

Thermogravimetric Study of the $\text{Ln}_2\text{O}_3\text{-Co-Co}_2\text{O}_3$ System

I. Ln = La

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Phase equilibria in the system La-Co-O at 1200°C are established by changing the oxygen partial pressure from 0 to 12.50 in $-\log(P_{\text{O}_2}/\text{atm})$ and are represented in the $\text{La}_2\text{O}_3\text{-Co-Co}_2\text{O}_3$ system. Under the present experimental conditions, La_2O_3 , CoO, Co, LaCoO_3 , La_2CoO_4 , and $\text{La}_4\text{Co}_3\text{O}_{10}$ phases are stable. Co_3O_4 and Co_2O_3 are not found. Nonstoichiometry of the compounds is discussed with respect to the oxygen partial pressure, and activities of the components in the solid solutions are obtained by using the composition-oxygen partial pressure relations. The standard Gibbs energies of six reactions appearing in the phase diagram are calculated and compared with previous values. © 1988 Academic Press, Inc.

The study of the phase equilibria on the La-Co-O system has been studied at 1130°C by Janecek and Wirtz (1), but the results were very rough as illustrated in Fig. 1 of Ref. (1). Judging from the report (1), their interests seemed to be more in the crystallographic properties of the ternary compounds than in the phase equilibrium.

On the other hand, compounds LaCoO_3 , La_2CoO_4 , and $\text{La}_4\text{Co}_3\text{O}_{10}$ in the La-Co-O system have been widely studied from the view point of the physical properties. In particular, LaCoO_3 has been proposed for application such as catalytic conversion of auto exhausts (2), oxygen electrodes (3), high temperature fuel cells (4), and MHD electrodes (5) and has been studied from the view point of defect structure and nonstoichiometry (6). The synthesis and the crystallographic properties of La_2CoO_4 and $\text{La}_4\text{Co}_3\text{O}_{10}$ were reported (1, 7, 8).

The present study was conducted to bring about a more exact understanding of

phase relations and to determine the oxygen partial pressure stability range of the ternary compounds and the thermochemical data at 1200°C.

Other objectives are to ascertain in the Ln-Co-O system whether phase diagram patterns would change with different lanthanoid elements and whether the linear trend of the standard Gibbs energy of reactions with lanthanoid ionic radius that is observed in the Ln-Fe-O (9) and Ln-V-O (10) systems will also be observed in the Ln-Co-O system.

Experimental

Analytical grade La_2O_3 (99.9%) and CoO (99.9%) are employed as starting materials. Both oxides are preliminarily dried at 1200°C in air. Desired ratios of $\text{La}_2\text{O}_3/\text{CoO}$ are obtained by mixing thoroughly in an agate mortar with ethyl alcohol. The mixtures thus obtained are calcined at 1200°C at sev-

eral times during the intermediate mixing and are treated by the same procedures as those described previously (11).

Mixed gases of CO_2 and H_2 and of CO_2 and O_2 are used to obtain the oxygen partial pressures in the present experiment. The actual oxygen partial pressures of the gas phase is measured by means of a solid electrolytic cell of $(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}$ (12).

The apparatus and procedures for controlling the oxygen partial pressures and keeping a constant temperature, the method of thermogravimetry, and the criterion for the establishment of equilibrium are the same as those described in the previous papers (11–13).

Phases in the quenched samples are identified by the powder X-ray diffraction method with Ni-filtered $\text{CuK}\alpha$ radiation. Lattice constants are also determined by the X-ray method with a slow scanning speed of 0.5° per minute in 2θ . Instrumental errors are calibrated by measuring the diffraction angles of a standard specimen of silicon.

