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Phase Equilibria and Thermodynamics of Coexisting Phases in Rare-Earth Element–Iron–Oxygen Systems. I. The Cerium–Iron–Oxygen System*

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In the present work it is shown that in the Ce–Fe–O system only one ternary compound with a perovskite structure, the orthoferrite $CeFeO_3$, is formed. We define the crystallographic properties of cerium ferroperovskite more accurately. The thermodynamics of its oxidation and reduction over a temperature range of 900–1200°C are studied using the emf method with a solid electrolyte.

It is shown that the free energy of cerium orthoferrite formation from the oxides according to the reaction $\frac{1}{2}Ce_2O_3 + \frac{1}{2}Fe_2O_3 = CeFeO_3$, derived from data on the equilibrium oxidation of $CeFeO_3$, differs very little from the value of $\Delta G°$, calculated from the magnitude of the equilibrium pressure of oxygen over the orthoferrite and reduction products coexisting with it.

Phase equilibria and the thermodynamics of coexisting phases in the Ce–Fe–O system have been investigated. Equilibrium diagrams are constructed which define the character of the changes taking place in the Ce–Fe–O system during changes in partial oxygen pressure, temperature, and composition of the initial oxide mixture. Thus, we have equilibrium diagrams of the type $P_{O_2} = f$(composition) with T = constant; $P_{O_2} = f(1/T)$ with one composition parameter fixed; and $T = f$(composition) with P_{O_2} = constant.

Introduction

Oxides of the rare-earth elements (r.e.e.) generally form two types of ferrites, "$RFeO_3$" and "$R_3Fe_5O_{12}$" (R = a rare earth element), having perovskite and garnet structure, respectively. Ferrites of the rare-earth elements have been the subject of a large number of investigations, which for the most part have a physical or technical character. However, practically no reports exist in the literature on the equilibrium conditions of formation and on the thermodynamics of coexisting phases in the ferrite-forming systems of the R–Fe–O type. Moreover, such reports are extremely necessary in choosing optical conditions for synthesis and thermal treatment of r.e.e. ferrogarnets and ferroperovskites.

The first element in the lanthanide series, cerium, has variable valency in oxide phases and, therefore, one can expect that the character of the ferrite-forming phases in the Ce–Fe–O system will be sensitive to change in temperature and the chemical potential of oxygen in the equilibrium gas phase.

Reports on the formation of ternary compounds in the system are contradictory. One series of references (*1–3*) indicates the possibility of forming only one $CeFeO_3$ compound with a perovskite structure and the instability of the ferrogarnet $Ce_3Fe_5O_{12}$ due to too-large dimensions of the Ce^{3+} ion. In Ref. (*4*), on the contrary, the possibility of forming cerium ferroperovskite is denied and it is affirmed that upon heating in air a mixture of hematite and cerium dioxide, containing 40–70% of the latter, the compound $Ce_2Fe_2O_7$ with pyrochlore structure is formed.

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The investigation which we undertook in Ref. (*5*) to establish the feasibility of making ferrogarnet $Ce_3Fe_5O_{12}$, orthoferrite $CeFeO_3$, and pyrochlore $Ce_2Fe_2O_7$, indicated that in the Ce–Fe–O system only one ternary compound with a perovskite structure, $CeFeO_3$, is formed and it is unstable in air and easily oxidizes with formation of a mechanical mixture of CeO_2 and α-Fe_2O_3 at temperatures of 800–1250°C and oxygen pressures of 0.21–1 atm.

The purpose of the present work is to investigate the phase equilibria and the thermodynamics of coexisting phases in the Ce–Fe–O system over the range Ce_2O_3–CeO_2–Fe_2O_3–Fe, to construct equilibrium diagrams which define the character of phase changes in the system during changes in partial oxygen pressure, temperature, and composition of the initial oxide mixtures, and also to determine the equilibrium conditions for forming an intermediate compound, the orthoferrite.

Experimental

The following methods were used in the study of the phase equilibria: (1) static and dynamic methods of attaining equilibrium with subsequent annealing and identification of the condensed phases by X-ray analysis; (2) the electromotive force method with solid electrolyte having pure anionic conductivity.

Preparation of the Test Specimens

Metals and oxides of high purity were used as initial materials for preparing the test specimens. The metallic cerium had an impurity content <0.002%; the cerium dioxide CeO_2, <0.001%; the iron carbonyl powder, <0.002% by weight. The iron oxide Fe_2O_3 was obtained by thermal dissociation of Mohr's salt at a temperature of 800°C for a period of 5 hr in air. The completeness of the dissociation of the sulfates was checked by reaction with $BaCl_2$.

