

ON THE STABILITY OF Mn_3O_4

By

GY. GRASSELLY and E. KLIVÉNYI

(Mineralogical—Petrographical Institute of the University, Szeged)

In a previous work (1) the authors deal with the thermal properties of the systems containing manganese oxides (MnO_2 , Mn_2O_3 , Mn_3O_4) of higher valencies. The examinations were carried out with artificially prepared pure oxides and their mixtures the composition of which was precisely known. The substances were precisely weighed and controlled by chemical analyses and X-ray examinations. The examinations showed that Mn_3O_4 alone is stable at every temperature not exceeding $1050^\circ C$ — the highest temperature employed in the course of the experiments — in the presence of MnO_2 and/or Mn_2O_3 , however it oxidises to Mn_2O_3 and presently at temperatures exceeding $940^\circ C$ gives off oxygen and turns again into Mn_3O_4 . In the course of the solid phase reaction in the presence of MnO_2 and/or Mn_2O_3 — if the experiments are performed in the free air — Mn_3O_4 presumably takes up the oxygen needed for the oxidation from the air.

However, the question arises whether there is some difference in the influence exerted on Mn_3O_4 by MnO_2 and Mn_2O_3 respectively, and if there is some relation between the extent and velocity of the oxygen consumption of Mn_3O_4 and between the ratio of the mentioned two oxides and the latter.

The mixtures employed at the work referred to (1) contained in the case of systems with two components 25, 50, 75 per cent Mn_3O_4 . At a temperature range of 670 — $780^\circ C$ in all the mixtures the Mn_3O_4 transformed into Mn_2O_3 , expressed more precisely the entire originally heterogenous mixture turned into Mn_2O_3 . The $+\Delta O$ values obtained from the results of the measurements associated with the transformation of the component of Mn_3O_4 contained in the mixtures, respectively, the averages of the values obtained at 670 , 780 , $880^\circ C$ are if the amount of Mn_3O_4 present (25, 50, 75 per cent) is taken into account in good agreement — within the limits of error — with the theoretically calculated $+\Delta O$ values.

Fig. 1 shows the change of the active O content of the MnO_2 — Mn_3O_4 and Mn_2O_3 — Mn_3O_4 systems (ΔO per cent) in the 460 — $880^\circ C$ temperature range.

