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Thermogravimetric Study of the *Ln*$_2$O$_3$–Co–Co$_2$O$_3$ System

IV. *Ln* = La at 1100 and 1150°C

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Phase equilibria in the system La–Co–O at 1100 and 1150°C are established by changing the oxygen partial pressure from 0 to 12.00 in $-\log(P_{O_2}/\text{atm})$, and a phase diagram of the La_2O_3–Co–Co_2O_3 system is represented. Under the experimental conditions, La_2O_3, CoO, Co, La_2CoO_4, $LaCoO_3$, and $La_4Co_3O_{10}$ phases are present. Nonstoichiometry of the compound is presented with respect to the oxygen partial pressure, and activities of the components in the solid solutions are calculated by using the composition–oxygen partial pressure relations obtained. The standard Gibbs energy changes of the reactions in the phase diagrams are calculated and their linearity with reciprocal temperature is confirmed under the present experimental conditions. © 1997 Academic Press

The phase equilibrium in the La–Co–O system was established at 1130°C by Janecek and Wirtz (1), but their phase diagram was very rough, as illustrated in Fig. 1 in Ref. 1. Recently the phase equilibrium of the La–Co–O system at 1200°C was presented (2). In that report, La_2O_3, Co, CoO, $LaCoO_3$, $La_4Co_3O_{10}$, and La_2CoO_4 were stable and the standard Gibbs energy changes were obtained based on reactions in the phase diagram.

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

EXPERIMENTAL

Analytical grade La_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 desired ratios of La_2O_3/CoO were prepared by thorough mixing in an agate mortar, calcined several times at 1100°C during the intermediate mixing, and treated by the same procedures as those described previously (3).

Mixed gases of CO_2 and H_2 and of CO_2 and O_2 were used to obtain the oxygen partial pressures. The actual oxygen partial pressures of the gas phase were measured by means of a solid electrolytic cell of $(ZrO_2)_{0.85}(CaO)_{0.15}$ (4).

The apparatus and procedures used to control the oxygen partial pressures and keep a constant temperature, the method of thermogravimetry, and the criterion for the establishment of equilibrium are the same as those described in a previous paper (5).

RESULTS AND DISCUSSION

(1) Phase Equilibria

(a) Co–O system. The Co–O system is a subsystem of the present system. The system is reinvestigated at 1100 and 1150°C by using the present apparatus and procedures. It is known that in this system the compounds CoO, Co_3O_4, and Co_2O_3 are present as stable phases, but under the present experimental conditions only the CoO phase is stable and it has a slight nonstoichiometric to oxygen-rich side. As shown in Table 1, for example, x is $\sim$1.00 and 1.011 in CoO_x at 10.33 and 0 in $-\log(P_{O_2}/\text{atm})$ at 1100°C. The weight in the atmosphere of $\log(P_{O_2}/\text{atm}) = -12.00$ at which Co metal is stable is chosen as the standard weight.

The oxygen partial pressures in equilibrium with CoO and Co metal at 1100 and 1150°C are 10.33 ± 0.03 and 9.70 ± 0.03 in $-\log P_{O_2}$, respectively.

(b) La_2O_3–Co–Co_2O_3 system at 1100°C. Nine samples with La_2O_3/CoO mole ratios of 6/4, 1, 45/55, 4/6, 3/5, 35/65, 1/2, 2/8, and 1/9 are prepared for use in thermogravimetry. 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 with four representative samples, 6/4 (Fig. 1a), 45/55 (Fig. 1b), 3/5 (Fig. 1c), and 2/8 (Fig. 1d). Here, W_{O_2} is the weight increase

