

Phase Equilibrium in the System La-Ni-O at 1100°C

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Phase equilibrium in La-Ni-O system was established at 1100 °C at the oxygen partial pressure ranging from $-\log(P_{O_2}/\text{atm}) = 0$ to 12.00, and a phase diagram for the corresponding $\text{La}_2\text{O}_3\text{-Ni-Ni}_2\text{O}_3$ system at 1100°C was constructed. Stable La_2O_3 , Ni, NiO, $\text{La}_2\text{Ni}_4\text{O}_7$, and $\text{La}_6\text{Ni}_5\text{O}_{15}$ phases were found in the La-Ni-O system.

$\text{La}_2\text{Ni}_2\text{O}_5$, LaNiO_2 , LaNiO_3 , $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_4\text{Ni}_3\text{O}_{10}$, $\text{La}_5\text{Ni}_4\text{O}_{13}$ were not found under the present experimental conditions.

Nonstoichiometric ranges were found in both $\text{La}_2\text{Ni}_4\text{O}_7$ and $\text{La}_6\text{Ni}_5\text{O}_{15}$ phases, with the composition of $\text{La}_2\text{Ni}_4\text{O}_7$ represented as functions of $\log(P_{O_2}/\text{atm})$, $N_{\text{O}}/N_{\text{La}_2\text{Ni}_4\text{O}_7} = -2.932 \times 10^{-4} (\log P_{O_2})^2 + 1.056 \times 10^{-2} \log P_{O_2} + 0.1318$, and with the composition of $\text{La}_6\text{Ni}_5\text{O}_{15}$ represented as functions of $\log(P_{O_2}/\text{atm})$, $N_{\text{O}}/N_{\text{La}_6\text{Ni}_5\text{O}_{15}} = 0.0641 \log P_{O_2} + 0.480$, respectively. Activity of the components in a solid solution was calculated from these equations.

Lattice constants of $\text{La}_2\text{Ni}_4\text{O}_7$ quenched at two different oxygen partial pressures were determined.

The standard Gibbs energy changes of the reactions, $\text{Ni} + \text{La}_2\text{O}_3 + 1/2 \text{O}_2 = \text{La}_2\text{Ni}_4\text{O}_7$ and $\text{NiO} + 3 \text{La}_2\text{Ni}_4\text{O}_7 + 1/2 \text{O}_2 = \text{La}_6\text{Ni}_5\text{O}_{15}$, appearing in the phase diagrams were calculated to be -133.8 and -20.1 kJmol^{-1} , respectively.

Key words: Phase equilibrium; Thermogravimetry; Lanthanum-nickel oxide; Gibbs energy.

1. INTRODUCTION

In the La-Ni-O system seven compounds, $\text{La}_2\text{Ni}_2\text{O}_5$, LaNiO_2 , LaNiO_3 , and a homologous series, $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ ($n = 1 \sim 4$), have been reported and their crystallographic and physical properties have been examined.

Low-temperature reduction of LaNiO_3 under hydrogen led to compounds such as $\text{La}_2\text{Ni}_2\text{O}_5$ (monoclinic) and LaNiO_2 (tetragonal) before total reduction (1).

LaNiO_3 , containing nickel in the trivalent state was prepared. The hexagonal form of this cell has the following dimensions, $a = 5.456 \text{ \AA}$, $c = 13.122 \text{ \AA}$ (2). Additionally, stoichiometric LaNiO_3 is an ideal cubic perovskite with cell parameter $a = 3.851 \text{ \AA}$

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(3). LaNiO_3 has a high catalytic activity for oxygen reduction and is used as an oxygen electrode (4) and is a good candidate for use as a fuel-cell electrode. LaNiO_3 has been prepared at 773 K and the calcination time necessary to prepare phase-homogeneous samples is 15 hrs (5). LaNiO_3 is stable at temperatures lower than 900 °C (6). The lanthanum nickelates provide an interesting compromise between high conductivity (LaNiO_3 has a conductivity comparable to graphite) and good thermal stability (La_2NiO_4) (6).

