

CONCERNING THE THERMAL PROPERTIES OF THE MANGANESE OXIDES OF HIGHER VALENCIES

By

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Introduction.

As regards the dependence upon the temperature of the stability of the three manganese oxides (Mn_3O_4 , Mn_2O_3 , MnO_2) of higher valency — not taking into account the different modifications of the single oxides — according to the literature it was established that on heating in the open air MnO_2 is only stable at temperatures below $500^\circ C$, and transforms at 550 — $600^\circ C$ with loss of oxygen into Mn_2O_3 , and this oxide in turn transforms at a temperature exceeding $940^\circ C$ with further loss of oxygen into Mn_3O_4 . Mn_2O_3 is namely stable at a temperature range of 530 — $940^\circ C$, whereas at higher temperatures all manganese oxides transform into Mn_3O_4 .

Whilst concerning the properties of the individual manganese oxides, as well as of those of the different iron oxide—manganese oxide systems fairly detailed investigations can be found in the literature, no reference is made regarding the interaction of the manganese oxides of different rate of oxidation. The question is not only of theoretical interest. If namely the interpretation of the mineral associations forming in the course of the metamorphism of the sedimentary manganese deposits should be attempted the examination of the interaction of the manganese oxides of different rate of oxidation, as function of the change of temperature ought to be carried out. On examining minerals of the manganese ore occurrences one of us already thought of performing such examinations.

It seemed expedient first to carry out the examinations on artificial well defined substances and on their mixtures the proportion of which was known. These circumstances seemed to ensure the reduction to a minimum of the interfering conditions due to the use of natural substances which could be expected, but not always controlled. The employment of pure artificial manganese oxides the composition of which corresponds to their formula warrants that the change in the composition and in the percentile quantity of the active oxygen is exclusively the result of the heat treatment determined and controlled by the investigators and only the function of the change which takes place in the rate of oxidation of the starting system.

Hence the purpose of the present study is to examine the thermal behaviour of the manganese oxides of different valency, in the first place in order to reveal the interaction they exert in the course of the heat treatment.

Experimental results and their evaluation

A. Pure substances: MnO_2 , Mn_2O_3 , Mn_3O_4

The behaviour in the course of the heat treatment at different temperatures of the pure components corresponded to what was anticipated according to the data reported in the literature.

MnO_2 already loses an appreciable amount oxygen at $460^\circ C$ and is present as ideal Mn_2O_3 at a temperature range of $670-880^\circ C$. Above this temperature starts with further loss of oxygen its transformation into Mn_3O_4 . The transformation can be considered to be complete at a temperature exceeding $1050^\circ C$. At the starting point the composition of MnO_2 is $MnO_{1,983}$ and that of the sample ignited at $1050^\circ C$ $MnO_{1,346}$, i. e. $Mn_3O_{4,028}$.

At the starting point the composition of Mn_2O_3 is $MnO_{1,502}$, i. e. $Mn_2O_{3,004}$. On increasing the temperature no difference in the composition of the heat treated samples was detected at temperatures not exceeding $880^\circ C$. At this temperature the transformation into Mn_3O_4 — associated with loss of oxygen — starts and can be considered to be complete at $1050^\circ C$. The composition of the sample heated at the latter temperature is $MnO_{1,335}$, i. e. $Mn_3O_{4,005}$.

In the course of the treatment at different temperatures Mn_3O_4 showed as expected fluctuations in its composition which remained, however, between the limits of error of measurements, but it did not show any fluctuations which could be attributed to changes due to the rate of oxidation of the substance. Its composition — $MnO_{1,335}$, i. e. $Mn_3O_{4,005}$ — appears to be constant at a temperature range of $20-1050^\circ C$.

Taking the results and the diagrams illustrating them into account the transformation of MnO_2 into Mn_3O_4 at the given temperature is apparently slower and less complete than that of Mn_2O_3 . This fact can easily be explained by the differences in the size of the granules. Under the conditions of its preparation MnO_2 is coarsely crystalline, whereas in comparison to the latter the physical condition of Mn_2O_3 is far more finely crystalline.

According to the literature in the case of systems with two components it may be anticipated that until the temperature does not exceed $880-900^\circ C$ a change will only occur in the systems which also contain MnO_2 as according to the reports of various authors as well as to the data illustrated on the Fig. 1. until this temperature both Mn_2O_3 and Mn_3O_4 are stable. Furthermore it may also be expected that the change in the extent of the rate of oxidation is in proportion with the amount of the only variable component — MnO_2 — present in the system. According to the above the same would hold for the systems containing all the three oxides of higher valency too, as this establishment served as starting point for the determination of the composition of $MnO_2-Mn_2O_3-Mn_3O_4$ systems carried out by one of us. The results of the present work point to the fact that certain amendments concerning the work referred to must be carried out.

Table 1

The change of the composition of the pure components depending upon the temperature.

Samples		°C							
		20°	460°	560°	670°	780°	880°	980°	1050°
MnO ₂	Mn	63,39	69,05	69,34	69,47	69,64	69,57	70,02	71,81
	O	36,61	30,95	30,66	30,53	30,36	30,43	29,98	28,19
	Mn/O	MnO _{1,980}	MnO _{1,537}	MnO _{1,517}	MnO _{1,508}	MnO _{1,496}	MnO _{1,500}	MnO _{1,468}	MnO _{1,346}
Mn ₂ O ₃	Mn	69,54	69,54	69,54	69,54	69,54	69,60	71,60	71,99
	O	30,46	30,46	30,46	30,46	30,46	30,40	28,40	28,01
	Mn/O	MnO _{1,502}	MnO _{1,502}	MnO _{1,502}	MnO _{1,502}	MnO _{1,502}	MnO _{1,499}	MnO _{1,361}	MnO _{1,335}
Mn ₃ O ₄	Mn	71,97			71,91		71,99		71,97
	O	28,03			28,09		28,01		28,03
	Mn/O	MnO _{1,335}			MnO _{1,339}		MnO _{1,335}		MnO _{1,335}

