45. *Observations upon the Mechanism of Permanganate Reduction and the Induced Oxidation of Chlorion.*

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The use of internal indicators in dichromate titrations (Knop, *J. Amer. Chem. Soc.*, 1924, **46**, 263) has removed most of the practical interest attached to the titration of ferrous chloride solutions by permanganate, but observations made in a study of the titration throw some light on the mechanism of oxidation by permanganate.

The excess consumption of permanganate in the titration of ferrous salts in presence of chloride was first noticed by Löwenthal and Lenssen (*Z. anal. Chem.*, 1862, **1**, 329). It is generally small, but has led to much investigation and speculation (Zimmermann, *Ber.*, 1881, **14**, 779; *Annalen*, 1882, **213**, 307; Wagner, *Z. physikal. Chem.*, 1889, **28**, 33; Manchot, *Annalen*, 1902, **325**, 93; Manchot and Wilhelms, *ibid.*, p. 105; Skrabal, *Z. anal. Chem.*, 1903, **42**, 359; Friend, J., 1909, **95**, 1228; Kolthoff and Smit, *Pharm. Weekblad*, 1924, **61**, 1082). Addition of manganese sulphate decreases the error; this device was first proposed by Kessler (*Pogg. Ann.*, 1863, **118**, 48; **119**, 225; *Z. anal. Chem.*, 1882, **21**, 381) and revived by Zimmermann (*loc. cit.*). Opinion differs as to the amount to be added (Treadwell, " Analytical Chemistry," 1905, Vol. II, 483; Harrison and Perkin, *Analyst*, 1908, **33**, 43; Friend, *loc. cit.*).

Liberation of small amounts of chlorine, induced in some way by the other reaction, is the cause of the phenomenon. This was at first attributed to a " peroxide " formed from the ferric salt (Zimmermann; Manchot; Skrabal; *locc. cit.*) or to a hydroferrochloric acid (*e.g.*, $HFeCl_3$), which was supposed to be oxidised more readily than chlorion to chlorine (Wagner, *loc. cit.*).

Such explanations are inadequate since, in the oxidation of oxalic acid by permanganate in presence of hydrochloric acid, excess of permanganate is always required, and manganese sulphate is as effective in diminishing the excess in this case as in the foregoing (Gooch and Peters, *Z. anorg. Chem.*, 1899, **21**, 185; Skrabal, *ibid.*, 1904, **42**, 1). In our opinion, the liberation of chlorine is due to tervalent manganese which probably plays as important a part in all reactions involving acid permanganate as Skrabal (*loc. cit.*, 1904) and Launer (*J. Amer. Chem. Soc.*, 1932, **54**, 2597) showed it to do in the reaction with oxalic acid.

Although compounds of tervalent manganese are very unstable, a few have been prepared in the solid state (Kehrmann, *Ber.*, 1887, **20**, 1594; Christensen, *Dansk Vid. Selsk. Förh.*, 1896, 94; *J. pr. Chem.*, 1887, **35**, 57; Fichter and Brunner, J., 1928, 1862; Mellor, " Comprehensive Treatise, etc.," 1932, Vol. XII, 460). They have a cherry-red colour either as solids or in solution, whereas salts of quadrivalent manganese are yellow or brown (Weinland and Lauenstein, *Z. anorg. Chem.*, 1899, **20**, 40; Fichter and Brunner, *loc. cit.*). We find that a cherry-red colour is produced when permanganate is added to solutions of manganese sulphate strongly acidified with sulphuric acid. This colour persists for several days in the absence of oxidisable material, but the solution gradually gets paler and deposits manganese dioxide.

The explanation appears to be that tervalent manganese, formed by the reaction $MnO_4' + 4Mn^{\cdot\cdot} + 8H^{\cdot} \longrightarrow 5Mn^{\cdot\cdot\cdot} + 4H_2O$, is converted into relatively stable mangani-sulphate complexes which, however, slowly undergo the change $2Mn^{\cdot\cdot\cdot} \rightleftharpoons Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot}$. In presence of zinc hydroxide to maintain neutrality and prevent adsorption of $Mn^{\cdot\cdot}$ by the precipitate, the reaction $2MnO_4' + 3Mn^{\cdot\cdot} + 2H_2O = 5MnO_2 + 4H^{\cdot}$ goes to completion and is used for estimating manganese (Volhard, *Annalen*, 1879, **198**, 218). On the above basis, at least two steps are involved :

$$\begin{cases} 2MnO_4' + 8Mn^{\cdot\cdot} + 16H^{\cdot} \longrightarrow 10Mn^{\cdot\cdot\cdot} + 8H_2O \\ 10Mn^{\cdot\cdot\cdot} + 10H_2O \longrightarrow 5Mn^{\cdot\cdot} + 5MnO_2 + 20H^{\cdot} \end{cases}$$