La_2NiO_4 , which has the tetragonal K_2NiF_4 -type structure (7), has a broad range of lattice constants, indicative of variations in composition and of the extent of oxygen nonstoichiometry. $\text{La}_2\text{NiO}_{4+x}$ was prepared and chemical analysis revealed the presence of about 5% of Ni^{3+} (8).

The oxygen pressure dependence of the composition (x) of $\text{La}_2\text{NiO}_{4+x}$ has been determined for the first time in the temperature range between 1000°C and 1200°C by thermogravimetry (9). A point defect model was proposed for the system.

Rao et al. (10) observed a monoclinic cell in a CO_2 -annealed crystal of La_2NiO_4 at 1470 K. Saez-Puche et al. (8) also found that $\text{La}_2\text{NiO}_{4+x}$ (tetragonal) changed to La_2NiO_4 (monoclinic) in H_2 at 430°C and in oxygen or air at 600 °C, in which the weight loss value was higher than 0.7%. Conversely, the structure of a reduced form of La_2NiO_4 , prepared under Po_2 between 10^{-7} and 10^{-6} Pa, was determined to be orthorhombic using X-ray and neutron diffraction (11). The tetragonal form of La_2NiO_4 is stabilized by the presence of a small amount of Ni^{3+} ions coming from the air preparation (11). Magnetic susceptibility studies on single crystals of nearly stoichiometric La_2NiO_4 with the applied field both parallel and perpendicular to the c axis show a transition at 204 K, below which a two-dimensional canted antiferromagnetic order seems to exist (12). The electrical properties of La_2NiO_4 have been studied with respect to the stoichiometry of the material (13). The crystal structure of $\text{La}_2\text{NiO}_{4+x}$ was studied by means of X-ray and neutron single crystal diffraction measurements. At room temperature, the tetragonal crystal structure is $\text{P4}_2/\text{ncm}$ -type (No. 138). The lattice parameters of a sample annealed and slowly cooled in an oxygen atmosphere from 673 K are $a = b = 5.4640$ (1) Å and $c = 12.6719$ (2) Å (14).

Heat capacities of $\text{La}_2\text{NiO}_{4.094}$ single crystal were measured in 15-400 K with an adiabatic calorimeter (15). Four anomalies were found, as due to a phase separation concerning the excess oxygen composition at around 285 K, a glass transition over a

wide temperature range of 150-300 K, a first-order structural transition from tetragonal to orthorhombic phases as 240 K, and an antiferromagnetic phase transition at around 55 K. Also, heat capacities of a single crystal of the stoichiometric compound La_2NiO_4 and the nonstoichiometric $\text{La}_2\text{NiO}_{4+x}$ were measured over the temperature range 14-500 K with an adiabatic calorimeter (16).

The existence of $\text{La}_3\text{Ni}_2\text{O}_7$ and $\text{La}_4\text{Ni}_3\text{O}_{10}$ were reported (17). $\text{La}_3\text{Ni}_2\text{O}_7$, orthorhombic type, was prepared by heating in air at 1150°C for 5 hrs and $\text{La}_4\text{Ni}_3\text{O}_{10}$ by heating at 1080°C for 12 hrs. The powder pattern of $\text{La}_4\text{Ni}_3\text{O}_{10}$ can be indexed on the orthorhombic cell (18). Samples of nominal composition $\text{La}_5\text{Ni}_4\text{O}_{13}$ were prepared by heating La_2O_3 and NiO in a K_2CO_3 flux at 1050°C for 24 hrs but it was difficult to determine whether or not a new phase existed (17).

The thermodynamic stability of ternary oxides in the La-Ni-O system was investigated by Petrov et al. (19) and a simple phase diagram was presented. In the diagram the nonstoichiometry of La_2NiO_4 was not clearly shown.

Thermogravimetric study of the La-Ni-O system at 1200°C has been reported (20). In the system La_2NiO_4 and $\text{La}_6\text{Ni}_5\text{O}_{15}$ were stable and La_2NiO_4 was nonstoichiometric.

As described above, the principal interest in the system seems to be surrounding the crystallographic and physical properties of the compounds which are stable in the system. Reliable information on the stability of these compounds is still limited and the range of nonstoichiometry of La_2NiO_4 between 1000 - 1200°C is still ambiguous.

