

51559

boroh

ACTA UNIVERSITATIS SZEGEDIENSIS

ACTA
MINERALOGICA—PETROGRAPHICA

TOMUS IX.



SZEGED, HUNGARIA

1956

51559

ACTA UNIVERSITATIS SZEGEDIENSIS

ACTA
MINERALOGICA—PETROGRAPHICA

TOMUS IX.



SZEGED, HUNGARIA

1956

Redigit
SÁNDOR KOCH

Edidit
Institutum Mineralogicum et Petrographicum Universitatis Szegediensis
(Szeged, Tácsics Mihály u. 2.)

Nota
Acta Min. Petr. Szeged

Szerkeszti
KOCH SÁNDOR

Kiadja
a Szegedi Tudományegyetem Ásvány-Kőzettani Intézete
(Szeged, Tácsics Mihály u. 2.)

Kiadványunk rövidítése
Acta Min. Petr. Szeged

A kiadásért felelős: Koch Sándor.

A kézirat nyomdába érkezett: 1956. december. Megjelenés: 1957. február. Példányszám: 350.
Szegedi Nyomda Vállalat — 4300.

F. v.: Gabnai János.

THE MINERAL COLLECTION OF THE HUNGARIAN NATIONAL MUSEUM

was already badly damaged in 1944 during the siege of Budapest. Now at the end of October 1956 the fire which broke out in the course of the fighting destroyed a considerable part of this mineral collection. It constituted an irreplaceable scientific and museum value. Not merely the Hungarian mineral collection, but one of the most beautiful and richest mineral collection of the world has been destroyed.

The Hungarian National Museum was founded in 1802 but only received its first minerals as a present in 1808. The wife of F. Széchenyi, the founder of the museum, gave the Nation the »Fossilia« collection.

The first enthusiastic expert of the gradually increasing mineral collection was *J. Jonas* to whose successful work the fruitful development of the young collection was due. Unfortunately, Jonas died as early as 1821 and as for several decades a well educated mineralogist appreciating his subjectmatter did not become member of the cabinet of the Natural Sciences the development of the collection did not advance, on the contrary it went back.

A change only occurs in 1866 when *J. Krenner* the eminent mineralogist becomes the leader of that time already independent fossil cabinet.

Krenner who was well acquainted with the more important foreign collections seeing the poor mineral collection of Hungary, otherwise such a rich country, made propaganda for the purchasing of the world-famous Lobkowitz private collection, which the Hungarian Parliament acquired for Hungary in 1871. To the 34 000 samples of this collection which had been kept in Bilin in Czecho-Slovakia particularly the old famous, partly already exhausted mines of Central Europe (Hungarian and Czecho-Slovakia) contributed numerous beautiful samples. This rich collection constituted the real very valuable basis of the mineral collection of the Hungarian National Museum.

The splendid samples of this collection aroused the interest for mineralogy of *A. Semsey*. Prompted by Krenner Semsey became for four decades the unselfish, generous maecenas of the collection of minerals, he devoted several hundred thousand of gold crowns to the enlargement of the collection and technical library of the collection of minerals.

In 1878 the »Golden Age« of the collection of minerals began. The scanty collection which was neglected over a long period became through

the work of two men; *J. Krenner* the scientist who could inspire and *A. Semsey* the maecenas who could become enthusiastic and who spend one of the most prominent collections of the world. Of the more valuable private collections they acquired those of *Schuchard*, *Frenzel*, *Fausser*, *Eszterházy*, *Schäffer*, *Damour*, *Uzlar*, *Marquis de Vobray*, *Norpe*, as well as the nicest samples of the collection of *Don Pedro*.

Besides these collections the experts of the museum always purchased from well-known firms from all over the world magnificent samples for the collection as owing to the generosity of Semsey they frequently made collection tours.

The engineers and miners from the Hungarian mines also sent continuously the most beautiful and valuable samples of their mines.

The collection obtained the splendid granates from the classical contact occurrences of the now already exhausted mines of the Banat and Rézbánya (Baița), furthermore, the unique hematite, pink aragonite crystals and bismuth- and bismuthtelluride ores, the rare native gold tellurides (crystallized nagyágit, sylvanit, hessite) of the Ore Mountains of Transsylvania, the rich sample of native tellure, the unique gold crystals of the Katronca lode of Verespatak (Rosia Montana) and the well-known beautiful minerals from Nagybánya (Baia Mare), Felsőbánya (Baia Sprie), Kapnikbánya (Capnic) and finally those from the once famous mines of Slovensko from Urvölgy (Spana Dolina), Libetbánya (Lubietova), Kalinka, Selmezbánya (Banska Stiavnica) which are nowadays no more available. The material of the communications of *J. Krenner*, *K. Zimányi*, *S. Schmidt*, *L. Tokody* and that of the other Hungarian mineralogists was all founded on the collection of the museum.

Apart from the Hungarian occurrences supplies from foreign mineral (before 1914 sometimes 3—4 batches arrived daily) warranted that the collection should contain selected samples of all well known mines.

The generosity of Semsey rendered it possible that the meteorite collection of the museum developed into one of the largest and most valuable of such collections. As can be seen in the book »Magyarország meteoritgyűjteményei« (Hungarian meteorite collections) by Tokody—Mrs. Dudich which appeared in 1951 the collection contains 1295 pieces from 484 falls.

The monumental development of the cabinet of minerals of the National Museum was interrupted by the outbreak of World War I. Shortly after the war was over *J. Krenner* (1920 January) and eventually *A. Semsey* (1923 August) died and the development was interrupted over a long period.

*

On returning from World War I. in 1919 I became a member of the staff of the cabinet of minerals of the National Museum and spent over two decades there, and now it is my sad duty to inform the experts of the destruction of this beautiful collection.

How often I guided colleagues from abroad round this wonderfully rich collection showing them the show-cases and together we admired the beautiful samples of the mineral world exhibited there.

And now when a great part of the collection, and even the catalogues, have become victims of the flames I feel I must emphasize again what I have already mentioned frequently to experts.

Of the valuable works of art of the Museum of Fine Arts, Museum of Industrial Arts and Historical Museum, furthermore of the more valuable samples of the libraries all related institutions possess photographs. Hence to the investigators, the students and the public numerous splendidly illustrated editions are available. Although mentioned I worked for nearly a quarter of a century in the museum containing the collection of minerals I never saw any reproductions of the beautiful samples of other collections. I have not, respectively hardly ever seen any issue illustrating the remarkably beautiful and valuable samples of the largest mineral collections.

Not only art, but nature has unique masterpieces too. Let us make the public acquainted with them! Nowadays when the production of coloured photos and reproductions does not meet with any significant obstacles and is not very expensive every museum ought to have pictures made of nature's most wonderful works of art, of the minerals, in their possession. I am sure that like in the case of the issues of art Museums, Universities, as well as interested specialists and even the public would be glad to purchase them.

The tragedy of the mineral collection of our museum is an example what a great pity it is if of a collection which has been destroyed even pictures of its mineral masterworks are no more available.

Prof. Dr. Sándor Koch

Director of the Mineralogical—Petrographical
Institute of the University, Szeged

DIFFERENTIAL THERMAL ANALYSIS OF ARTIFICIAL MANGANESE COMPOUNDS

By

M. FÖLDVÁRI—VOGL, and V. KOBLENCZ

(Hungarian Geological Institute, Budapest)

A previous paper [2] dealt with the examinations of the DTA of natural manganese minerals. The present measurements carried out on artificial manganese compounds, manganese-oxides and carbonates supplement partly the work mentioned above and are also associated closely with the examinations of Gy. Grasselly and E. Klivényi [1].

Grasselly and his co-worker prepared three manganese-oxides the thermal properties of which they studied in detail in addition they also prepared manganese carbonate and a mixture series in which the proportion of the prepared oxides and carbonates varied. The authors mentioned above described in their paper in detail the manner of preparation and the change which the prepared oxides and their mixtures undergo on the action of heat.

Authors also carried out their DTA examinations on the samples prepared by Grasselly and Klivényi, in this way well defined and chemically thoroughly examined compounds could be studied and our DTA curves supplemented the work of Grasselly and co-worker.

The detailed description of the DTA equipment used for the examinations has been already reported elsewhere [3]. The DTA examinations were carried out at a temperature ranging between room temperature and 1000°C. The results of the examinations are shown on the figures.

Fig. 1. shows the DTA curves of the four prepared manganese compounds. The first curve was prepared from MnO_2 . The curve corresponds with that of pyrolusite the only difference being that particularly the first peak illustrating the transformation of MnO_2 to Mn_2O_3 appears in the present case at a temperature about 60–80°C below the one it appears as in the case of natural pyrolusite. This phenomenon which can be frequently observed on comparing DTA curves of artificial and natural substances can obviously be explained by the fact that the size of the granule of the artificially produced compound is more minute than that of the natural mineral. The second peak of MnO_2 indicates the transformation of Mn_2O_3 into Mn_3O_4 .

The second curve of Fig. 1. was prepared of Mn_2O_3 , until 1000°C it only shows a single peak a little below 1000°C at this peak Mn_2O_3 transforms into Mn_3O_4 .

The third curve was prepared from artificial Mn_3O_4 . Until 1000° C the curve does not show any characteristic peak, at the most, only an insig-

nificant endothermic bend between 950—1000° C. This bend may be either due to a small part of the Mn_3O_4 having oxidised during the heating to Mn_2O_3 and that over 950°C this is retransformed into Mn_3O_4 , or it may be the consequence of a transformation $\alpha \rightarrow \beta$, a fact which is also referred to in the book of Rode [4].

The fourth curve is the artificial curve of MnCO_3 . The endotherm peak indicating the decomposition of the carbonate and the exotherm peak following it appear earlier than in the curve of the natural MnCO_3 mineral. The small peaks appearing between 900—1000° C are striking they could not be detected on the DTA curves of natural rodochrosite.

The other Figs. illustrate the DTA examinations of mixtures of the four ground substances mentioned above and their investigation purposes the establishment to what extent these compounds may be determined simultaneously and to what an extent they interfere or influence one another.

Fig. 2. shows the DTA curves of the mixtures containing MnO_2 , Mn_2O_3 and Mn_3O_4 in different proportion. The curves form as anticipated, it should only be remarked that the duplicated broadening of the peaks appearing between 950—1000° C is in agreement with the establishment of Grasselly and co-worker that if the size of the granules of MnO_2 and Mn_2O_3 varies they do not transform into Mn_3O_4 at exactly the same temperature.

