

# High-Temperature Vaporization Behavior of Oxides II. Oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, Zn, Cd, and Hg

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# High-Temperature Vaporization Behavior of Oxides II. Oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, Zn, Cd, and Hg

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In order to assess the high-temperature vaporization behavior and equilibrium gas phase compositions over the condensed oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, Zn, Cd, and Hg, the relevant thermodynamic and molecular constant data have been compiled and critically evaluated. Selected values of the Gibbs energy functions of condensed and vapor phases are given in the form of equations valid over wide temperature ranges, along with the standard entropies and enthalpies of formation. These data were used to generate plots of equilibrium partial pressures of vapor species as functions of temperature for representative environmental conditions ranging from reducing to oxidizing. The calculated partial pressures and compositions agree, for the most part, with experimental results obtained under comparable conditions. Maximum vaporization rates have been calculated using the Hertz-Knudsen equation. Literature references are given.

Key words: critically reviewed data; enthalpy increment; enthalpy of formation; entropy; Gibbs energy function; high temperature; oxide; partial pressure; thermodynamic data; vaporization; vaporization rate.

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## 1. Introduction

### 1.1. Background

Oxide materials are used or encountered in a wide variety of high-temperature applications where vaporization rates and thermodynamic stabilities are often limiting factors. The efficient design and operation of high-temperature devices and processes requires reliable information about the stability and volatility of these oxides so that vaporization losses and component lifetimes can be predicted.

Despite continuing research efforts and the use of increasingly sophisticated techniques, there are still many gaps in our knowledge and understanding of the detailed vaporization thermodynamics of metal oxide systems. This puts a premium on critical review of the literature and selection of the necessary thermodynamic data. However, even in

cases where most of the requisite data are compiled, the user must resort to a significant amount of additional calculations, sometimes unfamiliar, in order to evaluate vapor composition and vaporization behavior for specific environmental conditions. Thus we perceive a definite need for critically evaluated data, presented in a format that gives users ready access to the detailed vaporization chemistry and equilibrium partial pressures of the various species. To this end, we present graphs of species partial pressures as functions of temperature under representative reducing, neutral, and oxidizing environments. We also give equations for calculating partial pressures and maximum vaporization rates for arbitrary conditions of temperature and oxygen potential.

The present work is the second publication in a program sponsored by the Office of Standard Reference Data of the National Bureau of Standards to provide critically re-

viewed thermodynamic data of oxides, along with overviews of their high-temperature vaporization phenomena. The previous article (Lamoreaux and Hildenbrand, 1984) on alkali metal oxide systems discussed the scope of the program, the relevant literature, methods of data evaluation, and the mathematics of vaporization calculations. This article covers oxide systems of the elements Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, Zn, Cd, and Hg.

Readers should note that revised JANAF Thermodynamic Tables (Chase *et al.*, 1985), the final CODATA Key Values for Thermodynamics, and the CODATA Thermochemical Tables (Garvin *et al.*, 1987) have been in preparation in the same time period as the present work and should appear concurrently. The minor differences in selected values of thermodynamic properties are immaterial to the purpose of this paper.

## 2. Properties of Individual Systems

### 2.1. Data Evaluation, Units, and Symbols

Molecular constants cited in the text are internuclear distances  $r$  in nm, vibrational wavenumbers  $\omega$  in  $\text{cm}^{-1}$ , the molecular symmetry number  $\sigma$ , electronic state quantum weights  $g_i$ , and excited electronic state term values  $T_e$  in  $\text{cm}^{-1}$ . Thermodynamic quantities are expressed in dimensionless units, e.g.,  $S^\circ/R$ ,  $G^\circ/RT$ , or in kelvin units, e.g.,  $\Delta H^\circ/R$ ,  $\Delta G^\circ/R$ . The symbols K and kK, where  $1 \text{ kK} = 10^3 \text{ K}$ , are used to represent kelvin units. Values of  $R$  used in the present work are  $1.987\ 19 \text{ cal/mol K}$  and  $8.3144 \text{ J/mol K}$ . The standard state pressure was taken as 1 atm ( $1.013\ 25 \times 10^5 \text{ Pa}$ ), although the unit for computed vaporization partial pressures is the bar ( $10^5 \text{ Pa}$ ).

The thermodynamic symbols used in the present work are the following:

$\Delta_f H_{298}^\circ/R$

The standard molar enthalpy of formation at 298.15 K divided by the molar gas constant. Units = kelvins.