The objectives of the present study are to: (1) establish detailed phase diagrams of the La-Ni-O system at 1100°C as a function of the oxygen partial pressure; (2) establish a phase diagram and compare the established diagram with the previous diagram at 1200°C ; (3) determine the thermochemical properties based on the phase equilibrium at 1100°C .

2. EXPERIMENTAL

Analytical grade La_2O_3 (99.9%), and NiO (99.9%) were used as starting materials. The both oxides were calcinated at 1100°C . Mixtures having desired ratios of $\text{La}_2\text{O}_3/\text{NiO}$ were prepared by mixing thoroughly in an agate mortar and performing repeated calcination during the intermediate mixing. This was followed by the same

procedures described previously (21). The thermogravimetric method was used in the present experiment; the oxygen partial pressure was varied passing a gas or mixed gases through the furnace.

The desired oxygen partial pressures were obtained by using the mixed gases CO_2 and H_2 and CO_2 and O_2 , and single-component gases of O_2 and CO_2 . The actual oxygen partial pressures of the gas phase were measured by means of a solid electrolytic cell composed of $(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}$ (22). The apparatus and procedures for controlling the oxygen partial pressure and maintaining a

constant temperature, that being the method of thermogravimetry, and the criterion for the establishment of equilibrium were the same as described in the previous paper (21). The method of establishing equilibrium can be briefly described as follows: To ensure equilibrium, the equilibrium weight of each sample at a particular oxygen partial pressure was determined from both sides of the reaction; that is, as the oxygen partial pressure was increased from a low value and as it was decreased from a high value. The balance, furnace, and gas mixer were schematically shown in (23). The furnace was installed vertically, and a mullite tube wound with Pt 60%-Rh 40% alloy wire served as its heating element. Mixed gases, which ensure the desired oxygen partial pressures, passed from the bottom of the furnace to the top.

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

3. RESULTS AND DISCUSSIONS

3-1. Phase equilibrium

3-1-1 Ni-O system

There is a known oxide phase, NiO, in the Ni-O system. The system was reinvestigated under the present experimental conditions. The relationships between the oxygen partial pressure, $-\log(\text{Po}_2/\text{atm})$, on the ordinate and the ratio of the mole fraction, $\text{No}/\text{N}_{\text{Ni}}$, on the abscissa are shown. Here, No is the mole fraction of the

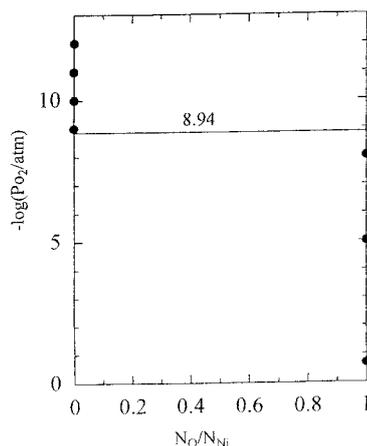


Fig. 1. The relationship between the oxygen partial pressure, $\log(\text{Po}_2/\text{atm})$, and the $\text{No}/\text{N}_{\text{Ni}}$ mole ratio.

oxygen in the sample and N_{Ni} is the mole fraction of nickel in the sample. The oxygen partial pressure in equilibrium with Ni-NiO was found to be $\log(\text{Po}_2/\text{atm}) = -8.94 \pm 0.05$ as shown in Fig. 1. The NiO seems to be slightly nonstoichiometric by the thermogravimetric analysis, being oxygen-rich with a NiO/N_{Ni} molar ratio. But the range of the nonstoichiometry is too small to be represented in the present phase diagram.

3-1-2 La_2O_3 -Ni- Ni_2O_3 system.

