[AMERICAN JOURNAL OF SCIENCE, VOL. 258, JANUARY 1960, P. 66-78]

STUDIES IN THE SYSTEM Mn–O: THE Mn_2O_3–Mn_3O_4 AND Mn_3O_4–MnO EQUILIBRIA*

W. C. HAHN, JR. and ARNULF MUAN
College of Mineral Industries.
The Pennsylvania State University, University Park, Pennsylvania

ABSTRACT. As a first step in an investigation of phase relations in the system Mn–O, the equilibria

$$6\ Mn_2O_3 = 4\ Mn_3O_4 + O_2$$

and

$$2\ Mn_3O_4 = 6\ MnO + O_2$$

have been studied in the temperature intervals 845 to 1029°C and 1248 to 1562°C, respectively, and at O_2 partial pressures ranging from 0.21 to 1 atm. and from $10^{-3.66}$ to 0.21 atm. respectively. The conditions for coexistence of two crystalline phases in stable univariant equilibria are expressed as follows:

$$Mn_2O_3, Mn_3O_4 : \log p_{O_2} = 8.05 - 10100 \cdot 1/T$$

$$Mn_3O_4, MnO : \log p_{O_2} = 13.31 - 26000 \cdot 1/T$$

Exploratory runs in the solidus temperature region for the composition range between MnO and Mn_3O_4 indicate the presence of a eutectic at approximately 1540°C.

An explanation is offered for the poor agreement among previously published data on these equilibria.

INTRODUCTION

The system Mn–O is of considerable economic importance. In addition to the role of manganese as an alloying element, it acts as a deoxidizer (as well as desulfurizer) in the production of steel; the oxide formed constitutes a part of the slag, and this in turn may have a serious fluxing effect on the furnace refractories. Thus precise knowledge of the reactions of manganese with oxygen is fundamental to the chemistry of steelmaking. The use of manganese dioxide as a depolarizer in the common dry cell has also stimulated considerable interest in the Mn–O system. The fact that the United States produces only a small percentage of the manganese it needs has caused a great deal of attention to be devoted to the effective utilization of manganese, improved recovery from its ores (which are principally oxides) and the recovery of manganese from slags and low grade deposits. For a scientific investigation of all these problems, a knowledge of the system Mn–O is necessary.

Inasmuch as manganese occurs in different states of oxidation, many of the problems encountered in determining and illustrating phase equilibria in the system Mn–O are similar to those in Fe–O. The latter system was studied very thoroughly by Darken and Gurry (1945, 1946), and methods for describing such systems have been discussed in several papers emanating from our laboratories during the past few years (see for instance a paper by Muan, 1958).

A complete study of phase relations in the system Mn–O involves work at relatively high temperatures and over a wide range of O_2 partial pressures. We have selected temperature and O_2 pressure limits for our present study with the following considerations in mind. First, while the entire range of O_2 partial pressures from approximately 10^{-20} to 1 atm. is of interest, it is ex-

---

* Contribution No. 58-44 from College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

perimentally easier to work at O_2 pressures in the upper part of this range. This is mainly because the high activity of manganese in oxide phases under strongly reducing conditions makes it difficult to find a crucible material in which to contain the samples. Therefore, the first step in our investigation was limited to O_2 pressures ranging from 1 atm. down to $10^{-3.66}$ atm. The temperature range for our study was also limited by practical considerations. The upper limit of approximately 1550°C is a temperature which can be conveniently reached in platinum-20 percent rhodium resistance furnaces, and the lower limit is that below which equilibrium cannot be reached within a "reasonable" period of time, say 1-2 weeks. With these chosen limitations in our investigation, we will be mainly concerned with the equilibria

$$6\ Mn_2O_3 = 4\ Mn_3O_4 + O_2$$

and

$$2\ Mn_3O_4 = 6\ MnO + O_2$$

as well as limited parts of the solidus temperature region in the composition range between MnO and Mn_3O_4.

PREVIOUS WORK

Numerous investigations have been reported in the literature dealing with various aspects of the chemistry of manganese oxides. However, nowhere does there exist a comprehensive account of the temperature-pressure-composition relations in the system Mn–O.

It is widely known that the oxides MnO, Mn_3O_4, Mn_2O_3 and MnO_2 exist as stable crystalline phases and can be converted from one to the other by suitable adjustments of temperature and O_2 partial pressure. It is also generally assumed that some of these oxide structures, notably MnO and Mn_3O_4, may exist over a range of compositions deviating from the stoichiometric ratios represented by the above formulas. However, an inspection of the quantitative data available for the various equilibria shows that discouragingly large discrepancies exist among these data. This may be partly a result of the fact that many of the equilibria have been estimated by addition and subtraction of heat of formation and entropy data, each of which has considerable limits of error, rather than by direct experimental observation of the equilibria in question. However, even data obtained by different authors using essentially the same technique are in very poor agreement. It is suspected that extreme difficulty in attainment of equilibrium in this system is the main reason for these discrepancies.

