

it is believed that the explanation here given is of general application and that it is not necessary to invoke the assistance of the older chemical compound theory of solution.

Summary.

In this paper the action of magnesium on solutions of potassium chloride has been investigated. The experimental work has involved (a) the measurement of the volume of hydrogen obtained by the action of magnesium on water prepared in a variety of ways, (b) the measurement of the volume of hydrogen obtained from solutions of potassium chloride of different concentrations, (c) the determination of the differences of potential between magnesium and solutions of potassium chloride, (d) the determination of the concentration of the hydrogen ion in both pure water and solutions of potassium chloride, and (e) the determination of the concentration of potassium chloride in a solution before and after the action of magnesium. The evidence furnished by these several lines of experimentation has led to the conclusion that the reaction between magnesium and water may be represented by the equation



and that the presence of the dissolved salt merely accelerates the reaction catalytically.

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OXIDATION-REDUCTION REACTIONS WITHOUT THE ADDITION OF ACID.

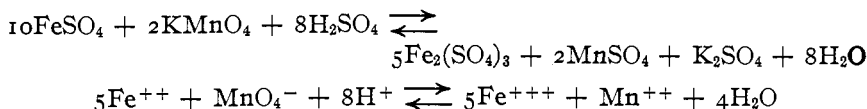
III. FERROUS CHLORIDE AND POTASSIUM PERMANGANATE.

A New Method for the Preparation of Colloidal Hydrous Ferric Oxide.

BY MARKS NEIDLE AND JOHN N. CROMBIE.

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The most familiar reaction involving the oxidation of ferrous ion by permanganate ion, is that between potassium permanganate and ferrous sulfate in the presence of an excess of sulfuric acid, and may be formulated by either of the following equations:



The data necessary for predicting whether a mixture of aqueous solutions of ferrous chloride and potassium permanganate contains a sufficient concentration of hydrogen ion to render the normal reaction possible, and to make it go practically to completion are not available. Nor was it possible to gain this information from the results of the oxidation-

reduction reactions¹ already studied, for, in the latter, potassium dichromate was employed, which gives a concentration of hydrogen ion greater than that given by equivalent solutions of ferrous chloride or potassium permanganate. From our knowledge that hydrated manganese dioxide is formed when permanganate reacts with certain substances, *e. g.*, sugar, oxalic acid, manganese sulfate, in neutral or slightly alkaline solution (and even in weakly acid solution),² we might expect a similar result in the reaction with ferrous chloride or ferrous sulfate, without the addition of acid. A few preliminary experiments, however, pointed to the contrary, indicating that the ionic equation for the reaction between ferrous chloride and potassium permanganate, without the addition of acid, is the same as that in which an excess of acid is added. Then, it was possible to predict that one of the products is colloidal hydrous ferric oxide, while in the corresponding reaction with ferrous sulfate, the colloid is precipitated.

Stoichiometric Relations.—Ferrous chloride solutions, approximately normal, half-normal, fifth-normal and tenth-normal, were prepared by dissolving the commercial C. P. salt in the proper amounts of water, and filtering off the insoluble residue. These solutions were titrated by potassium permanganate of approximately the same normalities: first, with the addition of an excess of acid, and second, without the addition of acid.

Twenty-five cubic centimeters of ferrous chloride solution were taken in all titrations. In those with acid, 10 cc. of concentrated hydrochloric acid, 50 cc. of preventative solution, and water to make a volume of 400 cc. were added to the ferrous chloride and the titration conducted in the usual way, *i. e.*, until the first appearance of pink throughout the solution.

In the titrations without the addition of acid, the permanganate was immediately run into the ferrous chloride contained in a beaker. The first few drops produced a light yellow color, which gradually changed to a clear deep brown as more permanganate was added. Potassium ferricyanide was used as an outside indicator, and the end point was considered reached when a brown color was obtained, which did not turn green on standing for a few minutes. With a little practice, the end points were easily detected with a fair degree of precision. The titrations with the normal solution, however, presented a little more difficulty than the others, because of the intense brownish red color produced as the permanganate was added to the ferrous chloride.

It will be seen from the results, given in Table I, that the volume of permanganate required in a titration depends upon the manner of its addition. This was evidently due to the collateral reaction between

¹ Neidle and Witt, *THIS JOURNAL*, 37, 2360-68; 38, 47-52.

