dye is necessary, but its original color in acid solution is not of sufficient intensity to interfere with the test. (2) Moderate amounts of calcium, magnesium or zinc salts do not affect the final color intensity. (3) Large quantities of iron and chromium salts and of phosphates interfere with the test. (4) The interference of iron and chromium may be prevented by the addition of a citrate before adding the ammonium hydroxide. Thus, the coloration given by 0.015 mg. of aluminum was not affected by 10 mg. of iron. (5) Since acetic acid slowly attacks the aluminum lake, especially in the presence of phosphates, the comparisons must be made within a short time. (6) The temperature at which the lake is formed does not affect the final color, if the acetic acid is added in the cold. (7) The glycerine prevents precipitation, which takes place readily in the presence of salts of other metals. (8) One part of aluminum in 10 million parts of water can be detected readily; suitable amounts for estimation are 0.005 to 0.05 mg.

The purpose of this paper is to present some specific data on the effects of varying the several factors in the procedure outlined above. The apparatus, method of attack and general procedure have been described in detail in a recent paper by Yoe and Hill.[2]



△, 0.1% of dye, 5 cc. of HAc in light; ▲, 0.1% of dye, 5 cc. of HAc in dark; ⊡, 0.1% of dye, 5 cc. of HAc and 10 cc. of glycerine; ⊙, 0.1% of dye, 10 cc. of HAc.

Fig. 1.—"Aging."

Experimental

Reagents.—1. Acetic acid, 5 *N*. 2. Hydrochloric acid, 1 *N*. 3. Ammonium hydroxide, 5 *N*. 4. Ammonium citrate, 5 *N*. 5. Standard aluminum chloride solution; 1 cc. contained 0.10 mg. of aluminum. For method of preparation and standardization, see ref. 2. 6. Solutions of the several salts used in the study of the effects of ions were prepared so that 1 cc. would contain 10 mg. of the desired ion if the salt were completely dissociated. In the study of positive ions chlorides were used, in all other cases sodium salts were employed. 7. Alizarin S solution. Four grams of Alizarin Red S, Schultz No. 780, National Aniline and Chemical Co., Inc., New York, N. Y., was dissolved in distilled water, filtered from the small amount of sediment and made up to a volume of 400 cc. This 1% stock solution was diluted to 0.1% and 0.2% solutions as needed. 8. Glycerine, clear white.

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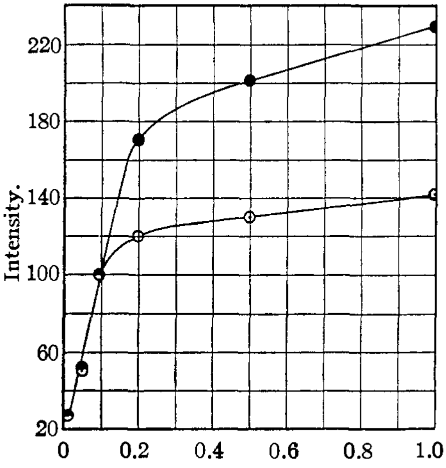
[2] Yoe and Hill, This Journal, **49**, 2395 (1927).

Procedure.—The order of addition of the reagents, as well as the quantities added, unless otherwise stated, was as follows. To 1 mg. of aluminum in a Nessler tube were added 5 cc. of 1 *N* hydrochloric acid, 5 cc. of a 0.1% Alizarin S solution and sufficient distilled water to bring the volume to 30 cc. Then 2 cc. of 5 *N* ammonium hydroxide was added with gentle stirring and after standing for five minutes 5 cc. of 5 *N* acetic acid was put in and mixed thoroughly. The solution was then diluted to 50 cc., thoroughly mixed and allowed to stand in the Nessler tube until time for comparison. In all instances where glycerine was employed it was added just after the hydrochloric acid and thoroughly mixed. Unless otherwise stated the temperature was 23°.



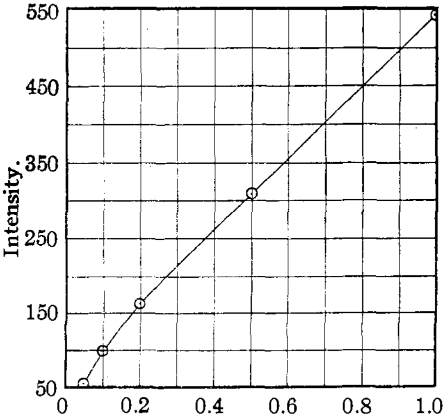
Mg. of aluminum.

○, with 0.1% of dye; ●, with 0.2% of dye.

Fig. 2.—Concentration of aluminum.

