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Estimation of The Standard Entropy Change on Complete Reduction of Oxide M_mO_n

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The standard entropy change $\Delta S°$ for the reduction of nonmagnetic, nonconducting oxides, $M_mO_n(s) = mM(s) + (n/2)O_2(g)$, has been estimated as a function of m, n, and temperature T from motional entropies of oxygen molecules and vibrational entropies of solid phases. An available formula of $\Delta S°_{calc} = a \cdot m + b \cdot n$ with constant a and b based on effective Debye temperatures, $\Theta_M = 165$ K for M and $\Theta_{OX} = 540$ K for M_mO_n, agrees well with the observed $\Delta S°_{obs}$ for M_2O, MO, M_2O_3, MO_2, M_2O_5, and MO_3 in the temperature range $T = 300$–1300 K. Possible electronic entropy corrections are applied to $\Delta S°_{calc}$ for M_2O_7 and MO_4.

1. Introduction

It is known that the standard entropy change $\Delta S°$ of a chemical equilibrium among the condensed phases is generally small compared to the change $\Delta S°$ of an equilibrium involving a release of gas. Schmalzried and Navrotsky (*1*) noticed a relative constancy of $\Delta S° = -22 \pm 4$ (cal/deg · mole) for standard formation reactions such as $M(s) + \frac{1}{2}O_2(g) = MO(s)$. They correlated the value $\Delta S° = -22 \pm 4$ (cal/deg · mole) with the molar standard entropy of oxygen gas to be $\Delta S° \simeq -\frac{1}{2}S°_{O_2}$.

Table I shows the standard entropy change $\Delta S°_{obs}$ of the following chemical equilibrium

$$M_mO_n(s) = mM(s) + (n/2)O_2(g) \quad (1)$$

for various nonmagnetic, nonconducting oxides obtained from thermochemical data (*2–4*). An inspection of Table I shows a systematic decrease in the entropy change per oxygen atom ($T = 300$ K) from $\Delta S°/n \simeq 31$(cal/deg · mole) for M_2O to $\Delta S°/n \simeq 18$ (cal/deg · mole) for MO_4, which suggests systematic variation of $\Delta S°/n$ rather than a constant value of $\Delta S° = 22n$ (cal/deg · mole) for Eq. (1). The thermochemistry gives formally the standard entropy change of Eq. (1) in the form

$$\Delta S° = [mS°(M) + (n/2)S°_{O_2}] - S°(M_mO_n), \quad (2)$$

where $S°(M)$, $S°_{O_2}$, and $S°(M_mO_n)$ are molar standard entropies of the respective phases.

The present paper proposes that the entropy change in Eq. (2) be written in the form $\Delta S° = a \cdot m + b \cdot n$ (a,b = constants under a constant temperature) for nonmagnetic, nonconducting oxides M_mO_n via taking the effects of vibrational entropies of solid phases into account. This paper also

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TABLE I

STANDARD ENTROPY CHANGE ΔS°_{obs} FOR $M_mO_n(s) = mM(s) + (n/2)O_2(g)$[a]

ΔS°_{calc}	T (K)	ΔS°_{obs} (cal/deg · mole)					
M_2O		Li_2O	Na_2O	K_2O			
32.6	300	29.36	31.02	32.91			
31.4	800	31.64[b]	31.57[b]	30.71[b]			
31.2	1300	28.7[b]					
MO		BeO	MgO	CaO	SrO	BaO	ZnO
25.9	300	23.41	25.88	24.95	24.00	23.90	24.05
24.4	800	23.34	25.39	24.19	22.73	23.64	
23.9	1300	22.80					
M_2O_3		B_2O_3	Al_2O_3	Sc_2O_3	Y_2O_3	La_2O_3	Ga_2O_3
71.0	300	63.41	74.87	73.02[c]	71.06	70.09	72.84
66.2	800		74.12	70.47[c]	67.85	66.51	
64.3	1300			69.64[c]	66.40		
MO_2		SiO_2	TiO_2	ZrO_2	HfO_2	CeO_2	ThO_2
45.1	300	43.41	44.35	46.27	45.31	49.60	46.16
41.8	800	42.18	42.84	44.52	42.54	48.23	44.10
40.4	1300	41.19	42.78	44.22	40.98		43.14
M_2O_5		P_2O_5	V_2O_5	Nb_2O_5	Ta_2O_5	As_2O_5	Sb_2O_5
109.4	300	106.08	104.96	107.10	108.10	114.12	114.38
101.0	800	100.71	98.29	101.67	102.01		
97.3	1300			97.85	97.34		
MO_3		MoO_3	WO_3	UO_3			
64.3	300	61.73	63.17	61.92			
59.2	800	58.12	59.61	59.00			
56.9	1300		56.79				
M_2O_7		Re_2O_7					
147.8	300	139.6[d]					
MO_4		RuO_4	OsO_4				
83.5	300	69.83[d]	71.41[d]				