Results and Discussions

(1) Phase Equilibria

(1) *Co–O system.* The Co–O system is the subsystem in the present system. The system is reinvestigated by using the present apparatus and procedures. Compounds CoO , Co_3O_4 , and Co_2O_3 have been reported in the system, but only CoO is stable under the present experimental conditions and has slight nonstoichiometric compositions. x , for example, is 0.992, 0.996, 1.001, and 1.005 at 9.30, 3.00, 0.68 (air) and 0 in $-\log(P_{\text{O}_2}/\text{atm})$, respectively. Here, x means the value in CoO_x . The weight in the atmosphere of $\log(P_{\text{O}_2}/\text{atm}) = -11.00$ in which Co metal is stable is taken as the standard state of the weight. The relation between the $\log P_{\text{O}_2}$ and the composition of the CoO solid solution will be presented in

the next section together with other solid solutions. The obtained oxygen partial pressure in equilibrium with CoO and Co metal is 9.30 ± 0.03 in $-\log P_{\text{O}_2}$.

(2) *La_2O_3 –Co– Co_2O_3 system.* Eight samples with $\text{La}_2\text{O}_3/\text{CoO}$ mole ratios of 6/4, 1, 45/55, 4/6, 3/5, 1/2, 3/7, and 2/8 are prepared for use in thermogravimetry. In Fig. 1 the relationships between the oxygen partial pressure, $-\log(P_{\text{O}_2}/\text{atm})$, on the ordinate and the weight change, $W_{\text{O}_2}/W_{\text{T}}$, on the abscissa are shown with four representative samples, 6/4 (Fig. 1a), 45/55 (Fig. 1b), 3/5 (Fig. 1c), and 3/7 (Fig. 1d). Here, W_{O_2} is the weight increase of the samples from reference weight at $\log P_{\text{O}_2} = -12.50$, at which La_2O_3 and Co metal are stable, and W_{T} is the total weight gain from the reference state to the weight at 1 atm O_2 , at which $\text{La}_2\text{O}_3 + \text{LaCoO}_3$ or $\text{LaCoO}_3 + \text{CoO}$ are stable depending upon the total composition of the samples.

Abrupt weight changes are observed at 10.02, 9.30, 4.70, 3.90, 3.05, and 1.87 in $-\log P_{\text{O}_2}$ from Fig. 1. These values correspond to the oxygen partial pressures in equilibrium with three solid phases.

The identification of phase is carried out with samples which are quenched under different conditions of the oxygen partial pressure. A part of the results is shown in Table I as the two phase combinations.

Based upon the above thermogravimetric results and the phase identification, a phase diagram is drawn and is represented in Fig. 2 as La_2O_3 –Co– Co_2O_3 although Co_2O_3 is not stable under the experimental conditions. Figure 2 is similar to Fig. 1 in Ref. (1) at 1130°C which had no information about solid solutions. The numerical values in the three solid fields in Fig. 2 are the six values in $-\log P_{\text{O}_2}$ described above. The thin-dotted lines in two-phase fields are the iso-oxygen partial pressure on which the values are indicated. Six phases, La_2O_3 (R), Co, La_2CoO_4 (A), $\text{La}_4\text{Co}_3\text{O}_{10}$ (B), LaCoO_3 (C), and CoO (D) are stable under the present condi-

