ART. IV. — *The Interaction of Hydrochloric Acid and Potassium Permanganate in the Presence of Ferric Chloride;* by JAMES BROWN.

[Contributions from the Kent Chemical Laboratory of Yale University—CXXXII.]

LÖWENTHAL* and LENSSEN were the first to show that the titration of ferrous salts by potassium permanganate in the presence of hydrochloric acid as proposed by Margueritte† does not admit of quantitative accuracy because of the evolution of chlorine by the interaction of hydrochloric acid and potassium permanganate, and to propose as a remedy for this source of error the titration of successive equal portions of the ferrous salt to be determined until the readings become constant.

This tendency toward evolution of chlorine in titrations of a ferrous salt by potassium permanganate in the presence of hydrochloric acid as compared with the alleged absence of such tendency in similar titrations of oxalic acid, was explained by Zimmermann‡ on the supposition that the oxidation of the iron proceeds so rapidly as to form oxides of iron higher than the sesquioxide which then react to oxidize more iron and liberate chlorine from hydrochloric acid. Quite recently Wagner§ explains this phenomenon by the assumed formation of chlor-ferrous acid (analogous to chlor-platinic and chlor-auric acids), which is more easily oxidized by the permanganate than is hydrochloric acid under similar conditions. Recent work‖ has shown that there is a slight though real waste of permanganate in titrations of oxalic acid under the conditions named, and that this loss is proportional to the amount of hydrochloric acid present. It still appears, however, that this loss is greater in titrations of ferrous salts than in those of oxalic acid under the conditions named.

Wagner's work in relation to the phenomenon mentioned above has been reviewed very carefully, and it has been found that, although as shown by him more permanganate is required to bring about final coloration against equal quantities of oxalic acid in experiments in which equal quantities of potassium permanganate are digested with a constant quantity of normal hydrochloric acid and a measured volume of tenth normal ferric chloride than when an equivalent quantity of tenth-normal hydrochloric acid is substituted for the tenth-normal ferric chloride, the differences vary within wide limits and disappear entirely if the chlorine formed by the interaction of the potas-

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* Zeit. Anal. Chem., i, 329.

† Ann. Chim. [3], xviii, 244.

‡ Ann. Chem., ccxiii, 311.

§ Maassanalytische Studien, Habilitationsschrift, Leipzig, 1898.

‖ Gooch and Peters: This Journal [4], vol. vii, 463.

sium permanganate and hydrochloric acid is removed during the digestion. When also the chlorine is thus removed the same quantity of permanganate is required to bring about final coloration whether ferric chloride is present or not. It is found also that the permanganate is entirely destroyed within the limits proposed by Wagner, and that after an hour's digestion, and in fact long before, the permanganate color has entirely disappeared and only the hydrated oxides of manganese, formed according to the Guyard reaction, are visible in the digestion liquid.

Wagner describes no special form of apparatus in his work, and gives no details as to size of flask used to contain the digestion liquids, form of bath, etc., pointing out the fact simply that he used a return-condenser 60^{cm} in length. It was found convenient in the experiments about to be described to use a 250^{cm^3} flask to contain the solutions during digestion, and to heat the solutions in an Ostwald thermostat.

TABLE I.

[$9{\cdot}91^{cm^3}$ $H_2C_2O_4 = 20{\cdot}25^{cm^3}$ $KMnO_4$]