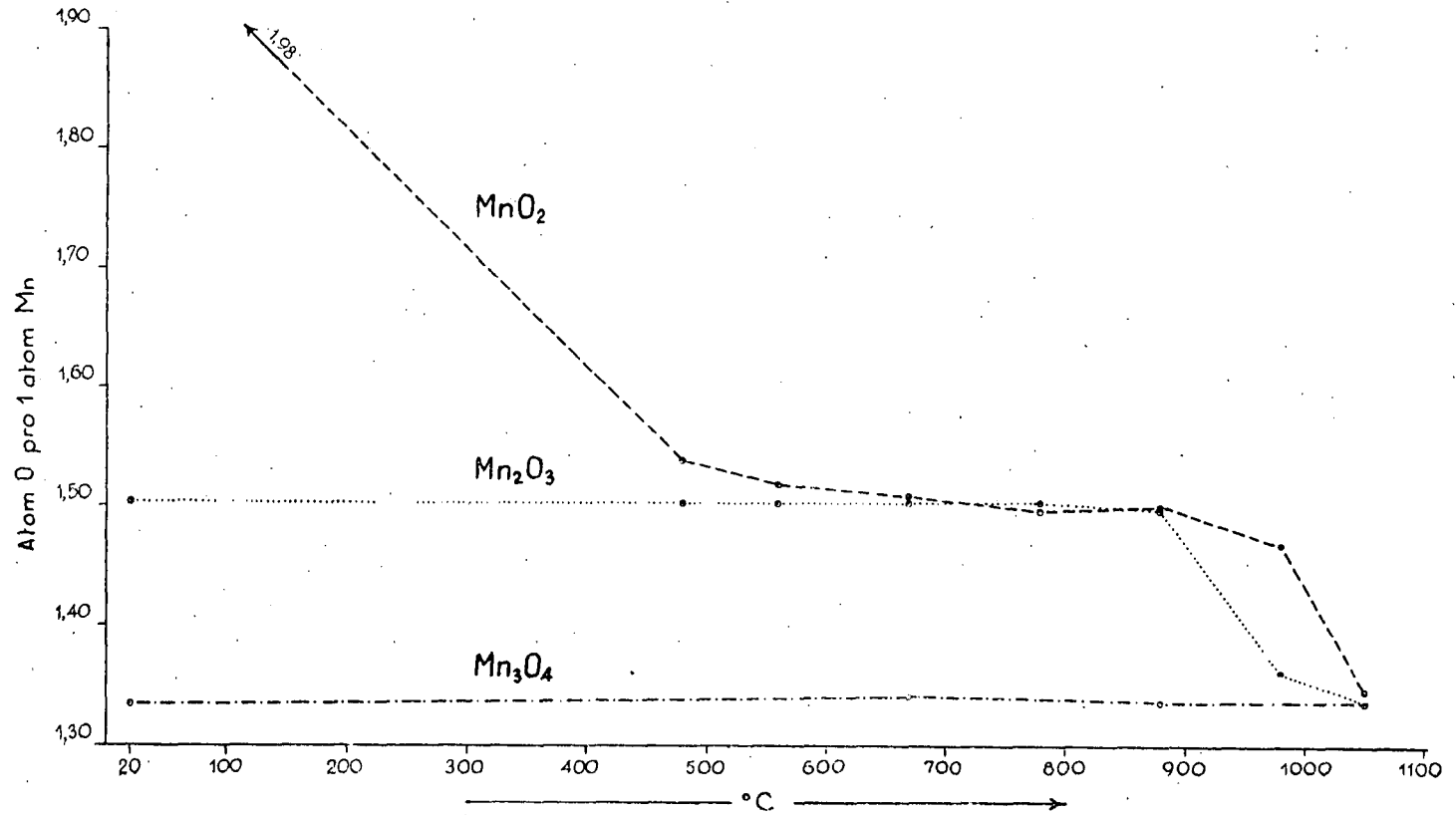


Fig. 1.
The change of the Mn:O ratio of the individual oxide
depending upon the temperature,

Table 2.
The change of the composition of the examined mixtures depending upon the temperatures.

Samples		°C		20°			460°			560°			670°			780°			880°			980°			1050°				
				C _C	C _F	Δ	C _C	C _F	Δ	C _C	C _F	Δ	C _C	C _F	Δ	C _C	C _F	Δ	C _C	C _F	Δ	C _C	C _F	Δ	C _C	C _F	Δ		
I	MnO ₂	1	25% +	Mn	67,98	69,42	69,37		69,49	69,33		69,53	69,47		69,57	69,62		69,59	69,61		71,21	71,29		71,94	72,08				
				O	32,02	30,58	30,63	+0,05	30,51	30,67	+0,16	30,47	30,53	+0,06	30,43	30,38	-0,05	30,41	30,39	-0,02	28,79	28,71	-0,08	28,06	27,92	-0,14			
				Mn/O	MnO _{1,616}	MnO _{1,514}			MnO _{1,517}			MnO _{1,508}			MnO _{1,497}			MnO _{1,498}			MnO _{1,381}			MnO _{1,329}					
	+	Mn ₂ O ₃	2	50% +	Mn	66,56	69,30	69,44		69,44	69,36		69,51	69,68		69,59	69,63		69,59	69,59		70,81	70,98		71,91	71,91			
					O	33,44	30,70	30,56	-0,14	30,56	30,64	+0,08	30,49	30,32	-0,17	30,41	30,37	-0,04	30,41	30,41	±0,00	29,19	29,02	-0,17	28,09	28,09	±0,00		
					Mn/O	MnO _{1,724}	MnO _{1,510}			MnO _{1,516}			MnO _{1,493}			MnO _{1,497}			MnO _{1,500}			MnO _{1,402}			MnO _{1,340}				
			3	75% +	Mn	64,85	69,18	69,21		69,40	69,33		69,49	69,45		69,62	69,58		69,58	69,50		70,42	70,30		71,86	71,84			
					O	35,15	30,82	30,79	-0,03	30,60	30,67	+0,07	30,51	30,55	+0,04	30,38	30,42	+0,04	30,42	30,50	+0,08	29,58	29,70	+0,12	28,14	28,16	+0,02		
					Mn/O	MnO _{1,859}	MnO _{1,525}			MnO _{1,517}			MnO _{1,508}			MnO _{1,503}			MnO _{1,506}			MnO _{1,449}			MnO _{1,345}				
II	MnO ₂	1	25% +	Mn	69,67	71,24	70,12		71,26	69,73		71,30	69,51		71,34	69,40		71,39	69,70		71,49	71,36		71,93	72,00				
				O	30,33	28,76	29,88	+1,12	28,74	30,27	+1,53	28,70	30,49	+1,79	28,66	30,60	+1,96	28,61	30,30	+1,69	28,51	28,64	+0,13	28,07	28,00	-0,07			
				Mn/O	MnO _{1,494}	MnO _{1,462}			MnO _{1,489}			MnO _{1,508}			MnO _{1,513}			MnO _{1,492}			MnO _{1,377}			MnO _{1,335}					
	+	Mn ₂ O ₄	2	50% +	Mn	67,62	70,52	69,85		70,63	69,61		70,70	69,59		70,78	69,60		70,79	69,59		71,00	71,38		71,90	72,01			
					O	32,38	29,48	30,15	+0,67	29,37	30,39	+1,02	29,30	30,41	+1,11	29,22	30,40	+1,18	29,21	30,41	+1,20	29,00	28,72	-0,38	28,10	27,99	-0,11		
					Mn/O	MnO _{1,643}	MnO _{1,450}			MnO _{1,497}			MnO _{1,499}			MnO _{1,499}			MnO _{1,500}			MnO _{1,376}			MnO _{1,338}				
			3	75% +	Mn	65,40	69,78	69,29		69,99	69,47		70,08	69,59		70,21	69,61		70,18	69,51		70,51	71,80		71,85	71,94			
					O	34,60	30,22	30,71	+0,49	30,01	30,53	+0,52	29,92	30,41	+0,49	29,79	30,39	+0,60	29,82	30,49	+0,67	29,49	28,20	-1,29	28,15	28,06	-0,09		
					Mn/O	MnO _{1,816}	MnO _{1,520}			MnO _{1,508}			MnO _{1,499}			MnO _{1,498}			MnO _{1,505}			MnO _{1,348}			MnO _{1,338}				
III	Mn ₂ O ₃	1	25% +	Mn	71,27	71,37	70,64		71,32	69,60		71,32	69,30		71,32	69,58		71,40	69,72		71,88	71,87		71,98	71,88				
				O	28,73	28,63	29,36	+0,73	28,68	30,40	+1,72	28,68	30,70	+2,02	28,68	30,42	+1,74	28,60	30,28	+1,68	28,12	28,13	+0,01	28,02	28,12	+0,10			
				Mn/O	MnO _{1,383}	MnO _{1,427}			MnO _{1,499}			MnO _{1,519}			MnO _{1,503}			MnO _{1,491}			MnO _{1,343}			MnO _{1,343}					
	+	Mn ₂ O ₄	2	50% +	Mn	70,69	70,76	70,01		70,73	69,56		70,73	69,43		70,73	69,55		70,80	69,68		71,79	71,81		71,99	72,08			
					O	29,31	29,24	29,99	+0,75	29,27	30,44	+1,17	29,27	30,57	+1,30	29,27	30,45	+1,18	29,20	30,32	+1,12	28,21	28,19	-0,02	28,01	27,92	-0,09		
					Mn/O	MnO _{1,422}	MnO _{1,469}			MnO _{1,502}			MnO _{1,511}			MnO _{1,501}			MnO _{1,493}			MnO _{1,346}			MnO _{1,329}				
			3	75% +	Mn	70,04	70,15	69,39		70,14	69,50		70,14	69,37		70,14	69,58		70,20	69,40		71,69	71,57		71,98	71,96			
					O	29,96	29,85	30,61	+0,76	29,86	30,50	+0,64	29,86	30,63	+0,77	29,86	30,42	+0,56	29,80	30,60	+0,80	28,31	28,43	+0,12	28,02	28,04	+0,02		
					Mn/O	MnO _{1,468}	MnO _{1,514}			MnO _{1,505}			MnO _{1,514}			MnO _{1,503}			MnO _{1,513}			MnO _{1,362}			MnO _{1,337}				
IV	MnO ₂	1	20% +	Mn	69,40	70,66	69,70		70,68	69,61		70,71	69,80		70,75	69,62		70,79	69,73		71,47	71,84		71,95	72,00				
				O	30,60	29,34	30,30	+0,96	29,32	30,39	+1,07	29,29	30,20	+0,91	29,25	30,38	+1,13	29,21	30,27	+1,06	28,53	28,16	-0,37	28,05	28,00	-0,05			
				Mn/O	MnO _{1,513}	MnO _{1,491}			MnO _{1,497}			MnO _{1,485}			MnO _{1,497}			MnO _{1,490}			MnO _{1,345}			MnO _{1,335}					
	+	Mn ₂ O ₃	2	50% +	Mn	66,84	69,78	69,12		69,91	69,55		69,98	69,68		70,06	69,57		70,07	69,63		70,88	71,80		71,90	71,98			
					O	33,16	30,22	30,88	+0,66	30,09	30,45	+0,36	30,02	30,32	+0,30	29,94	30,43	+0,49	29,93	30,37	+0,44	29,12	28,20	-0,92	28,10	28,02	-0,08		
					Mn/O	MnO _{1,703}	MnO _{1,533}			MnO _{1,502}			MnO _{1,493}			MnO _{1,490}			MnO _{1,497}			MnO _{1,348}			MnO _{1,335}				
			3	40% +	Mn	67,94	70,32	69,43		70,41	69,61		70,46	69,81		70,53	69,62		70,55	69,57		71,11	71,72		71,91	71,98			
					O	32,06	29,68	30,57	+0,89	29,59	30,39	+0,80	29,54	30,39	+0,85	29,47	30,38	+0,91	29,45	30,43	+0,98	28,89	28,28	-0,51	28,09	28,02	-0,07		
					Mn/O	MnO _{1,619}	MnO _{1,511}			MnO _{1,497}			MnO _{1,498}			MnO _{1,497}			MnO _{1,500}			MnO _{1,353}			MnO _{1,335}				
O atoms pro 1 atom Mn (average)					MnO _{1,496}			MnO _{1,503}			MnO _{1,502}			MnO _{1,500}			MnO _{1,498}			MnO _{1,369}			MnO _{1,356}						
Average composition					Mn ₂ O _{2,992}			Mn ₂ O _{3,006}			Mn ₂ O _{3,004}			Mn ₂ O _{3,000}			Mn ₂ O _{3,000}			Mn ₂ O _{2,996}			Mn ₂ O _{4,107}			Mn ₂ O _{4,008}			

