

REMARKS ON THE DETERMINATION OF THE COMPOSITION OF MnO_2 — Mn_2O_3 — Mn_3O_4 SYSTEMS

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In a previous paper (1) the author describes a procedure for the determination of the composition of MnO_2 — Mn_2O_3 — Mn_3O_4 systems. The procedure is based on literary data concerning the thermal properties of the manganese oxides of higher valencies according to which MnO_2 already transforms into Mn_2O_3 at a temperature range of 600—700°C, whereas Mn_2O_3 and Mn_3O_4 remain unchanged.

As a basis for the determination of the composition the author employs the change which the active oxygen content undergoes when the sample is heated at temperatures of 600—700°C. According to the data of the literature this change can only be due to MnO_2 transforming into Mn_2O_3 and the extent of the change is proportional with the amount of MnO_2 .

Originally (1) it was suggested to determine the composition as follows. The MnO and active O content of the substance to be examined is determined and recalculated to 100 per cent. Another part of the sample is heated for three hours at 600—700°C and its active O content is also determined, furthermore by means of calculation (taking the loss on ignition and the original MnO content into account) the MnO content is obtained too and these results are recalculated to 100 per cent. The difference of the active O content of the heated and starting sample — ΔO — plotted on the diagram of the paper (1) mentioned above shows which of the possible systems is involved thus indicating the rate of oxidation of the manganese oxides present and their amount.

The behaviour during the heating of the pure MnO_2 , Mn_2O_3 , Mn_3O_4 seems to confirm the theoretical starting point of the determination which is also supported by the behaviour of the mixtures containing MnO_2 — Mn_2O_3 . The soundness of the starting basis was also supported by the results of examinations carried out on natural substances (manganite from Ilfeld). The DTA curves of these oxides and their mixtures did not either show phenomena which would seem to render necessary the revision of the above considerations (2). In the case of pure MnO_2 and of mixtures containing MnO_2 at a temperature of about 560°C the high endothermal peak indicating the transformation of MnO_2 into Mn_2O_3 appears distinctly

on the curves, Mn_2O_3 does not show any change until a temperature of $950^\circ C$, whereas in the case of mixtures containing MnO_2 and/or Mn_2O_3 the second characteristic high endothermal peak appears at $950^\circ C$ indicating the transformation of Mn_2O_3 into Mn_3O_4 . The DTA curve of Mn_2O_3 does not show any essential change.

The author also dealt with the thermal properties of manganese oxides of higher valency (3). The examinations showed that whilst pure MnO_2 , Mn_2O_3 , Mn_3O_4 behave according to the data reported in the literature Mn_3O_4 if it is pure is only stable at higher temperatures (exceeding $400^\circ C$), this fact considerably influences the method of determination mentioned above. Should MnO_2 or Mn_2O_3 also be present they already oxidise the Mn_3O_4 to Mn_2O_3 at $600-700^\circ C$.

Author also dealt in detail with the problem of the oxidation taking place as the result of the reaction between Mn_3O_4 and the two other oxides in a solid phase (4). At the present regarding the determination of the composition of artificial mixtures, or ore mixtures containing oxides of higher valency it is only essential to note that not like at the original starting conditions of the determination at a temperature of $600-700^\circ C$ merely MnO_2 , but in the presence of MnO_2 and/or Mn_2O_3 , Mn_3O_4 must also be considered to be a variable component. Hence the change and the extent of the active oxygen content cannot be considered to be an unequivocal factor for the determination of the composition — as was believed in the first communication — because at the change of the active oxygen content in the presence of one or both other oxides in addition to MnO_2 the oxygen change connected with the oxidation of Mn_3O_4 into Mn_2O_3 also plays a role.

Thus the following facts must be taken into account:

a) At a temperature of $600-700^\circ C$ MnO_2 on giving off oxygen is entirely transformed into Mn_2O_3 .

b) At the given temperature the Mn_2O_3 is stable and does not undergo any change.

c) If the system only contains Mn_3O_4 there is also no change at the given temperature, but in the presence of MnO_2 and/or Mn_2O_3 , Mn_3O_4 takes up oxygen and is transformed into Mn_2O_3 .