$\frac{N}{1}$ HCl cm³.	$\frac{N}{10}$ HCl cm³.	$\frac{N}{10}$ $FeCl_3$ cm³.	$KMnO_4$ before digestion. cm³.	Temperature C°.	Time digestion. min.	$\frac{N}{10}$ $H_2C_2O_4$ cm³.	$KMnO_4$ to color. cm³.	$KMnO_4$ apparently reduced during digestion. cm³.
100	9·91	---	9·91	50	60	9·91	15·89	5·55
100	9·91	---	9·91	“	“	9·91	15·11	4·77
100	9·91	---	9·91	“	“	9·91	15·15	4·81
100	9·91	---	9·91	“	“	9·91	15·07	4·73
100	9·91	---	9·91	“	“	9·91	15·13	4·79
100	9·91	---	9·91	“	“	9·91	15·07	4·73
100	9·91	---	9·91	“	“	9·91	15·08	4·74
100	9·91	---	9·91	“	“	9·91	15·02	4·68
100	9·91	---	9·91	“	“	9·91	14·85	4·51
100	9·91	---	9·91	“	“	9·91	14·40	4·06
100	9·91	---	9·91	“	“	9·91	15·05	4·71
100	---	9·91	9·91	“	“	9·91	15·60	5·26
100	---	9·91	9·91	“	“	9·91	15·35	5·01
100	---	9.91	9·91	“	“	9·91	15·32	4·98
100	---	9.91	9·91	“	“	9·91	15·88	5·54
100	---	9·91	9·91	“	“	9·91	15·42	5·08
100	---	9·91	9·91	“	“	9·91	15·45	5·11
100	---	9·91	9·91	“	“	9·91	15·95	5·61
100	---	9·91	9·91	“	“	9·91	15·41	5·07
100	---	9·91	9·91	“	“	9·91	15·95	5·61
100	---	9·91	9·91	“	“	9·91	16·65	6·31
100	---	9·91	9·91	“	“	9·91	15·75	5·41
100	---	9·91	9·91	“	“	9·91	15·79	5·45

The experiments of Table I were conducted, as outlined by Wagner, in the following manner: To a 250^{cm^3} flask were added 100^{cm^3} of normal hydrochloric acid (that is a solution containing 36·4575 grams of the acid to the liter), and in addition either 9·91$^{cm^3}$ of tenth normal hydrochloric acid (prepared by diluting 100$^{cm^3}$ of the normal solution to one liter) or 9·91$^{cm^3}$ of tenth normal ferric chloride. Of approximately twentieth normal potassium permanganate, carefully standardized against ammonium oxalate, 9·91$^{cm^3}$ were then added, and the flask, fitted in a ground joint to a return-condenser 60^{cm} in length and with a bore approximately 3^{cm} in diameter, was heated for one hour in the Ostwald thermostat at a temperature of 50° C. Of tenth normal oxalic acid, 9·91$^{cm^3}$ were then added to the digestion liquid and a measured volume of the same permanganate solution as was added before digestion was run in to color. The difference between the total permanganate used (that is the permanganate added before digestion plus that added to bring about final coloration against the oxalic acid) and the permanganate equivalent of the oxalic acid added gives, according to Wagner, the permanganate reduced during the digestion. The results of these experiments are recorded in the above table.

Here it may be seen that although in general more permanganate is required to bring about final coloration in those experiments in which ferric chloride was used than in its absence, the results show at best wide variation among themselves, and the amounts of permanganate apparently destroyed during the digestion are at all events considerably greater than in the experiments conducted by Wagner under similar conditions. In the experiments recorded in Table I, in the average 4·73$^{cm^3}$ of permanganate were apparently destroyed where ferric chloride was not used, and 5·37$^{cm^3}$ in the presence of ferric chloride; while in Wagner's experiments 0·96$^{cm^3}$ of permanganate was apparently reduced without use of ferric chloride and 1·41$^{cm^3}$ in its presence.

Since, as has been noted above, the permanganate color entirely disappeared in the experiments of Table I, long before the termination of the hour's digestion, while only small amounts of hydrated oxides of manganese varying in color from brown to black were visible in the digestion liquid, it seemed probable that more permanganate was really reduced during the digestion than is indicated in these experiments. Moreover a strong odor of chlorine was noticeable in these experiments and it seemed probable that some of the chlorine, formed by the interaction of the potassium permanganate and hydrochloric acid during the digestion, remained to take part in the oxidation of the oxalic acid introduced, and that, therefore, on running in permanganate solution to color, less of the latter was required than corresponded to the oxalic acid left unoxidized by the residual oxides of manganese. It was, therefore, decided to remove if possible this chlorine, and to this end a vigorous current of carbon dioxide or air was passed through the digestion liquid while heating. In this way the chlorine was readily removed and starch and potassium iodide paper held in the current of carbon dioxide or air gave no test for chlorine.

The experiments of the following table (II), in which no ferric chloride was used, were conducted precisely as were those of Table I above, except that a vigorous current of carbon dioxide generated in a Kipp generator by action of hydrochloric acid on marble, and washed and dried by passing first through a bottle filled with water and then through a calcium chloride tube, was passed through the liquid during the process of digestion. Because also of the greater ease of measuring out accurately 9·90$^{cm^3}$ rather than the 9·91$^{cm^3}$ used by Wagner and in the experiments of Table I above, the former volume of reagents was substituted for the latter in the experiments to follow. It will readily be seen that in the case of tenth normal hydrochloric acid 0·01$^{cm^3}$ is negligible as compared with the large amount of hydrochloric acid used in the experiments.

