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Isothermal Decomposition of Ternary Oxide $A_xB_yO_z$ on an Isobar—Stability of Perovskite ABO_3 (A = La, Sm, Dy; B = Mn, Fe) in a Reducing Atmosphere

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The isothermal decomposition of any ternary oxide $A_xB_yO_z$ on liberation of n moles of oxygen at a constant pressure is found to be driven by the mixing entropy $\Delta S_m = -nR \ln P_{O_2}$ of the total entropy change $\Delta S = \Delta S^\circ + \Delta S_m$. The stability of $A_xB_yO_z$ towards isothermal decomposition into a biphasic solid mixture is derived from the equilibrium condition $\Delta G^* = 0$ as functions of standard changes ΔH° and ΔS°. Assuming $\Delta S^\circ = 44n$ and calculating ΔH° in terms of lattice energies $U(ABO_3)$ and $U(A_2O_3)$, the stability of perovskites $\mathrm{St}(ABO_3) = -\log P^*_{O_2}$ (A = La, Sm, Dy; B = Mn, Fe) is given as a function of the ionic radius of the A^{3+} ion. The calculated stability agrees well with that observed. The effect of electronic entropy change ΔS_e on ΔS° is demonstrated for $A\mathrm{FeO_3}$ (A = La, Sm, Dy).

1. Introduction

Studies on isothermal dissociation equilibria of perovskite-type compounds ABO_3 under P_{O_2}-controlled atmospheres have been reported for $A\mathrm{MoO_3}$ (A = Ba, Sr, Ca) (*1*), $A\mathrm{MnO_3}$ (A = La, Sm, Dy) (*2–4*), and $A\mathrm{FeO_3}$ (A = rare earth ions) (*5–7*). Chemical formulas of their equilibria at $T = 1473$K and $P = 1$ bar are as follows:

$$A\,\mathrm{MoO_3(s)} = A\,\mathrm{O(s)} + \mathrm{Mo(s)} + \mathrm{O_2(g)} \quad (A = \mathrm{Ba, Sr, Ca}), \quad (1)$$

$$A\mathrm{MnO_3(s)} = \tfrac{1}{2}A_2\mathrm{O_3(s)} + \mathrm{MnO(s)} + \tfrac{1}{4}\mathrm{O_2(g)} \quad (A = \mathrm{La, Sm, Dy}), \quad (2)$$

$$A\mathrm{FeO_3(s)} = \tfrac{1}{2}\mathrm{A_2O_3(s)} + \mathrm{Fe(s)} + \tfrac{3}{4}\mathrm{O_2(g)} \quad (A = \mathrm{La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y}). \quad (3)$$

Although the critical oxygen partial pressure $P^*_{O_2}$ for each dissociation equilibrium of ABO_3, that is, its standard Gibbs free energy change

$$\Delta G^\circ = -nRT \ln P^*_{O_2} \quad (4)$$

has been known, yet the reason why the compound ABO_3 decomposes isothermally at a constant pressure $P = 1$ bar when the oxygen partial pressure P_{O_2} varies has not basically been understood. In the present paper the thermochemical meaning of the stability of ternary oxide $A_xB_yO_z$, $\mathrm{St}(A_xB_yO_z) = -\log P^*_{O_2}$, towards isothermal decomposition on an isobar is discussed and the effect of isovalent A substitution on the $\mathrm{St}(ABO_3)$ for perovskites ABO_3 is evaluated via estimation of lattice energies of solid phases.

2. Isothermal Decomposition of $A_xB_yO_z$ on an Isobar

Whether the isothermal reaction at a constant pressure,

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$$A_xB_yO_z(\mathrm{s}) = [A,B,\mathrm{O}](\mathrm{s}) + n\mathrm{O}_2(\mathrm{g}), \quad (5)$$

proceeds spontaneously or not at a particular P_{O_2}- atomsphere depends on the sign of its Gibbs free energy change

$$\Delta G = \Delta H - T\Delta S, \quad (6)$$

where $[A,B,\mathrm{O}]$ is generally a biphasic solid mixture and rarely a single-phase solid solution. Since free energies or enthalpies of the solid phases in Eq. (5) do not change as P_{O_2} varies unless they liberate oxygen in the isothermal process on an isobar, the only possible way to get a negative ΔG, that is, the force to drive the reaction Eq. (5) foward, is inferred to be a positive entropy change ΔS in Eq. (6) associated with the liberation of n moles of oxygen into a P_{O_2} atomsphere.

For any isothermal chemical reaction which liberates oxygen at constant pressure, the free energy change in the surrounding atmosphere δG associated with the acceptance of the liberated oxygen is very important for the chemical reaction to proceed.