Seven samples having $\text{La}_2\text{O}_3/\text{NiO}$ molar ratios of 0.7/0.3, 0.6/0.4, 0.45/0.55, 0.4/0.6, 0.3/0.7, 0.2/0.8, and 0.1/0.9 were prepared for thermogravimetric analysis. The relationships between the oxygen partial pressure, $-\log(\text{Po}_2/\text{atm})$, on the ordinate and the ratio of weight changes, $W_{\text{O}_2}/W_{\text{T}}$, on the abscissa are shown for the four representative samples of 0.3/0.7, 0.4/0.6, 0.45/0.55, and 0.7/0.3 in Figs. 2(a), 2(b), 2(c), and 2(d), respectively. Here, W_{O_2} is the weight increase of the samples from the reference weight at $\log(\text{Po}_2/\text{atm}) = -12.00$, at which La_2O_3 and Ni are stable, and W_{T} is the total weight gain from the reference state to the weight at 1 atm O_2 , at which La_2O_3 and La_2NiO_4 or La_2NiO_4 and $\text{La}_6\text{Ni}_5\text{O}_{15}$ or $\text{La}_6\text{Ni}_5\text{O}_{15}$ and NiO are stable depending on the total composition of the samples. Weight breaks are found at $-\log$

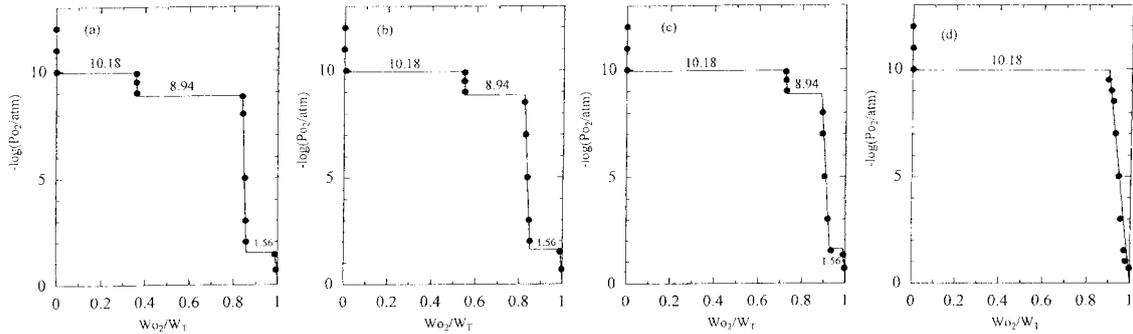


Fig. 2. The relationship between the oxygen partial pressure, $\log(\text{Po}_2/\text{atm})$, and the weight change of samples, $W_{\text{O}_2}/W_{\text{T}}$. (a) $\text{La}_2\text{O}_3/\text{NiO} = 0.3/0.7$, (b) $\text{La}_2\text{O}_3/\text{NiO} = 0.4/0.6$, (c) $\text{La}_2\text{O}_3/\text{NiO} = 0.45/0.55$, (d) $\text{La}_2\text{O}_3/\text{NiO} = 0.7/0.3$.

$(\text{Po}_2/\text{atm}) = 10.18, 8.94, \text{ and } 1.56$. These values correspond to the oxygen partial pressure, in which the three phases $\text{La}_2\text{O}_3 + \text{La}_2\text{NiO}_4 + \text{Ni}$, $\text{La}_2\text{NiO}_4 + \text{Ni} + \text{NiO}$, and $\text{La}_2\text{NiO}_4 + \text{NiO} + \text{La}_6\text{Ni}_5\text{O}_{15}$, are in equilibrium, respectively. The pressure, $\log(\text{Po}_2/\text{atm}) = -8.94$, at which the three solid phases, $\text{NiO} + \text{La}_2\text{NiO}_4 + \text{Ni}$, are in equilibrium, corresponds to the value at which Ni and NiO are in equilibrium described above.

Table 1 shows the results of phase identification in the La-Ni-O system. Samples of approximately 500 mg were prepared for the identification of phases using the quenching method. Five phases, La_2O_3 , Ni, NiO, La_2NiO_4 and $\text{La}_6\text{Ni}_5\text{O}_{15}$ were found to be stable. Other phases, for example $\text{La}_2\text{Ni}_2\text{O}_5$, LaNiO_2 , and LaNiO_3 , are not present under the present experimental conditions.

