

Some Oxidation Properties of Manganese and its Lower Oxides

ROBERT POMPE

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden

Oxidation of the pulverised samples of Mn, MnO and the equilibrium Mn_2O_3 - Mn_3O_4 have been studied. The investigations were made in the temperature range 200–1000 °C and at oxygen partial pressures of 0.01, 0.20 and 1 atm. The techniques employed were thermogravimetry and differential thermal analysis. Mn_2O_3 was found to be the oxide finally formed by oxidation of the metal, MnO and Mn_3O_4 in the temperature range from 400 °C to the equilibrium temperature of decomposition. The equilibrium temperature for the system Mn_2O_3 - Mn_3O_4 could be determined by decomposing the partially oxidized MnO or Mn_3O_4 using the TG-DTG technique. The thermodynamic aspects are discussed.

The ability of manganese to appear in different oxidation states gives rise to the existence of various solid oxide phases. The methods of preparation and the properties of these phases have been comprehensively described by Moore *et al.*¹ It was further established²⁻⁵ that the oxide phases appeared as crystalline compounds which might be represented by ideal formulae MnO, Mn_2O_3 , Mn_3O_4 and MnO_2 . MnO and Mn_3O_4 were shown to exhibit a considerable non-stoichiometry. The higher oxides were found to be convertible to the lower ones and *vice versa*, by a proper choice of temperature and oxygen pressure.⁶⁻⁹

The experimental results of many authors, however, differ somewhat as to which type of the oxide is formed and which temperature corresponds to the equilibrium value of decomposition. Mn_2O_3 or Mn_3O_4 are thus reported to form from MnO up to ca. 850 °C, while MnO₂ should be the product up to ca. 500 °C. Similarly, Mn_2O_3 is said to decompose to Mn_3O_4 at 920–970 °C. Hahn and Muan¹⁰ found the equilibrium Mn_2O_3 - Mn_3O_4 to be attainable in both direc-

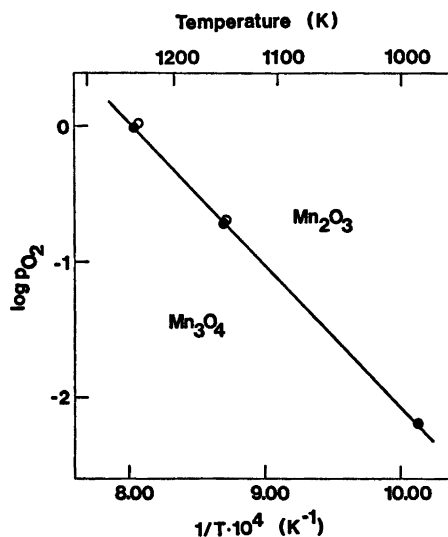


Fig. 1. Diagram showing the equilibrium oxygen pressure of the system Mn_2O_3 - Mn_3O_4 as a function of reciprocal temperature. ● This work, ○ Hahn and Muan.¹⁰

tions and determined approximately the equilibrium temperatures as indicated in Fig. 1. Kim *et al.*¹¹ confirmed by a different method their values.

The oxidation of pure manganese in air was studied by Baldwin and co-workers.¹² By X-ray and metallographic analysis they identified MnO, Mn_3O_4 and Mn_2O_3 in the oxide scale below 825 °C and MnO with some Mn_3O_4 above this temperature. According to Païdassi and Echeverria¹³ the oxide scale up to 850 °C consists of MnO, Mn_2O_3 and MnO_2 , while at 900–1200 °C the oxides present are MnO and Mn_3O_4 .

The purpose of the present work was to determine what kind of oxide is formed at various oxygen partial pressures (p_{O_2}) in the temperature range 200–1000 °C when samples of pulverized Mn metal or MnO are heated either continuously or at selected temperatures. A further objective was to explore the possibility of investigating the equilibrium Mn_3O_4 - Mn_2O_3 by the TG-DTG technique.

