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Thermodynamic Study of the Ln_2O_3–Co–Co_2O_3 System
II. *Ln* = Nd and Gd

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Phase equilibria in the system Ln_2O_3–Co–Co_2O_3 (*Ln* = Nd and Gd) at 1200°C were studied at oxygen partial pressures ranging from 1 to 10^{-12} atm O_2. $NdCoO_3$ and $Nd_4Co_3O_{10}$ are stable ternary compounds in the Nd_2O_3–Co–Co_2O_3 system, while only $GdCoO_3$ is stable in the Gd_2O_3–Co–Co_2O_3 system. $Nd_4Co_3O_{10}$ was found to be a new compound; its lattice constants have been determined from data on $La_4Co_3O_{10}$. The standard Gibbs energies ($\Delta G°$) of the reactions appearing in the systems were also determined from the oxygen partial pressures in equilibrium with three solids. The variation of $\Delta G°$ with the ionic radius of *Ln* with 12 coordination is linear.

In a previous study (*1*), the system La_2O_3–Co–Co_2O_3 was studied at 1200°C at oxygen partial pressures ranging from 1 to 10^{-12} atm O_2. In that system La_2CoO_4, $LaCoO_3$, and $La_4Co_3O_{10}$ were stable as ternary compounds, and the standard Gibbs energies of reactions which appeared in the system were also determined.

In this paper Nd_2O_3 and Gd_2O_3 are chosen as Ln_2O_3. According to the previous studies, Nd_2CoO_4 (*2, 3*), $NdCoO_3$ (*4–6*), and $GdCoO_3$ (*4, 6–8*) are known as the ternary compounds in these systems. Nd_2CoO_4 is monoclinic (*2, 3*) while La_2CoO_4 is orthorhombic. The $Ln_4Co_3O_{10}$-type compounds for Nd and Gd have not been reported and little information about phase equilibria in these systems is available.

The objectives of the present study are (1) to establish the detailed phase equilibria in these systems at 1200°C as a function of the oxygen partial pressure; (2) to determine the thermochemical properties based upon the phase equilibria; (3) to ascertain whether the phase diagrams in the *Ln*–Co–O systems change with different lanthanoid elements; and (4) to discover whether a linear trend of the standard Gibbs energy of reactions with lanthanoid ionic radius, observed in the systems *Ln*–Fe–O (*9*) and *Ln*–V–O (*10*), is also encountered in the *Ln*–Co–O system.

Experimental

Analytical-grade Nd_2O_3 (99.9%), Gd_2O_3 (99.9%), and CoO (99.9%) were used as starting materials. These oxides were dried by heating at 1200°C in the air. Mixtures with desired ratios of Nd_2O_3/CoO and Gd_2O_3/CoO were prepared by mixing thoroughly in an agate mortar and then were calcined several times at 1200°C during the intermediate mixing and treated by the same procedures as described previously (*11*).

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The thermobalance and means for controlling the oxygen partial pressures, temperature, and criterion for the establishment of equilibrium are the same as those described in previous papers (*11*, *12*).

X-ray powder analysis using Ni-filtered Cu$K\alpha$ radiation for the Nd–Co–O system and Mn-filtered Fe$K\alpha$ radiation for the Gd–Co–O system was employed to characterize the phases in the quenched samples. Lattice constants were also determined by the X-ray powder method with a slow scanning speed of 0.5° per minute in 2θ. The instruments were calibrated by measuring the diffraction angles of a standard specimen of silicon.

Mixed gases of CO_2 and H_2 and of CO_2 and O_2 were used to achieve the required oxygen partial pressure in the present experiment. The actual oxygen partial pressure of the gas phase was measured by means of a solid electrolytic cell, $(ZrO_2)_{0.85} \cdot (CaO)_{0.15}$ (*13*).