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

Component	Compositions	Symbol	$-\log P_{O_2}$ (atm)	$\log a_i$
	1100°C			
La_2CoO_4	$La_2CoO_{4.00}$	A_1	11.05	0
	$La_2CoO_{4.02}$	A_2	10.33	~0
	$La_2CoO_{4.17}$	A_3	5.70	−0.222
	$La_2CoO_{4.20}$	A_4	4.65	−0.318
$La_4Co_3O_{10}$	$La_4Co_3O_{10.01}$	B_1	5.70	0
	$La_4Co_3O_{10.03}$	B_2	4.95	-8×10^{-3}
	$La_4Co_3O_{10.04}$	B_3	4.65	−0.0137
	$La_4Co_3O_{10.10}$	B_4	2.70	−0.0848
$LaCoO_3$	$LaCoO_{2.92}$	C_1	4.95	0
	$LaCoO_{2.96}$	C_2	2.70	0.0666
	$LaCoO_{3.00}$	C_3	0.680 ~ 0	0.0919
CoO	$CoO_{1.00}$	D_1	10.33	0
	$CoO_{1.00}$	D_2	5.70	~0
	$CoO_{1.00}$	D_3	4.95	~0
	$CoO_{1.01}$	D_4	1.50 ~ 0	~0
	1150°C			
La_2CoO_4	$La_2CoO_{4.01}$	A'_1	10.50	0
	$La_2CoO_{4.02}$	A'_2	9.70	-7.44×10^{-3}
	$La_2CoO_{4.17}$	A'_3	5.00	−0.189
	$La_2CoO_{4.20}$	A'_4	3.80	−0.212
$La_4Co_3O_{10}$	$La_4Co_3O_{9.93}$	B'_1	5.00	0
	$La_4Co_3O_{9.94}$	B'_2	4.30	0.0218
	$La_4CoO_{9.96}$	B'_3	3.80	−0.0381
	$La_4Co_3O_{9.99}$	B'_4	2.20	0.0561
$LaCoO_3$	$LaCoO_{2.91}$	C'_1	4.50	0
	$LaCoO_{2.97}$	C'_2	2.20	0.0726
	$LaCoO_{3.00}$	C'_3	0.68 ~ 0	0.0819
CoO	$CoO_{1.00}$	D'_1	9.70	0
	$CoO_{1.00}$	D'_2	5.00	~0
	$CoO_{1.00}$	D'_3	4.30	~0
	$CoO_{1.01}$	D'_4	4.30 ~ 0	~0

of the samples from the reference weight at $\log P_{O_2} = -12.00$, at which La_2O_3 and Co are stable, and W_T is the total weight gain from the reference state to the weight at 1 atm O_2, at which $La_2O_3 + LaCoO_3$ or $LaCoO_3 + CoO$ are stable depending on the total composition of the samples. Abrupt weight changes are observed at 11.05, 10.33, 5.70, 4.95, 4.65, and 2.70 in $-\log P_{O_2}$ in Fig. 1. These values correspond to the oxygen partial pressure in equilibrium with three solid phases.

The compositions of the ternary compounds, symbols, stability ranges in $\log P_{O_2}$, and activities of the components in solid solutions are shown in Table 1.

Based on the above thermogravimetric results, a phase diagram was drawn and is illustrated in Fig. 2 as La_2O_3–Co–Co_2O_3 although Co_2O_3 is not stable under the experimental conditions. The numerical values in the three solid fields in Fig. 2 are the six values in $-\log P_{O_2}$ described above. Six phases, La_2O_3, Co, La_2CoO_4, $La_4Co_3O_{10}$, $LaCoO_3$, and CoO, are stable under the present conditions. The stable phases are the same as those at 1200°C (2). Co_3O_4 is not found. Except for Co and La_2O_3, the other phases have nonstoichiometric compositions. The relationship between the composition of a solid solution and the oxygen partial pressure is represented by a linear equation such as $N_O/N_{\text{component}} = a \log P_{O_2} + b$, which can be used to calculate the activity of the components in the solid solutions with the Gibbs–Duhem equation (6). Here, N_O and $N_{\text{component}}$ are the mole fraction of oxygen and component (cf. Table 1) in the solid solutions, respectively. The a and b values for each solid solution, which are obtained from the thermogravimetric results, are tabulated in Table 2.

As for the oxygen deficiency of the $LaCoO_3$ phase, Seppanen *et al.* (7) expressed the deficiency by a general equation, $LaCoO_{3-d}$, as $d = kP_{O_2}^{-1/2}$ and at 1300 K reaches the value 0.091 at the phase boundary $LaCoO_{3-d}$–CoO–$La_4Co_3O_{10}$. The present value 0.08 ($LaCoO_{2.92}$ (C_1)) in Table 1 might be reasonable considering the difference in temperature.