C_C = composition calculated
C_F = composition found on the basis of the measuring
Δ = difference between the values calculated and found.

*B. Systems not containing Mn₃O₄
MnO₂—Mn₂O₃ systems*

In view of the above facts it could be anticipated that in the case of the different mixtures at any temperature not exceeding the critical temperature of 800—900°C the Mn₂O₃ component of the system remains unchanged, whereas the loss of oxygen of the MnO₂ component already starts at 460°C and it also transforms completely at a temperature exceeding 560—600°C into Mn₂O₃, i. e. instead of two phases the system will have only one which will transform at higher temperature into Mn₃O₄.

Table 2. shows the change of the composition of the various mixtures due to the heat treatment. The heading »found composition« (C_F) shows the actually measured values recalculated to 100 per cent, whereas the »calculated composition« (C_C) heading — considering according to the above, at temperatures not exceeding 880° C merely MnO₂ and from this temperature on also Mn₂O₃ to be variable — contains the calculated composition. The calculations were based partly on the composition of the given mixture (i. e. whether it contained 25, 50 or 75 per cent of the variable component) and on the extent of the change observed in the composition of the single pure components at the various temperature values (Table 1.) For the establishment of the calculated compositions only the composition of Mn₃O₄ was considered at all temperatures to remain unchanged.

Taking the change of the mixtures (I) demonstrated on Table 2. into consideration on comparing the actually found oxygen values with the calculated ones — based on the above consideration — it can be established that at any temperature in the case of all mixtures both values agree well within the limits of error. (Concerning the remark about the limit of error see the experimental part.) In the case of these mixtures too the transformation towards the composition of Mn₂O₃ already starts at 460°C and at temperatures of 600—800°C Mn₂O₃ is present almost in a homogeneous state independently of the mixture ratio as this was also confirmed by the X-ray examinations.

The established mean values of the Mn:O ratios of the various mixtures at 670—880°C:

25 per cent MnO ₂ — 75 per cent Mn ₂ O ₃	MnO _{1.501}
50 per cent MnO ₂ — 50 per cent Mn ₂ O ₃	MnO _{1.496}
75 per cent MnO ₂ — 25 per cent Mn ₂ O ₃	MnO _{1.503}

The average value of the values of the Mn:O ratios of all these mixtures obtained at the above temperatures is: MnO_{1.500}, i. e. in the above temperature limits the mixture transformed independently of the original composition uniformly into Mn₂O₃. Of the above mixtures the one the starting composition of which was 75 per cent MnO₂ and 25 per cent Mn₂O₃ was found on the basis of X-ray investigation of a sample heated at 780° C to be identical with the pure starting Mn₂O₃.

Although the chemical analysis and the X-ray examinations confirm unequivocally that after heating at 670—880°C the original mixtures may be considered to be homogeneous Mn₂O₃, nevertheless at the transformation of this system into Mn₃O₄ which starts at 980°C, the MnO₂ content of the starting mixture exerts an influence. Hence after having been heated at

980°C the composition of the original mixture of 25 per cent MnO_2 and 75 per cent Mn_2O_3 is $\text{MnO}_{1,381}$ and that of the 50 per cent mixture $\text{MnO}_{1,402}$ and finally that of the mixture containing 75 per cent MnO_2 $\text{MnO}_{1,449}$, although according to the above on being heated at 670—880°C the composition of each mixture including a fluctuation within the limit of error was $\text{MnO}_{1,500}$. On the other hand, in the case of the samples heated at 980°C the Mn:O ratio shifts always more in favour of O the more MnO_2 is contained in the starting substance. This seems to be due to the fact — as has already been mentioned above with reference to the pure substances — that not only the starting MnO_2 material is coarser crystalline as compared to the starting Mn_2O_3 one, but that the same holds too for Mn_2O_3 transformed from MnO_2 . Hence in spite of the fact that chemical and X-ray examinations have shown that at a temperature of 880°C only Mn_2O_3 is present, at higher temperatures than this when the transformation into Mn_2O_3 has already started, the difference of the size of the granules results in the originally finely granular Mn_2O_3 giving off also as mixture its oxygen more rapidly and also transforming quicker into Mn_3O_4 than Mn_2O_3 which has larger granules and formed from MnO_2 .

C. Systems also containing Mn_3O_4

1. MnO_2 — Mn_3O_4 systems

The examinations of the pure substances show that Mn_3O_4 remains unchanged in the course of the heating. The literature also refers to this oxide as being at high temperatures a stable oxide of manganese. Thus it could be anticipated that like in that of the above mixtures in this case also only the MnO_2 component of the mixture will undergo a change and that the change in the Mn:O ratio will be in proportion with the MnO_2 content of the mixture. Taking this into account from the composition of the pure components determined at the given temperature the anticipated Mn and O content, respectively, was calculated at the given temperatures. (Table (2. II.)). The measurements showed that at 400°C a transformation towards the ideal $\text{MnO}_{1,500}$ composition also sets in here. There are still essential differences in the composition of the starting mixtures (20°C) but at the above mentioned temperature these differences are already far smaller and all tend towards $\text{MnO}_{1,500}$. The composition of the heat treated mixtures at a temperature range of 560—880°C again corresponds to the composition of Mn_2O_3 .

At the individual mixtures the mean values of the Mn:O ratios established for substances heated at 670—780—880°C are as follows:

25 per cent MnO_2 — 75 per cent Mn_3O_4	$\text{MnO}_{1,503}$
50 per cent MnO_2 — 50 per cent Mn_3O_4	$\text{MnO}_{1,499}$
75 per cent MnO_2 — 25 per cent Mn_3O_4	$\text{MnO}_{1,500}$

The average of the values of the Mn:O ratios of all these mixtures obtained at the above temperatures is $\text{MnO}_{1,500}$, i. e. between the above temperature limits independently of the original composition the mixtures transformed uniformly into Mn_2O_3 . Of the above mixtures the one containing originally 50 per cent of MnO_2 and 50 per cent Mn_3O_4 which was heated at 780°C proved according to X-ray examinations to be identical with pure Mn_2O_3 .