² C. W. R. Powell, *J. Proc. Roy. Soc., New S. Wales*, 48, II, 223-41 (1914).

the permanganate and the chloride ion. We therefore decided to run similar titrations, using ferrous sulfate instead of ferrous chloride.

TABLE I.

Normality (approximate).	FeCl. Cc.	Titrations with acid. KMnO ₄ . Cc.	Titrations without addition of acid.	
			Nearly sufficient KMnO ₄ added all at once, stirred, and titrated to completion. KMnO ₄ . Cc.	KMnO ₄ added 1 cc. at a time and stirred vigorously after each addition. KMnO ₄ . Cc.
0.1	25.00	26.13	29.27	27.66
		26.15	29.25	27.61
0.2	25.00	25.12	26.82	25.34
		25.11	26.83	25.40
0.5	25.00	24.00	25.12	23.97
		23.97	25.12	23.99
1.0	25.00	25.54	25.74	25.56
		25.52

Titration of Ferrous Sulfate by Potassium Permanganate with and without the Addition of Acid.—The procedure was identical with that followed in the ferrous chloride titrations, except that in those with acid, 5 cc. of concentrated sulfuric acid were substituted for the hydrochloric acid, and no preventative solution was employed. The ferrous sulfate solutions, in the titrations without acid, at first behaved exactly like those of ferrous chloride, but later gave a precipitate as indicated in Table II.

TABLE II.

Normality (approximate).	FeSO ₄ . Cc.	Titrations with acid. KMnO ₄ . Cc.	Titrations without addition of acid.	
			KMnO ₄ . Cc.	Remarks.
0.1	25.00	24.88	24.90	Decided turbidity appeared when 15 cc. KMnO ₄ were added. Precipitate settled gradually on standing.
		24.80	24.80	
0.2	25.00	22.97	22.95	Solution became cloudy when end point was nearly reached, and on standing a short time after completion of titration, a brown gelatinous precipitate formed.
		23.00	22.97	
0.5	25.00	25.63	25.60	Cloudiness did not appear until a short time after the completion of titration. Turbidity gradually increased and a precipitate finally formed.
		25.67	25.63	

Discussion of Results.—Since the ferrous sulfate titrations gave the same results (Table II, Columns 3 and 4), whether acid was used or not, we may conclude that the stoichiometric relations in the reaction between ferrous ion and permanganate ion are the same with and without the addition of acid. We may also conclude that, even in 0.1 *N* concentrations, ferrous sulfate and potassium permanganate react practically instantaneously.

The results of the ferrous chloride titrations, without acid, show the

same variations as found by Birch¹ and Friend² in their studies on the action of permanganate on ferrous salts in presence of hydrochloric acid. Birch attributes the larger amounts of permanganate to the loss of elementary chlorine. He also observes that "the results are, if anything, slightly better in concentrated than in dilute solution." This is also the case in the ferrous chloride reaction, without acid, as is seen from Column 5, Table I. Our data thus show that the greater the concentrations of the solutions, the less does the chloride ion interfere with the titrations. This may be explained by the greater speed of reaction between elementary chlorine formed in the side reaction and ferrous ion at the higher concentrations, and the consequent smaller proportionate loss of elementary chlorine.

The latter will also explain why the discrepancy in the results, due to the difference in the manner of adding the permanganate, decreases with increasing concentration. Friend has observed that the results in titrating ferrous salts by permanganate in the presence of hydrochloric acid are high when the permanganate is added rapidly, and more nearly theoretical when it is added slowly. He ascribes this discrepancy to the formation of an intermediate perchloride of manganese. We are inclined to attribute it to the presence of large local excesses of permanganate in the rapid titrations, resulting in considerable oxidation of chloride ion and loss of elementary chlorine.

The products in the ferrous sulfate-permanganate reaction are potassium sulfate, manganese sulfate, ferric sulfate and colloidal hydrous ferric oxide. Ferric sulfate, or rather the ferric ion, protects the colloid while the other salts are good colloid precipitants. A definite concentration of ferric ion is necessary to protect the colloid against precipitation by the sulfate ion. The amount of ferric ion in a ferric sulfate solution gradually diminishes because of hydrolysis.³ Furthermore, colloidal hydrous ferric oxide accelerates the hydrolysis of ferric salts.⁴ These considerations immediately furnish an explanation of the gradual appearance of a turbidity and ultimate precipitation in the ferrous sulfate-permanganate titrations without acid.

