649. *The Oxidation of Manganous Sulphate by Chromic Acid in Sulphuric Acid Solution.*

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The amount of manganous sulphate oxidised by chromates has been measured, for various concentrations of sulphuric acid and reactants by two different methods. In all the solutions an equilibrium is attained which may be represented by the equation, $Cr^{6+} + 3Mn^{++} \rightleftharpoons Cr^{3+} + 3Mn^{3+}$; the constants, $K = \{[Mn^{3+}]^3[Cr^{3+}]/[Mn^{2+}]^3[Cr^{6+}]\}^{0 \cdot 25}$, are summarised in Tables I and II. The percentage of the manganous sulphate oxidised increases with increasing concentration of sulphuric acid and decreases with rise of temperature. The influence of the sulphuric acid is explained by the formation of sulphato-complexes of the tervalent manganese ion. The extinctions of the equilibrium solutions were also measured.

In view of the frequent use of chromates and manganic salt solutions as standard oxidising agents, it is of interest to know their relative powers of oxidation at different concentrations of sulphuric acid and at different temperatures. The standard redox potential for the reaction

$$Mn^{2+} = Mn^{3+} + e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in 4·55M-sulphuric acid is given by Grube and Huberich (*Z. Elektrochem.*, **1923**, **29**, 8) as 1·503 v., whilst the normal electrode potential of the reaction,

$$Cr^{3+} + 4H_2O = HCrO_4^- + 7H^+ + 3e \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is given in various handbooks (*e.g.*, Landolt–Börnstein's " Tabellen ") as 1·3 v. These values are sufficiently close to lead to the expectation that an equilibrium would be established in a solution containing the reduced and oxidised forms. Also, as both potentials depend on the acidity of the solution, the equilibrium should vary with the concentration of the sulphuric acid present.

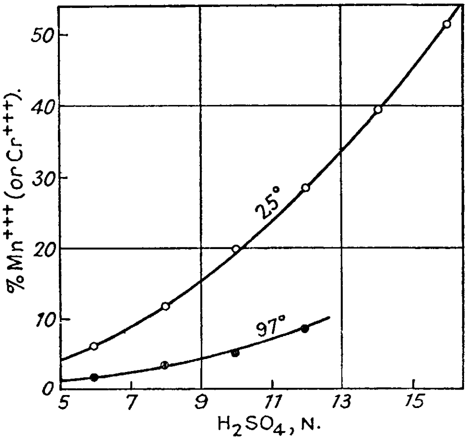
Lang (*Z. anorg. Chem.*, 1928, **170**, 387) states that a chromate solution did not react with an excess of manganous salt in N-H_2SO_4, but, on adding an alkali fluoride or metaphosphoric acid, he observed the formation of red manganic salts (owing to complex formation).

Fridland (Thesis, Hebrew Univ., Jerusalem, 1940) observed that, in moderately concentrated solutions of sulphuric acid, chromic acid and manganous salts reacted, giving an equilibrium which changed with the concentration of sulphuric acid in favour of the manganic and chromic salt, in agreement with equation (2), but that at a temperature near the boiling point of water the equilibrium shifts greatly in the direction of sexavalent chromium.

The general equation for the equilibrium could thus be written :

$$Cr^{6+} + 3Mn^{2+} = Cr^{3+} + 3Mn^{3+} + \text{heat} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

% *Amount of manganic salt* (*or* Cr^{3+}) *at equilibrium in equivalent mixtures of manganous sulphate and chromic acid in sulphuric acid solutions.*



The shift to the right in equilibrium (3) with increasing concentration of sulphuric acid may be explained by the formation of sulphato-complexes, thus :

$$Mn^{3+} + nSO_4^{2-} = [Mn(SO_4)_n]^{2(n-3)-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Further, the dehydrating effect of sulphuric acid should be taken into consideration, as the destruction of the aqueous shell of the [Mn, aq.]$^{2+}$ ion might assist in the formation of the sulphato-complexes, enabling tervalent manganese to be formed.