To express the chemical composition of the three ternary compounds, Janecek *et al.* (1) presented the general formula $La_{n+1}Co_nO_{3n+1}$ ($LaO(LaCoO_3)_n$) as the perovskite-related layered structure. The phase diagram suggests that the compositions $LaCoO_3$, $La_4Co_3O_{10}$, and La_2CoO_4 can be represented by the compositions $La_2O_3\cdot Co_2O_3$, $2La_2O_3\cdot Co_3O_4$, and $La_2O_3\cdot CoO$, respectively, that is, a two-component system of La_2O_3–cobalt oxide, although there is no crystallographic evidence for it now.

Recently, Lewandowski *et al.* (8) reported that the composition of La_2CoO_4 did not exist in the range of temperatures and P_{O_2} investigated and proposed a lanthanum cation-deficient composition, $La_{1.83}CoO_4$. As shown in Fig. 2 in the present case, lanthanum-cation deficiency is not found. Both lines, which originate from Co and La_2O_3 apices and go through the experimental points, join at A_1 and have the composition 20 mol% Co, 60 mol% La_2O_3, and 20 mol% Co_2O_3, that is, La_2CoO_4. The result is the same as those at 1200°C.

(*c*) *La_2O_3–Co–Co_2O_3 system at 1150°C.* Five samples with La_2O_3/CoO mole ratios of 6/4, 1, 4/6, 1/2, and 2/8 were prepared for use in thermogravimetry, although they were anticipated to have the same pattern as those at 1100 and 1200°C. In Fig. 1 the relationships between the oxygen partial pressure and weight changes are shown for four representative samples, La_2O_3/CoO mole ratios of 6/4 (Fig. 1e), 1 (Fig. 1f), 4/6 (Fig. 1g), and 2/8 (Fig. 1h). The reference weight at $\log P_{O_2} = -12.00$ was chosen here also. Based on Figs. 1e–1h, a pattern the same as that in Fig. 2 at 1100°C can be easily seen. The oxygen partial pressures in equilibrium with three solid phases and the activities of the component in the solid solutions are also given in Table 1.