Fig. 3. illustrates the DTA curves of the MnO_2 and MnCO_3 mixtures. In the case of these curves it is striking that the peak indicating the decomposition of MnCO_3 , particularly in the case of mixture 3, decreases irregularly.

The curves of the mixtures visible on Fig. 4. seem to support the establishments of Grasselly and co-worker that if Mn_3O_4 is present together with other manganese-oxides it oxidises into Mn_2O_3 at the stability temperature range of Mn_2O_3 and that the whole Mn_2O_3 only retransforms into Mn_3O_4 at temperatures exceeding 950° C. This statement seems also to be supported by the fact that e. g. the peaks between 950—1000°C appear to be duplicated too, furthermore that if the mixture contains 25 per cent of Mn_2O_3 the peak mentioned is higher than if it would only derive from Mn_2O_3 . However, the question arises why the DTA curve does not indicate the oxidation of Mn_3O_4 ? The blunting of the exothermic peak following the decomposition of MnCO_3 on curve No. 4 of Fig. 4. can be attributed to the reducing effect of Mn_2O_3 . A similar phenomenon can be seen on curves 2 and 3 of Fig. 5. on which the oxidation following the decomposition of the manganese carbonate appears also to be less distinct.

The three last curves of Fig. 5. show the oxide mixtures with three components. In these the duplicated broadening of the second peak appears, its presumable reason has already been referred to.

The investigations lead to the conclusion that with due care carbonate and manganese oxide may be determined simultaneously by means of DTA curves, however, owing to their interaction quantitative determinations based on the DTA peaks may become unreliable.

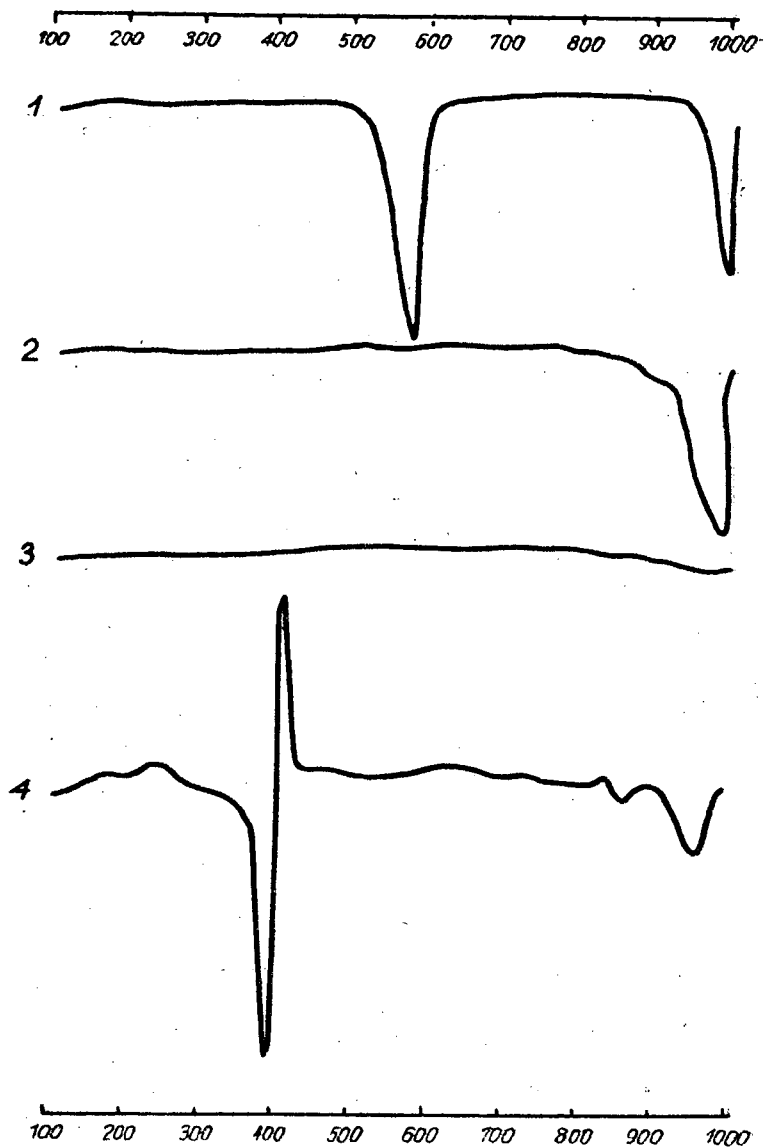


Fig. 1.

DTA curves of artificial manganese oxides and that of manganese carbonate.

1. MnO_2 , 2. Mn_2O_3 , 3. Mn_3O_4 , 4. MnCO_3 .



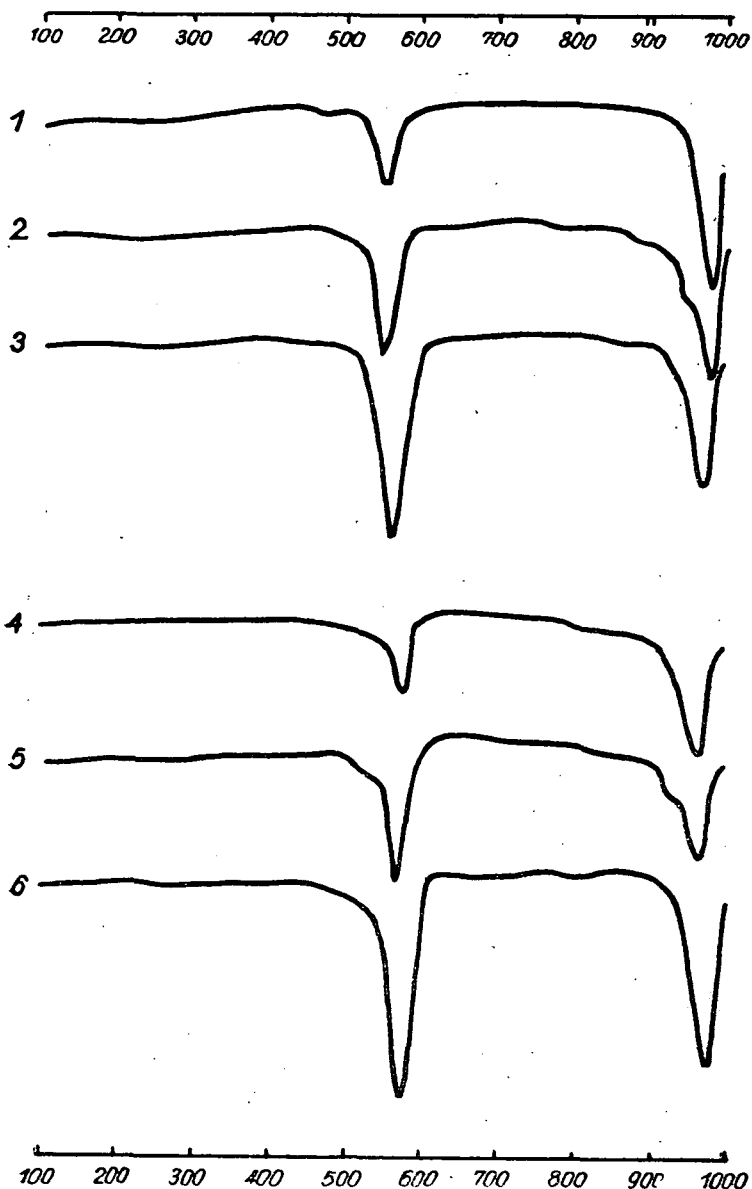


Fig. 2. DTA curves of mixtures of manganese oxides.

1. 25% MnO_2 + 75% Mn_2O_3
2. 50% MnO_2 + 50% Mn_2O_3
3. 75% MnO_2 + 25% Mn_2O_3
4. 25% MnO_2 + 75% Mn_3O_4
5. 50% MnO_2 + 50% Mn_3O_4
6. 75% MnO_2 + 25% Mn_3O_4

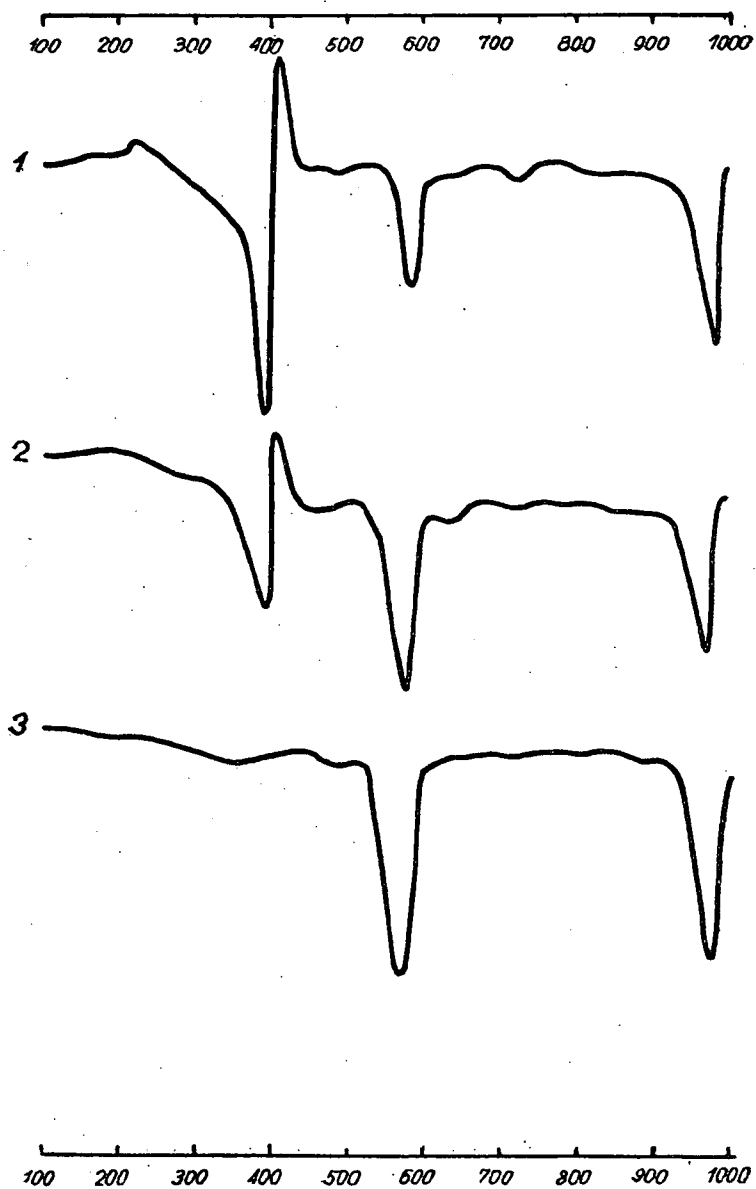


Fig. 3.

