Summary

1. The catalytic decomposition of hydrogen peroxide by potassium dichromate is promoted by manganese salts. The reaction does not follow a simple unimolecular course.

2. The nature of the separate reactions has been investigated and discussed. Anomalous effects due to the solubility of the glass capsules and beads were avoided by the use of bakelite.

3. The promotion effect has been shown to consist of two superimposed reactions. The results agree with the explanation previously advanced for the relations between promoter and catalyst, and by resolving the promotion effect into two parts, one related to the concentration of intermediate due to the promoter, and the other, a rate related to the specific velocity constant of the promotion reaction, the interpretation offers a striking confirmation of the earlier work.

4. The addition of promoter causes the diminution of the concentration of the first intermediate. In the simpler reaction the nature of the intermediate due to the catalyst is not known definitely. When the concentration of manganese is higher, the relation is much more complex. The intermediate in this case is probably a permanganate, as shown by spectroscopic studies.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE ATOMIC WEIGHT OF SCANDIUM[1]

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Introduction

Until 1919 there had been considerable doubt as to the true value for the atomic weight of scandium. The atomic weight adopted by the International Committee on Atomic Weights was 44.1, which was considered to be a representative value based upon determinations made by previous investigators. These investigators had employed the usual sulfate method and had obtained values ranging from 43.90 to 45.23 as follows. Cleve, 44.96;[2] Nilson, 44.13;[3] Meyer and Winter, 44.94;[4] Meyer and Goldenberg, 44.09;[5] Meyer and Schweig, 45.23.[6]

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[1] From a thesis done in coöperation with Hiram S. Lukens, and submitted by Nicol H. Smith, in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Pennsylvania.

[2] Cleve, *Compt. rend.*, **89**, 419 (1879).

[3] Nilson, *ibid.*, **91**, 56, 118 (1880).

[4] Meyer and Winter, *Z. anorg. Chem.*, **67**, 398 (1910).

[5] Meyer and Goldenberg, *ibid.*, **102**, 12 (1912).

[6] Meyer and Schweig, *ibid.*, **108**, 303 (1919).

Such was the information concerning the atomic weight of scandium prior to Hönigschmid's series of determinations in 1919.[7] He determined the ratio of scandium bromide to silver and from this value obtained for the atomic weight a mean value of 45.099 ± 0.014, his values ranging from a minimum of 45.054 to a maximum of 45.122. Hönigschmid's scandium bromide was contaminated with small quantities of scandium oxide, formed by the action of scandium bromide on the quartz apparatus at the high temperature of sublimation. On this account he had to apply a correction to every determination.

Since scandium chloride sublimes at a much lower temperature (850°) its action on the quartz apparatus, if any, should be very slight. Therefore, the ratio of scandium chloride to silver should give a better method for the determination of the atomic weight of scandium, even though the nephelometric end-point is not as sharp as in the bromide to silver ratio.

Purification of Scandium Oxide

The scandium oxide used in this investigation was obtained from a sample of scandium oxalate on hand in this Laboratory. In order to test the purity of this oxide a preliminary determination of the atomic weight was made. From the ratio of scandium oxide to scandium sulfate, the value of 45.29 was obtained, and from the ratio of scandium chloride to silver the values of 45.16 and 45.28 were obtained. These values indicated that the scandium oxide was reasonably pure to begin with. However, this fairly pure oxide was subjected to two methods of purification: first, by means of ammonium fluoride, and second, by means of ammonium tartrate.