EXPERIMENTAL

Starting materials. MnO was prepared by heating manganese powder in the nitrogen atmosphere containing about 100 ppm oxygen at 800 °C for 18 h. The product was obtained as a hard grey-green mass containing 4.1 weight % manganese metal. Mn_2O_3 and Mn_3O_4 were produced by complete oxidation of Mn, MnO or Mn_2O_3 , and by decomposition of Mn_2O_3 , respectively.

The grain size of the manganese powder and the oxides varied between 1 and 3 μ for about 90 % of the grains.

Apparatus and experimental procedure. The investigations were made using a micro-thermo-balance (Mettler) with the additional equipment enabling TG, DTG and DTA curves to be simultaneously recorded as a function of temperature and time. The experimental and instrumental parameters used were as follows: Weight of the samples: 50–80 mg; reference substance: Cr_2O_3 , $BaCO_3$ (estimation of ΔH for the reactions); crucibles of S platinum; sensitivity of the measurements: TG, 5×10^{-2} mg; DTG, 10 mg/min; DTA, 100 μ V (Pt-Rh thermocouples); temperature control: ± 1.5 °C; the heating rates used: 1–15 °C/min; the gas atmospheres employed: O_2 ; Ar + O_2 , $p_{O_2} = 0.20$ atm; N_2 + O_2 , $p_{O_2} = 0.01$ atm; gas flow: 6 l/h.

In studying the oxidation of MnO, Mn_3O_4 and Mn_2O_3 , TG, DTG and DTA curves were recorded during heating of the samples up to 1000 °C. Systematic runs were made then at temperatures corresponding to the maxima of the appearing exothermic peaks, as well as some other selected temperatures.

Manganese powder was oxidized continuously up to 1000 °C and also at some lower, constant temperatures in the atmospheres of $p_{O_2} = 0.20$ atm and 0.01 atm.

Each run was terminated when the DTG curve essentially stabilized close to its initial value. This indicated either a zero or insignificant weight change of the sample. The heating of the furnace was then interrupted and the samples were cooled as quickly as possible in the furnace atmosphere.

The products were examined by X-ray diffractometry, IR-spectroscopy and optical microscopy. Calculations, where feasible, were

also made on the basis of weight gain or loss (TG) or the peak areas of the DTA curves.

RESULTS

Oxidation of Mn. On continuous heating of the samples up to 1000 °C the thermograms were such as schematically depicted in Fig. 2. The data for the subsequent runs are presented in Table 1. The weight increase appeared to be most pronounced in the temperature range of about 400–600 °C. At $p_{O_2} = 0.01$ atm the weight gain in this range was a linear function of time because of the limited oxygen supply. At the temperatures following from the figure a well-defined decomposition of the higher oxide took place. The diffraction patterns of the products before and after this decomposition were those of α - Mn_2O_3 and Mn_3O_4 , respectively. One or two strongest reflections for Mn_3O_4 often appearing in the Mn_2O_3 pattern suggested the occurrence of a layer of Mn_3O_4 beneath that of Mn_2O_3 . The IR spectra taken on Mn_2O_3 and Mn_3O_4 agreed with those published.¹⁴

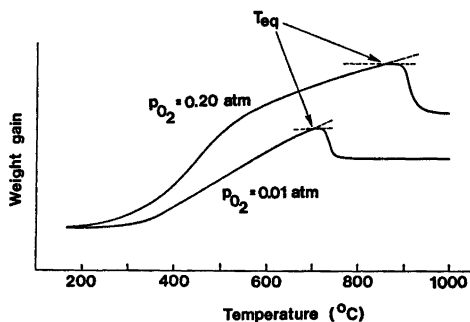


Fig. 2. The TG curves obtained in oxidizing the pulverized Mn up to 1000 °C at $p_{O_2} = 0.20$ atm and 1 atm.