Compositions of Mn_3O_4 have been studied by Millar (1928), Le Blanc and Wehner, (1934), and Shomate (1943), and by Moore, Ellis and Selwood (1950). While Le Blanc and Wehner found the Mn_3O_4 to contain a considerable amount of excess oxygen over stoichiometric, the other investigators reported the Mn_3O_4 in air to contain essentially the amount of oxygen corresponding to the formula Mn_3O_4.

Le Blanc and Wehner (1934), as well as Moore, Ellis and Selwood (1950), also studied the MnO phase and concluded that the compositions varied with conditions of preparation, without giving any reliable quantitative data for the limits.

A structural transformation is known to take place in Mn_3O_4 in the temperature interval between 1100 and 1200°C. Southard and Moore (1942), on the basis of heat content data, estimated that the transition takes place at 1172±40°C. McMurdie and Golovato (1948) showed that the low temperature tetragonal form inverts to a high temperature cubic form. They found the transition to take place at 1170°C upon heating, but at temperatures as low as 1100°C upon cooling. Van Hook and Keith (1958) re-investigated this reaction recently and placed the transformation temperature at 1160±5°C.

Mn_2O_3 is also known to exist in at least two polymorphic forms, as pointed out as early as in 1934 by Dubois. One form, generally called α, has a "C" type cubic structure, while the other, generally called γ, has a cation deficient, tetragonal, distorted spinel structure. According to Mason (1943) the α form is stable relative to the γ form under all conditions. The γ form was not encountered in the present investigation.

The melting point of metallic manganese is 1244±3°C (from data compiled by Sully, 1955). Various "melting points" of MnO and Mn_3O_4 have been reported in the literature although these have little meaning unless the O_2 pressure of the atmosphere is specified. This is particularly the case with "MnO"[1], the "melting point" of which probably varies by several hundred degrees depending on the O_2 pressure used. Indications are, however, that the maximum temperature on the MnO liquidus curve is 1750°C or higher (White, Howat and Hay, 1934, Glasser, 1958). The melting point of stoichiometric Mn_3O_4 has been reported by Van Hook and Keith (1958) to be 1562°C, while v. Wartenburg and Prophet (1932) determined the melting point in air as 1560°C.

Temperatures for decomposition of Mn_2O_3 to Mn_3O_4 in air and at 1 atm. O_2 pressure have been reported by Meyer and Rötgers (1908), Saito (1927) and by Drucker and Hüttner (1927). These authors indicate that decomposition takes place at approximately 940 and 1090°C in air and at 1 atm. O_2 pressure, respectively. However, these temperatures represent those at which the decomposition proceeds at an easily observable rate rather than defining the equilibrium existence of the two crystalline phases Mn_2O_3 and Mn_3O_4, at these O_2 partial pressures. Coughlin (1954) has compiled free energy tables, based mainly on heat of formation and entropy data, that permit calculation of the Mn_2O_3–Mn_3O_4 equilibrium. On the basis of his data the temperatures of equilibrium coexistence of the two crystalline phases are approximately 1170 and 1280°C in air and at 1 atm. O_2 pressure, respectively.

Even greater discrepancies exist regarding the equilibrium between Mn_3O_4 and MnO. Coughlin (1954) has very ably compiled the data that seem to be most reliable. His free energy tabulations for MnO are based on the heat of formation data of Southard and Shomate (1942), the entropy measurements of Todd and Bonnickson (1951) and the high temperature equilibrium studies of Aoyama and Oka (1933). Uncertainties regarding the composition of the MnO used in the latter experiments detract from the reliability of the data for calculating the equilibrium between MnO and Mn_3O_4.

[1] This phase will be designated MnO in the present paper for sake of convenience.

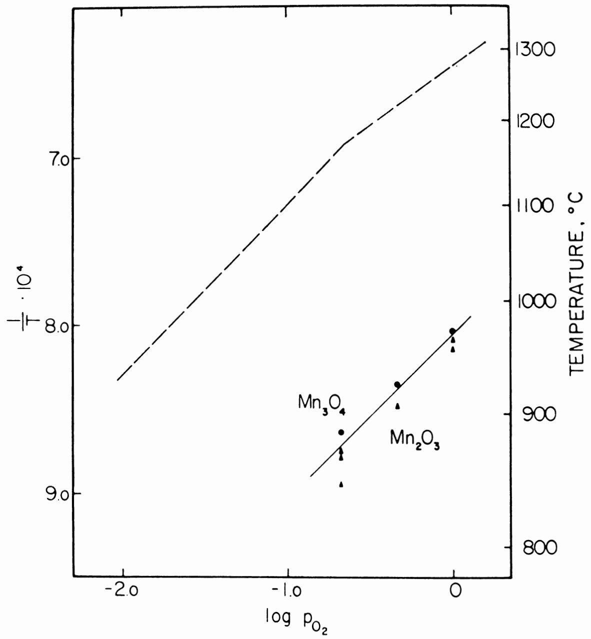

Fig. 1. Diagram showing the equilibrium relations of Mn_2O_3 and Mn_3O_4 as a function of O_2 pressure (log scale in atm.) and temperature (inverse °K scale). Solid triangles and circles represent observed stable occurrence of Mn_2O_3 and Mn_3O_4 respectively, and the solid line is drawn to fit the experimental data as well as possible. The dash curve is drawn to represent the same equilibrium on the basis of data tabulated by Coughlin (1954).