To investigate phase equilibria in the Ce–Fe–O system, mixtures corresponding to specific ratios of Ce : Fe : O were prepared in the following manner: Weighed amounts of powders $Ce + CeO_2 + Fe$ or of $CeO_2 + Fe_2O_3 + Fe$ were homogenized in an agate mortar under ethyl ether for a period of 3 hr, pressed into tablets (diameter, 9 mm; pressing pressure, 2 t/cm^2), and sealed into ampoules evacuated to 10^{-3} atm. For firing, double quartz ampoules containing a getter (tantalum chip) in the space between were used. The heating was done at a temperature of 1300°K for a period of 48 hr, after which the specimens were rapidly quenched by immersing the ampoules in water.

The single-phase cerium orthoferrite $CeFeO_3$ was obtained by heating the $3CeO_2 + Fe_2O_3 + Fe$ mixture in evacuated quartz ampoules for 50 hr at a temperature of 1300°K. The product of the heating, according to X-ray analysis, had the structure of a single-phase perovskite.

X-Ray Analysis

X-ray analysis of the condensed phases was carried out using FeK_α radiation. Filming by the photographic method was done in a high-resolution camera of diameter 143.25 mm using FeK_α radiation.

Study of the Equilibria with the emf Method

For measuring the equilibrium pressure of oxygen over the condensed phases of the Ce–Fe–O system we chose an electromotive force method with a solid electrolyte of $ZrO_2(Y_2O_3)$, which has pure anionic-oxygen conductivity. The construction of the galvanic cell with separate gas space, shown in Fig. 1, has been described by one of the authors in Ref. (*8*). The basic part of the cell is the solid electrolyte (tube 1) of zirconium dioxide, stabilized with yttrium oxide. This tube is joined with epoxy resin in a vacuum seal to the joint (3), through which is carried the lead of the specimen and its conditioning for the experiment. The specimen is placed in a platinum container (6) connected to the internal current lead. A quartz capillary rod (5) compressed by a spring assured reliable contact of the platinum container with the inner wall of the solid electrolyte tube and simultaneously isolated the inner current conductor (8) from the walls of the electrolyte tube. Good contact of the platinum container with the solid electrolyte is an important factor affecting the sensitivity of the cell. The end of the cell was placed in the nongradient heating zone of an electric fur-

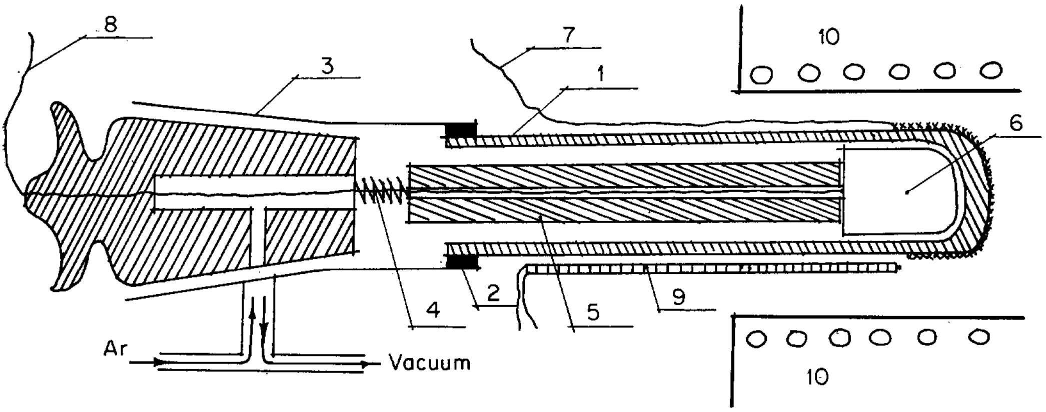


FIG. 1. Galvanic cell with separated electrode space for measuring the emf (the reference electrode is air with $P_{O_2} = 0.21$ atm): 1, solid electrolyte; 2, vacuum-tight seal of the electrolyte with the joint; 3, glass tube; 4, spring; 5, quartz capillary tube; 6, platinum container; 7, 8, current leads; 9, thermocouple; 10, furnace.