The results of these experiments are recorded in Table II.

TABLE II.

	$\frac{N}{1}$ HCl cm³.	$\frac{N}{10}$ HCl cm³.	KMnO$_4$ before digestion. cm³.	Temperature. C°.	Time of digestion. min.	H$_2$C$_2$O$_4$ cm³.	KMnO$_4$ to color cm³	KMnO$_4$ apparently reduced during digestion. cm³.
[9·90^{cm3} approximately $\frac{N}{10}$ H$_2$C$_2$O$_4$ =23·52^{cm3} KMnO$_4$]								
I	100	9·90	9·90	50	60	9·90	22·19	8·57
II	100	9·90	9·90	“	“	9·90	22·10	8·48
III	100	9·90	9·90	“	“	9·90	22·15	8·53
IV	100	9·90	9·90	“	“	9·90	22·11	8·49
[9·90^{cm3} approximately $\frac{N}{10}$ H$_2$C$_2$O$_4$ = 23·65^{cm3} KMnO$_4$]								
V	100	9·90	9·90	50	60	9·90	22·15	8·40
VI	100	9·90	9·90	“	“	9·90	21·79	8·04
VII	100	9·90	9·90	“	“	9·90	22·24	8·49
VIII	100	9·90	9·90	“	“	9·90	22·21	8·46
IX	100	9·90	9·90	“	“	9·90	22·24	8·49
X	100	9·90	9·90	“	“	9·90	22·23	8·48
XI	100	9·90	9·90	“	“	9·90	22·25	8·50
XII	100	9·90	9·90	“	“	9·90	22·15	8·40
XIII	100	9·90	19·80	“	“	9·90	19·77	15·92
XIV	100	9·90	19·80	“	“	9·90	19·83	15·98
XV	100	9·90	50·0	“	“	25·00	44·53	34·81
XVI	100	9·90	50·0	“	“	25·00	44·47	34·75
XVII	100	9·90	50·0	“	“	25·00	44·44	34·72
XVIII	100	9·90	50·0	“	“	25·00	44·58	34·86

From these results the conclusion may be drawn that the low indications of the amount of permanganate apparently reduced during digestion in the experiments recorded in Table I, at least so far as concerns those experiments in which no ferric chloride was used, were in all probability due to the oxidizing action of the unexpelled chlorine on the oxalic acid, and that the large variations in results were due to the greater or less retention of the chlorine. In experiments XIII to XVIII it is seen further that amounts of permanganate very much greater than those used in Wagner's experiments and in the experiments of Table I above can be reduced by the same amount of hydrochloric acid, and under the same conditions of temperature and time as in those other experiments; for, in these last experiments, also, the permanganate color entirely disappeared during the digestion.

In order to ascertain if a current of air is equally as effective in removing the chlorine as is carbon dioxide, and also because of the greater availability of the former, the experiments recorded in Table III were conducted in a manner identical with those of Table II, except that a current of air dried and purified was substituted for the carbon dioxide. When also the success of the air current was apparent, ferric chloride was again used and the effect noted.

Results are outlined in the following table.

TABLE III.

[$9·90^{cm^3}$ approximately $\frac{N}{10}$ $H_2C_2O_4 = 20·09^{cm^3}$ $KMnO_4$.]

