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Thermochemical Properties of Lanthanoid-Iron-Perovskite at High Temperatures

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The standard Gibbs energy of formation of $\bar{C}FeO_3$($\bar{C}$=La, Nd, Sm, Eu, Gd, Tb, and Dy) from metallic iron, $\bar{C}_2O_3$, and oxygen has been determined at temperatures from 1473 to 1673 K. Based on the free-energy data, the heat of reaction and the entropy change resulting from the reaction have been calculated. The values of the heat of reaction of $LaFeO_3$, $NdFeO_3$, $SmFeO_3$, $EuFeO_3$, and $GdFeO_3$ (the first group) were identical, −107 kcal/mol, at the present temperature interval. However, the values of the heat of reaction of $TbFeO_3$ and $DyFeO_3$ (the second group) decreased with an increase in the temperature. The entropy change of each reaction in the first group was constant, independent of the temperature, and each value decreased in the sequence from $LaFeO_3$ to $GdFeO_3$. The entropy change of the second group decreased with an increase in the temperature. The change of the standard Gibbs energy was intimately related to the ionic radii of $\bar{C}$-ions, and the relationship between the Gibbs energy and the tolerance factor has been clarified.

Recently, Kimizuka and Katsura[1,2] and Sugihara *et al.*[3] have determined the standard Gibbs energy of the formation of $LaFeO_3$, $YFeO_3$, $Y_3Fe_5O_{12}$, $EuFeO_3$, and $Eu_3Fe_5O_{12}$ at 1200 °C on the basis of the phase equilibria in the Fe–Fe_2O_3–La_2O_3, Fe–Fe_2O_3–Y_2O_3, and Fe–Fe_2O_3–Eu_2O_3 systems. Sugihara *et al.*[3] suggested that the standard Gibbs energy of formation of lanthanoid-iron-perovskite from metallic iron, lanthanoid sesquioxides and oxygen would decrease in negative value with a decrease in the ionic radii of lanthanoid ions with 12 coordination number. Kimizuka and Katsura[2] and Kimizuka *et al.*[4,5] have found two series of new compounds, $\bar{A}Fe_2O_4$ ($\bar{A}$=Y, Ho, Er, Tm, Yb, and Lu) and $\bar{B}_2Fe_3O_7$ ($\bar{B}$=Yb and Lu), and determined the standard Gibbs energy of formation of YFe_2O_4. Tannieres *et al.*[6] and Evrard *et al.*[7] have also found the $\bar{A}Fe_2O_4$ and $Lu_2Fe_3O_7$ compounds, but they did not show any equilibrium relation in the Fe–Fe_2O_3–$\bar{A}_2O_3$ systems which could be used for calculating the standard Gibbs energy. It would be expected from the present knowledge about lanthanoid-iron-complex oxides that the $\bar{C}FeO_3$($\bar{C}$= La, Nd, Sm, EU, Gd, Tb, and Dy) would decompose straightforwardly to form metallic iron and $\bar{C}_2O_3$ at any definite oxygen partial pressure. On the other hand, the situation with $\bar{A}FeO_3$ is somewhat complicated because of the presence of the $\bar{A}Fe_2O_4$ and $\bar{B}_2Fe_3O_7$ compounds, and we can determine the standard Gibbs energy of formation of $\bar{A}FeO_3$ only after determining the standard Gibbs energy of formation of $\bar{A}Fe_2O_4$ and $\bar{B}_2Fe_3O_7$.

In the present study, we determine the standard Gibbs energy of formation of $\bar{C}FeO_3$ from metallic iron, $\bar{C}_2O_3$, and oxygen by the method of controlling the oxygen partial pressure by using a mixed gas of CO_2 and H_2. Temperatures were changed from 1473 to 1673 K. Based on the standard Gibbs energy data, we calculate the heat of reaction and entropy change resulting from the reaction, $Fe+1/2\ \bar{C}_2O_3+3/4\ O_2=\bar{C}FeO_3$. The relationship between the tolerance factor of the $\bar{C}FeO_3$ compounds and the standard Gibbs energy will also be presented.

Experimental

The experimental methods and apparatus adopted in this study are the same as those described by Kimizuka and Katsura.[1] Every equilibrium value of p_{O_2} was measured by means of a solid electrolyte cell composed of $(ZrO_2)_{0.85}(CaO)_{0.15}$. The values of P_{O_2} calculated from the thermochemical data[8] were in good agreement with those measured, and the differences were within ±0.02 at most in terms of $\log P_{O_2}$ over the temperature and P_{O_2} ranges studied. The temperature was kept constant within ±1 °C and was calibrated against the gold point.