The cherry-red colour can also be noticed in an ordinary titration of ferrous sulphate in presence of sulphuric acid. If the permanganate is added, drop by drop, while the ferrous solution is rotated in the flask, the purple colour is seen to give rise to quite a distinct red colour which is quickly bleached. As this red colour can be seen from the beginning of the titration, it appears that $Mn^{\cdot\cdot\cdot}$ is the first identifiable stage in the acid reduction of permanganate and probably precedes the complete reduction to $Mn^{\cdot\cdot}$ in all cases. There is no indication that a yellowish stage due to quadrivalent manganese intervenes between the purple and the cherry-red stage.

Manganese sulphate solutions strongly acidified with phosphoric acid show the same colour changes as do sulphuric acid solutions on treatment with permanganate. The precipitate slowly formed as the cherry-red solutions gradually lose their colour is not manganese dioxide, however. It is of a greenish-buff colour and of somewhat variable composition. A typical sample, washed with dilute phosphoric acid, then with acetone, and air-dried, gave on analysis : Available oxygen, 4·06; P_2O_5, 41·73; MnO, 35·97; loss on ignition, 22·22%. Consideration of various possibilities suggests that the material is a mixture of manganous salts of complex quadrivalent-manganese–phosphoric acids. Mixtures of $[Mn^{II}(H_2O)_4]^{\cdot\cdot}[Mn^{IV}(PO_4)_2]''$, $[Mn^{II}(H_2O)_4]^{\cdot\cdot}{}_2[Mn^{IV}(HPO_4)_4]''''$, and MnO_2 in suitable proportions would account for the analytical figures.

Christensen (*Dansk Vid. Selsk. Skr.*, 1883, **2**, 148, 151), by a somewhat similar method at 100°, obtained a product of the same character as ours, to which, however, he attributed the formula $MnPO_4,H_2O$, with only tervalent manganese. Although the product is of rather variable composition, the evidence appears to favour our view of its nature rather than Christensen's.

The insolubility of this substance in strongly acid solutions led us to try whether phosphoric acid could be removed from acid solution by means of manganese and nitric acid, as it can be by tin and nitric acid (Reynoso, *Compt. rend.*, 1851, **33**, 385; *J. pr. Chem.*, 1851, **54**, 261). This is indeed the case, and either metallic manganese or a soluble manganese salt may be used. A mixture of 0·5 g. of manganese (metal), 0·4 g. of diammonium hydrogen phosphate, 10 c.c. of concentrated nitric acid, and 10 c.c. of water was heated to about 70° for 12 hours; a dark buff-coloured precipitate formed, which was filtered off and washed with dilute nitric acid, and the filtrate contained no phosphate. In another experiment, 2·5 g. of manganese chloride tetrahydrate were used in place of the metallic manganese, but otherwise the procedure was the same; in this case the filtrate contained 0·0031 g. of P_2O_5.

Analysis showed the buff precipitate to be essentially similar in character to that obtained by decomposition of the cherry-red manganic phosphate solutions. A typical sample contained : Available oxygen, 4·91; P_2O_5, 41·86; MnO, 39·38; loss on ignition, 18·96%.

When permanganate is added to solutions containing oxalic acid and manganese sulphate, a cherry-red colour is obtained which gradually or rapidly (according to the concentrations, etc.) becomes brownish-yellow. Addition of alkali oxalate or acetate causes the cherry-red colour to return. The observations set out above make it likely that the colour change from red to yellow is due to the change $2Mn^{\cdot\cdot\cdot} \rightleftharpoons Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot}$. Both the $Mn^{\cdot\cdot\cdot}$ and the $Mn^{\cdot\cdot\cdot\cdot}$ ions would be mainly in the form of complex oxalate anions. Decomposition on the above lines of the $Mn^{\cdot\cdot\cdot}$ complex might well involve liberation of oxalate ions. This would explain why addition of these restores the red colour. Acetate ions would act in the same way owing to formation of acetate complexes. Skrabal (*loc. cit.*) considered that he had some kinetic evidence for the above change. The kinetics of the oxalate reaction have recently been re-examined by Lidwell and Bell (J., 1935, 1303).

