[Contribution from the School of Chemistry, University of Pittsburgh.]

OXIDATION AND REDUCTION WITHOUT THE ADDITION OF ACID.

I. THE REACTION BETWEEN FERROUS SULFATE AND POTASSIUM DICHROMATE.

By Marks Neidle and Joshua C. Witt.

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The first use of the reaction between ferrous salts and dichromate for the determination of iron was made by Penny.[1] In the method, as described in his paper, a sample of "iron stone" was dissolved in hydrochloric acid, and the iron reduced by adding sodium sulfite in excess. After boiling off the excess sulfurous acid, he titrated with dichromate solution, using potassium ferricyanide as an outside indicator. It is interesting to note that this method is essentially the same as that in use today for the determination of iron in iron ore.

Whenever the reaction between ferrous salts and dichromate has been studied a mineral acid has been added. Penny employed excess of free acid in dissolving the iron ore, and the equation for the reaction demands free acid for the formation of the normal salts of potassium, chromium, and iron. Since no mention of any investigation of the reaction in the absence of free acid could be found in the literature, it was decided to perform a few preliminary experiments in which a quantity of ferrous sulfate was titrated by 0.1 *N* dichromate, with and without acid.

It was considered preferable to weigh out a separate portion of ferrous sulfate for each titration, rather than to keep a standard solution of the salt. As soon as a portion was weighed out it was rapidly transferred to a beaker containing water, and titrated at once with the dichromate solution, using potassium ferricyanide as an outside indicator. The following results were obtained showing the effect of acid:

$FeSO_4.7H_2O$ (g.).	Cc. $K_2Cr_2O_7$.	H_2SO_4.
0.8	29.52	Excess present
0.8	29.54	Excess present
0.8	36.16	None present
0.8	36.25	None present

The end point is obtained when the amount of ferrous salt remaining at the time the drop test is made is insufficient to affect the indicator. When no acid is added, an excess of dichromate is required to give an end point, which means that with the theoretical amount of dichromate necessary to completely oxidize the ferrous sulfate, enough of the latter remains to affect the indicator, *i. e.*, the reaction is incomplete. A brown precipitate appears after a few drops of the dichromate have been added.

The following results show the effect of the volume of ferrous sulfate solution on the titration, 0.8 g. of salt being used in each experiment.

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[1] *Brit. Assoc. Rep.*, [2] 1850, 58, 59.

Cc. water added to $FeSO_4$.	Cc. dichromate sol. with H_2SO_4.	Cc. dichromate sol. without H_2SO_4.
0	29.67	29.89
5	.....	29.88
15	.....	30.03
30	.....	30.62
100	.....	32.12
1000	.....	53.00

This increase in the dichromate was to be expected, since the reaction is slower the greater the volume, and larger amounts of dichromate are required to drive the reaction to the end point. When no water is added the result of the titration is nearer theoretical, and in several experiments, in which more than 0.8 g. was taken and the solid titrated, the result was exactly the theoretical. We may therefore conclude that the precipitate formed does not adsorb the ferrous ion appreciably. Adsorption of ferrous ion would vitiate the results on the velocity of the reaction.

Considerable difficulty was encountered in finding the end point at the higher concentrations when the titration was made in the absence of sulfuric acid. The brown precipitate had a tendency to mask the end point. To overcome this, when the end point was nearly reached, it was found necessary to filter a few drops of the mixture each time before it was applied to the indicator.

Measurement of the Velocity of the Reaction.—The problem which presented itself at this point was to find a method of determining the unoxidized ferrous salt or unreduced dichromate in a solution containing ferric salts, ferrous salts, chromic salts, and dichromate. Three methods suggested themselves:

(1) To stop the reaction by the addition of ammonium hydroxide, filter the precipitated hydroxides of iron and chromium, and determine the chromium in the precipitate.

(2) To add ammonium hydroxide as in (1) and titrate the unchanged dichromate in the filtrate.

(3) To precipitate the unchanged dichromate with lead acetate, dissolve the precipitate of the reaction in acetic acid, and determine chromate in the residue.

The second method, being more direct and therefore more accurate, was adopted.

It is well known that ferrous salts, in common with salts of other divalent metals, cannot be completely precipitated by ammonium hydroxide in the presence of ammonium salts in consequence of the repression of hydroxyl ion by the latter. In order to be certain of completely precipitating ferrous iron, the necessary conditions were investigated.

It was found that ferrous salts may be completely precipitated with ammonium hydroxide provided,

(1) The solution is neutral.