Classical thermostatistics (*8, 9*) instructs us that an isothermal addition of an infinitesimal amount of oxygen δn into a perfect gas mixture whose oxygen mole fraction is $X_{O_2} = P_{O_2}/P$ produces an increase in the free energy of the gas mixture by the amount

$$\begin{aligned}\delta G &= \delta n \cdot \mu_{O_2} = \delta n(\mu^\circ{}_{O_2} + RT \ln X_{O_2}) \\ &= \delta n(\mu^\circ{}_{O_2} + RT \ln P_{O_2} - RT \ln P), \quad (7)\end{aligned}$$

where μ_{O_2} is the molar chemical potential of oxygen in the gas mixture. Since $\mu^\circ{}_{O_2}$, the standard molar chemical potential of oxygen, is given by

$$\begin{aligned}&\mu^\circ{}_{O_2} = RT[\ln P - \ln f(T)] \\ &f(T) = (1/h^3)(2\pi m_{O_2})^{3/2}\,(kT)^{5/2} \cdot Z_{O_2}(T), \quad (8)\end{aligned}$$

where $Z_{O_2}(T)$ is the internal partition function and m_{O_2} is the mass of the oxygen molecule O_2, the free energy increase δG in Eq. (7) is independent of the total pressure P in the perfect gas mixture. When n moles of oxygen gas are added into the perfect gas mixture whose oxygen partial pressure P_{O_2} is kept at a constant value, the total free energy increase in the gas mixture, therefore, amounts to

$$\delta G = nRT\,[\ln P_{O_2} - \ln f(T)]. \quad (9)$$

The first term in Eq. (9) obviously comes from the mixing entropy of the added oxygen.

It follows from Eq. (9) that the entropy change in Eq. (6) associated with the reaction Eq. (5) can be written generally as

$$\Delta S = \Delta S^\circ - nR \ln P_{O_2}, \quad (10)$$

where

$$\Delta S^\circ = \Delta S(\text{solid}) + nR\,\frac{d}{dT}[T \ln f(T)] \quad (11)$$

is the standard entropy change of Eq. (5) at $P_{O_2} = P = 1$ bar. Here, ΔS(solid) in Eq. (11) is the entropy change between the solid phases associated with the reaction Eq. (5), contributed mainly by the vibrational entropy change ΔS_L and partly by the electronic entropy change ΔS_e. The second term in Eq. (11) is the standard entropy of oxygen molecules composed of translational, rotational, and vibrational terms. An attempt to calculate ΔS° for oxides M_mO_n on their complete reduction is given elsewhere (*10*). ΔS in Eq. (10) is a linear function of $\ln P_{O_2}$ in contrast with a constant ΔH in the isothermal decomposition Eq. (5) at constant pressure. Such a situation is schematically shown in Fig. 1 for $AB\mathrm{O}_3$, where the simplifications $\Delta H^* = \Delta H^\circ$ and $(\Delta S^\circ)^* = \Delta S^\circ$, which exclude nonstoichiometries versus P_{O_2} for solid phases, are employed. Here, ΔH^* and $(\Delta S^\circ)^*$ are the changes at the equilibrium state and ΔH° and ΔS° are the standard changes at $P_{O_2} = P = 1$ bar.

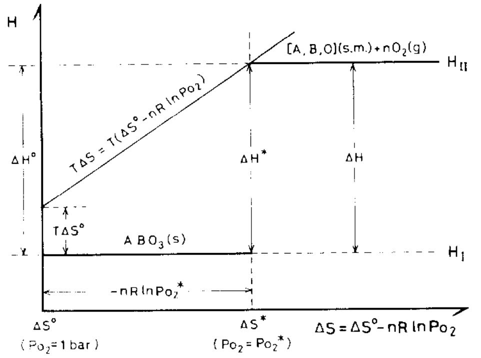

FIG. 1. The thermochemical meaning of isothermal decomposition of ABO_3 into a biphasic solid mixture $[A,B,\mathrm{O}]$ at a constant pressure. The reaction is directly driven by the mixing entropy $\Delta S_m = -nR \ln P_{O_2}$.

From the critical condition $P_{O_2} = P^*_{O_2}$, where $\Delta G^* = \Delta H^* - T\Delta S^*$ in Eq. (6) vanishes, the stability of $A_xB_yO_z$ toward decomposition Eq. (5) is given by

$$\begin{aligned}\mathrm{St}(A_xB_y\mathrm{O}_z) &= -\log P^*_{O_2} = \frac{\Delta H^* - T(\Delta S^\circ)^*}{2.303\, nRT} \\ &= \frac{\Delta H^\circ - T\Delta S^\circ}{2.303\, nRT}. \qquad (12)\end{aligned}$$

The final form of Eq. (12), which is equivalent to Eq. (4), followed from the simplifications excluding nonstoichiometries versus P_{O_2}. Schmalzried and Navrotsky (*11*) gave empirically the standard entropy change per liberation of 1 mole of oxygen from oxides to be 44 ± 8 cal/deg · mole, that is,

$$\Delta S^\circ = (44 \pm 8)n \text{ cal/deg} \cdot \text{mole}. \qquad (13)$$

Putting Eq. (13) into Eq. (12), a working formula for the stability of ternary oxide $A_xB_y\mathrm{O}_z$ is obtained.

$$\begin{aligned}\mathrm{St}(A_xB_y\mathrm{O}_z) &= \frac{1}{2.303}\left(\frac{\Delta H^\circ}{nRT} - 22\right) \pm 2. \qquad (14)\end{aligned}$$

Eq. (14) indicates that the stability $-\log P^*_{O_2}$ is mainly determined by the factor $\Delta H^\circ/n$.

