

Thermogravimetric Study of the Ln_2O_3 –Co– Co_2O_3 System

V. $Ln = Nd$ at 1100 and 1150°C

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Phase equilibria in the system Nd–Co–O at 1110 and 1150°C are established by changing the oxygen partial pressure from 0 to 12.00 in $-\log(P_{O_2}/\text{atm})$ and phase diagrams are presented for the Nd_2O_3 –Co– Co_2O_3 system. Under the experimental conditions, Nd_2O_3 , CoO, Co, $Nd_4Co_3O_{10}$, and $NdCoO_3$ phases are present at both temperatures. The nonstoichiometry of the compounds $Nd_4Co_3O_{10}$ and $NdCoO_3$ is represented with respect to the oxygen partial pressure, and activities of the components in the solid solutions are calculated using the composition–oxygen partial pressure relations obtained. The changes of the standard Gibbs energies of the reactions in the phase diagrams are calculated and their linearity with temperature is confirmed under the present experimental conditions. The relationship between the change of the standard Gibbs energy of a reaction and the ionic radius of the lanthanoid element is discussed. © 1998 Academic Press

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According to previous studies, Nd_2CoO_4 (1,2) and $NdCoO_3$ (3–5) exist as ternary compounds in the Nd–Co–O system. Kitayama studied (6) the phase equilibria in the Nd–Co–O system at 1200°C and established that Nd_2O_3 , Co, CoO, $Nd_4Co_3O_{10}$, and $NdCoO_3$ phases are stable. Moreover, the changes of the standard Gibbs energies of the reactions were determined based on the phase diagram obtained and the lattice constants of $Nd_4Co_3O_{10}$ and $NdCoO_3$. The pattern of the system is different from that of the La–Co–O system with respect to the absence of an Ln_2CoO_4 type compound (7).

The objectives of the present study are (1) to establish detailed phase equilibria in the system at 1100 and 1150°C as a function of the oxygen partial pressure, (2) to determine the thermochemical properties based on the phase equilibria at different temperatures, and (3) to ascertain whether the isothermal pattern of the phase diagram of the Nd–Co–O system changes with temperature.

EXPERIMENTAL

Analytical grade Nd_2O_3 (99.9%) and CoO (99.9%) were used as starting materials. These oxides were dried by heating at 1100°C in air. Mixtures with the desired Nd_2O_3 /CoO ratios were prepared by mixing thoroughly in an agate mortar, calcining several times during the mixing, and treated by the same procedures as described previously (8).

CO_2/H_2 and CO_2/O_2 gas mixtures were used to obtain the oxygen partial pressures in the present experiment.

The apparatus and procedures for controlling the oxygen partial pressures and keeping a constant temperature, the thermogravimetric method, and the criterion for the establishment of equilibrium were the same as those described in the previous paper (9). Briefly, the method of establishment of equilibrium is as follows: To ensure equilibrium, the equilibrated point of each sample at a given oxygen partial pressure was established from both sides of reaction, that is to say, from low oxygen partial pressures to high oxygen partial pressures and from high to low.

The balance, furnace, and gas mixer are schematically shown in Fig. 1. The furnace which has a mullite tube wound with 60% Pt–40% Rh alloy wire as heater is used vertically. Mixed gases, which make the desired oxygen partial pressures, pass from the bottom of the furnace to the top.

RESULTS AND DISCUSSION

(1) Nd_2O_3 –Co– Co_2O_3 System at 1100°C

The Co–O system was reinvestigated at 1100 and 1150°C by using the present apparatus and procedures (10). As shown in Table 1 in ref 10, the oxygen partial pressures in equilibrium with CoO and Co metal at 1100 and 1150°C were 10.33 ± 0.03 and 9.70 ± 0.03 in $-\log(P_{O_2}/\text{atm})$, respectively. At 1100°C, x in CoO_x was ~ 1.000 at $-\log P_{O_2} = 10.33$ and 1.012 at $-\log P_{O_2} = 0$ whereas at 1150°C x was 1.000 at $-\log P_{O_2} = 9.70$ and 1.011 at $-\log P_{O_2} = 0$.