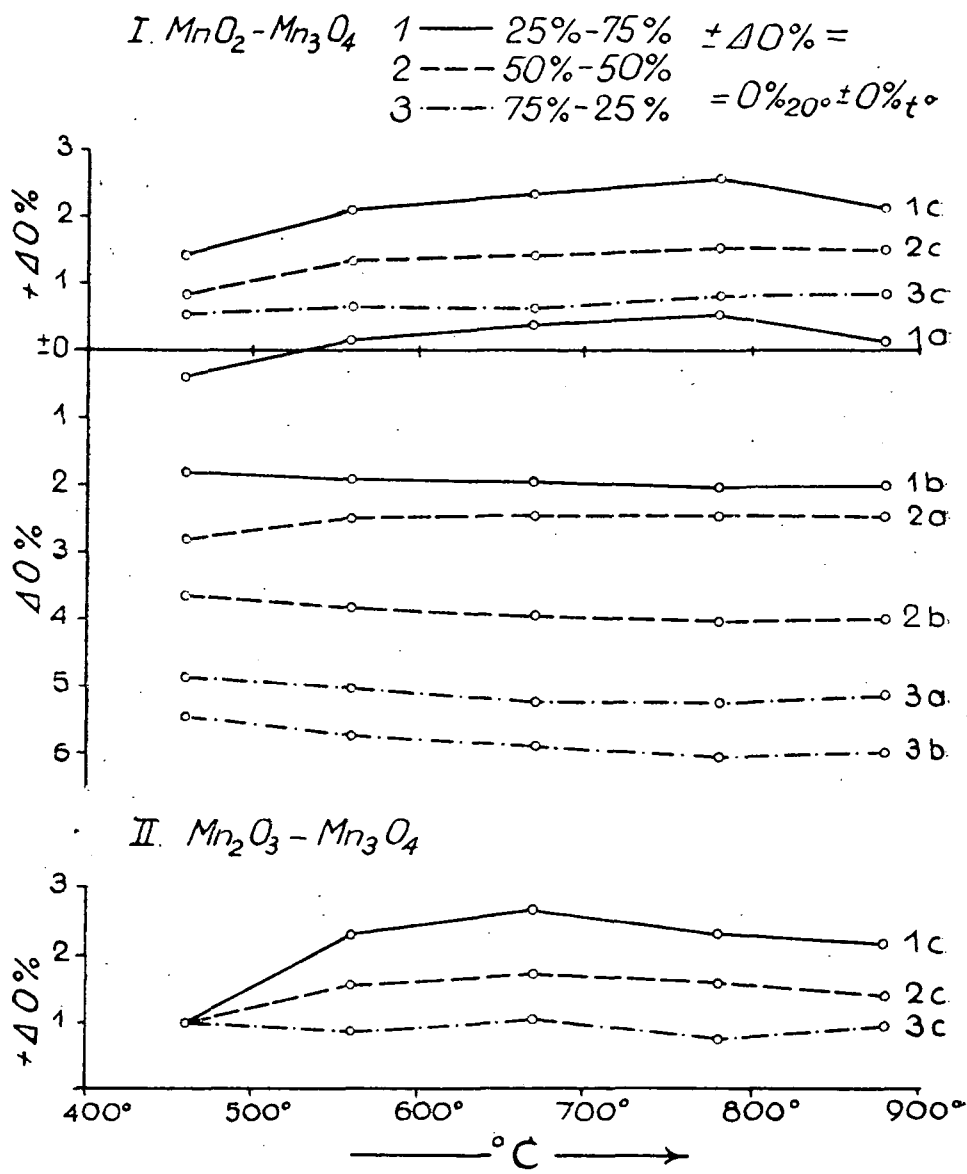


Fig. 1.

The change of the active oxygen content respectively that of the single components (ΔO per cent) of the $MnO_2 - Mn_3O_4$ (I) and $Mn_2O_3 - Mn_3O_4$ (II) systems.

On Fig. 1/I. 1, 2, 3 represent the different mixtures and a denotes the measured active oxygen change of the given mixtures, b denotes the $-\Delta O$ values representing the transformation of the MnO_2 component of the same mixtures, c represents the $+\Delta O$ values proportional to the Mn_3O_4 amount present in the same mixtures.

On Fig. 1/II. 1, 2, 3, again represent the different mixtures, however, in this case curve a denotes identical values as curve c, i. e. the $+\Delta O$ values measured in the mixtures correspond with the $+\Delta O$ values representing the characteristic transformation of the Mn_3O_4 present. At the given temperature range the Mn_2O_3 component does not change the slight change occurring at $880^\circ C$ is negligible, hence curve b coincides with the abscisse.

The Fig. only shows that at the given temperature limits — mainly at $670-880^\circ C$ — the amount of Mn_3O_4 present has already transformed into Mn_2O_3 . The mean values (I) of the $+\Delta O$ values associated with the transformation of Mn_3O_4 measured at $670, 780, 880^\circ C$ are in good agreement with the theoretically calculated corresponding values (II) — assuming that the entire amount of Mn_3O_4 present transforms — this is also illustrated on Table 1.

Table 1.

Samples		I	II
		mean values of the $+\Delta O\%$ measured at $670, 780, 880^\circ C$	$+\Delta O\%$ calculated
$MnO_2 + Mn_3O_4$	25% + 75%	2,37	2,36
	50% + 50%	1,51	1,57
	75% + 25%	0,78	0,78
$Mn_2O_3 + Mn_3O_4$	25% + 75%	2,36	2,36
	50% + 50%	1,54	1,57
	75% + 25%	0,90	0,78

The data contained in the Table and Fig. 1 are based — according to the composition of their pure components — on the calculated active oxygen content of the different mixtures. However, the above Fig. and the previous data only show that Mn_3O_4 transforms completely into Mn_2O_3 , but it is not revealed what influence the components of higher oxidation rate exert on Mn_3O_4 . Namely, in the presence of the given amounts — on heating the different samples at $700^\circ C$ — the active oxygen content of

the mixtures already reaches in the case of some mixtures the oxygen content corresponding to the composition of Mn_2O_3 , provided that the heating was immediately interrupted when the temperature attained $700^\circ C$ (for which about 40 minutes was needed). If on the other hand, the mixtures were kept for 1 hour at a temperature of $700^\circ C$ the active O content measured in the case of the samples treated in this way corresponded for all the mixtures — within the limit of error — with the oxygen content of Mn_2O_3 . If on reaching the temperature of $700^\circ C$ the heating was immediately interrupted the O value corresponding to the composition of Mn_2O_3 was only not attained in the case of the samples containing a larger quantity of Mn_3O_4 .

Table 2.