Since the discussions in Part 2 contain nothing about the structural information on the solid phases, the conclusions obtained in this part are applicable to the isothermal decomposition of any type of complex oxide liberating n moles of oxygen at a constant pressure.

3. Effect of Isovalent *A* Substitution on the Stability of Perovskite ABO_3

The stability of ABO_3 toward decomposition, Eq. (2) or (3), depends not only on the stability of reactants, e.g., on the lattice energy $U(ABO_3)$, but also on the stability of products, e.g., on the lattice energy $U(A_2O_3)$, as demonstrated by $\Delta H^\circ/n$ in Eq. (14). In this part the order of stability for ABO_3 on A substitution is studied on the basis of Eq. (14) via estimation of $\Delta H^\circ(A)$ of reaction Eq. (2) or (3) as functions of lattice energies $U(ABO_3)$ and $U(A_2O_3)$, regarding the semiconducting perovskites (*12*) $A\mathrm{MnO}_3$ and $A\mathrm{FeO}_3$ (A = La, Sm, Dy) to be ionic crystals of the $A^{3+}B^{3+}O^{2-}{}_3$-type.

3.1. Stability Order in $A\mathrm{MnO}_3$ (A = La, Sm, Dy)

For convenience in the calculation of the cation-A-dependent $\Delta H^\circ(A)$ in terms of lattice energies $U(A\mathrm{MnO}_3)$ and $U(A_2O_3)$, the thermochemical reference state for every stage in reaction Eq. (2) has been chosen as

$$A^{3+}(\mathrm{g}) + \mathrm{Mn}^{3+}(\mathrm{g}) + 3\mathrm{O}^{2-}(\mathrm{g}). \qquad (15)$$

Figure 2 shows an enthalpy diagram for the reaction Eq. (2) based on the reference state Eq. (15).

Since the PV term at P = 1 bar in each solid phase is negligibly small compared to its internal energy, the enthalpy of each solid phase is given in terms of the negative of its lattice energy with an adjusting factor $(1 - 1/h)$, associated with the Born-type repulsion energy (*13*) at the equilibrium separations,

$$W(r) = b/r^h. \qquad (16)$$

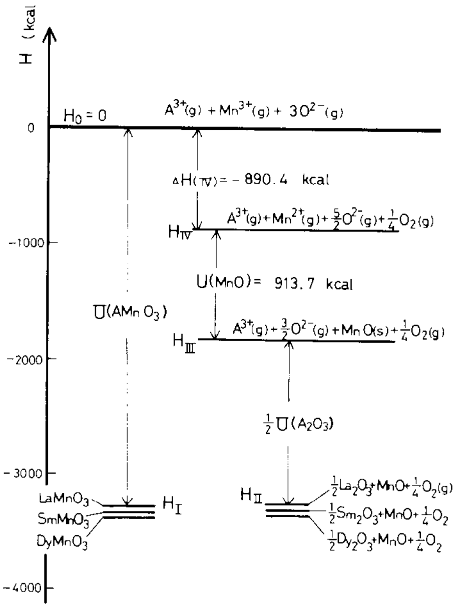

FIG. 2. An enthalpy diagram relative to the state $A^{3+}(g) + Mn^{3+}(g) + 3O^{2-}(g)$ for reaction Eq. (2). The standard enthalpy change $\Delta H°(A)$, and lattice energies $U(A\mathrm{MnO_3})$, $U(A_2O_3)$, and $U(\mathrm{MnO})$ are shown as enthalpy differences between the states.

Each state in Fig. 2 is interpreted as follows.