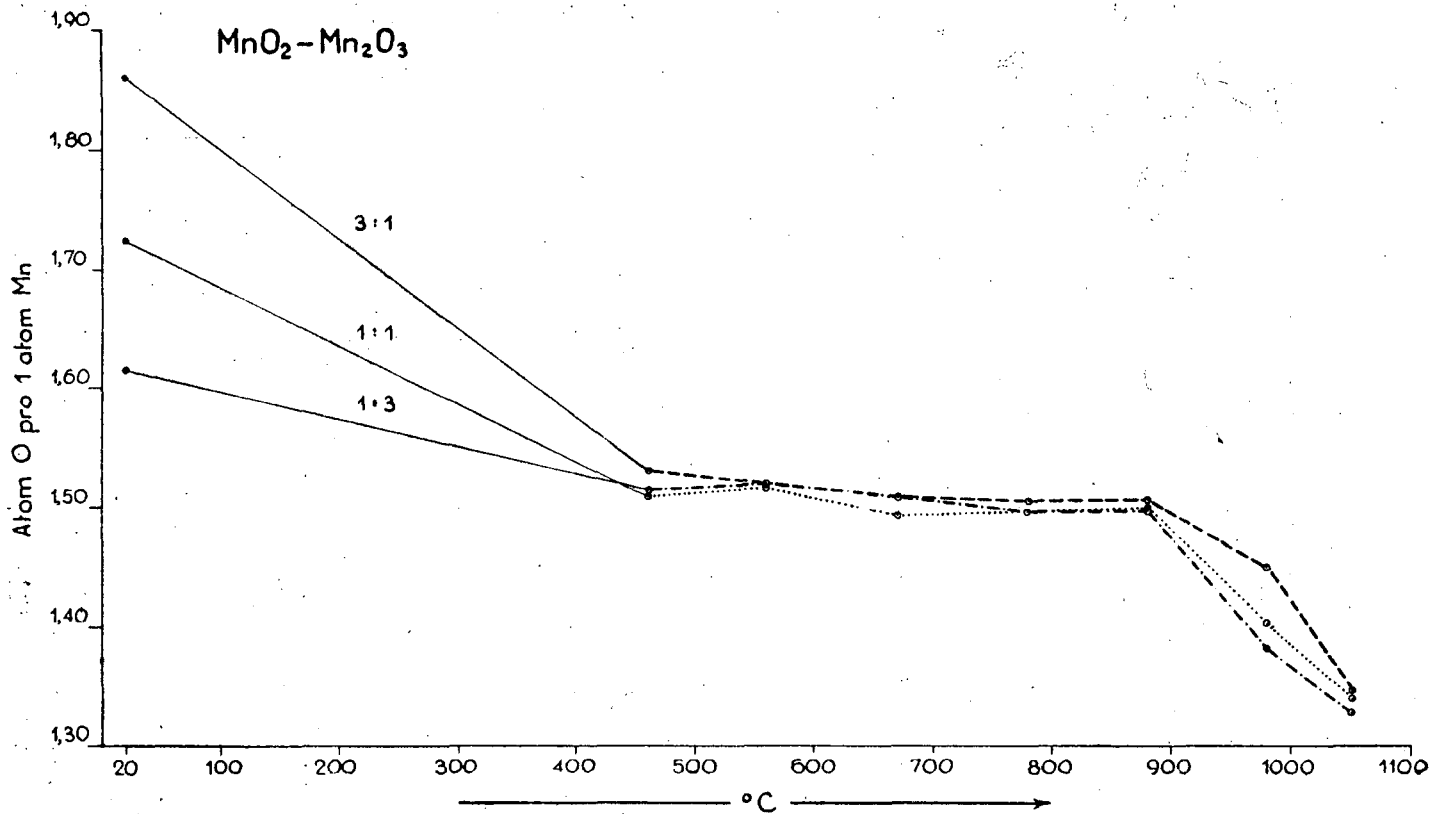


Fig. 2.
The change of the Mn:O ratio of the MnO₂-Mn₂O₃ systems depending upon the temperature.

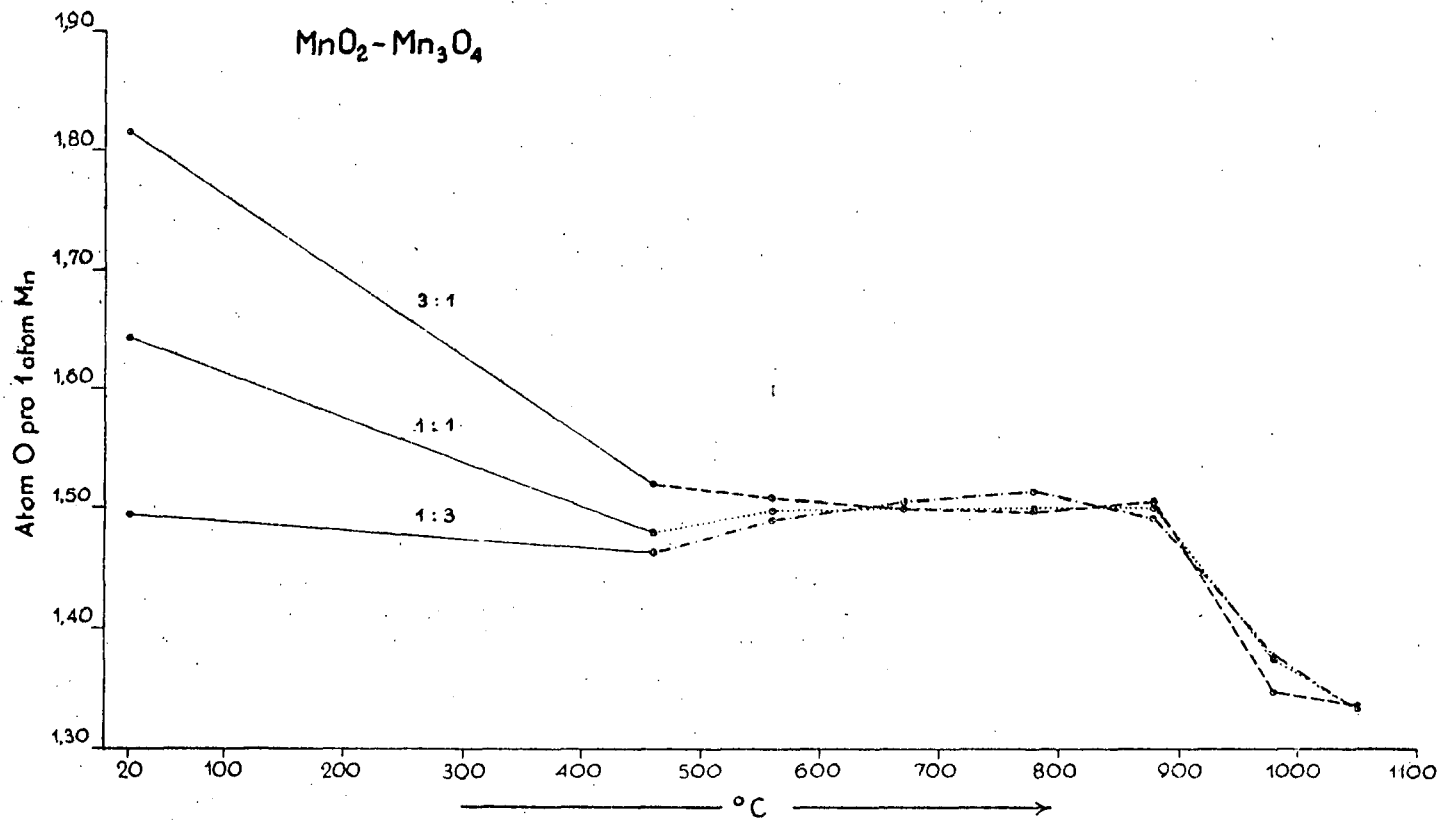


Fig. 3.
The change of the Mn:O ratio of the $\text{MnO}_2\text{-Mn}_3\text{O}_4$ systems
depending upon the temperature.

2. Mn_2O_3 — Mn_3O_4 systems

According to the primary assumption and the behaviour of the single pure components in the course of the heat treatment of the given systems until the temperature does not exceed 880°C no change in the rate of oxidation can be expected as at a temperature range of 20 — 1050°C the Mn_3O_4 component and at one of 880°C the Mn_2O_3 one remain unchanged. The differences between of the calculated and experimentally established values as well as those of the composition of the heat treated mixtures prove on the other hand — as has also been experienced so far — that whatever may be the composition of the original mixture its Mn:O ratio begins already at 460°C to shift and at 560°C the transformation of the mixture into Mn_2O_3 can already be considered to be almost complete, this composition remains unchanged until 880°C . (Table 2. III.)