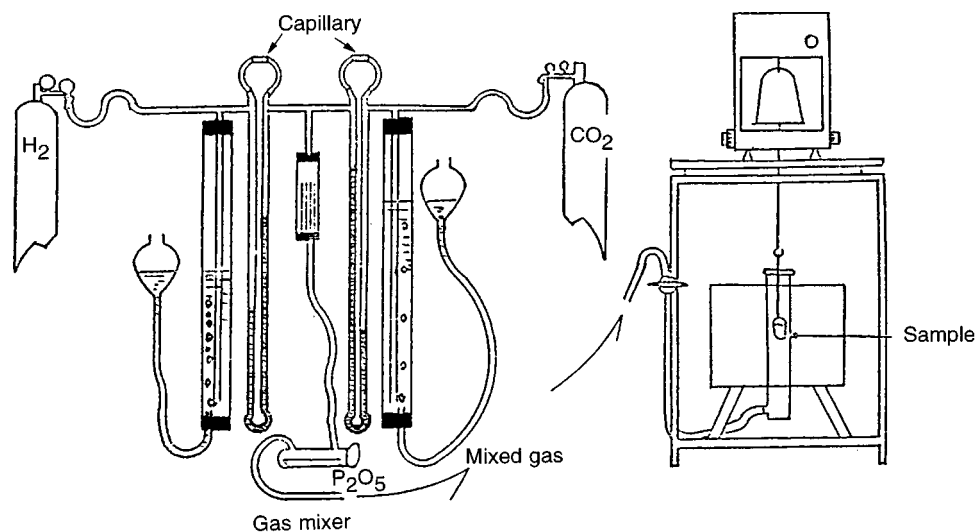


FIG. 1. Schematic of the apparatus: left, gas mixer; right, furnace and balance. Mixed gases, which make various oxygen partial pressures, are led to the furnace from the bottom to the top.

Six samples with $\text{Nd}_2\text{O}_3/\text{CoO}$ mole ratios of 6/4, 5/5, 4/6, 35/65, 1/2, and 2/8 were prepared for use in thermogravimetry. In Fig. 2 the relationships between the oxygen

partial pressure, $-\log(P_{\text{O}_2}/\text{atm})$, on the ordinate and the weight change, W_{O_2}/W_T , on the abscissa are shown with three representative samples, 6/4 (Fig. 2a), 4/6 (Fig. 2b), and