Samples		The active O% of the samples heated at $700^\circ C$			
		duration of ignition in hours			
		0h	1h	3h	$5\frac{1}{2}h$
MnO_2 + Mn_3O_4	25%+75%	9,81	10,16	10,22	10,20
	75%+25%	10,21	10,21	10,25	10,24
Mn_2O_3 + Mn_3O_4	25%+75%	9,73	10,32	10,18	10,12
	50%+50%	9,98	10,29	10,19	10,15
	75%+25%	10,08	10,20	10,25	10,20
MnO_2 + Mn_2O_3 + Mn_3O_4	20%+30%+50%	10,22	10,23	10,20	10,09
	50%+30%+20%	10,20	—	10,30	10,21

To decide how long the oxidation lasts if the oxides present in addition to the Mn_3O_4 occur in amounts not exceeding 25 per cent the oxidation of Mn_3O_4 was examined at $700^\circ C$ in the presence of 2, 5, 10 per cent MnO_2 and Mn_2O_3 , respectively, as a function of the time of the heating.

Assuming that the Mn_3O_4 present in the mixtures transforms through oxygen consumption from the air completely into Mn_2O_3 , in the mixture containing 98 per cent Mn_3O_4 the oxygen content ought to increase by 3,8 per cent, in the mixture containing 95 per cent it ought to show an increase of 2,99 per cent and finally in the one containing 90 per cent the increase should amount to 2,83 per cent.

It is also obvious that in the case of the MnO_2 — Mn_3O_4 mixtures the transformation of MnO_2 into Mn_2O_3 represents on the contrary to the above increase in the active oxygen content, a reduction of it, i. e. $-\Delta O$. The above examinations showed that at this temperature the transformation of MnO_2 is already complete, hence from the O value measured in the mixture — taking the $-\Delta O$ value corresponding to the quantity of

the MnO_2 present into account — the $+\Delta O$ values associated with the transformation into Mn_2O_3 of the amount of Mn_3O_4 present may be calculated.

If on the other hand, Mn_2O_3 — Mn_3O_4 mixtures are involved the change between the active O content of the starting substance and the heat treated one — which in this case always represents an increase, i. e. $+\Delta O$ — is exclusively in proportion with the amount of the Mn_3O_4 present considering that Mn_2O_3 does not undergo any change at the given temperature. The results of the respective measurements are summarized in Table 3. Fig. 2 shows the change of the ΔO values of the different mixtures as a function of the duration of the heating.

Table 3.

Samples	O ^{0/1000} calc.	the change of the active oxygen content					Remarks		
		duration of ignition at 700° C in hours							
		0	3	12	16	24			
$MnO_2 + Mn_3O_4$	2%+98%	7,27	-0,15	+1,09	+2,55	+2,66	+2,90	a	a: the measured ΔO of the mixtures b: ΔO values concerning the MnO_2 content of the mixtures c: ΔO values concerning the Mn_3O_4 content calculated from a and b.
			-0,13	-0,16	-0,16	-0,16	-0,16	b	
			-0,02	+1,25	+2,71	+2,82	+3,06	c	
	5%+95%	7,60	-0,18	+1,20	+2,26	+2,33	+2,54	a	
			-0,34	-0,41	-0,41	-0,41	-0,41	b	
			+0,16	+1,61	+2,67	+2,74	+2,95	c	
	10%+90%	8,16	-0,25	+1,16	+1,80	+1,93	+1,98	a	
			-0,68	-0,82	-0,82	-0,82	-0,82	b	
			+0,43	+1,98	+2,62	+2,75	+2,80	c	
$Mn_2O_3 + Mn_3O_4$	2%+98%	7,11	+0,16	+0,91	+2,81	+2,87	+2,98	a	
			0	0	0	0	0	b	
			+0,16	+0,91	+2,81	+2,87	+2,98	c	
	5%+95%	7,21	+0,28	+1,49	+2,74	+2,81	+2,94	a	
			0	0	0	0	0	b	
			+0,28	+1,49	+2,74	+2,81	+2,94	c	
	10%+90%	7,37	+0,47	+2,41	+2,66	+2,69	+2,76	a	
			0	0	0	0	0	b	
			+0,47	+2,41	+2,66	+2,69	+2,76	c	