[a] Obtained from thermochemical data (*2*) and compared with those from Eq. (10): $\Delta S^\circ_{calc} = 6.68m + 19.21n$ ($T = 300$ K), etc.

[b] Entropy of fusion ΔS_f was corrected for metals M since it is molten.

[c] Standard entropies S°_M for Sc were taken from Ref. (*4*).

[d] Data were taken from Ref. (*3*) for $T = 298$ K.

examines possible contributions of electronic entropies.

2. Entropy Generation via Oxygen Release

Statistical thermodynamics gave the entropy per mole of a perfect gas G as follows (*5*),

$$S_G = R\left[\frac{5}{2} + \frac{5}{2}\ln T - \ln P + \ln\frac{(2\pi m_G)^{3/2}k^{5/2}}{h^3}\right] + R\frac{d}{dT}[T\ln Z_G(T)], \quad (3)$$

where $R = 1.987$ (cal/deg · mole) is the gas constant, m_G the mass of molecule G, $k = 1.3806 \times 10^{-16}$ (erg/deg) the Boltzmann constant, $h = 6.6262 \times 10^{-27}$ (erg · sec) Plank's constant, $P = 1$ bar $= 1{,}013{,}250$ (dynes/cm^2) the pressure and $Z_G(T)$ the internal partition function of the molecule G.

The rotational partition function Z_{rot} for a diatomic oxygen molecule for high-temperature limit is given by (5)

$$Z_{rot} = \frac{8\pi^2 IkT}{h^2}, \quad \text{with} \quad \Theta_{rot} = \frac{h^2}{4\pi^2 Ik} = 4.17 \text{ K}, \tag{4}$$

while the vibrational partition function for the oxygen molecule is given by (5)

$$Z_{vib} = \exp(-h\nu/2kT)[1 - \exp(-h\nu/kT)], \quad \text{with } \Theta_{vib} = h\nu/k = 2260 \text{ K}, \tag{5}$$

where I is the moment of inertia and ν the vibrational frequency of the oxygen molecule. Putting $m_G = 32.00 \times 1.6605 \times 10^{-25}$g and inserting it with the other numerical constants into Eq. (3), the entropy per mole of oxygen gas is given by

$$\begin{aligned} S^\circ_{O_2}(T) &= S_{trans} + S_{rot} + S_{vib} \\ &= R\left[4.034 + \frac{5}{2}\ln T\right] \\ &\quad + R\left[1 + \ln\frac{2T}{\Theta_{rot}}\right] \\ &\quad + R\left[\frac{\Theta_{vib}}{2T}\coth\frac{\Theta_{vib}}{2T} - \ln 2\sinh\frac{\Theta_{vib}}{2T}\right]. \end{aligned} \tag{6}$$

This entropy is considered to provide the standard entropy per mole of oxygen because the entropy due to electronic excitations is negligible. Thus, one obtains the entropy increase on liberation of $n/2$ moles of oxygen $(n/2)S^\circ_{O_2}$ as a function of T. The entropies calculated from Eq. (6) $S^\circ_{O_2}$ are compared with the observed ones (2) in Table II for T = 300, 800, and 1300 K.