EXPERIMENTAL METHOD

General procedure.—Subsolidus equilibria were investigated by making runs at selected temperatures and O_2 partial pressures. Two samples, either Mn_2O_3 and Mn_3O_4 or Mn_3O_4 and MnO, were equilibrated side by side in the furnace. After a suitable time, determined by experience, the samples were quenched and the phases present determined by x-ray methods. In addition, runs were made in a thermal balance which permitted a direct observation of weight changes and hence the approach toward equilibrium as oxygen was added to or subtracted from the samples by reaction with the gas phase.

Charges for the investigation of solidus relations in the composition range between MnO and Mn_3O_4 were prepared by mixing various proportions of the two oxides. These charges were sealed in platinum-20 percent rhodium tubes, equilibrated in the furnace and quenched in water. The samples were then polished and examined microscopically under reflected light to determine the phases present.

Control of atmosphere.—The method used for controlling O_2 pressures was essentially the same as that used by Darken and Gurry (1945), and later by Muan (1955). Runs at 1 atm. O_2 were made by passing commercial tank oxygen through the furnace. Runs at 0.21 atm. O_2 were made by opening the bottom of the furnace tube to allow air to circulate through. Runs at other pressures in the range 1-$10^{-2.00}$ atm. were made by mixing O_2 and CO_2 in required proportions. In these cases the partial pressure of O_2 is determined directly from its partial pressure in the mixture at room temperature because at these concentrations of O_2 the dissociation of CO_2 can be neglected. Runs at lower O_2 partial pressures were made in CO_2 and in an atmosphere obtained by mixing CO_2 and H_2. The partial pressures of O_2 in these cases were calculated from the data compiled by Coughlin.

The gases used were of reported compositions 99.5 percent O_2, 99.956 percent CO_2, and 99.5 percent H_2. It was found necessary to remove O_2 from the CO_2 by passing the gas over copper gauze heated to 500°C.

The rate of flow of each of the two gases was measured separately by two capillary flow meters with bleeder tubes on both ends of the capillaries to maintain a constant pressure drop. A series of mutually interchangeable capillaries of different openings was at hand, so that a wide range of mixing ratios could be obtained with manometer readings of convenient magnitude. A third manometer was inserted in the line to measure the rate of flow of gas through the furnace. The flow meters were calibrated individually with the various capillaries, using a standard wet test meter.

Furnaces and temperature control.—Vertical tube furnaces with platinum-20 percent rhodium resistance windings were used throughout this investigation. The furnace used for the quenching experiments was provided in the upper end with a brass head through which sample holder or thermocouple protection tube could be inserted and clamped in gas tight connection. The lower end of the furnace was provided with a gas inlet device which permitted quenching of the sample without disturbing the atmosphere in the furnace. The gas escaped through a side arm attachment in the upper part of the furnace tube, and was passed through a bubbling bottle before going to the atmosphere.

The furnace used for the thermal balance experiments was equipped with ground glass joints fused to the top and bottom of the furnace tube. The upper glass attachment was drawn out to a long, relatively narrow tube to prevent air from diffusing into the furnace. In this furnace a sample could be suspended from an analytical balance by means of a fine platinum wire leading through the opening for the gas outlet. The approach to equilibrium could then be followed by weighing the sample periodically.

The furnace temperatures were regulated by means of control couples connected in the case of one furnace to a Celectray controller and in the other to a Brown Pyr-O-Vane controller. The thermal gradient at the hot spot did not exceed 2°C over 1 inch at 1400°C in either furnace.

Temperatures were measured before and after each run with a platinum-90 percent platinum 10 percent rhodium thermocouple. This was calibrated periodically at melting points defined as follows: Au, 1063°C; $CaMgSi_2O_6$, 1391.5°C; $CaSiO_3$, 1544°C. The tables compiled by Shenker, et al. (1955) were used for temperature interpolations.

Starting materials.—All oxides of manganese used in the present investigation were made from "Baker Analyzed" reagent grade manganese dioxide of reported analysis as follows: Assay (MnO_2), 100.0%; Fe, 0.020%; insoluble in HCl. 0.015%; chloride, 0.002%; nitrate, 0.050%; sulfate, 0.040%; earths and alkalies (as SO_4), 0.015%. Starting materials were made by igniting this oxide in air at approximately 800°C to produce Mn_2O_3 and at approximately 1100°C to produce Mn_3O_4. The MnO used as starting material was prepared by heating of MnO_2 at approximately 1100°C in an atmosphere with a CO_2/H_2 mixing ratio of approximately 10. In accordance with the results of Le Blanc and Wehner (1934) it was found necessary to cool the MnO in the furnace atmosphere to prevent the formation of higher oxides.