Now ter- and quadri-valent manganese are more potent oxidising agents than permanganate under comparable conditions. The normal potential for the reduction $MnO_4' + 8H^{\cdot} + 5e \rightleftharpoons Mn^{\cdot\cdot} + 4H_2O$ is $+ 1{\cdot}761$ volts on the absolute zero scale (normal calomel electrode $= 0{\cdot}56$ volt), while that for reduction only to $Mn^{\cdot\cdot\cdot}$ would be $+ 1{\cdot}755$ volts. The normal potentials for the reactions $Mn^{\cdot\cdot\cdot\cdot} + 2e \rightleftharpoons Mn^{\cdot\cdot}$ and $Mn^{\cdot\cdot\cdot} + e \rightleftharpoons Mn^{\cdot\cdot}$ are said to be $+ 1{\cdot}854$ and $+ 1{\cdot}788$ volts respectively on the same scale (see Grube and Huberich, *Z. Elektrochem.*, 1923, **29**, 8, and "International Critical Tables," 1929, vol. VI, 333, where the potentials are given with reference to the normal hydrogen electrode). Since the normal potential of $MnO_4' \longrightarrow Mn^{\cdot\cdot\cdot}$ is little less than that of $Mn^{\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot}$, it is evident that relatively small changes in concentration (*e.g.*, of $Mn^{\cdot\cdot}$) would enable the latter to be oxidised to $Mn^{\cdot\cdot\cdot}$ by permanganate. Any process converting $Mn^{\cdot\cdot\cdot}$ into a complex would be particularly favourable. Since there is not enough difference between the normal potentials of $MnO_4' \longrightarrow Mn^{\cdot\cdot\cdot}$ and of $Mn^{\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot}$ to explain why $Mn^{\cdot\cdot\cdot}$ can apparently oxidise chloride ion so much more rapidly than can MnO_4', some other explanation for this is necessary. It may well depend upon the much greater simplicity of the change $Mn^{\cdot\cdot\cdot} + Cl' \longrightarrow Mn^{\cdot\cdot} + Cl$ than of $MnO_4' + 4Cl' + 8H^{\cdot} \longrightarrow Mn^{\cdot\cdot\cdot} + 2Cl_2 + 4H_2O$.*

Any factor which increases the stability of $Mn^{\cdot\cdot\cdot}$ will also lower its oxidation potential and its capacity for liberating chlorine. Ions able to form complex ions with $Mn^{\cdot\cdot\cdot}$ should have this effect. The stability of $Mn^{\cdot\cdot\cdot}$ would also be increased, and its oxidation potential reduced, by addition of $Mn^{\cdot\cdot}$. This effect is allowed for in the usual expression for the potential of an electrode at which the reaction $Mn^{\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot}$ is proceeding reversibly (*viz.*, $1{\cdot}788 + 0{\cdot}058 \log [Mn^{\cdot\cdot\cdot}]/[Mn^{\cdot\cdot}]$ volts at 17°, 1·788 being the normal potential). Although the normal potential for $\frac{1}{2}Cl_2 \longrightarrow Cl'$ (Cl_2 at 1 atm.) is $+ 1{\cdot}635$ volts, yet that for $Fe^{\cdot\cdot\cdot} \longrightarrow Fe^{\cdot\cdot}$ is only $+ 1{\cdot}025$ volts, so that ferrous iron is readily and rapidly oxidised by any of the possible stages in the reduction of MnO_4' to $Mn^{\cdot\cdot}$.

Normal potentials can only be used as qualitative guides as to what may happen in permanganate titrations, since the actual oxidation potentials will depend upon various concentrations which are usually unknown.

A series of titrations summarised in the tables showed that the excess consumption of permanganate in ferrous chloride–permanganate titrations could, in fact, be substantially eliminated by addition of considerable amounts of sulphuric, phosphoric, or hydrofluoric acids, and even, somewhat paradoxically, of hydrochloric acid, all of which give rise to complex manganic anions. Lithium chloride was found to be effective (last table), and the effect of manganous salts is shown in the two preceding tables.