The mean value of the Mn:O ratios of the individual mixtures measured at 670 — 780 — 880°C :

25 per cent Mn_2O_3 — 75 per cent Mn_3O_4	$MnO_{1,503}$
50 per cent Mn_2O_3 — 50 per cent Mn_3O_4	$MnO_{1,501}$
75 per cent Mn_2O_3 — 25 per cent Mn_3O_4	$MnO_{1,510}$

The mean value of the values of the Mn:O ratios of the mixtures — obtained at the above temperature — is: $MnO_{1,503}$, i. e. between the above temperature limits independently of their composition these mixtures transformed uniformly into Mn_2O_3 too. Of the mixtures the sample containing an original composition of 25 per cent Mn_2O_3 and 75 per cent Mn_3O_4 , heated at 780°C proved also according to the X-ray examinations to be identical with pure Mn_2O_3 .

3. MnO_2 — Mn_2O_3 — Mn_3O_4 systems

So far the establishments concerning the behaviour of the binary systems also hold good for those with three components. When the temperature exceeds 880°C not only MnO_2 transforms with loss of oxygen into Mn_2O_3 , but the Mn_3O_4 present does this too consuming oxygen. On the basis of the chemical analysis the mixtures of different compositions can already at a temperature exceeding 560°C be considered to be homogeneous Mn_2O_3 , this is confirmed by X-ray examinations of a mixture heated to 780°C the original composition of which was 50 per cent MnO_2 , 30 per cent Mn_2O_3 and 20 per cent Mn_3O_4 .

The mean values of the Mn:O ratios established with mixtures heated at 670 — 780 — 880°C also point to the fact that at this temperature independently of their original composition the mixtures transform into Mn_2O_3 , i. e. not only MnO_2 was reduced to Mn_2O_3 , but Mn_3O_4 also oxidised to it. (Table 2. IV.)

20 per cent MnO_2 — 30 per cent Mn_2O_3 — 50 per cent Mn_3O_4	$MnO_{1,490}$
50 per cent MnO_2 — 30 per cent Mn_2O_3 — 20 per cent Mn_3O_4	$MnO_{1,496}$
40 per cent MnO_2 — 20 per cent Mn_2O_3 — 40 per cent Mn_3O_4	$MnO_{1,498}$

The mean value of the Mn:O ratios of the mixtures obtained at the above temperatures is $MnO_{1,494}$, i. e. within the limit of error all correspond to the composition of Mn_2O_3 .

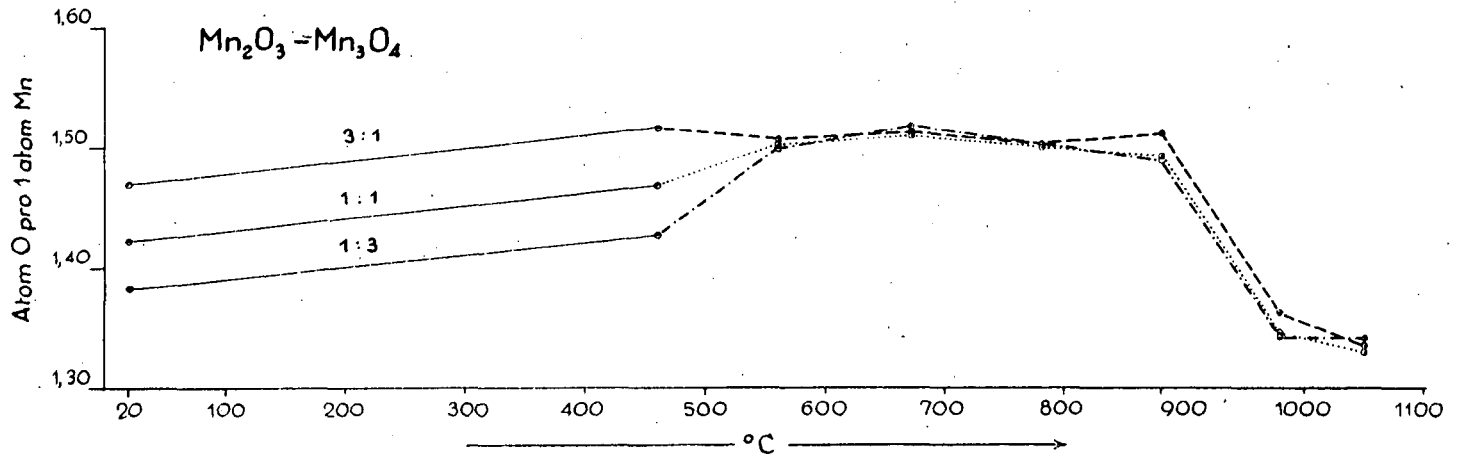


Fig. 4:
The change of the Mn:O ratio of the $Mn_2O_3 - Mn_3O_4$ systems
depending upon the temperature.

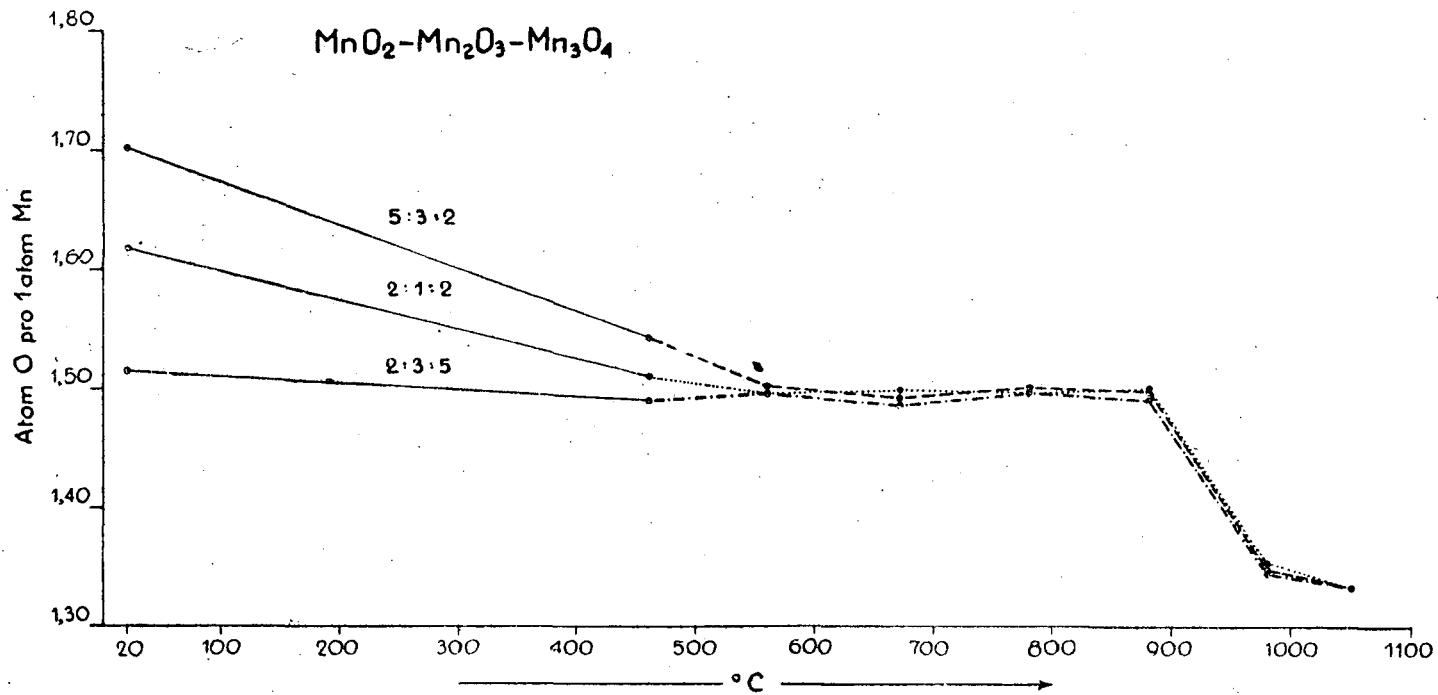


Fig. 5.
The change of the Mn:O ratio of the $\text{MnO}_2\text{-Mn}_2\text{O}_3\text{-Mn}_3\text{O}_4$ systems
depending upon the temperature.

Finally if the mean value of the Mn:O ratios of all the samples of the mixtures heated to 670—780—880°C contained in Table 2 is taken value $\text{MnO}_{1,500}$ is obtained corresponding exactly to the composition of Mn_2O_3 . All these experimental facts prove that Mn_3O_4 per se is indeed stable, however, in the presence of other manganese oxides — either MnO_2 or Mn_2O_3 or both — it begins to oxidise at 460°C (the lowest temperature in the course of these examinations) and at temperatures exceeding 560°C oxidises to Mn_2O_3 , to transform finally at temperatures exceeding 950°C again into Mn_3O_4 . The fact that at a temperature range of 670—880°C the systems originally also containig Mn_3O_4 have actually been transformed into one phase systems essentially only containig Mn_2O_3 is supported by the chemical analyses as well as by X-ray examinations. For the carrying out and evaluation of the latter work authors express their sincere thanks to *Mr. K. Sasvári*.

