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The Thermodynamic Properties of the Nonstoichiometric Ceric Oxide at Temperatures from 900 to 1300°C

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Oxygen partial pressure in equilibrium with nonstoichiometric ceric oxide of a definite composition were determined by equilibration with pure oxygen, air, CO_2, and CO_2-H_2 mixtures at 900, 1000, 1100, 1227, and 1300°C, using a thermobalance. The values for the activities and the relative partial enthalpies and entropies of both Ce_2O_3 and CeO_2 were calculated on the basis of the relation between the Po_2 and its composition.

During the last 10 years, studies of nonstoichiometric ceric oxide have been made by many investigators, especially from a view to clarifying the behavior of the solid solution in the Ce_2O_3-CeO_2 system at high temperatures. Brauer *et al.*,[1] for example, determined oxygen-dissociation pressures in the Ce_2O_3-CeO_2 system at temperatures from 600 to 1050°C by a thermogravimetric technique and calculated the enthalpy of oxidation of Ce_2O_3 to CeO_2. Furthermore, Brauer and Gingerich[2] determined the phase relations in the same system at temperatures from 20 to 1000°C using a high-temperature X-ray diffractometer and constructed a phase diagram. Kuznetsov *et al.*[3] reported on oxygen-dissociation pressures in the same system at temperatures from 694 to 1010°C; their results were based on emf measurements. Bevan and Kordis[4] reported their results on the same system at temperatures from 636 to 1169°C; these results were based on thermogravimetry.

These investigations have indeed revealed the presence of an extensive solid solution with a definite structure of CeO_2, but it is still desirable to study in more detail the relationship between the composition and the oxygen partial pressure at which the composition is equilibrated, especially at temperatures above 1100°C, in order to determine the precise thermodynamic properties. It is also necessary to measure directly the actual oxygen partial pressure in the furnace instead of using the calculated oxygen partial pressure based on the thermochemical data.

The objectives of the present study are, therefore, to determined the oxygen partial pressure in equilibrium with the ceric oxide of a definite composition by means of a solid electrolyte cell and thermogravimetry at temperatures from 900 to 1300°C, and to present some thermodynamic properties of the present solid solution.

Experimental

The ceric oxide obtained from the Nichisan Rare Element Co., was 99.9% pure. The oxide sample was heated at 1200°C in the air for 2 hr to make a suitable pellet.

The details of the procedure have been described by Katsura and Muan,[5] Katsura and Kimura,[6] and Katsura and Hasegawa.[7] A brief description will suffice for the general procedure.

A thermobalance was used to measure the isothermal weight change of a pellet as a function of the oxygen partial pressure. A quenching method was also used to check the thermogravimetric result.

As a results of the preliminary work, it was found that the weight of a pellet remained constant over a range of oxygen partial pressures from 0.2 to 1 atm at all the temperatures used. In addition, the chemical analysis of the quenched samples obtained from this range of oxygen partial pressures always had the stoichiometric composition of $CeO_{2.00}$, as may be seen in Table 1. On the basis of these facts, we chose the $CeO_{2.000}$ prepared under an oxygen partial pressure of 0.2 or 1 atm as the reference-weight standard.

The desired partial pressures of oxygen were obtained by using pure oxygen, air, carbon dioxide, and CO_2-H_2 mixtures. The actual oxygen partial pressures in the CO_2 and CO_2-H_2 mixtures at 900 to 1227°C were measured by an improved solid electrolyte cell composed of $(ZrO_2)_{0.85}(CaO)_{0.15}$.[7] It had been found previously[7,8] that the actual oxygen partial pressures produced by the CO_2-H_2 mixtures at 1300°C agreed well with the values calculated on the basis of the thermochemical data within the limits of experimental error. Thus, the oxygen partial pressures in the mixtures at 1300°C were calculated from the data summarized by Elliott and Gleiser[9] and by Coughlin.[10]

The O/Ce ratio in the weight-standard material, $CeO_{2.000}$ was determined volumetrically by using the persulfate method.[11] The O/Ce ratios in samples quenched in various atmospheres were determined thermogravimetrically by a weight-gain method as follows: the samples of the inner parts obtained by being taking the outer parts out of the the quenched samples were heated at 1000°C for 2 hr in the air until complete oxidation to $CeO_{2.000}$ had been achieved. The weight-gain corresponds to the increase in oxygen content in the quenched samples.