(2) No ammonium salts are present to begin with.

(3) The concentration is sufficiently low.

(4) The solution is boiled and the precipitate allowed to settle before filtration is attempted.

If 0.5 g. portions of ferrous sulfate were dissolved in various volumes of water, and an excess of ammonium hydroxide added, the precipitation was complete only when the volume was at least 100 cc.

Solutions.

Potassium Dichromate.—A 0.1 *N* solution, standardized against iron wire, was kept in a ten-liter bottle fitted with a siphon. All air entering the bottle came through a cotton plug to avoid contamination.

Sodium Thiosulfate.—A 0.01 *N* solution was standardized each time before using against the dichromate solution.

Ferrous Sulfate.—At first it was thought advisable to make up a standard solution of ferrous sulfate and attempt to protect it from oxidation, but it was finally decided to use the dry salt and weigh out a portion for each determination. To avoid difficulty from any variation in quality, a fresh pound bottle of the c. p. salt was taken, and used for all the work. The surface layer was discarded, a weighing bottle filled and kept in the balance until used, then refilled when necessary. In weighing out a sample, a slight excess was placed on the balance and the stopper of the weighing bottle replaced at once. The excess salt was removed as quickly as possible and discarded to avoid any possible contamination. The salt was analyzed from time to time and found to remain constant in composition, as shown by the following results obtained with 0.8 g. samples:

Date	April 5.	May 3.	June 9.
Titration with 0.1014 *N* $K_2Cr_2O_7$	29.53 cc.	29.67 cc.	29.63 cc.

Manipulation.—A large, electrically controlled bath was maintained at 30° ± 0.05°. A ten-liter bottle of distilled water was kept in this bath that no delay might be caused by waiting for water to assume the correct temperature.

Nearly as much water as was needed for the experiment was placed in a liter flask corrected for temperature, and a given amount of standard dichromate solution was run into an Erlenmeyer flask. Both flasks were immersed in the bath and allowed to assume constant temperature. In the meantime a portion of the ferrous sulfate was weighed and rapidly transferred to the liter flask. When solution was complete, the dichromate was added and the volume adjusted. The flask was kept in the bath and. at intervals, 100 cc. portions were removed and run into beakers containing excess of ammonium hydroxide.

The precipitate formed by the ammonium hydroxide was very finely divided and would pass very readily through the filter. It was found necessary to let it stand some time—preferably over night—or to boil it a few minutes before a complete filtration could be made. It was preferable to filter at once, without heating, but no method could be found which gave the desired result. The precipitate passed through an alundum Gooch, and would not settle when kept in a centrifuge for 15–20 minutes.

In order to determine whether the potassium dichromate still in solution was in any way affected by the precipitated ferrous iron, 25 cc. of 0.1 *N* dichromate was added to 0.8 g. of ferrous sulfate dissolved in water in a liter flask, and, after introducing an excess of ammonium hydroxide, the mixture was made up to volume. A number of 100 cc. portions were withdrawn and placed in beakers. They were filtered at various intervals and titrated with 0.01 *N* thiosulfate by the method already described. Some were boiled before filtering, and others were filtered in the cold. The following are the results obtained:

Time.	Titration. 0.01 *N* thiosulfate.	Remarks.
2 hours	0.90 cc.	Not boiled
2 hours	1.00	Boiled
24 hours	0.94	Not boiled
24 hours	1.00	Boiled

It is seen from the above that the final result is not altered by allowing the mixture to stand for many hours, or by boiling, before filtration.

Results.—All measurements were made at 30°. The ferrous sulfate and dichromate solution were in the ratio of 0.8 g. of the former to 25 cc. of the latter, or 2.878 mols to 0.4225 mol. It was not thought advisable to attempt any measurements with more dichromate than would be required for the normal end point, since in this case a very large volume of 0.01 *N* thiosulfate would be required. The ratio of the reacting substances was maintained constant. The volume of dichromate reduced is represented by *x* and that unreduced by *a* — *x*.

Table I.

Total Volume Containing 25 cc. of 0.1014 *N* $K_2Cr_2O_7$ and 0.8 g. $FeSO_4$.

