PREPARATION OF IRON SOLUTIONS FREE FROM CHLORIDE FOR TITRATION WITH PERMANGANATE[1,2]

EARLE R. CALEY AND CHARLES D. OVIATT

Department of Chemistry, The Ohio State University, Columbus 10

It is commonly recognized that the most accurate results in the titration of ferrous iron with permanganate are obtained when chloride is not present. Since hydrochloric acid is the best solvent for iron ores and certain other materials containing iron, the chloride must ordinarily be removed in some way in order to obtain such results. It may be removed, as suggested by Willard (1912), by evaporating the solution of the sample with an excess of perchloric acid, but this procedure does not appear to have been commonly adopted. One disadvantage of this procedure is that the evaporation must be conducted with some care in order to avoid removal of all the excess of perchloric acid, as this may lead to decomposition of the ferric perchlorate. Another disadvantage is that with ores or other materials containing unsuspected organic matter there is a possibility of mechanical loss from violent reaction. The usual procedure is to evaporate the solution of the sample with an excess of sulfuric acid. The advantages, aside from the minor one of low cost, are that no special attention is required during evaporation and that there is no such possibility of mechanical loss. However, it does have a serious disadvantage that the iron sulfate so obtained is usually difficult to dissolve, especially when the residue has been heated with the concentrated sulfuric acid at a high temperature for an unusually long time. Even with careful technique it may take as long as half an hour to bring the iron sulfate completely into solution on adding the proper amount of water and heating. With careless technique the time required may be much longer (Willard and Furman, 1940). Another difficulty arises if the sample contains silica. Some of this goes into colloidal suspension in the hydrochloric acid, becomes dehydrated during the evaporation with the sulfuric acid, and appears as an insoluble residue that is very similar in color and general appearance to the iron sulfate, so that it is not easy to decide when all the difficultly soluble iron sulfate has been dissolved. The primary purpose of this investigation was to study methods for dissolving the iron sulfate obtained by evaporating an iron solution containing chloride with sulfuric acid. An incidental purpose was to determine the composition of this iron sulfate, about which some uncertainty appears to exist.

COMPOSITION OF THE SALT

Some investigators have stated or suggested, but without citing experimental evidence, that the iron sulfate obtained by evaporating iron chloride solutions with hot concentrated sulfuric acid is difficultly soluble in water or dilute sulfuric acid solution because it is a basic salt, or a mixture of basic salts of indefinite composition. That such a basic salt or mixture of basic salts could be formed and exist in the presence of an excess of sulfuric acid seems unlikely, but not unlikely that such could be formed if all the free sulfuric acid were removed by evaporation and the dry residue were further heated at an elevated temperature. However, from the standpoint of normal analytical procedure the composition of the salt produced in this latter way is of small importance. To settle this question about its composition, analyses were made of specimens of the salt isolated by different methods.

A solution of pure ferric chloride in dilute hydrochloric acid, to which had been added an excess of concentrated sulfuric acid, was evaporated until hydrogen chloride was no longer expelled, and the mixture of the residual sulfate and concentrated sulfuric acid was heated at the decomposition temperature of this acid for five minutes longer. After cooling to room temperature, the salt was isolated from the mixture by these two methods:

I. By the use of a porcelain filter crucible most of the sulfuric acid was separated from the salt. The remainder of the acid was removed by washing with 95 per cent ethyl alcohol, and the alcohol by washing with ethyl ether. To make sure that all the sulfuric acid and solvents had been removed and to stimulate somewhat extreme conditions of treatment from the standpoint of analytical procedure, the salt was then heated to constant weight at 300° C in a muffle. The product was yellowish white and noticeably crystalline.

II. Most of the sulfuric acid was removed by the use of a filter crucible, but the remainder was removed directly by heating at 300° C to constant weight. This product was also crystalline but had an orange tint.

