

Phase Equilibrium in the System Ln–Mn–O

II. Ln = Nd at 1100°C

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Phase equilibrium is established in a Nd–Mn–O system at 1100°C by changing the oxygen partial pressure from 0 to 12.00 in $-\log(\text{P}_{\text{O}_2}/\text{atm})$; a phase diagram at 1100°C is presented for a Nd_2O_3 –MnO– MnO_2 system. Under the experimental conditions, Nd_2O_3 , MnO, Mn_3O_4 , and NdMnO_3 phases are present at 1100°C, but Nd_2MnO_4 , Mn_2O_3 , and MnO_2 are not stable in the system. Wide ranges of nonstoichiometry were found in the NdMnO_3 phase, which coexisted with Nd_2O_3 . X ranges from -0.006 at $\log \text{P}_{\text{O}_2} = -10.85$ to 0.104 at $\log \text{P}_{\text{O}_2} = 0$ in the form of NdMnO_{3+x} . The nonstoichiometry is represented by the equation $\text{No}/\text{N}_{\text{NdMnO}_3} = 4.34 \times 10^{-5}(\log \text{P}_{\text{O}_2})^3 + 1.99 \times 10^{-3}(\log \text{P}_{\text{O}_2})^2 + 2.65 \times 10^{-2}(\log \text{P}_{\text{O}_2}) + 0.104$; the activities of the components in the solid solution are also calculated with this equation. NdMnO_3 has a composition range to the Nd_2O_3 -rich or Nd_2O_3 -poor side of LaMnO_3 . Lattice constants of NdMnO_3 made in different oxygen partial pressures were determined. © 2001 Academic Press

Key Words: phase equilibrium; thermogravimetry; neodymium–manganese compound; standard Gibbs energy change of reaction.

Many reports have been published on LaMnO_3 from the view of magnetic, electronic, and crystallographic properties (1–11). In contrast, on other lanthanoid–manganese perovskites, very few reports have been published though the same physical and chemical properties would be expected.

In a Nd–Mn–O system, there is a stable ternary phase NdMnO_3 . NdMnO_{3+y} has been prepared and characterized by powder X-ray and neutron diffraction together with thermogravimetric and chemical titration analysis by Cherepanov *et al.* (12). In addition, the ternary oxide has an orthorhombically distorted perovskite-like structure; also, a small manganese deficiency has been found along with an oxygen excess that can likely be described by the cation disorder: $\text{Nd}_{0.97}\text{Mn}_{0.95}\text{O}_3$.

The nonstoichiometry of the NdMnO_3 phase has been studied by a gravimetric method at 1273 K (13). This earlier work revealed the existence of a hyperstoichiometric phase and the homogeneity range of the phase NdMnO_{3+x} from

$x = 0$ to 0.065 at 1273 K under various oxygen partial pressures. Furthermore, the effect of oxygen nonstoichiometry on the phase transition at high temperature has been studied by electrical conductivity and DTA measurements. However, fewer physical and chemical studies have been conducted on NdMnO_3 than on LaMnO_3 .

Although the nonstoichiometry of the compound was well represented by the phase diagram, no detailed phase equilibrium for a Nd–Mn–O system at high temperatures has been determined under the controlled oxygen partial pressure described above.

Due to the difficulty in making higher oxygen partial pressure, for example a level higher than 10^{-14} atm at 800°C, and the low reaction rate from Mn_3O_4 to Mn_2O_3 and from Mn_2O_3 to MnO_2 and vice versa at lower temperatures, a temperature of 1100°C was chosen.

Considering the above circumstances, the objectives of the present study are (1) to establish a detailed phase diagram of a Nd–Mn–O system at 1100°C as a function of the oxygen partial pressure and ascertain the nonstoichiometric range of NdMnO_3 , and (2) to determine the thermochemical properties based on the established phase diagram.