"Aging."—In Fig. 1 the curves show the decrease in color intensity with time after the addition of acetic acid, both in the light and in the dark, for different concentrations of acetic acid, and also when 10 cc. of glycerine was added. The intensities for each curve have been expressed in terms of the two minute intensity with 5 cc. of acetic acid and "aged" in the light.

Effects of Varying the Quantities of the Reagents.—The quantities of the reagents were varied one at a time, all other conditions being kept constant. All solutions were "aged" for twenty-five minutes and the intensities are expressed in terms of the intensity of the standard at the end of twenty-five minutes. The results are shown in Figs. 2, 3 and 4, and in Table I.



Alizarin solution, %.

Fig. 3.—Concentration of Alizarin S.

Conditions During Lake Formation.—In Figs. 5 and 6 are shown the curves for the three variable conditions: namely, (1) time allowed for the lake to form, (2) the temperature at which the lake was formed and (3)

TABLE I

VARIATIONS IN QUANTITIES OF REAGENTS

Hydrochloric Acid		Ammonium Hydroxide	
Reagent, cc.	Intensity, %	Reagent, cc.	Intensity, %
0	102	1.5	52
3	105	2.0	100
5	100	2.5	130
8	97		

the volume of the solution when the lake was formed. For (1) and (2) measurements were made at the end of twenty-five minutes and sixty minutes, respectively.

Presence of Other Ions.—The intensity of solutions containing 15 mg. of chloride, nitrite, normal phosphate, orthophosphate, sulfate or sulfite ions or of silica was sensibly the same as that of the standard containing only aluminum. Furthermore, the presence of these ions caused no appreciable decrease in intensity at the end of one hour. The final color was not altered by 45 mg. of the orthophosphate ion.

With 5 mg. of nitrate ion the intensity was 99% and had not decreased at the end of one hour; with 15 mg. the intensity was 96%, and with 30 mg. it was 39%. With 1 mg. of sulfur as sulfide the intensity was 100%, decreasing to 97% at the end of one hour. Greater quantities yielded a turbid solution.

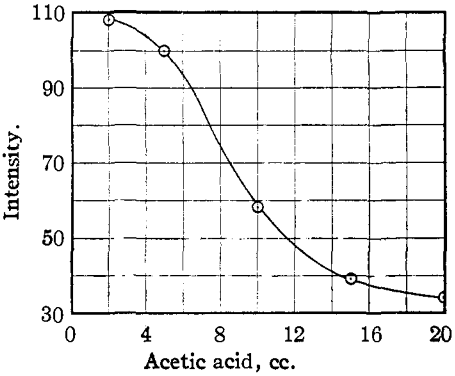


Fig. 4.—Concentration of acetic acid.

Solutions containing 15 mg. of chromium as chromate, zinc, calcium or magnesium gave readings in accord with that of the standard. The effects of some other positive ions are summarized in Table II.

An effort was made to prevent iron from interfering by adding ammonium citrate before the ammonium hydroxide. Some representative results are given in the following table:

Citrate, cc.	0	10	10	20	20	20
Aluminum, mg.	0.1	0.0	0.1	0.1	0.1	0.1
Iron, mg.	.0	.0	.0	.0	1.0	5.0
Intensity, %	100	128	131	320	314	388

Limits of the Test for Colorimetric Work.—The data for the sensitivity curve, Fig. 7, are shown in Table III.

At the left is shown the volume of solution in liters containing one gram atomic weight of aluminum; *B* is mg. of aluminum in 50 cc. of the

TABLE II

PRESENCE OF OTHER IONS

Ion[a]	Intensity, %, 15 mg.		Intensity, % 10 mg.	Intensity, % 5 mg.	Intensity, % 1 mg.
Fe^{+++}	heavy ppt.	...	brown ppt.	brown ppt.	100 (0.01 mg.)
Co^{++}	....	177[b]	deeply col.	204	185
Ni^{++}	120	161[b]	103	100	100
Mn^{++}	69	130[b]	69	70	88
Cr^{+++}	deeply col.	...	....	deeply col.	150
Cu^{++}	deep red	...	deep red	200	110
Sn^{++++}	very turbid	...	very turbid	107 (turb.)	103

[a] A 0.1% solution of alizarin used unless otherwise indicated.

[b] A 0.2% solution of alizarin used.