The oxidation of chromic salts by permanganate in 2·92M-sulphuric acid was studied by Fales and Roller (*J. Amer. Chem. Soc.*, 1929, **51**, 345). They showed that the rate of oxidation increases with the increase of the relative amount of quadrivalent manganese in the solution and assumed that the oxidation by the tervalent manganic ion is preceded by disengagement of the manganic ion from a sulphato-complex, followed by its disproportionation according to the equation

$$2Mn^{3+} \rightleftharpoons Mn^{2+} + Mn^{4+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The constants of this equilibrium in sulphuric acid solution of various concentration were measured by Grube and Huberich (*loc. cit.*). They found that the amount of tervalent manganese increases with increase in the concentration of sulphuric acid, and thus all the considerations regarding the sulphato-complexes mentioned above should apply to equilibrium (5) as well.

Fales and Roller used, in all their solutions, a large excess of chromic salt and expected the reaction to go to completion in one direction. Actually only about five-sixths of the theoretical amount of dichromate was obtained, after which the reaction slowed down greatly. No explanation for this phenomenon is given; it could be most easily accounted for by a back-reaction.

We investigated three analytical methods :

(*a*) The photometric method. The extinction of the series of solutions containing 0·00139M-potassium chromate and 0·0333M-manganous sulphate in various concentrations of sulphuric acid was measured after attainment of equilibrium at 25°. The results were compared with the extinction of 13N-sulphuric acid containing a very large excess of manganous sulphate in order to reduce all the available chromate to the chromic state, while oxidising the manganese to either tervalent or quadrivalent manganic salts. On the assumption that all the oxidised manganese was present in the tervalent state, the following percentages of the theoretically available manganic salt were calculated, from the photometric measurements, to be present in the various sulphuric acid solutions :

N-H_2SO_4	6	8	10	12	14	16	18	20
Mn^{3+}, %	16·9	42·5	69·3	88·1	107·2	111·8	122·6	125·6

These results show that a valuation of the photometric measurements will be practicable only when further data on the forms and extinctions of the tervalent and quadrivalent manganese present in these solutions are available.

(*b*) The bromine-oxidation method. Fales and Roller (*loc. cit.*; cf. Bobtelsky and Glasner, *J.*, 1948, 1376) observed that, whilst oxidation of hydrobromic acid by chromates is rather slow, manganic salts are reduced instantaneously. We have exploited this difference to measure the amount of manganic salt in the equilibrium mixtures. The results are given in Table I. The equilibrium constants K were calculated according to equilibrium (3) by the equation

$$K = \{[Mn^{3+}]^3(Cr^{3+}]/[Mn^{2+}]^3[Cr^{6+}]\}^{0{\cdot}25} = [x^4/(a - x)^3(3b - x)]^{0{\cdot}25},$$

where a and b = moles of manganous sulphate and potassium chromate, respectively, introduced into the solution, and x = the equivalent of manganese in the oxidised state present at equilibrium. The good agreement of the K for each concentration of sulphuric acid proved the validity of this method.

TABLE I.

Equilibrium constants $K = x/[(a - x)^{0{\cdot}75}(3b - x)^{0{\cdot}25}]$ by the bromine-oxidation method.
Volume : 15 c.c. Temperature : 25°.