TABLE II

STANDARD ENTROPIES OF OXYGEN $S^\circ_{O_2}$ (cal/deg · mole) CALCULATED FROM EQ. (6) AND COMPARED WITH THOSE S°_{obs} (cal/deg · mole) FROM REF. (2)

T (K)	S_{trans}	S_{rot}	S_{vib}	$S^\circ_{O_2}$	S°_{obs}	$\frac{1}{2}S^\circ_{O_2}$
300	36.348	11.860	0.009	48.217	49.048	24.11
800	41.221	13.809	0.475	55.505	56.380	27.75
1300	43.632	14.774	1.121	59.527	60.337	29.76

3. Role of Lattice Vibration in Entropy Change ΔS°

The Debye theory of specific heat gives the entropy of every solid due to its lattice vibration $S_L(\Theta_D/T)$ as a function of $x = \Theta_D/T$ irrespective of its crystal structure or its chemical kind (6);

$$\begin{aligned} S_L(x) &= \int_0^T \frac{C_v}{T}\,dT \\ &= R\left[\frac{12}{x^3}\int_0^x \frac{y^3}{e^y - 1}\,dy - 3\ln(1 - e^{-x})\right], \end{aligned} \tag{7}$$

where C_v is its specific heat per gram-atom under a constant volume and Θ_D its characteristic (Debye) temperature. The one-to-

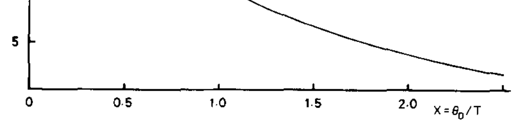

FIG. 1. Entropy $S_L(x)$ in (cal/deg · g-atom) associated with lattice vibration is drawn as a function of $x = \Theta_D/T$.

one correspondence between $x = \Theta_D/T$ and $S_L(x)$ is shown in Fig. 1 which is based on the numerical table in Ref. (*6*).

Since electronic entropies are negligibly small for metals M with Fermi temperatures of $T_F \simeq 5 \times 10^4$ K (*7*) and also for nonmagnetic, nonconducting oxides M_mO_n at relatively low temperatures, the molar standard entropies of solid phases in Eq. (2) are mostly made of their vibrational entropies. In the simple Debye model both cations and anions in oxide M_mO_n take part equally in the thermal vibration. Hence 1 mole of M_mO_n can be regarded as if it is made of $(m + n)$ gram-atoms of the same kind of atoms. Therefore, it follows that

$$S^\circ(M) = S^\circ_M(\Theta_M/T)$$

$$\text{and} \quad S^\circ(M_mO_n) = (m + n)S^\circ_{OX}(\Theta_{OX}/T), \quad (8)$$

where $S^\circ_M(\Theta_M/T)$ and $S^\circ_{OX}(\Theta_{OX}/T)$ respectively are vibrational entropies per $N_0 = 6.022 \times 10^{23}$ atoms of M and M_mO_n. Thus, it follows from Eqs. (2) and (8) that

$$\Delta S^\circ(T) = [S^\circ_M(\Theta_M/T) - S^\circ_{OX}(\Theta_{OX}/T)]m + [\tfrac{1}{2}S^\circ_{O_2}(T) - S^\circ_{OX}(\Theta_{OX}/T)]n. \quad (9)$$

Equation (9) gives the entropy change on reduction of oxide M_mO_n in question as functions of m, n, and T.

The spread of Debye temperature Θ_M is appreciable even for metals (*6*) ranging from 38 K for Cs to 630 K for Cr. The highest $\Theta_M = 1440$ K for Be may be an exception. Little is known of the Debye temperature Θ_{OX} for oxides (*4*, *6*). The known examples of Θ_{OX} are listed in Table III, together with their corresponding entropy change $\Delta S^\circ(T)$ calculated from Eq. (9) using $S^\circ_{O_2}(T)$ in Table II and $S^\circ_L(x)$ in Ref. (*6*).