nace controlled to ±0.5°. The constancy of temperature was assured by a regulating system. Temperature measurement was done with a calibrated platinum/platinum–rhodium (10% Rh) thermocouple by the potentiometric method. Measurement of the emf was also carried out by the potentiometric method. Removal of oxygen from the gas phase was accomplished by means of prolonged degassing of the specimen at a temperature of 300°C and a dynamic vacuum of $\sim 10^{-2}$ mm of mercury. After degassing, the working chamber of the unit was flushed with especially pure argon and filled to a pressure of $P_{Ar} = 1 \pm 0.05$ atm. The cell was heated to the working temperature at a rate of 300°/hr. The specimens were kept at constant temperature until the equilibrium value of the emf was attained over the temperature range 1173–1473°K. The working temperature range was examined during heating as well as cooling of the cell. Equilibrium in the system was considered to be attained if a change in the magnitude of the emf did not have a monotonic character and did not exceed ±0.5 mV at the constant temperature.

Basic Results and Discussion

Considering the fact that one ternary compound, orthoferrite $CeFeO_3$, is formed in the Ce–Fe–O system, we attempted to determine the equilibrium condition for its formation using the emf method. X-ray analysis of the products of oxidation of the orthoferrite, which are found in equilibrium with the perovskite phase, indicated the presence of the fluorite type "CeO_2" plus magnetite. Therefore, for determining the equilibrium phases of the reaction

$$CeFeO_3 + \tfrac{1}{6}O_2 \rightarrow CeO_2 + \tfrac{1}{3}Fe_3O_4 \quad (1)$$

we studied a galvanic cell of the type:

$$Pt|CeFeO_3, CeO_2, Fe_3O_4|ZrO_2(Y_2O_3)|Pt \quad (P_{O_2} = 0.21\ \text{atm}) \quad (2)$$

Since the solid electrolyte $ZrO_2(Y_2O_3)$ has pure anionic-oxygen conductivity, the emf of the cell (2) is expressed by the equation

$$E = \frac{1}{4F}(\mu'_{O_2} - \mu''_{O_2}) = \frac{RT}{4F}\ln\frac{P'_{O_2}}{P''_{O_2}} \quad (3)$$

where μ'_{O_2} (P'_{O_2}) and μ''_{O_2} (P''_{O_2}) equal the chemical potentials (the equilibrium pressures of the oxygen) over the standard and the studied electrodes, respectively; F = the Faraday number; R = universal gas constant, and T = absolute temperature in degrees Kelvin.

The results of measuring the emf of cell (2) can be expressed by the equation:

$$E_{cell}(\text{mV}) = 1541.7 - 0.739T. \quad (4)$$

Combining Eq. (4) with Eq. (3) and keeping in mind that $P'_{O_2} = 0.21$ atm and $4F = 92.26$ cal/mV, we find that the equilibrium pressure of oxygen over the orthoferrite and the products of its oxidation is given by

$$\log P_{O_2}(\text{atm}) = 14.23 - (31085/T). \qquad (5)$$

A phase analysis of the reduction products of $CeFeO_3$ found in equilibrium with the perovskite phase indicated the presence of a phase of the fluorite type "CeO_{2-x}" and of metallic iron. The galvanic cell was studied to determine the equilibrium pressure of oxygen over the $CeFeO_3$ + "CeO_{2-x}" + Fe mixture

$$\text{Pt}|CeFeO_3, \text{"}CeO_{2-x}\text{"}, \text{Fe}|ZrO_2(Y_2O_3)|\text{Pt} \quad (P_{O_2} = 0.21 \text{ atm}). \qquad (6)$$

The emf of cell (6) can be expressed by the equation

$$E_{\text{cell}}(\text{mV}) = 1495.3 - 0.432T \qquad (7)$$

from which, according to Eq. (3), we find the equilibrium pressure of oxygen over orthoferrite and its reduction products:

$$\log P_{O_2}(\text{atm}) = 8.02 - (30150/T) \quad (1173\text{–}1473°\text{K}) \qquad (8)$$