State I: $A\mathrm{MnO_3(s)}$, is the initial state of reaction Eq. (2). Its enthalpy relative to Eq. (15) is given by

$$H_{\mathrm{I}} = -U(A\mathrm{MnO_3})$$
$$= -\frac{Ne^2M(ABO_3)}{a_{\mathrm{p}}(r_A)}\left(1 - \frac{1}{h_{\mathrm{p}}}\right), \quad (17)$$

where N and e are Avogadro's number and the electronic charge, respectively, Ne^2 = 331.984 kcal/mole, $M(ABO_3)$ = 44.544 is the Madelung constant for the $A^{3+}B^{3+}O_3^{2-}$-type perovskite structure (*14*), h_{p} is the hardness parameter in the repulsion potential Eq. (16) for $A\mathrm{MnO_3}$, and

$$a_{\mathrm{p}}(r_A) = 0.75329\,r_A + 3.0241 \text{ Å}, \quad (18)$$

the averaged pseudocubic perovskite parameter $a_{\mathrm{p}} = (abc/4)^{1/3}$ for orthorhombic $A\mathrm{MnO_3}$ (*15*) is indicated as a linear function of r_A, the 9-coordinated Shannon's radius of A^{3+} ion (*16*). The a_{p} data employed in the mean-square averaging treatments are listed in Table I.

State II: $\frac{1}{2}A_2O_3(s) + \mathrm{MnO(s)} + \frac{1}{4}O_2(g)$, is the final state of the reaction Eq. (2). The enthalpy difference between States I and II is the very quantity in question;

$$\Delta H°(A) = H_{\mathrm{II}} - H_{\mathrm{I}}. \quad (19)$$

State III: $A^{3+}(g) + \frac{3}{2}O^{2-}(g) + \mathrm{MnO(s)} + \frac{1}{4}O_2(g)$, is an imaginary state, the enthalpy of which H_{III} is given by the sum of H_{II} and the lattice energy $\frac{1}{2}U(A_2O_3)$;

$$H_{\mathrm{III}} - H_{\mathrm{II}} = \tfrac{1}{2}U(A_2O_3)$$
$$= \frac{Ne^2M(AO_{1.5})}{a_{\mathrm{c}}(r_A)}\left(1 - \frac{1}{h_{\mathrm{c}}}\right), \quad (20)$$

where $M(AO_{1.5})$ = 56.5332 (*17*) is the Madelung constant per 0.5 A_2O_3 of C-type rare-earth oxide (cubic Bixbyite structure) (*15*) and

$$a_{\mathrm{c}}(r_A) = 5.2561 r_A + 4.9675 \text{ Å}, \quad (21)$$

the averaged lattice parameter of the C-type A_2O_3 is a linear function of the 9-coordinated Shannon's radius of the A^{3+} ion. The data used for averaging are tabulated in Table I. Each A^{3+} ion in the C-type A_2O_3 is surrounded by 6 oxygen ions, whereas it is surrounded by 12 oxygen ions in the ideal perovskite structure ABO_3 (*15*). The employed coordination number 9 for A^{3+} ion is midway between them.

State IV: $A^{3+}(g) + \frac{5}{2}O^{2-}(g) + \mathrm{Mn^{2+}}(g) + \frac{1}{4}O_2(g)$, is an another imaginary state the enthalpy of which H_{IV} is given by the sum of H_{III} and the lattice energy $U(\mathrm{MnO})$;

$$H_{\mathrm{IV}} - H_{\mathrm{III}} = U(\mathrm{MnO})$$
$$= \frac{Ne^2M(\mathrm{MnO})}{r_0}\left(1 - \frac{1}{h_0}\right), \quad (22)$$

where $M(\mathrm{MnO}) = 4 \times 1.747565$ is the Madelung constant of the rock-salt structure and r_0 = 2.2224 Å (*15*) is the nearest-

TABLE I

LATTICE CONSTANTS OF C-TYPE A_2O_3 (a_C), PSEUDOCUBIC PEROVSKITE PARAMETERS OF ORTHORHOMBIC ABO_3 [$a_p = (abc/4)^{1/3}$], AND THEIR MEAN-SQUARES FITS TO A LINEAR FUNCTION OF r_A

A Rare earth element	r_A Shannon's radius of 9-coordination (Å)	a_C lattice constant of A_2O_3 (Å)	$a_C(r_A)$ averaged constant from Eq. (21)	a_p constant for AMnO$_3$(Å)	$a_p(r_A)$ averaged constant from Eq. (18)	a_p constant for AFeO$_3$ (Å)	$a_p(r_a)$ averaged constant from Eq. (30)
La	1.216	11.38	11.3589	3.940^a	3.9401	3.930^a	3.9325
Pr	1.179	11.136				3.912	
Nd	1.163	11.048		3.896^b		3.894^g	
Sm	1.132	10.932	10.9174	3.879^c	3.8768	3.874	3.8753
Eu	1.120	10.866		3.872^d		3.869	
Gd	1.107	10.813		3.862^e		3.861	
Tb	1.095	10.728					
Dy	1.083	10.667	10.6598	3.834^f	3.8399	3.839^h	3.8418
Y	1.075	10.604				3.836	
Ho	1.072	10.607					
Er	1.062	10.547					
Tm	1.052	10.488					
Yb	1.042	10.439					
Lu	1.032	10.391					

Note. Remarks for lattice constants. *a*, Ref. (*3*); *b*, ASTM card 25–565; *c*, ASTM card 25–747; *d*, ASTM card 26–1126; *e*, ASTM card 25–337; *f*, ASTM card 25–330; *g*, ASTM card 25–1150; *h*, ASTM card 19–433. Constants without remarks are taken from Ref. (*15*).

neighbor separation of Mn^{2+}–O^{2-} in MnO(s).