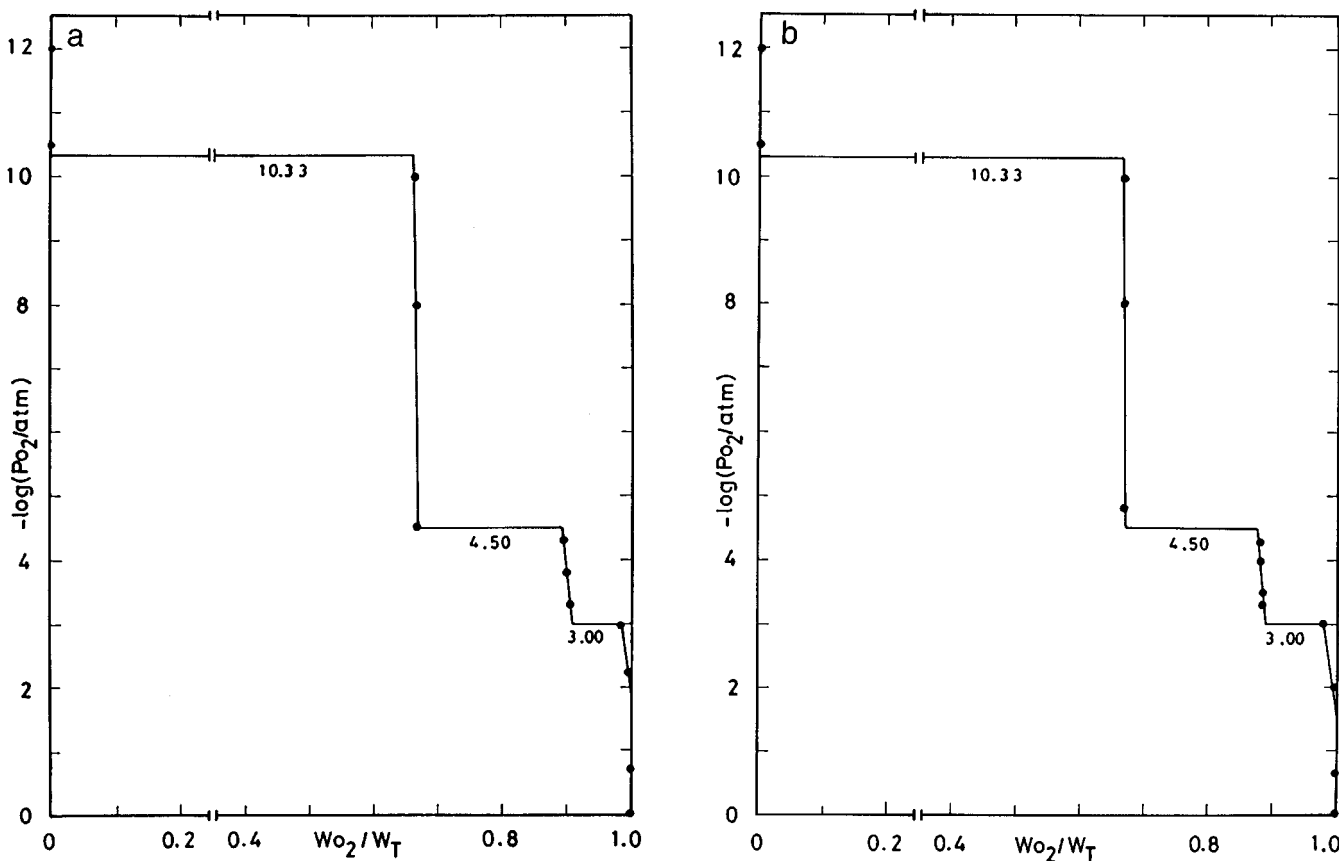


FIG. 2. Relationship between the oxygen partial pressure, $\log(P_{\text{O}_2}/\text{atm})$, and the weight changes of the samples, W_{O_2}/W_T . At 1100°C: (a) $\text{Nd}_2\text{O}_3/\text{CoO} = 6/4$, (b) $\text{Nd}_2\text{O}_3/\text{CoO} = 4/6$, and (c) $\text{Nd}_2\text{O}_3/\text{CoO} = 1/2$. At 1150°C: (d) $\text{Nd}_2\text{O}_3/\text{CoO} = 5/5$, (e) $\text{Nd}_2\text{O}_3/\text{CoO} = 1/2$, and (f) $\text{Nd}_2\text{O}_3/\text{CoO} = 2/8$.