Chemical analysis.—The oxides were analyzed by determination of "excess oxygen", i.e., weight percent oxygen in excess of that corresponding to stoichiometric MnO. Approximately 0.1 gm of the oxide sample and 0.75 gm of $Fe\ (NH_4)_2\ (SO_4)_2 \cdot 6H_2O$ were added to 25 ml of H_2O, 10 ml of 1:4 H_2SO_4 and 3 ml of 49 percent HF, and the solution was allowed to boil for 10 minutes to dissolve all the sample. Upon cooling to room temperature 25 ml of distilled water and 15 ml of 2 percent boric acid were added and the solution was titrated with 0.05-normal $KMnO_4$. The value of the equivalents of excess oxygen was calculated as the difference between the equivalents of ferrous iron added and that reacting with $KMnO_4$. The addition of HF was necessary in order to avoid the difficulty encountered by Siemonsen (1939) in dissolving samples of Mn_3O_4 which had been prepared at high temperatures. Boric acid was added to complex the iron in order that the faint pink color of the end point in the titration with $KMnO_4$ could be observed. The $Fe\ (NH_4)_2\ (SO_4)_2 \cdot 6H_2O$ had to be standardized under the conditions of the analysis each time analyses were made because it will lose or gain water on standing.

Preliminary tests were made to determine whether the oxygen of the air affects the analytical results as it does in the use of the arsenate method as discussed by Stalzer and Vosburgh (1951). Duplicate samples boiled in air and in CO_2 gave identical results within limit of experimental error.

RESULTS

The composition of Mn_3O_4 in air and in 1 atm. O_2 was determined over the temperature interval from about 1100 to 1500°C. In preliminary experiments, starting samples of MnO and Mn_3O_4 were equilibrated side by side in the furnace until the compositions of both samples were the same. This was done at a high temperature and at the lowest temperature in the interval concerned. Once the time necessary to reach equilibrium at these two chosen temperatures had been determined, it was assumed than any run at intermediate temperatures would require no longer time to reach equilibrium than at the lowest temperature. Also, in succeeding runs only Mn_3O_4 was used as starting material. It was found necessary to quench these samples in water, for air quenching caused results which were inconsistent because of the reaction of the samples with the oxygen of the air upon cooling. The results of these runs appear in table 1.

The phase transformation in Mn_3O_4 occurs rapidly, and the high temperature form cannot be quenched to room temperature. It is inferred, however, that although the structure of Mn_3O_4 changes upon quenching, the composition does not change appreciably. The basis for this inference is that

TABLE 1

Analyses of Samples of Mn_3O_4 Produced at Different Temperatures in Air ($p_{O_2} = 0.21$ atm.) and at $p_{O_2} = 1$ atm.

	Temperature (°C)	Starting Material	Duration of Run (hours)	% Excess Oxygen (duplicate analyses)		Value of x in Calculated Formula (MnO_x) of Oxide	
				#1	#2	#1	#2
Runs in Air:	1099	MnO	40	6.94	6.97	1.331	1.332
	1099	Mn_3O_4	52	6.99	7.00	1.333	1.334
	1252	Mn_3O_4	43	6.93	6.96	1.330	1.332
	1393	MnO	53	6.98	7.03	1.333	1.334
	1393	Mn_3O_4	39	6.91	7.03	1.329	1.335
	1463	Mn_3O_4	34	6.90	—	1.329	—
	1535	Mn_3O_4	54	6.85	6.96	1.326	1.329
Runs at p_{O_2} = 1 atm.:	1085	Mn_3O_4	41	6.85	7.07	1.326	1.337
	1251	Mn_3O_4	72	6.95	6.94	1.331	1.331
	1383	Mn_3O_4	94	6.83	6.85	1.325	1.326
	1456	Mn_3O_4	36	6.87	6.91	1.327	1.329
	1505	Mn_3O_4	38	6.92	—	1.330	—

Saito (1927) and Meyer and Rötgers (1908), who followed the decomposition of MnO_2 on continuous heating in air by means of a thermal balance, found no abrupt change in weight in the vicinity of 1160°C.

Inasmuch as all compositions of Mn_3O_4 determined in the present investigation were in the range $MnO_{1.326}$ to $MnO_{1.334}$ and there was no systematic variation with temperature or O_2 partial pressure, it is concluded that the composition of this phase is essentially constant, corresponding to that of stoichiometric Mn_3O_4, under the conditions of temperature and O_2 pressure used in this investigation. Additional evidence of the constancy of composition was obtained in the present investigation by means of the thermal balance arrangement. A sample of Mn_3O_4, weighing approximately 1 gm, was equilibrated for two days in air at 1348°C. It showed no change in weight at the end of 17 hours after the atmosphere was changed to oxygen at 1 atm.