Purification by Means of Ammonium Fluoride.[8]—The scandium oxide obtained by igniting scandium oxalate was dissolved in redistilled hydrochloric acid and evaporated to a sirupy consistency on the water-bath in a platinum dish. The solution was then diluted and any undecomposed oxide filtered out. The clear solution was then treated with redistilled ammonium hydroxide until the excess of acid was neutralized. This clear solution was then poured slowly with stirring into a hot solution of ammonium fluoride (using 8 to 9 g. of ammonium fluoride for every gram of scandium oxide). A gelatinous precipitate of scandium fluoride is first formed but this dissolves in the excess of ammonium fluoride. The solution was kept hot for about an hour on the water-bath, then filtered through a platinum funnel into another platinum dish. The residue should consist of the fluorides of thorium and the rare earths. The filtrate contained the complex fluoride of scandium and was evaporated almost to solidification. The residue, consisting of ammonium scandium fluoride and an excess of ammonium fluoride, was then treated cautiously with concd. sulfuric acid and evaporated slowly to fuming, first on a water-bath until all hydrofluoric acid had been expelled, and then on a hot-plate, taking care to prevent bumping and loss by spattering. Owing to the large excess of ammonium sulfate, the double ammonium scandium sulfate separated out. In order to avoid using a large volume of water to take this into solution, the greater

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[7] Hönigschmid, *Z. Elektrochem.*, **25**, 91 (1919).

[8] Meyer and Wassjuchnow, *Z. anorg. Chem.*, **86**, 257 (1914).

part of the ammonium salts was volatilized by heating. The residue was treated with a small amount of concd. hydrochloric acid and heated. The scandium sulfate could then be easily dissolved in a small amount of water.

The solution was filtered free from any basic salt and ammonia gas was passed into the clear filtrate. The precipitated scandium hydroxide was filtered and washed free from ammonia with hot, redistilled water and then dissolved in pure, redistilled nitric acid, using only a very slight excess. An excess of pure, recrystallized oxalic acid was then added to the solution, heated almost to boiling and allowed to stand for 24 hours. The precipitated scandium oxalate was then filtered on a Büchner funnel, washed with pure water, sucking dry after each washing. The dried scandium oxalate was then ignited to oxide in a platinum dish. The oxide thus obtained was pure white and was supposedly free from cerium and yttrium earths and thorium.

This purified oxide was again dissolved in redistilled hydrochloric acid, the excess of acid removed by evaporating almost to dryness and the above purification with ammonium fluoride repeated. Scandium hydroxide was again precipitated by passing ammonia into the scandium sulfate solution. After thoroughly washing the scandium hydroxide, it was transposed to oxalate by boiling with a solution of oxalic acid. After standing it was filtered, washed thoroughly, dried and ignited to oxide. The oxide obtained was pure white and after two treatments with ammonium fluoride was considered to be free from thorium. This was called Sample I.

Purification by Means of Ammonium Tartrate.[5]—The scandium oxide was dissolved in redistilled hydrochloric acid and the excess of acid removed by evaporation on the water-bath to a sirupy consistency. The solution was diluted and any excess of acid removed by neutralization with redistilled ammonium hydroxide. The neutral scandium chloride solution was then poured very slowly with vigorous stirring into 750 cc. of a 15% solution of pure ammonium tartrate. The solution was filtered, since a slight precipitate was formed. The clear filtrate was heated to boiling and freshly distilled ammonium hydroxide added to the boiling solution until the solution was faintly ammoniacal. The scandium separated as the difficultly soluble scandium ammonium tartrate, thorium remaining in solution. The solution was digested for 15 minutes and the scandium ammonium tartrate filtered out, washed with a dilute solution of ammonium tartrate, dried and ignited to scandium oxide.

This oxide was again dissolved in pure hydrochloric acid, the excess of acid removed by evaporation and the ammonium tartrate purification repeated. The pure scandium ammonium tartrate was again ignited to oxide and dissolved in hydrochloric acid. Ammonia was then passed into the hot, diluted solution and the precipitated scandium hydroxide filtered out, washed well with pure hot water, sucking dry after each washing, and then converted to oxalate by boiling with a solution of oxalic acid in slight excess. After standing for 24 hours the scandium oxalate was filtered, washed with pure water, dried and then ignited to oxide. The oxide obtained was pure white and was considered to be free from thorium. This was called Sample II.