The method of analyzing these products was to heat weighed samples at 800° C to constant weight. Their iron content in terms of ferric oxide was given directly by the weight of ferric oxide thus obtained. Their sulfur content in

TABLE 1

Analyses of Samples of Iron Sulfate

Method of Preparation	Samples Taken g.	Fe_2O_3 Found g.	Fe_2O_3 Content %	SO_3 Content %	Ratio of Fe_2O_3 to SO_3
I	2.1191	0.8444	39.85	60.15	0.332
	0.8142	0.3246	39.87	60.13	0.332
II	2.6870	1.0692	39.79	60.21	0.331
	0.6960	0.2764	39.71	60.29	0.330
Calculated for $Fe_2(SO_4)_3$:			39.94	60.06	0.333

terms of sulfur trioxide was found by difference. The results are shown in table 1.

From these results it is evident that the salt, when isolated by the methods described, is simply anhydrous normal ferric sulfate. In spite of the difference in the color of the products prepared by the two methods, no significant difference in composition is indicated by the analyses. The reason for this difference in color was not investigated further. The possibility still remained that the difficultly soluble sulfate formed in the presence of a large excess of sulfuric acid is a complex salt containing additional combined sulfuric acid, similar in composition to the very slightly soluble complex salt formed when chromic chloride solutions are evaporated with an excess of sulfuric acid, and that the treatment at 300° C in the absence of sulfuric acid had decomposed this salt. To test this possibility some of the sulfate isolated by filtration and washing was dried at room temperature and at 110° C. Analyses of this product indicated that it had the same composition as the others. All the experiments therefore showed that anhydrous normal ferric sulfate is the only salt formed when ferric chloride solutions are evaporated with an excess of sulfuric acid.

METHODS OF DISSOLVING THE SULFATE

Experiments were made both on isolated samples of the sulfate, prepared by the methods just described, and on mixtures of the salt and sulfuric acid such as would be obtained in the usual procedure for the determination of iron.

According to the personal knowledge of the senior author, some analysts add finely divided zinc to the dilute sulfuric acid solution containing the ferric sulfate in suspension in order to increase the rate at which the salt dissolves. He has used this procedure himself and has observed many students using it under his direction. Under apparently similar conditions, the time required to dissolve the salt varies considerably, and sometimes for no apparent reason the procedure appears to be of little help. As no published account of this procedure could be located, it was systematically studied to determine under what conditions it would give satisfactory results.

In a typical group of experiments, ferric chloride solutions, each containing 0.100 g. of iron, were evaporated down with different volumes of concentrated sulfuric acid on a steam plate until no further reduction in volume was observed. Next, the residual solutions were evaporated on an electric hot plate for 30 min. at a temperature such that fumes of sulfur trioxide were continually evolved. After cooling, different volumes of water were added to the samples along with different weights of 20-mesh granulated zinc, and the mixtures were heated on steam plate and stirred at regular intervals to the same extent until all the ferric sulfate had dissolved. The results of many such experiments are summarized in table 2. The figures for the times in the last column are average figures, often

TABLE 2

Effect of Metallic Zinc in Accelerating the Rate of Solution of Anhydrous Ferric Sulfate

Series No.	Volume of H_2SO_4 used ml.	Volume of H_2O added ml.	Weight of Zinc g.	Time required min.
1	3	25	none	28
2	3	25	0.5	9
3	3	50	0.3	30
4	3	50	0.5	20
5	5	25	none	19
6	5	25	0.5	12
7	7	25	none	37
8	7	25	0.5	22
9	7	100	none	53
10	7	100	0.5	32

of a considerable number of individual experiments. For example, in Series 6 the times of the individual experiments were as follows: 6, 8, 8, 9, 9, 10, 10, 12, 13, 13, 15, 15, 15, 16, and 19 min. Numerous variables, difficult to control by the method of experiment, such as the temperature of evaporation, the amount of acid lost on evaporation, the sizes of the particles of the salt and the zinc, and the amount of contact of these on stirring, affect the rate of solution. However, since the same procedure would be followed in actual practice it seemed better to design the experiments in this way rather than to attempt a more rigorous control of the variables. Even though there is some overlapping of individual times from one series to another, the average times are distinctly different and clearly significant.