The phase present in the inner parts of the quenched samples were identified by an X-ray diffraction method using CuKα.

The rate of approach to the equilibrium state was studied thermogravimetrically. To ensure the equilibrium, the

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Table 1. Comparisons of O/Ce ratios determined by various methods and of the phases present in the quenched samples

Temp., °C	$-\log P_{O_2}$	O/Ce by thermogravimetry	O/Ce by weight-gain method	phase present[a]
1300±3	0	2.000±0.001	2.00 ±0.01[b]	cubic
	9.03	1.901±0.001	1.926±0.002	cubic
	12.14	1.792±0.001	1.814±0.001	cubic
	15	1.697±0.001	1.722±0.002	cubic
1000±3	19.14±0.05	1.775±0.001	1.801±0.002	cubic
900±3	19.78±0.05	1.900±0.001	1.909±0.002	cubic+pseu.
	20.47±0.05	1.824±0.001	——	cubic+pseu.
	20.77±0.05	1.804±0.001	1.832±0.001	cubic+pseu.

a) Abbreviations used have the following meanings: cubic=cubic fluorite structure and pseu.=pseudo-cubic fluorite structure.

b) Obtained by volumetric analysis.

equilibrium composition was established from two courses, *i.e.*, the course from a reduced state to an oxidized, and the reverse course. It was found that, in general, the equlibrium was approached quickly, even in the slowest case, in which the time of equilibration was approximately 2 hr.

The weight-loss due to the vaporization of the nonstoichiometric ceric oxide could not be observed even in the case of the lowest oxygen partial pressure at 1300°C.

Results

Table 1 compares the O/Ce ratios determined by various methods and the phases present in the quenched samples, together with the maximum uncertainties in the measurements. As is shown in Table 1, the O/Ce ratios obtained by a weight-gain method are slightly larger than the thermogravimetric results. As an O/Ce ratio is found to become slightly larger with a falling temperature at a given ratio of CO_2 to H_2 in the atmosphere, and as the reaction rate is rapid, as has been described previously, these results obtained by a weight-gain method are considered to be due to oxidation during quenching. As may be seen in Table 1, the cubic form of the sample at 900°C could not be quenched to ice temperature without an exsolution of the pseudo-cubic form. Judging from the shape of the curve of the oxygen partial pressure against CeO_{2-x} at 900°C in Fig. 1, as will be seen later, and the phase diagram obtained by a high-temperature X-ray-diffraction method,[2] the phase assemblages of the CeO_{2-x} obtained in the present study at all the temperatures used are considered to be a single solid solution.

Table 2 shows the experimental results obtained thermogravimetrically at various temperatures.

Table 2. Equilibrium oxygen partial pressures over the nonstoichiometric ceric oxide of a given composition at 900, 1000, 1100, 1227, and 1300°C