EXPERIMENTAL

Analytical grade Nd_2O_3 (99.9%) and MnO (99.9%) were used as starting materials. MnO was dried by heating at 110°C in air. The Nd_2O_3 was also dried at 1100°C. Mixtures with desired ratios of $\text{Nd}_2\text{O}_3/\text{MnO}$ were prepared by thorough mixing in an agate mortar and then repeated calcination during the intermediate mixing. This was followed by the same procedures as described previously (14).

Mixed gases of CO_2 and H_2 and of CO_2 and O_2 , and one atmosphere of O_2 and of CO_2 , respectively, were used to obtain the oxygen partial pressures in the present experiment.

The apparatus and procedures for controlling the oxygen partial pressure and keeping a constant temperature, the method of thermogravimetry, and the criterion for the establishment of equilibrium were the same as those described

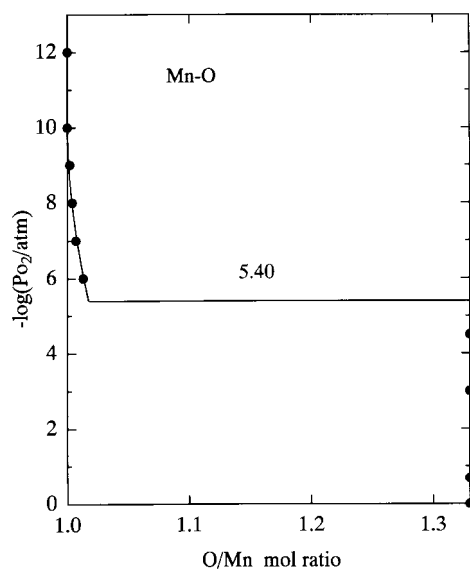


FIG. 1. Relationship between oxygen partial pressure, $\log(P_{O_2}/\text{atm})$, and O/Mn mole ratio.

in a previous paper (15). The method of establishing equilibrium can be briefly described as follows. To ensure equilibrium, the equilibrated point of each sample at an oxygen partial pressure was determined from both sides of the reaction, that is, from low oxygen partial pressures to high oxygen partial pressures and vice versa. The balance, furnace, and gas mixer are schematically shown in (14). The furnace is installed vertically and has a mullite tube wound with Pt 60%–Rh 40% alloy wire as its heating element. Mixed gases, which ensure the desired oxygen partial pressures, pass from the bottom of the furnace to the top.

The identification of phases and the determination of lattice constants were performed with a Rigaku X-ray diffractometer Rint 2500 apparatus, employing Ni-filtered $\text{CuK}\alpha$ radiation. A standard specimen of silicon was used to calibrate 2θ .

RESULTS AND DISCUSSIONS

1. Phase Equilibrium

a. Mn–O system. In the Mn–O system, there are four known oxides: MnO, Mn_3O_4 , Mn_2O_3 , and MnO_2 . The results of a system that was reinvestigated were reported in a previous paper (16). These results can be summarized as follows. Figure 1 shows the relationship between the oxygen partial pressure, $-\log(P_{O_2}/\text{atm})$, and the O/Mn mol ratio. The oxygen partial pressure in equilibrium with MnO and Mn_3O_4 is -5.40 ± 0.05 in $\log(P_{O_2}/\text{atm})$ and Mn_3O_4 is stoichiometric in the $-\log(P_{O_2}/\text{atm})$ range at least from 0 to 5.40. On the other hand, MnO has a slight nonstoichiometric composition to the oxygen-rich side. The O/Mn mol ratio is 1.020 at -5.40 in $\log(P_{O_2}/\text{atm})$, and an equation,

$$\text{No}/\text{N}_{\text{MnO}} = 9.83 \times 10^{-4} (\log P_{O_2})^2 + 1.914 \times 10^{-2} (\log P_{O_2}) + 0.0933,$$
 was obtained for the MnO solid solution in the oxygen partial pressure range from -10.00 to -5.40 using the least squares method. Here, No and N_{MnO} are the mole fraction of oxygen and MnO, respectively. It was confirmed that MnO and Mn_3O_4 phases are stable under the present experimental conditions, but the higher oxides, Mn_2O_3 and MnO_2 , are not stable. This fact was also pointed out by van Roosmalen *et al.* (11), who presented the pseudobinary $\text{La}_2\text{O}_3\text{--Mn}_2\text{O}_3$ phase diagram in air (Fig. 6 of (11)) and showed that below about 1150 K Mn_2O_3 is stable, but in the range from about 1150 to 1450 K, the tetragonal Mn_3O_4 is stable.