DTA curves of mixtures of MnO_2 and MnCO_3

1. 25% MnO_2 + 75% MnCO_3
2. 50% MnO_2 + 50% MnCO_3
3. 75% MnO_2 + 25% MnCO_3

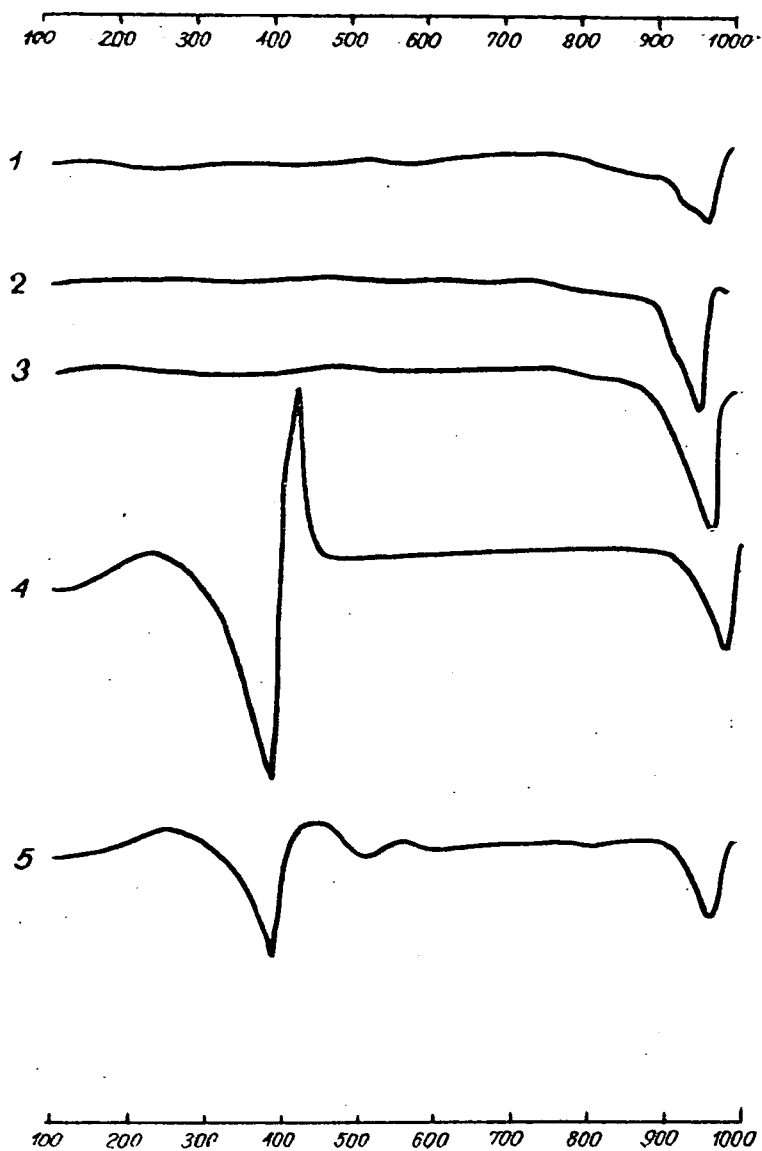


Fig. 4. DTA curves of mixtures of manganese oxides and carbonate, respectively.

1. 25% Mn_2O_3 + 75% Mn_3O_4
2. 50% Mn_2O_3 + 50% Mn_3O_4
3. 75% Mn_2O_3 + 25% Mn_3O_4
4. 25% Mn_2O_3 + 75% MnCO_3
5. 50% Mn_2O_3 + 50% MnCO_3

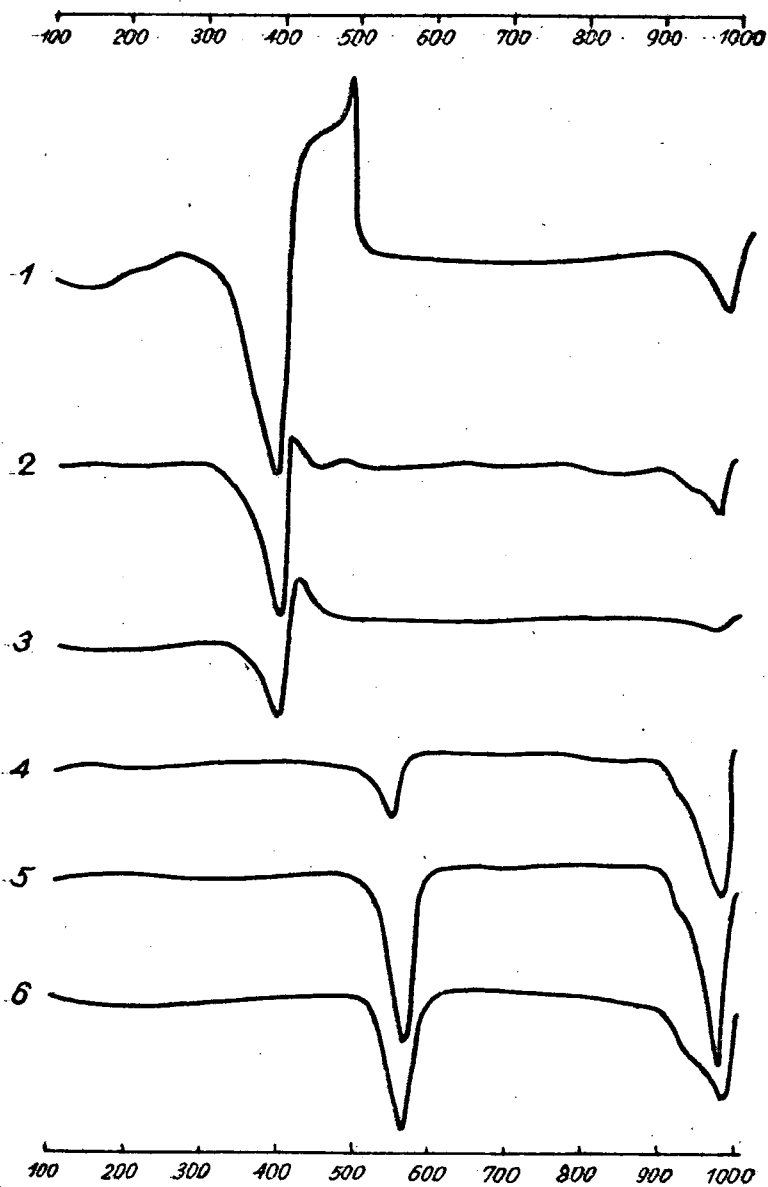


Fig. 5. DTA curves of mixtures of manganese oxides and carbonate, respectively.

1. 25% Mn_3O_4 + 75% MnCO_3
2. 50% Mn_3O_4 + 50% MnCO_3
3. 75% Mn_3O_4 + 25% MnCO_3
4. 20% MnO_2 + 30% Mn_2O_3 + 50% Mn_3O_4
5. 50% MnO_2 + 30% Mn_2O_3 + 20% Mn_3O_4
6. 40% MnO_2 + 20% Mn_2O_3 + 40% Mn_3O_4

REFERENCES:

1. Grasselly, Gy., Klivényi, E.: Acta Mineralogica—Petrographica Univ. Szegediensis, Tom. IX. 1956. 15—32.
2. Földvári Vogl, M., Koblencz, V.: Acta Geologica Acad. Sci. Hung. Tom. IV. Fasc. 1. 1955. 85—93.
3. Földvári—Vogl, M., Kliburszky, B.: Acta Geologica Acad. Sci. Hung. Tom. II. Fasc. 3—4. 1954. 215—229.
4. Rode E. JA.: Kiszlorodnűe szoedinenija marganca. (Iszkusztvennűe szoedinenija mineralű i rudű.) Izdatelysztvo akademii nauk SzSzSzR Moszkva 1952.

Received July 5, 1956.

CONCERNING THE THERMAL PROPERTIES OF THE MANGANESE OXIDES OF HIGHER VALENCIES

By

GY. GRASSELLY and E. KLIVÉNYI

(Mineralogical—Petrographical Institute of the University, Szeged)

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. $Mn_3O_{4.038}$.

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.

<div> <div>°C</div> <div>Samples</div> </div>		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}