The data obtained on the equilibrium pressure of oxygen over cerium orthoferrite and its coexistent oxidation products, on the one hand, and reduction products, on the other, were used to construct the phase diagram. It is apparent that the state of the Ce–Fe–O system, like that of any other three-component system, is fixed by four variables: T, P, and two composition parameters (for example, mole fractions of cerium N_{Ce} and iron N_{Fe}). Therefore, the full equation of state of the system is a function of the type $P = f(T, N_{Ce}, N_{Fe})$, $T = f(P, N_{Ce}, N_{Fe})$, or $N_{Ce} = f(T, P, N_{Fe})$, in addition to which, over the entire composition range (with the exception of pure Ce and Fe), the relations $P_{Fe} \ll P_{O_2}$, $P_{Ce} \ll P_{O_2}$, and, consequently, $P \simeq P_{O_2}$ hold true. It is apparent that the geometric representation of a full state diagram demands four-dimensional space, so in practice one uses partial diagrams or projections of diagrams on determined planes. Diagrams of the type $P_{O_2} = f(N_1, N_2)$, which are projections of isothermal diagrams onto a phase composition triangle (*11*), are extremely popular. We undertook the construction of just such a diagram.

Using data in the literature on the behavior of the Ce–O (*6*) and Fe–O (*9*, *10*) binary systems and the information we obtained ourselves on the nature of the intermediate phases, we examined possible ways of triangulating the composition triangle and then verified them by heating mixtures of condensed phases corresponding to determined ratios of Ce:Fe:O in sealed and carefully evacuated quartz ampoules. The compositions studied and their phase composition after attaining equilibrium at 1300°K followed by rapid quenching are presented in Table I. The equilibrium phase diagram of the Ce–Fe–O system at 1300°K constructed on the basis of these data is presented in Fig. 2. Here the Arabic

TABLE I

OVERALL AND INDIVIDUAL PHASE COMPOSITIONS IN THE Ce–Fe–O SYSTEM

	Overall composition			
N	Ce	Fe	O	Phase composition (data from X-ray analysis)
1	0.300	0.200	0.500	Ce_2O_3 + "C" + Fe
2	0.280	0.250	0.520	CeO_{2-x} + $CeFeO_3$ + Fe
3	0.120	0.400	0.480	$CeFeO_3$ + $Fe_{1-x}O$ + Fe
4	0.150	0.280	0.570	$Fe_{1-x}O$ + $CeFeO_3$ + Fe_3O_4
5	0.180	0.220	0.600	CeO_2 + $CeFeO_3$ + Fe_3O_4
6	0.140	0.250	0.610	CeO_2 + Fe_2O_3 + Fe_3O_4
7	0.270	0.010	0.630	CeO_{2-x} + $CeFeO_3$

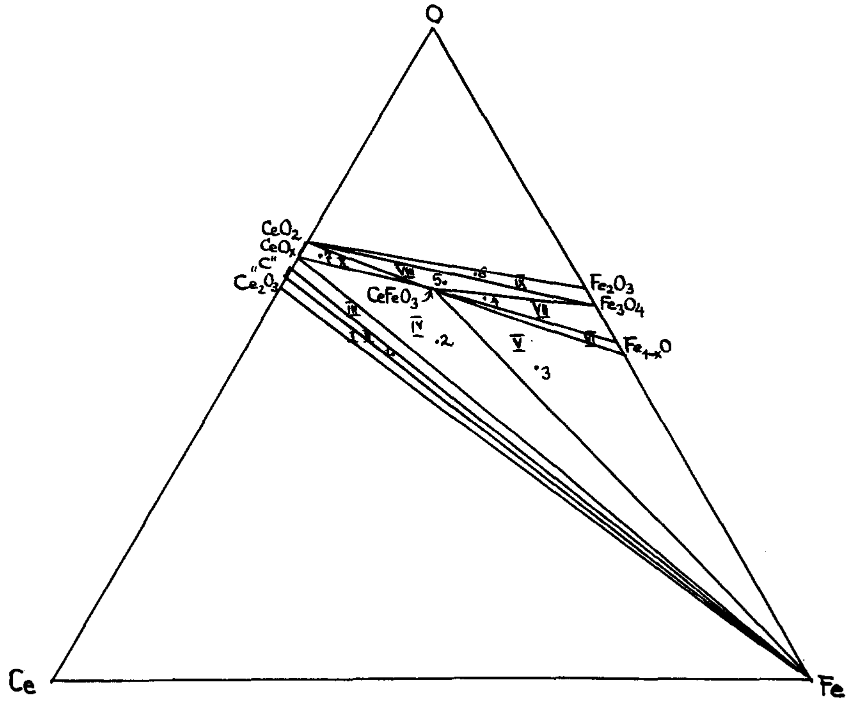


FIG. 2. Isothermal cross section of the phase diagram of the Ce–Fe–O system at 1300°K.

numerals indicate the compositions studied and the Roman numerals indicate the coexisting phases as given in Table II. Cerium sesquioxide Ce_2O_3, a phase of type "C", a nonstoichiometric phase of the fluorite type "CeO_{2-x}", and orthoferrite $CeFeO_3$ coexist with metallic iron. $CeFeO_3$ coexists also with wustite $Fe_{1-x}O$ and solid solutions of Fe_3O_4. Moreover, orthoferrite forms a triangle of coexisting phases with cerium dioxide CeO_2 and magnetite Fe_3O_4. The only ternary compound stable at 1300°K is the perovskite orthoferrite $CeFeO_3$, for which the measured unit-cell parameters are presented in Table III.