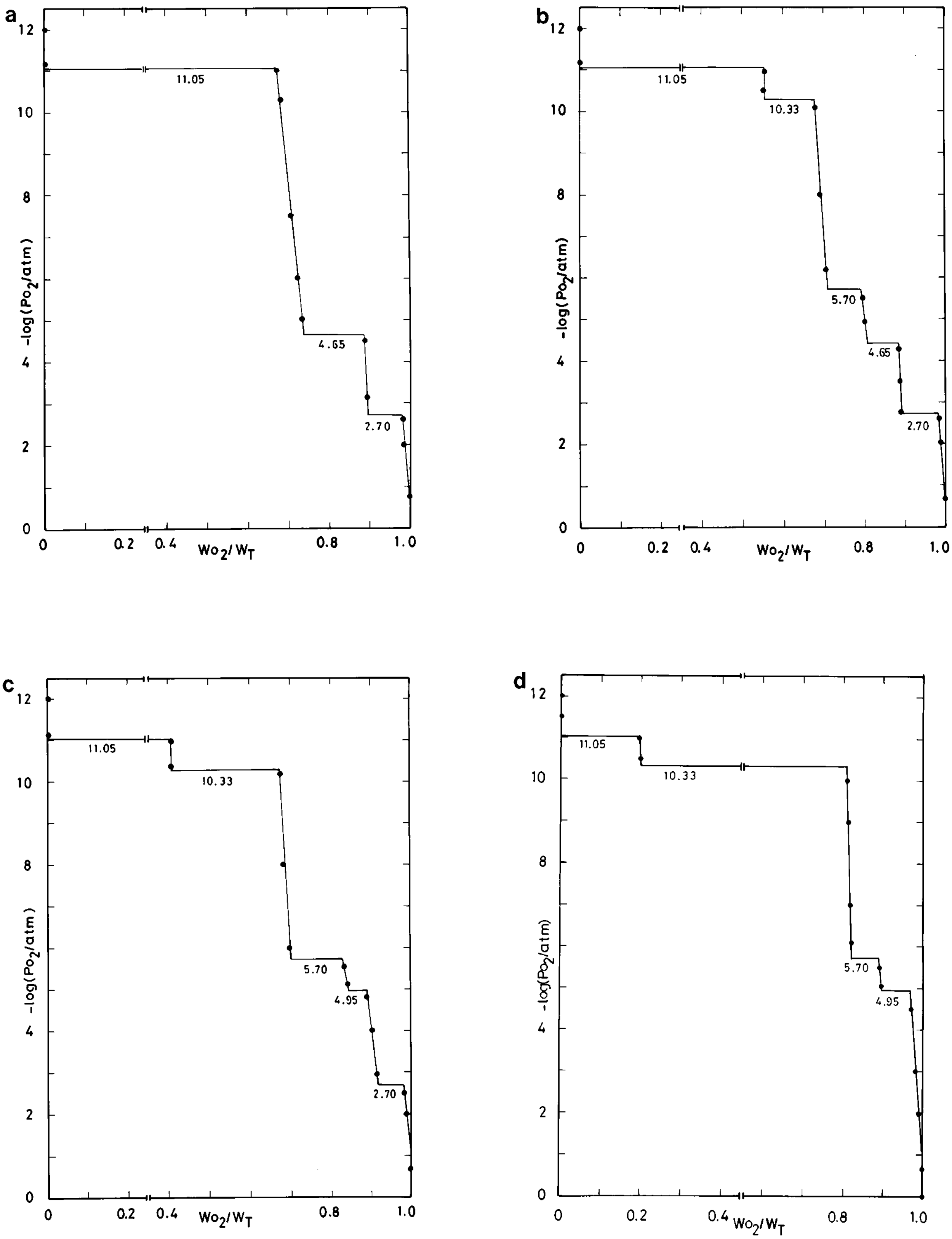

FIG. 1. The relationship between the oxygen partial pressure, log(P_{O_2}/atm), and the weight change of the samples, W_{O_2}/W_T. At 1100°C: (a) $La_2O_3/CoO = 6/4$, (b) $La_2O_3/CoO = 45/55$, (c) $La_2O_3/CoO = 3/5$, and (d) $La_2O_3/CoO = 2/8$. At 1150°C: (e) $La_2O_3/CoO = 6/4$, (f) $La_2O_3/CoO = 5/5$, (g) $La_2O_3/CoO = 4/6$, and (h) $La_2O_3/CoO = 2/8$.