The enthalpy level H_{IV} relative to the reference state Eq. (15), on the other side, is equal to the enthalpy change ΔH(IV) of the following reaction

$$Mn^{3+}(g) + \tfrac{1}{2}O^{2-}(g) = Mn^{2+}(g) + \tfrac{1}{4}O_2(g), \quad (23)$$

which amounts to

$$H_{IV} = \Delta H(\text{IV}) = -890.4 \text{ kcal/mole}. \quad (24)$$

The value in Eq. (24) is obtained from the ionization potential of $Mn^{2+}(g)$ = 776.4 kcal/g-ion (*18*), the dissociation energy of $\tfrac{1}{4}O_2(g)$ = 29.8 kcal (*18*), and the electron affinity of $\tfrac{1}{2}O(g)$ = 84.2 kcal (*18*).

Thus, it follows from Eqs. (20), (22), and (24) that

$$H_{II} = -\tfrac{1}{2}U(A_2O_3) - U(\text{MnO}) - 890.4 \text{ kcal}. \quad (25)$$

Insertion of Eqs. (17) and (25) into Eq. (19) gives

$$\begin{aligned} \Delta H^\circ(A) &= U(A\text{MnO}_3) - \tfrac{1}{2}U(A_2O_3) - U(\text{MnO}) - 890.4 \\ &= \frac{Ne^2M(ABO_3)}{a_p(r_A)}\left(1 - \frac{1}{h_p}\right) - \frac{Ne^2M(AO_{1.5})}{a_c(r_A)}\left(1 - \frac{1}{h_c}\right) \\ &\quad - \frac{Ne^2M(\text{MnO})}{r_0}\left(1 - \frac{1}{h_0}\right) - 890.4 \text{ kcal}. \quad (26) \end{aligned}$$

Referring to Eqs. (18) and (21), this equation consequently gives the enthalpy change of the reaction Eq. (2) as a function of the ionic radius of A^{3+} ion, r_A.

The hardness parameter h in Eq. (16), which has been taken for granted in simple oxides (*13*), ranges from $h = 6.0$ for Li_2O to $h = 9.5$ for BaO with an average value of $h = 8.00$. Therefore, putting $h_p = h_c = h_0 = 8.00$ in Eq. (26) in the first place, one can calculate the enthalpy change $\Delta H°(A)$ for A = La, Sm, Dy. Table II shows the calculated enthalpy change $\Delta H°(A)$, along with the stability $\mathrm{St}(A\mathrm{MnO}_3) = -\log P^*_{\mathrm{O}_2}$ according to the working formula Eq. (14). The calculated stabilities $\mathrm{St}(A\mathrm{MnO}_3)_{\mathrm{calc}}$ agree well with the observed $\mathrm{St}(A\mathrm{MnO}_3)_{\mathrm{obs}}$ (*4*), not only in their stability order,

$$\mathrm{St}(\mathrm{LaMnO_3}) > \mathrm{St}(\mathrm{SmMnO_3}) > \mathrm{St}(\mathrm{DyMnO_3}), \quad (27)$$

but also in their values. If we put $h_p = 8.026$ for $A\mathrm{MnO}_3$(s) in Eq. (26) and $h_c = h_0 = 8.00$ for simple oxides A_2O_3(s) and MnO(s), better agreement between the calculated and the observed values is obtained as shown in Table II.

3.2. Stability Order in AFeO₃ (A = La, Sm, Dy)

An enthalpy diagram for the reaction Eq. (3) relative to the reference state

$$A^{3+}(g) + \mathrm{Fe}^{3+}(g) + 3\mathrm{O}^{2-}(g) \quad (28)$$

is shown in Fig. 3.

State I: $A\mathrm{FeO}_3$(s), is the initial state of the reaction Eq. (3). Its enthalpy is given by

$$H_{\mathrm{I}} = -U(A\mathrm{FeO}_3) = -\frac{Ne^2M(ABO_3)}{a_p(r_A)}\left(1 - \frac{1}{h_p}\right), \quad (29)$$

where $M(ABO_3) = 44.544$ is the Madelung constant, h_p is the hardness parameter in Eq. (16) for $A\mathrm{FeO}_3$(s), and

$$a_p(r_A) = 0.68202\, r_A + 3.10321 \quad (30)$$

is the averaged pseudocubic perovskite parameter $a_p = (abc/4)^{1/3}$ for orthorhombic $A\mathrm{FeO}_3$ (*15*). The data a_p used for the averaging procedure are listed in Table I.