ΔS°_{calc} for BeO, MgO, TiO_2, and Fe_2O_3

TABLE III

CALCULATION OF THE ENTROPY CHANGE ΔS°_{calc} ACCORDING TO EQ. (9) BY USE OF THE REPORTED DEBYE TEMPERATURES Θ_{OX} AND Θ_M (*4*, *6*)

T (K)	M_mO_n	Θ_{OX} (K)	S°_{OX}	M	Θ_M (K)	S°_M	ΔS°_{calc}	ΔS°_{obs}
300	BeO	1553[b]	0.901	Be	1440	1.068	23.38	23.41
800	BeO	1553	4.523	Be	1440	4.901	23.61	23.34
1300	BeO	1553	7.096	Be	1440	7.519	23.09	22.80
300	MgO	946	2.366	Mg	400	6.496	25.87	25.88
800	MgO	946	7.155	Mg	400	12.117	25.56	25.39
300	SiO_2	470	5.624	Si	640	4.062	35.41	43.41
800	SiO_2	470	11.180	Si	640	9.372	31.33	42.18
1300	SiO_2	470	14.089	Si	640	12.218	29.47	41.19
300	TiO_2	760	3.268	Ti	420	6.225	44.64	44.35
800	TiO_2	760	8.395	Ti	420	11.849	42.16	42.84
1300	TiO_2	760	11.211	Ti	420	14.745	40.63	42.78
300	Y_2O_3	178[b]	11.121	Y	280	8.497	33.72	71.06
300	Fe_2O_3	660	3.913	Fe	467	5.659	64.08	65.57
800	Fe_2O_3	660	9.203	Fe	467	11.220	59.68	60.04
1300	Fe_2O_3	660	12.035	Fe	467	14.129	57.36	59.70

Note. Entropies are described in calories per degree per mole.

[b] The data were taken from Ref. (*4*).

agrees well with the observed ΔS°_{obs}, whereas the descrepancies between ΔS°_{calc} and ΔS°_{obs} are considerable for SiO_2 and Y_2O_3. This author has no evidence for the present to judge whether the descrepancies come from the inadequacy of the simple Debye model to describe vibrations in the SiO_2 and Y_2O_3 frameworks or from the inadequacy of the reported values of Θ_{OX} for SiO_2 (*6*) and Y_2O_3 (*4*) to characterize their vibrations in terms of the simple Debye model.

4. Available Solutions for Entropy Change ΔS°

Because of the irregularities of Debye temperatures in both metals and oxides, no rigorous guiding principles for choosing the typical values of Θ_M and Θ_{OX} have been found.

For convenience and simplicity, the effective Debye temperature for every metal M in Eq. (1) is a priori set equal to Θ_M = 165 K and that for every oxide M_mO_n to Θ_{OX} = 540 K. Then, referring to Table II for $S^\circ_{O_2}$ and Fig. 1 or the numerical table in Ref. (*6*) for S°_M and S°_{OX}, one can evaluate the Eq. (9) to be

$$\begin{aligned}\Delta S^\circ &= 6.68m + 19.21n \text{ cal/deg} \cdot \text{mole} \\ &\qquad (T = 300\text{ K}), \\ \Delta S^\circ &= 7.03m + 17.38n \text{ cal/deg} \cdot \text{mole} \\ &\qquad (T = 800\text{ K}), \\ \Delta S^\circ &= 7.33m + 16.53n \text{ cal/deg} \cdot \text{mole} \\ &\qquad (T = 1300\text{ K}). \quad (10)\end{aligned}$$

The numerical values ΔS°_{calc} calculated from Eq. (10) for M_mO_n were already tabulated in Table I, which agree generally well with the observed data ΔS°_{obs} except for oxides M_2O_7 and MO_4.

5. Effects of Electronic Excitations on ΔS°

Disagreements of Eq. (10) in Table I with the observed entropy change ΔS°_{obs} in oxides of high-valence cations such as M_2O_7 and MO_4 may be caused by a thermal electronic excitation via a transient radiationless electron transfer from a closed shell anion O^{2-} into its neighboring cation $M^{(2n/m)+}$ as shown schematically in Fig. 2.