$(H_{298}^\circ - H_0^\circ)/R$

The standard molar enthalpy increment between 0 and 298.15 K divided by the molar gas constant. Units = kelvins.

$-(G_T^\circ - H_{298}^\circ)/RT$  The standard molar Gibbs energy function divided by the molar gas constant.

$S_T^\circ/R$

The standard molar entropy at  $T$  K divided by the molar gas constant.

$T_{us}, \Delta_{us} H^\circ/R$

Solid-phase transition temperature and standard molar enthalpy of transition divided by the molar gas constant.

$T_{fus}, \Delta_{fus} H^\circ/R$

Melting temperature and standard molar enthalpy of fusion divided by the molar gas constant.

### 2.2. Thermodynamic Data and Vaporization Equilibria

Selected values of thermochemical properties of the relevant chemical species involved in the high-temperature vaporization equilibria are shown in Tables 1–3. Table 1 lists the reported melting points and enthalpies of fusion of high-temperature oxide phases. Table 2 presents Gibbs energy functions fit to the equation

$$-(G_T^\circ - H_{298}^\circ)/RT = A + BT + CT^2 + DT^3 + ET^4. \quad (1)$$

Values of  $\Delta_f H_{298}^\circ/R$ ,  $S_{298}^\circ/R$ , and  $(H_{298}^\circ - H_0^\circ)/R$  are presented in Table 3.

After careful review and comparison of the literature, Vols. 2 and 3 of the IVTAN compilation (Glushko *et al.*, 1978, 1979a, 1981, 1983) and recent JANAF (Stull *et al.*, 1971) supplements (Chase *et al.*, 1974, 1975, 1978, 1982, and dated individual issues) were chosen as the primary sources of data for the oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Tl, Si, Ge, Sn, and Pb. This choice was due to the uniform coverage of the recent literature and to the thoroughness of the reviews presented; agreement of recent JANAF issues with the IVTAN selected values is excellent. Other literature examined included reviews cited in the first paper (Brewer, 1953; Coughlin, 1954; Kelley, 1960; Schick, 1960; Ackermann and Thorn, 1961; Brewer and Rosenblatt, 1961; Kelley and King, 1961; Olette and Ancey-Moret, 1963; Wicks and Block, 1963; Brewer and Rosenblatt, 1969; Barin and Knacke, 1973; Samsonov *et al.*, 1978) and the 1982 NBS compilation (Wagman *et al.*, 1982). As described below, data from the selected sources were supplemented by our own analyses for a few of the minor gaseous species not

Table 1. Melting temperatures and enthalpies of fusion of oxide phases <sup>a</sup>

	$T_{fus}$ (K)	$\Delta_{fus} H/R$ (kK)
BeO	2851 $\pm$ 12	10.3 $\pm$ 0.7
MgO	3100 $\pm$ 25	9.3 $\pm$ 0.7
CaO	2900 (-50,+300)	6.3 $\pm$ 0.6
SrO	2930 $\pm$ 30	8.4 $\pm$ 0.8
BaO	2290 $\pm$ 30	7.1 $\pm$ 0.7
B <sub>2</sub> O <sub>3</sub>	723 $\pm$ 1	2.95 $\pm$ 0.02
Al <sub>2</sub> O <sub>3</sub>	2327 $\pm$ 4	13.40 $\pm$ 0.36
Ga <sub>2</sub> O <sub>3</sub>	2080 $\pm$ 20	12.0 $\pm$ 2.4
In <sub>2</sub> O <sub>3</sub>	2186 $\pm$ 10	12.6 $\pm$ 1.2
Tl <sub>2</sub> O	852 $\pm$ 10	3.64 $\pm$ 0.12
Tl <sub>2</sub> O <sub>3</sub>	1107 $\pm$ 10	6.37 $\pm$ 1.20
SiO <sub>2</sub> (qu)	1726 $\pm$ 10	0.9 $\pm$ 0.1
SiO <sub>2</sub> (cr)	1996 $\pm$ 5	1.15 $\pm$ 0.25
GeO <sub>2</sub>	1388 $\pm$ 3	2.07 $\pm$ 0.3
SnO	1250 $\pm$ 30	3.33 $\pm$ 0.6
SnO <sub>2</sub>	1903 $\pm$ 10	2.81 $\pm$ 0.6
PbO	1160 $\pm$ 10	3.08 $\pm$ 0.05
ZnO	2242 $\pm$ 25	
CdO	>1500	

<sup>a</sup>See Table 4 for references.