Purification of Other Materials

Silver.—The silver used in these analyses was prepared according to the method outlined by Richards and Wells.[9]

Silver chloride was precipitated from twice recrystallized silver nitrate by redistilled hydrochloric acid and then reduced by heating with sodium hydroxide and glucose solution. The silver oxide and silver thus obtained was fused on a block of pure sugar carbon. After solution of this silver in pure, redistilled nitric acid, it was again precipi-

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[9] Richards and Wells, THIS JOURNAL, **27**, 459 (1905).

tated by warming the solution with a solution of pure ammonium formate, prepared by passing ammonia into redistilled formic acid. The silver was then fused on a block of pure lime before the blast lamp, and the silver bars thus obtained scrubbed with sea-sand, etched with dil. nitric acid, washed with dil. ammonium hydroxide and finally with pure water. Part of this silver was dissolved in pure nitric acid and used as the electrolyte; the other part of the silver was used as the anode and pure silver was deposited on a cathode consisting of a platinum wire. The silver crystals thus obtained were washed with pure water and fused in a pure lime boat in a current of hydrogen. The buttons obtained were washed with water, scrubbed with sea-sand, then etched with dil. nitric acid, washed with dil. ammonia and finally with pure water. The buttons were then cut into suitable sizes and heated to 400° in a vacuum and kept over potassium hydroxide until used. All precautions were taken for the purification of the materials used as prescribed by Richards and Wells.

Nitric Acid.—Concd. nitric acid was redistilled, the middle portion being collected, and was tested in a nephelometer to prove the absence of halogen.

Hydrochloric Acid.—Concd. hydrochloric acid was diluted and redistilled, the middle portion being collected.

Oxalic Acid.—Oxalic acid was recrystallized thrice from solution, acidified with hydrochloric acid and finally once from pure water, centrifuging after each crystallization.

Ammonium Tartrate.—Ammonium tartrate was recrystallized twice from pure water, centrifuging after each crystallization.

Ammonium Fluoride.—The ammonium fluoride used was the purest that could be obtained. Upon examination it yielded only a trace of non-volatile material and for this reason was not subjected to a purification.

Water.—The laboratory distilled water was redistilled from alkaline permanganate. Water to be used for the nephelometer was distilled once more from dil. sulfuric acid. The condensers were made of pure block tin fitted to Pyrex flasks with constricted necks. The water was collected in Pyrex flasks and was used immediately.

Carbon Tetrachloride.—Pure carbon tetrachloride, sulfur-free, was dried for two weeks over anhydrous calcium chloride and then fractionated, collecting the middle fraction within 0.1°.

Preparation of Anhydrous Scandium Chloride

Anhydrous scandium chloride has been prepared by the action of a mixture of sulfur monochloride and chlorine on the heated oxide.[10] The scandium chloride used in this investigation was prepared by the action of carbon tetrachloride on scandium oxide at a temperature of 750–800°. At first, attempts were made to prepare the chloride by the action of chlorine on an intimate mixture of scandium oxide and sugar carbon, but the yields of anhydrous chloride obtained were so small that this method of preparation was abandoned. The action of carbon tetrachloride on the heated oxide proceeds very smoothly. The apparatus used for the preparation of anhydrous scandium is a bottling apparatus, as shown in Fig. 1.

It consists of a quartz tube A, 36 cm. long with a side tube (c) 22 cm. long and 2 cm. wide. This quartz tube was ground to fit a Pyrex end B, 19 cm. long with two side tubes (a) 10 cm. long to hold the weighing

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[10] Matignon and Bourion, *Compt. rend.*, **138**, 631 (1904).