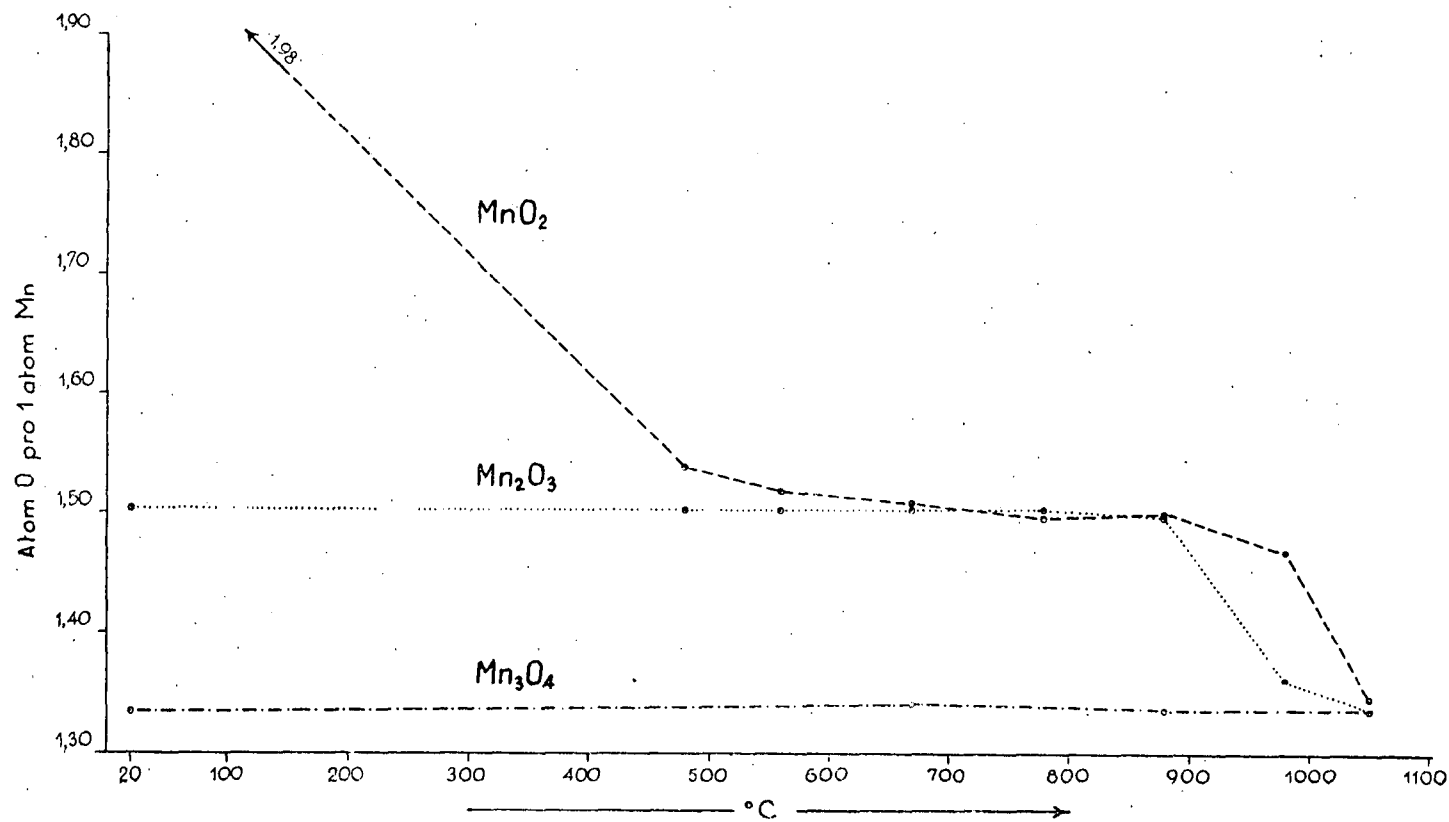


Fig. 1.
The change of the Mn:O ratio of the individual oxide
depending upon the temperature,

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 + Mn ₂ O ₃	1	25% + 75%	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 _{1,610}	MnO _{1,614}			MnO _{1,617}			MnO _{1,608}			MnO _{1,497}			MnO _{1,498}			MnO _{1,381}			MnO _{1,329}					
		2	50% + 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% + 25%	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 _{1,839}	MnO _{1,625}			MnO _{1,517}			MnO _{1,508}			MnO _{1,503}			MnO _{1,506}			MnO _{1,449}			MnO _{1,343}						
II	MnO ₂ + Mn ₃ O ₄	1	25% + 75%	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 _{1,505}			MnO _{1,513}			MnO _{1,492}			MnO _{1,377}			MnO _{1,335}					
		2	50% + 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 _{1,460}			MnO _{1,497}			MnO _{1,499}			MnO _{1,499}			MnO _{1,500}			MnO _{1,376}			MnO _{1,335}					
	3	75% + 25%	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 + Mn ₃ O ₄	1	25% + 75%	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}					
		2	50% + 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% + 25%	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 + Mn ₂ O ₃ + Mn ₃ O ₄	1	20% + 30% + 50%	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 _{1,355}					
		2	50% + 30% + 20%	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 _{1,500}			MnO _{1,497}			MnO _{1,348}			MnO _{1,335}					
	3	40% + 20% + 40%	Mn	67,94	70,32	69,43		70,41	69,61		70,46	69,61		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 _{2,996}			Mn ₃ O _{4,107}			Mn ₃ 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 Mn_3O_4 MnO_2 — Mn_2O_3 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 Mn_2O_3 component of the system remains unchanged, whereas the loss of oxygen of the MnO_2 component already starts at 460°C and it also transforms completely at a temperature exceeding 560—600°C into Mn_2O_3 , i. e. instead of two phases the system will have only one which will transform at higher temperature into Mn_3O_4 .

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 MnO_2 and from this temperature on also Mn_2O_3 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 Mn_3O_4 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 Mn_2O_3 already starts at 460°C and at temperatures of 600—800°C Mn_2O_3 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_2O_3	$MnO_{1.501}$
50 per cent MnO_2 — 50 per cent Mn_2O_3	$MnO_{1.496}$
75 per cent MnO_2 — 25 per cent Mn_2O_3	$MnO_{1.505}$

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 Mn_2O_3 . Of the above mixtures the one the starting composition of which was 75 per cent MnO_2 and 25 per cent Mn_2O_3 was found on the basis of X-ray investigation of a sample heated at 780° C to be identical with the pure starting Mn_2O_3 .

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 Mn_2O_3 , nevertheless at the transformation of this system into Mn_3O_4 which starts at 980°C, the MnO_2 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 .

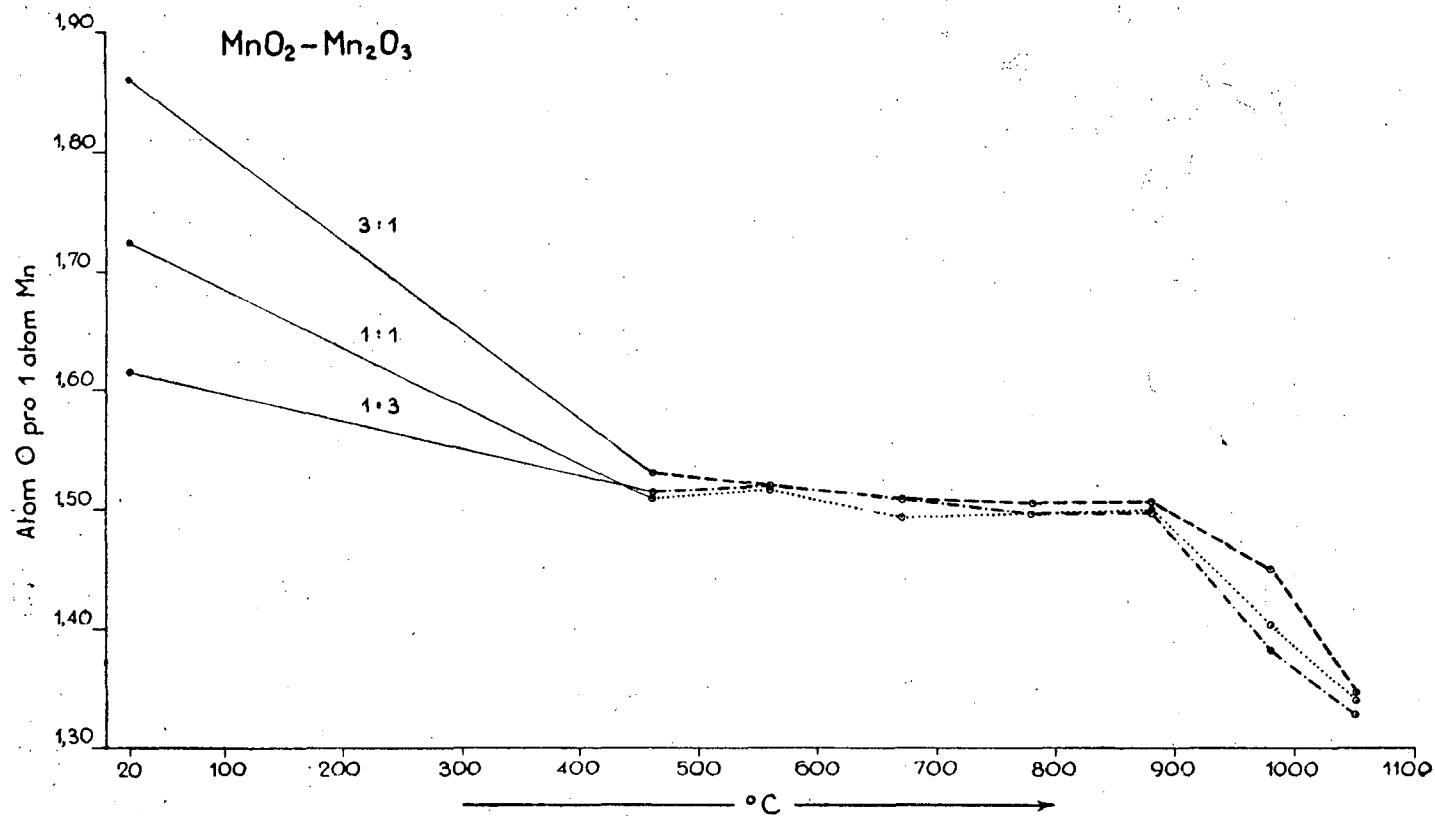


Fig. 2.
The change of the Mn:O ratio of the $\text{MnO}_2 - \text{Mn}_2\text{O}_3$ systems
depending upon the temperature.