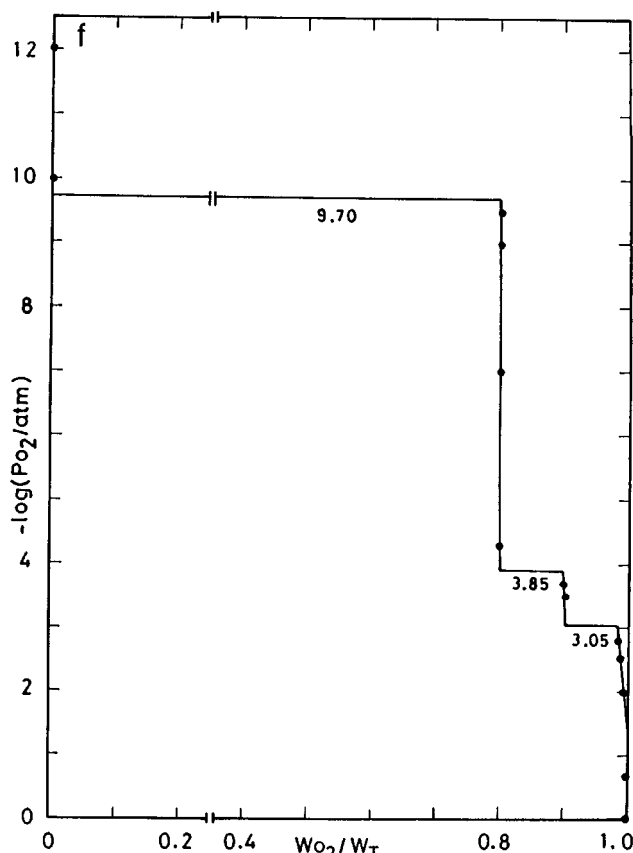
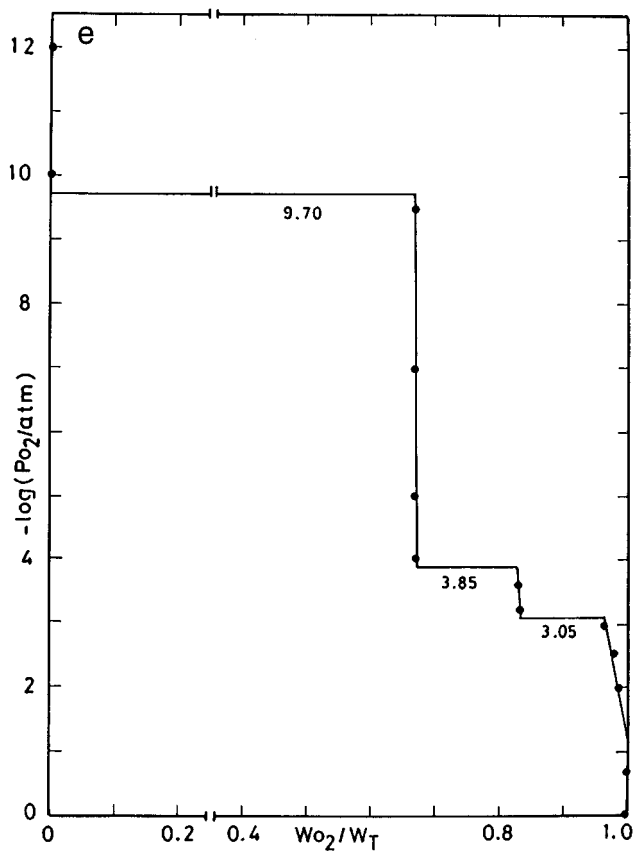
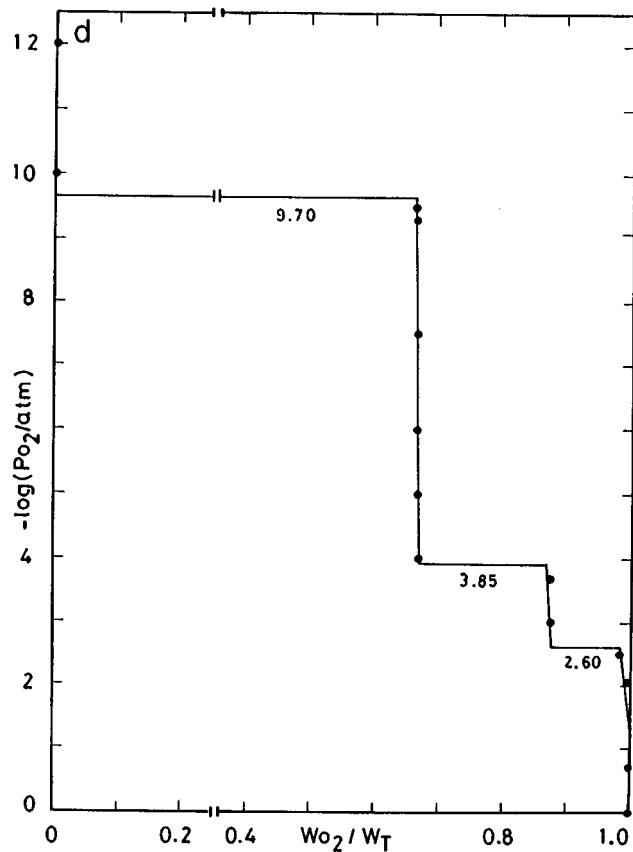
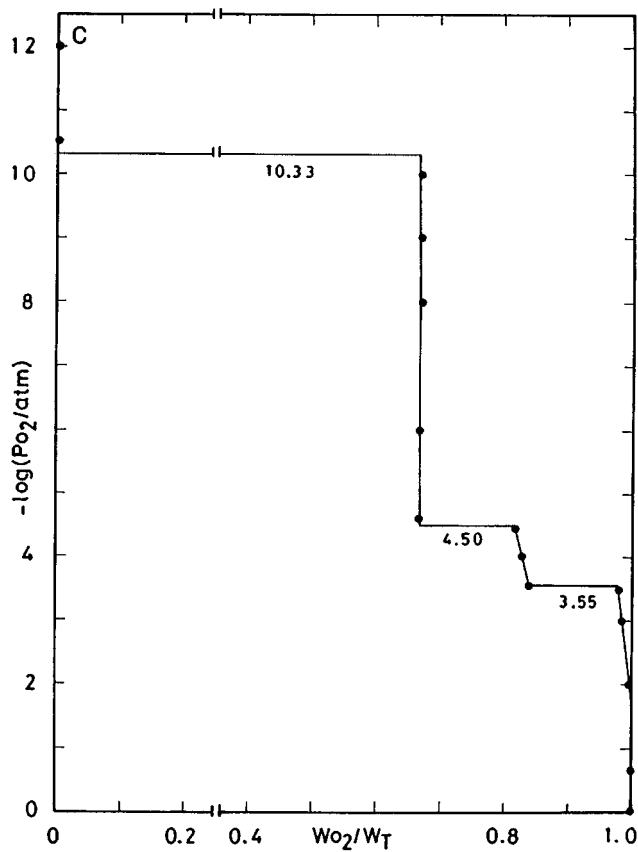