In principle, Fig. 2 allows us to establish the equilibrium phase composition of any combination of condensed phases with a known ratio of Ce:Fe:O. At the same time, it does not allow us to evaluate the character of phase

TABLE II

COEXISTING PHASES IN THE Ce–Fe–O SYSTEM AT 1300°K

Region	Phase composition
I	Ce_2O_3 + "C" + Fe
II	"C" + Fe
III	"C" + CeO_{2-x} + Fe
IV	CeO_{2-x} + $CeFeO_3$ + Fe
V	$CeFeO_3$ + $Fe_{1-x}O$ + Fe
VI	$CeFeO_3$ + $Fe_{1-x}O$
VII	$CeFeO_3$ + Fe_3O_4 + $Fe_{1-x}O$
VIII	CeO_2 + Fe_3O_4 + $CeFeO_3$
IX	CeO_2 + Fe_2O_3 + Fe_3O_4
X	CeO_2 + CeO_{2-x} + $CeFeO_3$

TABLE III

CRYSTALLOGRAPHIC PROPERTIES OF $CeFeO_3$

Unit-cell parameters			Volume of unit cell (Å³)	Reference
a (Å)	b (Å)	c (Å)		
5.520	5.539	7.820	239.1	(*5*)
5.541	5.577	7.809	241.3	(*12*)
5.519	5.536	7.819	238.9	(*1*)

changes during a change in P_{O_2} when the temperature is maintained constant or when it too changes. To solve these problems we constructed equilibrium diagrams of the type $P_{O_2} = f(\text{composition})$ with $T = \text{constant}$, $P_{O_2} = f(1/T)$ with one composition parameter fixed and $T = f(\text{composition})$ with $P_{O_2} = \text{constant}$.

Figure 3 presents the isothermal diagram $\log P_{O_2} = f(\xi_{Fe})$, where the composition parameter $\xi_{Fe} = n_{Fe}/(n_{Fe} + n_{Ce})$. Also, Fig. 3a shows the isothermal diagram $\xi_O = f(\xi_{Ce})$ where $\xi_O = n_O/(n_{Fe} + n_{Ce})$. It is understood that the latter diagram does not contain additional information compared with the phase diagram shown in Fig. 2, but it is more convenient for use with Fig. 3.

From Fig. 3, it is seen that under very low oxygen pressures ($-\log P_{O_2} < 21.2$ at 1300°K) Ce_2O_3 and metallic iron are found in equilibrium; with a rise in oxygen pressure, the sesquioxide goes back to a phase of the "C"-type structure, then to a phase of the fluorite type "CeO_{2-x}", remaining indifferent to the iron. Only when $-\log P_{O_2} < 15.2$ does an orthoferrite form, which, for compositions with $\xi_{Fe} < 0.5$, coexists with the fluorite phase and, for compositions with $\xi_{Fe} > 0.5$, coexists again with metallic iron and, proportional to the increase in P_{O_2}, with wustite and, finally, magnetite. When $-\log P_{O_2} < 9.6$, cerium orthoferrite decomposes, during which process oxidation of the perovskite phase is accompanied by a peculiar disproportionation. In fact, as shown by the reaction