A guaranteed reagent-grade Fe_2O_3 and a 99.9% pure-grade of each lanthanoid sesquioxide were used as the starting substances. The mixture of $Fe_2O_3/\bar{C}_2O_3=1$ was thoroughly mixed under ethyl alcohol and calcined at 1200 °C for from 20 to 30 hr in air. The subsequent procedures were the same as those described by Kimizuka and Katsura.[1] The weight change accompanying the reaction was followed by the thermogravimetric method within an error of ±0.5 mg per about 3 g of every sample. The equilibrated sample was quenched rapidly, and the phases present were identified by an X-ray powder method.

Results and Discussion

The $\bar{C}FeO_3$ compounds decomposed straightforwardly to form metallic iron and $\bar{C}_2O_3$ at any definite oxygen partial pressure, and the reverse reaction occurred at the same P_{O_2} value.

We may write the general reaction scheme as follows:

$$Fe(s) + 1/2\bar{C}_2O_3(s) + 3/4O_2(g) = \bar{C}FeO_3(s) \qquad (1)$$

In Equation (1), $Fe(s)$ is in the form of γ-iron at temperatures from 910 to 1390 °C, while it is in the form of δ-iron from 1390 to 1534 °C.[9] Thus, in the present study, metallic iron is almost in the form of γ-iron except for $LaFeO_3$ at 1673 K. A recent study by Roth and Schneider[10] showed that La_2O_3 and Nd_2O_3 belong to the A-type with the hexagonal crystal system, Sm_2O_3, Eu_2O_3, and Gd_2O_3 to the B-type with the monoclinic crystal system, and Tb_2O_3 and Dy_2O_3, to the C-type with the cubic crystal system at the temperatures covered by the present study. The $\bar{C}FeO_3$ compounds are all perovskite-like compounds and all belong to the orthorhombic crystal system. McCarthy and White[11] have studied the lower oxides of the Sm, Eu, Yb, Bedford anf Catalano[12] have also studied the Eu–Eu_2O_3, Sm–Sm_2O_3, and Yb–Yb_2O_3 systems at 1500 °C. As verified by them, $\bar{C}_2O_3$ is so stable at very low oxygen partial pressures that we cannot reduce them to lower oxidation states by the present techniques.

The most interesting fact in Equation (1) is that all the Fe^{3+} ions with the coordination numbers of 6 in the perovskite structure are reduced to metallic iron without passing through the state of Fe^{2+} ions.

Non-stoichiometry in $\bar{C}FeO_3$. It has been pointed out by Sugihara *et al.*[3] that $EuFeO_3$ has a non-stoichiometric composition, represented by $EuFeO_{3-x}$. This is also found in $\bar{C}FeO_3$, when the $\bar{C}$'s are Gd, Tb, and Dy. The deviated compositions of these compounds were determined to be approximately $\bar{C}FeO_{2.98}$ when the compounds were in equilibrium with metallic iron and Gd_2O_3, Tb_2O_3, or Dy_2O_3. We ascertained in addition no significant solubility of other components in the $\bar{C}_2O_3$ phases. The lattice constants of these non-stoichiometric compounds, synthesized at various temperatures and oxygen partial pressures, were obtained by the least-squares method. The results were almost identical with those for stoichiometric compounds. The lattice constants of stoichiometric $\bar{C}FeO_3$ were identical with those reported by Geller and Wood[13] and by Eibschütz.[14]

The Standard Gibbs Energy of Formation of $\bar{C}FeO_3$ *from Metallic Iron,* $\bar{C}_2O_3$*, and Oxygen.* In the present study, we define the activity of each $\bar{C}FeO_3$ component as being unity at the composition where each $\bar{C}FeO_3$ component is in equilibrium with both metallic iron and $\bar{C}_2O_3$ at the respective definite oxygen partial pressure. Thus, the standard Gibbs energy of formation $\bar{C}FeO_3$ from metallic iron, $\bar{C}_2O_3$, and oxygen can readily be calculated by measuring the equilibrium oxygen partial pressure in each assembly. Here, the $\bar{C}_2O_3$ phases are all in the stoichiometric composition, as has been mentioned before. The results are given in Table 1. The errors due to the fluctuations of both temperature and oxygen partial pressure may be estimated to be ±200 cal at most.

Figure 1 shows the relationship between $\Delta G^0/T$ and $1/T$, where T is the absolute temperature. As may be seen in Fig. 1, the slope for each $\bar{C}FeO_3$ except for $TbFeO_3$ and $DyFeO_3$ is straight and identical with all others. This means that the heat of reaction of each compounds except for $TbFeO_3$ and $DyFeO_3$ is constant, with an identical value of −107 kcal per mol. In the cases of $TbFeO_3$ and $DyFeO_3$, the heats of reaction change with temperature. The calculated heats of reaction at various temperatures are given in Table 1.