FIG. 2—Continued

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

Component	Composition	Symbol	$-\log P_{O_2}$ (atm)	$\log a_i$
1100°C				
Nd ₄ Co ₃ O ₁₀	Nd ₄ Co ₃ O _{9.92}	B ₁	4.50	0
	Nd ₄ Co ₃ O _{9.95}	B ₂	3.55	0.0287
	Nd ₄ Co ₃ O _{9.97}	B ₃	3.00	0.0388
NdCoO ₃	NdCoO _{2.96}	C ₁	3.55	0
	NdCoO _{2.97}	C ₂	3.05	0.0099
	NdCoO _{3.00}	C ₃	2.04-0	0.016
CoO	CoO _{1.00}	D ₁	10.33	0
	CoO _{1.00}	D ₂	4.50	~ 0
	CoO _{1.00}	D ₃	3.55	~ 0
	CoO _{1.01}	D ₄	3.55-0	~ 0
1150°C				
Nd ₄ Co ₃ O ₁₀	Nd ₄ Co ₃ O _{9.89}	B _{1'}	3.85	0
	Nd ₄ Co ₃ O _{9.94}	B _{2'}	3.05	0.0343
	Nd ₄ Co ₃ O _{9.98}	B _{3'}	2.60	0.0439
NdCoO ₃	NdCoO _{2.99}	C _{1'}	3.05	0
	NdCoO _{2.99}	C _{2'}	2.60	0.0123
	NdCoO _{3.00}	C _{3'}	0.73-0	0.0350
CoO	CoO _{1.00}	D _{1'}	9.70	0
	CoO _{1.00}	D _{2'}	3.85	~ 0
	CoO _{1.00}	D _{3'}	3.05	~ 0
	CoO _{1.01}	D _{4'}	3.05-0	~ 0

1/2 (Fig. 2c). Here, W_{O_2} is the weight increase of the samples from the reference weight at $\log P_{O_2} = -12.00$, at which Nd₂O₃ and Co metal are stable, and W_T is the total weight gain from the reference weight to the weight at 1 atm of O₂, at which Nd₂O₃ and NdCoO₃ or NdCoO₃ and CoO are stable, depending upon the total composition of the samples. Abrupt weight changes occurred in equilibrium with three solid phase regions at 10.33, 4.50, 3.55, and 3.00 in $-\log P_{O_2}$. The value 10.33 corresponds to the oxygen partial pressure of the reaction $Co + \frac{1}{2}O_2 = CoO$ described earlier. The linear line in Fig. 2b between -4.50 and -3.00 in $\log P_{O_2}$ represents the change of composition of the Nd₄Co₃O₁₀ phase with oxygen partial pressure, and the linear line in Fig. 2c between -3.55 and -2.04 in $\log P_{O_2}$ represents the change of composition of the NdCoO₃ phase with oxygen partial pressure.