Hahn and Muan (21) presented a general equation, $\log(P_{O_2}/\text{atm}) = 13.31 - 26,000/T$, for the $\text{Mn}_3\text{O}_4\text{--MnO}$ equilibrium. $\log P_{O_2} = -5.62$ is obtained from this equation at 1100°C. This value is in fairly good agreement with the present value, -5.40 . They also reported the oxygen partial pressures in equilibrium with Mn_3O_4 and Mn_2O_3 by using an equation $\log P_{O_2} = 8.05 - 10100/T$. At 1373 K, $\log(P_{O_2}/\text{atm}) = 0.694$ ($P_{O_2} = 4.94$ atm) is obtained from the equation. Therefore, it seems reasonable that Mn_2O_3 is not stable in the present experimental conditions.

The compositions, symbols, stability ranges of the solid solution in the oxygen partial pressures, and the activities of components in the MnO solid solution are tabulated in Table 1 together with the activities of the NdMnO_3 solid solutions. These are necessary to calculate the equilibrium constant K. The calculation method using the Gibbs–Duhem equation was described in a previous paper (15).

b. $\text{Nd}_2\text{O}_3\text{--MnO--MnO}_2$ system. Five samples with $\text{Nd}_2\text{O}_3/\text{MnO}$ mole ratios of 6/4, 45/55, 3/7, 25/75, and 15/85 were prepared for thermogravimetry. In Fig. 2, the relationships between the oxygen partial pressure, $-\log(P_{O_2}/\text{atm})$, on the ordinate and the weight changes, W_{O_2}/W_T , on the abscissa are shown with three representative samples: 15/85 (Fig. 2a), 25/75 (Fig. 2b), and 45/55 (Fig. 2c). Here, W_{O_2} is

TABLE 1
Compositions, Symbols, Stability Ranges in Oxygen Partial Pressures, and Activities of Components in Solid Solutions

Component	Compositions	Symbols	$-\log(P_{O_2}/\text{atm})$	$\log a_i$
MnO	$\text{MnO}_{1.00}$	A_1	15.00 ~ 10.00	0
	$\text{MnO}_{1.02}$	A_2	5.40	-0.0137
NdMnO_3	$\text{NdMnO}_{2.995}$	B_1	10.85	0
	$\text{NdMnO}_{3.012}$	B_2	5.40	2.50×10^{-3}
	$\text{NdMnO}_{3.048}$	B_3^a	0	—
	$\text{NdMnO}_{3.104}$	B_4^b	0	-0.133

^aCoexisting with Mn_3O_4 .

^bCoexisting with Nd_2O_3 .