The data of the Table and Fig. respectively, show that in the presence of both MnO_2 and Mn_2O_3 , Mn_3O_4 behaves in a fairly similar manner. Namely, in the case of the corresponding mixture pairs (2 per cent MnO_2 — 98 per cent Mn_3O_4 , respectively 2 per cent Mn_2O_3 — 98 per cent Mn_3O_4 , etc.) the $+\Delta O$ values concerning the change of Mn_3O_4 agree within the

limit of error, although the mixtures illustrated on the Table only attained after heating for 24 hours at a temperature of 700°C the composition corresponding to Mn_2O_3 . As at a temperature of 560°C MnO_2 has essentially already transformed into Mn_2O_3 it seems as if from the point of view of the oxidation of Mn_3O_4 practically only Mn_2O_3 plays a role, MnO_2 itself only takes part inasmuch as that with the rising of the temperature it also transforms into Mn_2O_3 . Mn_3O_4 consumes the oxygen required for its

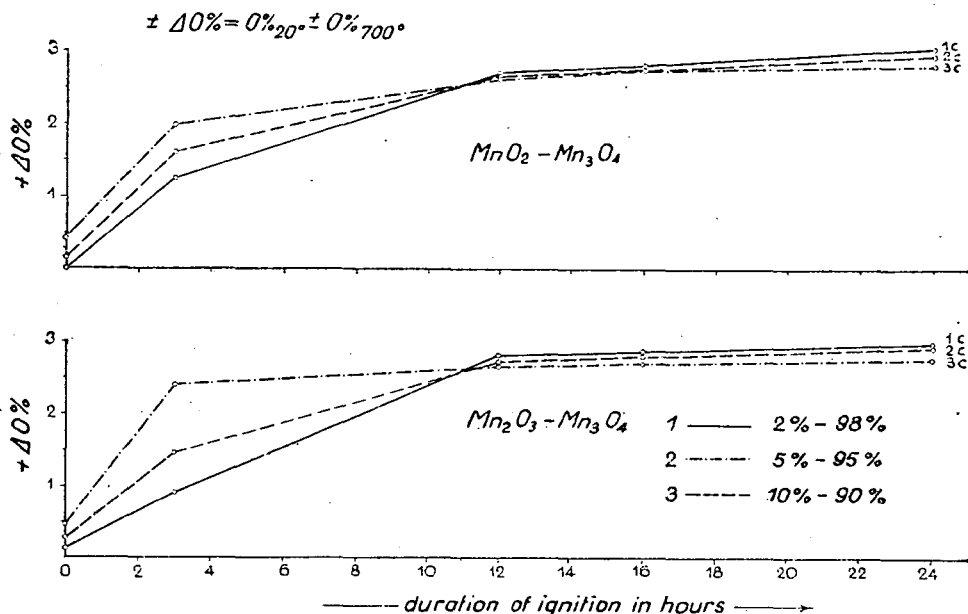


Fig. 2.

The change of the active oxygen content of the mixtures, i. e. the change concerning the Mn_3O_4 component depending upon the time of the heating in the presence of 2, 5, 10 per cent MnO_2 and Mn_2O_3 , respectively.

transformation into Mn_2O_3 from the air the oxygen diffuses gradually into the surface layers and through them into the interior of the single granules. The velocity of the procedure is in correlation with the size of the granules, i. e. with the relative size of the surface of the granules. As can be seen from the Table this is a fairly slow procedure particularly if larger Mn_3O_4 amounts are involved and just through this slowness of the process the fact can be interpreted that the oxidation of Mn_3O_4 described above is not indicated by the DTA curves prepared in the case of the most various mixtures under normal conditions (2). Therefore, the authors increased the temperature in their DTA apparatus at uniform velocity to 700°C and kept it for three hours at this temperature. The curve on comparing with the groundline from 560—600°C rises uniformly. This slow rise also seems to support the above explanation.

Summarizing the above it may be stated that at the same temperature the complete transformation of Mn_3O_4 in the presence of MnO_2 and/or Mn_2O_3 is the slower the greater the relative quantity of the Mn_3O_4 present. This is comprehensive owing to the slow diffusion of the oxygen taken up from the air and is in agreement with the work of Simon and Fehér (3). These authors examined the transformation of MnO_2 into Mn_2O_3 and the stability of the oxides respectively as a function of the pressure and temperature. At the decomposition of MnO_2 they established that the tension occurring at the same temperatures depends to a great extent upon the amount of the weighed substance which in turn is in relation with the velocity of the diffusion.

In the following it must only be proved that Mn_3O_4 consumes oxygen from the free air. This is already proved by the fact that also in the presence of Mn_2O_3 which does not give off oxygen, complete oxidation takes place, furthermore, that it also occurred in the presence of such slight amounts of MnO_2 which could in no case give off as much oxygen as required for the oxidation of the entire amount of Mn_3O_4 present. To support this statement examinations were also carried out in a nitrogen current under conditions in which the air was completely excluded.