On dealing with the oxidation of Mn_3O_4 it was confirmed (4), that Mn_3O_4 takes up the oxygen required for its transformation into Mn_2O_3 from the air. Hence if the heating is carried out in an atmosphere free of oxygen presumably only MnO_2 will undergo a change whilst Mn_3O_4 will remain unchanged consequently it will only be possible to carry out the determination according to the original considerations. The only difference is that the heating at a temperature of $600-700^\circ C$ must be accomplished in an indifferent atmosphere with the exclusion of air.

Pure substances and their mixtures, respectively, were heated for three hours at $650-720^\circ C$ in a nitrogen current.

The results obtained in the course of the heating in a nitrogen current are summarized in Table 1.

Table 1.

Samples	Composition at 20° C recalc. to 100 per cent		sample treated at 670° C (three hours)								
			in air			in N ₂					
			loss on ignition	compo- sition	ΔO	loss on ignition	composition	ΔO			
								meas.	calc.		
MnO ₂	MnO	81,86	-11,82	89,72	-7,86	-11,73	MnO	89,76	-7,90		
	O	18,14		10,28			O	10,24			
Mn ₂ O ₃	MnO	89,80	±0,00	89,80	±0,00	±0,00	MnO	89,91	-0,11		
	O	10,20		10,20			O	10,09			
Mn ₃ O ₄	MnO	92,94	±0,00	92,87	+0,07	±0,00	MnO	92,94	±0,00		
	O	7,06		7,13			O	7,06			
MnO ₂ +Mn ₃ O ₄	25%+75%	MnO	89,97	-0,48	89,77	+0,20	-2,87	MnO	91,84	-1,87	-1,97
		O	10,03		10,23			O	8,16		
	50%+50%	MnO	87,33	-4,01	89,87	-2,54	-5,77	MnO	91,40	-4,07	-3,95
		O	12,67		10,13			O	8,60		
	75%+25%	MnO	84,46	-7,76	89,87	-5,41	-8,65	MnO	90,25	-5,79	-5,85
		O	15,54		10,13			O	9,75		
Mn ₂ O ₃ +Mn ₃ O ₄	25%+75%	MnO	92,04	+2,41	89,49	+2,55	±0,00	MnO	92,02	+0,02	±0,00
		O	7,96		10,51			O	7,98		
	50%+50%	MnO	91,29	+1,61	89,66	+1,63	±0,00	MnO	91,45	-0,16	±0,00
		O	8,71		10,34			O	8,55		
	75%+25%	MnO	90,45	+0,73	89,58	+0,87	±0,00	MnO	90,26	+0,19	±0,00
		O	9,55		10,42			O	9,74		
MnO ₂ +Mn ₂ O ₃ + +Mn ₃ O ₄	20%+30%+50%	MnO	89,63	-0,62	90,14	-0,51	-2,26	MnO	91,02	-1,51	-1,58
		O	10,37		9,86			O	8,86		
	50%+30%+20%	MnO	86,32	-5,04	89,99	-3,67	-5,84	MnO	90,11	-4,11	-3,95
		O	13,68		10,01			O	9,57		
	40%+20%+40%	MnO	87,74	-3,27	89,89	-2,15	-4,63	MnO	90,99	-3,25	-3,16
		O	12,26		10,11			O	9,01		

The Table 1. shows that in a nitrogen current at 600—700°C MnO_2 also transforms with oxygen loss into Mn_2O_3 . Mn_2O_3 remains unchanged at this temperature like when it is heated in air. Mn_3O_4 also remains unchanged and what is the most essential not only pure Mn_3O_4 remains unchanged but the same holds for mixtures too, hence it does not either change in the presence of MnO_2 and/or Mn_2O_3 .

Consequently the precise composition of systems consisting of components of MnO_2 — Mn_2O_3 — Mn_3O_4 may be determined if the procedure described in paper (1) is merely modified so far as the heating at 600—700°C is carried out in a nitrogen current and not in free air. When heated in a nitrogen current merely the MnO_2 component changes the two other components remain unchanged. Hence after determining the active oxygen content of a sample heated in a nitrogen current and knowing the active oxygen content of the untreated sample after having carried out the suitable calculations (the MnO and the O content is recalculated to 100 per cent in both cases whether the sample is heated or not) according to the trend of thought described in the previous paper and if ΔO is plotted on the diagram also described in this paper the exact composition of the sample examined may be determined.