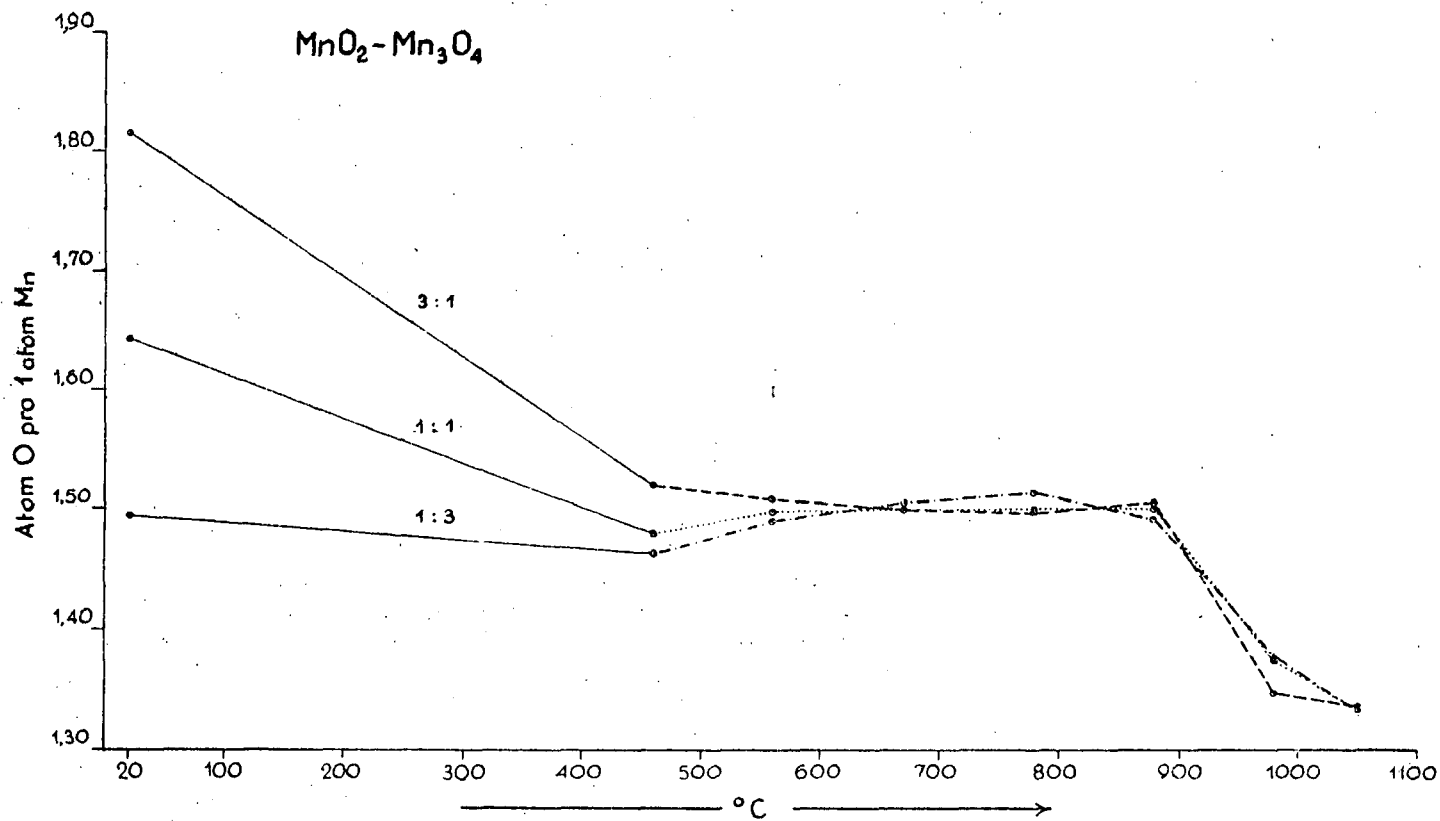


Fig. 3.
The change of the Mn:O ratio of the $\text{MnO}_2 - \text{Mn}_3\text{O}_4$ systems
depending upon the temperature.

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 .

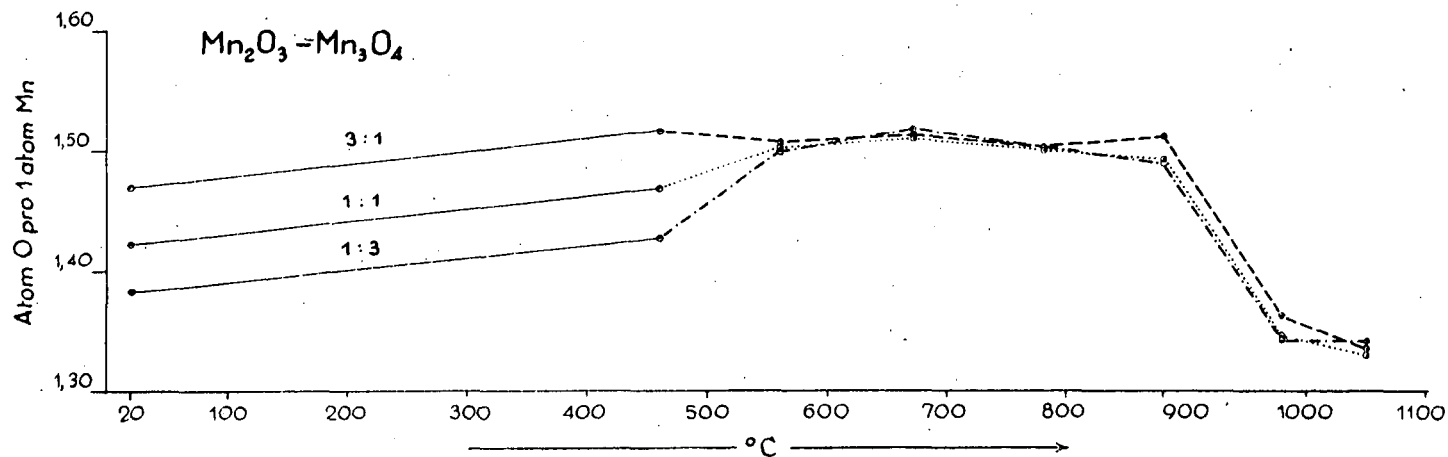


Fig. 4:
The change of the Mn:O ratio of the $\text{Mn}_2\text{O}_3 - \text{Mn}_3\text{O}_4$ systems
depending upon the temperature.

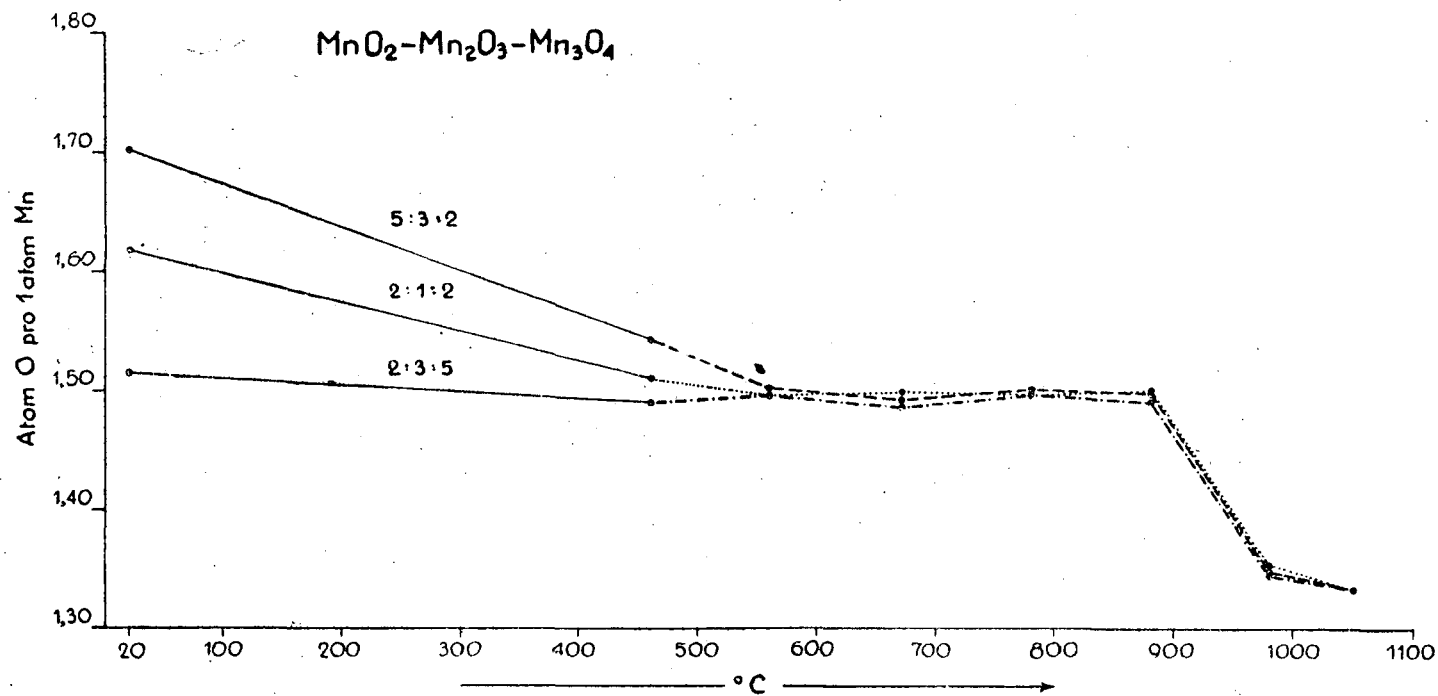


Fig. 5.
The change of the Mn:O ratio of the $\text{MnO}_2\text{--Mn}_2\text{O}_3\text{--Mn}_3\text{O}_4$ systems
depending upon the temperature.

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 containing Mn_3O_4 have actually been transformed into one phase systems essentially only containing 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 gravimetric 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} meas.	l _{estim}	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} calc.	hkl
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°C into Mn_2O_3 (which it never does in itself):

The composition of Mn_3O_4 at 20°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°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°C and 880°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 $560-880^\circ C$ 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.

<div> <div>°C</div> <div>Samples</div> </div>				20°		460°		560°		670°		780°		880°		980°		1050°	
						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 + Mn ₂ O ₃	1	25% + 75%	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
				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% + 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
				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
		3	75% + 25%	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
				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 + Mn ₃ O ₄	1	25% + 75%	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
				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% + 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
				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
		3	75% + 25%	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
				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 + Mn ₃ O ₄	1	25% + 75%	MnO	92,04	91,23	91,24	89,88	89,82	89,49	89,44	89,86	89,79	90,04	89,93	92,61	92,76	92,83	92,79
				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% + 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
				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
		3	75% + 25%	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
				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 + Mn ₂ O ₃ + Mn ₃ O ₄	1	20% 30% 50%	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
				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% 30% 20%	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
				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
		3	40% 20% 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
				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%
$\text{MnO}_{1,511}$		$\text{MnO}_{1,500} \pm 0,011$		$\text{MnO}_{1,489}$	

REFERENCES:

- Dubois, P.: Comptes Rendus 199. 1934. 1416—1418.
 Dubois, P.: Comptes Rendus 200. 1935. 1107—1110.
 Földvári—Vogl, M., Koblenz, V.: Acta Geologica Academiae Scientiarum Hungaricae Tom. IV. Fasc. 1. 1956. 85—93.
 Grasselly, Gy.: Acta Mineralogica—Petrographica Univ. Szegediensis, Tom. VIII. 1955. 13—26.
 Le Blanc, M., Wehner, G.: Z. für phys. Chem. A. 168. 1933. 59—78.
 Mason, B.: Mineralogical Aspects of the System $\text{FeO—Fe}_2\text{O}_3\text{—MnO—Mn}_2\text{O}_3$. Acad. Dissertation. 1943. Stockholm.
 Pavlovitch, St.: Comptes Rendus 200. 1935. 71—73.
 Simon, A., Fehér, F.: Z. f. Electrochemie, 38. 1932. 137—148.

Received May 15, 1956.

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°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°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°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 $+\Delta\text{O}$ 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°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 $+\Delta\text{O}$ 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°C temperature range.