Results and Discussions

(*1*) *Phase Equilibria*

Nd_2O_3–Co–Co_2O_3 system. Six samples with Nd_2O_3/CoO mole ratios of 6/4, 4/6, 3/5, 1/2, 3/7, and 2/8 were prepared and studied thermogravimetrically. In Fig. 1 the relationships between the oxygen partial pressure, $-\log (P_{O_2}/\text{atm})$, on the ordinate and the weight change, W_{O_2}/W_T, on the abscissa are shown for three representative samples, Nd_2O_3/CoO = 6/4, 3/5, and 2/8. W_{O_2} is the weight increase of the samples relative to the reference weight at $\log P_{O_2} = -12.00$, at which Nd_2O_3 and Co metal coexist, and W_T is the total weight gain from the reference weight to the weight at 1 atm O_2 pressure, at which $Nd_2O_3 + NdCoO_3$ or $NdCoO_3 + CoO$ are stable, depending upon the total composition of the samples. Nd_2O_3 is stable under the present experimental conditions (*9*).

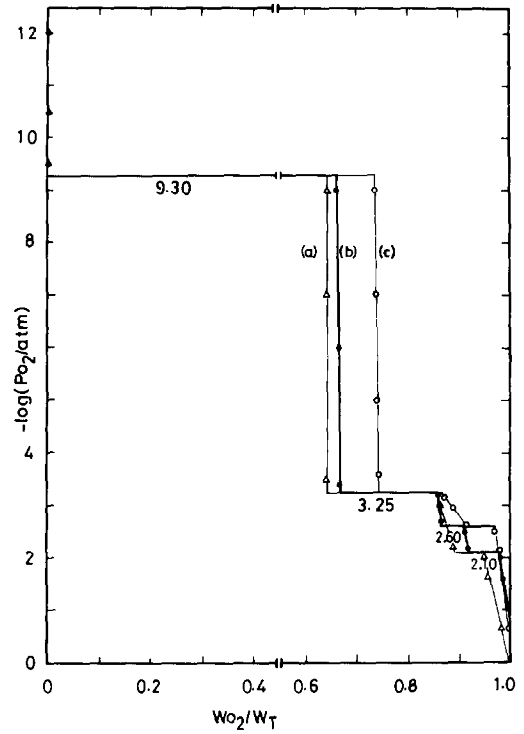

FIG. 1. The relationships between the composition, $W_{O_2}W_T$ and the oxygen partial pressure in the system Nd_2O_3–Co–Co_2O_3 at 1200°C with ratios of Nd_2O_3/CoO of (a) 6/4, (b) 3/5, and (c) 2/8.

As is shown in Fig. 1, abrupt weight changes take place at values of $-\log P_{O_2}$ of 9.30, 3.25, 2.60, and 2.10. These values reflect the oxygen partial pressures at which solid phases are in equilibrium. It is apparent from previous data (*1*) that $\log P_{O_2} = -9.30$ corresponds to the oxygen partial pressure of the reaction, $Co + 1/2\ O_2 = CoO$.

The identification of phases was carried out on samples which were quenched at different conditions of the oxygen partial pressure. Part of the results is shown in Table I as the two-phase combinations.

Based upon the thermogravimetric results and the phase identifications, the phase diagram shown in Fig. 2 was constructed. Numerical values in the three

TABLE I

THE IDENTIFICATION OF PHASES

Ln_2O_3 (mole%)	CoO (mole%)	$-\log P_{O_2}$ (atm)	Time (hr)	Phase
Nd_2O_3				
60	40	10.00	9	Nd_2O_3 + Co
		9.00	37	Nd_2O_3 + CoO
		3.70	17	Nd_2O_3 + CoO
		3.00	23	Nd_2O_3 + $Nd_4Co_3O_{10}$
		2.00	23	Nd_2O_3 + $NdCoO_3$
		0.68	23	Nd_2O_3 + $NdCoO_3$
37.5	62.5	2.40	27	$NdCoO_3$ + $Nd_4Co_3O_{10}$
20	80	10.00	9	Nd_2O_3 + Co
		9.00	37	Nd_2O_3 + CoO
		3.70	17	Nd_2O_3 + CoO
		3.00	23	CoO + $Nd_4Co_3O_{10}$
		2.00	23	CoO + $NdCoO_3$
		0.68	23	CoO + $NdCoO_3$
Gd_2O_3				
60	40	10.00	7	$Gd_2O_3{}^a$ + Co
		9.00	10	$Gd_2O_3{}^a$ + CoO
		2.00	30	Gd_2O_3 + CoO
		0.68	45	$Gd_2O_3{}^a$ + $GdCoO_3$
20	80	10.00	7	$Gd_2O_3{}^a$ + Co
		9.00	10	$Gd_2O_3{}^a$ + CoO
		2.00	30	Gd_2O_3 + CoO
		0.68	45	CoO + $GdCoO_3$