Table 1. Oxidation of Mn powder up to 1000 °C at $p_{O_2} = 0.20$ atm and 0.01 atm.

p_{O_2} (atm)	Temp. (°C)	Time at const. temp. (h)	Products
0.20	1000	(heat. rate 1 °C/min)	Mn_3O_4
0.01	1000	(12 at 600 °C)	Mn_3O_4
0.01	600	16	Mn_2O_3
0.20	470	18	Mn_2O_3

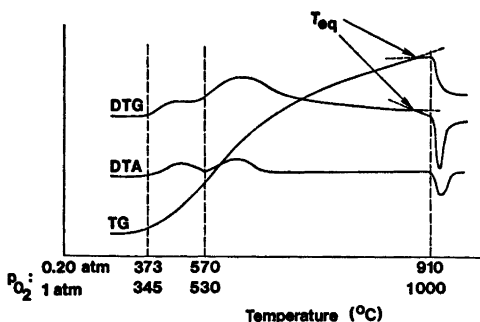


Fig. 3. The TG, DTG and DTA curves obtained in oxidizing MnO up to 1000 °C at $p_{O_2} = 0.20$ atm and 1 atm.

Oxidation of MnO. The essential appearance of the thermograms when oxidizing MnO at $p_{O_2} = 1$ atm and 0.20 atm at 1000 °C is shown in Fig. 3. Two exothermic peaks and one endothermic peak are apparent on the DTA curves at the temperatures indicated in the figure. The data characteristic of the constant temperature runs at $p_{O_2} = 0.20$ atm are given in Table 2.

In the run made at a temperature corresponding to the first exothermic reaction (480 °C) the DTG curve levelled off after ca. 1 h. X-Ray analysis revealed the presence of a small amount of Mn_2O_3 and the weight gain corresponded to almost complete oxidation of the Mn metal present in MnO, to Mn_2O_3 .

The reaction corresponding to the second exothermic peak was suggested by X-ray patterns and thermogravimetical calculations to be that of oxidation of MnO over Mn_2O_3 to Mn_3O_4 .

Table 2. Oxidation of MnO at constant temperatures and $p_{O_2} = 1$ atm and 0.20 atm.

Temp. (°C)	Time at const. temp. (h)	Products
480	1	MnO, Mn_2O_3
610	4	Mn_2O_3 , some MnO
780	6	Mn_2O_3
450	23	Mn_2O_3 , MnO
330	12	MnO (some Mn_2O_3 and Mn_3O_4 of strongly distorted X-ray patterns)

The product after the endothermic reaction was always found to be Mn_3O_4 .

$Mn_2O_3 - Mn_3O_4$ system. Mn_3O_4 was oxidized at a heating rate of 10 °C/min up to 870 °C at $p_{O_2} = 0.20$ atm. The oxygen uptake was most rapid in the range of 650–770 °C. Increasing the temperature out of this range produced a decreased oxidation rate. Mn_3O_4 could be converted into Mn_2O_3 within 2 h at 700 °C.

When the temperature of a partially oxidized sample of MnO or Mn_2O_3 attained the value determined as the equilibrium temperature (T_{eq}), the DTG curve showed an abrupt change in the slope. The TG curve, at the same time, formed a small plateau before the onset of an observable decomposition. The plateau was more prolonged when Mn_2O_3 , prepared by incomplete oxidation of MnO, was decomposed.

The values of the equilibrium temperature of decomposition obtained at $p_{O_2} = 1$ atm, 0.20 atm and 0.01 atm corresponded to 1246 K, 1151 K and 983 K, respectively, with a mean deviation of 3 K. The plot of their reciprocal values versus $\log p_{O_2}$ is shown in Fig. 1. ΔH° for the reaction $3Mn_2O_3 \rightarrow 2Mn_3O_4 + \frac{1}{2}O_2$ was evaluated from the peak area of the DTA curve. Using the reference value of 4.3 kcal/mol for $BaCO_3$,¹⁶ the ΔH° value was found to be 24.6 kcal/3 mol Mn_2O_3 . The value obtained from the slope of the plot in Fig. 1 was 21.8 kcal/3 mol Mn_2O_3 , being thus close to that commonly accepted (21.6 kcal/3 mol Mn_2O_3),^{11,15}