$$CeFeO_3 + \tfrac{1}{6}O_2 \rightarrow CeO_2 + \tfrac{1}{3}Fe_3O_4$$

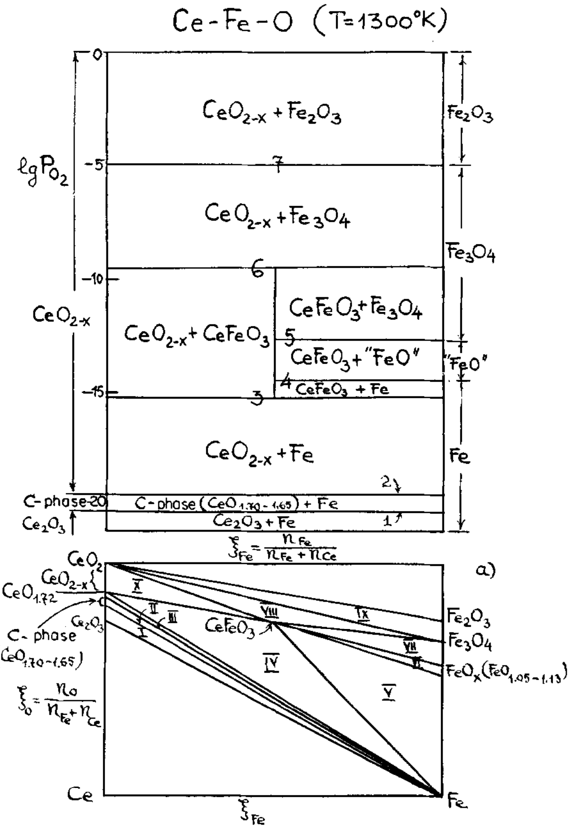


FIG. 3. (Top) Equilibrium phase diagram of $\log P_{O_2} = f(\xi_{Fe})$ and (bottom, marked a) $\xi_O = f(\xi_{Fe})$ for the Ce–Fe–O system at 1300°K.

TABLE IV

SUMMARY OF FIXED POINTS OF THE Ce–Fe–O DIAGRAM (FIG. 3)

Point	Equation $\log P_{O_2} = A - B/T$		$-\log P_{O_2}$ at 1300°K	Source
	A	B		
1			20.20	(*6*)
2			19.60	(*6*)
3	8.02	30150	15.20	Our data
4	6.78	27600	14.45	(*9*, *10*)
5	11.06	31090	12.80	(*9*, *10*)
6	14.23	31085	9.60	Our data
7	14.90	25900	5.00	(*9*, *10*)

that Ce^{3+} goes to Ce^{4+}, but simultaneously part of the Fe^{3+} is restored to Fe^{2+}. Table IV presents a summary of the fixed points of the Ce–Fe–O diagram in Fig. 3.

Figure 4 shows the equilibrium diagram $\log P_{O_2} = f(1/T)$ for various ratios of Ce:Fe, i.e., for various values of ξ_{Ce}. It is apparent that the stability zone of single-phase ferroperovskite is rather narrow, and the interval of oxygen pressure which does not cause destruction of orthoferrite is very sensitive to temperature.

Up to this point we have suggested that ferroperovskite is realized only when $\xi_{Ce} = 0.5$, i.e., there is no tendency to appearance of cationic nonstoichiometry and formation of a phase of the type $Ce_{1-x}Fe_{1-x}O_3$ or $Ce_{1-x}Fe_{1-x}O_3$. The parameters of the lattice, which turned out to be identical both for stoichiometric and nonstoichiometric compositions, can serve as a well-known confirmation of this. Table III presents the measured values of the unit cell parameters, which turned out to be in good correspondence with Bertaut's data (*1*) but differed from the values obtained in Ref. (*12*).

The state diagrams of the Ce–Fe–O system constructed on coordinates of $T = f(\xi_{Fe})$ for three values of the oxygen partial pressure ($P_{O_2} = 0.21$, 10^{-6}, and 10^{-10} atm) are presented in Fig. 5. The same illustration gives rather accurate temperature values of the phase changes.

Using the data on the equilibrium pressure of oxygen over orthoferrite and the oxidation products coexisting with it, we have calculated the free energy for cerium orthoferrite formation from the sesquioxides, i.e., the change in the free energy of the reaction