TABLE III

SENSITIVENESS

Volume, liters	B	Δ	S	B'	B/B'	Δ/B'	$\sqrt{V}/4$	$\sqrt{S}/4$
2,710	0.500	too intense for comparison						
6,775	.200	0.027	37.04	0.227	0.880	0.119	20.6	1.52
13,550	.100	.012	83.33	.112	.893	.107	29.0	2.28
135,500	.010	.0011	909.1	.0111	.900	.099	91.3	7.54
271,000	.005	.0010	1000	.006	.834	.167	130	7.90
1,355,000	.001	.0005	2000	.0015	.733	.500	291	11.12
3,387,500	.0004	barely distinguishable from "blank"						
With 10 cc. of glycerine								
13,550	.100	.015	66.7	.115	.870	.150	29.0	2.04
With 0.2% dye								
13,550	.100	.016	62.5	.116	.862	.137	29.0	1.98

solution; Δ is the increment in mg. of aluminum necessary to produce a perceptible difference in the color intensity of 50 cc. of solution, $S = 1/\Delta$ = Sensitivity, and $B' = B + \Delta$. For convenience in plotting, one-fourth of the square root of the volume and the sensitivity has been taken.

With 1 mg. of aluminum present the lake had coagulated and settled 1 cm. at the end of two hours; with 5 mg. the precipitate began to settle before the addition of acetic acid, was dispersed by the acid and after two hours had settled, leaving a clear yellow liquid.

For purposes of comparison the aluminum content of three solutions, as determined by Alizarin S and by "Aluminon" are given in Table IV.

TABLE IV

DETERMINATION OF ALUMINUM IN SOLUTION

Solution	Al, mg.	Found by Alizarin S,	by "Aluminon"[a]
I	0.10	0.08	0.12
II	.05	.05	.06
III	.03	.03	.03

[a] The ammonium salt of aurintricarboxylic acid.

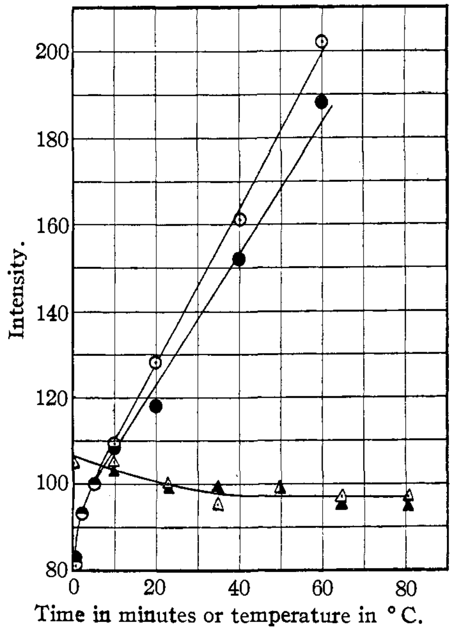
Discussion

The "aging" effects in the light and in the dark are about the same. An increase in the excess of acetic acid increases the rate of change in the color intensity during the first twenty minutes; however, after this time interval all the curves run almost parallel with the axis of time.

Fig. 2 indicates that the intensity is directly proportional to the aluminum content, provided that an excess of the dye is present. With 0.1% of dye the curve breaks at 0.1 mg. of aluminum, and with 0.2% of dye it breaks in the vicinity of 0.2 mg. of aluminum, supporting Atack's opinion[1] that a definite chemical compound is formed, or more likely simply representing an equilibrium condition.

Atack[1] recommends a 1% alizarin solution, but we have found, working with a liquid volume of 50 cc. in Nessler tubes, or in a colorimeter of the Kennicott-Campbell-Hurley type, that it is impossible to use the dye solution stronger than 0.4% on account of the very intense color. Weaker solutions yielded more satisfactory results. Fig. 3 shows a curve for the variation in the amount of dye used.

Variations of less than 1 cc. in the quantity of hydrochloric acid produce a negligible effect on the results; however, the final intensity is very sensitive to slight variations in the concentration of ammonium hydroxide. This is probably due to the alteration of the excess acetic acid by the ammonia.



○, Time, "aged" 25 min.; ●, time, "aged" 1 hour; △ temperature, "aged" 25 min.; ▲, temperature, "aged" 1 hour.

Fig. 5.—Conditions at lake formation.

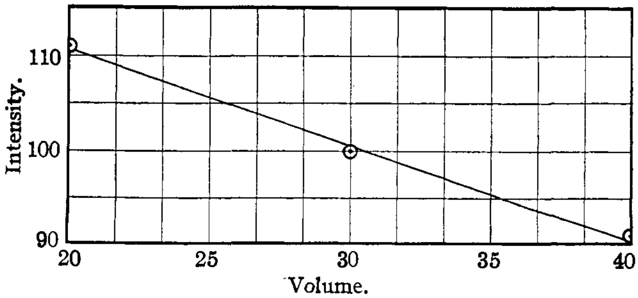


Fig. 6.—Volume at lake formation.

The temperature effect (Fig. 5) is very slight, while the intensity increases quite rapidly with the time given for the lake to form. The volume effect (Fig. 6) is practically the same as in the case of "Aluminon."