Table 2. Gibbs energy function equation parameters<sup>a</sup>

	(G° - H° <sub>298</sub> )/RT = A + BT + CT <sup>2</sup> + DT <sup>3</sup> + ET <sup>4</sup>					
	A	10 <sup>3</sup> B	10 <sup>6</sup> C	10 <sup>9</sup> D	10 <sup>12</sup> E	T range, K
O(g)	20.151 18.210	-7.110 3.296	19.800 -1.0262	-18.16 0.2027	5.987 -0.01724	298-1000 1000-3000
O <sub>2</sub> (g)	25.757 22.987	-9.743 4.5769	26.812 -1.2107	-24.157 0.2154	7.8845 -0.01666	298-1000 1000-3000
O <sub>3</sub> (g)	30.370 26.052	-14.222 7.018	38.373 -1.806	-33.85 0.3086	10.885 -0.01934	298-1000 1000-3000
Be( <sup>n</sup> )	2.034	-7.475	19.873	-17.976	5.957	298-1000
Be( <sup>n</sup> , <sup>l</sup> )	8.537	-24.584	31.968	-16.899	3.292	1000-1560
Be(l)	-3.236	7.078	-2.489	0.5080	-0.0430	1560-3000
Be(g)	17.144 15.252	-6.845 3.199	18.997 -0.377	-17.344 0.1904	5.697 -0.01602	298-1000 1000-3000
BeO(s)	2.967 -0.674	-10.99 5.719	28.75 -1.379	-24.57 0.223	7.723 -0.0138	298-1000 1000-2851
BeO(l)	-7.346	9.280	-1.810	0.21594	-0.01098	2851-4400
BeO(g)	24.867 21.973	-9.832 4.9765	27.028 -1.4770	-24.330 0.3176	7.933 -0.0281	298-1000 1000-3000
Be <sub>2</sub> O(g)	29.774 24.427	-20.1565 8.0534	54.3939 -2.1884	-50.1244 0.3926	16.7664 -0.0312	298-1000 1000-3000
Be <sub>2</sub> O <sub>2</sub> (g)	32.854 26.667	-22.425 9.150	59.774 -2.102	-54.066 0.312	17.870 -0.020	298-1000 1000-3000
Be <sub>3</sub> O <sub>3</sub> (g)	38.097 28.589	-33.9177 13.9546	89.8539 -3.0033	-80.6047 0.4051	26.4901 -0.0221	298-1000 1000-3000
Be <sub>4</sub> O <sub>4</sub> (g)	40.566 28.776	-40.846 17.0115	107.050 -3.0276	-94.434 0.2743	30.696 -0.0017	298-1000 1000-3000
Be <sub>5</sub> O <sub>5</sub> (g)	96.513	4.049	11.077	-5.7094	0.610	298-2900
Be <sub>6</sub> O <sub>6</sub> (g)	38.503	5.485	14.664	-7.0016	1.001	298-2900
Mg(s)	4.906	-8.577	23.50	-21.153	6.92	298-922
Mg(l)	0.000	8.49	-3.460	0.657		922-1500
Mg(g)	18.632 16.939	-6.845 2.7458	18.997 -0.6073	-17.344 0.06217	5.697 -0.0221	298-1000 1000-3000
MgO(s)	4.853 0.762	-13.977 6.6356	37.705 -1.7527	-33.422 0.3108	10.77 -0.0238	298-1000 1000-3100
MgO(l)	-0.804	5.1067	-0.3615			3100-3500
MgO(g)	26.832 23.16	-10.45 5.90	28.20 -1.175	-24.40 0.1043	7.81 -0.0205	298-1000 1000-3000
Mg <sub>2</sub> (g)	28.571	2.357	0.784	-0.597	0.0973	298-2900
Ca(s)	6.000	-8.551	22.703	-19.356	5.980	298-1115
Ca(l)	-0.150	11.003	-5.641	1.669	-0.205	1115-2000
Ca(g)	18.715 17.84	-2.045 2.537	7.181 -0.5155	-5.2376 0.0494	1.29 -0.0217	298-1500 1500-3000
CaO(s)	6.367 1.882	-15.53 7.3304	42.175 -2.0518	-37.723 0.3837	12.225 -0.0316	298-1000 1000-2900
CaO(l)	0.924	5.922	-0.7316	0.0436		2900-3800
CaO(g)	27.663 24.83	-11.194 4.579	30.70 -0.9895	-27.673 0.1144	9.013 -0.0193	298-1000 1000-3000
Ca <sub>2</sub> (g)	29.904	3.031	0.551	-0.5714	0.098	298-2900
Sr(s)	7.933	-10.5795	28.7422	-26.6189	8.9849	298-1041
Sr(l)	2.377	9.314	-4.345	1.2437	-0.1513	1041-2000
Sr(g)	20.556 18.670	-5.845 3.179	18.997 -0.9560	-17.344 0.1807	5.697 -0.01433	298-1000 1000-3000
SrO(s)	8.476 3.963	-15.857 7.379	43.313 -1.9765	-38.867 0.367	12.64 -0.0304	298-1000 1000-2930
SrO(l)	6.386	3.146				2930-3000
SrO(g)	28.947 25.602	-11.39 5.676	31.289 -1.840	-28.261 0.3974	9.22 -0.03455	298-1000 1000-3000
Sr <sub>2</sub> (g)	32.729	2.547	0.1393	-0.329	0.0609	298-2900
Sr <sub>2</sub> O(g)	36.732 31.201	-22.190 8.216	60.226 -2.092	-55.941 0.328	18.803 -0.021	298-1000 1000-3000
Ba(s)	8.902	-11.77	31.280	-27.375	8.74	298-1000
Ba(l)	3.426	9.095	-3.429	0.7557	-0.0695	1000-3000
Ra(d)	21.217 19.512	-6.78 2.82	18.914 -0.6830	-17.317 0.0871	5.703 -0.02184	298-1000 1000-3000
BaO(s)	10.518 5.843	-16.350 7.712	44.77 -2.160	-40.27 0.4227	13.115 -0.0376	298-1000 1000-2290
BaO(l)	1.172	9.907	-1.7986	0.1491		2290-3000
BaO(g)	29.592 26.393	-11.342 5.305	31.147 -1.5133	-28.132 0.2776	9.177 -0.02184	298-1000 1000-3000
Ba <sub>2</sub> (g)	36.295 33.641	-11.287 4.200	31.634 -1.518	-30.544 0.335	10.529 -0.031	298-1000 1000-3000