State II: $\frac{1}{2}A_2O_3(s) + \mathrm{Fe}(s) + \frac{3}{4}O_2(g)$, is the final state of the reaction Eq. (3). The enthalpy difference between States I and II is the enthalpy change in question:

$$\Delta H°(\mathrm{A}) = H_{\mathrm{II}} - H_{\mathrm{I}}. \quad (31)$$

State III: $\mathrm{A}^{3+}(g) + \frac{3}{2}\mathrm{O}^{2-}(g) + \mathrm{Fe}(s) + \frac{3}{4}O_2(g)$, is an imaginary state, the enthalpy of which H_{III} is defined by the sum of H_{II} and $\frac{1}{2}U(A_2O_3)$:

$$H_{\mathrm{III}} - H_{\mathrm{II}} = \frac{1}{2}U(A_2O_3) = \frac{Ne^2M(AO_{1.5})}{a_c(r_A)}\left(1 - \frac{1}{h_c}\right). \quad (32)$$

This equation is the same as Eq. (20). $a_c(r_A)$ has been given by Eq. (21). The enthalpy H_{III} relative to Eq. (28), on the other side, is equal to the enthalpy difference between State III and the reference state, Eq. (28),

TABLE II

THE STABILITY OF $A\mathrm{MnO}_3$ (A = La, Sm, Dy) CALCULATED AT T = 1473 K IS COMPARED WITH THE OBSERVED VALUES (*4*)

A	r_A	$\Delta H°(A)^a$ $h_p = h_c = h_0 = 8.00$	$\mathrm{St}(A\mathrm{MnO}_3)$ $h_p = h_c = h_0 = 8.00$	$\Delta H°(A)^a$ $h_p = 8.026$, $h_c = h_0 = 8.00$	$\mathrm{St}(A\mathrm{MnO}_3)$ $h_p = 8.026$, $h_c = h_0 = 8.00$	$\mathrm{St}(A\mathrm{MnO}_3)_{\mathrm{obs}} = -\log P^*_{\mathrm{O}_2}$
La	1.216	34.18	10.73	35.71	11.64	11.65
Sm	1.132	29.32	7.85	30.87	8.77	8.51
Dy	1.083	25.06	5.32	26.62	6.24	6.60

[a] $\Delta H° = \Delta H°(A)$ is given in kcal/mole.

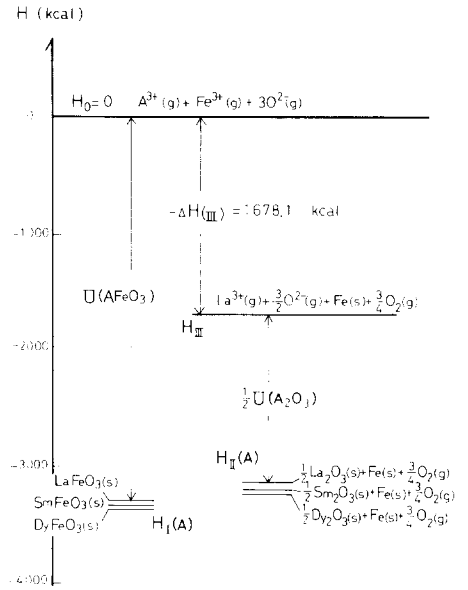

FIG. 3. An enthalpy diagram for reaction Eq. (3). The standard enthalpy change $\Delta H°(A)$, and lattice energies $U(AFeO_3)$ and $U(A_2O_3)$ are shown as enthalpy differences between the states.

which is given by the enthalpy change $\Delta H°(\text{III})$ of the following reaction;

$$Fe^{3+}(g) + \tfrac{3}{2}O^{2-}(g) = Fe(s) + \tfrac{3}{4}O_2(g), \quad (33)$$

with

$$H_{\text{III}} = \Delta H(\text{III}) = -1687.1 \text{ kcal/mole}. \quad (34)$$

The value of Eq. (34) is obtained from the heat of vaporization of Fe(s) = 83.90 kcal/g-atom (*18*), the ionization potentials from Fe(g) to $Fe^{3+}(g)$ = 1261.46 kcal/g-atom (*18*), the dissociation energy of $\frac{3}{4}O_2(g)$ = 89.33 kcal (*18*), and the electron affinity of $\frac{3}{2}O(g)$ = 252.45 kcal (*18*).

Thus, it follows from Eqs. (29), (31), (32), and (34) that

$$\begin{aligned}\Delta H°(A) &= U(AFeO_3) - \tfrac{1}{2}U(A_2O_3) - 1687.1 \text{ kcal/mole} \\ &= \frac{Ne^2M(ABO_3)}{a_p(r_A)}\left(1 - \frac{1}{h_p}\right) - \frac{Ne^2M(AO_{1.5})}{a_c(r_A)}\left(1 - \frac{1}{h_c}\right) - 1687.1 \quad (35)\end{aligned}$$

According to Eqs. (21) and (30), Eq. (35) gives the enthalpy change of the reaction Eq. (3) as a function of ionic radius of A^{3+} ion, r_A.