	$\frac{N}{1}$ HCl cm³.	$\frac{N}{10}$ HCl cm³.	$\frac{N}{10}$ $FeCl_3$ cm³.	$KMnO_4$ before digestion. cm³.	Temperature. C°.	Time of digestion. min.	Residual $KMnO_4$ color after digestion.	Cl Test after digestion.	$H_2C_2O_4$ cm³.	$KMnO_4$ to color. cm³.	KMnO apparently reduced during digestion. cm³.
I	100	9·90	---	9·90	50	60	none	none	9·90	18·88	8·69
II	100	9·90	---	9·90	“	“	“	“	9·90	18·87	8·68
III	100	9·90	---	9·90	“	“	“	“	9·90	18·80	8·61
IV	100	9·90	---	9·90	“	“	“	“	9·90	18·81	8·62
V	100	9·90	---	9·90	“	“	“	“	9·90	18·80	8·61
VI	100	9·90	---	9·90	“	“	“	“	9·90	18·82	8·63
VII	100	9·90	---	9·90	“	30	“	“	9·90	18·77	8·58
VIII	100	9·90	---	9·90	“	“	“	doubtful	9·90	18·70	8·51
IX	100	9·90	---	9·90	“	15	“	very faint	9‘90	18·70	8·51
X	100	9·90	---	9·90	“	“	“	“	9·90	18·68	8·49
XI	100	---	9·90	9·90	“	60	“	none	9·90	18·87	8·68
XII	100	---	9·90	9·90	“	“	“	“	9·90	18·85	8·66
XIII	100	---	9·90	9·90	“	“	“	“	9·90	18·81	8·62
XIV	100	---	9·90	9·90	“	“	“	“	9·90	18·81	8·62
XV	100	---	9·90	9·90	“	“	“	“	9·90	18·87	8·68
XVI	100	---	9·90	9·90	“	“	“	“	9·90	18·85	8·66
XVII	100	---	9·90	9·90	“	30	“	“	9·90	18·80	8·61
XVIII	100	---	9·90	9·90	“	“	“	doubtful	9‘90	18·72	8·53
XIX	100	---	9·90	9·90	“	15	“	very faint	9·90	18·65	8·46
XX	100	---	9·90	9·90	“	“	“	“	9·90	18·67	8·48

Here again may be noted the concordance of results when the chlorine is all removed before the addition of oxalic acid, as well as the fact that under these conditions substantially the same amount of permanganate is required to bring about the end reaction, whether ferric chloride is present or not; and that consequently as much permanganate is reduced during the digestion in the latter case as in the former. Also by a comparison of experiments VIII–X and XVIII–XX, in which a slight trace of chlorine remained, with experiments I–VI and XI–XVI, in which the chlorine was entirely removed, we again see the oxidizing effect of the residual chlorine on the oxalic acid; for even in the former sets of experiments, in which the digestion was carried on only fifteen or thirty minutes, the permanganate color had entirely disappeared at the end of the digestion. The variations in the amount of permanganate apparently reduced during the digestion in the experiments recorded in Table I are, therefore, doubtless due to the interfering action of the residual chlorine held in solution. The "$KMnO_4$ apparently reduced during digestion" in the experiments of Table II, and in those of Table III in which the chlorine was entirely removed during the digestion, represents the amounts of permanganate entirely reduced to manganous chloride, while the differences between these amounts and the "$KMnO_4$ before digestion" represent the residual oxides of manganese. Similar differences in the experiments of Table I, and in those of Table III in which the chlorine was only partially removed, represent the residual oxides of manganese and the chlorine retained in solution.

The amount of chlorine held in solution when no means are employed to remove it, depends largely on the form and size of the flask used to contain the solutions during digestion, also on the dimensions of the return-condenser, and will vary according to the greater or less amount of shaking to which the flask is subjected during the entire course of the experiment. It is, therefore, evident that Wagner's experiments are in no way indicative of the relative amounts of potassium permanganate reduced in the presence or absence of ferric chloride other conditions being constant, but are an indication simply of the greater or less retention of chlorine in solution in the form of apparatus used by him; for it has been shown that in all experiments conducted within the limits proposed by Wagner the permanganate is entirely destroyed and that any variations in the amount of permanganate apparently destroyed during digestion disappear when the chlorine is entirely removed from the sphere of action. The possibility of any interfering action of ferric chloride in titrations of oxalic acid by potassium permanganate is excluded by the results of the experiments of

Table III, in which we find no variations in results whether ferric chloride is present or not. The cause of the apparently greater destruction of potassium permanganate in those experiments of Table I in which ferric chloride was used than in those in which ferric chloride was not used, is now under investigation.

TABLE IV.