[a] B-form (monoclinic) often appears together with C-form (cubic).

solid fields in Fig. 2 indicate the four equilibrium oxygen partial pressures as $-\log P_{O_2}$ described above. Five phases, Nd_2O_3(R), Co, CoO(D), $Nd_4Co_3O_{10}$(B), and $NdCoO_3$(C) are stable in the system. Co_2O_3 and Co_3O_4 are not found. The existence of $Nd_4Co_3O_{10}$ has not previously been reported, and it might be a new compound. The corresponding phase of $La_4Co_3O_{10}$ is well known. Flamand *et al.* (*3*) have prepared Nd_2CoO_4 in a high-temperature imaging furnace at 1800°C in 1 atm and 30 atm O_2, but this phase was not encountered in the present system under the experimental conditions. That Nd_2CoO_4 is not stable is a remarkable difference between the diagrams of the Nd_2O_3-Co-Co_2O_3 and the La_2O_3-Co-Co_2O_3 system. As is shown in Fig. 2, $NdCoO_3$ and $Nd_4Co_3O_{10}$ phases have nonstoichiometric compositions. The relationship between the composition and the oxygen partial pressure is represented by the linear equations, $N_O/N_{NdCoO_3} = 0.0319 \log P_{O_2}$ for the $NdCoO_3$ solid solution and $N_O/N_{Nd_4Co_3O_{10}} = 0.0833 \log P_{O_2} + 0.180$ for the $Nd_4Co_3O_{10}$ solid solution, respectively. Here, N denotes the mole fraction of the subscripts. Data for the linear equation concerning the CoO solid solution were reported earlier (*1*).

Lattice constants of the ternary compounds are listed in Table II. The present results for $NdCoO_3$ are in good agreement with previous values (*4–6*). The values did not depend measurably on the oxygen partial pressure. The assignment of indices for $Nd_4Co_3O_{10}$ was based on the data for $La_4Co_3O_{10}$; the resulting spacings and relative intensities are shown in Table III, in which other weak peaks are not indicated. These weak peaks appear at about 28.5, 46.7, 59.4, 61.5, 68.9 in 2θ which could not be determined by the usual slow scanning method described above. No effect from other coexisting phases on the lattice constants of $Nd_4Co_3O_{10}$ is found. This suggests that the width of its composition range toward Nd_2O_3 and CoO might be small.

In Table IV the compositions of the com-

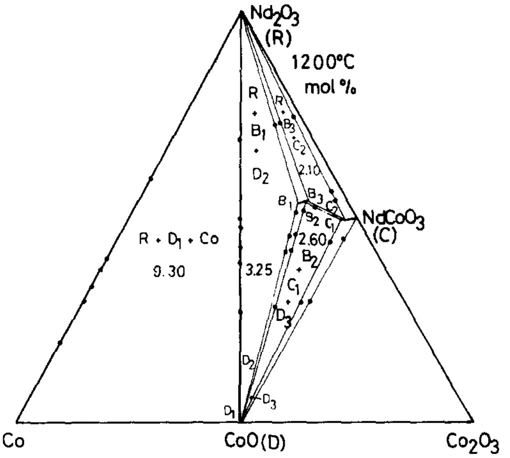

FIG. 2. Phase equilibria in the Nd_2O_3-Co-Co_2O_3 system at 1200°C. Numerical values in the three-phase regions are the oxygen partial pressure in $-\log (P_{O_2}/\text{atm})$ in equilibrium with the three solid phases. Symbols are the same as those in Table IV.