On the basis of the foregoing thermogravimetric results, a phase diagram is drawn and is illustrated in Fig. 3 as Nd₂O₃-Co-Co₂O₃, although Co₂O₃ is not stable under the experimental conditions. The numerical values in the three solid phases in Fig. 3 are the four values in $-\log P_{O_2}$ shown in Fig. 2 and described above. Five phases, Nd₂O₃, Co, Nd₄Co₃O₁₀, NdCoO₃, and CoO, are stable.

The compositions of the ternary compounds, their symbols, the stability ranges in $\log P_{O_2}$, and the activities of the components in the solid solutions are shown in Table 1. Stable phases are the same as those at 1200°C (6). Co₃O₄ is not found. Except for Co and Nd₂O₃, the other phases have

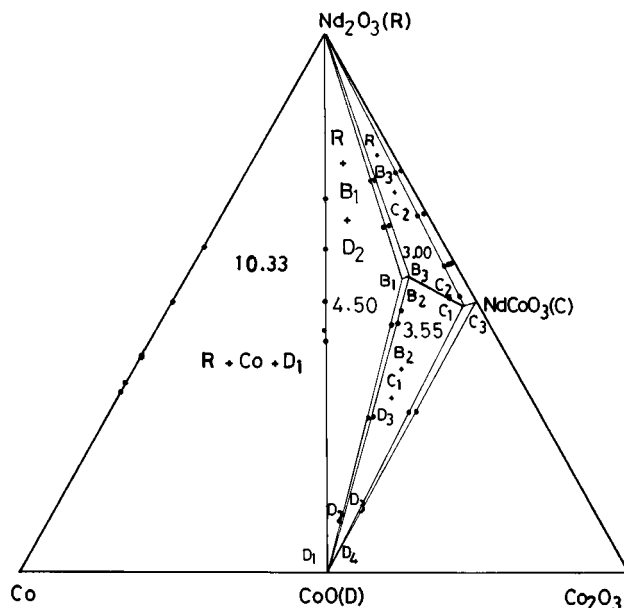


FIG. 3. Phase equilibrium in the Nd₂O₃-Co-Co₂O₃ system at 1100°C. Numerical values in the three-phase regions are the oxygen partial pressures in $-\log(P_{O_2}/\text{atm})$ in equilibrium with the three solid phases. Abbreviations are the same as those in Table 1.

nonstoichiometric compositions. The composition of the solid solutions as a function of the oxygen partial pressure may be represented by the equation, $N_O/N_{\text{component}} = a \log P_{O_2} + b$, which, together with the Gibbs-Duhem equation, can be used to calculate the activity of the components in the solid solutions (11). Here, N_O and $N_{\text{component}}$ are the mole fractions of oxygen and component (cf. Table 1) in the solid solutions, respectively. The a and b values for each solid solution, which were obtained from thermogravimetric results, are tabulated in Table 2.

(2) Nd₂O₃-Co-Co₂O₃ System at 1150°C

Five samples with Nd₂O₃/CoO mole ratios of 5/5, 4/6, 35/65, 1/2, and 2/8 were prepared for use in thermogravimetry. The thermogravimetric results for representative samples with Nd₂O₃/CoO ratios of 5/5 (Fig. 2d), 1/2

TABLE 2
 a and b Values of Solid Solutions

Temp (°C)	Component	a	b
1100	Nd ₄ Co ₃ O ₁₀	0.0312	0.0653
	NdCoO ₃	0.0291	0.0593
1150	Nd ₄ Co ₃ O ₁₀	0.0692	0.153
	NdCoO ₃	0.0260	0.0190

(Fig. 2e), and 2/8 (Fig. 2f) are shown in Fig. 2 together with those of 1100°C.

The phase diagram depicted based on these thermogravimetric results shows the same pattern as those at 1100 and 1200°C. The stability range of oxygen partial pressure of the solid solutions and the activities of the components in the solid solutions are tabulated in Table 1.