If it holds good that Mn_3O_4 takes up the oxygen from the air on heating the different samples in a nitrogen current only the MnO_2 component can change through transformation into Mn_2O_3 and giving off of oxygen. However, both Mn_2O_3 (as if heated in the free air) and Mn_3O_4 must remain unchanged. In the course of the examinations the following results were obtained.

Table 4.

Samples		active O in per cent of the samples		$\Delta O\%$	
		at 20° C	ignited in nitrogen at 700°C	measured	calculated
MnO ₂		18,14	10,24	-7,90	--
Mn ₂ O ₃		10,20	10,09	-0,11	--
Mn ₃ O ₄		7,06	7,06	0	--
MnO ₂ + Mn ₃ O ₄	25%+75%	10,03	8,16	-1,87	-1,97
	50%+50%	12,67	8,60	-4,07	-3,95
	75%+25%	15,54	9,75	-5,79	-5,85
Mn ₂ O ₃ + Mn ₃ O ₄	25%+75%	7,96	7,98	+0,02	±0,00
	50%+50%	8,71	8,55	-0,16	±0,00
	75%+25%	9,55	9,74	+0,19	±0,00
MnO ₂ + Mn ₂ O ₃ + Mn ₃ O ₄	20%+30%+50%	10,37	8,86	-1,51	-1,58
	50%+30%+20%	13,68	9,57	-4,11	-3,95
	40%+20%+40%	12,26	9,01	-3,25	-3,16

As can be seen in the Table the $-\Delta O$ values obtained at the actual measurements in the different mixtures are in good agreement with the $-\Delta O$ values calculated (only taking the change of MnO_2 into account) on the basis of the amount of MnO_2 present. This accordance confirms in part the fact, that in an atmosphere free of air (oxygen) only MnO_2 undergoes a change the other two oxides not and that in the course of its transformation Mn_3O_4 actually consumes the oxygen from the air.

Concerning the stability of Mn_3O_4 — taking into account the presence or absence of MnO_2 and Mn_2O_3 respectively — the following can be stated:

1. If the mentioned two oxides of higher valency are absent Mn_3O_4 is stable at every temperature (on carrying out the examinations in the free air till $1050^\circ C$).

2. In the presence of MnO_2 and/or Mn_2O_3 Mn_3O_4 already takes up oxygen at a temperature of about $400^\circ C$ and consequently its composition gradually shifts towards that of Mn_2O_3 .

3. The transformation of Mn_3O_4 into Mn_2O_3 can be stated to be complete at a temperature of about $600^\circ C$ (only taking the dependence on the temperature of the transformation into account) and presently at higher temperatures (exceeding $940^\circ C$) it transforms again into Mn_3O_4 .

4. The transformation also takes place in the presence of smaller amounts of MnO_2 and/or Mn_2O_3 . In the course of the examinations the smallest amount of MnO_2 and Mn_2O_3 respectively contained in the mixtures is 2 per cent, the largest 75 per cent. The amount of the MnO_2 and Mn_2O_3 present does not influence the extent of the transformation of Mn_3O_4 , their role only consists in the bringing about of the solid-phase reaction for which, however, the slightest quantity sufficient. Mn_2O_3 plays an essential role as at a temperature of $460^\circ C$ MnO_2 also begins to transform into Mn_2O_3 .

5. The velocity of the transformation — on examining the extent of the oxygen consumption at a stable temperature as the function of time — is in correlation with the amount of Mn_3O_4 contained in the mixture. The more Mn_3O_4 is in the mixture the longer heating is required until the transformation into Mn_2O_3 is complete.

6. Mn_3O_4 consumes the oxygen from the air. On carrying out the heating in an oxygen free atmosphere (e. g. in nitrogen) there occurs no change although MnO_2 and/or Mn_2O_3 are present.

References:

1. Grasselly, Gy., Klivényi, É.: Acta Mineralogica—Petrographica Univ. Szegediensis Tom. IX. 1956. 15—32.
 2. Földvári—Vogl, M., Koblenz, V.: Acta Mineralogica—Petrographica Univ. Szegediensis Tom. IX. 1956. 7—14.
 3. Simon, A., Fehér, F.: Zeitschrift für Elektrochemie, Bd. 38. Nr. 3. 137—148. 1932.
- Received August 20, 1956.