TABLE II

LATTICE CONSTANT OF THE TERNARY COMPOUNDS

Compound	$-\log P_{O_2}$ (atm)	a (Å)	b (Å)	c (Å)	V (Å^3)	Ref.
$NdCoO_3$	0.68	5.337 ± 0.004	5.341 ± 0.005	7.555 ± 0.004	215.4 ± 0.3	Present
	2.40	5.340 ± 0.002	5.342 ± 0.003	7.552 ± 0.002	215.5 ± 0.2	Present
		5.345 ± 0.002	5.345 ± 0.002	7.560 ± 0.003	216.0 ± 0.2	*(5)*
		5.331	5.339	7.548		*(6)*
		5.336	5.336	7.547		*(4)*
$Nd_4Co_3O_{10}$	3.00[a]	5.361 ± 0.002	5.454 ± 0.001	27.22 ± 0.01		Present
	3.00[b]	5.366 ± 0.002	5.450 ± 0.002	27.24 ± 0.02		Present
$GdCoO_3$	0.68[c]	5.224 ± 0.002	5.391 ± 0.002	7.454 ± 0.002	209.9 ± 0.1	Present
	0.68[a]	5.227 ± 0.002	5.389 ± 0.002	7.456 ± 0.002	210.1 ± 0.1	Present
		5.217	5.388	7.446		*(7)*
		5.222	5.390	7.462		*(6)*
		5.221 ± 0.005	5.385 ± 0.005	7.465 ± 0.005		*(8)*
		5.228	5.401	7.436		*(4)*

[a] Coexists with CoO.

[b] Coexists with Nd_2O_3.

[c] Coexists with Gd_2O_3.

pounds at representative points, their symbols, the stability of the compounds, and activities of the components in the solid solutions are tabulated. The CoO data were determined using the experimental results from a previous study *(1)*. The activities of the components in the solid solutions are calculated with the Gibbs–Duhem equation involving the variation of the above ratio $N_O/N_{\text{Component}}$ with $\log P_{O_2}$ *(14)*.

Gd_2O_3–Co–Co_2O_3 system. In Fig. 3 the relationship between the oxygen partial pressure and the composition is represented by three mixtures, $Gd_2O_3/CoO = 6/4$ (a), 4/6 (b), and 2/8 (c). The reference weight was also set at $\log P_{O_2} = -12.00$, at which Gd_2O_3 and Co metal are stable. The patterns are very simple, in which two oxygen partial pressures 9.30 and 1.14 in $-\log P_{O_2}$ are found in equilibrium with three solid

TABLE III

SPACINGS AND RELATIVE INTENSITIES OF $Nd_4Co_3O_{10}$

$h\ k\ l$	d_{obs}	d_{cal}	I_{obs}
1 1 1	3.7857	3.7861	22
0 0 8	3.4040	3.4025	19
1 1 7	2.7254	2.7262	100
2 0 0	2.6811	2.6805	33
	1.9429		15
2 2 0	1.9113	1.9116	39
1 3 7	1.57429	1.57429	22

TABLE IV

COMPOSITIONS OF COMPOUNDS, SYMBOLS, STABILITY RANGES IN OXYGEN PARTIAL PRESSURES, AND ACTIVITIES OF COMPONENTS IN THE SOLID SOLUTIONS

Component	Composition	Symbol	$-\log P_{O_2}$ (atm)	$\log a_i$
$Nd_4Co_3O_{10}$	$Nd_4Co_3O_{9.91}$	B_1	3.25	0
	$Nd_4Co_3O_{9.96}$	B_2	2.60	0.0207
	$Nd_4Co_3O_{10.0}$	B_3	2.10	0.0247
$NdCoO_3$	$NdCoO_{2.92}$	C_1	2.60	0
	$NdCoO_{2.93}$	C_2	2.10	0.0187
	$NdCoO_{3.00}$	C	0–0.68	0.0502
$GdCoO_3$	$GdCoO_{3.00}$	E	0	~0
	$GdCoO_{2.995}$	E_1	1.14	0
CoO	$CoO_{0.991}$	D_1	9.30	0
	$CoO_{0.998}$	D_2	3.25	0.0155
	$CoO_{0.999}$	D_3	2.60	0.0159
	$CoO_{1.001}$	D_4	1.14	0.0158