La_2O_3 NiO (Mol ratio)	$-\log P_{\text{O}_2}$ (atm)	Time (h)	Phase
0.0 1.0	0.68	23.0	NiO
	8.00	17.5	NiO
	12.00	6.0	Ni
0.2 0.8	0.68	87.5	NiO + $\text{La}_6\text{Ni}_5\text{O}_{15}$
	5.00	23.0	NiO + La_2NiO_4
	8.00	49.0	NiO + La_2NiO_4
	9.00	72.0	Ni + La_2NiO_4
	12.00	8.5	Ni + La_2O_3
0.4 0.6	0.68	87.5	La_2NiO_4 + $\text{La}_6\text{Ni}_5\text{O}_{15}$
	5.00	23.0	NiO + La_2NiO_4
	8.00	49.0	NiO + La_2NiO_4
	9.00	72.0	Ni + La_2NiO_4
	12.00	8.5	Ni + La_2O_3
0.6 0.4	0.68	87.5	La_2NiO_4 + La_2O_3
	5.00	23.0	La_2O_3 + La_2NiO_4
	9.00	72.0	La_2O_3 + La_2NiO_4
	12.00	8.5	Ni + La_2O_3

Based on the results of thermogravimetry and phase identification, a phase diagram was constructed for the La_2O_3 -Ni-Ni₂O₃ system, even though Ni₂O₃ was not stable under the experimental conditions. The results are shown in Fig. 3. The numerical

values shown in the three solid fields in Fig. 3 were the values of $-\log(P_{\text{O}_2}/\text{atm})$ in the three solid phase regions in equilibrium indicated. As shown in Fig. 3, there are three three-phase regions, R + A + Ni, A₁ + C + Ni, and A₂ + C + B, in which the oxygen partial pressures in equilibrium are 10.18, 8.94, and 1.56 in $-\log(P_{\text{O}_2}/\text{atm})$, respectively. It is imperative to note that there are six two-phase regions, La_2O_3 -Ni, La_2O_3 - La_2NiO_4 , Ni- La_2NiO_4 , NiO- La_2NiO_4 , La_2NiO_4 - $\text{La}_6\text{Ni}_5\text{O}_{15}$, and $\text{La}_6\text{Ni}_5\text{O}_{15}$ -NiO.

Zinkevich et al.(24) reported the calculated isothermal section of the La-Ni-O system at 1373 K and $P_{\text{O}_2} = 1$ bar (Fig.

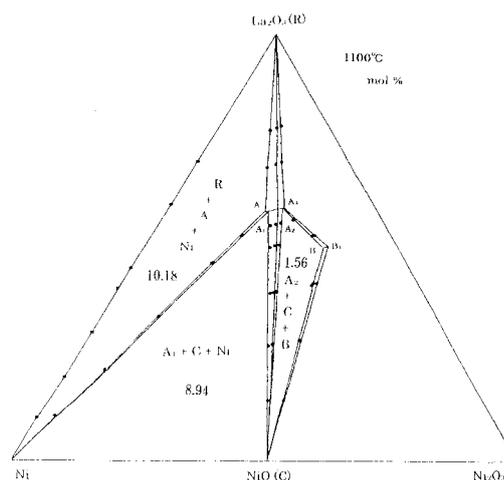


Fig. 3. Phase equilibrium in the La_2O_3 -Ni-Ni₂O₃ system at 1100°C. Numerical values indicated in the three-solid phase regions are oxygen partial pressures in $-\log(P_{\text{O}_2}/\text{atm})$ which are in equilibrium with solid phases shown in each region. Abbreviations are the same as those in Table 2.

8) on the basis of the study conducted by Cherepanov et al.(25). That figure (Fig. 8) has a gross mistake which shows that Ni-metal is stable in $P_{O_2} = 1$ bar.