From the above facts a practical conclusion can be drawn. One of the methods of determining manganese gravimetrically is to heat the precipitated manganese dioxide hydrate at a temperature of about 1000°C and to weigh it as Mn_3O_4 . The results of our examinations show that on heating MnO_2 at temperature of about 700°C the ideal Mn_2O_3 composition can be approached far nearer than by heating at 1050°C the composition of Mn_3O_4 . Thus it seems more expedient — if for some reason or other the gravimetical determination of manganese as oxide should be required — not to measure in the course of the determination the precipitate heated to 1000°C as Mn_3O_4 , but in the form of Mn_2O_3 at a temperature of about 700°C.

Against the so far enumerated experimental facts and the conclusions drawn the objection could be raised that the agreement of the composition of the heat treated mixtures with the composition of Mn_2O_3 — based on the chemical analyses — does not necessarily mean that the different mixtures varying in composition transform uniformly into almost homogeneous one phase systems of Mn_2O_3 when heated at a temperature range of 560—880°C. According to this point of view it could at the most be stated definitely that during the heat treatment the original mixture and the single components, respectively, underwent such a change in the state of their oxidation that at the analysis of the heat treated mixture the Mn:O ratio approaches the value of $\text{MnO}_{1,500}$, without that the system containing several components turns into one only containing a single component. It is true that theoretically it may be assumed that of the systems with three components containing the above oxides numerous ones may have compositions in which independently of the proportion of the components the Mn:O ratio the whole mixture may be $\text{MnO}_{1,500}$.

In view of the fact, however, that whatever the composition of the starting system with two or three components might have been when heated at temperature ranges of 560—880°C almost always within the limit of error the composition $\text{MnO}_{1,500}$ was obtained. Thus the conclusion was drawn that the agreement of the composition of the various mixtures after heat treatment at a temperature range of 670—880°C can only be explained by the fact that all mixtures transform at the given temperature range into Mn_2O_3 . This assumption — which was only suggested at the beginning owing to the behaviour of a few samples — has been confirmed by the unequi-

Table 3.

Starting composition of the samples heated at 670°C (three hours)								Mn ₂ O ₃ lit.	
MnO ₂ +Mn ₃ O ₄ 50%+50%		Mn ₂ O ₃ +Mn ₃ O ₄ * 25%+75%		Mn ₂ O ₃		MnO ₂ +Mn ₃ O ₄ 1:1 mol			
(Cr Kα)		(Cr Kα)		(Cr Kα)		(Fe Kα)		sin ² θ _{cr} calc.	hkl
sin ² θ _{cr} meas.	l _{estim}	sin ² θ _{cr} meas.	l _{estim}	sin ² θ _{cr} meas.	l _{estim}	sin ² θ _{cr} meas.	l _{estim}		
0886	2	0904	2—3	0882	2	0871	2—3	0886	112
1464	3—4	1468	4	1460	4	1482	0,25	1476	130 β222
1773	10	1777	12	1771	12	1752	10	1772	222
2049	0,25	2066	0,5	2056	0,25	2071	0,5	—	—
2365	2—3	2365	3	2368	2	2346	2	2363	400
—	—	2958	0,25	—	—	2917	0,25	2953	024
3224	0,25	3192	0,25	3176	0,25	—	—	—	—
3274	2	3254	3	3254	1—2	3241	2	3248	233
—	—	3458	0,25	—	—	—	—	—	—
3558	0,25	3558	0,25	3530	0,25	3538	0,25	3543	224
3844	2	3847	3	3838	2	3829	2—3	3840	150
—	—	4192	0,25	—	—	—	—	—	134
4440	0,5—1	4431	1	4449	0,25	4431	0,5	4430	125
4771	7	4738	8	4735	8	4711	7	4723	044
5035	0,25	5029	0,5—1	5011	0,25	5021	0,25	5020	350
5636	2	5624	2	5618	1	5610	0,5—1	5610	334
5917	0,25	5917	0,5	5882	0,25	—	—	5905	116
6224	3	6219	3—4	6210	2	6204	2	6200	026
6517	6	6512	6—7	6501	6	6503	4—5	6490	145
6816	2	6813	2—3	6792	1—2	6792	1	6793	226
7110	1	7105	2	7097	1	7089	0,5	7089	136
7401	0,25	7401	0,5	7393	0,25	—	—	7383	444
									170
									550

* The same diagram was obtained by examining of the samples (also heated at 670°C) of following original composition: MnO₂ 75% — Mn₂O₃ 25% and MnO₂ 50%
— Mn₂O₃ 30% — Mn₃O₄ 20%.

vocal results of the chemical analyses and has also been proved by the X-ray examinations according to which the samples heated at 780°C regardless of them being originally systems with two or three components and/or their starting composition were after heating essentially homogeneous Mn_2O_3 .

Summarising it can be said that at the critical temperature range (670—800°C) the systems containing also Mn_3O_4 transform into Mn_2O_3 too, when MnO_2 under loss of oxygen and Mn_3O_4 with oxygen consumption transform into Mn_2O_3 and that the original Mn_2O_3 content remains unchanged.

For the elucidation of the question the following considerations may be taken into account.

At the beginning pure MnO_2 is taken which in the course of the heat treatment, e. g. at 880°C transforms completely into Mn_2O_3 .

Using our own pure substances:

The composition of MnO_2 at 20° C.		→	The composition of Mn_2O_3 formed in the course of the heating.	
		880° C		
Mn	63,39 per cent		Mn	69,57 per cent
O	36,61 per cent		O	30,43 per cent

i. e. the change in the oxygen content during the heating amounts to -6.18 per cent. Thus if a mixture containing MnO_2 and Mn_3O_4 components contains 25 per cent MnO_2 a -1,54 per cent, in the case of 50 per cent MnO_2 a -3,09 per cent and finally in that of 75 per cent MnO_2 a -4,63 per cent oxygen change will be undergone by the MnO_2 component, i. e. changes of such extent must be taken into account for the whole mixture if besides the MnO_2 the other component does not change at the given temperature range. This later consideration actually holds good for the MnO_2 — Mn_2O_3 mixtures in which the calculated and experimentally determined values showed very good agreement.

On the other hand, in the case of the MnO_2 — Mn_3O_4 , or Mn_2O_3 — Mn_3O_4 systems the differences between the calculated and found values are far too appreciable than that they could simple be due to errors of measuring, furthermore — and this is very essential — a certain regularity can be detected in the differences. Hence the conclusion can be drawn that a component is responsible for these differences the changing of which has so far not been taking into account.

It has already been mentioned above that in Table 2. the calculated compositions were based on the changes of the pure MnO_2 and at higher temperatures those of the Mn_2O_3 content of the given mixture, and finally on their percentage in the given mixtures. In these calculations Mn_3O_4 is considered to be an always unchanged component. Hence if between the calculated and measured values an essential and what is more important a regular difference can be found for all the mixtures which contain Mn_3O_4 the establishment holds that in the presence of MnO_2 and/or Mn_2O_3 , Mn_3O_4 oxidises.

Let us assume for the following that the initial Mn_3O_4 completely transforms at $880^\circ C$ into Mn_2O_3 (which it never does in itself):

The composition of Mn_3O_4 at $20^\circ C$.

Mn 71,97 per cent
O 28,03 per cent

The composition of the Mn_2O_3 presumably formed in the course of the heat treatment

Mn 69,54 per cent
O 30,46 per cent

i. e. the assumed entire transformation of the pure Mn_3O_4 is associated with an oxygen change of +2.43 per cent. Thus for a mixture containing 25 per cent Mn_3O_4 a change of oxygen of +0.60 per cent, for one containing 50 per cent one of +1.21 per cent and finally for one containing 75 per cent one of +1.82 per cent is involved for the Mn_3O_4 component.