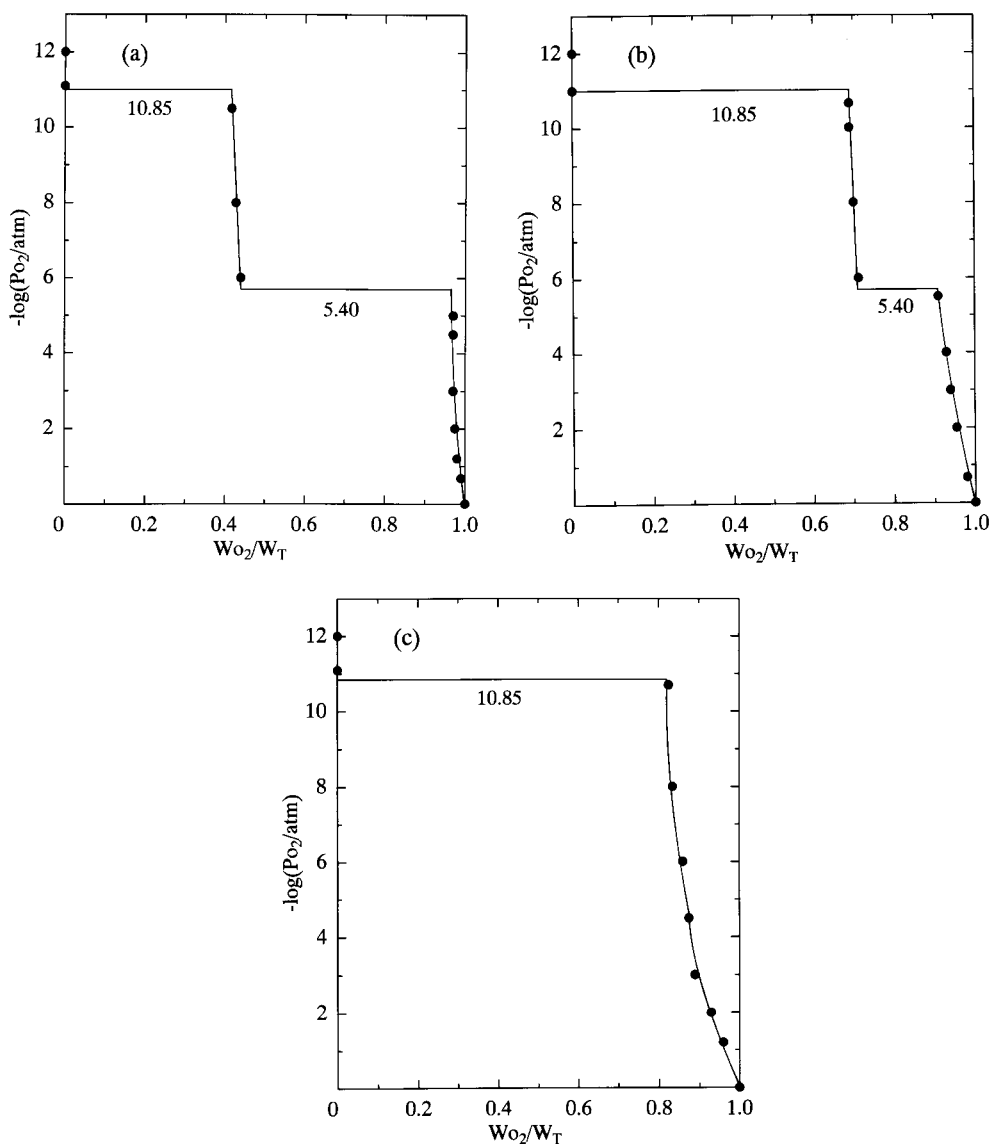


FIG. 2. Relationship between oxygen partial pressure, $\log(P_{O_2}/\text{atm})$, and weight change of the samples, W_{O_2}/W_T . (a) $\text{Nd}_2\text{O}_3/\text{MnO} = 15/85$, (b) $\text{Nd}_2\text{O}_3/\text{MnO} = 25/75$, and (c) $\text{Nd}_2\text{O}_3/\text{MnO} = 45/55$.

the weight increase of the samples from the reference weight at $\log(P_{O_2}/\text{atm}) = -12.00$, at which Nd_2O_3 and MnO are stable, and W_T is the total weight gain from reference state to the weight at 1 atm O_2 , at which Nd_2O_3 and NdMnO_3 or NdMnO_3 and Mn_3O_4 are stable depending on the total composition of the samples. Weight breaks are found at 10.85 and 5.40 in $-\log(P_{O_2}/\text{atm})$. These values correspond to the oxygen partial pressure in equilibrium with the three solid phases, $\text{Nd}_2\text{O}_3 + \text{NdMnO}_3 + \text{MnO}$ and $\text{NdMnO}_3 + \text{MnO} + \text{Mn}_3\text{O}_4$, respectively.