Products of the Ferrous Chloride-Potassium Permanganate Reaction.

—An amount of commercial C. P. ferrous chloride, containing an equivalent weight of ferrous iron, was dissolved in about a liter of water and filtered. An equivalent weight of permanganate ($1/5\text{KMnO}_4$) was dissolved in about 600 cc. of water, and the resulting solution added in small portions—to avoid oxidation of chloride ion—to the ferrous chloride solution which

¹ *Chem. News*, **99**, 61, 73 (1909).

² *J. Chem. Soc.*, **95**, 1218 (1909).

³ Schneider, *Ann.*, **257**, 362 (1890).

⁴ Goodwin and Grover, *Phys. Rev.*, **11**, 193 (1900).

was shaken vigorously during the addition. Considerable heat was generated by the reaction, which yielded a perfectly clear, deep, brownish red solution. This solution, diluted to two liters, will be referred to as the "reaction mixture."

The reaction mixture became turbid after several weeks. The turbidity gradually increased, until, after nearly five months, two layers formed, the upper one being a perfectly clear yellow solution, and the lower one a brown ochery suspension, which could not be filtered off but did separate out on centrifuging for many hours. Boiling the original mixture gave a brown gelatinous precipitate, which was filterable. This precipitate readily dissolved in water to a solution, which was perfectly clear red by transmitted light, and turbid by reflected light, and from which the colloid could not be separated by centrifuging for many hours at about 2000 revolutions per minute.

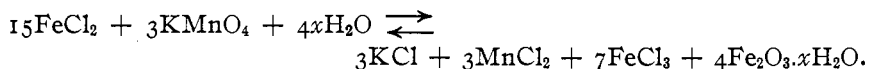
Dialysis.—Immediately after its preparation, 400 cc. of the reaction mixture were introduced into a parchment paper membrane and dialyzed with intermittent changing of the diffusate. The dialysis was continued for thirty-five days, and the perfectly clear reddish brown colloidal solution, which now suffered no change on boiling, was analyzed for iron, manganese, potassium and chlorine. The manganese and potassium were barely detectable, and therefore were not determined. The ratio of iron to chlorine in gram equivalents ($\frac{1}{3}$ Fe, 1 Cl) was 26.3, and the colloidal solution contained 68.4% of the iron in the original mixture. We have thus obtained the common hydrosol of hydrous ferric oxide, protected, as usual, by a small amount of hydrochloric acid.

The percentage of the total iron in the mixture, obtainable in the form of the hydrosol, depends on the nature of the membrane and the method of dialysis. By continuous dialysis in the cold, using a parchment paper membrane, 82.1% of the total iron remained in the colloidal solution. The equation for the reaction points to only 53.3% of iron in the form of the hydrous oxide. The additional 15.1% obtained in intermittent dialysis and 28.8% in continuous dialysis, is due to hydrolysis of the ferric chloride. It has been mentioned that the reaction mixture gradually becomes turbid, and finally separates into two layers. Until the latter stage is reached, dialysis will readily yield a perfectly clear colloidal solution. After that, the colloidal solution obtainable by mixing the two layers and dialyzing, is slightly turbid in reflected light, though perfectly clear in transmitted light.

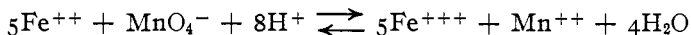
Addition of an Excess of Permanganate to Ferrous Chloride.—A slight excess of permanganate has no apparent effect other than a slight change in color, and, on dialysis, it rapidly diffuses through the membrane, leaving a clear hydrosol. A large excess does not cause an immediate change, but an odor of chlorine is observed, and the entire solution gels—within

an hour for 0.5 *N* solutions, and after several days for 0.1 *N* solutions. When such solutions have gelled, dialysis will not yield a hydrosol.