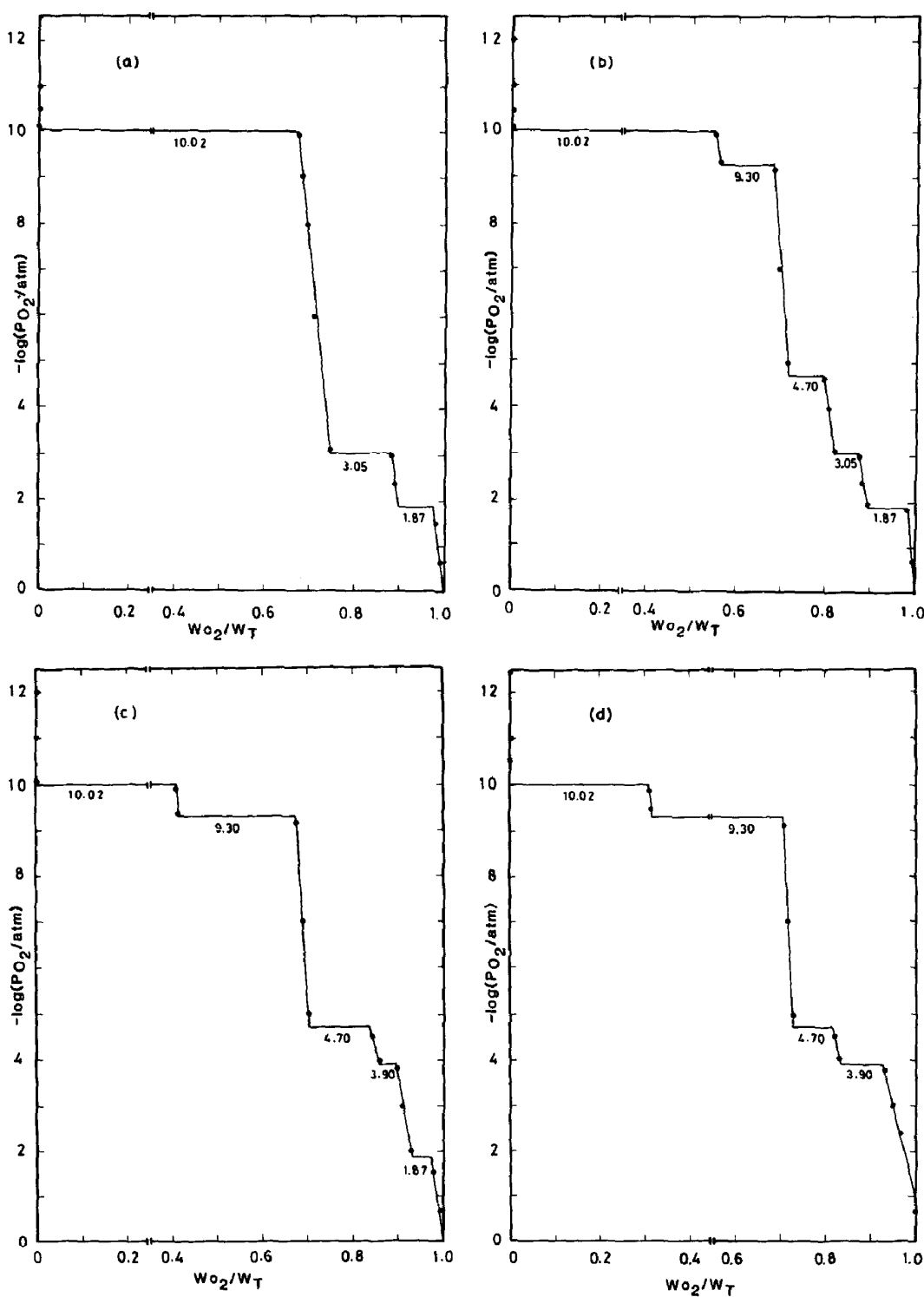


FIG. 1. The relationship between the oxygen partial pressure, $\log(P_{O_2}/\text{atm})$, and the weight change of the samples, W_{O_2}/W_T . (a) $\text{La}_2\text{O}_3/\text{CoO} = 6/4$, (b) $\text{La}_2\text{O}_3/\text{CoO} = 45/55$, (c) $\text{La}_2\text{O}_3/\text{CoO} = 3/5$, (d) $\text{La}_2\text{O}_3/\text{CoO} = 3/7$.