The Entropy Change. The entropy change, ΔS^0, is determined either by $(\Delta H^0-\Delta G^0)/T$ or $d\Delta G^0/dT$. The results are given in Table 1. As may be seen in Table 1, the entropy value of each compounds except for $TbFeO_3$ and $DyFeO_3$ is independent of the temperature and is constant with a good accuracy when we adopt the values of $(\Delta H^0-\Delta G^0)/T$.

Table 1. Values of standard Gibbs energy, heat of reaction, and entropy change

	Temp. (K)	$-\log P_{O_2}$ (atm.)	$-\Delta G^0$ (kcal/mol)	$-\Delta H^0\left(\frac{d\Delta G^0/T}{d(1/T)}\right)$ (kcal/mol)	$-\Delta S^0$ (eu) $-(\Delta H^0-\Delta G^0)/T$		$-\Delta S^0$ (eu) $(d\Delta G^0/dT)$
$LaFeO_3$	1473	13.63	68.9	107±2	26.14	26.2±0.1	28
	1523	12.91	67.5		26.21		
	1570	12.27	66.1		26.30		
	1673	11.04	63.4		26.31		
$NdFeO_3$	1473	12.99	65.7		28.33	28.3±0.1	28
	1523	12.27	64.1		28.41		
	1570	11.67	62.9		28.36		
	1620	11.08	61.6		28.27		
$SmFeO_3$	1473	12.68	64.1		29.40	29.4±0.05	29
	1523	11.99	62.7		29.37		
	1570	11.38	61.3		29.35		
$EuFeO_3$	1473	12.52	63.3		29.95	29.9±0.08	29
	1497	12.21	62.7		29.84		
	1523	11.86	62.0		29.82		
	1570	11.24	60.6		29.83		
$GdFeO_3$	1473	12.49	63.1		30.05	30.0±0.05	30
	1497	12.15	62.4		30.05		
	1523	11.80	61.7		30.02		
	1570	11.18	60.2		30.04		
$TbFeO_3$	1473	12.22	61.8	76	10		8
	1497	11.96	61.5	94	22		18
	1523	11.62	60.7	117	37		38
	1548	11.21	59.6	138	51		(63±5)
$DyFeO_3$	1473	12.11	61.2	78	11		10
	1497	11.83	60.8	96	24		24
	1523	11.46	59.9	123	41		48
	1548	11.04	58.7	147	57		(65±5)

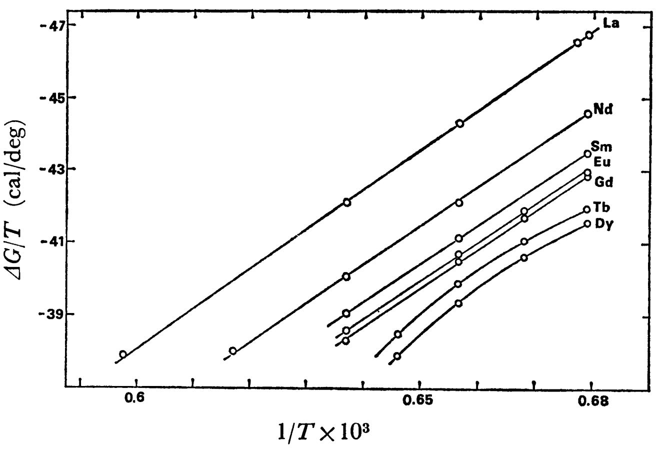

Fig. 1. The relationship between $\Delta G^0/T$ and $1/T$. The value at 1204 °C was cited from the paper by Kimizuka and Katsura.[1]

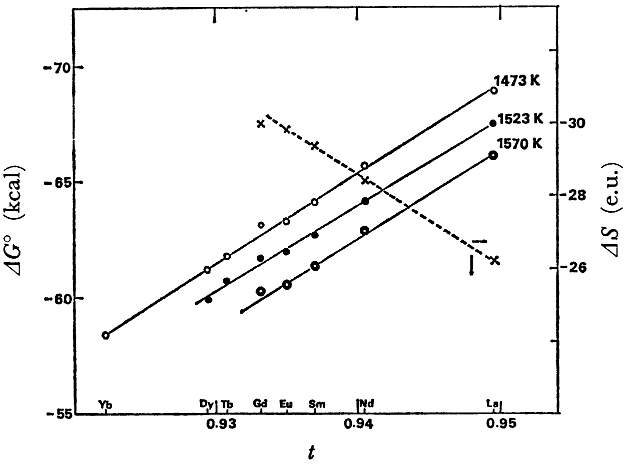

Fig. 2. The relationship between ΔG^0 and the tolerance factor *t*.