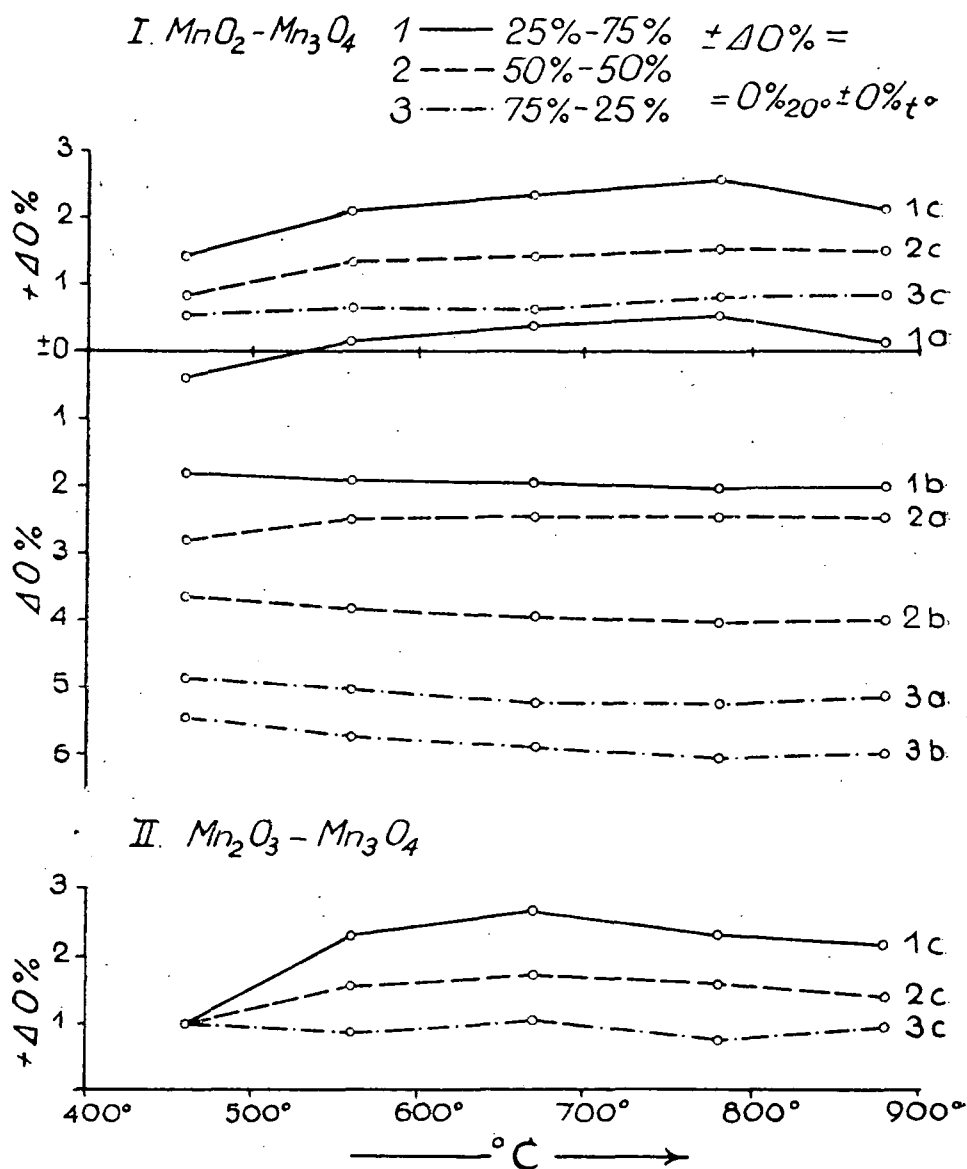


Fig. 1.

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 $+\Delta\text{O}$ 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. $+\Delta\text{O}$ — 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 /O ₉₀₀ 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 ₃ O 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 ₃ O 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 ₂ O ₃ +Mn ₃ O 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 $+\Delta\text{O}$ 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

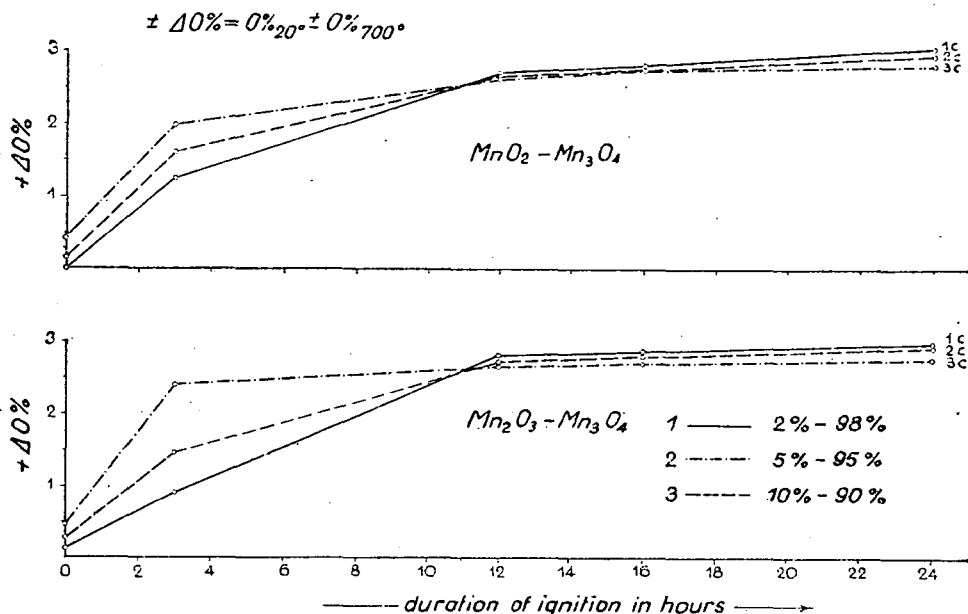


Fig. 2.

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_2O_3		10,20	10,09	-0,11	--
Mn_3O_4		7,06	7,06	0	--
MnO_2 + Mn_3O_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_2O_3 + Mn_3O_4	25%+75%	7,96	7,98	+0,02	$\pm 0,00$
	50%+50%	8,71	8,55	-0,16	$\pm 0,00$
	75%+25%	9,55	9,74	+0,19	$\pm 0,00$
MnO_2 + Mn_2O_3 + Mn_3O_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.

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

By

GY. GRASSELLY

(Mineralogical—Petrographical Institute of the University, Szeged)

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°C , whereas in the case of mixtures containing MnO_2 and/or Mn_2O_3 the second characteristic high endothermal peak appears at 950°C indicating the transformation of Mn_2O_3 into Mn_3O_4 . The DTA curve of Mn_3O_4 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°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 $600\text{--}700^\circ\text{C}$.

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 $600\text{--}700^\circ\text{C}$ 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 $600\text{--}700^\circ\text{C}$ 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 $600\text{--}700^\circ\text{C}$ must be accomplished in an indifferent atmosphere with the exclusion of air.

Pure substances and their mixtures, respectively, were heated for three hours at $650\text{--}720^\circ\text{C}$ 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
		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
		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
		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
		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
		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
		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
		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
		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
		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_2O_3	$-\Delta O\%$	Mn_2O_3	no change
Mn_2O_3	Mn_2O_3	no change	Mn_2O_3	no change
Mn_3O_4	Mn_3O_4	no change	Mn_3O_4	no change
$MnO_2-Mn_2O_3$	Mn_2O_3	$-\Delta O\%$	Mn_2O_3	no change
$MnO_2-Mn_3O_4$	$Mn_2O_3-Mn_3O_4$	$-\Delta O\%$	Mn_2O_3	$+\Delta O\%$
$Mn_2O_3-Mn_3O_4$	$Mn_2O_3-Mn_3O_4$	no change	Mn_2O_3	$+\Delta O\%$
$MnO_2-Mn_2O_3-Mn_3O_4$	$Mn_2O_3-Mn_3O_4$	$-\Delta O\%$	Mn_2O_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 MnO_2 — 30 per cent Mn_2O_3 — 20 per cent Mn_3O_4 . 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 MnO_2 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:

$\text{Mn}_2\text{O}_3\% = 100 - (\text{MnO}_2\% + \text{Mn}_3\text{O}_4\%) = 29,7\%$ 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:

$$\text{MnO}_2\% = \frac{3,26 \cdot 100}{8,27} = 39,4\%$$

$$\text{Mn}_3\text{O}_4\% = \frac{1,24 \cdot 100}{3,15} = 39,3\%$$

$$\text{Mn}_2\text{O}_3\% = 100 - 78,7\% = 21,3\%.$$

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

$$\text{MnO}_2\% = \frac{1,51 \cdot 100}{8,27} = 18,2\%$$

$$\text{Mn}_3\text{O}_4\% = \frac{1,34 \cdot 100}{3,15} = 42,5\%$$

$$\text{Mn}_2\text{O}_3\% = 100 - 60,7 = 39,3\%$$

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.

$$\text{MnO}_2\% = \frac{4,07 \cdot 100}{8,27} = 49,2\%$$

$$\text{Mn}_3\text{O}_4\% = \frac{1,58 \cdot 100}{3,15} = 50,1\%$$

$$\text{Mn}_2\text{O}_3\% = 100 - 99,3 = 0,7\%$$

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 caused, 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., Koblenz, 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.

Received September 10, 1956.

THE DETERMINATION OF KAOLINITES BASED ON COLOUR REACTIONS

By

J. MEZŐSI

(Mineralogical—Petrographical Institute of the University, Szeged)

As is known from the literature different organic substances stain the different components of clays and conclusions can be drawn from this as to the different mineral groups to which they belong. Particularly in the case of montmorillonites a vivid and in most cases quick discolourisation can be observed. The disadvantage of these examinations is that they only indicate the presence of montmorillonite thus rendering it possible to distinguish it from kaolinite and illite, respectively. However, it cannot be established if kaolinite, illite or a mixture of these minerals is involved.

Vedenejeva and *Ratejev* (7) believe that for the distinguishing of the single clay mineral groups spectrophotometry is the only reliable means.

Vedenejeva (6) distinguishes kaolinite, montmorillonite and illite from one another on the basis of the shift of the adsorption band. As staining material she uses benzidine, chrizoidine and methylene blue the latter also in the presence of KCl.

Vikulova (8) mainly on the basis of *Vedenejeva's* examinations uses methylene blues for staining. In such cases methylene blue stains the kaolinite clays pale light violet, this colour does not change even on the addition of KCl, a mixture of hydromica on the other hand turns according to the increase of the quantity of the hydromicas on the addition of KCl into violet blue, blue, or skyblue. However, the determination of this colour renders the method very unreliable.