Table 2 shows the results of identifying phases in the Mn-O and Nd-Mn-O systems together with the experimental conditions. Samples of about 500 mg were made for

the identification of phases by the quenching method. Four phases, Nd_2O_3 , MnO , Mn_3O_4 , and NdMnO_3 , were stable under the experimental conditions.

Based on the above results of thermogravimetry and the identification of the phase, a phase diagram was drawn (Fig. 3), as an $\text{Nd}_2\text{O}_3\text{-MnO-MnO}_2$ system, although MnO_2 is not stable under the experimental conditions. The numerical values in the three solid fields in Fig. 3 are the two values in $-\log P_{O_2}$ in equilibrium with the three solid phases described above, and those in the two-phase regions are the oxygen partial pressures, which are shown by dotted lines. The nonstoichiometry of MnO is ascertained by the results of thermogravimetry of the other two samples,

TABLE 2
Identification of Phase

Sample		- log (Po ₂ /atm)	Time/h	Phases
Nd ₂ O ₃	MnO			
0.15	0.85	12.00	9	MnO + Nd ₂ O ₃
		10.00	19	MnO + NdMnO ₃
		6.00	23	MnO + NdMnO ₃
		4.35	23	Mn ₃ O ₄ + NdMnO ₃
		0.68	9	Mn ₃ O ₄ + NdMnO ₃
0.30	0.70	12.00	9	MnO + Nd ₂ O ₃
		10.00	19	MnO + NdMnO ₃
		6.00	23	MnO + NdMnO ₃
		4.35	23	Mn ₃ O ₄ + NdMnO ₃
		0.68	9	Mn ₃ O ₄ + NdMnO ₃
0.45	0.55	12.00	9	MnO + Nd ₂ O ₃
		10.00	19	Nd ₂ O ₃ + NdMnO ₃
		4.35	23	Nd ₂ O ₃ + NdMnO ₃
		0.68	9	Nd ₂ O ₃ + NdMnO ₃
		0.00	1.00	12.80
6.50	23			MnO
5.00	14			Mn ₃ O ₄
0.68	15.5			Mn ₃ O ₄

shown in Figs. 2a and 2b. That is, this is represented with slight changes in the composition in the range of the oxygen partial pressure from 10.85 to 5.40 in -log Po₂.

NdMnO₃ has a large nonstoichiometric composition in the range from -10.85 to 0 in log Po₂. Furthermore, as indicated in the enlarged inset of Fig. 3, when the oxygen partial pressures are in equilibrium, the NdMnO₃ solid solutions at the rich side and at the poor side of Nd₂O₃ are not the same composition. It is assumed that this results from the width of the NdMnO₃ composition toward the Nd₂O₃ side or Mn₃O₄. Van Roosmalen *et al.* (11) reported that a perovskite-type LaMnO_{3+δ} solid solution can be formed with excess La as well as with excess Mn. The same phenomenon was also found in the La-Mn-O system (16). A tentative detailed figure of the NdMnO₃ part is drawn in the upper-left side of Fig. 3 in an exaggerated drawing. However, its width has not been detected by the present experimental techniques. The curved lines of log Po₂ result from the Gibbs Phase Rule, that is, one phase area of three component systems has two degrees of freedom. Consequently, the oxygen partial pressure lines in one phase area, the NdMnO₃ phase, could be curved.

Figure 4 shows the relationship between the oxygen partial pressure and the composition of the NdMnO₃ solid solution, which coexisted with Nd₂O₃. This curve is represented by this equation: $No/N_{NdMnO_3} = 4.34 \times 10^{-5} (\log Po_2)^3 + 1.99 \times 10^{-3} (\log Po_2)^2 + 2.65 \times (\log Po_2) + 0.104$. Here, No and N_{NdMnO₃} represent the mole fraction of oxygen and NdMnO₃ in the solid solution. From this equation,