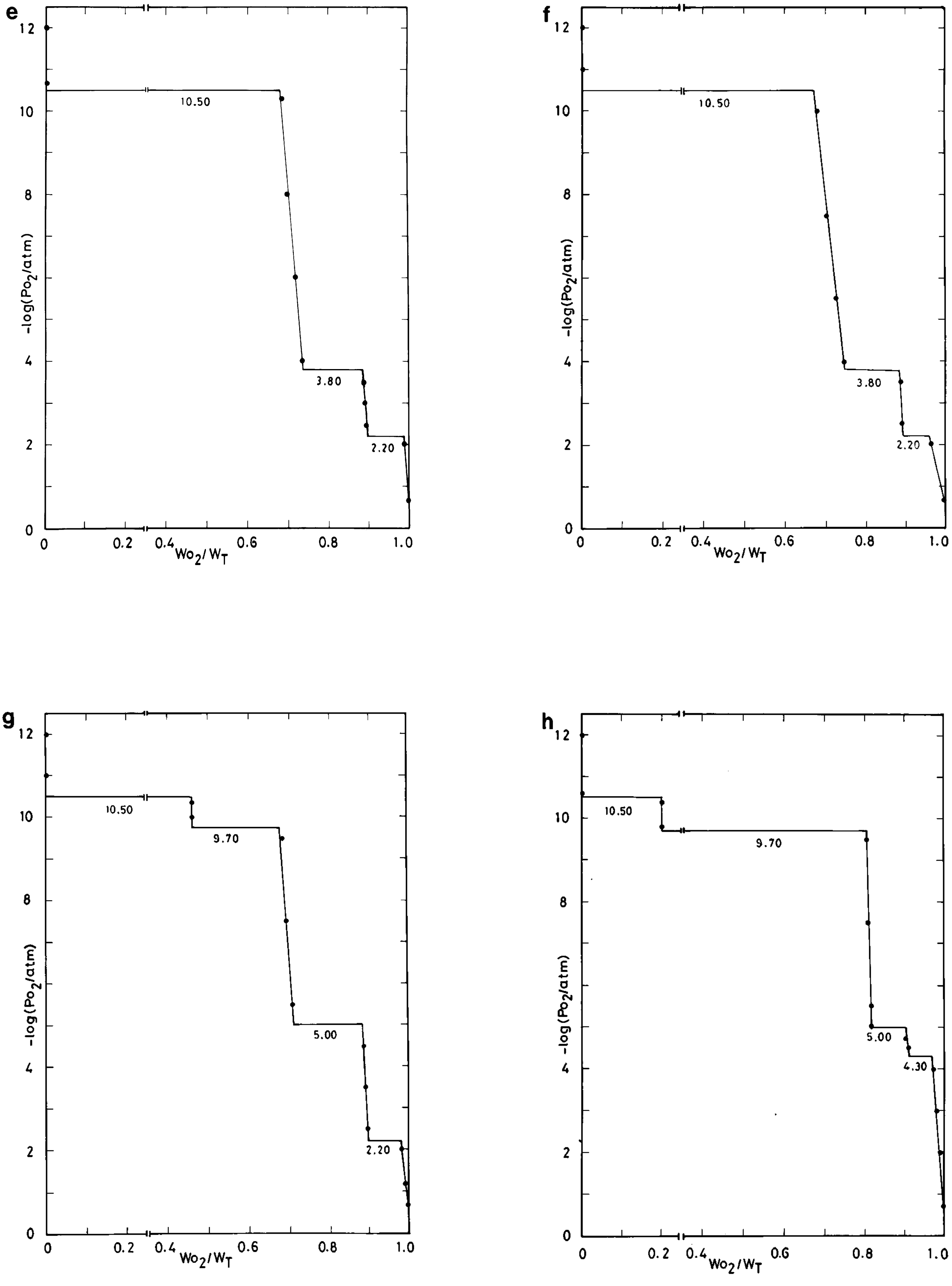

FIG. 1—*Continued*

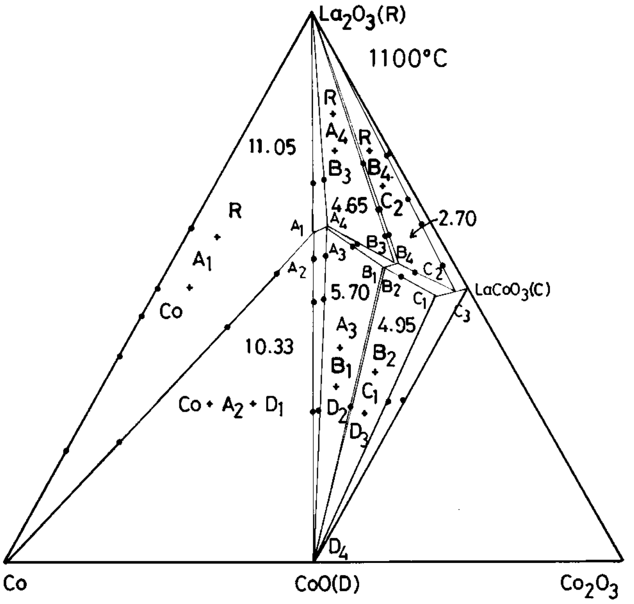

FIG. 2. Phase equilibrium in the La_2O_3–Co–Co_2O_3 system at 1100°C. Numerical values in the three phase regions are the oxygen partial pressures in $-\log(P_{O_2}/\text{atm})$ in equilibrium with three solid phases. Abbreviations are the same as those in Table 1.

TABLE 2
***a* and *b* Values of Solid Solution**

Component	*a*	*b*
	1100°C	
La_2CoO_4	0.0313	0.345
$La_4Co_3O_{10}$	0.0313	0.188
$LaCoO_3$	0.0160	0.002
	1150°C	
La_2CoO_4	0.0151	0.171
$La_4Co_3O_{10}$	0.0210	0.0355
$LaCoO_3$	0.0266	0.0260

Note. $N_O/N_{\text{component}} = a \log P_{O_2} + b$.