The values from $d\Delta G^0/dT$ seem to have some larger errors than those from $(\Delta H^0-\Delta G^0)/T$. On the other hand, the entropy change of $TbFeO_3$ and $DyFeO_3$ increases in negative value with an increases in the temperature.

It should be emphasized here that there are two groups of compounds in $\bar{C}FeO_3$ in respect to thermochemistry; the first includes $LaFeO_3$, $NdFeO_3$, $SmFeO_3$, $EuFeO_3$, and $GdFeO_3$, and the second, $TbFeO_3$ and $DyFeO_3$. This trend should be investigated furthermore with reference to the $\bar{A}FeO_3$ compounds.

The Relationship between the Tolerance Factor and the Standard Gibbs Energy of Formation of $\bar{C}FeO_3$. Figure 2 shows the relationship between the tolerance factor defined by Goldschmidt,[15] $[r_a+r_o=t\sqrt{2}(r_b+r_o)]$, and the standard Gibbs energy of formation of $\bar{C}FeO_3$ from metallic iron, $\bar{C}_2O_3$, and oxygen. In the tolerance-factor equation, r_a, r_b, and r_o mean the ionic radii of $\bar{C}$, Fe, and O ions in the perovskite structure respectively, and *t* is the tolerance factor. Here, we adopt the values reported by Espinosa[16] for ions of $\bar{C}$ with the coordination number of 12 in the perovskite structure. The ionic radii of Fe^{3+} and O^{2-} are 0.645 Å and 1.40 Å respectively; these values are given by Shannon and Prewitt.[17] The ΔG^0 value of $YbFeO_3$[18] is also given in Fig. 2. As may be seen in Fig. 2, the ΔG^0 value is proportional to the tolerance factor except for the case of $GdFeO_3$. The deviation in $GdFeO_3$ from the general trend is significant though within the range of experimental error; we cannot explain the reason for this deviation.

The entropy change resulting from the reaction is also plotted in Fig. 2. As is illustrated in Fig. 2, the entropy change decreases with a decrease in the tolerance factor.

References

1) N. Kimizuka and T. Katsura, This Bulletin, **47**, 1801 (1974).

2) N. Kimizuka and T. Katsura, *J. Solid State Chem.*, **13**, 176 (1975).

3) T. Sugihara, N. Kimizuka, and T. Katsura, This Bulletin, **48**, 1806 (1975).

4) N. Kimizuka, A. Takenaka, Y. Sasada, and T. Katsura, *Solid State Commun.*, **15**, 1321 (1974).

5) N. Kimizuka, A. Takenaka, Y. Sasada, and T. Katsura, *ibid.*, **15**, 1199 (1974).

6) N. Tannieres, O. Evrard, and J. Aubry, *C. R. Akad. Sc. Paris*, **278**, 241 (1974).

7) O. Evrard, B. Malaman, F. Jeannot, N. Tannieres, and J. Aubry, *ibid.*, **278**, 413 (1974).

8) "JANAF" Thermochemical Tables, U. S. Department of Commerce/Nat. Bur. Stand. (1965—1966).

9) M. Hansen, "Contribution of Binary Alloys," McGraw-Hill Book Co., New York (1958).

10) R. S. Roth and S. J. Schneider, *J. Res. Nat. Bur. Stand., A. Phys. Chemi.*, **64A**, 309 (1960).

11) G. J. McCarthy and W. B. White, *J. Less Common Metals*, **22**, 409 (1970).

12) R. G. Bedford and E. Catalano, *J. Solid State Chem.*, **3**, 112 (1971).

13) S. Geller and E. A. Wood, *Acta Crystallogr.*, **9**, 563 (1956).

14) M. Eibschutz, *ibid.*, **19**, 337 (1965).

15) V. M. Goldschmidt, T. Barth, G. Lunde, and W. Zachariasen, Pt. VII Skrifter Norske Videnskaps-Akad. Oslo, I. Mat. Naturv. K. I. No. 2 (1926).

16) G. P. Espinosa, *J. Chem. Phys.*, **37**, 2344 (1962).

17) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, B **25**, 925 (1969); *ibid.*, B **26**, 1046 (1970).

18) N. Kimizuka and T. Katsura, *J. Solid State Chem.*, **13**, in press.