DISCUSSION AND CONCLUSIONS

The solid oxide phases obtainable by oxidation of Mn or MnO may be summarily written as MnO_{1+x} , where, for ideal stoichiometric molar ratios, x equals to 0.33, 0.50 and 1.00. Using the tabulated data¹⁵ and the formula for the computation of ΔG° in the form

$$\Delta G^\circ = \Delta H_0 + (2.303a \log T + I)T + b \times 10^{-3}T^2 + c \times 10^5/T \quad (A)$$

a comparison was made of the thermodynamic stability of the oxides. ΔG -values per mol MnO were calculated at 700 K and $p_{O_2} = 0.20$ atm for Mn_3O_4 , Mn_2O_3 and MnO, and also at 600 K and 800 K for the latter two oxides. The formula used was

$$\Delta G = x \Delta G^\circ(MnO_{1+x}) - \Delta G^\circ(MnO) - (x/2)RT \ln p_{O_2} \quad (B)$$

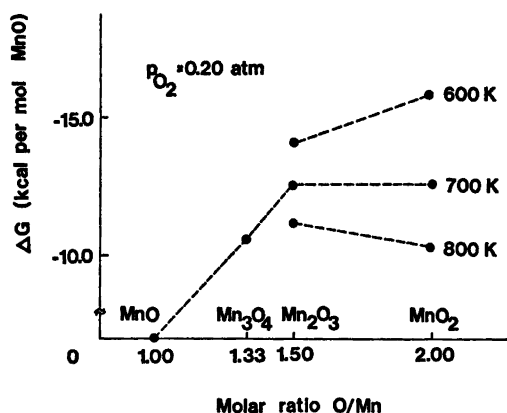


Fig. 4. The free enthalpy of formation per mol MnO for the higher manganese oxides at $p_{\text{O}_2} = 0.20$ atm.

and the values obtained were plotted in Fig. 4. Above 700 K Mn_2O_3 appears to be the most stable oxide while below this temperature the existence of MnO_2 should be favoured. The limiting value of p_{O_2} , estimated for the system $\text{Mn}_2\text{O}_3\text{-Mn}_3\text{O}_4$ from the formula (B) is of the order of 10^{-6} atm at 700 K.

The experimental results obtained tend to confirm that Mn_2O_3 is the only oxide finally formed above 700 K. The yield of Mn_2O_3 per unit time is then a function of the grain size, the operating time and the oxygen supply. No evidence of the formation of MnO_2 has been found. The oxidation, however, proceeds extremely slowly at lower temperatures (< 700 K) and a considerably longer time is therefore required to attain equilibrium.

In studying the system $\text{Mn}_2\text{O}_3\text{-Mn}_3\text{O}_4$ Hahn and Muan¹⁰ equilibrated the samples side by side at selected temperatures for between 40 and 300 h. In this investigation the duration of the measurements was reduced to less than 2 h. The change in the slope of the TG and DTG curves during heating was used to indicate the attainment of equilibrium. In order to obtain observable slope changes on the curves, partially oxidized samples of Mn_2O_3 were employed. Prepared by the oxidation of Mn, MnO or Mn_3O_4 they consisted of grains containing layers of MnO, Mn_3O_4 and Mn_2O_3 or Mn_2O_3 and Mn_3O_4 , respectively.

The presumed oxidation mechanism behind this method of determining the T_{eq} values is

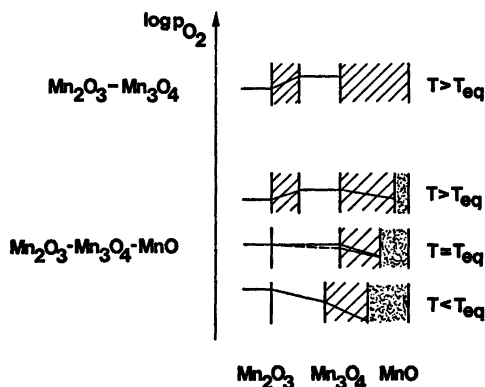


Fig. 5. The profiles of the oxygen pressure inside the grains of incompletely oxidized samples of Mn_2O_3 in the region of the equilibrium temperature of decomposition (T_{eq}) of Mn_2O_3 to Mn_3O_4 .

outlined in Fig. 5. When approaching the region of equilibrium the profiles of p_{O_2} within a grain are assumed to be approximately as illustrated in the figure. At temperature $T < T_{\text{eq}}$ the oxidation of Mn_3O_4 to Mn_2O_3 and MnO to Mn_2O_3 takes place and the weight change occurs continuously. On reaching the equilibrium temperature T_{eq} the oxidation of Mn_3O_4 to Mn_2O_3 is stopped resulting in the slope change of the DTG curve.