Titrations by permanganate of ferrous chloride solutions containing small amounts of extra hydrochloric acid are most accurate when the solutions are made 2—3*N* with regard to sulphuric acid. No manganese sulphate need be added. The concentration of the iron should be between 0·05 and 0·1*N*. The end-point is then sharp and lasts for some minutes. The instability of the end-point is a serious difficulty in all titrations of ferrous chloride solutions with permanganate. By the methods indicated above, the rate of oxidation of chlorion can be repressed so much, relatively to that of the ferrous ion, that a very close approximation to the correct end-point is obtainable, but when all ferrous iron is removed, slow oxidation of chlorion continues, with the result that the pink end-point colour fades whether it be due to MnO_4' or to $Mn^{\cdot\cdot\cdot}$ ions. Increased acidity caused by acid addition should have little, if any, effect on the fading, for although the rate of the reduction stage $MnO_4' \longrightarrow Mn^{\cdot\cdot\cdot}$ depends on the eighth power of the hydrogen-ion concentration, that of the $Mn^{\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot}$ stage is independent of it.

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* This point has been considered by Ubbelohde (J., 1935, 1605), though he does not attribute loss of chlorine in permanganate titrations to the $Mn^{\cdot\cdot\cdot}$ ion, as we do. He recommends the use of a manganic sulphate solution instead of permanganate for the titration of ferrous iron in presence of chloride, but the concentration of sulphuric acid in this solution is such as gave good results with permanganate in the present investigation.

It appears likely that the rapidity of the fading is mainly due to the change $2Mn^{\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot}$ (possibly accelerated by hydrogen ions). The normal potential of $Mn^{\cdot\cdot\cdot\cdot}$ being so high (+ 1·854 volts), its capacity to liberate chlorine would be much less checked by the methods which were reasonably effective for $Mn^{\cdot\cdot\cdot}$. The $Mn^{\cdot\cdot\cdot\cdot}$ ion, formed from $Mn^{\cdot\cdot\cdot}$, could hardly appear so long as any ferrous iron remained unoxidised, and it is unlikely that it plays any part in an ordinary permanganate titration of ferrous iron although it may well do so in the slower oxalate reaction.

With high chlorion concentration, the end-point is also obscured by formation of reddish-brown $[FeCl_4]'$ ions. This can be prevented by addition of phosphoric acid, which forms much more stable but nearly colourless ferriphosphoric anions (Reinhardt, *Chem.-Ztg.*, 1889, **13**, 323).

EXPERIMENTAL.

The ferrous chloride solution was made by dissolving pure iron wire in hydrochloric acid, an excess of the latter being used which ranged from about 10 to 20 c.c. of 4*N*-acid per litre of ferrous chloride solution. The solutions were standardised by means of potassium dichromate,

(I) $FeCl_2$–HCl–$KMnO_4$ Series.

(*a*) $KMnO_4$ = 0·1322*N*; $FeCl_2$ = 0·1520*N*;
20 c.c. $FeCl_2$ = 22·99 c.c. $KMnO_4$ (calc.).

Acid added.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
20 c.c. (water)	23·41	0·42	>3 mins.
20 ,, 1·8*N*-HCl	23·20	0·21	2½ ,,
20 ,, 1·8 ,,	23·24	0·25	2½ ,,
20 ,, 2·9 ,,	23·19	0·20	1½ ,,
20 ,, 2·9 ,,	23·18	0·19	1½ ,,
20 ,, 3·5 ,,	23·16	0·17	40 secs.
20 ,, 4·8 ,,	23·10	0·11	20 ,,
20 ,, 4·8 ,,	23·10	0·11	20 ,,
20 ,, 5·4 ,,	23·20	0·21	15 ,,

(*b*) $KMnO_4$ = 0·09755*N*; $FeCl_2$ = 0·09375*N*;
20 c.c. $FeCl_2$ = 19·22 c.c. $KMnO_4$ (calc.).

Acid added.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
20 c.c. 0·59*N*-HCl	19·50	0·28	7 mins.
20 ,, 0·59 ,,	19·48	0·26	
20 ,, 0·71 ,,	19·48	0·26	
20 ,, 1·8 ,,	19·38	0·16	3 mins.
20 ,, 2·5 ,,	19·32	0·10	*ca.* 3 ,,
20 ,, 2·7 ,,	19·32	0·10	2 ,,
20 ,, 2·7 ,,	19·33	0·11	2 ,,
20 ,, 3·6 ,,	19·25	0·03	*ca.* 1½ ,,

(II) $FeCl_2$–H_2SO_4–$KMnO_4$ Series.

(*a*) $KMnO_4$ = 0·1332*N*; $FeCl_2$ = 0·1514*N*;
20 c.c. $FeCl_2$ = 22·91 c.c. $KMnO_4$ (calc.).