The equilibrium between Mn_3O_4 and Mn_2O_3 was investigated at 1 atm. O_2 pressure, in air, and in an atmosphere of intermediate O_2 partial pressure. The data for the critical runs appear in table 2. These data are plotted in figure 1 along with the values of log p_{O_2} calculated from the data compiled by Coughlin (1954). The value for the heat of reaction for the process $6Mn_2O_3 = 4Mn_3O_4 + O_2$ as calculated from the data of the present investigation is 46,200 ± 3,300 cal. The equilibrium decomposition temperatures of Mn_2O_3 to Mn_3O_4 as determined in the present investigation are 968 ± 5°C in oxygen at 1 atm. and 877 ± 8°C in air.

Data for the equilibrium between Mn_3O_4 and MnO appear in table 3. These data are plotted in figure 2 along with the values of log p_{O_2} calculated from the data compiled by Coughlin (1954). The high temperature limit of the experimental curve is that at which a liquid phase develops, as described later. The low temperature limit of the present investigation was the temperature of the Mn_3O_4–MnO equilibrium in pure CO_2. The mixing ratios,

TABLE 2

Critical Runs for Determination of the Equilibrium

$6Mn_2O_3 = 4Mn_3O_4 + O_2$

	Temperature (°C)	$1/T \cdot 10^4$	Duration of Run (hours)	Phase Present at Equilibrium
Runs in Air:	845	8.95	61	Mn_2O_3
	865	8.79	60	Mn_2O_3
	870	8.75	98	Mn_2O_3
	874	8.72	244	no change in either sample
	885	8.64	47	Mn_3O_4
	972	8.03	43	Mn_3O_4
Runs at pO_2 = 0.46 atm.:	906	8.48	308	Mn_2O_3
	924	8.35	288	Mn_3O_4
Runs at pO_2 = 1 atm.:	955	8.14	46	Mn_2O_3
	964	8.08	66	Mn_2O_3
	972	8.03	86	Mn_3O_4
	1029	7.68	42	Mn_3O_4

CO_2/H_2, necessary to obtain partial pressures of O_2 in the vicinity of the curve at lower temperatures would have to be greater than 500/1. In the case of such mixtures, serious doubts concerning the accuracy of the gas mixer would arise.

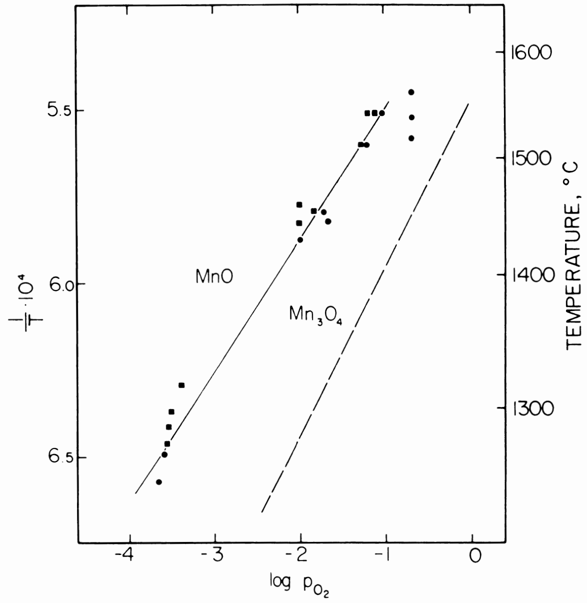

Fig. 2. Diagram showing stability relations of the phases Mn_3O_4 and MnO as a function of O_2 pressure (log scale in atm.) and temperature (inverse °K scale). Solid dots and squares represent observed stable occurrence of Mn_3O_4 and MnO, respectively, and the solid straight line is drawn to fit the data as well as possible. The dash straight line represents the equilibrium curve as calculated from data tabulated by Coughlin (1954).

The value of the heat of reaction for the process $2Mn_3O_4 = 6MnO + O_2$ as calculated from the data of the present investigation is 118,500 ± 2,500 cal.

Runs in sealed 80 percent platinum 20 percent rhodium tubes with mixtures intermediate in composition between MnO and Mn_3O_4 permitted the determination of lowest liquidus temperatures in this region. An invariant situation (eutectic) exists at 1540 ± 6°C with Mn_3O_4, MnO, liquid and gas present together in equilibrium. The O_2 partial pressure of the gas phase is determined as the intersection between the 1540°C isotherm and the MnO—Mn_3O_4 equilibrium curve in figure 2; the value is approximately 0.1 atm.