There is, however, also a more simple way for the determination of the composition rendering the use of a diagram unnecessary.

If the samples to be examined are heated in a nitrogen current at 700° C according to the above paper (4) only MnO_2 will undergo a change. It gives off oxygen and transforms into Mn_2O_3 . The Mn_2O_3 and/or Mn_3O_4 components remain unchanged. Hence the observed $-\Delta\text{O}$ per cent is proportional with the amount of the MnO_2 present. If no change can be detected MnO_2 is not present, thus the substance examined is pure Mn_2O_3 or pure Mn_3O_4 , or a mixture of the two. Considering that the MnO and active O content (recalculated to 100 per cent) of the not heat-treated examined substance must be known it can immediately be established which of the mentioned cases is involved.

One half of the sample heated in a nitrogen current is used for the determination of the active O, the other half is weighed into a crucible and is heated for three hours at 700°C in the free air and then its active O content is determined too. Knowing the MnO content these values are also recalculated to 100 per cent.

Hence the following values are known:

a = the active O content of the original substance examined

b = the active O content of the sample heated in a nitrogen current at 700°C

c = the active O content of the sample heated in a nitrogen current and subsequently in air also at 700°C.

The $\pm\Delta\text{O}$ values formed from these values represent the amount of MnO_2 and Mn_3O_4 , respectively, i. e. on complementing the sum of the percentage of their amount to 100 per cent the Mn_2O_3 quantity is obtained. On heating in nitrogen if a change occurs this can only be $-\Delta\text{O}$ and only derive from MnO_2 ($a-b$); after heating in nitrogen and subsequently in air if there occurs a change as compared with the oxygen content of the

sample heated in nitrogen it can only be $+\Delta O$ and only derive from Mn_3O_4 (c—b). On the basis of the character of the changes occurring in the course of the treatment, or through their non-occurrence, conclusions can be drawn concerning the components of the substance investigated as this is shown in the Table below (Table 2.). On the other hand, from the extent of the changes the amount of the respective component may be calculated on the basis that in the case of 100 per cent MnO_2 the $-\Delta O=8,27$ per cent (a—b) and in that of 100 per cent Mn_3O_4 $+\Delta O=3,15$ per cent (c—b).

Table 2.

Original composition of the samples	Ignition in nitrogen at a temperature of 700° C		Ignition in free air at 700° C of the product ignited in N ₂	
	composition of the product obtained	character of the change	composition of the product obtained	character of the change
MnO ₂	Mn ₂ O ₃	$-\Delta O\%$	Mn ₂ O ₃	no change
Mn ₂ O ₃	Mn ₂ O ₃	no change	Mn ₂ O ₃	no change
Mn ₃ O ₄	Mn ₃ O ₄	no change	Mn ₃ O ₄	no change
MnO ₂ —Mn ₂ O ₃	Mn ₂ O ₃	$-\Delta O\%$	Mn ₂ O ₃	no change
MnO ₂ —Mn ₃ O ₄	Mn ₂ O ₃ —Mn ₃ O ₄	$-\Delta O\%$	Mn ₂ O ₃	$+\Delta O\%$
Mn ₂ O ₃ —Mn ₃ O ₄	Mn ₂ O ₃ —Mn ₃ O ₄	no change	Mn ₂ O ₃	$+\Delta O\%$
MnO ₂ —Mn ₂ O ₃ — —Mn ₃ O ₄	Mn ₂ O ₃ —Mn ₃ O ₄	$-\Delta O\%$	Mn ₂ O ₃	$+\Delta O\%$

In the following a few examples are stated to illustrate the above:

a) The composition of the starting mixture: 50 per cent MnO₂ — 30 per cent Mn₂O₃ — 20 per cent Mn₃O₄. The active O content of the mixture $a=13,68$ per cent. The sample was heated for three hours in a nitrogen current at 700° C and then its active O content was determined from one half of the sample, $b=9,57$ per cent. Finally the second half of the sample which had previously been heated in nitrogen was also heated in free air for three hours at 700° C. Its active O content was $c=10,22$ per cent. Calculating on the basis of the above consideration the MnO₂ content of the mixture:

$$MnO_2\% = \frac{(a-b) \cdot 100}{8,27} = \frac{4,11 \cdot 100}{8,27} = 49,7\%$$

$$\text{Similarly: } Mn_3O_4\% = \frac{(c-b) \cdot 100}{3,15} = \frac{0,65 \cdot 100}{3,15} = 20,6\%$$