$$\tfrac{1}{2}Ce_2O_3 + \tfrac{1}{2}Fe_2O_3 \rightarrow CeFeO_3. \qquad (9)$$

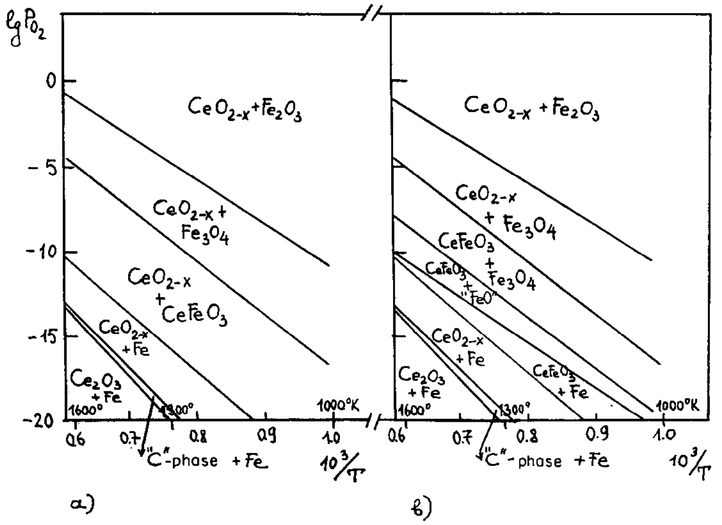
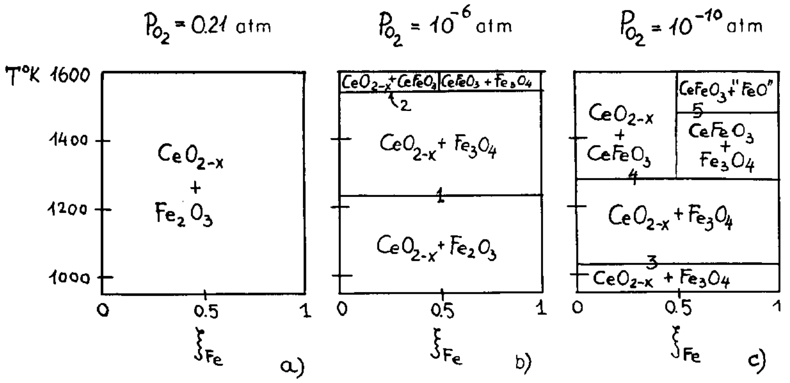


FIG. 4. State diagram of $\log P_{O_2} = f(1/T)$ for the equilibrium mixture of condensed phases of the Ce–Fe–O system (a) $\xi_{Ce} > 0.5$ and (b) $\xi_{Ce} < 0.5$.



Point	T°K
1	1234
2	1537
3	1036
4	1283
5	1477

FIG. 5. State diagram of the Ce–Fe–O system in coordinates $T = f(\xi_{Fe})\ P_{O_2}$ = constant for the three values of oxygen partial pressure: (a) $P_{O_2} = 0.21$ atm; (b) $P_{O_2} = 10^{-6}$ atm; (c) $P_{O_2} = 10^{-10}$ atm.

It is apparent that

$$\Delta G^\circ_{(9)} = \Delta G^\circ_{(11)} - \Delta G^\circ_{(12)} - \Delta G^\circ_{(13)} \quad (10)$$

where $\Delta G^\circ_{(11)}$, $\Delta G^\circ_{(12)}$, and $\Delta G^\circ_{(13)}$ are the changes in free energy of the reactions:

$$\tfrac{1}{2}Ce_2O_3 + \tfrac{1}{4}O_2 \rightarrow CeO_2, \quad (11)$$

$$\tfrac{1}{3}Fe_3O_4 + \tfrac{1}{12}O_2 \rightarrow \tfrac{1}{2}Fe_2O_3, \quad (12)$$

$$CeFeO_3 + \tfrac{1}{6}O_2 \rightarrow CeO_2 + \tfrac{1}{3}Fe_2O_4. \quad (13)$$

According to Holley's data (*13*) at 1300°K, $\Delta G^\circ_{(11)} = -23.5 \pm 2.5$ kcal/mole; at the same temperature the tabulated values of $\Delta G^\circ_{(12)} = -2.43 \pm 0.3$ kcal/mole (*9*). Finally,

$$\Delta G^\circ_{(13)} = -RT\ln K_p = -4.575\,T \log P_{O_2}^{1/6} = -0.766\,T \log P_{O_2}. \quad (14)$$

Realizing that for reaction (13) the equilibrium pressure of oxygen over the orthoferrite and the oxidation products coexisting with it is expressed by Eq. (5), we find from Eq. (14) that at 1300°K, $\Delta G^\circ_{(13)} = -9.64 \pm 0.20$ kcal/mole. In accordance with Eq. (10), the free energy of formation of cerium orthoferrite from the oxides is $\Delta G^\circ_{(9)} = -11.43 \pm 3.0$ kcal/mole.