La_2NiO_4 and $La_6Ni_5O_{15}$ exhibit nonstoichiometric compositions in the range of $\log(P_{O_2}/atm) = -10.18$ ($La_2NiO_{2.985}$, A) to 0 ($La_2NiO_{4.00}$, A_3) and -1.56 ($La_6Ni_5O_{15.38}$, B) to 0 ($La_6Ni_5O_{15.48}$, B_1) as shown in Fig. 3. The $\log(P_{O_2}/atm) = -10.18$ is in good agreement with ~ -10.50 which can be seen in Fig. 2 in (9). The homologous series, $La_{n+1}Ni_nO_{3n+1}$, has been reported in many reports. On the basis of the series, $La_6Ni_5O_{15.38}$ and $La_6Ni_5O_{15.48}$ could be represented as $La_6Ni_5O_{16-x}$ ($x = 0.62$ and 0.52). However, x is larger than 0.5. Therefore, the compound could be represented as $La_6Ni_5O_{15+x}$ in the present case, because of the instability of $La_6Ni_5O_{16}$.

The solid solution range of $La_6Ni_5O_{15}$ is smaller than that of La_2NiO_4 . The composition of La_2NiO_4 is represented as a function of $\log(P_{O_2}/atm)$: $N_o/N_{La_2NiO_4} = -2.932 \times 10^{-4}(\log P_{O_2})^2 + 1.056 \times 10^{-2} \log P_{O_2} + 0.1318$, and the composition of $La_6Ni_5O_{15}$ is represented as a function of $\log(P_{O_2}/atm)$: $N_o/N_{La_6Ni_5O_{15}} = -0.0641 \log P_{O_2} + 0.480$. Here, N_o , $N_{La_2NiO_4}$, and $N_{La_6Ni_5O_{15}}$ indicate the mole fraction of the solid solution. In Fig 4 the relationship between N_o and $N_{La_2NiO_4}$ was

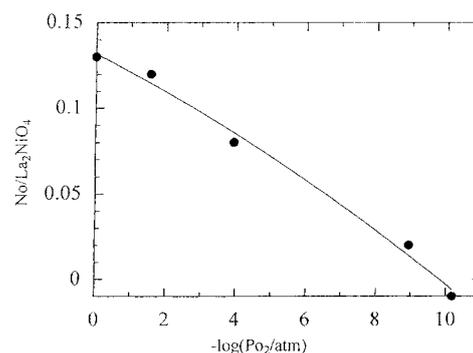


Fig. 4 The relationship between the mole fraction ratio, $N_o/N_{La_2NiO_4}$ and the oxygen partial pressure, $-\log(P_{O_2}/atm)$

Table 2. Compositions, Symbols, Stability Ranges in Oxygen Partial Pressures, and Activities of Components in Solid Solutions

Component	Compositions	Symbols	$-\log(P_{O_2}/atm)$	$\log a_i$
La_2NiO_4	$La_2NiO_{3.99}$	A	10.18	0
	$La_2NiO_{4.02}$	A_1	8.94	-2.49×10^{-3}
	$La_2NiO_{4.12}$	A_2	1.56	-0.250
	$La_2NiO_{4.13}$	A_3	0	-0.346
$La_6Ni_5O_{15}$	$La_6Ni_5O_{15.38}$	B	1.56	0
	$La_6Ni_5O_{15.48}$	B_1	0	0.335

shown. Activities of the components in the solid solution were calculated from these equations.

Table 2 lists the compositions, oxygen partial pressures in equilibrium and activities of the components in solid solution applying the same symbols as used in Fig. 3. Lattice constants of the hexagonal La_2NiO_4 are listed in Table 3 together with the values of Odier et al.(6) and Rebenau et al.(7). Two quenching samples were prepared at two different oxygen partial pressures, $-\log P_{O_2} = 9.00$ and 0.68 at $1100^\circ C$. The phases coexisting with La_2NiO_4 are shown in the last column in Table 3. The values prepared in the different oxygen partial pressures are in good agreement

with each other. The lattice constants are also in fairly good agreement with previous values. Odier et al. (6) reported that the crystal structure of La_2NiO_4 was depend upon the stoichiometry or nonstoichiometry of the compound. The present sample made in $\log(\text{Po}_2/\text{atm}) = -9.00$ could be regarded as being hexagonal.