bottle and (b) 12 cm. long to hold the stopper for the weighing bottle. The quartz boat containing scandium oxide was placed in the quartz side tube (c) and the air completely displaced from the apparatus by a stream of pure nitrogen. The nitrogen was prepared according to the usual laboratory method,[11] by passing a current of air through concd. ammonium hydroxide, then through a silica tube filled with copper spirals heated to 400–500°, then through a large quantity of dil. sulfuric acid, followed by passing through another silica tube containing copper spirals and copper oxide heated to 400–500°. The nitrogen was then passed through alkaline pyrogallate solution to remove the last traces of oxygen, through a tower containing silver nitrate solution to remove any sulfur compounds and finally through two towers containing concd. sulfuric acid, two soda lime towers filled with fused potassium hydroxide and then through two long tubes containing phosphorus pentoxide. The dried nitrogen was passed through the quartz and Pyrex bottling apparatus for six hours, heating the whole apparatus to remove any traces of moisture. The stopcocks in the inlet tubes e and g were then closed and the nitrogen was by-passed through a flask containing pure, anhydrous carbon tetrachloride. The carbon tetrachloride was heated to a temperature of 50–60° and the nitrogen bubbled through it. The stream of nitrogen and carbon tetrachloride vapors was passed over the scandium oxide which was heated to about 700°. The temperature was increased to about 850° towards the end so that just a little scandium chloride sublimed from the boat to the top of the tube above the boat. Within

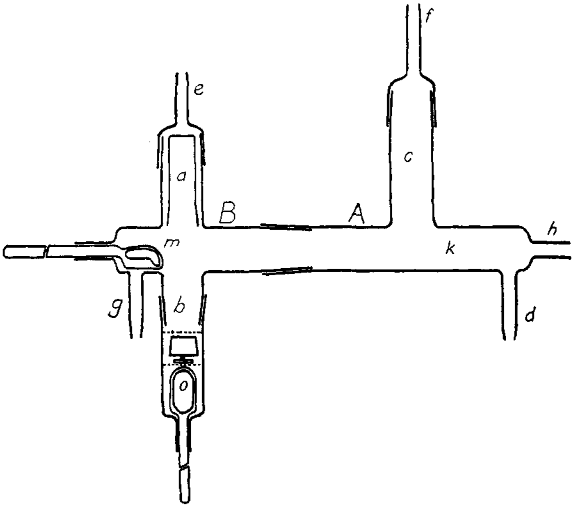

Fig. 1.

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[11] Richards and Krepelka, This Journal, **42,** 2221 (1920).

an hour 1.5 g. of scandium oxide could be completely converted to chloride. The complete conversion to chloride could be attained in a much shorter time by using more carbon tetrachloride and a higher temperature. At higher temperatures (900–950°), however, it was found that considerable carbon tetrachloride was decomposed and carbon deposited in the quartz tube and on the scandium chloride. In order to obviate this, a lower temperature (750–850°) was used, and the action of carbon tetrachloride on the oxide was continued for an hour, using only a small quantity of carbon tetrachloride. During the formation of the scandium chloride some material sublimed and was carried into the horizontal quartz tube (k) with the nitrogen stream. At the end of an hour the stopcocks in the inlet tubes e and g were opened and the stopcock in the by-pass tube through the carbon tetrachloride flask was closed. Nitrogen was passed through the entire quartz and Pyrex apparatus through the inlet tubes e, f and g, heating the entire apparatus to 150–200° in order to drive out the last traces of carbon tetrachloride. The horizontal quartz tube k was heated to a high temperature to remove the small quantity of sublimed material which had come over during the formation of the chloride. Before the sublimation of the chloride this part of the quartz tube was clean and free from any sublimate which had come over during the formation of the anhydrous scandium chloride. At the end of two hours all of the carbon tetrachloride and oxidation products had been removed from the system. The stopcocks in the inlet tubes e and g were then closed, only the inlet tube f being open. The anhydrous scandium chloride in the boat in the quartz tube c was then sublimed to the horizontal quartz tube k in a current of dry nitrogen (at a temperature not exceeding 900–950°). Nearly all of the scandium chloride sublimed into the tube k, opposite and within an inch on either side of the tube c. Half an hour was necessary for a complete sublimation of the scandium chloride.