The magnitude of $\Delta G^\circ_{(9)}$ can be calculated from the magnitude of the equilibrium pressure of oxygen over the orthoferrite and the reduction products that coexist with it. This equilibrium can be described by the reaction

$$CeFeO_3 = CeO_{1.72} + Fe + 0.64\ O_2 \quad (15)$$

if one presupposes that the fluorite phase which is in equilibrium with the orthoferrite and metallic iron has the greatest possible deficit of oxygen at 1300°K (*6*). It is apparent that the change in free energy of reaction (9) is

$$\Delta G^\circ_{(9)} = \Delta G^\circ_{(17)} - \Delta G^\circ_{(18)} - \Delta G^\circ_{(19)}, \quad (16)$$

where $\Delta G^\circ_{(17)}$, $\Delta G^\circ_{(18)}$, and $\Delta G^\circ_{(19)}$ are the free-energy changes of the reactions:

$$0.5\,Ce_2O_3 + 0.11\ O_2 = CeO_{1.72}, \quad (17)$$

$$Fe + \tfrac{3}{4}O_2 = \tfrac{1}{2}Fe_2O_3, \quad (18)$$

$$CeFeO_3 = CeO_{1.72} + Fe + 0.64\ O_2. \quad (19)$$

Correspondingly, for reaction (17) we have

$$\Delta G^\circ_{(19)} = -RT\ln K_p = -RT\ln P_{O_2}^{-0.11} = 0.11\ RT\ln P_{O_2}.$$

Using Bevan's experimental data (*6*) for the magnitude of log $P_{O_2} = f$(composition) we have found that at 1300°K, $\Delta G^\circ_{(17)} = -12.95 \pm 0.50$ kcal/mole.

At the same temperature, the tabulated values of $\Delta G^\circ_{(18)} = -98.24 \pm 31.29 \times 10^{-3}\ T = 57.6 \pm 0.1$ kcal/mole (at 1300°K) (*9*). Finally,

$$\Delta G^\circ_{(19)} = -RT\ln P_{O_2}^{-0.64} = -3.04\,T \log P_{O_2}. \quad (20)$$

Knowing that for reaction (19) the equilibrium pressure of oxygen over the orthoferrite and its reduction products is expressed by Eq. (18), we find from Eq. (20) that at 1300°K, $\Delta G^\circ_{(19)} = 57.8 \pm 0.2$ kcal/mole.

In agreement with Eq. (16), the free energy of formation of cerium orthoferrite from the oxides is $\Delta G^\circ_{(19)} = -13.15 \pm 0.80$ kcal/mole.

It is easy to be convinced that, within the limits of the indicated probable errors, this value differs little from the value of $\Delta G^\circ_{(9)}$ which was obtained by using the data on equilibrium oxidation of orthoferrite. Moreover, if one considers that, in equilibrium with orthoferrite and metallic iron, there is found not $CeO_{1.72}$ but a phase richer in oxygen of the fluorite type, then the difference in evaluation of $\Delta G^\circ_{(9)}$ for reduction and oxidation decreases. If one assumes that, in equilibrium with the orthoferrite and metallic iron, there is found the stoichiometric dioxide CeO_2, i.e.,

$$CeFeO_3 = CeO_2 + Fe + \tfrac{1}{2}O_2 \qquad (21)$$

then a calculation analogous to the one presented above leads to the value $\Delta G^\circ_{(9)} = -10.7 \pm 0.8$ kcal/mole. In fact, the fluorite-type phase in equilibrium with orthoferrite and metallic iron should have a certain deficiency of oxygen CeO_{2-x}, which, at 1300°K, according to Bevan's data (*6*), corresponds to $x < 0.01$ and, according to the data of (*7*), to $x \simeq 0.03$. Therefore, the real value of $\Delta G^\circ_{(9)}$, evaluated from data on the equilibrium reduction, should lie between −13.15 and −10.7 kcal/mole. The data obtained confirm the consideration above that the composition of orthoferrite in the direction of reduction actually does not differ from the orthoferrite composition in the direction of oxidation.

Conclusions

It has been shown that in the Ce–Fe–O system only one ternary compound with a perovskite structure, orthoferrite $CeFeO_3$, is formed. The emf method with solid electrolyte $ZrO_2(Y_2O_3)$ was used to study the thermodynamics of oxidation and reduction of cerium orthoferrite in the temperature range 900–1200°C. The phase equilibria and the thermodynamics of coexisting phases in the Ce–Fe–O system have been studied. Equilibrium diagrams have been constructed which define the character of the changes that take place in the Ce–Fe–O system when the partial oxygen pressure, temperature, and composition of the initial mixture of oxides change.

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