In the presence of only Mn_3O_4 the oxygen pressure gradient (∇p_{O_2}) is removed and the TG curve stabilizes since no more oxygen can be taken up. When, however, MnO is also present a certain Δp_{O_2} still exists through the Mn_2O_3 layer. The TG curve then increases slightly giving rise to a prolonged plateau at a low heating rate. At temperatures $T > T_{\text{eq}}$ a negative p_{O_2} is built up within the Mn_2O_3 layer and the decomposition of Mn_2O_3 to Mn_3O_4 is then a rather rapid process.

From the data compiled¹⁵ the value of T_{eq} can be evaluated. Using the formula (A) T_{eq} at $p_{\text{O}_2} = 1$ atm is calculated to be about 1530 K. The experimentally determined $T_{\text{eq}} = 1246$ K at $p_{\text{O}_2} = 1$ atm gives a value of ΔG° equal to 1.6 kcal/mol Mn_2O_3 . This is about 1% of the ΔG° values for Mn_2O_3 or Mn_3O_4 and may represent a measure of the error in the determination of these values. Since the ΔG° ($\text{Mn}_2\text{O}_3\text{-Mn}_3\text{O}_4$) is calculated as a difference of ΔG° values for the oxides this formula may be in-

appropriate to an accurate calculation of T_{eq} .

The values of T_{eq} obtained in this investigation compare well with those reported.^{10,11} This indicates that the above TG-DTG technique may provide a simple method for investigating solid oxide equilibria.

Acknowledgements. I wish to express my warmest thanks to Prof. Nils-Gösta Vannerberg for many helpful discussions and to Dr. John Wood for correction of the English text.

The investigation was performed in connection with a research project on nitrides in steel supported financially by the Swedish Board for Technical Development (Contr. No. EKB-U-287-74/75).

REFERENCES

1. Moore, T. E., Elis, M. and Selwood, P. W. *J. Am. Chem. Soc.* 72 (1950) 856.
2. LeBlanc, M. and Wehner, G. *Z. Phys. Chem. Abt. A* 168 (1934) 59.
3. Holtermann, X. X. *Ann. Chim. (Paris)* 14 (1940) 121.
4. Dubois, P. *C. R. Acad. Sci.* 199 (1934) 1416.
5. Drucker, C. and Hüttner, R. *Z. Phys. Chem. Leipzig* 131 (1927) 237.
6. Hed, A. Z. and Tannhauser, D. S. *J. Electrochem. Soc.* 114 (1967) 314.
7. Bergstein, A. and Vintera, I. *Chem. Listy* 50 (1956) 1530.
8. Mackenzie, R. C. *The Diff. Therm. Inv. of Clays*, Mineral. Soc., London 1957, p. 320.
9. Dollimore, D. and Tonge, K. H. *Thermal Analysis* 2 (1971) 91.
10. Hahn, W. C. and Muan, A. *Am. J. Sci.* 258 (1960) 66.
11. Kim, D. O., Wilbert, Y. and Marion, F. *C. R. Acad. Sci. Paris Ser. C* 262 (1966) 756.
12. Evans, E. B., Phalnikar, C. A. and Baldwin, W. M. *J. Electrochem. Soc.* 103 (1956) 367.
13. Paidassi, I. and Echeverria, A. *Acta Metall.* 7 (1959) 293.
14. Gattow, G. and Glemser, O. *Z. Anorg. Allg. Chem.* 309 (1961) 143.
15. *Handbook of Chemistry and Physics*, 47th Ed., The Chem. Rubber Co., Cleveland.
16. Mackenzie, R. C. and Ritchie, P. F. S. *Thermal Analysis* 1 (1971) 442.

Received November 19, 1975.