(4) When the metal is immersed in a solution of a salt, the cation of which is less electro-positive than magnesium, the metal of the salt is displaced by the magnesium. Solutions of such salts generally have an acid reaction, in which case the hydrogen of the acid is also displaced by the magnesium.

Summary of Results.

(1) A 0.1 *M* solution of potassium chloride was found to react quite as readily with chemically pure magnesium prepared by distillation *in vacuo* as with a sample of the metal containing less than 0.5% of impurity.

(2) The behavior of magnesium when immersed in 0.1 *M* solutions of a variety of typical electrolytes was found to be similar to its behavior in solutions of potassium chloride previously investigated. This is considered as additional evidence in favor of the hypothesis already advanced that in the reaction represented by the equation

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2,$$

the solute acts catalytically.

(3) In solutions of salts which undergo hydrolysis, the evolution of hydrogen was found to be accelerated if the base of the salt was weak and retarded if the base of the salt was strong.

(4) Non-electrolytes appear to exert no appreciable influence on the rate of the reaction. This suggests that the effective catalytic agency is ionic.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

DIFFERENTIAL IODIMETRY.

II. THE TITRATION OF CHROMIC ACID IN THE PRESENCE OF FERRIC IRON AND THE ANALYSIS OF CHROMITE FOR ITS CHROMIUM CONTENT.[1]

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In a previous paper[2] the rate of reaction of ferric iron and iodide in phosphoric acid solution was shown to be a very slow one. The reaction is so slow indeed that interaction of iodic acid and iodide could be allowed to proceed and the liberated iodine titrated with thiosulfate without the ferric iron present causing interference. The principle of utilizing regulated acidities with iodide to determine various oxidizing agents has also been applied in the determination of periodates, iodates, bromates and chlorates in the presence of each other.[3]

When potassium iodide is added in excess to chromic acid the amount

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[1] Read at the Urbana meeting of the American Chemical Society.

[2] THIS JOURNAL, **37**, 1503 (1915).

[3] *Ibid.*, **38**, 330 (1916).

of iodine liberated depends essentially upon the concentration of the reacting substances and the temperature. The character of the acid also is a deciding factor inasmuch as salts may be formed which are very sparingly dissociated. Or complex acid formations may accompany the use of certain acids, thus converting a previously active ion to an acid radical which is very slightly dissociated and, hence, more or less inactive with iodide. The conversion of ferric iron to a soluble acid phosphate in a phosphoric acid solution eliminates the effect of ferric iron on iodide due to interaction such as above mentioned.

Of all the acids used to obtain a differential effect between chromic acid and ferric iron, phosphoric acid has proven to be the best. If the acid used is too strong ferric iron reacts with the iodide, and if it is too weak the liberation of iodine by the chromic acid is entirely too slow for the purposes at hand. In this respect the minimum concentration of phosphoric acid which will give a complete reaction in a short time is important. Fig. 1 shows the effect of the varying acidity factor in establishing a safe minimum concentration for the chromate titration at ordinary temperatures. The amount of chromate and iodide, the volume and the time are constant and the acidity is variable. From this curve it is concluded that a minimum acidity of the solution in the presence of 0.1 *N* iodide is 2.5 *N*, allowing three minutes for reaction. If a longer time is allowed for completion of the reaction the minimum acidity is

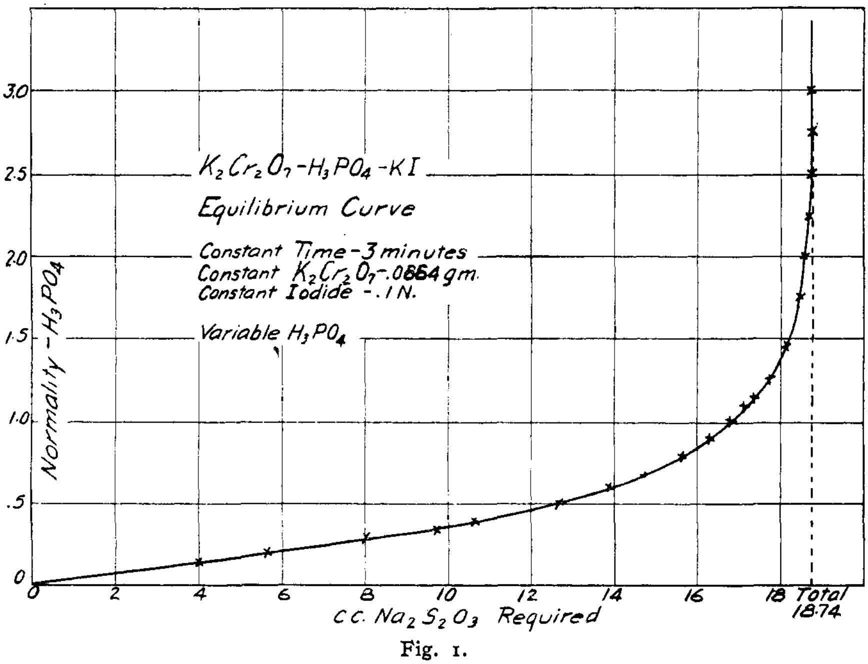

Fig. 1.

correspondingly reduced. However, for titration purposes a prolonged procedure is not desirable.

One of the best reagents used for oxidation of iron and chromium is sodium peroxide. An aqueous solution of the sample to be analyzed is made just alkaline with sodium hydroxide, then solid Na_2O_2 is added in slight excess. The solution is heated to boiling for a few minutes to decompose the excess of peroxide, and is then made acid with phosphoric acid, a sufficient excess of which is added to completely dissolve the phosphate of iron and have an acidity of about 3 *N*. 10 cc. of normal iodide for each 100 cc. of solution are then added, and the liberated iodine is titrated with thiosulfate.

The following procedure can be applied to the determination of chromium in chromite: A sodium peroxide fusion of the sample is made in a porcelain or silver crucible. The fusion is extracted with water, and the excess of peroxide is removed by boiling. The solution is acidified with phosphoric acid in sufficient excess to make the acidity about 3 *N*. Potassium iodide is added as before mentioned and the liberated iodine is titrated with thiosulfate. The thiosulfate used in the experiments of Table I was standardized against both pure potassium dichromate and potassium iodate. The results tabulated are typical of a large number obtained.

TABLE I.—ANALYSIS OF CHROMATE.

		% Cr_2O_3 found.	
Expt. No.	Sample.	With filtration.	Without filtration.
1	No. 13	6.22	6.16
		...	6.20
2	No. 1	56.26	56.12
		...	56.12
3	No. 9	45.00	45.04
		...	44.93
4	No. 2	49.25	49.23
		...	49.20

The third column contains the results obtained by filtering off the iron and titrating iodimetrically the chromate in the filtrate. The last column contains the results obtained by titrating directly in the presence of the iron.

Summary.

These results show:

1. That chromic acid can be titrated accurately in the presence of ferric iron by an iodimetric method.

2. That this principle can be applied to the determination of chromium in chromite, thus giving a rapid reliable method.

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