It is tentatively postulated that the *i*th electronic excitation energy E_i (i = 1,2) in M_mO_n is lower for the oxide with higher valence cation $M^{(2n/m)+}$, and is inversely proportional to the cation valence

$$E_i = \frac{m}{n} E_i^0. \qquad (11)$$

The probability of the electronic excitations in Fig. 2, on the other hand, is proportional to the coordination number $C(m/n)$, the number of cations $M^{(2n/m)+}$ around an oxygen ion O^{2-}, which is assumed to be

$$C\left(\frac{m}{n}\right) = 6 \times \frac{m}{n}, \qquad (12)$$

through oxide series from M_2O to MO_4.

From the assumptions in Eqs. (11) and (12), the electronic partition function for an oxygen ion in M_mO_n is written as functions of m/n and T;

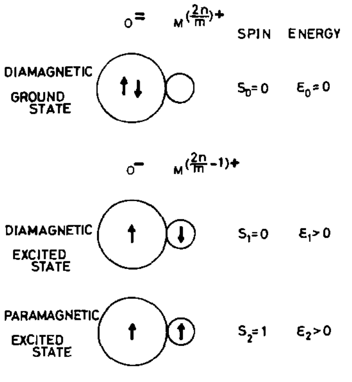

FIG. 2. Possible electronic excitations in oxide of high valence cation $M^{(2n/m)+}$ with rare-gas-type outer electronic shell.

$$
\begin{aligned}
Z_e &= \sum_{i=0}^{2} C_i(m/n)\cdot(2S_i+1)\cdot\exp(-E_i/kT) \\
&= 1 + 6\cdot(m/n)\cdot\exp[-(m/n)(E_1^\circ/kT)] \\
&\quad + 18\cdot(m/n)\cdot\exp[-(m/n)(E_2^\circ/kT)], \qquad (13)
\end{aligned}
$$

where $(2S_i + 1)$ is the spin multiplicity for the ith excited state, and $S_0 = 1$, $C_0(m/n) = 1$, $E_0 = 0$ for the ground state.

If the electronic excitations in individual oxygen ions in M_mO_n are independent of each other, statistical thermodynamics gives the Helmholtz free energy A_e of the electronic state of the whole system M_mO_n,

$$A_e = -kT \ln [Z_e]^{nN_0} = -nRT \ln Z_e, \qquad (14)$$

and its corresponding electronic entropy,

$$
\begin{aligned}
S_e(\mathrm{OX}) &= -\left(\frac{\partial A_e}{\partial T}\right)_v \\
&= nR \ln Z_e + \frac{nR}{Z_e}\left(\frac{\partial Z_e}{\partial T}\right)_v. \qquad (15)
\end{aligned}
$$

On reduction of M_mO_n according to Eq. (1), $2nN_0$ valence electrons on the oxygen ions are returned to metallic band in metal M. Since the electron specific heat for N free electrons obeying the Fermi–Dirac distribution law is known as (7)

$$C_e = (\pi^2/2)NkT/T_F,$$

the contribution of the $2nN_0$ electrons to the electronic entropy of M is given by

$$S_e(M) = \int (C_e/T)dT = \pi^2\, nRT/T_F, \qquad (16)$$

which amounts to

$$S_e(M) = 0.1177\, n \text{ (cal/deg} \cdot \text{mole)}$$

at $T = 300$ K for the Fermi temperature of $T_F = 5 \times 10^4$ K.

In order to fit in the observed entropy change $\Delta S^\circ_{\mathrm{obs}}$ of M_mO_n in Table I for $T = 300$ K, the coefficients of m and n of the entropy change due to atomic motions ΔS°_a in Eq. (9) for $T = 300$ K are chosen as

$$\Delta S^\circ_a = 6m + 20n \text{ (cal/deg} \cdot \text{mole)}. \qquad (17)$$

Their relating Debye temperature $\Theta_M = 207$ K ($S^\circ_M = 10.23$ cal/deg · mole) and $\Theta_{\mathrm{OX}} = 618$ K ($S^\circ_{\mathrm{OX}} = 4.23$ cal/deg · mole) seem to be quite normal for mean values of metal M and oxide M_mO_n.