20 c.c. (water)	23·25	0·34	
20 ,, 0·62*N*-H_2SO_4	23·12	0·21	
20 ,, 0·62 ,,	23·10	0·19	
20 ,, 1·3 ,,	23·08	0·17	*ca.* 2 mins.
20 ,, 1·3 ,,	23·03	0·12	
20 ,, 3·4 ,,	23·02	0·11	
20 ,, 6·0 ,,	23·02	0·11	*ca.* 2 mins.

(*b*) $KMnO_4$ = 0·09725*N*; $FeCl_2$ = 0·05825*N*;
20 c.c. $FeCl_2$ = 11·97 c.c. $KMnO_4$ (calc.).

20 c.c. (water)	12·15	0·18	
20 ,, 0·62*N*-H_2SO_4	12·08	0·11	
20 ,, 1·3 ,,	12·01	0·04	
20 ,, 1·3 ,,	11·98	0·01	
20 ,, 3·4 ,,	12·00	0·03	
20 ,, 4·7 ,,	12·01	0·04	
20 ,, 4·7 ,,	12·02	0·05	
20 ,, 6·0 ,,	11·99	0·02	*ca.* 12 mins.

(III) $FeCl_2$–H_3PO_4–$KMnO_4$ Series.

(*a*) $KMnO_4$ = 0·1332*N*; $FeCl_2$ = 0·1680*N*;
20 c.c. $FeCl_2$ = 25·23 c.c. $KMnO_4$ (calc.).

20 c.c. (water)	25·78	0·55	
20 ,, 1·1*N*-H_3PO_4	25·50	0·27	40 secs.
20 ,, 2·1 ,,	25·33	0·10	20 ,,
20 ,, 3·1 ,,	25·27	0·04	16 ,,
20 ,, 3·1 ,,	25·30	0·07	16 ,,
20 ,, 5·2 ,,	25·25	0·02	*ca.* 5 ,,
20 ,, 5·2 ,,	25·25	0·02	*ca.* 5 ,,

(*b*) $KMnO_4$ = 0·09725*N*; $FeCl_2$ = 0·05286*N*;
20 c.c. $FeCl_2$ = 11·90 c.c. $KMnO_4$ (calc.).

20 c.c. 1·1*N*-H_3PO_4	11·99	0·09	*ca.* 2½ mins.
20 ,, 2·1 ,,	12·00	0·10	
20 ,, 2·6 ,,	11·94	0·04	
20 ,, 2·6 ,,	11·97	0·07	
20 ,, 3·1 ,,	11·95	0·05	30 secs.
20 ,, 3·1 ,,	11·97	0·07	30 ,,
20 ,, 5·2 ,,	11·91	0·01	*ca.* 7 ,,
20 ,, 5·2 ,,	11·90	0·00	

(IV) $FeCl_2$–HF–$KMnO_4$ Series.

(*a*) $KMnO_4$ = 0·1641*N*; $FeCl_2$ = 0·1914*N*;
20 c.c. $FeCl_2$ = 23·34 c.c. $KMnO_4$ (calc.).

20 c.c. 0·3*N*-HF	23·66	0·32	*ca.* 3 mins.
20 ,, 0·3 ,,	23·65	0·31	*ca.* 3 ,,
20 ,, 0·6 ,,	23·64	0·30	2—3 mins.
20 ,, 0·6 ,,	23·60	0·26	
20 ,, 2·1 ,,	23·41	0·07	*ca.* 7 secs.
20 ,, 2·1 ,,	23·41	0·07	*ca.* 7 ,,

(*b*) $KMnO_4$ = 0·07565*N*; $FeCl_2$ = 0·05946;
20 c.c. $FeCl_2$ = 15·72 c.c. $KMnO_4$ (calc.).

20 c.c. 0·20*N*-HF	16·04	0·32	colour slightly faded after 3 mins.
20 ,, 0·20 ,,	16·00	0·28	
20 ,, 0·60 ,,	15·92	0·20	30 secs.
20 ,, 0·60 ,,	15·94	0·22	30 ,,
20 ,, 2·1 ,,	15·85	0·13	5 ,,
20 ,, 2·1 ,,	15·88	0·16	

(V) $FeCl_2$–$MnSO_4$–$KMnO_4$ Series.

1 C.c. of Mn solution = 0·60 g. $MnSO_4,4H_2O$. 20 C.c. 0·7*N*-HCl were added to the 20 c.c. of $FeCl_2$ solution. $KMnO_4$ = 0·1332*N*; $FeCl_2$ = 0·1711*N*; 20 c.c. $FeCl_2$ = 25·54 c.c. $KMnO_4$ (calc.).