One mg. of sulfur as sulfide, or 10 mg. of nitrate ion may be present in 50 cc. of solution without the results being impaired. One mg. of stannic tin is allowable, but the copper content must be considerably less than 1 mg. Ten mg. of nickel is permissible; iron, chromium, cobalt and manganese must be removed if present in more than a trace. The use of a citrate to prevent the interference by iron and chromium was not successful. Fifteen mg. of the other positive ions studied do not interfere with the determination.

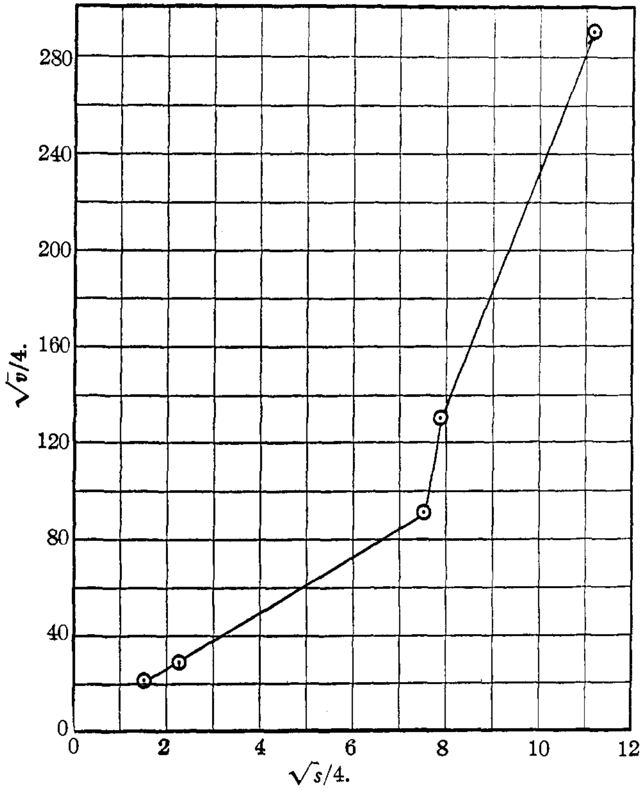


Fig. 7.—Sensitivity curve.

With 50cc. Nessler tubes the range of the test is from 0.0004 to 0.2 mg. of aluminum; with a volume of 50 cc. in the Kennicott-Campbell-Hurley colorimeter 0.005 to 5 mg. may be determined. The lake produced by 10 mg. of aluminum remains in suspension long enough for a reading to be taken, but a smaller volume of the liquid must be employed. By using glycerine greater quantities may be kept in suspension.

According to the method of Horn,[3] the sensitivity curve (Fig. 7) shows that with 50cc. Nessler tubes the best range of the test is from 0.01 to 0.2 mg. When glycerine or a stronger solution of the dye is employed, the sensitiveness is decreased considerably.

Summary

An experimental study of the reaction of Alizarin Red S with aluminum under various conditions has been made, and quantitative measurements on the following effects were obtained: (1) time, (2) temperature, (3) volume, (4) concentration of reagents and (5) the presence of other ions. The range and the sensitiveness of the test have been determined.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. I. THE PREPARATION AND STABILITY OF SOLUTIONS OF CERIC SULFATE (CONTAINING FREE SULFURIC ACID). II. POTENTIOMETRIC STUDY OF THE REACTIONS BETWEEN CERIC AND FERROUS OR OXALATE ION. APPLICATION TO THE STANDARDIZATION OF CERIC SOLUTIONS. III. THE POTENTIOMETRIC DETERMINATION OF CERIUM

BY N. HOWELL FURMAN

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Introduction

Barbieri[1] was apparently the first to propose the use of a solution of ceric sulfate in volumetric analysis. He described the direct titration of nitrite with ceric sulfate. The end-point was determined by the disappearance of the yellow color of the ceric ion (the nitrite solution was placed in the buret). He found that more exact results could be obtained by adding an excess of ceric solution. The excess of ceric salt was then determined iodimetrically. It was stated that the nitrite solution could contain nitrates and that the ceric solution need not be free from other rare earths. No experimental data were given.

A solution of ceric sulfate, or of other ceric salts, was found by Sommer and Pincas[2] "to be ideal" for the quantitative oxidation of hydrazoic acid. The volume of nitrogen that was evolved was measured.

Quite recently Martin[3] has used ceric sulfate for the oxidation of hydra-

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[3] Horn, *Am. Chem. J.*, **36**, 195 (1906).

[1] Barbieri, *Chem.-Ztg.*, **29**, 668 (1905).

[2] Sommer and Pincas, *Ber.*, **48**, 1963 (1915).

[3] Martin, THIS JOURNAL, **49**, 2133 (1927).