Finally:

$Mn_2O_3\%$ = 100 — ($MnO_2\%$ + $Mn_3O_4\%$) = 29,7% is obtained.

b) The composition of the starting mixture: 40 per cent MnO_2 — 20 per cent Mn_2O_3 — 40 per cent Mn_3O_4 . On carrying out the examinations one after another a = 12,26 per cent, b = 9,00 per cent and c = 10,24 per cent. On this basis:

$$MnO_2\% = \frac{3,26 \cdot 100}{8,27} = 39,4\%$$

$$Mn_3O_4\% = \frac{1,24 \cdot 100}{3,15} = 39,3\%$$

$$Mn_2O_3\% = 100 - 78,7\% = 21,3\%.$$

c) The composition of the starting mixture: 20 per cent MnO_2 — 30 per cent Mn_2O_3 — 50 per cent Mn_3O_4 . On carrying out the examinations: a = 10,37 per cent, b = 8,86 per cent and c = 10,20 per cent. Hence

$$MnO_2\% = \frac{1,51 \cdot 100}{8,27} = 18,2\%$$

$$Mn_3O_4\% = \frac{1,34 \cdot 100}{3,15} = 42,5\%$$

$$Mn_2O_3\% = 100 - 60,7 = 39,3\%$$

d) The composition of the starting substance: 50 per cent MnO_2 — 50 per cent Mn_3O_4 . On carrying out the examinations: a = 12,67 per cent, b = 8,60 per cent and c = 10,18 per cent.

$$MnO_2\% = \frac{4,07 \cdot 100}{8,27} = 49,2\%$$

$$Mn_3O_4\% = \frac{1,58 \cdot 100}{3,15} = 50,1\%$$

$$Mn_2O_3\% = 100 - 99,3 = 0,7\%$$

At the determination the following two circumstances must be carefully taken into consideration:

1. In the paper referred to (4) it was mentioned that in the presence of large amounts of Mn_3O_4 and slight ones of MnO_2 and/or Mn_2O_3 on heating the mixture in the free air for three hours Mn_3O_4 does not completely transform into Mn_2O_3 . If therefore, the sample contains a large amount of hausmannite and presumably only a slight quantity of pyrolusite or manganite then the heating for three hours in nitrogen is enough, but the heating in the free air of the half of the heated sample which follows must last at least 24 hours, more exactly it is advisable to heat it to constant weight. If on the other hand, pyrolusite, manganite and psilomelane dominate then both the heating in nitrogen and the following one in air at 700° C need not exceed three hours. For pure manganese ores about 0,3—0,5 g is sufficient.

2. At the volumetric determination of the active oxygen content the error is $\pm 0,2$ per cent. This does not represent an essential error, in the determination of the chemical composition, but an inaccurate determination of the different values an essential error in the determination of the mineral composition can be cause, both if the method with the diagramm, or the previously mentioned more simple one is used. The fluctuation $\pm 0,2$ per cent of the ΔO values — on the basis of which the mineral composition is determined — represents at the determination of the quantity of MnO_2 , a fluctuation of $\pm 2,5$ per cent and at that of the quantity of Mn_3O_4 , a fluctuation of $\pm 6,4$ per cent. For an informative determination this is suitable and even more precise than the measurements carried out by means of the recording micrometer stage the more so as a picture is gained of the average mineral composition of the whole substance and not only of the composition observed in the plane of the ore section as on using the recording micrometer stage. However, if we want to be very precise examinations carried out parallel should be made and the mean value of their results should be used for the calculation.

References:

1. Grasselly, Gy.: Acta Mineralogica—Petrographica Univ. Szegediensis Tom. VIII. 1955. 13—26.
2. Földvári—Vogl, M., Koblencz, V.: Acta Mineralogica—Petrographica Univ. Szegediensis Tom. IX. 1956. 7—14.
3. Grasselly, Gy., Klivényi, E.: Acta Mineralogica—Petrographica Univ. Szegediensis Tom. IX. 1956. 15—32.
4. Grasselly, Gy., Klivényi, E.: Acta Mineralogica—Petrographica Univ. Szegediensis Tom. IX. 1956. 33—40.

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