TABLE I
THE IDENTIFICATION OF PHASES

La ₂ O ₃ /CoO (mole ratio)	-log P _{O₂} (atm)	Time (hr)	Phase	
6/4	10.50	16	Co	+ La ₂ O ₃
	9.50	22	La ₂ O ₃	+ La ₂ CoO ₄
	2.70	23	La ₂ O ₃	+ La ₄ Co ₃ O ₁₀
5/5	0.68	21	La ₂ O ₃	+ LaCoO ₃
	2.70	23	La ₂ O ₃	+ La ₄ Co ₃ O ₁₀
9/11	4.50	24	La ₂ CoO ₄	+ La ₄ Co ₃ O ₁₀
4/6	10.50	16	Co	+ La ₂ O ₃
	9.50	22	Co	+ La ₂ CoO ₄
	9.00	19	CoO	+ La ₂ CoO ₄
	5.50	23	CoO	+ La ₂ CoO ₄
	0.68	21	La ₂ O ₃	+ LaCoO ₃
	3/5	3.00	30	LaCoO ₃
3/7	4.50	24	CoO	+ La ₄ Co ₃ O ₁₀
	2.70	23	CoO	+ LaCoO ₃
	0.68	21	CoO	+ LaCoO ₃
	2/8	9.50	22	Co
2/8	9.00	19	CoO	+ La ₂ CoO ₄
	4.50	24	CoO	+ La ₄ Co ₃ O ₁₀
	2.70	23	CoO	+ LaCoO ₃
	0.68	21	CoO	+ LaCoO ₃

tions. Co₃O₄ is not found. Except for Co and La₂O₃, the other phases have nonstoichiometric compositions. The stoichiometry of Co-metal and La₂O₃ was ascertained by preliminary experiments and a previous report (14) under the present experimental conditions. The relationship between the composition of the 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 is available in the calculation of activities of the components. Here, N_O and $N_{\text{Component}}$ are the mole fractions of oxygen and the component, respectively. Activities of the components in the solid solutions were calculated with the Gibbs-Duhem equation using N_O vs $\log P_{O_2}$ (15). The a and b values for each solid solution, which are obtained with thermogravimetric results, are tabulated in Table II together with those of CoO.

In particular, LaCoO₃ phase has a large oxygen deficiency. Seppänen *et al.* (16)

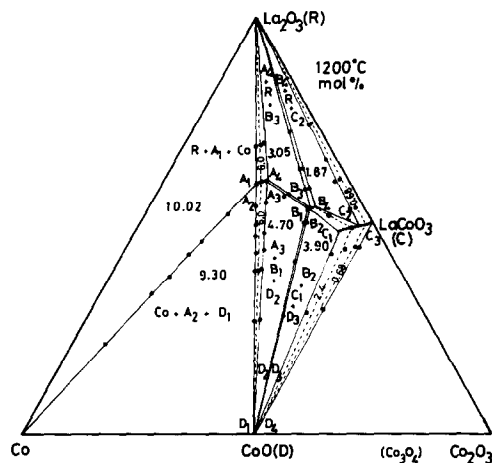


FIG. 2. Phase equilibrium in the La₂O₃-Co-Co₂O₃ system at 1200°C. Numerical values in the three solid phase regions are the oxygen partial pressures in -log (P_{O₂}/atm) in equilibrium. Abbreviations are the same as those in Table III. The dotted lines in the two solid phase regions are the iso-oxygen partial pressure lines shown by numerical values on the lines.

represented the deficiency using LaCoO_{3-Δ} and the deficiency can be expressed as $\Delta = kP_{O_2}^{-1/2}$ and at 1300 K reaches the value $\Delta = 0.091$ at the phase boundary LaCoO_{3-Δ}-CoO-La₄Co₃O₁₀. The present value 0.14 in Table III might be reasonable considering the difference in temperature.

In order to express the chemical composition of the three ternary compounds, Janacek *et al.* (1) have presented a general formula La_{n+1}Co_nO_{3n+1}(LaO(LaCoO₃)_n) as the perovskite-related layered structure. The phase diagram suggests that LaCoO₃, La₄Co₃O₁₀, and La₂CoO₄ consist of La₂O₃ ·

TABLE II
 a AND b VALUES OF SOLID SOLUTIONS

Component	a	b
CoO	1.2×10^{-3}	2.4×10^{-3}
La ₂ CoO ₄	0.0121	0.117
La ₄ Co ₃ O ₁₀	0.094	0.205
LaCoO ₃	0.0419	0.0213