Mn soltn. added, c.c.	H_2O added, c.c.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.	Mn soltn. added, c.c.	H_2O added, c.c.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
—	10	26·10	0·56		3	7	25·71	0·17	1½ mins.
1	9	25·82	0·28	Pink colour not bleached after 5 mins.	3	7	25·70	0·16	1½ ,,
1	9	25·81	0·27		5	5	25·71	0·17	45 secs.
2	8	25·71	0·17	2 mins.	7	3	25·70	0·16	20 ,,
2	8	25·72	0·18	2 ,,	10	—	25·71	0·17	3 ,,

(VI) $FeCl_2$–$MnCl_2$–$KMnO_4$ Series.

1 C.c. of Mn solution = 0·6 g. $MnCl_2,4H_2O$. 20 C.c. 0·7*N*-HCl were added to the 20 c.c. of $FeCl_2$ solution. $KMnO_4$ = 0·1332*N*; $FeCl_2$ =0·1680*N*; 20 c.c. $FeCl_2$ = 25·23 c.c. $KMnO_4$ (calc.).

—	10	25·65	0·42		4	6	25·44	0·21	20 secs.
1	9	25·52	0·29	2 mins.	5	5	25·45	0·22	20 ,,
2	8	25·46	0·23	30 secs.	7	3	25·45	0·22	7 ,,

(VII) $FeCl_2$–LiCl–$KMnO_4$ Series.

1 C.c. of solution = 0·55 g. LiCl. 20 C.c. of 0·23*N*-HCl were added to the 20 c.c. of $FeCl_2$ solution. $KMnO_4$ = 0·05609*N*; $FeCl_2$ = 0·07655*N*; 20 c.c. $FeCl_2$ = 27·34 c.c. $KMnO_4$ (calc.).

LiCl soltn. added, c.c.	H_2O added, c.c.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.	LiCl soltn. added, c.c.	H_2O added, c.c.	$KMnO_4$ required, c.c.	Error, c.c.	Duration of end-point.
—	20	27·82	0·48		10	10	27·44	0·10	20 secs.
10	10	27·41	0·07	20 secs.	20	—	27·33	0	

diphenylamine being used as internal indicator. The calculated permanganate values in the tables are based on the dichromate titrations. 20 C.c. of the ferrous chloride solution were used in each experiment; other additions are shown in the tables. Permanganate was run in slowly and, towards the end of the titration, drop by drop. The duration of the end-point colour was determined by means of a stop-clock. The experiments with hydrofluoric acid were carried out in wax beakers.

SUMMARY.

1. In the interaction of ferrous iron and permanganate, the first identifiable product of reduction of the latter is manganic ion, $Mn^{\cdot\cdot\cdot}$. This may also be formed by direct oxidation of $Mn^{\cdot\cdot}$ by permanganate.

2. The quadrivalent $Mn^{\cdot\cdot\cdot\cdot}$ ion may be formed from $Mn^{\cdot\cdot\cdot}$ by the change $2Mn^{\cdot\cdot\cdot} \rightleftarrows Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot}$; but indications appear to be against its being a direct and intermediate product of reduction of permanganate in acid solution.

3. Ter- and quadri-valent manganese are more potent oxidising agents than permanganate under comparable conditions, and the induced oxidation of chlorion in permanganate reactions is attributed to them, especially to the former. This may be partly because reduction of $Mn^{\cdot\cdot\cdot}$ to $Mn^{\cdot\cdot}$ is a simpler process than reduction of MnO_4' to $Mn^{\cdot\cdot\cdot}$.

4. A more correct end-point in the titration of ferrous chloride solutions by permanganate can be obtained by increasing the stability of $Mn^{\cdot\cdot\cdot}$ ions and thus lowering their oxidation potential. This can be done by addition either of manganous ions or of anions which can form stable complexes with $Mn^{\cdot\cdot\cdot}$, such as sulphate, phosphate, fluoride, or even chloride.

5. The end-point colour is always very unstable. It is considered that this is mainly due to the change $2Mn^{\cdot\cdot\cdot} \rightleftarrows Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot}$ and production of $Mn^{\cdot\cdot\cdot\cdot}$ ions with a much higher oxidation potential.

6. The most satisfactory titrations of ferrous chloride solutions with permanganate are obtained after making them 2—3*N* with respect to sulphuric acid.

7. Phosphate can be practically completely removed from solutions by digestion with concentrated nitric acid and manganese metal or salts. An insoluble product is formed which appears to be a manganous salt of a quadrivalent-manganese–phosphoric acid.

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