Expt. no.	Normality of H_2SO_4.	Orig. mixt. (millimoles). $MnSO_4$.	K_2CrO_4.	Equilib. mixt. (millimoles). Mn^{3+}.	Cr^{6+}.	K.
1	6	1	0·250	0·056	(0·231)	0·0647
2	6	1	0·667	0·072	(0·643)	0·0649
3	6	4	0·167	0·141	(0·120)	0·0663
4	6	4	0·250	0·162	(0·196)	0·0673
5	6	4	1·667	0·258	(1·581)	0·0649
	6			average		0·0656
6	8	1	0·250	0·111	(0·213)	0·1352
7	8	1	0·667	0·146	(0·618)	0·1406
8	8	1	1·667	0·176	(1·608)	0·1387
9	8	4	0·167	0·252	(0·083)	0·1326
10	8	4	0·250	0·296	(0·151)	0·1351
11	8	4	1·667	0·498	(1·501)	0·1337
12	8	8	0·250	0·454	(0·099)	0·1353
	8			average		0·1359
13	10	1	0·250	0·188	(0·187)	0·2531
14	10	1	1·667	0·292	(1·570)	0·2563
15	10	4	0·250	0·443	(0·102)	0·2324
16	10	4	0·333	0·504	(0·165)	0·2487
17	10	4	1·667	0·817	(1·395)	0·2397
	10			average		0·2460
18	12	1	0·250	0·274	(0·159)	0·3948
19	12	1	0·667	0·348	(0·551)	0·4231
20	12	2	0·167	0·362	(0·046)	0·4121
21	12	4	0·250	0·600	(0·050)	0·3850
	12			average		0·4048
22	14	1	0·250	0·375	(0·125)	0·6439
23	14	1	0·667	0·464	(0·512)	0·6662
	14			average		0·6550
24	16	1	0·250	0·466	(0·095)	1·020
25	16	1	0·667	0·619	(0·461)	1·179
	16			average		1·10

TABLE II.

Equilibrium constants, $K = x/[(a - x)^{0{\cdot}75}(3b - x)^{0{\cdot}25}]$ by manganese dioxide precipitation method.

All the original mixtures in these series contained 4 millimoles of $MnSO_4$ and 1·667 millimoles of K_2CrO_4 per 15 c.c. of solution. Temperature : 25° or 97°.

		Equilib. mixt. (millimoles).						
		25°.		97°.				
Expt. no.	Normality of H_2SO_4.	$MnSO_4$.	K_2CrO_4.	$MnSO_4$.	K_2CrO_4.	$K_{25°}$.	$K_{97°}$.	$K_{25°}/K_{97°}$.
31	6	(0·303)	1·566	(0·060)	1·647	0·0764	0·0144	5·3
32	8	(0·492)	1·503	(0·159)	1·614	0·1313	0·0387	3·4
33	10	(0·858)	1·381	(0·240)	1·587	0·2579	0·0594	4·3
34	12	(1·245)	1·252	(0·378)	1·541	0·4171	0·0983	4·2
35	16	(1·869)	1·044	—	—	1·118	—	—

(*c*) The manganese dioxide precipitation method. The attainment of the equilibrium studied is rather slow compared with equilibrium (5). Therefore, if the solutions are quickly diluted to weaker than 2·6N-sulphuric acid, all the manganic salts present are precipitated as hydrated manganese dioxide. After centrifugation, the concentration of the chromate could be determined volumetrically in the supernatant diluted solution. The results thus obtained at 25° and at 97° are given in Table II and show good agreement with the bromine-oxidation method. The latter method is, however, more reliable, especially for the lower concentrations of sulphuric acid, because of the relatively small amount of manganese present in the oxidised state at equilibrium. The difference lies in the fact that in the bromine method the manganese oxidised is determined directly, whilst in the manganese dioxide method the chromic acid is titrated. The large difference in the equilibrium constants caused by a relatively small error in the titration of the chromic acid is seen in the following figures from experiments Nos. 5, 31; 11, 32; and 17, 33 :

Nos. :	5, 31.	11, 32.	17, 33.
ΔK	15%	1·8%	7·1%
ΔMn^{3+}	14·8%	1·2%	4·8%
ΔCr^{6+}	0·94%	0·13%	1·02%

Because of the low accuracy of the constants calculated from the results obtained by the manganese dioxide method, caution is required in drawing conclusions from the temperature coefficient given in Table II. Yet it will be seen that they are fairly constant for the range of sulphuric acid concentration measured, namely, from 6 to 12N.

Owing to the complexity of the equilibrium expression it will be cumbrous to calculate the concentrations of the respective components of the equilibrium under all conditions, but, if the manganous sulphate and the potassium chromate are mixed in stoicheiometrically equivalent amounts (*i.e.*, $3b = a$), the percentage of the chromic salt present at equilibrium is $100K/(K + 1)$. The results thus obtained at 25° and at 97° are given in the figure.