(2) The Standard Gibbs Energy Change of Reaction and Its Dependency on Temperature

On the basis of the established phase diagram, the standard Gibbs energy changes of reactions, which appear in the diagram and are shown in Table 3, are determined with the equation $\Delta G^\circ = -RT\ln K$. Here, R is the gas constant, T the absolute temperature, and K the equilibrium constant of the reaction. Activities of the components in solid solutions, which are necessary to calculate ΔG° values, are given in Table 1. The standard state of the components in solid solution can be chosen arbitrarily in each solid solution as $\log a_i = 0$ in Table 1.

ΔG° values obtained for each reaction are given in Table 3 together with those at 1200°C (1). Assuming that the activity of the components in the solid solutions is unity, ΔG° values for reactions [3]–[5] in Table 3 are -17.7, -74.9, and -61.1 kJ mol^{-1}, at 1100°C, and -15.0, -70.5, and -51.8 kJ mol^{-1} at 1150°C. The differences in

TABLE 3
The Standard Gibbs Energy Change of Reactions

Reaction	Temperature (°C)	$-\log P_{O_2}$ (atm)	$-\Delta G^\circ$ (kJ)
[1] $Co + La_2O_3 + \frac{1}{2}O_2 = La_2CoO_4$	1100	11.05	145.3
	1150	10.50	143.1
	1200	10.02	141.1
[2] $Co + \frac{1}{2}\ O_2 = CoO$	1100	10.33	135.8
	1150	9.70	132.2
	1200	9.30	131.1
[3] $La_4Co_3O_{10} + \frac{1}{4}O_2 = \frac{1}{2}La_2O_3 + 3LaCoO_3$	1100	2.70	25.2
	1150	2.20	19.4
	1200	1.87	17.5
[4] $2La_2CoO_4 + CoO + \frac{1}{2}O_2 = La_4Co_3O_{10}$	1100	5.70	86.6
	1150	5.00	76.2
	1200	4.70	70.1
[5] $3La_2CoO_4 + \frac{1}{2}O_2 = La_2O_3 + La_4Co_3O_{10}$	1100	4.65	85.8
	1150	3.80	70.1
	1200	3.05	57.8
[6] $La_4Co_3O_{10} + CoO + \frac{1}{2}O_2 = 4LaCoO_3$	1100	4.95	65.1
	1150	4.30	58.6
	1200	3.90	52.3

Note. Values at 1200°C are quoted from Ref. 2.