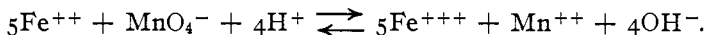
Discussion of Results.—Since all the manganese and potassium in the reaction mixture diffuse through the dialysis membrane, it may be concluded that they are present in the mixture as chlorides. Hence the products of the reaction are the chlorides of potassium, manganese and ferric iron, and colloidal hydrous ferric oxide. The reaction may now be written,



The ionic reaction, with acid, is usually formulated by the equation

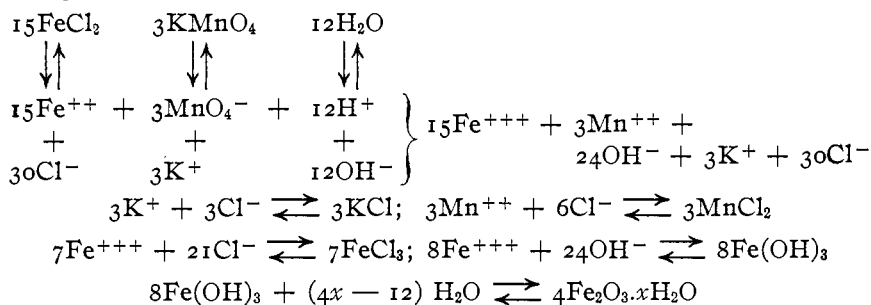


but is possibly better represented by the equation



If the concentration of hydrogen ion is very high, due to the presence of a strong acid, the concentration of hydroxyl ion will be kept at an exceedingly low value, as required by the ionic product constant for water. When no acid is employed, our results show that sufficient hydrogen ion for the reaction is furnished by the dissociation of the water, and by the hydrolysis of the ferrous chloride and potassium permanganate. But here hydroxyl ion accumulates, and soon the solubility product constant of ferric hydroxide is exceeded, when colloidal hydrous ferric oxide is formed.

The complete reaction between ferrous chloride and potassium permanganate may be represented ionically as follows:



The turbidity which appears in the reaction mixture, gradually in the cold and rapidly in the hot, is due to the hydrolysis of the ferric chloride. The ferric chloride, or rather the ferric ion, protects the colloid against precipitation by the manganese and potassium chlorides. Hydrolysis of the ferric chloride decreases the concentration of ferric ion, and, when it is reduced below the value necessary for protection, the colloid coagulates. This coagulation is, however, reversible, for the turbid reaction

mixture, on dialysis, will yield a practically clear sol. The reversibility in this case is due to the greater diffusion velocities of manganese and potassium chlorides as compared with ferric chloride. As the manganese and potassium chlorides diffuse, the residual ferric ion peptizes the coagulated colloid, and the sol is again formed.

Summary.

The stoichiometric relations in the permanganate-ferrous sulfate and permanganate-ferrous chloride reactions are the same with or without the addition of acid. In the permanganate-ferrous chloride reaction, the collateral oxidation of chloride ion is practically avoided by adding the permanganate gradually and with vigorous stirring.

The products of the permanganate-ferrous chloride reaction are the chlorides of potassium, manganese and ferric iron, and colloidal hydrous ferric oxide, while in the permanganate-ferrous sulfate reaction, the corresponding sulfates are formed, and also hydrous ferric oxide, which is precipitated by the sulfate ion.

A gram equivalent of permanganate, dissolved in about 600 cc. water, was slowly added to a gram equivalent of ferrous chloride, dissolved in about a liter of water, and the resulting clear, deep brownish red solution diluted to two liters. This solution remained perfectly clear for several weeks, then gradually became more and more turbid, until finally a suspension settled out. Until the latter stage is reached, dialysis yields a perfectly clear brownish red hydrosol of hydrous ferric oxide. After a suspension settles out, dialysis will give a hydrous ferric oxide hydrosol which is slightly turbid in reflective light, but perfectly clear in transmitted light.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

FURTHER STUDY OF THE ATOMIC WEIGHT OF LEAD OF RADIOACTIVE ORIGIN.

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The recent independent and almost simultaneous investigations upon the atomic weights of lead from radioactive minerals have proved with very little room for doubt that the substance derived from this source has a much lower atomic weight than ordinary lead.¹ This conclusion is so important in its theoretical relations that its every aspect should be carefully investigated. Accordingly, the present paper represents further

¹ Richards and Lembert, *THIS JOURNAL*, **36**, 1329 (1914); Hönigschmid and St. Horovitz, *Compt. rend.*, **158**, 1798 (1914); M. Curie, *Ibid.*, **158**, 1676 (1914); Soddy and Hyman, *J. Chem. Soc.*, **105**, 1402 (1914); also especially, Hönigschmid, *Sitzb. k. Akad. Wiss, Wien, IIa*, **123**, 1 (Dec., 1914).