EXPERIMENTAL.

Mixtures of known amounts of potassium chromate, manganous sulphate, and sulphuric acid were made up to 15·0 c.c. in ground-stoppered flasks. The solutions varied from 6 to 20N. in respect of sulphuric acid. They were kept in a water-bath at a constant automatically-controlled temperature (±0·1°) for 3 days (at first some of the solutions were kept at constant temperature for a week, but experience showed that at 25° three days sufficed for the slowest solutions to attain equilibrium). After this period the " equilibrium solutions " were treated, each according to the method adopted.

The Photometric Method.—The extinction of the " equilibrium solution " was measured, in a Hellige pan-photometer, with use of filters corresponding to the wave-lengths 530 and 550 mμ. At these wave-lengths the extinction of chromic salts of corresponding concentrations was negligible, and the extinction of pure chromate solutions varied only very slightly in the range of the concentrations of sulphuric acid used. Therefore the diminution of transmission must have been due to the oxidation of the manganese.

To ensure that there were no changes in temperature during a measurement, the photometer tube was enclosed by a specially designed container through which a constant water-flow from an ultra-thermostat was maintained.

The comparison standard chosen was 13N-H_2SO_4 + 0·00139M-K_2CrO_4 + 0·1333M-$MnSO_4$; thus it contained a 32-fold excess of manganous sulphate (in equivalents). This solution had an extinction exceeding that of the pure chromate solution by 0·995 unit at 530 mμ. and by 0·969 unit at 550 mμ. In a series of solutions containing varying amounts of manganous sulphate, maximum extinction was reached in the solution mentioned. We assumed, therefore, that under these conditions very nearly 100% of the chromate has been reduced. Measurements were made at 25° (±0·1°).

The Bromine Oxidation Method.—The glass stopper was removed from the reaction flasks, and a mechanically-moved glass stirrer (1800 r.p.m.) was inserted into the " equilibrium solutions." With continued stirring, 10 c.c. of carbon tetrachloride and 20 c.c. of 0·05M-potassium bromide were introduced in quick succession. The stirring was stopped 15 seconds after the latter reagent had begun to run into the solution. The manganic ions were reduced instantaneously as expected (judging by the disappearance of the red colour of the solutions), and an equivalent amount of bromide was oxidised to elementary bromine and extracted by the carbon tetrachloride. The added bromide solution served, at the same time, to dilute the concentration of acid in the " equilibrium solutions," and thus reduced the velocity of oxidation of hydrogen bromide by chromic acid. In control experiments with similar sulphuric acid solutions, which contained chromate but no manganous salt, no oxidised bromine could be detected even after 30 seconds. For example, in 0·0333M-potassium bromide containing a five-fold excess of chromic acid but no manganese, the oxidation of 1% of the bromine required the following times :

Normality of H_2SO_4	6	5	4	3
Time, seconds	43·6	109	272	680

Mixing for 15 seconds was sufficient to extract the free bromine. The carbon tetrachloride first formed an emulsion with the aqueous solution, and, when the stirring was stopped, separated as a lower layer. The concentration of the bromine in the tetrachloride layer was determined colorimetrically in a Hellige pan-photometer. Two coloured filters corresponding to the wave-lengths 530 mμ. and 550 mμ. were used, the two measurements serving as a check on each other. The extinction of a bromine solution in carbon tetrachloride, obtained by allowing the reduction of a similar chromate solution to go to completion, was used as a standard of comparison. Measurements were made at 25° (±0·1°).

The Manganese Dioxide Precipitation Method.—The " equilibrium solutions " were quickly diluted with a known amount of distilled water to a concentration less than 2N. with respect to sulphuric acid, yielding by hydrolysis an extremely fine, hydrated manganese dioxide suspension. An aliquot amount of the suspension was centrifuged for 15 minutes at 2000 r.p.m. The chromic acid in the clear solutions was then determined by addition of potassium iodide solution and titration with 0·1N-thiosulphate. Measurements were made at 25° (±0·1°) and at 97° (boiling water).

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[*Received, May 26th,* 1949.]