Minutes.	100 cc.		250 cc.		500 cc.		1,000 cc.		2,000 cc.		4,000 cc.		5,000 cc.	
	a — *x*.	*x*.	*a* — *x*.	*x*.	*a* — *x*.	*x*.	*a* — *x*.	*x*.	*a* — *x*.	*x*.	*a* — *x*.	*x*.	*a* — *x*.	*x*.
1	0.06	24.94	0.22	24.78	0.35	24.65	1.50	23.50	1.93	23.07	....	.....	....	.....
5	0.03	24.97	0.18	24.82	0.34	24.66	1.46	23.50	....	.....	1.99	23.01	2.69	23.31
15	0.04	24.96	0.23	24.77	0.30	24.70	0.93	24.07	1.74	23.26	1.65	23.35	2.20	23.80
30	0.04	24.96	0.22	24.78	0.29	24.71	0.80	24.20	1.36	23.64	1.57	23.43	2.20	23.80
60	0.04	24.96	0.19	24.81	0.26	24.74	0.61	24.37	....	.....	1.06	23.94	2.31	23.69

One series of experiments was made with method number three as a check. The work was carried on in the same way up to the time when 100 cc. portions were removed from the liter flask. In this case they were run into beakers containing lead acetate solution, which precipitated the sulfate ion and the chromate ion. The mixture was then acidified with a few cubic centimeters of acetic acid and boiled to dissolve all the iron salts. The lead salts were then filtered out and the lead chromate dissolved in dilute hydrochloric acid. The resulting dichromate was titrated, after cooling, with 0.01 *N* thiosulfate. The results given in Table II compare satisfactorily with those previously obtained and given in Table I.

TABLE II.

	$a - x$.	
Minutes.	Method III.	Method II.
5	1.49	1.46
15	0.98	0.93
60	0.59	0.61

Comments on Velocity Measurements and the Order of the Reaction.—From Table I it is seen that in the titration of 0.8 g. of ferrous sulfate with dichromate, the reaction is 99.8% complete at the end of one minute, provided the final volume is 100 cc. This statement may be made even though in our experiments the dichromate taken was a little less than equivalent to the ferrous sulfate. At all other concentrations except the most dilute, the reaction is more than 90% complete at the end of the first minute.

The data as obtained are not of a nature to permit ready calculation of the order of the reaction, although those in the last column of Table I seemed sufficiently regular to justify an attempt at such a calculation. No constant could be obtained by assuming the reaction to be of the first order with respect to each of the reacting substances, of the first order with respect to one and of the second with respect to the other, and, finally, of the second order with respect to both. Our conclusion, therefore, is that this reaction is probably of an order higher than the fourth.

The rate of oxidation of ferrous sulfate by dichromate with the addition of more than the sulfuric acid required by the normal equation has been investigated by Benson.[1] It is stated in his conclusions that the rate is proportional to the second power of the concentration of ferrous salt, and to the second power of that of the acid, and that the order is variable with respect to the dichromate. Benson also found that the order is much retarded by the presence of ferric salts. If the velocity of this reaction is strictly proportional to the square, or any other power, of the concentration of acid added it should be zero when no acid is employed.

There can be no question, however, that the velocity is proportional to some power of the hydrogen-ion concentration, in which case the velocity of the reaction without the addition of acid is due to the hydrogen-ion concentration arising from the hydrolytic dissociation of both dichromate and ferrous salt. The concentration of hydrogen ion must play an

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[1] *J. Phys. Chem.*, 1, 1 (1903).

important part in the reaction, even in very low concentration. Our reaction is most probably accompanied by a change in the concentration of hydrogen ion, which was disregarded in our velocity calculations. For this reason, we can not conclude with certainty that the reaction is of an order higher than the fourth.

The great velocity of the reaction without the addition of acid is partly due to the fact that less than one-third of the iron remains in solution as ferric salt, which has a retarding influence, while the remainder precipitates in the form of hydrous ferric oxide and adsorbed ferric sulfate.

The Products of the Reaction.—Preliminary experiments showed that all the brown precipitate, ultimately formed when solutions of dichromate and ferrous sulfate are mixed, does not come down instantly, but gradually, reminding one of the precipitation of suspensoids by small quantities of electrolytes. Upon filtering the mixture after it had stood for several days, the filtrate still yielded apparently the same precipitate on standing. The precipitation, it was found, could be rendered complete by boiling, when a reddish brown, gelatinous precipitate, resembling ferric hydroxide, appeared.

One-tenth of the equivalent weights of potassium dichromate and ferrous sulfate were dissolved in water and the solutions mixed, diluted nearly to a liter and heated to boiling for several minutes to bring about complete precipitation. After cooling, the mixture was made up to a liter exactly. The precipitate was brown and very abundant. The supernatant liquid had the purplish green color characteristic of chromium salts.