Table 2. Gibbs energy function equation parameters (Continued)

	(G° - H° <sub>298</sub> )/RT = A + BT + CT <sup>2</sup> + DT <sup>3</sup> + ET <sup>4</sup>					
	A	10 <sup>3</sup> B	10 <sup>6</sup> C	10 <sup>9</sup> D	10 <sup>12</sup> E	T range, K
Ba <sub>2</sub> O(g)	37.386 31.635	-21.957 8.710	59.433 -2.509	-55.081 0.472	18.489 -0.039	298-1000 1000-3000
Ba <sub>2</sub> O <sub>2</sub> (g)	41.823 33.968	-30.205 11.925	81.896 -3.500	-76.084 0.668	25.574 -0.056	298-1000 1000-3000
B(s)	0.892 -0.229	-1.883 2.270	4.894 -0.268	-2.125 -0.011	0.006	298-1000 1000-2348
B(l)	-7.187	8.2887	-2.211	0.3219	-0.01906	2348-4300
B(g)	19.205 17.518	-6.828 2.739	18.957 -0.6037	-17.304 0.0616	5.684	298-1000 1000-3000
BO(g)	25.538 22.855	-9.80 4.4204	26.50 -1.1536	-23.978 0.2032	7.85 -0.01593	298-1000 1000-3000
BO <sub>2</sub> (g)	29.430 24.906	-15.38 7.330	41.697 -1.830	-36.995 0.3033	11.94 -0.02227	298-1000 1000-3000
B <sub>2</sub> (g)	25.560 22.213	-11.10 5.509	30.027 -1.503	-26.55 0.274	8.53 -0.022	298-1000 1000-3000
B <sub>2</sub> O(g)	29.513 24.277	-19.7041 7.8803	53.1825 -2.1006	-48.9668 0.3700	16.3750 -0.0288	298-1000 1000-3000
B <sub>2</sub> O <sub>2</sub> (g)	32.412 26.390	-21.030 9.761	57.385 -2.4205	-51.320 0.4048	16.664 -0.03025	298-1000 1000-3000
B <sub>2</sub> O <sub>3</sub> (s)	11.447	-42.021	117.728	-123.930	49.645	298-723
B <sub>2</sub> O <sub>3</sub> (l)	-4.535	24.99	-9.642	2.399	-0.262	723-2000
B <sub>2</sub> O <sub>3</sub> (g)	37.087 30.144	-23.536 11.050	63.490 -2.479	-55.990 0.3720	18.015 -0.0248	298-1000 1000-3000
Al(s)	4.343	-8.33	22.815	-20.197	6.705	208-033.61
Al(l)	-0.766	8.831	-3.7837	0.9296	-0.0931	933.61-2900
Al(g)	20.759 18.649	-8.4641 3.2317	23.2158 -0.9905	-21.8534 0.193	7.4094 -0.0162	298-1000 1000-3000
Al <sub>2</sub> O(g)	27.467 24.765	-10.673 4.254	29.229 -0.8087	-26.310 0.0793	8.575	298-1000 1000-3000
Al <sub>2</sub> O <sub>2</sub> (g)	29.114 24.765	-21.304 4.254	32.4785 -2.8728	-21.4446 0.7043	0.22084	298-2900
Al <sub>2</sub> O <sub>3</sub> (g)	29.637 25.767	-13.690 6.399	37.430 -1.866	-33.720 0.3566	10.970 -0.0299	298-1000 1000-3000