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

TABLE III
COMPOSITIONS, SYMBOLS, STABILITY RANGES IN
OXYGEN PARTIAL PRESSURES AND ACTIVITIES IN
SOLID SOLUTIONS

Component	Composition	Symbol	$-\log P_{O_2}$ (atm)	$\log a_i$
La ₂ CoO ₄	La ₂ CoO _{4.00}	A ₁	10.02	0
	La ₂ CoO _{4.00}	A ₂	9.30	~0
	La ₂ CoO _{4.06}	A ₃	4.70	-0.074
	La ₂ CoO _{4.08}	A ₄	3.05	-0.13
La ₄ Co ₃ O ₁₀	La ₄ Co ₃ O _{9.74}	B ₁	4.70	0
	La ₄ Co ₃ O _{9.84}	B ₂	3.90	0.079
	La ₄ Co ₃ O _{9.92}	B ₃	3.05	0.130
	La ₄ Co ₃ O _{10.0}	B ₄	1.87	0.145
LaCOO ₃	LaCoO _{2.86}	C ₁	3.90	0
	LaCoO _{2.94}	C ₂	1.87	0.101
	LaCoO _{3.00}	C ₃	0-0.68	0.12
CoO	CoO _{0.992}	D ₁	9.30	0
	CoO _{0.994}	D ₂	4.70	0.0138
	CoO _{0.998}	D ₃	3.90	0.0149
	CoO _{1.005}	D ₄	0	0.0148

Co₂O₃, 2La₂O₃ · Co₃O₄, and La₂O₃ · CoO, respectively, although there is no crystallographic evidence for it now. Other compounds with different mole ratios might be found at temperatures at which Co₂O₃ and Co₃O₄ were stable.

Recently, Lewandowski *et al.* (17) reported that the composition La₂CoO₄ did not exist for the range of temperatures and P_{O₂}'s investigated and proposed a lanthanum cation-deficient composition, La_{1.83}CoO₄.

As is shown in Fig. 2, for the present case both lines, which originate from Co apex through the experimental points and which originate from La₂O₃ apex through an experimental point, join at A₁, having as its composition Co 20 mol%, La₂O₃ 60 mol%, and Co₂O₃ 20 mol%, La₂CoO₄. The differences in the temperature might show both facts. A detailed phase diagram at ~1000°C is being established by Lewandowski *et al.* (17) to solve the problem.

The data of compositions of the ternary compounds, the symbols, the stability ranges in log P_{O₂}, and the activities of the components in the solid solutions are shown in Table III.

LaCoO₃ shows a rhombohedral modification of the perovskite structure, whereas La₄Co₃O₁₀ and La₂CoO₄ have perovskite-related structures based on a face-centered orthorhombic lattice (1). The X-ray powder pattern of La₂CoO₄, which was prepared at 1200°C in log P_{O₂} = -9.80, is orthorhombic, being similar to the pattern of Ortho-1 and Ortho-2 in Fig. 6 of Ref. (17).

Lattice constants of the ternary compounds are determined with the aid of the above information. The results are shown in Table IV together with values from previous reports. Owing to different preparation conditions, the earlier data cannot be directly compared with the present results, but the present values are comparable to the previous values. As shown in Table IV, lower oxygen partial pressure causes the lattice constants to increase for the ternary compounds. This corresponds to the increasing content of Co²⁺ of larger ionic radius.

(2) The standard Gibbs Energy of Reaction

On the basis of the established phase diagram, the standard Gibbs energies of reactions, which appear in the diagram and are shown in Table V, are determined from an 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 the solid solutions, which are necessary to calculate ΔG° values, are tabulated in Table III. The standard state of the components can be chosen arbitrarily in each solid solution because $\log a_i = 0$ in Table III.