By heating in this manner, a fractional sublimation of the scandium chloride was carried out. The more volatile impurities such as iron and thorium, were removed during the formation of the scandium chloride. Since the temperature of sublimation did not exceed 950° any rare earth impurities would remain behind in the boat. The tube was then allowed to cool in nitrogen and the stream of nitrogen was displaced by a stream of dry air. The air was first passed through an acid permanganate solution, then through a soda lime tower filled with fused potassium hydroxide, a tower of concd. sulfuric acid, and finally through two long tubes filled with glass beads covered with phosphorus pentoxide. During the passage of the air through the system, the anhydrous chloride was transferred from the quartz tube k to the weighing bottle. This was accomplished by means of the two scoops m and o. The anhydrous scandium chloride was picked up with the scoop m and transferred to the scoop o. Scoop o was then inserted into the weighing bottle and the chloride deposited there. The outlet tubes for the scoop handles were closed by means of a short piece of rubber tubing wired to the scoop handle. In order to facilitate the working of the scoop m, a quartz rod could be inserted at (h), by means of which the scandium chloride could be pushed into the scoop. In only one or two cases was this necessary. After a little experience in manipulating these scoops, the transfer of chloride from one scoop to another could be carried out with very little loss. Some chloride, however, is lost along the quartz tube k. Only the sublimate which collected around the outlet of Tube c was collected and placed in the weighing bottle. Any chloride which had been carried along the tube k was not collected. After passing air through Tube a for two hours, Tube b containing the stopper for the weighing bottle was inverted and the stopper pushed into the weighing bottle. The weighing bottle was then removed from the Pyrex tube and placed in a large desiccator containing phosphorus pentoxide. It was necessary to remove the stopper from the weighing bottle and clean the ground joint free from scandium chloride. After the stopper had been cleaned and inserted tightly into the weighing bottle, it was removed from the desiccator and cleaned with a damp cloth, dried carefully with a lintless cloth and allowed to stand in a desiccator in the balance room overnight. All joints were fused together throughout the system, except the Pyrex to soft glass, or Pyrex to quartz, which were ground joints.

Weighing.—All weighings were made on a Christian Becker balance No. 9 with weights standardized to 0.02 mg. according to the Richards method.[12] All weights were corrected to a vacuum, vacuum corrections being applied as follows.

	Weights	Silver	Scandium chloride	Air
Density	8.3	10.49	2.733	0.001293
Vac. corr. per g.	...	−0.000031	+0.000318	......

The density of scandium chloride was determined and the value 2.733 was obtained from an average of three determinations. All weighings were made by the method of substitution.

Analysis

After standing overnight in a desiccator in the balance room, the weighing bottle was placed in the balance and, after two hours, was carefully weighed. One hundred and fifty to two hundred cc. of pure, redistilled water was then frozen in a 2-liter Erlenmeyer flask with a tight-fitting ground stopper. A mixture of ammonium nitrate and crushed ice was used as a freezing mixture free from large quantities of chlorides. The stopper of the weighing bottle was then removed and the weighing bottle

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[12] Richards, This Journal, **22**, 144 (1900).

and stopper dropped onto the ice. In order to remove the stopper it was necessary to heat gently around the ground joint. The ice was slowly melted and reaction between the anhydrous scandium chloride and water proceeded mildly. After standing for 24 hours, the stopper of the precipitation flask was removed and the solution diluted to about 1 liter. The scandium chloride dissolved in the water to a perfectly clear solution. The weighing bottle and stopper were removed, washing with much water. Silver was weighed out in the form of buttons to within 0.1–0.2 mg. of the exact equivalent, dissolved in pure, redistilled nitric acid in a flask fitted with a Richards bulb tower, diluted so that the silver was less than 0.1 *N*, and added very slowly to the chloride solution with vigorous shaking after all of the silver had been added. The solution was allowed to stand for four to six days, shaking three or four times a day. The solution was then cooled in ice for three to four hours, samples were withdrawn with a pipet and examined in the nephelometer, adding either silver nitrate or potassium chloride solutions until equilibrium was reached. The solution was allowed to stand for three to four weeks to make sure that it was in equilibrium and that no more "soaking out" had taken place. The silver nitrate and potassium chloride solutions were equivalent to 0.6 g. of silver per liter and were added from a calibrated buret. After equilibrium had been verified two or three times over a period of two weeks, 0.3 mg. of silver threw the equilibrium well over to one side. All operations involving silver chloride were carried out in the dark room lighted with a ruby light. The data for one of the analyses are given in full in order to make clear the corrections applied.

