sity increases with an increase in hydrogen-ion concentration up to a maximum value at about P_H 5.0, after which the density curves drop toward a minimum (probably coming at P_H 4.7, although more data are necessary before a definite statement may be made).

2. The curves for the variation of viscosity of proteins with change in Sörensen values also have a maximum at P_H 3.0–3.2 dropping to a minimum at the iso-electric point, P_H 4.7, as shown by Loeb and Pauli. The similarity of the density curves to the viscosity curves adds further verification to Pauli's theory of hydration of proteins.

3. The acids may be arranged in a series as to their effect on hydration: acetic < phosphoric < hydrochloric < sulfuric < and < nitric.

4. It was shown that the effect of alkali and alkaline earth chlorides on hydration is of the same order as for acids and that the cations may be arranged in a series in the order of their effectiveness: Sr > Ca > Na,K > Li.

5. Non-electrolytes did not affect the hydration to nearly as great an extent as did the acids and salts. The anomalous action of methyl and ethyl alcohols seemed to indicate that they favored the hydration.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE DETERMINATION OF TITANIUM BY REDUCTION WITH ZINC AND TITRATION WITH PERMANGANATE[1]

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RECEIVED AUGUST 18, 1923

Introduction

Most texts leave the impression that the reduction of titanium by zinc in acid solution, as in a Jones reductor,[2] is a slow and difficult process. As a matter of fact, titanium is no more difficult so to reduce than iron[3] and the reduction proceeds quickly and quantitatively to the trivalent stage.

The treatment of the reduced titanium solution is also usually made a matter of special precautions, such as catching the liquid in a measured excess of a standard permanganate solution or in an atmosphere of hydrogen or of carbon dioxide. Here, precautions are well taken, as trivalent titanium is very easily oxidized. The question, therefore, concerns the choosing of the most effective preventive and is answered by the use of

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[1] Published by permission of the Director of the Bureau of Standards of the United States Department of Commerce.

[2] For details concerning the construction of a Jones reductor, consult such texts as Treadwell-Hall, "Analytical Chemistry," Vol. II, 5th Ed., J. Wiley and Sons, p. 638, or Scott, "Standard Methods of Chemical Analysis," Vol. I, 3rd Ed., p. 320.

[3] W. F. Hillebrand in *U. S. Geol. Survey, Bull.*, **700**, p. 169, calls attention to this fact and to a communication from Mr. J. A. Holladay, Chief Chemist of the Electro Metallurgical Co., on the same subject.

a solution of ferric sulfate in the receiving flask in the same way that was recommended by Randall[4] for the determination of molybdenum. The use of permanganate in the receiver is unsatisfactory, as is generally recognized. The maintenance of an atmosphere of hydrogen or of carbon dioxide entails extra labor and expense and is desirable only when both iron and titanium have been reduced and a direct titration of titanium is desired, or when a titanous solution is wanted for volumetric work.

In view of the above remarks and of the increasing use of titanium in various products, it seems desirable to present the following data which demonstrate the ease with which titanium can be quantitatively reduced in a Jones reductor and quantitatively determined by catching the solution under ferric sulfate and then titrating with permanganate.

Experimental Part

A solution of titanic sulfate in sulfuric acid of 5% by volume was prepared from potassium titanium fluoride by repeated crystallizations of the salt, followed by evaporations with sulfuric acid. Tests demonstrated the absence of iron and zirconium and the solution was standardized both by precipitation with ammonia and by cupferron.[5] With ammonia, three precipitations were made and the weighed oxide was freed from silica. The results obtained by the two methods agreed within 1 part in 2000. Weight burets were used in all of the work.

The reductions were made in a reductor having a bore of 19 mm. and a zinc column 43 cm. in length. Our experience has been that satisfactory reduction can be obtained in any reductor which provides a reasonable contact with amalgamated zinc. The reductor was always washed out with dil. sulfuric acid before runs in order to eliminate reducing compounds which are formed as the reductor stands idle. The usual reduction procedure was then followed and there were added in order, 25–50 cc. of dil. sulfuric acid 3–5% by volume, 150 cc. of the same solution containing the titanium, 100 cc. more of acid, and finally 100 cc. of water. The reduction was performed at a speed of approximately 100 cc. per minute or 4 minutes for the passage of all solutions through the reductor.

The reduced solution was caught under a 3–5-fold excess of ferric sulfate[6]

[4] Randall, *Am. J. Sci.*, [4] **24**, 313 (1907).

[5] Thornton, *Am. J. Sci.*, [4] **37**, 173, 407 (1914). Lundell and Knowles, *J. Ind. Eng. Chem.*, **12**, 346 (1920).