O/Ce	$-\log P_{O_2}$	O/Ce	$-\log P_{O_2}$	O/Ce	$-\log P_{O_2}$	O/Ce	$-\log P_{O_2}$	O/Ce	$-\log P_{O_2}$
900°C		1000°C		1100°C		1227°C		1300°C	
2.000	0.68	2.000	0.68	2.000	0	2.000	0	2.000	0
1.998	3.12	1.997	3.20	1.999	2.41	1.998	2.77	2.000	0.68
1.996	11.05	1.993	10.18	1.993	6.79	1.991	6.25	1.995	3.43
1.995	13.15	1.987	13.82	1.989	8.78	1.988	6.63	1.976	6.29
1.994	14.12	1.983	15.04	1.981	10.14	1.980	7.48	1.967	6.87
1.993	15.85	1.973	15.77	1.970	10.92	1.976	7.96	1.959	7.32
1.992	17.13	1.959	16.18	1.960	11.56	1.965	8.49	1.953	7.48
1.990	18.00	1.933	16.60	1.938	12.35	1.946	9.17	1.949	7.65
1.978	19.07	1.893	17.04	1.915	12.76	1.926	9.72	1.946	7.82
1.964	19.33	1.871	17.34	1.899	13.08	1.895	10.45	1.940	7.96
1.940	19.56	1.857	17.60	1.886	13.35	1.876	10.90	1.929	8.21
1.925	19.64	1.837	18.00	1.870	13.70	1.861	11.29	1.924	8.38
1.913	19.71	1.803	18.64	1.851	14.13	1.848	11.60	1.901	9.03
1.907	19.74	1.775	19.14	1.803	15.52	1.834	11.97	1.886	9.46
1.900	19.78			1.777	16.27	1.817	12.46	1.875	9.73
1.870	20.00					1.797	13.08	1.860	10.14
1.850	20.18					1.790	13.32	1.847	10.51
1.824	20.47					1.768	13.84	1.830	10.96
1.804	20.77					1.742	14.61	1.816	11.40
								1.792	12.14
								1.776	12.55
								1.769	12.70
								1.738	13.81
								1.727	14.13

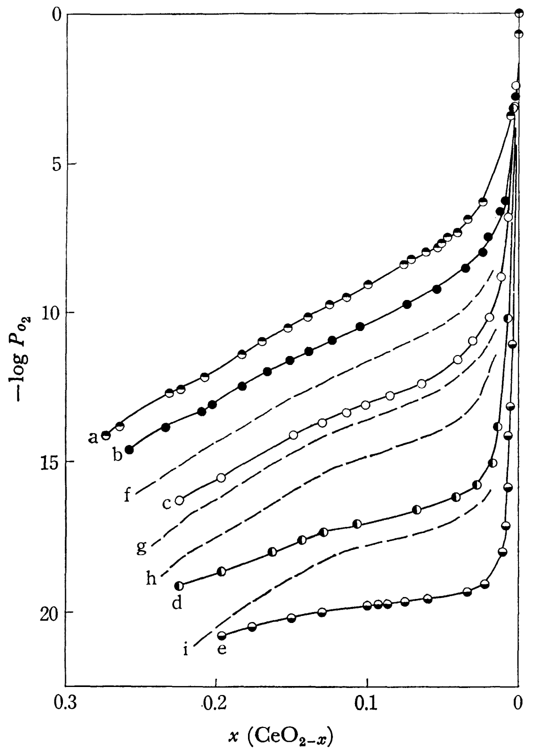

Fig. 1. −log P_{O_2} vs. x in CeO_{2-x} at each temperature.
—— This work; Temp.: (a) 1300°C, (b) 1227°C, (c) 1100°C, (d) 1000°C, (e) 900°C
---- Data of Bevan and Kordis: Temp.: (f) 1169°C, (g) 1080°C, (h) 1023°C, (i) 916°C

Discussion

Variation in the Composition of CeO^{2-x} *with the Oxygen Partial Pressure.* Figure 1 shows the variation in the composition of the nonstoichiometric ceric oxide with the oxygen partial pressures at various temperatures, together with the results of Bevan and Kordis.[4] These curves above 1100°C nearly agree with those of Bevan and Kordis[4] in shape, but the curves below 1000°C are inconsistent with each other, especially from 0.1 to about 0.2 of x. This might be largely the result of the oxygen partial pressure calculated in the study of Bevan and Kordis,[4] because, in the case of such a low temperature, the establishment of the equlibrium within the gas phase may be suspicious, even at a usual flow-rate of gases of, say, about 1 cm/sec. Therefore, the P_{O_2} must be actually measured by the solid electrolyte cell used in the present study. We will use the present results in respect to composition and P_{O_2} as the most reliable relation to calculate the thermodynamic properties of the Ce_2O_3-CeO_2 system, as will be seen later.