Table 3. Lattice constants of Quenched La_2NiO_4

Sample	$-\log \text{Po}_2$ (atm)	a/A	b/A	c/A	V/A^3	Other Phase
La_2O_3 NiO						
0.6 0.4	9.00	3.862(2)		12.64(2)	188.5(3)	La_2O_3
	0.68	3.8621(7)		12.682(3)	189.16(5)	La_2O_3
Ref. 7		3.855(1)		12.652(3)		
Ref. 6		5.4614	5.5322	12.527		

3-2. The Standard Gibbs Energy Change of Reaction

Based on the established phase diagrams, standard Gibbs energy changes of the reactions in the corresponding phase diagrams were determined from the equation, $\Delta G^\circ = -RT \ln K$, where R is the gas constant, T the absolute temperature, and K the equilibrium constant of the reaction. The results obtained were listed in Table 4.

Table 4. The standard Gibbs Energy Changes of Reaction at 1100°C.

Reaction	$-\log \text{Po}_2$ (atm)	$-\Delta G^\circ$ (kJ/mol)
(1) $\text{Ni} + 1/2 \text{O}_2 = \text{NiO}$	8.94 (8.93) (8.94) (8.92) (8.93)	117.5 117.4 ^a 117.5 ^b 117.3 ^c 117.4 ^d
(2) $\text{Ni} + \text{La}_2\text{O}_3 + 1/2 \text{O}_2 = \text{La}_2\text{NiO}_4$	10.18 10.45 ^e (10.04)	133.8 (137.4) 132.0 ^b
(3) $2 \text{NiO} + 3 \text{La}_2\text{NiO}_4 + 1/2 \text{O}_2 = \text{La}_6\text{Ni}_5\text{O}_{15}$	1.56	20.1

^a Ref. 25; ^b Ref. 16; ^c Ref. 23; ^d Ref. 24; ^e Ref. 29

Values in parenthesis are calculated from the quoted ΔG° or $-\log(\text{Po}_2/\text{atm})$.

The standard state of the activities of components in the solid solutions can be arbitrarily chosen for each solid solution as indicated by $\log a_i = 0$ in Table 2. Values of $-\log(\text{Po}_2/\text{atm})$ and ΔG° shown with parenthesis in Table 4 are calculated from the quoted values.

Concerning reaction 1) many reports have been published: for example, Kemori et al (26) derived a general equation, $\Delta G^\circ = -55,560 + 19.98 T$ (calmol⁻¹, 1173 ~ 1726 K) by e.m.f. measurements of the galvanic cell with the solid oxide electrolyte (ZrO_2

+ CaO) and Holmes et al. (27) also derived a general equation, $\Delta G^0 = -239,885 + 122.350 T - 4.584 T \ln T$ (Jmol⁻¹) by means of galvanic cell with an oxygen-specific solid electrolyte made of calcia-stabilized zirconia. The present value and previous values are in good agreement. As for reaction 2), Petrov et al.(19) reported -132.0 kJmol⁻¹ which is slightly higher than our value of, -133.8 kJmol⁻¹.

4. CONCLUSION

- 1) Phase equilibrium in the system La-Ni-O at 1100°C were established under an oxygen partial pressure from 0 to -12.00 in log(P_{O2}/atm)
- 2) Under the present experimental conditions, the La₂O₃, Ni, NiO, La₂NiO₄, and La₆Ni₅O₁₅ phases are stable in the system.
- 3) NiO, La₂NiO₄, and La₆Ni₅O₁₅ all have nonstoichiometric composition. However, the change in the composition of NiO solid solution is too small to show in Fig. 2 and 3. The composition of the La₆Ni₅O₁₅ solid solution is represented as the composition of La₆Ni₅O_{15+x}, although, in view of the homologous series, La_{n+1}Ni_nO_{3n+1}, the composition of the solid solution may in fact be represented as La₆Ni₅O_{16-x}.
- 4) Lattice constants of La₂NiO₄ were determined and compared with previous values.
- 5) Standard Gibbs energies of reactions found in the diagram were calculated with the oxygen partial pressure in equilibrium with two or three solid phases. The value of reaction (1) is in good agreement with previously recorded values. This fact shows that the present experimental facilities were well established and worked well.

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