[6] Randall (Ref. 4) and various texts prescribe the use of a solution of ferric ammonium sulfate. Our experience goes to show that a sulfuric acid solution of ferric sulfate prepared from ingot iron or plain carbon steel is preferable in that it is less expensive, the absence of ferrous salts and chlorides is assured, and the solution has a clearer color when used alone or with phosphoric acid. Such a solution is made by dissolving the material in aqua regia, evaporating to the fuming point with sulfuric acid, and diluting to proper volume after chlorides have been expelled; 0.02 g. of iron per cc. of 8% (by volume) sulfuric acid is a convenient strength and this will satisfactorily provide for 0.004 g. of titanium.

solution and then titrated with 0.1 N permanganate which had been standardized against sodium oxalate. No phosphoric acid was used in the receiver because of the insolubility of titanium phosphate. All titrations were corrected by careful runs on the reagents and end-point.

The data are given in Table I.

TABLE I

THE REDUCTION OF TITANIUM BY ZINC

Acidity of solution, 5%. All solutions were thoroughly boiled except where otherwise indicated

Titanium			Reducing conditions	
Taken G.	Found G.	Error G.	Temperature °C.	Ferric iron used × theoretical
0.1108	0.1110	+0.0002	90–100	5
.0551	.0555	+ .0004	90–100	5
.0051	.0053	+ .0002	90–100	5
.1052[a]	.1053	+ .0001	90–100	5
.0529[a]	.0532	+ .0003	90–100	5
.0059[a]	.0058	− .0001	90–100	5
.1022[b]	.1024	+ .0002	22–25	5
.0506[b]	.0508	+ .0002	22–25	5
.1025[a,b]	.1028	+ .0003	22–25	5
.0999[c]	.1010	+ .0001	22–25	5
.1053[d]	.1056	+ .0003	75–80	5
.1089[d]	.1092	+ .0003	75–80	5
.1012	.0854	− .0158	90–100	None
.0542[a,b]	.0503	− .0039	22–25	None
.1063	.1045	− .0018	90–100	1
.1074[b]	.1062	− .0012	22–25	1
.1071	.1071	± .0000	90–100	3
.1061[b]	.1061	± .0000	22–25	3

[a] Acidity of solution, 3%.

[b] Solutions cooled after boiling.

[c] Solutions not boiled.

[d] Solutions quickly warmed.

The data in Table I show that a rapid, quantitative reduction of titanium can be had in a Jones reductor, provided the reduced solution is caught under a solution containing at least three times more ferric salt than is necessary to oxidize the reduced titanium. The slight errors average no more than one drop of titrating solution and are undoubtedly due to experimental errors which could be largely eliminated if it were necessary to do so. The data also show that the reduction can be done with sulfuric acid of 3–5% by volume at any temperature between 25° and 100°, that it is not necessary to expel air from the solutions used in the reductor, and that an excess of ferric sulfate must be used in the receiving flask.

When titanium is reduced in the Jones reductor and then titrated as above, it should be borne in mind that the results will be in error if other reducible compounds are present. Such are: certain organic compounds, nitric acid, tin, arsenic, antimony, molybdenum^{III}, iron^{II}, chromium^{II}, vanadium^{II}, tungsten, uranium and columbium. Of these, the effect of the first five is indefinite and depends on experimental conditions; molybdenum, iron, chromium and vanadium are quantitatively reduced to the valences which are indicated; the reduction of the last three is not definite, tungsten approaching the quinquevalent, and uranium and columbium the trivalent state. The list seems large and formidable, but in reality it is not so. Some of the compounds are uncommon and all, save columbium, can be removed with but little effort. For example, it is obvious that nitric acid can be easily removed by evaporations with sulfuric acid and that organic compounds can be destroyed by evaporation with the same acid together with oxidizing agents such as nitric, permanganic or persulfuric acids. The simple remedy for tin, arsenic, antimony and molybdenum is, of course, treatment with hydrogen sulfide in a solution sufficiently acid to prevent hydrolysis of titanium. The elimination of iron is a little more laborious, as it involves three treatments: reduction of the iron by hydrogen sulfide in acid solution, its precipitation by ammonium sulfide in the presence of tartrate, and the removal of the tartrate as outlined above. The separation of titanium from chromium, vanadium, tungsten and uranium is conveniently done by filtration after oxidation in alkaline solution as, for example, with sodium carbonate and sodium peroxide; in this separation, it is to be borne in mind that at first titanium is also oxidized and rendered soluble and that thorough boiling of the solution is necessary to effect its complete precipitation. It is fortunate that columbium is rarely met, as its separation from titanium is a difficult matter.

In conclusion, it is interesting to record that the preparation of titanous solutions for use in volumetric work should not be much more difficult than the task of preparing the corresponding titanic solutions. This follows because any volume of the acidified titanic solution can be run through a Jones reductor and caught in a bottle of suitable size fitted with a 3-hole stopper carrying the outlet of the Jones reductor, and inlet and outlet tubes for maintaining the necessary neutral atmosphere of carbon dioxide or hydrogen.

Summary

The reduction of titanium in a Jones reductor proceeds rapidly and is quantitative, provided the reduced solution is caught under a 3–5-fold excess of ferric sulfate.

The reduction is conveniently carried on in solutions containing 3–5% by volume of sulfuric acid and may be done at any temperature between 25° and 100°.

Attention is called to interfering compounds and their removal, and to the ease with which titanous solutions can be prepared for volumetric use.

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