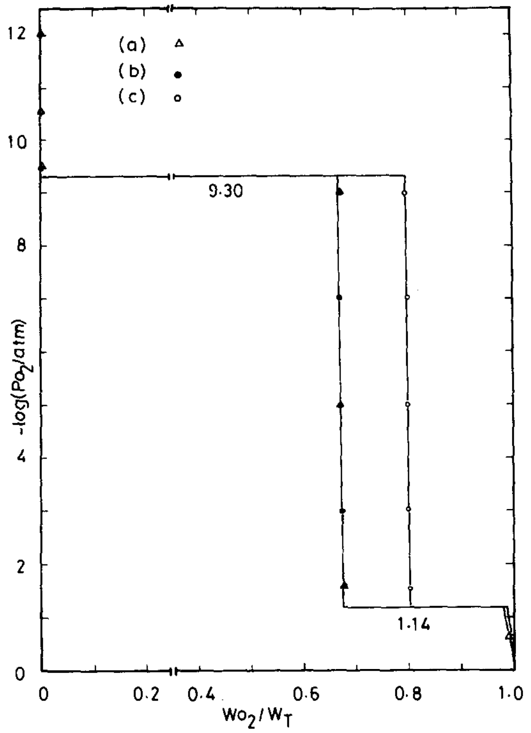

FIG. 3. The relationships between the composition, W_{O_2}/W_T, and the oxygen partial pressure in the system Gd_2O_3–Co–Co_2O_3 at 1200°C with ratios of Gd_2O_3/CoO of (a) 6/4, (b) 4/6, and (c) 2/8.

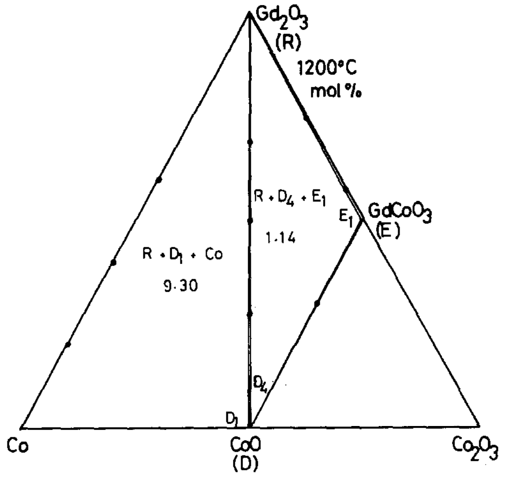

FIG. 4. Phase equilibria in the Gd_2O_3–Co–Co_2O_3 system at 1200°C. Numerical values in the three-phase regions are the oxygen partial pressure in −log (P_{O_2}/atm) in equilibrium with the three solid phases. Symbols are the same as those in Table IV.

phases. The results of the phase identification are tabulated in a lower part of Table I. The Gd_2O_3–Co–Co_2O_3 diagram is illustrated in Fig. 4. Only $GdCoO_3$ is stable as a ternary compound; Gd_2CoO_4 and $Gd_4Co_3O_{10}$ are not encountered. A small range of the composition is observed in $GdCoO_3$ but it is too small to deduce a linear relation as was done for $NdCoO_3$. The range as shown in Fig. 4 is exaggerated to indicate the range explicitly. The numerical values in the three solid-phase areas are also the oxygen partial pressures in equilibrium with three solid phases in −log P_{O_2}.

(2) *The Standard Gibbs Energy of Reaction*

On the basis of the established phase diagrams, the standard Gibbs energy of reactions which appear in the systems are calculated by the equation, $\Delta G° = -RT \ln K$ and are shown in Table V. Here, the R is the gas constant, the T the absolute temper-