In view of the fact, that in Table 2. in the case of the calculated values at the given temperatures the oxygen changes due to the MnO_2 and at higher temperatures to the Mn_2O_3 components have already been taken into account the difference between the calculated and found values must be ascribed to the change of Mn_3O_4 , all the more as the differences are in proportion with the percentage of Mn_3O_4 in the mixture. If the composition of the initial mixtures of MnO_2 — Mn_3O_4 and Mn_2O_3 — Mn_3O_4 respectively, are considered as well as the differences between the calculated and found oxygen values found at 670 — 780 — $880^\circ C$ and these differences and their mean values respectively compared with the values of the oxygen changes presumably due to the oxidation of Mn_3O_4 the following are obtained:

Mixtures	Differences between the calculated and measured oxygen content at the different temperatures; the mean value of the differences:				The theoretically calculated values derived from the Mn_3O_4 component
	670°	780°	880°	Average	
25% MnO_2 —75% Mn_3O_4	+1,79	+1,96	+1,69	+1,81	+1,82
50% MnO_2 —50% Mn_3O_4	+1,11	+1,18	+1,20	+1,16	+1,21
75% MnO_2 —25% Mn_3O_4	+0,49	+0,60	+0,67	+0,58	+0,60
25% Mn_2O_3 —75% Mn_3O_4	+2,02	+1,74	+1,68	+1,81	+1,82
50% Mn_2O_3 —50% Mn_3O_4	+1,30	+1,18	+1,12	+1,20	+1,21
75% Mn_2O_3 —25% Mn_3O_4	+0,77	+0,56	+0,80	+0,71	+0,60

The good agreement between the mean value of the observed and calculated values points to the fact that the Mn_3O_4 present in the mixture is completely oxidised at the given temperatures. Also in the case of the systems with three components the calculated and measured differences are in good agreement. In the case of the samples heated at $780^\circ C$ and $880^\circ C$ for the mixture containing 40 per cent Mn_3O_4 the found value is +0.91 per cent and +0.98 per cent respectively instead of the calculated +0.97 per cent difference; for the mixture containing 20 per cent Mn_3O_4 the found one is +0.49 per cent and +0.44 per cent respectively, instead of the calculated +0.48 per cent difference; finally for the mixture containing 50 per cent Mn_3O_4 instead of the calculated difference of +1.21 per cent the found differences between the calculated and measured oxygen content are +1.13 per cent and +1.06 per cent respectively.

At the temperatures mentioned MnO_2 gives off oxygen and therefore could be imagined that this oxygen oxidises the Mn_3O_4 . However in the case of a mixture of 25 per cent MnO_2 and 75 per cent Mn_3O_4 the oxygen given off by MnO_2 would be too little to oxidise the whole amount of Mn_3O_4 present in the mixture into Mn_2O_3 , nevertheless, in fact the whole amount is oxidised. If further it is taken into consideration that in the case of the Mn_2O_3 — Mn_3O_4 mixtures under the given temperatures limits Mn_2O_3 does not give off any oxygen and yet in every examined mixture of Mn_3O_4 it was uniformly and completely oxidised into Mn_2O_3 it must be established that the oxidation of Mn_3O_4 in the presence of one or possibly both oxides takes place through the oxygen consumed from the air.

At higher temperatures (880°C) the transformation into Mn_3O_4 of any substance transforming uniformly with loss of oxygen at the given temperature ranges into Mn_2O_3 starts and is almost complete at 1050°C . Among the lower temperature ranges the change was examined at 460°C . At this temperature equilibrium cannot yet be mentioned as MnO_2 has not yet even transformed into Mn_2O_3 , whilst the oxidation of Mn_3O_4 has started, but cannot yet be considered to be complete. Considering the changes taking place at these higher and lower temperatures at which equilibrium has not set in (460 and 980°C respectively) it seems that concerning the rate of the oxidation of Mn_3O_4 and that of the reduction of Mn_2O_3 formed at a temperature range of 560 — 880°C the mixtures containing Mn_3O_4 and also MnO_2 as well as those free of MnO_2 do not behave in the same manner.

Summary

The literature dealing with the thermal behaviour of manganese oxides of different rate of oxidation establishes unequivocally that at 560°C MnO_2 is transformed with loss of oxygen into Mn_2O_3 and that at 950°C it transforms further into Mn_3O_4 , whereas Mn_2O_3 is stable until 950°C , but at temperatures exceeding this also transforms into Mn_3O_4 . Mn_3O_4 is at high temperatures the stable oxide of manganese.

In the course of the examinations the above oxides were not only examined separately, but their mixtures containing in different proportions two and three components, respectively, were also heat treated.

The pure oxides tabulated on Table 1. as well as the mixtures on Table 2. were heat treated at each given temperature in the open air for three hours.

After the heat treatment at each determination the active oxygen content was established. Knowing this and after establishing the MnO content of the starting pure substances and also knowing the proportion of the pure oxides in the single mixtures besides the active O, the MnO content was also given, and the results were always recalculated to 100 per cent. Table 4. shows these results. In the case of each sample taking into account the change in the rate of oxidation in the course of the heating the MnO and active O content of the starting and of the heat treated samples could be observed.

The behaviour of the pure components corresponded to the data in the literature and the mixtures containing MnO_2 — Mn_2O_3 also behaved as anticipated.

On the other hand, the change of the active oxygen content of the mixtures containing Mn_3O_4 — whether MnO_2 or Mn_2O_3 were present alone or both together in addition to the Mn_3O_4 — showed that in the course of the heating Mn_3O_4 does not remain unchanged, but oxidises. The oxidation already starts at the lowest temperature ($460^\circ C$) at which examinations were carried out, what more, at a temperature range of $560-830^\circ C$ it oxidises completely into Mn_2O_3 . Between these temperature limits all examined mixtures independently of their original composition transformed into homogeneous Mn_2O_3 . The chemical analyses as well as X-ray examinations also prove this.

In the course of further examinations on the basis of above results the authors as mentioned above will investigate in detail the mechanism of the oxidation of Mn_3O_4 , as well as deal with the interpretation of the metamorphism of the sedimentary manganese deposits.

Experimental

1. The preparation of the oxides used for the examinations

a) The preparation of MnO_2

To a solution of manganous chloride in concentrated nitric acid solid potassium chlorate is carefully added during the boiling in portions. The manganese dioxide separates soon. When the precipitate has settled a little of the pure solution is taken out and if on adding nitric acid and a small amount of potassium chlorate precipitate still forms the boiling of the solution and the adding of potassium chlorate is continued. During the operation the solution must be constantly stirred. When the precipitation is complete after the precipitate has settled the pure solution is poured off and the precipitate decanted several times with water then it is put onto a filter and washed with water until it reacts neutrally and finally dried at $100^\circ C$. The precipitate obtained in this manner is crystalline and coarsely granular.

b) The preparation of Mn_2O_3

The preparation is started with manganese carbonate. To a dilute boiling aqueous solution of manganous chloride a solution of ammonium carbonate is added until the precipitation is complete and then it is placed for a long time on the water bath. Subsequently it is filtered and the precipitate washed with water until the chloride reaction disappears. The washed pale pink precipitate prepared in this manner is suspended in hot water and a saturated oxalic acid solution is added in small portions to the hot solution until the bubbling stops. After the addition of the oxalic acid the solution must be very acid. The precipitate consisting of $MnC_2O_4 \cdot 2H_2O$ settles rapidly, it is coarsely granular and crystalline, it is filtered and washed with water until the washing liquid reaches the neutral reaction and then dried at $100^\circ C$. The manganous oxalate obtained in this manner is poured into a platinum dish and slowly and carefully heated under continual stirring over an open flame. In the course of the heating a vigorous evolution of gas may be observed when this begins to decrease the

Table 4.
The change of the MnO and O content of the examined samples depending upon the temperature.