Al <sub>2</sub> O <sub>3</sub> (s)	20.123	3.475	2.389	-1.4244	0.1005	290-2900
Al <sub>2</sub> O <sub>2</sub> (g)	32.197	4.484	3.337	-1.9575	0.2996	298-2900
Al <sub>2</sub> O <sub>3</sub> (s)	9.758 4.866	-31.19 2.744	83.503 -6.5295	-73.15 -4.602	23.40 0.7695	298-1000 1000-2327
Al <sub>2</sub> O <sub>3</sub> (l)	232.345	-336.622	193.572	-48.1032	4.4461	2327-3000
Ga(s)	6.263	-9.1060	15.305			298-302.92
Ga(l)	1.849 3.535	13.267 6.8206	-12.531 -2.8728	7.426 0.7043	-1.894 -0.0706	302.92-1000
Ga(O(g)	29.008 25.976	-11.095 4.886	30.43 -1.1755	-27.423 0.1976	8.95 -0.0154	298-1000 1000-3000
Ga <sub>2</sub> O(g)	36.155 31.272	-17.11 8.088	46.857 -2.305	-42.177 0.4269	13.723 -0.0346	298-1000 1000-3000
Ga <sub>2</sub> O <sub>3</sub> (s)	15.061 4.223	-41.0724 16.0456	110.124 -4.0362	-100.900 0.6755	33.6291 -0.0461	298-1000 1000-2080
Ga <sub>2</sub> O <sub>3</sub> (l)	-10.369	29.837	-8.766	1.5334	-0.11264	2080-3000
In(s)	9.404	-19.929	50.346	-37.888		298-429.78
In(l)	4.824 4.868	6.051 6.448	-1.300 -2.797	-0.896 0.743	0.500 -0.083	429.78-1000
In(g)	21.643 19.733	-6.722 3.058	18.523 -0.6107	-16.645 0.05655	5.44	298-1000 1000-2400
In(O(g)	30.031 26.955	-11.23 4.92	30.807 -2.305	-27.77 0.4269	9.074 -0.1685	298-1000 1000-3000
In <sub>2</sub> O(g)	37.892 32.940	-17.434 8.220	47.814 -2.3696	-43.124 0.4428	14.05 -0.0361	298-1000 1000-3000
In <sub>2</sub> O <sub>3</sub> (s)	18.200 6.558	-44.122 17.425	118.710 -4.7585	-109.295 0.8572	35.522 -0.0665	298-1000 1000-2186
In <sub>2</sub> O <sub>3</sub> (l)	-7.619	30.010	-8.791	1.522	-0.1108	2186-3000
Tl(s)	11.701	-36.5875	119.523	-164.816	86.659	298-576
Tl(l)	4.748	8.265	-4.264	1.295	-0.1576	576-1800
Tl(g)	22.520 20.659	-6.856 3.087	19.028 -0.8375	-17.381 0.1135	5.712	298-1000 1000-1800
TlO(g)	31.052 27.683	-11.364 5.489	31.000 -1.3467	-27.614 0.2058	8.946 -0.0134	298-1000 1000-3000
Tl <sub>2</sub> O(s)	22.540	-42.731	119.855	-123.107	46.613	298-852
Tl <sub>2</sub> O(l)	5.805	25.652	-10.338	2.4806	-0.2451	852-3000

Table 2.Gibbs energy function equation parameters (Continued)