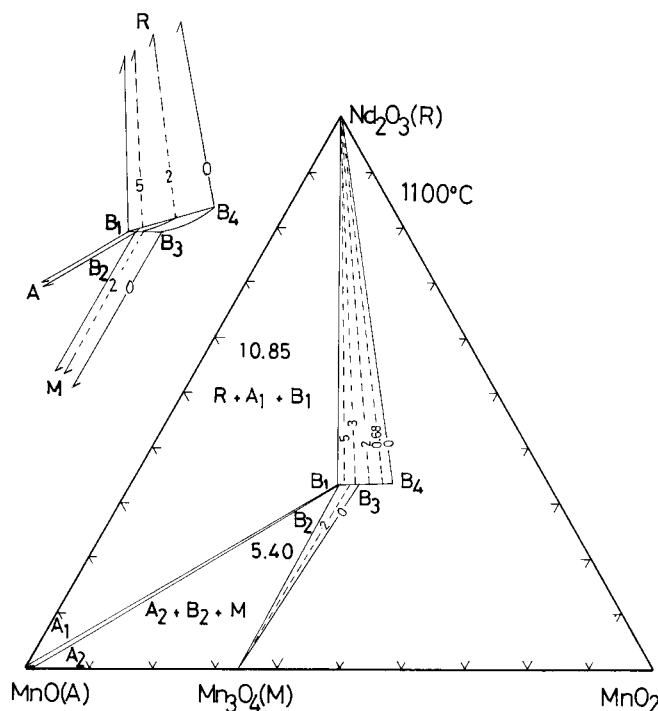


FIG. 3. Phase equilibrium in the Nd₂O₃-MnO-MnO₂ system at 1100°C. Numerical values in the three phase regions are the oxygen partial pressures in -log (Po₂/atm) in equilibrium with three solid phases, which are shown in the regions. Dotted lines in two-phase regions are also the oxygen partial pressures indicated on the lines. Abbreviations are the same as those in Table 1. A tentative detailed figure of the NdMnO₃ solid solution part is shown at the upper-left side in an exaggerated drawing.

neodymium-manganese perovskite would be stoichiometric at -5.83 in log (Po₂/atm).

Lattice constants of NdMnO₃ perovskite were determined as orthorhombic at 0.68, 5.83, and 10.00 in -log Po₂ using two mixtures of Nd₂O₃/MnO, mole ratio = 0.45/0.55 and 0.30/0.70. These samples were selected in order to coexist with Nd₂O₃ and MnO or Mn₃O₄. The results are

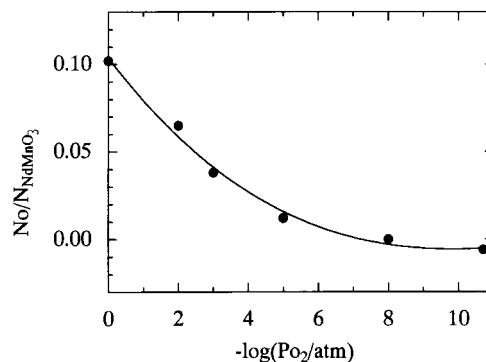


FIG. 4. Relationship between oxygen partial pressure, -log (Po₂/atm), and composition of NdMnO₃ solid solution, No/N_{NdMnO₃}.

TABLE 3
Lattice Constants of Quenched NdMnO₃

No.	$-\log P_{O_2}/\text{atm}$	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$	Source
1	0.68	5.398(6)	5.779(10)	7.547(10)	235.4(6)	This work ^a
2	0.68 ^c	5.526(4)		13.27(1)	351.0(4)	This work ^a
3	0.68	5.400(7)	5.729(7)	7.567(4)	234.1(3)	This work ^b
4	5.83	5.409(7)	5.814(7)	7.555(7)	237.3(5)	This work ^a
5	5.83	5.405(6)	5.823(3)	7.542(2)	237.6(1)	This work ^b
6	10.00	5.414(2)	5.837(3)	7.547(3)	238.6(2)	This work ^a
7	10.00	5.413(1)	5.846(1)	7.544(1)	238.7(1)	This work ^b
		5.4116(9)	5.6928(9)	7.599(1)		Ref. (12)
		5.378	5.554	7.653		Ref. (17)
		5.414(2)	5.811(3)	7.558		Ref. (18)
		5.406	5.789	7.556		Ref. (19)

^aQuenched sample of 0.45Nd₂O₃-0.55MnO that coexists with Nd₂O₃.