DISCUSSION

The compositions of the Mn_3O_4 phase determined in the present investigation agree well with those found by Shomate (1943) who prepared Mn_3O_4 by heating manganese dioxide in air to 1050°C, and Millar (1920) as well as Moore, Ellis and Selwood (1950) who prepared Mn_3O_4 by heating manganese sulphate in air at about 1000°C. Their results along with the calculated values for stoichiometric Mn_3O_4 are as follows (compare data in table 1):

	Percent excess oxygen	Value of x in calculated formula (MnO_x) of oxide	
Calculated :	6.99	1.333	
Shomate :	7.00, 7.01	1.334	1.334
Millar :	7.01, 7.03	1.334	1.335
Moore, Ellis and Selwood :	7.0	1.33	

In contrast to these results, the data of Le Blanc and Wehner (1934) indicate the existence of a Mn_3O_4 phase with considerable excess oxygen over stoichiometric in the temperature interval 400-500°C.

The melting temperature of Mn_3O_4 in air, 1567 ± 4°C, as determined in the present investigation, as in fair agreement with the value of 1560°C found by v. Wartenberg and Prophet (1932). It is also worth noting that Van Hook and Keith (1958) reported a melting temperature of 1562°C for stoichiometric Mn_3O_4 prepared by mixing MnO_2 and powdered manganese in the correct proportions and heating in tubes that were assumed to be gas tight.

The data for the reaction between Mn_2O_3 and Mn_3O_4 reported in the present paper we believe represent true equilibrium conditions, as distinguished from most data previously reported in the literature. We succeeded in attaining equilibrium in both directions, equilibrating samples of Mn_2O_3 and Mn_3O_4 as starting materials side by side and keeping them in the furnace up to two weeks.

The discrepancies between our data on this equilibrium and those of previous workers can probably be ascribed mainly to this difficulty of obtaining equilibrium. Meyer and Rötgers (1908), who reported decomposition temperatures of 940 and 1090°C in air and at 1 atm. O_2, respectively, stated specifically that the phase changes they observed were not reversible, but proceeded only from Mn_2O_3 to Mn_3O_4. Therefore, the decomposition temperatures reported by them were those at which the reaction took place in a "reasonable" period of time rather than true equilibrium values. Many other investigators, e.g., Saito (1927) and Drucker and Hüttner (1927), have confirmed or approximated the temperatures determined by Meyer and Rötgers. Unfortunately, some of these later investigators have failed to appreciate the significance of the reservations made by Meyer and Rötgers regarding the lack of equilibrium conditions. The transformation temperatures determined in the present investigation are also significantly lower than the values of approximately 1280°C at 1 atm. O_2 pressure and 1170°C in air calculated from the data of Coughlin (1954). The reasons for this discrepancy cannot be checked because Coughlin has omitted certain sources for the data which he has compiled for Mn_3O_4. However, in the light of the previous discussion concerning the transformation temperatures as reported in the literature, it can be suspected that if an experimentally determined transformation temperature was used by Coughlin in compiling his data, it was too high.

The ΔH° value of 46,200 ± 3,300 cal. for the reaction

$$6Mn_2O_3 = 4Mn_3O_4 + O_2$$

determined in the present investigation (for the temperature interval 845-1029°C) agrees well with the value of 44300 ± 13600 cal. calculated from the data compiled by Coughlin.

An observation which was made during study of the Mn_3O_4—MnO equilibrium deserves special discussion. In preliminary experiments for determination of the equilibrium between Mn_3O_4 and MnO, the transformations of MnO to Mn_3O_4 and vice versa were studied under conditions of constant temperature and O_2 partial pressures which were later found to be well within the regions of stability of the respective oxides. These transformations were followed by means of the thermal balance and x-ray examination. The complete transformation in both directions took place in three to four hours in tests run at 1300°C. (The transformations were called complete when the sample had reached a constant weight and the quenched sample consisted of only one phase according to x-ray analysis.) It was later discovered that when the two starting materials, MnO and Mn_3O_4, were run simultaneously in the furnace at combinations of temperature and O_2 partial pressure representing conditions near the boundary curve on the MnO side (see fig. 2), both quenched samples turned out to be mixtures of MnO and Mn_3O_4 as determined by x-ray analysis. In other words, each of the phases (MnO and Mn_3O_4) seemed to be unstable with respect to the other—apparently a contradictory situation.

Experience showed that if both quenched samples were a mixture the first time they were removed from the furnace, the amount of the MnO phase increased and the amount of the Mn_3O_4 phase decreased in every case upon further time in the furnace at the same temperature and O_2 partial pressure. On the basis of this observation it was assumed that MnO is the truly stable phase under the conditions of O_2 partial pressure and temperature which resulted in this anomalous behavior of the samples.

Inasmuch as the composition of Mn_3O_4 is known to remain essentially constant and the composition of MnO has been reported to vary considerably (Le Blanc and Wehner, 1934), it is suspected that the MnO phase is the cause of the difficulty encountered near the boundary conditions. Exsolution of Mn_3O_4 from the oxygen-rich MnO phase near the boundary curve during quenching may be thought of as a cause of the anomalous observation discussed above. However, indications are that the observed phenomenon instead is related to the complex kinetics of the transformation of an MnO phase of one composition to another. It is important to note that the MnO used as starting material in these runs was made up under conditions of temperature and O_2 partial pressure which are known to be far removed from the conditions in which MnO is in equilibrium with Mn_3O_4. Runs in the thermal balance furnace showed that the weight of the MnO sample under these boundary conditions first increased rapidly, then remained essentially constant for a long period of time before finally decreasing. This observation together with the fact that x-ray analysis of quenched samples showed decreasing amounts of Mn_3O_4 with increasing time of equilibriation strongly suggests that MnO of low oxygen content first transforms partly to Mn_3O_4 before reacting with oxygen of the atmosphere to form MnO of higher equilibrium oxygen content at the conditions near the boundary curve. This problem will be dealt with in more detail in a later paper.