Activities of Ce_2O_3 *and* CeO_2 *in Nonstoichiometric Ceric Oxide.* To begin with, we assume that the nonstoichiometric ceric oxide is a mixture of two components, CeO_2 and O_2. The real composition of the CeO_2 phase is, however, CeO_{2-x}, and the reaction between these components may be written as follows;

$$CeO_2 = CeO_{2-x} + x/2O_2 \qquad (1)$$

Thus, from the Gibbs-Duhem Equation, the activity of CeO_2 in the solution may be related as follows;

$$\log a_{CeO_2} = \int_2^x (2-x)\,d\log {P_{O_2}}^{1/2} \qquad (2)$$

where x is related to Eq. (1). The activity of CeO_2 is planimetrically measured by the integration of Eq. (2) from the stoichiometric composition to that under consideration.

Next, we may take the present solid solution as a homogeneous mixture of two components, CeO_2 and Ce_2O_3. Since the activity of CeO_2 has already been determined as a function of Po_2, the activity of the other component, Ce_2O_3, may be determined directly. However, the α-function method[12] is more reliable

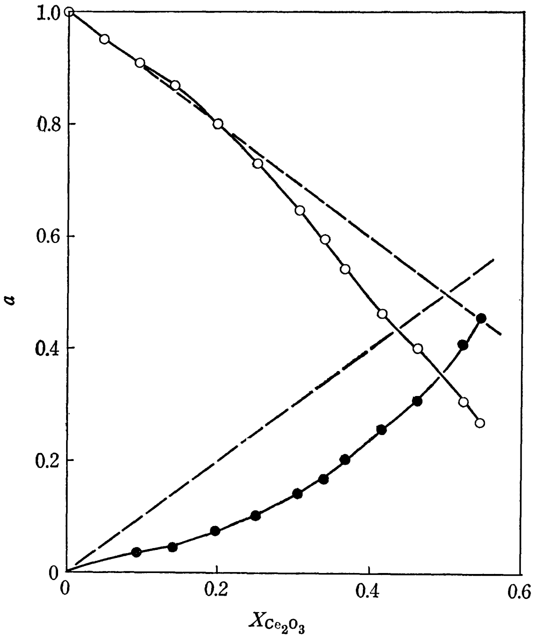

Fig. 2. Activity vs. mol fraction at 1300°C.
—— ● $a_{Ce_2O_3}$, ○ a_{CeO_2}, ---- Raoult's law

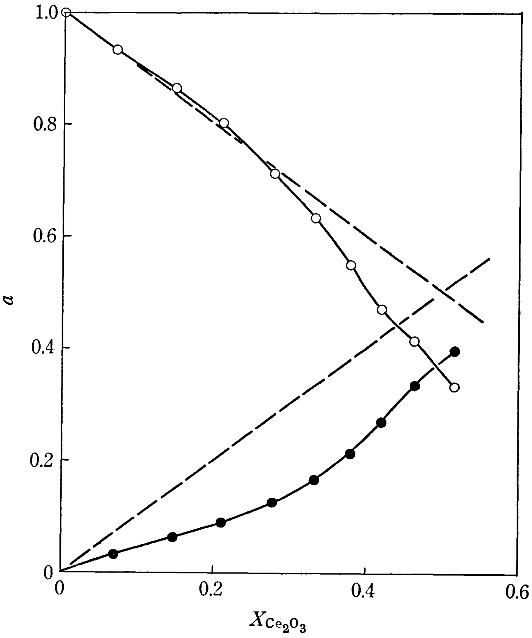

Fig. 3. Activity vs. mol fraction at 1227°C.
—— ● $a_{Ce_2O_3}$, ○ a_{CeO_2}, ---- Raoult's law

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[12] L. S. Darken and R. W. Gurry, "Physical Chemistry of Metals," McGraw-Hill Book Co., New York, N. Y. (1953), p. 264.