^bQuenched sample of 0.3Nd₂O₃-0.7MnO that coexists with Mn₃O₄ or MnO.

^cHexagonal.

tabulated in Table 3 together with the previous values. No large differences were found in lattice constants and volume in these samples.

Furthermore, as shown in Table 3, the lattice constant c does not show any large difference with the change in oxygen partial pressure. However, the constants a and b seemed to increase with a change in pressure from high to low. This tendency could result from the difference in the ionic radius, that is, Mn³⁺ 0.72 Å and Mn⁴⁺ 0.68 Å with coordination number 6, respectively (20).

Samples No. 1 and 2 are the same; the lattice constants of No. 1 were determined to be orthorhombic while those of No. 2 were hexagonal based on LaMnO₃ (JCPDS Card No. 32-484). The standard deviations of lattice constants of No. 1 are larger than those of No. 2, indicating that the crystal structure would shift from orthorhombic to hexagonal with the increase in oxygen content, that is, the increase in lower ionic radius Mn⁴⁺ content.

2. Standard Gibbs Energy Change of Reaction

On the basis of the established phase diagram, the standard Gibbs energy changes of reactions in Table 4 were determined by the equation $\Delta G^\circ = -RT \ln K$. Here, R is the gas constant, T is the absolute temperature, and K is the equilibrium constant of the reaction. The standard state of the activities of components in the solid solutions can be arbitrarily chosen for each solid solution and is indicated as $\log a_i = 0$ in Table 1.

The values of ΔG° and the oxygen partial pressure in equilibrium with MnO and Mn₃O₄ are quoted from Ref. (16). The standard Gibbs energy change for reaction (1) is -75.8 ± 0.3 kJ/mol. Assuming that the activity of MnO of the composition (A_2) is unity, this value is -75.0 ± 0.3 kJ/mol. Due to the small solid solution range, this difference is within experimental error. By calculating with the

data from (22) and (23), -60.4 kJ mol⁻¹ and 50.9 kJ mol⁻¹ are obtained, respectively. The reason for these large differences have not yet been found.

The ΔG° value for reaction (2) is -71.3 kJ mol⁻¹. This value is larger than that of -85.3 for LaMnO₃, as expected from the higher oxygen partial pressure in equilibrium.

3. Conclusions

1. A phase equilibrium in the system Nd-Mn-O at 1100°C was established in an oxygen partial pressure from 0 to -13.00 in log (P_{O_2}/atm).

2. Under the present experimental conditions, Nd₂O₃, MnO, Mn₃O₄, and NdMnO₃ phases are stable (Table 1 and Fig. 3).

3. MnO and NdMnO₃ have nonstoichiometric composition. However, Mn₃O₄ is stoichiometric.

4. Standard Gibbs energies of reactions found in the diagram were calculated with the oxygen partial pressure in equilibrium (Table 4).

TABLE 4
The Standard Gibbs Energy Changes of Reaction at 1100°C

Reaction	$-\log P_{O_2}$ (atm)	$-\Delta G^\circ$ (kJ/mol)
(1) 3MnO + 1/2 O ₂ = Mn ₃ O ₄	5.40	75.8 ± 0.3
	5.62	73.9 ^a
	(4.60) ^d	60.4 ^b
	(3.83) ^d	50.9 ^c
(2) 1/2 Nd ₂ O ₃ + MnO + 1/4 O ₂ = NdMnO ₃	10.85	71.3

^aRef. (20).

^bRef. (21).

^cRef. (22).

^dThese values are calculated from $-\Delta G^\circ$ values.

5. Lattice constants of NdMnO₃ were determined and discussed in relation to their dependency on the oxygen partial pressure.

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