Putting hardness parameters in Eq. (35) to be $h_p = h_c = 8.00$ and calculating $\Delta H°(A)$ for A = La, Sm, Dy, one obtains the stability $St(AFeO_3) = -\log P^*_{O_2}$ from Eq. (14), which is shown in Table III. The calculated stability order,

$$St(LaFeO_3) > St(SmFeO_3) > St(DyFeO_3), \quad (36)$$

agrees with that observed (*6*), but the value of $St(AFeO_3)$ does not agree with the observed value. If one puts $h_p = 7.45$ and $h_c =$

TABLE III

THE STABILITY OF $AFeO_3$ (A = La, Sm, Dy) CALCULATED AT T = 1473 K IS COMPARED WITH THE OBSERVED VALUES (*6*)

A	r_A	$\Delta H°(A)$‡	$St(AFeO_3)$	$\Delta H°(A)$‡	$St(AFeO_3)$	$St(AFeO_3)_{obs}$
		$h_p = h_c = 8.00$		$h_p = 7.45$ $h_c = 8.00$		$= -\log P^*_{O_2}$
La	1.216	157.49	21.60	122.79	14.74	13.63
Sm	1.132	147.67	19.66	112.45	12.69	12.68
Dy	1.083	140.37	18.21	104.85	11.19	12.11

‡ $\Delta H°(A)$ is given in kcal/mole.

8.00 in Eq. (35) and recalculates $\Delta H°(A)$ and $\mathrm{St}(A\mathrm{FeO_3})$, the agreement between the calculated and the observed $\mathrm{St}(A\mathrm{FeO_3})$ is excellent. This is also shown in Table III.

4. Discussion

4.1. Role of the Repulsion Parameter

The general agreement in the stability $\mathrm{St}(AB\mathrm{O_3})$ of perovskite-type oxides $AB\mathrm{O_3}(A$ = La, Sm, Dy; B = Mn, Fe) between calculated and observed data (see Tables II and III) indicates that the present treatment is valid.

Such agreement in $\mathrm{St}(AB\mathrm{O_3})$ is based on a suitable choice of the unknown hardness parameter h_{p} for $AB\mathrm{O_3}$ in the Born-type repulsion energy in Eq. (16). This choice of the multiplying factor $(1 - 1/h_{\mathrm{p}})$ for the Coulomb energy in Eqs. (17) and (29) is advantageous because it involves the simultaneous adjustment of thermal energy which is reflected on the lattice parameter $a_{\mathrm{p}}(r_A)$ via thermal expansion caused by lattice vibrations and defect formations.

4.2. Effect of A Substitution on St(ABO₃)

In our simple model with a constant standard entropy change $\Delta S° = 44n$ in Eq. (14), the stability order on A substitution in $AB\mathrm{O_3}$ is equal to the order of $\Delta H°(A)$. This approximation is based on the idea that the effect of A substitution on $\Delta S°$ is smaller than that on $\Delta H°(A)$. The variation of $\Delta H°(A)$ according to Eq. (26) or (35) is schematically drawn in Fig. 4 as a function of the ionic radius of A^{3+} ion, r_A. Figure 4 suggests the existence of a maximum $\Delta H°(A)$, i.e., a stability maximum, at a value of r_A greater than that of $\mathrm{La^{3+}}$, $r(\mathrm{La^{3+}}) = 1.216$ Å.

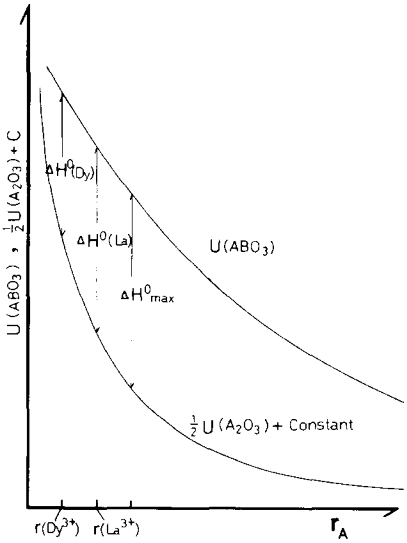

FIG. 4. The standard enthalpy change $\Delta H°(A)$ in terms of lattice energies $U(AB\mathrm{O_3})$ and $U(A_2\mathrm{O_3})$ for decomposition of perovskite $AB\mathrm{O_3}$ as a function of ionic radius of A^{3+} ion, r_A.