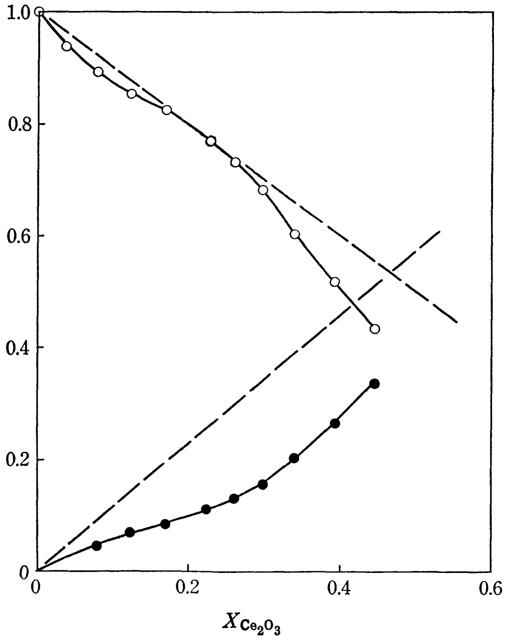

Fig. 4. Activity *vs*. mol fraction at 1100°C.
—— ● $a_{Ce_2O_3}$, ○ a_{CeO_2}, ---- Raoult's law

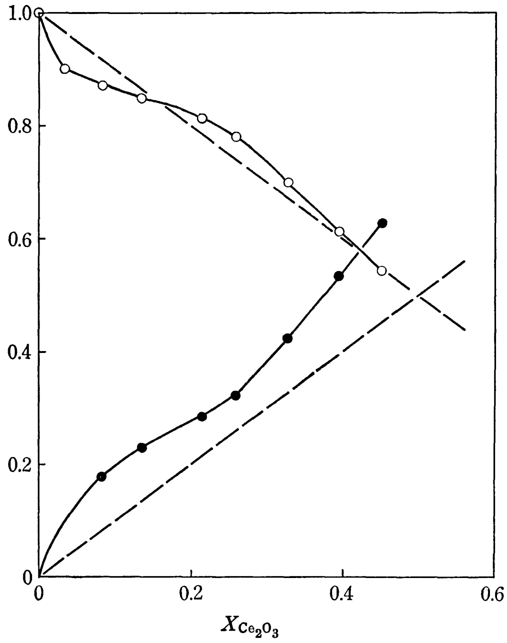

Fig. 5. Activity *vs*. mol fraction at 1000°C.
—— ● $a_{Ce_2O_3}$, ○ a_{CeO_2}, ---- Raoult's law

for graphic integration, and here we may adopt the equation proposed by Wagner,[13] which may, in order to calculate the activity of Ce_2O_3, be written as follows;

$$\log a_{Ce_2O_3} = \int_0^Y \frac{\log a_{CeO_2}}{(1-Y)^2}\,dY - \frac{Y}{1-Y}\log a_{CeO_2} \qquad (3)$$

where Y is the mol fraction of CeO_2 in the binary system.

The first term on the right side of Eq. (3) is obtained by integration from the stoichiometric composition of Ce_2O_3 to that under consideration. The value of $(\log a_{CeO_2})/(1-Y)^2$ at the stoichiometric composition of Ce_2O_3 is an extrapolated value.

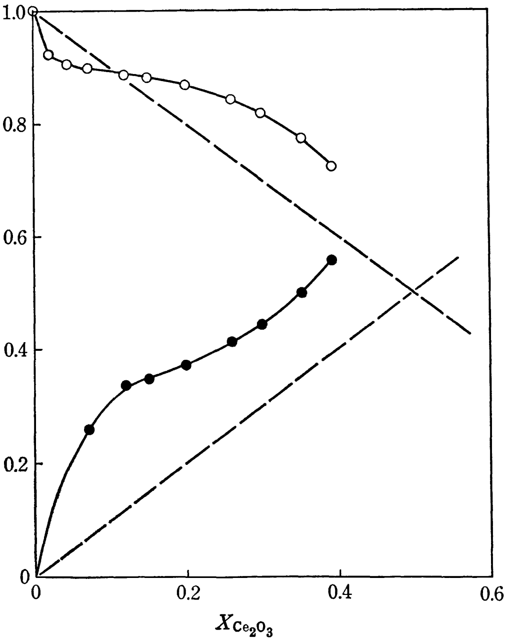

Fig. 6. Activity *vs*. mol fraction at 900°C.
—— ● $a_{Ce_2O_3}$, ○ a_{CeO_2}, ---- Raoult's law