TABLE I

Wt. of $ScCl_3$ in air, g.	1.02924	Wt. of Ag in air	2.19894
Correction for vacuum (d., 2.733)	+0.00032	Correction for vacuum (d., 10.49)	−0.00007
Wt. of $ScCl_3$ in vacuum, g.	1.02956	Wt. of Ag in vacuum	2.19887
		Nephelometric test	+0.00047
		Total amount of Ag in vacuum, g.	2.19934

The atomic weights of chlorine and silver were taken as 35.457 and 107.880, respectively; $ScCl_3:3Ag = 0.468120$; atomic weight of scandium, 45.132. The results are summarized in Table II.

The average results obtained using the scandium oxide purified by the ammonium fluoride method gave 45.173; the average of results obtained using the oxide purified by the ammonium tartrate method gave 45.142, which are in fairly close agreement. The average of these two values gave 45.160; although a little higher than Hönigschmid's value, 45.099, this is a fairly close check, considering the previous values for the atomic weight of scandium.

TABLE II

Sample	Analysis	Wt. of $ScCl_3$ in vac., g.	Wt. of Ag in vac., g.	Nephelometric test Ag, g.	Wt. of Ag in vac. g. (corr.)	Ratio $ScCl_3$:3Ag	At. wt. of Sc
I	1	0.59311	1.26725	−0.00036	1.26689	0.46815	45.142
I	2	1.13724	2.43079	− .00289	2.42790	.46838	45.225
I	3	2.14857	4.59452	− .00528	4.58924	.46817	45.149
I	4	1.10970	2.36999	− .00054	2.36945	.46832	45.202
II	5	1.02956	2.19887	+ .00047	2.19934	.46811	45.132
II	6	1.50457	3.21502	− .00016	3.21486	.46801	45.094
II	7	0.90557	1.93452	− .00043	1.93409	.46822	45.161
II	8	1.79432	3.83723	− .00466	3.83257	.46817	45.151
II	9	1.71420	3.66193	− .00110	3.66083	.46826	45.174
				Av. for Sample I			45.179
				Av. for Sample II			45.142
				Av. of all			45.160

The author desires to express his sincere thanks to Dr. Hiram S. Lukens, under whose direction and kindly encouragement this work was carried out.

Summary

1. Anhydrous scandium chloride was prepared by the action of pure anhydrous carbon tetrachloride on scandium oxide.
2. A new type of bottling apparatus is described for filling the weighing bottle with scandium chloride in the presence of dry air.
3. The ratio of pure scandium chloride to pure silver was determined and the average of nine analyses gave 45.160 as the atomic weight of scandium.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 137]

THE THERMAL DECOMPOSITION OF OZONE. III. THE TEMPERATURE COEFFICIENT OF REACTION RATE

BY OLIVER R. WULF[1] AND RICHARD C. TOLMAN

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1. Introduction

In two earlier papers,[2] the authors have presented the results of investigations on the thermal rate of ozone decomposition, which to a considerable extent explain the lack of agreement among the earlier researches in this field. The resulting clarification of the problem, as well as our discovery of certain improvements in technique, including in particular the discovery of a relatively reproducible source of ozone, have led us also to carry out a new investigation of the temperature coefficient of the rate of this decomposition.

[1] National Research Fellow in Chemistry.

[2] Wulf and Tolman, THIS JOURNAL, **49,** (a) 1183, (b) 1202 (1927).