ΔG° values obtained for each reaction are tabulated in Table V. In the last column of the table, ΔG° values are also tabulated, which are calculated with equations presented by Seppänen *et al.* (16). These values are obtained by extrapolation because 1200°C is the out of range given for these equations. The difference between the

TABLE IV
 LATTICE CONSTANTS OF TERNARY COMPOUNDS

Compound	$-\log P_{O_2}$ (atm)	a (Å)	b (Å)	c (Å)	V (Å ³)	Ref.
La ₂ CoO ₄	3.10	5.529 ± 0.002	5.479 ± 0.002	12.632 ± 0.004	382.6 ± 0.3	Present
	9.80	5.600 ± 0.002	5.466 ± 0.002	12.646 ± 0.003	387.1 ± 0.2	Present ^a
		5.530	5.470	12.55		(7)
		5.602	5.471	12.65		(1) ^a
		5.539	5.482	12.66		(8)
La ₄ Co ₃ O ₁₀		5.490	5.488	12.548		(22)
	4.80	5.423 ± 0.003	5.479 ± 0.003	27.91 ± 0.04	829.4 ± 1.4	Present
	1.98	5.411 ± 0.002	5.472 ± 0.002	27.75 ± 0.02	921.9 ± 0.7	Present
		5.414	5.471	27.81		(1)
		5.425	5.484	27.89		(1) ^b
LaCoO ₃	0.68	5.422 ± 0.001		13.089 ± 0.002	335.7 ± 0.1	Present ^c
	3.80	5.450 ± 0.002		13.079 ± 0.010	336.0 ± 0.9	Present
		5.424		13.068		(20)
		5.441		13.088		(21)

^a Coexists with La₂O₃.

^b Coexists with La₂CoO₄ and CoO.

^c The hexagonal form is adopted.

present and the quoted values is in the range 2.7 to 13.3 kJ. Assuming that the activities for the solid solutions are each unity, ΔG° values for reactions 3–5 of Table V are -13.2 , -66.3 , and -43.0 kJ, respectively. As the phase equilibria are not known exactly, Seppänen *et al.* (16) did not consider these activities in the derivation of their equations.

Combinations of the six reactions given in Table V can form new reactions, for ex-

ample, (7) $La_2O_3 + CoO = La_2CoO_4$ and (8) $CoO + \frac{1}{2} La_2O_3 + \frac{1}{4} O_2 = LaCoO_3$, and ΔG° values are easily obtained as -10.2 and -34.8 kJ, respectively. For reaction (7), Sreedharan and Pankajavalli (18) reported the equation, $\Delta G^\circ = 12.24 - 0.0149 T$ (973 – 1373 K, ± 1.02 kJ). Extrapolating the equation to 1200°C, the ΔG° value is -9.7 kJ and is in fairly good agreement with the present one.

As for reaction (2), $\Delta G^\circ = -111,800 +$

 TABLE V
 THE STANDARD GIBBS ENERGY OF REACTIONS AT 1200°C

Reaction	$-\log P_{O_2}$ (atm)	$-\Delta G^\circ$ (kJ)	$-\Delta G^{\circ a}$ (kJ)
(1) $Co + La_2O_3 + \frac{1}{2} O_2 = La_2CoO_4$	10.02 ± 0.03	141.1 ± 0.6	138.6
(2) $Co + \frac{1}{2} O_2 = CoO$	9.30 ± 0.03	131.1 ± 0.6	128.3
(3) $La_4Co_3O_{10} + \frac{1}{4} O_2 = \frac{1}{2} La_2O_3 + 3 LaCoO_3$	1.87 ± 0.07	17.5 ± 0.4	8.6
(4) $2 La_2CoO_4 + CoO + \frac{1}{2} O_2 = La_4Co_3O_{10}$	4.70 ± 0.03	70.1 ± 0.5	59.4
(5) $3 La_2CoO_4 + \frac{1}{2} O_2 = La_2O_3 + La_4Co_3O_{10}$	3.05 ± 0.03	57.8 ± 0.4	44.5
(6) $La_4Co_3O_{10} + CoO + \frac{1}{2} O_2 = 4 LaCoO_3$	3.90 ± 0.07	52.3 ± 1.1	42.5

^a Extrapolated values from equations presented by Ref. (16).

33.8 T (± 2 kcal, 298 – 1400 K) was reported (19). A value of -129.7 kJ is obtained at 1200°C for that reaction. This value and -128.3 are in good agreement with the present one.

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