(G°-H°298)/RT = A + BT + CT² + DT³ + ET⁴						
	A	10³B	10⁶C	10⁹D	10¹²E	T range,K
Tl₂O(g)	39.860 34.842	-17.750 8.350	48.76 -2.4334	-44.064 0.4584	14.375 -0.03765	298-1000 1000-3000
Tl₂O₃(s)	23.752 13.305	-39.353 15.999	107.127 -2.626	-96.004	31.16	298-1000 1000-1107
Tl₂O₃(l)	-0.743	40.917	-18.715	5.250	-0.627	1107-2000
Si(s)	3.101 1.052	-7.304 3.254	19.833 -0.7263	-17.696 0.0850	5.73	298-1000 1000-1687
Si(l)	-8.152	13.849	-5.0426	0.961	-0.07316	1687-3600
Si(g)	20.984 19.039 19.959	-7.130 3.32 1.9552	19.901 -1.0484 -0.2806	-18.28 0.2128 0.01899	6.03 -0.0165	298-1000 1000-3000 3000-5600
SiO(g)	26.584 23.682	-10.123 4.7876	27.755 -1.2880	-24.936 0.2291	8.113 -0.01797	298-1000 1000-3000
SiO₂(qu.)	6.947 1.394	-16.833 9.002	44.87 -2.166	-38.893 0.271	12.413	298-1000 1000-1726
SiO₂(cr.)	7.605 1.937	-19.79 8.590	51.495 -1.935	-44.403 0.225	10.91	290-1000 1000-1996
SiO₂(l)	2.120	7.6492	-1.2588	0.0998		1996-3000
SiO₂(g)	29.295 24.696	-15.684 7.467	42.55 -1.898	-37.810 0.3194	12.21 -0.0238	298-1000 1000-3000
Si₂(g)	28.945 25.520	-11.627 5.589	31.790 -1.3680	-28.374 0.210	9.206 -0.01386	298-1000 1000-3000
Si₂O₂(g)	40.398 33.340	-26.536 10.626	71.564 -2.860	-65.861 0.509	22.009 -0.040	298-1000 1000-3000
Cl₃(g)	34.490 29.042	-10.44 9.140	63.590 -2.788	-49.516 0.5832	15.962 -0.05276	298-1000 1000-3000
Ge(s)	5.484 2.896	-15.1302 1.8154	43.7517 1.6577	-48.3508 -1.5224	20.0263 0.3924	298-700 700-1210.4
Ge(l)	-5.426	15.1874	-6.5705	1.4859	-0.13343	1210.4-3200
Ge(g)	21.363 18.485	-10.534 4.992	29.285 -1.8107	-26.974 0.3906	8.883 -0.0351	298-1000 1000-3200
GeO(g)	28.117 25.086	-10.587 5.008	29.000 -1.385	-26.066 0.251	8.48 -0.020	298-1000 1000-3000
GeO₂(s)	7.621 118.948	-23.827 -403.336	63.421 538.497	-57.714 -313.567	19.138 68.097	298-1000 1000-1388
GeO₂(l)	-7.387	21.608	-8.362	1.844	-0.167	1388-3000
GeO₂(g)	30.914 26.045	-16.700 7.971	45.425 -2.142	-40.53 0.3796	13.12 -0.0298	298-1000 1000-3000
Ge₂(g)	32.229 28.103	-15.564 7.132	43.747 -2.398	-40.584 0.4977	13.465 -0.0437	298-1000 1000-3000
Ge₂O₂(g)	40.990 33.146	-28.642 12.193	77.350 -3.875	-71.242 0.630	23.759 -0.079	298-1000 1000-2000
Ge₃O₃	55.839 41.917	-48.258 22.959	130.774 -9.814	-121.600 3.022	40.908 -0.420	298-1000 1000-2000
Sn(s)	9.860	-34.0554	110.534	-151.014	79.2152	298-505.12
Sn(l)	1.684 4.201	14.256 6.483	-11.690 -2.3645	5.627 0.5071	-1.122 -0.0450	505.12-1400 1400-3000
Sn(g)	21.052 18.77	-6.998 3.667	18.881 -0.7262	-16.378 0.0646	5.221	298-1000 1000-3000
SnO(s)	10.425 4.990	-30.8313 4.5034	89.3685 1.9568	-99.1119 -0.2017	41.2146 0.5137	298-700 700-1250
SnO(l)	-3.168	19.3711	-9.1257	2.5224	-0.2917	1250-2000
SnO(g)	29.148 26.025	-10.96 5.173	30.054 -1.461	-27.070 0.2692	8.816 -0.0217	298-1000 1000-3000
SnO₂(s)	8.410 2.201	-21.510 9.576	57.480 -2.092	-50.560 0.236	16.203	298-1000 1000-1903
SnO₂(l)	-1.715	13.943	-3.931	0.6916	-0.0523	1903-3000