Mielenz and *King* (3) use for the determination of kaolinite and for its separation from montmorillonite and illite resp. malachit green dissolved in nitrobenzine and safranine »y«. The adsorption of these dyes brings about a pleochroismus. The extent of crystallization influences the intensity. With malachit green the characteristic colours are blue and yellowish red perpendicularly to the cleavage surface and with safranine »y« yellowish green and purple parallel to the cleavage surface. Benzidine did not give a characteristic colour reaction.

The single dickite crystals did not absorb either malachit green nor safranine »y«. Benzidine does not either produce a change in the colour in the presence of dickite.

Nacrite if it is in large crystals does not adsorb the above dyes, however, small samples presumably show a colour reaction. In this case also benzidine cannot be used for the production of colour reactions.

Halloysite in its original state adsorbs characteristically malachit green and safranin »y« showing blue-green and reddish blue-purple colours. Between benzidine and untreated halloysites colour reactions do not occur.

In their preliminary report *Mielenz, King and Schieltz* (3) attempt to determine the individual minerals of the kaolin group with an essentially identical method.

The difficulty of this determination is that the dye solution may only be used in a concentration which is just enough for the required colouration to appear, but that it may not be in excess which would lead to anomalous results. For example, if in the case of malachit green the colouration is weak the yellow and green colours cannot always be distinguished from the original colour thus rendering the determination unreliable.

These difficulties were already mentioned previously. To produce a good colouration experiments with different organic compounds were carried out, first with paramethyl-aminophenol and para-dioxybenzol and recently with benzidine which proved to be very suitable for the determination of montmorillonites.

In a previous paper it has already been referred to that these kaolinite determinations are not quite reliable and that further investigations are required.

Our recent investigations were based on the following geochemical factors which are also referred to by *Szádeczky* (5) in his book.

Among the clay minerals the cation exchange capacity of the kaolin mineral group is only slight it depends on the free OH anions on the surface of the lattice. On the other hand, the phosphor binding aptitude and the PO₄ and other anion exchange capacity of the OH groups is by virtue of their anion character great. The base exchange and adsorption capacity of the montmorillonites is far greater. In this case the binding is mainly carried out by the ions of the lattice structure. Owing to the deficiency of the valencies caused by the substitution in the crystal lattice of ions of higher value by ones of lower value a cation exchange may be brought about.

The hydromicas and illites mainly bind ammonium and the large alkali ions.

Taking the above into consideration, if a molecule can be bound by means of a phosphate ion on the surface of a kaolinite producing under certain circumstances a colour reaction then among the clay mineral groups the presence of kaolinite can be certainly determined, respectively it can be separated from montmorillonite. In this case the group of hydromicas is the only one which does not show under such conditions a colouration.

The experiments were carried out as follows:

To a dilute solution of phosphoric acid (5 per cent) so much benzidine was added that the solution corresponded to one of 0.1 per cent. In every case a suspension of powdered kaolinite, montmorillonite and illite was prepared from this solution. Immediately at the beginning a few drops of

H₂O₂ (3 per cent) was added. After a few minutes the kaolinite showed a colour reaction, whereas the montmorillonite only changed its colour after some time, however, it always differed distinctly from the colour of kaolinite. Illite never showed any colour reaction.

The following results were obtained for kaolinite from Zettlitz, bentonite from Istenmezeje and illite from Füzérradvány.

	kaolinite	montmorillonite	illite
wet	lilac red (10 pa)	colourless	colourless
dry	lilac ochre	greenish yellow (1 pc)	colourless

After some time the lilac red colour of kaolinite deepened. Simultaneously the montmorillonite suspension showed lilac patches if the montmorillonite contained kaolinite. Otherwise the colour turned into greenish yellow.

If not pure kaolinite is involved, but it may be contaminated with montmorillonite — a very frequent occurrence in the Hungarian kaolinites — then concerning montmorillonite it is advisable to carry out examinations with an aqueous benzidine solution and for kaolinite the phosphoric acid benzidine reaction should be employed with the same material. If the sample contains kaolinite at the one test a lilac colour appears and if it contains montmorillonite at the other one instead of the characteristic dark blue colour a lighter blue is obtained.

Another organic substance suitable for the determination of kaolinite is p-methylamino-phenol it is well known as methol in photography. This is used in the same way as benzidine, it is dissolved in dilute phosphoric acid and to the suspension prepared in this manner a few drops of H₂O₂ are added. After a short time a change in colour may be observed. Kaolinite from Zettlitz, bentonite from Istenmezeje and illite from Füzérradvány produce the following colour reaction:

	kaolinite	montmorillonite	illite
wet	ochre	light green	unchanged
dry	darker ochre	green	unchanged

After standing for some time similar as at the benzidine test in this case also the colours deepen, whereas illite does not show for a certain time any change.

At these examinations the pH value must not be particularly taken into consideration as a phosphoric acid solution, even, in such concentrations, ensures a pH of 1—2.



Taking the above into account some of the more important Hungarian and foreign kaolin samples were examined with a phosphoric acidic solution of benzidine and methol (p-methyl-aminophenol). The following results were obtained:

Deposites	In the presence of benzidine	In the presence of methol
Telkibánya Baglyas völgy	lilac	ochre brown
Mád Istenhegyi táró	the lilac colour developed slowly	no change
Mád Bomboly	no change	no change
Sárospatak Királyhegy	lilac	light ochre
Sárospatak Cinegehegy	lilac	brown
Sárospatak Megyerhegy	lilac	brown
Gyöngyössolymos Asztagkő	slower development of lilac	lighter ochre brown
Velencei hegység Nadap	slower development of lilac	lighter ochre brown
Zettlitz Czecho-Slovakia	lilac	brown
Szászabánya Roumania	the lilac colour developed slower	brown

Generally the reaction with phosphoric acidic benzidine showed a more characteristic colourisation than that with methol, although in certain cases the colour reaction appeared more slowly. The disadvantage of the phosphoric acidic-methol method is that the methol oxidises fairly rapidly and that independently of the clay mineral and the substance contained in the suspension the whole sample turned dark brown after 5—6 hours. In this case the change of colour appearing after half an hour had elapsed was not always characteristic.

It is, however, essential that if this method is used montmorillonite only shows a colourisation after some time has elapsed and illite does not show any change of colour, i. e. after a certain time no change can be observed in the suspension.

The procedure was also examined to establish if Fe^{++} , Fe^{+++} and Mn interfere and concerning the kaolin occurrences whether the frequent pyrite impregnation influences the colourisation.

Ferrous iron which can be detected with α — α' dipyridil interferes, namely H_2O_2 oxidises ferrous iron into ferric iron. Hence the employment of H_2O_2 proved to be disadvantageous. Luckily ferro could mostly not be detected.

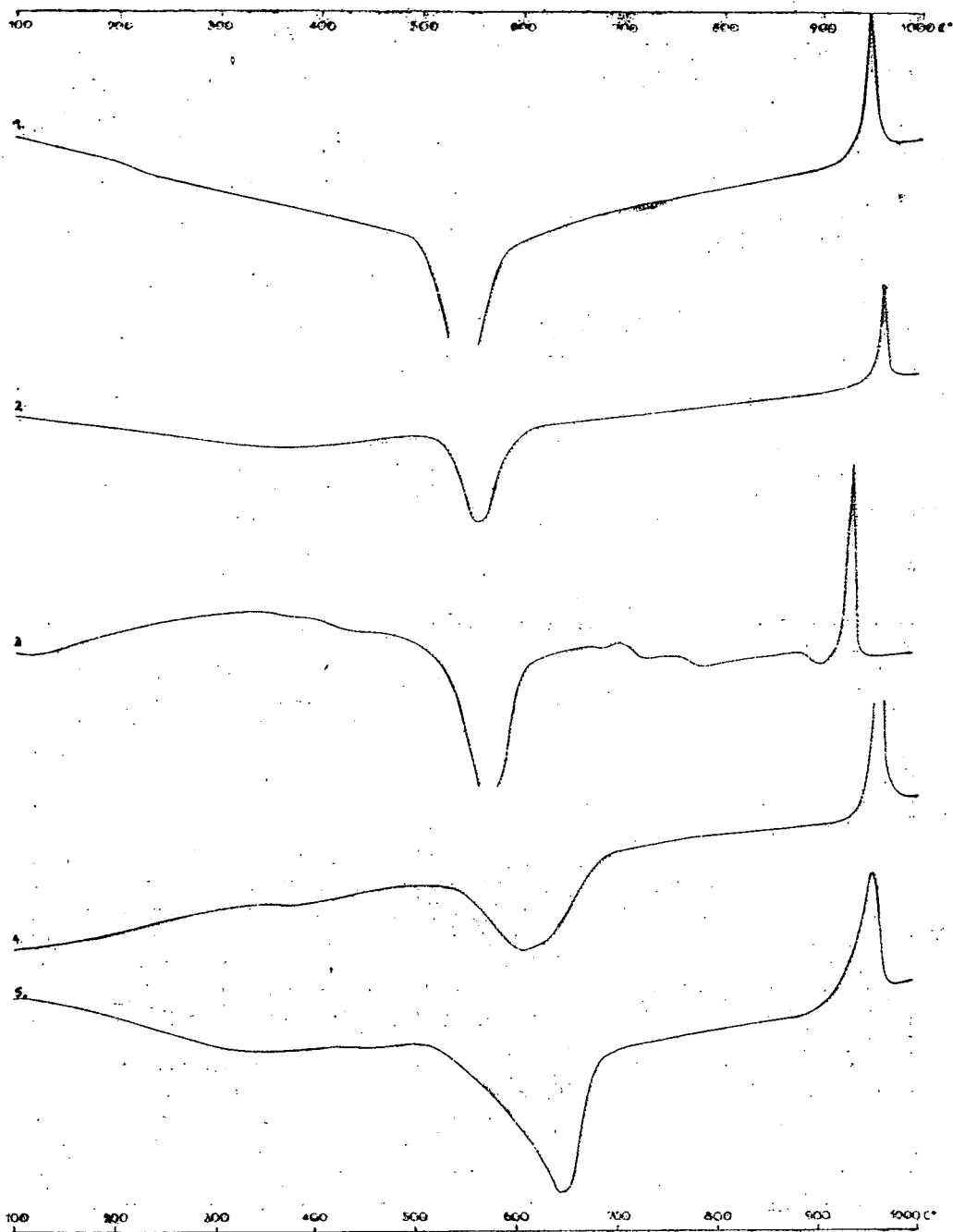


Fig. 1.