The heat of reaction for the process

$$2Mn_3O_4 = 6MnO + O_2$$

determined in the present investigation, 118,500 ± 2,500 cal., (in the temperature interval 1248-1540°C) does not agree well with the value of 94800 ± 1500 cal. calculated from the data compiled by Coughlin (1954). This, however, may be mainly an apparent discrepancy caused by differences in composition of the MnO phase involved in the reaction.

Table 3
Critical Runs for Determination of the Equilibrium
$2Mn_3O_4 = 6MnO + O_2$

Temperature (°C)	$1/T \cdot 10^4$	$\log p_{O_2}$	Duration of Run (hours)	Phase Present at Equilibrium
1248	6.58	−3.66	47	Mn_3O_4
1267	6.49	−3.59	22	Mn_3O_4
1274	6.46	−3.56	40	MnO
1286	6.41	−3.54	17	MnO
1297	6.37	−3.51	15	MnO
1315	6.30	−3.38	22	MnO
1429	5.88	−1.99	70	Mn_3O_4
1443	5.83	−1.99	22	MnO
1444	5.82	−1.66	26	Mn_3O_4
1453	5.79	−1.70	17	Mn_3O_4
1453	5.79	−1.82	20	MnO
1458	5.78	−1.99	72	MnO
1512	5.60	−1.20	17	Mn_3O_4
1512	5.60	−1.26	10	MnO
1517	5.59	−0.68	17	Mn_3O_4
1538	5.52	−0.68	11	Mn_3O_4
1542	5.51	−1.03	23	Mn_3O_4
1542	5.51	−1.10	7	MnO
1542	5.51	−1.10	9	MnO
1562	5.45	−0.68	7	Mn_3O_4

SUMMARY

Equilibria among the phases Mn_2O_3, Mn_3O_4 and MnO have been investigated as a first step in a study of phase relations in the system Mn—O. The investigation was limited to the temperature interval 845 to 1562°C and O_2

partial pressures ranging from $10^{-3.66}$ to 1 atm. The equilibria were studied mainly by the quenching technique, using microscopic, x-ray and chemical analysis for identification of phases in the quenched samples. These experiments were supplemented with weighing experiments carried out in a thermal balance setup.

Runs of long duration permitted equilibrium to be reached in both directions for the reaction

$$6Mn_2O_3 = 4Mn_3O_4 + O_2$$

The temperature of equilibrium coexistence of Mn_2O_3 and Mn_3O_4 in air is 877 ± 8°C and at 1 atm. O_2 pressure 968 ± 5°C. The $\Delta H°$ for the reaction above as calculated from the data of this investigation is 46,200 ± 3,300 cal.

The composition of Mn_3O_4 was found to be essentially constant and equal to that of the stoichiometric formula at all temperatures studied (1085 to 1535°C) in air and at 1 atm. O_2 pressure.

The equilibrium between Mn_3O_4 and MnO according to the equation

$$2Mn_3O_4 = 6MnO + O_2$$

was studied in the temperature interval 1248 to 1562°C. A curve representing the equilibrium coexistence of these two crystalline phases as a function of temperature and O_2 partial pressure has been obtained. The $\Delta H°$ for the reaction as calculated from the data of this investigation is 118,500 ± 2,500 cal.

Exploratory runs in the solidus temperature region showed that an invariant situation exists in the Mn–O system at approximately 1540°C., with the following phases present together in equilibrium: Mn_3O_4, MnO, liquid and a gas phase with an O_2 partial pressure of approximately 0.1 atm.

During the study of the Mn_3O_4–MnO equilibrium it was observed that MnO used as starting material and equilibrated under conditions of temperature and O_2 pressure in the stability field of the MnO phase, but close to the Mn_3O_4–MnO boundary curve, upon quenching to room temperature gave a mixture of Mn_3O_4 and MnO (as revealed by x-ray examination). It is tentatively suggested that this phenomenon is related to the complicated reaction kinetics for transformation of a MnO phase of one oxygen content to another rather than a simple exsolution of Mn_3O_4 from the MnO phase during quenching.

ACKNOWLEDGMENTS

This work was carried out as part of a research project on steel plant refractories systems sponsored by the American Iron and Steel Institute. The helpful assistance of A. M. Byström in developing the method of chemical analysis is gratefully acknowledged. The authors are also indebted to E. F. Osborn for his critical reading of the manuscript.