(3) Change of the Standard Gibbs Energy of Reaction and Its Dependency on Temperature and Ionic Radius of the Lanthanoid

On the basis of the established phase diagram, ΔG° of the reactions, which appear in the phase diagram and are shown in Table 3, is determined with 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 activities of the components in the solid solutions, which are necessary to calculate K values, are tabulated in Table 1. The standard state of the component in the solid solution can be arbitrarily chosen for each solid solution and this is indicated as $\log a_i = 0$ in Table 1. ΔG° values for the reactions are tabulated in Table 3 together with those at 1200°C (6). Assuming that the activities of the components in the solid solutions are unity, ΔG° values for reactions [2] and [3] in Table 3 are -46.7 and -19.7 kJ mol⁻¹ at 1100°C, and -41.6 and -17.7 kJ mol⁻¹ at 1150°C, re-

spectively. The differences between these values and the corresponding values in Table 3 are not significant. These differences are a little larger than experimental error. This is probably caused by the narrow solid solution ranges.

Reaction [4] in Table 3 is obtained as reaction [2] minus reaction [3], and ΔG° [4] is -26.4 and -23.7 kJ mol⁻¹ at 1100 and 1150°C, respectively. Reaction [4] is also obtained by a reaction $\{[1] + [2]\}/4$ and a reaction $\{[1] + [3]\}/3$. In these cases the ΔG° [4] values are -26.3 and -26.2 kJ mol⁻¹ at 1100°C and -23.3 and -23.1 kJ mol⁻¹ at 1150°C, respectively. These values are in good agreement with one another within the experimental error. This means that the present results, which were obtained independently, are reasonable.

Reaction [5] is also obtained by the procedure $\{[1] - [2]\}/2$. ΔG° [5] for reaction [5] is -6.7 kJ mol⁻¹ at 1100°C and -6.0 kJ mol⁻¹ at 1150°C. As shown in reaction [5], the oxygen partial pressure does not take part in the reaction, and the negative values of ΔG° show that Nd₄Co₃O₁₀ is stable at these temperatures compared to the mixture of Nd₂O₃, CoO, and NdCoO₃.

In Fig. 4 the change of the standard Gibbs energy of reactions [1], [2], [3], and [4] with absolute temperature is

TABLE 3
Standard Gibbs Energy Change of Reactions

Reaction	Temp (°C)	$-\log P_{O_2}$ (atm)	$-\Delta G^\circ$ (kJ mol ⁻¹) ^a
2Nd ₂ O ₃ + 3CoO + ½O ₂ = Nd ₄ Co ₃ O ₁₀ [1]	1100	4.50	59.2
	1150	3.85	52.5
	1200	3.25	44.5
Nd ₄ Co ₃ O ₁₀ + CoO + ½O ₂ = 4NdCoO ₃ [2]	1100	3.55	45.9
	1150	3.05	40.6
	1200	2.60	35.6
Nd ₄ Co ₃ O ₁₀ + ¼O ₂ = ½Nd ₂ O ₃ + 3NdCoO ₃ [3]	1100	3.00	19.5
	1150	2.60	16.9
	1200	2.10	15.7
½Nd ₂ O ₃ + CoO + ¼O ₂ = NdCoO ₃ ^b [4]	1100		26.4
	1150		23.7
	1200		19.9
Nd ₂ O ₃ + CoO + 2NdCoO ₃ = Nd ₄ Co ₃ O ₁₀ ^c [5]	1100		6.7
	1150		6.0
	1200		4.5
Co + ½O ₂ = CoO ^d [6]	1100	10.33	135.8
	1150	9.70	132.2
	1200	9.30	131.1

^a ± 0.6 kJ mol⁻¹.

^b [4] = [2] - [3].

^c $\{[1] - [2]\}/2$.

^d Values for reaction [6] are quoted from ref 5. Values at 1200°C are quoted from ref 1.