TABLE V

THE STANDARD GIBBS ENERGY OF REACTIONS

Reaction	−log P_{O_2} (atm)	−$\Delta G°$ (kJ)
(1) 2 Nd_2O_3 + 3 CoO + 1/2 O_2 = $Nd_4Co_3O_{10}$	3.25 ± 0.05	44.5 ± 0.7
(2) $Nd_4Co_3O_{10}$ + CoO + 1/2 O_2 = 4 $NdCoO_3$	2.60 ± 0.05	35.6 ± 0.7
(3) $Nd_4Co_3O_{10}$ + 1/4 O_2 = 1/2 Nd_2O_3 + 3 $NdCoO_3$	2.10 ± 0.05	15.7 ± 0.4
(4) 1/2 Gd_2O_3 + CoO + 1/4 O_2 = $GdCoO_3$	1.14 ± 0.05	7.6 ± 0.4

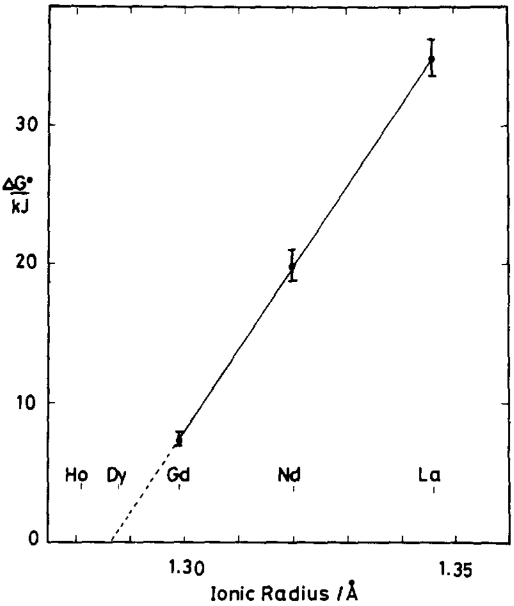

FIG. 5. The relationship between the ionic radius of lanthanoid elements in 12 coordination and ΔG° values of reaction, 1/2 Ln_2O_3 + CoO + 1/4 O_2 = LnCoO$_3$.

ature, and the K the equilibrium constant of the reaction. The activities which were used to calculate K values are tabulated in Table III. ΔG° values obtained are shown in Table V. The combination of reactions (2) and (3) yields reaction (5), 1/2 Nd_2O_3 + CoO + 1/4 O_2 = $NdCoO_3$ for which $\Delta G^\circ = -19.9$ kJ.

(3) *The Relationship between* ΔG° *and Ionic Radius*

A common reaction, 1/2 Ln_2O_3 + CoO + 1/4 O_2 = LnCoO$_3$, is found in the previous (*1*) and present systems. The relationship between ΔG° values for the reactions and the ionic radius of lanthanoid elements with 12 coordination in the perovskite structure (*15*) is shown in Fig. 5 where the ionic radii of Dy and Ho are also shown for reference. Although only three data points have been obtained so far, the figure indicates a linear relation between ΔG° and the ionic radius. The ΔG° value for $LaCoO_3$ also fits in the linear relationship despite the difference of the crystal system from other LnCoO$_3$. This means that the crystal structure does not affect the energy as much as the ionic radius. The sign of ΔG° changes from negative to positive between Dy and Ho. This suggests that LnCoO$_3$ from Ho to Lu might not be stable under the present conditions. The mixture of composition Tm_2O_3/CoO = 4/6 quenched in air shows no peaks corresponding to the perovskite structure in X-ray powder diffraction. Figure 5 also suggests that other systems which contain Dy and Tb might have only LnCoO$_3$ as the stable form.

(4) *Classification of the Pattern of the Phase Diagram*

The Ln_2O_3–Co–Co_2O_3 system at 1200°C was investigated, with Ln = La, Nd, and Gd. Each has a different pattern as described above. From the view point of stability of ternary compounds under the present experimental conditions, the diagram can be divided into three types: the A type which has three ternary compounds, Ln_2CoO_4, $Ln_4Co_3O_{10}$, and LnCoO$_3$; the B type which has two ternary compounds, $Ln_4Co_3O_{10}$ and LnCoO$_3$; and the C type which has only one compound, LnCoO$_3$.

It is of further interest to discover what other types of the diagram appear in other systems, and to what types other systems belong. As described above, systems of Ho to Lu might not be encountered even as LnCoO$_3$. The other systems will be examined in the near future.

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