4.3. Contribution of Electronic Entropy to ΔS°

The stability $\mathrm{St}(AB\mathrm{O_3}) = -\log P^*_{\mathrm{O_2}}$ in Eq. (14) assumes $\Delta S° = 44n$, which gives $\Delta S° = 11$ cal/deg · mole for $n = \frac{1}{4}$ in the case of $A\mathrm{MnO_3}$ in Eq. (2). The value of assumption $\Delta S° = 11$ cal/deg · mole agrees with the observed value of $\Delta S° = 11.5$ cal/deg · mole for $\mathrm{LaMnO_3}$ (*3*). This agreement is a fortunate case because the contributions of $3d$ electrons from $\mathrm{Mn^{3+}}$ $(3d^4)$ ions via thermal excitations in semiconducting $A\mathrm{MnO_3}$ to its $\Delta S°$ on the left side of Eq. (2) has been canceled by those from $\mathrm{Mn^{2+}}$ $(3d^5)$ ions in semiconducting MnO on the right side of Eq. (2). Consequently, the $3d$ electrons contribute little to $\Delta S°$ and do not affect the assumption $\Delta S° = 44n$ with $n = \frac{1}{4}$.

In the case of $A\mathrm{FeO_3}$ on the other hand, the contribution of $3d$ electrons from $\mathrm{Fe^{3+}}$ $(3d^5)$ ions in semiconducting $A\mathrm{FeO_3}$ to its $\Delta S°$ on the left side of Eq. (3), however, does not cancel with those in metallic Fe on the right side of Eq. (3) because of the Fermi–Dirac distribution of electrons in Fe. This is the reason why the observed values of $\Delta S°$ for $A\mathrm{FeO_3}$ (*6*) are smaller than $\Delta S° = 44n = 33$ cal/deg · mole, with $n = \frac{3}{4}$

TABLE IV

THE STANDARD CHANGES ΔS° AND ΔH° CALCULATED FROM THE OBSERVED ΔG° AT T = 1473 AND 1523 K (*7*)

$A\mathrm{FeO}_3$	ΔG° (kcal/mole) 1473 K	ΔG° (kcal/mole) 1523 K	ΔS°	ΔH° (kcal/mole)
$LaFeO_3$	68.9	67.5	28.0	110.1
$NdFeO_3$	65.7	64.1	32.0	112.8
$SmFeO_3$	64.1	62.7	28.0	105.3
$EuFeO_3$	63.3	62.0	26.0	101.6
$GdFeO_3$	63.1	61.7	28.0	104.3
$TbFeO_3$	61.8	60.7	22.0	94.2
$DyFeO_3$	61.2	59.9	24.0	99.5
$HoFeO_3$	60.5	59.2	26.0	98.8
$TmFeO_3$	58.7	57.4	26.0	97.0
$LuFeO_3$	57.5	56.1	28.0	98.7

Note. The ΔS° is smaller than the value of 33 cal/deg · mole expected from Eq. (13).

expected from Eq. (*13*). Table IV shows the ΔS° and ΔH° for $A\mathrm{FeO}_3$ on decomposition Eq. (3) which were calculated from the observed values of ΔG° at T = 1473 and 1523 K by Katsura *et al.* (*7*). The effect of 4*f* electrons on ΔS° is neglected in the present discussion because they are hardly excited, and if they are thermally excited their effects cancel on both sides of Eq. (3).

5. Conclusions

Thermostatistical discussions indicate that the isothermal decomposition of any type of ternary oxide $A_xB_yO_z$ into a biphasic solid mixture $[A,B,\mathrm{O}]$ at a constant pressure,

$$A_xB_yO_z(\mathrm{s}) = [A,B,\mathrm{O}](\mathrm{s}) + n\mathrm{O}_2(\mathrm{g}), \quad \text{(I)}$$

is driven by the mixing entropy $\Delta S_\mathrm{m} = -nR \ln P_{O_2}$ of the total entropy change of Eq. (I) $\Delta S = \Delta S^\circ + \Delta S_\mathrm{m}$, where ΔS° is the standard entropy change.

The stability of $A_xB_yO_z$ toward isothermal decomposition of Eq. (I)

$$\mathrm{St}(A_xB_yO_z) = -\log P^*_{O_2} = \frac{\Delta H^\circ - T\Delta S^\circ}{2.303\, nRT}, \quad \text{(II)}$$

contains two independent variables, ΔH° and ΔS°. ΔH° is strongly dependent upon the structures of the solid phases, whereas ΔS° depends strongly on the quantity of liberated O_2 and depends weakly on the solid structures. Therefore, in the approximation of putting $\Delta S^\circ = 44n$, the stability Eq. (II) is controlled only by the factor $\Delta H^\circ/n$.

The stability of perovskite-type ABO_3 on A substitution is approximately calculable from $\Delta H^\circ = \Delta H^\circ(A)$ in terms of lattice energies of solid phases, e.g., $U(ABO_3)$ and $U(A_2O_3)$, upon the assumption of $\Delta S^\circ = 44n$.

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