The activity relations thus obtained at various temperatures are illustrated in Figs. 2—6, together with the lines giving the behavior of an ideal solution. It is clear from these figures that the activity of CeO_2 obeys Raoult's law up to a 0.2 mol fraction of Ce_2O_3 at temperatures above 1200°C, but at 1000 and 900°C the activity of CeO_2 changes in a singular manner and

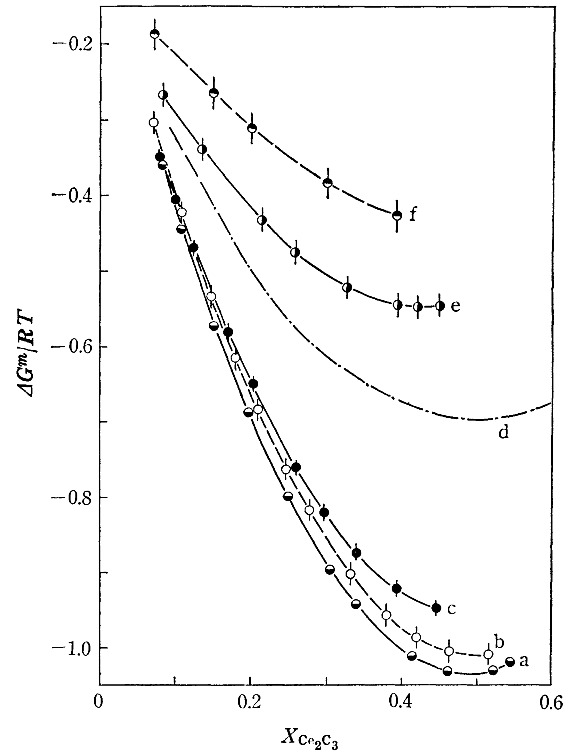

Fig. 7. $\Delta G^m/RT$ *vs*. mol fraction at each temperature.
Temp.: (a) 1300°C, (b) 1227°C, (c) 1100°C, (d) $\Delta G^m/RT$ of an ideal solution, (e) 1000°C, (f) 900°C

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[13] C. Wagner, "Thermodynamics of Alloys," Addison-Wesley Publ. Co., Reading, Mass. (1952), p. 16.

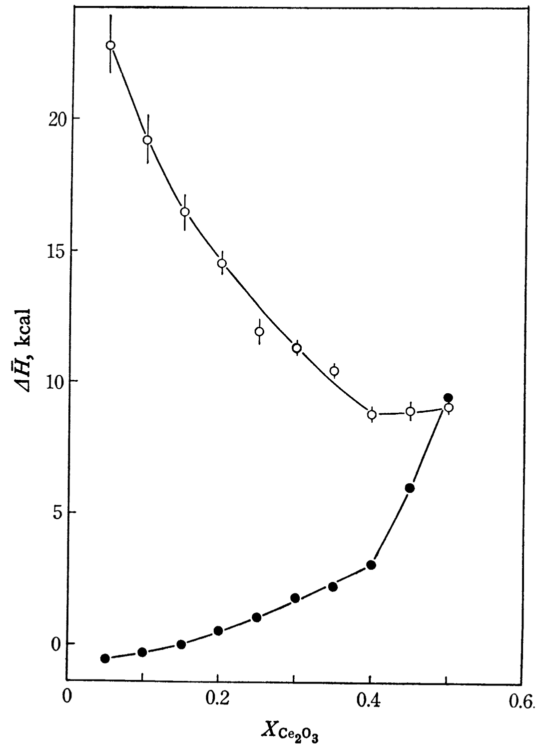

Fig. 8. Relative partial molal enthalpy *vs.* mol fraction.
● $\Delta\bar{H}_{Ce_2O_3}$, ○ $\Delta\bar{H}_{CeO_2}$