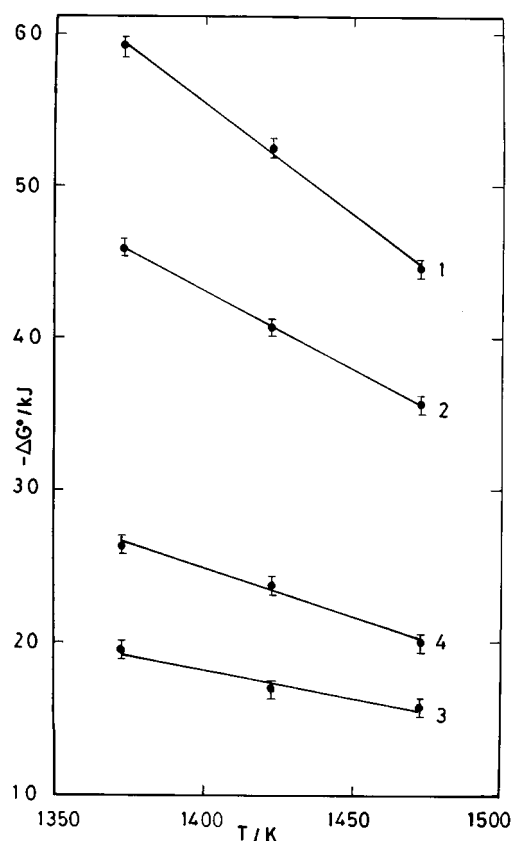


FIG. 4. Relationship between Gibbs energy change ($-\Delta G^\circ$) and temperature. The numbers in the figure correspond to the reactions [1]–[4] in Table 3.

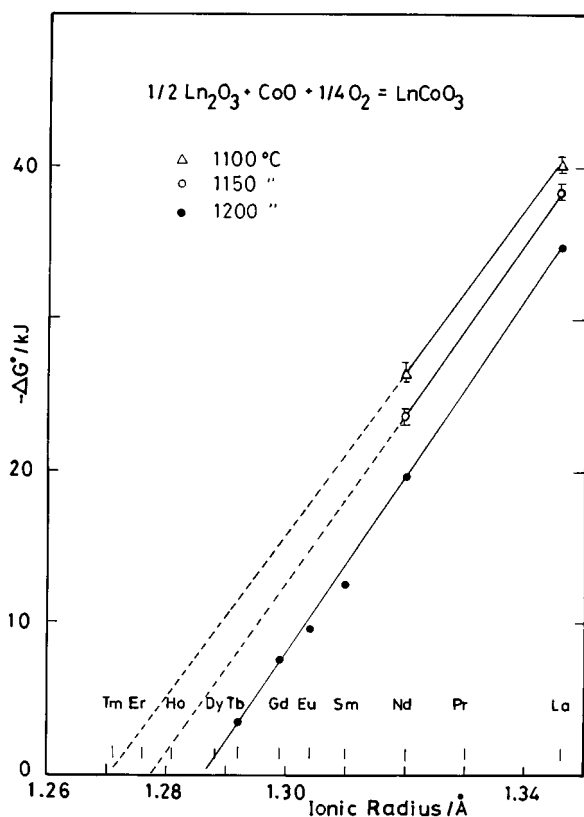


FIG. 5. Relationship between the ionic radius of lanthanoid elements in 12-coordination and ΔG° values of the reaction $\frac{1}{2}Ln_2O_3 + CoO + \frac{1}{4}O_2 = LnCoO_3$.

shown. Although the temperature range is limited, linear relations are observed. Tentative empirical formulae are as follows: for reaction [1], $\Delta G^\circ[1] = 0.147T - 261.2$ (kJ mol^{-1} , 1100–1200°C); for reaction [2], $\Delta G^\circ[2] = 0.103T - 187.3$; for reaction [3], $\Delta G^\circ[13] = 0.038T - 71.4$;

for reaction [4], $\Delta G^\circ[4] = 0.065T - 115.8$; for reaction [5], $\Delta G^\circ[5] = 0.022T - 37.04$; and for reaction [6], $\Delta G^\circ[6] = 0.044T - 195.7$.

As for reaction [4], the relationship between the ionic radius of the lanthanoid element and $\Delta G^\circ[4]$ is very interesting. This type of reaction would be common in all phase diagrams of a $Ln-Co-O$ system if $LnCoO_3$ were stable. At 1200°C it was found that the Gibbs energy change of the reaction was linearly changed with the ionic radius (12) of the lanthanoid element with 12-coordination (13). As shown in Fig. 5, with only two values of La and Nd, there would be a linear relation like that at 1200°C. In addition, as the values become smaller with decreasing temperature, $LnCoO_3$ with a smaller ionic radius would be stable at lower temperatures. At least $TmCoO_3$ would be stable at 1100°C.

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