It was thought that heating the mixture might have some effect on the reaction. To settle this point, another solution was made up exactly like the one already described, except that it was not heated. After standing over night, it was filtered and both precipitate and filtrate were analyzed along with those of the first mixture, giving practically the same results. Although the precipitation was not complete, the difference was practically negligible. The work on this second solution was dropped, therefore, and only the first carried on.

The brown precipitate from the first mixture was dried to constant weight at 100–105°, giving a very hygroscopic amorphous powder. This solid and also the filtrate were analyzed for SO_3, Cr_2O_3, and Fe_2O_3.

The SO_3 was determined as $BaSO_4$. To determine iron and chromium, the hydrochloric acid solution was neutralized with sodium hydroxide and the chromium oxidized by sodium peroxide. After boiling, the ferric hydroxide was filtered out and washed with hot water. The precipitate was then dissolved in hot hydrochloric acid, reprecipitated with sodium hydroxide, again treated with sodium peroxide, filtered and washed. The two filtrates were combined, boiled, acidified with hydrochloric acid (5 cc. in excess) and again boiled for some time. After cooling, 10 cc. of a 10% potassium iodide solution was added, and the solution titrated with 0.1 *N* thiosulfate, using starch as the indicator.

The iron was again dissolved, brought nearly to dryness on the hot plate, reduced by stannous chloride and titrated with 0.1 *N* potassium permanganate.

FILTRATE.

	Grams.	Gram equivalents.	Grams originally present.	Percentage of total in precipitate.
SO_3	6.241	0.1560	8.006	22.05
Fe	1.176	0.0631	5.590	78.96
Cr	1.122	0.0647	1.733	35.26

PRECIPITATE.

	Grams.	Gram equivalents.	Percentage.
Fe_2O_3	6.313	0.2369	56.03
Cr_2O_3	0.894	0.0353	7.93
SO_3	1.755	0.0440	15.58
Loss on ignition (except SO_3)	2.239	....	19.87
Undetermined (K_2O)	0.067	0.0015	0.59

Further Investigation of the Precipitate.—It is seen that the precipitate contains quantities of all the salts produced in the reaction. In order to ascertain the nature of these adsorbed salts, a weighed portion of the precipitate was boiled in water for some minutes, and filtered. The filtrate was made up to 250 cc., and 25 cc. portions removed for analysis. It was found that the filtrate contained 2.11% SO_3, calculated on the basis of the amount of precipitate taken; or, 13.54% of the SO_3 present in the original precipitate had been removed by the first boiling.

A 50 cc. portion of the filtrate, analyzed for iron, gave 0.69%, approximately the amount required to correspond to the formula $Fe_2(SO_4)_3$. We may therefore conclude that the adsorbed salt is mainly $Fe_2(SO_4)_3$.

Discussion of Results on the Products of the Reaction.—The value 35.26% for the amount of chromium in the precipitate suggests that one-third of the total is precipitated as Cr_2O_3 and the remaining 1.93% adsorbed as $Cr_2(SO_4)_3$. If we add the number of equivalents corresponding to the adsorbed potassium sulfate and chromium sulfate, and subtract the sum from the total number of equivalents of SO_3 in the precipitate, the result gives the number of equivalents of $Fe_2(SO_4)_3$ adsorbed. This value is 0.0407, which, added to the number of equivalents of $Fe_2(SO_4)_3$ in the filtrate (0.0631), gives the number of equivalents of this salt formed in the reaction (0.1038). The mixture contained sufficient iron for 0.3 equivalents of $Fe_2(SO_4)_3$. Thus two-thirds of the iron forms hydrous ferric oxide, and one-third forms ferric sulfate.

The following equation completely harmonizes with the above results:

$$3K_2Cr_2O_7 + 18FeSO_4 + (x + 6y)H_2O =$$
$$3K_2SO_4 + Cr_2O_3.xH_2O + 2Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6Fe_2O_3.yH_2O,$$

where $Cr_2O_3.xH_2O$ and $Fe_2O_3.yH_2O$ stand for the colloidal oxides of chromium and iron, each carrying adsorbed water.

The products of the reaction between potassium dichromate and ferrous sulfate without the addition of acid are: potassium sulfate, chromium sulfate and colloidal chromic oxide in the molar ratio of 2:1; and ferric sulfate and colloidal ferric oxide in the molar ratio of 1:2. The colloids are precipitated by the sulfate ion in the solution.