	$\frac{N}{1}$ HCl cm³.	$\frac{N}{10}$ HCl cm³.	$KMnO_4$ before digestion. cm³.	H_2O cm³.	Volume during digestion. cm³.	Temperature. C°.	Time of digestion min.	Residual $KMnO_4$ color after digestion.	Cl test after digestion.	$H_2C_2O_4$ cm³.	$KMnO_4$ to color. cm³.	$KMnO_4$ apparently reduced during digestion. cm³.
$[40^{cm3} \frac{N}{10} (H_4N)_2C_2O_4 = 37{\cdot}64^{cm3}\ KMnO_4$ $100^{cm3}\ H_2C_2O_4 = 101{\cdot}40^{cm3}\ KMnO_4]$												
I	100	9·90	100	--	210	50	60	none	faint	100	59·52	58·12
II	100	9·90	100	--	210	"	"	"	"	100	58·44	57·04
$[40^{cm3} \frac{N}{10} (H_4N)_2C_2O_4 = 18{\cdot}35^{cm3}\ KMnO_4$ $50^{cm3} \frac{N}{5} H_2C_2O_4 = 49{\cdot}26^{cm3}\ KMnO_4.]$												
III	100	9·90	50	--	160	50	60	none	none	50	30·72	31·46
IV	100	9·90	50	--	160	"	"	"	"	50	30·75	31·49
V	100	9·90	50	--	160	"	"	"	"	50	30·76	31·50
VI	100	9·90	50	--	160	"	"	"	"	50	30·78	31·52
VII	100	9·90	50	--	160	"	"	"	"	50	30·88	31·62
VIII	100	9·90	50	50	210	"	"	faint	faint	50	27·11	27·85
IX	100	9·90	50	50	210	"	"	"	"	50	27·92	28·66
X	100	9·90	50	50	210	"	"	"	"	50	28·52	29·26
XI	100	9·90	50	50	210	"	"	"	"	50	28·54	29·28
XII	100	9·90	50	50	210	"	"	"	"	50	29·14	29·88
XIII	100	9·90	50	50	210	"	"	"	"	50	28·98	29·72
XIV	100	9·90	50	50	210	"	"	"	"	50	28·56	29·30
XV	100	9·90	50	50	210	"	"	"	"	50	29·96	30·70
XVI	100	9·90	50	50	210	"	85	none	very faint	50	29·96	30·70
XVII	100	9·90	50	50	210	"	60	faint	faint	50	30·22	30·96
XVIII	100	9·90	75	--	185	"	"	none	marked	50	20·72	46·46
XIX	100	9·90	50	50	210	"	120	none	none	50	30·31	31·05
XX	100	9·90	100	--	210	"	60	marked	marked	60	19·58	60·47
XXI	100	9·90	75	50	235	"	220	none	faint	50	21·84	47·58
XXII	100	9·90	100	50	260	"	180	marked	marked	60	10·18	51·07
	$\frac{2N}{1}$ HCl											
XXIII	50	9·90	50	--	110	"	60	none	faint	50	30·23	30·97
XXIV	50	9·90	75	--	135	"	60	"	marked	--	--	--
XXV	50	9·90	75	--	135	"	60	"	"	50	30·69	56·43

Since in all experiments thus far conducted the permanganate color has been entirely destroyed, the experiments of Table IV were made to ascertain if possible how much permanganate can be destroyed by the amount of hydrochloric acid used in the experiments of Table I, II, and III, under the same conditions of time and temperature, and also during greater periods of time. It will readily be seen from the evident oxidation of oxalic acid by chlorine in previous experiments that an exact measure of the maximum amount of permanganate reduction during a given period of time can be obtained only when all the chlorine is removed and at the same time the permanganate color just disappears—a condition difficult to attain. The results recorded in Table IV should therefore be regarded as approximate only.

Thus it may be seen that the same amount of hydrochloric acid as was used in the experiments of Table I, II, and III is capable of breaking down approximately thirty times as much permanganate as was used in those experiments and in the experiments of Wagner, conditions of time and temperature being the same. Changes of volume are of course involved in the use of varying amounts of permanganate but an increase in volume would in all probability be attended by a decrease in the relative amount of permanganate reduced by a constant quantity of hydrochloric acid. In any case the results show a more extensive reduction than is indicated in Wagner's experiments and in those of Tables I, II, and III above.

The conclusion must be drawn, then, that Wagner's experiments in no way show the catalytic effect of ferric chloride in the interaction between hydrochloric acid and potassium permanganate, nor do they furnish evidence in support of the assumed formation of chlor-ferrous acid. They afford simply an indication of the greater or less retention of chlorine in solution, and the greater or less oxidizing action of this chlorine on the oxalic acid in the presence or absence of ferric chloride.

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