Table 2.Gibbs energy function equation parameters (Continued)

(G°-H°298)/RT = A + BT + CT² + DT³ + ET⁴						
	A	10³B	10⁶C	10⁹D	10¹²E	T range,K
SnO₂(g)	32.251 27.190	-17.54 8.322	47.834 -2.301	-42.85 0.4159	13.90 -0.033	298-1000 1000-3000
Sn₂(g)	32.827 28.634	-12.85 7.03	34.68 -1.967	-30.297 0.3357	9.65 -0.0245	298-1000 1000-3000
Sn₂O₂(g)	35.752	6.440	1.070	-1.011	0.171	298-3000
Sn₃O₃(g)	44.474	0.177	14.80	-7.926	1.264	298-3000
Sn₄O₄(g)	51.729	6.476	9.775	-5.144	0.772	298-3000
Pb(s)	9.762	-17.085	49.44	-54.63	22.66	298-600.65
Pb(l)	4.814	8.045	-3.983	1.191	-0.1493	600.65-2200
Pb(g)	21.847 19.914	-6.85 3.308	19.007 -1.080	-17.354 0.2288	5.70 -0.0197	298-1000 1000-3000
PbO(red)	11.492	-28.7693	82.3965	-89.2160	36.1111	298-762
PbO(yel)	6.081	4.9700	1.5284	-1.8198	0.4842	762-1160
PbO(l)	-1.494	19.2561	-9.2613	2.6476	-0.3178	1160-2000
PbO(g)	30.128 26.949	-11.204 5.276	30.750 -1.5062	-27.740 0.2792	9.040 -0.0225	298-1000 1000-3000
PbO₂(s)	10.231	-15.016	41.48	-33.24	9.446	298-1200
PbO₂(g)	33.462 28.252	-18.196 8.606	49.746 -2.440	-44.714 0.450	14.536 -0.0364	298-1000 1000-3000
Pb₂(g)	34.777 31.381	-12.426 5.687	34.43 -1.6535	-31.38 0.3116	10.30 -0.02454	298-1000 1000-3000
Pb₂O₂(g)	35.958	4.176	7.238	-4.146	0.658	298-3000
Pb₂O₃(s)	24.026	-48.4163	129.197	-117.502	39.0413	298-1000
Pb₃O₃(g)	44.777	6.271	10.844	-6.210	0.985	298-3000
Pb₃O₄(s)	26.958	-20.333	64.277	-45.386	11.00	298-1500
Pb₄O₄(g)	50.677	8.367	14.449	-8.274	1.312	298-3000
Pb₅O₅(g)	54.313	10.462	18.055	-10.338	1.639	298-3000
Pb₆O₆(g)	62.478	12.557	21.661	-12.401	1.966	298-3000
Zn(s)	5.763	-6.350	15.47	-8.73		298-692.73
Zn(l)	1.150	9.66	-4.862	1.132		692.73-1200
Zn(g)	19.791 18.184	-4.396 3.2905	12.606 -1.0522	-10.378 0.2166	3.000	298-1200 1200-3000
ZnO(s)	8.676 3.215	-29.783 5.346	86.988 -0.145	-98.618 -0.494	42.157 0.123	298-693 693-2000
ZnO(g)	28.337 25.163	-11.610 5.166	31.807 -1.4237	-28.827 0.2511	9.43 -0.01924	298-1000 1000-3000
Cd(s)	5.195	10.13	-40.49	74.52	-45.76	298-594.26
Cd(l)	2.511	10.22	-5.823	1.538		594.26-1100
Cd(g)	20.748 19.318	-5.4625 2.349	15.305 -0.035	-13.216 -0.263	4.055 0.064	298-1100 1100-2000
CdO(s)	6.887	-5.035	16.921	-12.132	2.97	298-1500
CdO(g)	29.305 26.054	-11.443 5.467	31.53 -1.6246	-28.494 0.3137	9.29 -0.0266	298-1000 1000-3000
Hg(l)	10.797	-14.507	41.32	-43.32	16.75	298-800
Hg(g)	21.798 19.906	-6.845 3.195	18.997 -0.9736	-17.344 0.1891	5.697 -0.01585	298-1000 1000-3000
HgO(s)	10.251	-15.674	42.5	-37.73	12.18	298-1000
HgO(g)	27.982	2.237	1.41	-0.8606	0.1332	298-2900

aSee Table 4 for references.