DTA curves of some kaolines of different localities:

1. Zettlitz (Czechoslovakia)
2. Sárospatak (Hungary)
3. Sasca montăna (Romania)
4. Gyöngyössolymos (Hungary)
5. Máđ, Bomboly (Hungary)

Ferric iron which can be detected with KSCN was also not contained in most of the samples. However, the attempt was made to add FeCl_3 to the suspension and the lilac colour appeared immediately, hence Fe^{+++} ions also interfere in this case as with the montmorillonite group if the determination is carried out with benzidine.

In the case of contamination with limonite the determination is difficult as the ochre yellow colour covers the whole suspension and it is difficult to detect any colourisation.

Like in the case of montmorillonite the interfering Fe^{+++} ion could not be reduced completely with sodium sulphite, at most, the lilac colour faded. Thus this question remained unsolved.

Pyrite always interfered. This could also be proved by adding a substance from Bomboly (Mád) to powdered pyrite in any other way this substance did not show any change of colour, however, on applying the phosphoric acid-benzidine procedure the lilac colouration appeared. What causes the interference can as yet not be explained.

MnO_2 , which may be present in the form of pyrolusite or psilomelane also interferes with the development of the true colour. As, however, as compared to the white kaolin these minerals always have a striking colour substances must be chosen for the test which do not contain minerals.

The silification which is particularly frequent in the case of the kaolins from Tokaj-Hegyalja did not influence the development of the colour.

The examination of the sample from Bomboly (Mád) proved interesting. Although its exterior has a show white colour like any other kaolin and its form is also identical it did not show any colourisation always remaining unchanged. With benzidine most of the kaolinites showed a pale blue colour, whereas this one did not show any change. Its DTA diagram diverged from the characteristic kaolinite curve, i. e. the endothermal peak between 500—600°C was missing and only appeared between 600—700°C. The exotherm peak like in the case of kaolinite appeared at 960°C. Hence the mineral is not kaolinite or at least not pure kaolinite, but probably dickite or a substance mixed with the latter. Consequently it can be stated that not every member of the kaolin group behaves in the same manner in the course of a reaction with phosphoric acid-benzidine. *Mielenz* and *King* also remark that dickite — at least some of its crystals — do not adsorb dyes. Unfortunately, nacrite and halloysite in a pure state are not available, hence their behaviour could not be compared with that of kaolinite.

According to the investigations of *Grofcsik* the clay mineral of the Velence mountain-range is monotermitite, which has also been described in the USSR. The difference is that the exothermal peak of kaolinite at 950°C is missing the rest of the curve is identical with that of kaolinite. Probably the structure of the mineral is a mixed one.

This substance like that of kaolinite underwent a reaction with phosphoric acid-benzidine. As, however, it is strongly impregnated with pyrite the examinations must be carried out with great care.

For the determination of kaolin by means of the phosphoric acid-benzidine method further investigations are, of course, still required. The mechanism of the reaction represents an important part of the detailed

examinations, the more so, as apparently the different structures influence it kaolinite-dickite-monotermite).

It seems important to examine whether the colourisation is only a surface adsorption phenomenon (which is probable) or whether these molecules or the solvent can also penetrate into the interlaminar layers. Furthermore, the investigation of minerals which had been examined with DTA, X-rays and chemical analysis and had unequivocally been proved to be belonging to a pure kaolin group seems desirable.

References

1. Grofcsik, János: Hazai előfordulású monotermit. agyagásvány vizsgálata. A veszprémi Vegyipari Egyetem tudományos ülészakának előadásai. 1956.
2. Mezősi, József: The qualitative determination of clay mineral groups based on colour reaction. (Preliminary report.) Acta Min. Petr. Tom. VII. Szeged. 1953/54.
3. Mielens, R. C. King, M. E. and Schieltz, N. C.: Staining Tests. (Preliminary Report) Amer. Petrol. Institute. 1950.
4. Mielenz, R. C. and King, M. E.: Identification of clay minerals by staining tests. Amer. Soc. Testing Materials. Vol. 51. 1951.
5. Szádeczky Kardoss Elemér: Geokémia. Budapest. 1955.
6. Vedenejeva, N. E.: Novig metod opredelenija mineralnogs tipa glin sz pomosju organicseszkih kraszitelej. Geoszgeolizdat. Moszkva. 1952.
7. Vedenejeva, N. E.—Ratejev, M. A.: Identifikacija diszpersznich mineralov glin sz pomoscsju kraszitelej na osnove szpektrofometrii. Dokladi Akademii Nauk. SzSzsZR 71. 1950.
8. Vikulova, M. F.: Metod okrasivanija glininszich mineralov organicseszхими kraszteljami i ego znacsenie pri analize oszadocsnich tolscs. Goszgeolizdat. Moszkva. 1952.

Received August 15, 1956.

INDEX

KOCH, S.: The Mineral Collection of the Hungarian National Museum	3
FÖLDVÁRI—VOGL, M., KOBLENCZ, V.: Differential Thermal Analysis of Artificial Manganese Compounds	7
GRASSELLY, GY., KLIVÉNYI, E.: Concerning the Thermal Properties of the Manganese Oxides of Higher Valencies	15
GRASSELLY, GY., KLIVÉNYI, E.: On the Stability of the Mn_2O_4	33
GRASSELLY, GY.: Remarks on the Determination of the Composition of MnO_2 — Mn_2O_3 — Mn_3O_4 Systems	41
MEZŐSI, J.: The Determination of Kaolinites Based on Colour Reactions	47

TOMUS I — 1943

- Koch S.*: A Fejér megyei Szárhegy ólomérc előfordulásai. — Das Bleierzvorkommen auf dem Szárhegy im Komitat Fejér.
- Mezősi J.*: Királyhelmecek környékének közettani viszonyai. — Die petrographischen Verhältnisse der Umgebung von Királyhelmecek.
- Maklári L.*: A legszebb magyar melanterit. — Der schönste ungarische Melanterit.
- Grasselly Gy.*: A kovásznai forrásüledék analízise módosított Winkler-féle eljárással.

TOMUS II — 1948

- Koch S.*: Bizmutásványok a Kárpátmedencéből. — Bismuth Minerals in the Carpathian Basin.
- Grasselly Gy.*: Analyses of some Bismuth Minerals.
- Mezősi J.*: Lápósbánya környékének geológiai felépítése. — Geological Structure of the Environment of Lápósbánya.
- Mezősi J.*: Rézérc előfordulás a Zempléni Sziget-hegységben. — Occurrence of Copper Ore in Mountain Sziget at Zemplén.

Tomus III — 1949

- Koch S., Mezősi J., Grasselly Gy.*: A gyöngyösoroszi Zgyerka altáró kőzetei és ásványai. — Rocks and Minerals exposed by the Zgyerka Adit of Gyöngyösoroszi.
- Koch S.*: A lévai (Levice, Csehszlovákia) és korondi (Corund, Románia) forráskövek. — Spring Limestones of Léva (Levice, Czechoslovakia) and Korond (Corund, Roumania).
-
- Pákozdy V.*: Kémiai vizsgálatok a tetraedrit család ásványain. — Chemical Examinations of the Minerals of the Tetrahedrite Group.
- Mezősi J., Grasselly Gy.*: A bajpataki (Mátra hgs.) termérsz előfordulás. — The Occurrence of Native Copper in the Mátra Mountains at Bajpatak.
- Mezősi J.*: A misztbányai (Nistru) Kisasszony-patak völgyi telércsoport geológiai helyzete és felépítése. — Geological Constitution and Position of the Kisasszony-creek Lode Group of Misztbánya (Nistru).

TOMUS IV — 1950

- Koch S., Grasselly Gy., Donáth É.*: Magyarországi vasércelőfordulások ásványai. — The Minerals of the Hungarian Iron Ore Deposites.
- Koch S., Donáth É.*: Adatok a Sacaramb-i (Nagyág, Románia) alabandin és a Kalinka-i (Csehszlovákia) hauerit ismeretéhez. — Data relating to the Alabandin Deposites in Sacaramb (Nagyág, Roumania) and those of Hauerite in Kalinka (Czechoslovakia).
- Koch S., Grasselly Gy.*: A stanija-i (Sztanizsa, Románia) altaít. — Altaite from Stanija (Sztanizsa, Roumania).
- Mezősi J.*: A borsodi Bükk hegység közettartományi helyzete. — The Rock Provincial Situation of the Bükk Mountain Range.

TOMUS V — 1951

- Koch S., Grasselly Gy.*: The Manganese Ore Mineral Occurrences of Hungary.
- Koch S., Grasselly Gy.*: Processes Occurring at the Decomposition of Sulphide Ores.
- Mezősi J., Donáth É.*: A Maros és a Tisza lebegtetett hordalékának ásványtani és vegyi vizsgálata. — The Mineralogical and Chemical Investigation of the Floating Material of the Maros and Tisza.
- Grasselly Gy.*: Elektrografiai vizsgálatok szulfidos ércsiszolatokon. — Electrographical Investigations of Sulphide Ore Polished Sections.

TOMUS VI — 1952

- Koch S., Grasselly Gy.:* The Minerals of the Sulphide Ore Deposit of Nagybörzsöny.
Koch S., Grasselly Gy.: Data on the Oxidation of Sulphide Ore Deposites.
Mezősi J., Donáth É.: Investigation of the Dissolved and Floating Material of the Tisza and Maros.
Grasselly Gy.: Electrographical Analysis of Ore Textures.

TOMUS VII — 1953/54

- Koch S.:* Minerals from Gyöngyösoroszi.
Koch S.: The Hungarian Mineral Occurrences.
Mezősi J.: The Qualitative Determination of Clay Mineral Groups Based on Colour Reaction.
Grasselly Gy.: Electrochemical Examination of the Oxidation Processes of Sulphide Ores. From the Electromotive Force Series of Sulphide Ores.
Erdélyi J., Tolnai V.: Jarosite from Mount Gécsi.
Vendl A.: Vorkommen von Fluorit bei Levice.

TOMUS VIII — 1955

- Erdélyi J.* Beiträge zur mineralogischen Kenntnis des Gebirges von Velence.
Grasselly, Gy.: The Determination of the Composition of the MnO_2 — Mn_2O_3 — Mn_3O_4 Systems.
Koch, S.: Liquid-magmatic pyrrhotite from Szarvaskő.
Mauritz, B.: Mineralogic and Petrographic Observations (1953).
Mauritz, B.: Recent Observations Dealing with the Zeolite Minerals of the Basalt Rocks in the Highlands of Lake Balaton.
Mezősi, J.: The Colouration of Montmorillonites at Various pH values.
Miháلتz, I.: Erosionszyklen—Anhäufungszyklen.
Vendl, A., Mándy, T.: Schnellmethode zur Unterscheidung von Pyrit und Markasit.