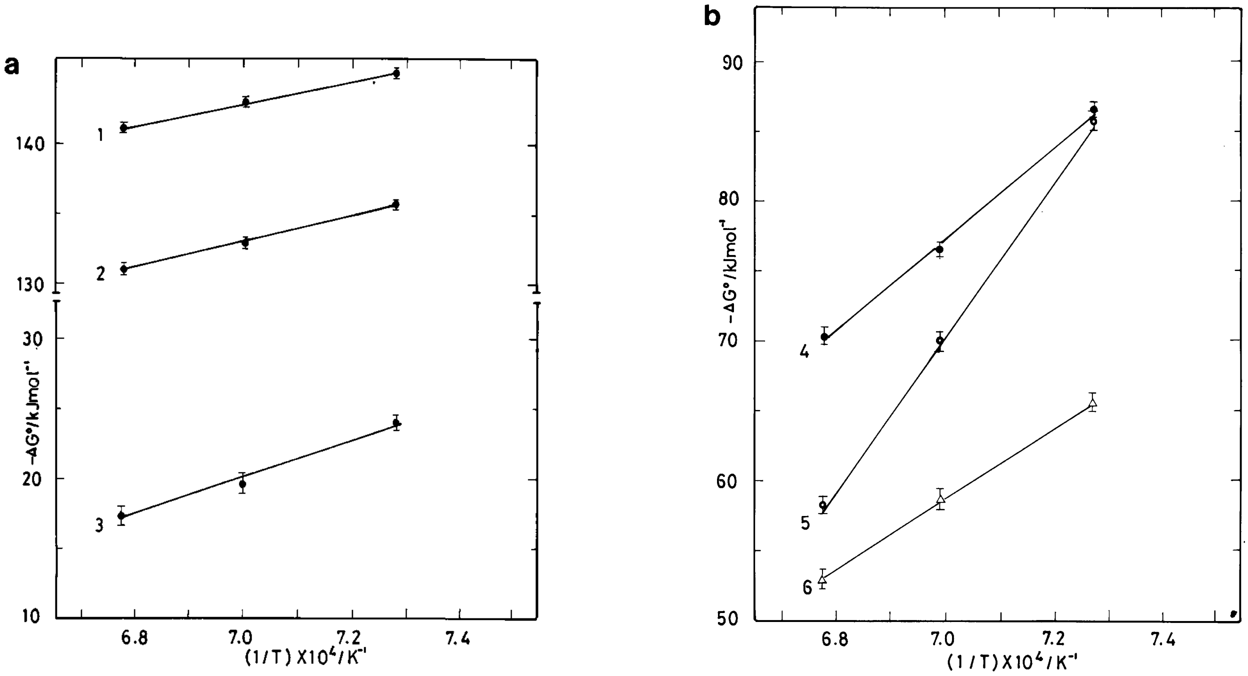

Fig. 3. The relationship between Gibbs energy change ($-\Delta G^\circ$) and reciprocal temperature ($1/T \times 10^4$). Numbers, 1–6 in the figures correspond to the reactions in Table 3.

these values are significant. As the phase equilibria are not known exactly, Seppanen *et al.* (7) did not use activity values in the calculation of Gibbs energy changes.

The combination of reactions given in Table 3 can form new equations, for example, reaction [7], $La_2O_3 + CoO = La_2CoO_4$ ([1]–[2]); and [8] $CoO + 1/2\,La_2O_3 + 1/4\,O_2 = LaCoO_3$ ([6]–[3]). ΔG° values are easily obtained as -9.5 and -10.9 kJ mol^{-1} for [7] at 1100 and 1150°C and -40.1 and -38.6 kJ mol^{-1} for [8] at 1100 and 1150°C, respectively. For reaction [7], Sreedharan *et al.* [9] presented the equation ΔG° (kJ mol^{-1}) $= 12.24 - 0.0149\,T$ (973–1373 K, ± 1.02 kJ). The ΔG° value for reaction [7] at 1100°C is -8.2 kJ and by extrapolating the equation to 1150°C we obtain a ΔG° value of -9.0 kJ. Both values are in fairly good agreement with the present results.

As for reaction [2] × 2, ΔG° (cal mol^{-1}) $= -111{,}800 + 33.8\,T$ (± 2 kcal, 298–1400 K) was reported (10). Values of -136.9 kJ at 1100°C and -129.8 kJ at 1150°C are obtained from the equation. These values are in good agreement with the present -135.8 and -132.2 kJ, respectively.

In Fig. 3 the standard Gibbs energy change versus reciprocal temperature is plotted. A linear relationship between both variables is observed.

REFERENCES

1. J. J. Janecek and C. P. Wirtz, *J. Am. Ceram. Soc.* **61,** 242 (1978).
2. K. Kitayama, *J. Solid State Chem.* **73,** 381 (1988).
3. N. Kimizuka and T. Katsura, *J. Solid State Chem.* **13,** 176 (1975).
4. T. Katsura and H. Hasegawa, *Bull. Chem. Soc. Jpn.* **40,** 561 (1967).
5. T. Katsura and A. Muan, *Trans. Am. Inst. Min. Metall. Pet. Eng.* **230,** 77 (1964).
6. K. Kitayama, K. Nojiri, T. Sugihara, and T. Katsura, *J. Solid State Chem.* **56,** 1 (1985).
7. M. Seppanen, M. Kyot, and P. Taskinen, *Scand. J. Metall.* **9,** 3 (1980).
8. J. Lewandowski, R. A. Beyerlein, J. M. Longo, and R. A. McCauley, *J. Am. Ceram. Soc.* **69,** 699 (1986).
9. O. M. Sreedharan and R. Pankajavalli, *J. Mater. Sci. Lett.* **3,** 388 (1984).
10. O. Kubaschewski and C. B. Alcock, “Metallurgical Thermochemistry,” 5th ed. Pergamon, Elsford, NY, 1979.