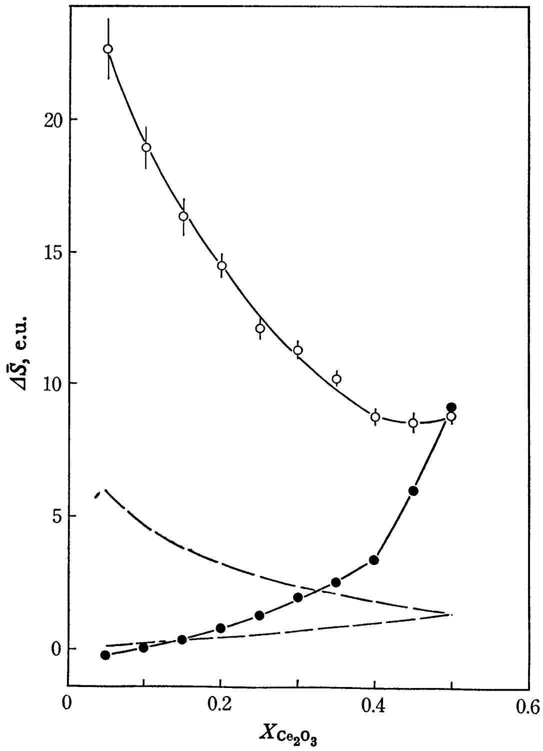

Fig. 9. Relative partial molal entropy *vs.* mol fraction.
—— ● $\Delta\bar{S}_{Ce_2O_3}$, ○ $\Delta\bar{S}_{CeO_2}$
---- Relative partial molal entropy of a regular solution

obeys Raoult's law only in a narrowly limited range of mol fractions of Ce_2O_3. The a_{CeO_2}-$X_{Ce_2O_3}$ relation at 1100°C seems to be intermediate between those obtained at higher and lower temperatures. Thus, the Ce_2O_3-CeO_2 solid solution will continuously change in its thermodynamic properties with a decrease in the temperature. However, the change in the same relation is very rapid at temperatures between 1000 and 1100°C compared with that at other intervals of temperature.

The activity of Ce_2O_3 reflects the behavior of the activity of CeO_2 at each temperature; it seems to obey Henry's law up to a 0.2 mol fraction of Ce_2O_3 above 1100°C.

Variation in the Free Energy of Mixing with the Temperature. In order to avoid a direct temperature effect, $\Delta G^m/RT$ was selected instead of the total free energy of mixing ΔG^m, where R is gas constant and T is the absolute temperature. Figure 7 shows the variation in $\Delta G^m/RT$ with the mol fraction of Ce_2O_3 at various temperatures, together with the curve showing the $\Delta G^m/RT$ of an ideal solution. The widths of the lines in Fig. 7 show the experimental errors.

As is shown in Fig. 7, these curves move upward with a fall in the temperature. Considered this fact and the activity relations shown in Figs. 2—6, this tendency seems to show a tendency toward the immiscibility of the solid solution. This inference is consistent with the fact that a miscibility-gap appears about 685°C at a composition of $CeO_{1.92}$.[2)]

As is shown in Fig. 7, these curves above 1100°C deviate negatively from the curve giving the ideal behavior. According to a quasi-chemical approach,[14)] this indicates an attractive interaction of the same atom. Thus, this may be assumed to be due to a tendency toward ordering or clustering in which cerium ions in normal sites enter interstitial sites.

Relative Partial Enthalpy and Entropy of Mixing. The relative partial enthalpies and entropies of the mixing of CeO_2 and Ce_2O_3 obtained by means of the mean least-squares method from the activity relations are shown in Figs. 8 and 9 respectively. The widths of the lines how the experimental errors. Curves showing the relative partial entropy of a regular solution are also included in Fig. 9.

As is shown in Fig. 9, these observed curves are similar in shape to those of a regular solution, but deviate too much from those of a regular solution.

The minimum of the curves of CeO_2 in Figs. 8 and 9 may be assumed to be due to a tendency toward compound formation.

Dr. Iwaji Iwasaki, Professor of chemistry, Toho University, encouraged us throughout the present study.

[14)] R. A. Swalin, "Thermodynamics of Solids," John Wiley & Sons, New York, N. Y. (1962), p. 109.