The normal ionic reaction is written

$$Cr_2O_7^{=} + 6Fe^{++} + 14H \rightleftarrows 2Cr^{+++} + 6Fe^{+++} + 7H_2O.$$

We believe that the reaction without acid proceeds in the same way, the hydrogen ion being derived from the water.

$$H_2O \rightleftarrows H^+ + OH^-.$$

As hydrogen ion is consumed by the reaction, more is formed, and at the same time hydroxyl ion accumulates. Soon the concentration of hydroxyl ion is sufficient to exceed the solubility products of the hydroxides of iron and chromium, and the colloidal hydrous oxides are formed.

$$Fe^{+++} + 3OH^- \rightleftarrows Fe(OH)_3;\ 2Fe(OH)_3 + (y-3)H_2O \rightleftarrows Fe_2O_3.yH_2O.$$
$$Cr^{+++} + 3OH^- \rightleftarrows Cr(OH)_3;\ 2Cr(OH)_3 + (x-3)H_2O \rightleftarrows Cr_2O_3.xH_2O.$$

The manner of the precipitation of the oxides led us to the belief that they were formed in the colloidal state in the reaction. Chloride ion is a far less powerful precipitant for positive colloids than sulfate ion. Hence in the reaction between ferrous chloride and potassium dichromate we may expect that the colloids will not be precipitated and, on dialysis, it should be possible to isolate a mixed hydrosol of chromium and ferric oxides. Such is actually the case. Work on this reaction is now in progress and the results will be duly reported.

The investigation of the reaction between stannous chloride and potassium dichromate has been completed and will be the subject of the second article of this series.

Summary.

1. The stoichiometric relations in the reaction between potassium dichromate and ferrous sulfate are the same with or without acid.

2. The experimental conditions for the complete precipitation of ferrous iron by ammonium hydroxide have been found and employed to determine dichromate in a mixture also containing ferrous, ferric, and chromium salts.

3. Without acid the reaction is instantaneous, except in very dilute solutions.

4. Disregarding the change of hydrogen-ion concentration accompanying the reaction, the order is higher than the fourth.

5. The rate of the reaction, with acid, can not be proportional to the second power of the concentration of acid added, for then it should be zero without acid.

6. The products of the reaction are the sulfates of potassium, chromium, and iron, and the colloidal hydrous oxides of iron and chromium. The latter are precipitated by the sulfate ion, and adsorb a large quantity of ferric sulfate and smaller quantities of the other two sulfates.

7. The equations for the reaction have been formulated.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

THE ELECTRONIC CONCEPTION OF POSITIVE AND NEGATIVE VALENCES.

BY HARRY SHIPLEY FRY.

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A paper recently published by Roger F. Brunel,[1] presents some general and some specific criticisms of the electronic conception of valence. The author states that the object of his paper[2] "is to call attention to certain weaknesses in the arguments put forward in support of this conception and certain difficulties that arise in applying it to chemical phenomena."

Brunel then subjects to criticism, either directly or indirectly, the opinions of a number of authors who have contributed to this subject None of Brunel's specific criticisms have any bearing upon the applications in which I am principally interested, namely the problem of substitution in the benzene nucleus[3] and the development of relationships between chemical constitution and absorption spectra.[4] But, on the other hand, some of his general criticisms call for comment, especially certain statements presented in a paragraph on page 718.[5] In quoting this paragraph, the assertions which it embodies have been numbered 1, 2, and 3 for facility in comment. Brunel states:

"Of the other applications of the theory to the more complex problems the author [Brunel] would mention only that of Fry to the question of substitution in the benzene ring. (1) The rule governing the positions of substituents which Fry puts forward with the utmost confidence is so simple as to arouse distrust at once. (2) It would appear sufficient to say that, in view of the extensive investigations carried on in this field in recent years by Holleman, Flürscheim, Obermüller and others, if any such rule could cover the facts it would have been discovered long ago empirically, even if not expressed in the same terms. (3) Holleman

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[1] THIS JOURNAL, **37**, 709 (1915).

[2] *Loc. cit.*, p. 710.

[3] Fry, THIS JOURNAL, **30**, 34 (1908); *Z. physik. Chem.*, **76**, 385 (1911); THIS JOURNAL, **34**, 664 (1912); *Ibid.*, **36**, 243, 262, 1035 (1914); *Ibid.*, **37**, 855. 863, 883 (1915).

[4] Fry, *Z. physik. Chem.*, **76**, 398, 591 (1911); *Ibid.*, **80**, 29 (1912); *Ibid.*, **82**, 665 (1913).

[5] *Loc. cit.*