REFERENCES

Aoyama, S., and Oka, Y., 1933, Oxidation reduction equilibrium of metallic manganese: Sci. Repts. Tâhoku Imp. Univ., v. 22, p. 824-834.

Coughlin, J. P., 1954, Contributions to the data on theoretical metallurgy: XII. heats and free energies of formation of inorganic oxides: U. S. Bur. Mines Bull. 542.

Darken, L. S., and Gurry, R. W., 1945, The system iron-oxygen I. The wüstite field and related equilibria: Am. Chem. Soc. Jour., v. 67, p. 1398-1412.

————, 1946, The system iron-oxygen II. Equilibrium and thermodynamics of liquid oxide and other phases: Am. Chem. Soc. Jour., v. 68, p. 798-816.

Drucker, C., and Hüttner, R., 1927, Die thermische Dissoziation des Mangandioxydes: Z. Physikal. Chem., Abt. A, v. 131, p. 237-266.

Dubois, P., 1934, Hydrate et variétés allotropiques du sesquioxyde de manganèse: Comptes Rendus, v. 199, p. 1416-1418.

Glasser, F. P., 1958, The system MnO—SiO_2: AM. JOUR. SCI., v. 256, p. 398-412.

Le Blanc, M., and Wehner, G., 1934, Beitrag zur Kenntis der Manganoxyde: Z. Physikal. Chem., Abt. A, v. 168, p. 59-78.

Mason, B., 1943, Mineralogical aspects of the system FeO—Fe_2O_3—MnO—Mn_2O_3: Geol. För. Stockholm Forh., v. 65, p. 97-180.

McMurdie, H. F., and Golovato, E., 1948, Study of the modifications of manganese dioxide: Nat. Bur. Standards Jour. Research, v. 41, p. 589-600.

Meyer, R. J., and Rötgers, K., 1908, Die Dissoziations-temperaturen der Manganoxyde MnO_2 und Mn_2O_3 in Luft und Sauerstoff: Z. Anorg. Chem., v. 57, p. 104-112.

Millar, R. W., 1928, The specific heats at low temperatures of manganous oxide, manganous-manganic oxide and manganese dioxide: Am. Chem. Soc. Jour., v. 50, p. 1875-1883.

Moore, T. E., Ellis, M., and Selwood, P. W., 1950, Solid oxides and hydroxides of manganese: Am. Chem. Soc. Jour., v. 72, p. 856-866.

Muan, Arnulf, 1958, Phase equilibria at high temperature in oxide systems involving changes in oxidation states: AM. JOUR. SCI., v. 256, p. 171-207.

————, 1955, Phase equilibria in the system FeO—Fe_2O_3—SiO_2: AIME Trans., v. 203, p. 965-976.

Saito, H., 1927, The thermobalance analysis of the change in various compounds heated in different gases: Sci. Repts. Tâhoku Imp. Univ., v. 16, p. 37-200.

Shenker, H., Lauritzen, J. I., Jr., Corruccini, R. J., and Lonberger, S. T., 1955, Reference tables for thermocouples: Natl. Bur. Standards Circ. 561.

Shomate, C. H., 1943, Heats of formation of manganomanganic oxide and manganese dioxide: Am. Chem. Soc. Jour., v. 65, p. 785-790.

Siemonsen, H., 1939, Neubestimmung der Bildungswärmen der Manganoxyde: Z. Elektrochem., v. 45, p. 637-643.

Southard, J. C., and Shomate, C. H., 1942, Heat of formation and high-temperature heat content of manganous oxide and manganous sulfate. High-temperature heat content of manganese: Am. Chem. Soc. Jour., v. 64, p. 1770-1774.

Southard, J. C., and Moore, G. E., 1942, High temperature heat content of Mn_3O_4, $MnSiO_3$ and Mn_3C: Am. Chem. Soc. Jour., v. 64, p. 1769-1770.

Stalzer, R. F., and Vosburgh, W. C., 1951, Determination of available oxygen and total manganese in manganese oxides: Anal. Chem., v. 23, p. 1880.

Sully, A. H., 1955, Manganese: London, Butterworths Scientific Publications.

Todd, S. S., and Bonnickson, K. R., Low temperature heat capacities and entropies at 298.16°K. of ferrous oxide, manganous oxide and vanadium monoxide: Am. Chem. Soc. Jour., v. 73, p. 3894-3895.

Van Hook, H. J., and Keith, M. L., 1958, The system Fe_3O_4—Mn_3O_4: Am. Mineralogist, v. 43, p. 69-83.

Wartenberg, H. v., and Prophet, E., 1932, Schmelzdiagramme höschstfeuerfester Oxyde. V. Systemme mit MgO: Z. Anorg. und Allg. Chem., v. 208, p. 369-379.

White, J., Howat, D. D., and Hay, R., 1934, The binary system, MnO—SiO_2: Royal Tech. Coll. Jour. (Glasgow), v. 3, p. 231-240.