Samples		°C		20°		460°		560°		670°		780°		880°		980°		1050°			
				a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b		
MnO ₂		MnO		81,86	89,17	89,15	89,55	89,75	89,72	89,74	89,94	89,94	89,85	89,85	90,43	90,49	92,74	92,95			
		O		18,14	10,83	10,85	10,45	10,25	10,28	10,26	10,06	10,06	10,15	10,15	9,57	9,51	7,26	7,05			
Mn ₂ O ₃		MnO		89,80	89,80	—	89,80	—	89,80	—	89,80	—	89,88	89,97	92,47	92,49	92,97	92,97			
		O		10,20	10,20	—	10,20	—	10,20	—	10,20	—	10,12	10,03	7,53	7,51	7,03	7,03			
Mn ₃ O ₄		MnO		92,94					92,87	—			92,97	—			92,94	—			
		O		7,06					7,13	—			7,03	—			7,06	—			
I	MnO ₂	1	25%+	MnO	87,79	89,59	89,56	89,54	89,52	89,72	89,68	89,91	89,86	89,89	89,84	92,06	92,13	93,08	93,04		
			75%	O	12,21	10,41	10,44	10,46	10,48	10,28	10,32	10,09	10,14	10,11	10,16	7,94	7,87	6,92	6,96		
	+	2	50%+	MnO	85,95	89,67	89,65	89,57	89,54	89,99	89,93	89,92	89,88	89,87	89,83	91,67	91,70	92,86	92,95		
			50%	O	14,05	10,33	10,35	10,43	10,46	10,01	10,07	10,08	10,12	10,13	10,17	8,33	8,30	7,14	7,05		
	Mn ₂ O ₃	3	75%+	MnO	83,75	89,38	89,37	89,54	89,52	89,69	89,68	89,86	89,82	89,75	89,73	90,78	90,80	92,78	92,75		
			25%	O	16,25	10,62	10,63	10,46	10,48	10,31	10,32	10,14	10,18	10,25	10,27	9,22	9,20	7,22	7,25		
II	MnO ₂	1	25%+	MnO	89,97	90,56	90,34	90,05	89,85	89,77	89,60	89,63	89,46	90,01	90,16	92,16	92,26	92,98	92,84		
			75%	O	10,03	9,44	9,66	9,95	10,15	10,23	10,40	10,37	10,54	9,99	9,84	7,84	7,74	7,02	7,16		
	+	2	50%+	MnO	87,33	90,21	90,16	89,89	89,82	89,87	89,79	89,88	89,80	89,87	89,79	92,18	92,19	92,99	92,95		
			50%	O	12,67	9,79	9,74	10,11	10,18	10,13	10,21	10,12	10,20	10,13	10,21	7,82	7,81	7,01	7,05		
	Mn ₃ O ₄	3	75%+	MnO	84,46	89,48	89,48	89,72	89,67	89,87	89,82	89,89	89,83	89,77	89,71	92,72	92,70	92,90	92,88		
			25%	O	15,54	10,52	10,52	10,28	10,33	10,13	10,18	10,11	10,17	10,23	10,29	7,28	7,30	7,10	7,12		
III	Mn ₂ O ₃	1	25%+	MnO	92,04	91,23	91,24	89,88	89,82	89,49	89,44	89,86	89,79	90,04	89,93	92,81	92,76	92,83	92,79		
			75%	O	7,96	8,77	8,76	10,12	10,18	10,51	10,56	10,14	10,21	9,96	10,07	7,19	7,24	7,17	7,21		
	+	2	50%+	MnO	91,29	90,41	90,35	89,83	89,77	89,66	89,60	89,82	89,74	89,99	89,91	92,73	92,70	93,08	93,03		
			50%	O	8,71	9,59	9,65	10,17	10,23	10,34	10,40	10,18	10,26	10,01	10,09	7,27	7,30	6,92	6,97		
	Mn ₃ O ₄	3	75%+	MnO	90,45	89,61	89,60	89,76	89,71	89,58	89,54	89,86	89,80	89,62	89,58	92,42	92,42	92,93	92,90		
			25%	O	9,55	10,39	10,40	10,24	10,29	10,42	10,46	10,14	10,20	10,38	10,42	7,58	7,58	7,07	7,10		
IV	MnO ₂	1	20%	MnO	89,63	90,01	89,96	80,89	89,82	90,14	90,03	89,91	89,83	90,05	89,97	92,78	92,74	92,98	92,94		
			30%	O	10,37	9,99	10,04	10,11	10,18	9,86	9,97	10,09	10,17	9,95	10,03	7,22	7,26	7,02	7,06		
	+	2	50%	MnO	86,32	89,26	89,28	89,82	89,77	89,99	89,92	89,84	89,80	89,92	89,86	92,72	92,70	92,95	92,93		
			30%	O	13,68	10,74	10,72	10,18	10,23	10,01	10,08	10,16	10,20	10,08	10,14	7,28	7,30	7,05	7,07		
	Mn ₃ O ₄	3	40%	MnO	87,74	89,66	89,63	89,89	89,81	89,89	89,82	89,91	89,84	89,85	89,78	92,62	92,60	92,95	92,94		
			20%	O	12,26	10,34	10,37	10,11	10,19	10,11	10,18	10,09	10,16	10,15	10,22	7,38	7,40	7,05	7,06		

a = composition on the basis of the measured active 0% recalculated to 100%.
b = composition on the basis of the active 0% of the weight-change occurred during the heat treatment, as well as on that of MnO contents of the original samples.

substance turns first on the surface and later completely brown, finally the development of gas ceases and the entire so far mobile substance forms a mass and glows mildly. It is cooled put into a porcelain dish and heated for a few hours in an electric oven at 700°C.

c) The preparation of Mn_3O_4

The starting material is manganese (II) — oxalate prepared as above. It is very slowly roasted as above and then placed into a porcelain dish and heated for 3—4 hours at 1050—1100°C in an electric oven.

2. The determination of MnO and the active O

The MnO content of the pure substances was determined both gravimetrically and volumetrically. The mixtures the ratios of which are demonstrated on the Tables (25—50—75 per cent indicates weight per cent) were prepared by precise weighing from the pure substances the MnO content of which was known. The mixtures were suitably homogeneous. Hence the MnO content of the mixtures was calculated on the basis of the MnO content of their components. The active O content of both the pure substances and the mixtures and of the starting materials as well as that of each single heat treated sample was determined by the oxalate method. In the Tables the results are in each case recalculated to 100 per cent thus enabling direct comparison.

3. The heat treatment of the samples

About 0.3 g of both the pure substances and the mixtures was heated for three hours at 460, 560, 780, 880, 980 and 1050°C in an electric oven. At each temperature all the samples were heated simultaneously. The given temperatures were chosen because MnO_2 transforms into Mn_2O_3 at a temperature exceeding 560°C and this is stable until 950°C. Furthermore as the measurements had also to be carried out at temperatures where presumably the transformation between the single rates of oxidation was complete and it seemed desirable to measure the change which ensues in the rate of oxidation as a function of the growing temperature by 100 degrees the above temperature values were obtained. Substances heated for ½, 1, 2, 3, 4 and 5 hours were examined. The results show that the change occurring at the given temperature was already complete after heating for three hours as the difference in the active O content of the substance heated for five and of that heated for three hours was only a difference due to error of measurement. The \pm change in weight was also measured in the case of the heated samples.

4. Calculations

Like at the description of the experimental conditions (described under 2) the MnO and active O content in the Tables was given for each sample recalculated to 100 per cent and from this the Mn and O values were then calculated. In view of the fact that at the preparation of the starting substances pro anal. substances were used besides the MnO and O content of the samples at most the water content could still be involved. For the

recalculation of the composition to 100 per cent there are two possibilities.

The one method of calculation is based on the consideration that as at a temperature of 460°C (the lowest temperature of the examinations) the water content must no more be taken into account it is justified to complete to 100 per cent the active O content determined of the heat treated samples and to identify this addition with the MnO content.

The other method of calculation is based on the MnO and O content of the sample which did not undergo heat treatment as well as on the change of weight measured after heating it at the given temperature. In the course of the heating only the effective oxygen amount of the sample may change, whereas the effective MnO amount remains unchanged only the percentage ratio changes. Thus taking the change of weight into consideration on the basis of the MnO and O content of the starting sample the MnO content of the heated sample is calculated, whilst the active O content is determined directly.

Both values were -within the limits of error- in good agreement as is shown in Table 4.

Table 4. shows at the various temperatures the composition of the examined samples expressed in percentage of MnO and O. For the establishment of the Mn:O ratio these values were recalculated to the Mn and O percentage and then from these values the number of O atoms for 1 manganese atom was calculated. Considering the exactness of the determination of the active oxygen carried out by the oxalate method to be ± 0.20 per cent then the following exactness is obtained for the calculations following the determination of the active oxygen: let the active oxygen content of Mn_2O_3 in an ideal case be 10,14 per cent. Thus on the basis of the above exactness the composition can be

a		A		b	
MnO	89,66%	MnO	89,86%	MnO	90,06%
O	10,34%	O	10,14% $\pm 0,20\%$	O	9,94%

For the calculation of the Mn:O ratio these values are recalculated to Mn and O:

a ₁		A ₁		b ₁	
Mn	69,43%	Mn	69,58%	Mn	69,73%
O	30,57%	O	30,42 $\pm 0,15\%$	O	30,27%
	MnO _{1,511}		MnO _{1,500 $\pm 0,011$}		MnO _{1,489}

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