Finally, it follows from Eqs. (15), (16), and (17) that the total entropy change ΔS° for Eq. (1) is given by

$$
\begin{aligned}
\Delta S^\circ &= \Delta S^\circ_a + \Delta S^\circ_e \\
&= \Delta S^\circ_a + S_e(M) - S_e(\mathrm{OX}). \qquad (18)
\end{aligned}
$$

Setting a priori, $E_1^\circ/kT = 9$ ($E_1^\circ = 0.233$ eV $= 5.37$ kcal for $T = 300$ K) and $E_2/kT = 12$ ($E_2^\circ = 0.310$ eV $= 7.15$ kcal for $T = 300$ K) in Eq. (13), one can evaluate $S_e(\mathrm{OX})$ from Eq. (15) as a function of m/n. In Table IV are listed the calculated entropies ΔS°_a from Eq. (17), $S_e(\mathrm{OX})$ from Eq. (15), $S_e(M)$ from Eq. (16) and the total entropy change ΔS° from Eq. (18).

Although its value is negligibly small compared to the total entropy change ΔS°, the electronic entropy of valence electrons in the metallic bond $S_e(M) = 0.118\, n$ is really present in all cases in Table IV, if one onece accepts the Fermi–Dirac distribution of electrons in metals, in contrast with a rather hypothetical entropy $S_e(\mathrm{OX})$ illustrated in Fig. 2.

Conclusions

Standard entropy change ΔS° on reduction of oxides of cations with rare-gas-type outer electronic shells, $M_mO_n(\mathrm{s}) = mM(\mathrm{s}) + (n/2)O_2(\mathrm{g})$, was shown to have a linear form of $\Delta S^\circ = a(T) \cdot m + b(T) \cdot n$ and to be calculable from motional entropies of oxygen molecules in the gas phase and vibrational entropies of solid phases if the correct average characteristic temperature of each phase are given.

An effective formula is available for the entropy change $\Delta S^\circ_{\mathrm{cal}} = a \cdot m + b \cdot n$ if one assumes constant Debye temperatures, $\Theta_M = 165$ K for every metal M and $\Theta_{\mathrm{OX}} = 540$ K for every oxide M_mO_n. It shows good agreement with the observed $\Delta S^\circ_{\mathrm{obs}}$ for ox-

TABLE IV

ESTIMATED TOTAL ENTROPY CHANGE ΔS° FOR $M_mO_n(s) = mM(s) + n/2 \cdot O_2(g)$ (T = 300 K),[a] BEING CONTRIBUTED BY ATOMIC MOTIONS ΔS_a° FROM EQ. (17) AND ELECTRONIC EXCITATIONS $\Delta S_e^\circ = S_e(M) - S_e(OX)$ FROM EQS. (15) AND (16)[a]

M_mO_n	M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_4
n	1	1	3	2	5	3	7	4
m/n	2	1	2/3	1/2	2/5	1/3	2/7	1/4
ΔS_a°	32	26	72	46	112	66	152	86
$S_e(OX)$	0	$0.0176\,n$ $= 0.018$	$0.2072\,n$ $= 0.623$	$0.6418\,n$ $= 1.28$	$1.153\,n$ $= 5.77$	$1.591\,n$ $= 4.77$	$1.909\,n$ $= 13.37$	$2.121\,n$ $= 8.48$
$S_e(M)$	0.118	0.118	0.353	0.235	0.588	0.353	0.824	0.471
ΔS°	32.1	26.1	71.7	45.0	106.8	61.6	139.5	78.0

[a] (Entropies are in cal/deg · mole.)

ides M_2O, MO, M_2O_3, MO_2, M_2O_5, and MO_3.

A possible entropy correction caused by electronic excitations, which are nonlinear in m and n, was applied to the estimation scheme in order to fit the $\Delta S_{\text{obs}}^\circ$ of all type of oxides including M_2O_7 and MO_4.

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