From the results shown in table 2, and from other experiments and observations, the following conclusions may be drawn:

1. Under any given set of conditions the presence of metallic zinc markedly accelerates the rate at which anhydrous ferric sulfate dissolves in dilute sulfuric acid. However, the time required for solution under one set of conditions when no zinc is present may be less than the time required under another set of conditions when zinc is present.
2. There is an optimum range of concentration of sulfuric acid. Not only must the concentration of the acid be high enough to prevent hydrolysis of the

salt on heating but it must be high enough to cause evolution of hydrogen. On the other hand, if the concentration of the acid is too high the rate of solution is retarded either in the presence or in the absence of zinc. Common-ion effect may account for this.

3. Sufficient zinc should be present to be in contact with all the salt. Though fine sub-division of the zinc improves the extent of contact, it cannot be too finely divided or else it will all be dissolved before the salt is dissolved. A large excess of zinc is not only unnecessary, but it may retard the rate of solution because it may reduce the concentration of the acid below the optimum range. However, if the concentration of the acid is initially too high, the addition of a large excess of zinc may have a favorable effect.

4. The efficiency of the process is markedly affected by relatively small changes in conditions. This explains why it is difficult to reproduce results and why such widely different results have been obtained by persons using this procedure for dissolving anhydrous ferric sulfate.

According to the experience of the authors, the following conditions lead to satisfactory results:

1. Add 3.0 ml. of concentrated sulfuric acid for each 0.1 g. of iron that is present.
2. Evaporate on a hot plate at a temperature such that only slight fumes of sulfur trioxide are evolved, and do not continue the evaporation for more than 15 min. after fuming begins.
3. Add 25 ml. of water and 0.5 g. of 20-mesh granulated zinc for each 0.1 g. of iron that is present.
4. Warm the mixture at about 75° C and stir continually in such a way that the salt and zinc remain in contact.

Under these conditions not more than 10 min. should be required for the complete solution of the ferric sulfate.

In solutions prepared in this manner the iron is largely in the ferrous state, and it seems probable that the ferric ions are reduced to ferrous ions at the interface between the solid ferric sulfate and the solution, and that this mechanism accounts for the acceleration of the rate of solution. However, it is also possible that some reduction occurs away from the interface and that this contributes to the shifting of the equilibrium between the ferric and ferrous ions. Other reducing agents, such as stannous sulfate, were tried for their effect on accelerating the rate of solution of anhydrous ferric sulfate in dilute sulfuric acid, but these generally were less effective than zinc and were not of practical utility because of the difficulty of removing the excess of reducing agent before titrating the ferrous iron.

Of all the reagents tried, concentrated hydriodic acid dissolved the isolated ferric sulfate most rapidly. When treated at room temperature with constant boiling hydriodic acid the salt dissolves at once with liberation of iodine but without detectable reduction of the sulfate ion. The following equation indicates the over-all reaction:

$$Fe_2(SO_4)_3 + 2HI \longrightarrow 2FeSO_4 + H_2SO_4 + I_2.$$
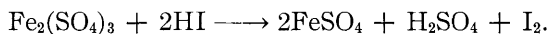
When the solution obtained in the cold is heated, or when the salt is treated with the hot acid, the sulfate ion is reduced to yield such products as hydrogen sulfide and sulfur dioxide. Unfortunately, this very rapid method of dissolving anhydrous ferric sulfate cannot conveniently be applied to the usual procedure in which the iron is titrated with permanganate, though it might be applied to a procedure in which the iron is determined indirectly through titration of the iodine liberated in the reaction.

<div align="center">LITERATURE CITED</div>

Willard, H. H.   1912.   The preparation of perchloric acid.   J. Am. Chem. Soc., 34: 1485.
Willard, H. H., and N. H. Furman.   1940.   Elementary Quantitative Analysis, 3rd ed., pp. 228–229.   Van Nostrand Co., New York.