Table 3. Values of  $\Delta fH^{\circ}298/R$ ,  $S^{\circ}298/R$ , and  $(H^{\circ}298-H^{\circ}0)/R$ <sup>a</sup>

	$\Delta fH^{\circ}298/R$ (kK)	$S^{\circ}298/R$	$(H^{\circ}298-H^{\circ}0)/R$ (kK)
O(g)	29.97 ± 0.01	19.3578 ± 0.0001	0.8092
O <sub>2</sub> (g)		24.660 ± 0.004	1.0440
O <sub>3</sub> (g)	17.1 ± 0.2	28.73 ± 0.01	1.2468
Be( <i>a</i> )		1.143 ± 0.006	0.2345
Be(g)	39.0 ± 0.6	16.3770 ± 0.0001	0.74538
BeO(s)	-73.29 ± 0.3	1.656 ± 0.005	0.3412
BeO(g)	16.1 ± 1.	23.756 ± 0.05	1.0449
Be <sub>2</sub> O(g)	-4.5 ± 0.3	27.403 ± 0.3	1.3459
Be <sub>2</sub> O <sub>2</sub> (g)	-46.3 ± 3.	30.19 ± 0.3	1.4697
Be <sub>3</sub> O <sub>3</sub> (g)	-123. ± 4.	34.045 ± 0.3	1.819
Be <sub>4</sub> O <sub>4</sub> (g)	-198. ± 5.	35.644 ± 0.3	1.9044
Be <sub>5</sub> O <sub>5</sub> (g)	-265. ± 15.	(38.87) ± 0.3	2.290
Be <sub>6</sub> O <sub>6</sub> (g)	-330. ± 15.	(41.26) ± 0.5	2.583
Mg(s)		3.931 ± 0.01	0.6014
Mg( <i>a</i> )	17.7 ± 0.1	17.8651 ± 0.0001	0.74538
MgO(s)	-72.34 ± 0.04	3.24 ± 0.02	0.6206
MgO(g)	7.0 ± 3.	25.637 ± 0.01	1.0715
Mg <sub>2</sub> (g)	34.7 ± 0.3	29.33 ± 0.05	1.2409
Ca(s)		5.003 ± 0.04	0.689
Ca(g)	21.4 ± 0.1	18.6154 ± 0.0004	0.74538
CaO(s)	-76.384 ± 0.1	4.582 ± 0.02	0.812
CaO(g)	5.3 ± 2.	26.412 ± 0.05	1.077
CaO <sub>2</sub> (s)	-79.6 ± 0.3	(7.8) ± 0.3	
Ca <sub>2</sub> (g)	41.6 ± 0.4	30.842 ± 0.2	1.316
Sr(s)		6.70 ± 0.02	0.7902
Sr(g)	19.8 ± 0.5	19.7886 ± 0.0002	0.74538
SrO(s)	-71.0 ± 0.1	6.658 ± 0.06	1.042
SrO(g)	-0.2 ± 3.	27.656 ± 0.002	1.0873
SrO <sub>2</sub> (s)	-77. ± 2.	(11.) ± 0.5	
Sr <sub>2</sub> (g)	37.3 ± 0.6	33.493 ± 0.6	1.3237
Sr <sub>2</sub> O(g)	-25.4 ± 3.	34.1 ± 1.	1.535
Ba(s)		7.517 ± 0.08	0.8311
Ba(g)	21.9 ± 1.	20.4627 ± 0.0001	0.74538
BaO(s)	-65.9 ± 0.3	8.66 ± 0.05	1.198
BaO(g)	-15.4 ± 1.	28.306 ± 0.05	1.084
Ba <sub>2</sub> (g)	41.9 ± 0.8	35.015 ± 0.6	1.3172
Ba <sub>2</sub> O(g)	-29. ± 5.	34.8 ± 1.	1.429
Ba <sub>2</sub> O <sub>2</sub> (g)	-72. ± 5.	38.3 ± 1.	1.882
B(s)		0.710 ± 0.01	0.1470
B(g)	67.9 ± 0.5	18.441 ± 0.001	0.7603
BO(g)	1.2 ± 1.	24.458 ± 0.003	1.0433
BO <sub>2</sub> (g)	-39.0 ± 2.	27.665 ± 0.01	1.2956
B <sub>2</sub> (g)	99.8 ± 4.	24.291 ± 0.1	1.0598
B <sub>2</sub> O(g)	33. ± 12.	27.20 ± 0.50	1.4172
B <sub>2</sub> O <sub>2</sub> (g)	-55.5 ± 1.	30.015 ± 0.2	1.6112
B <sub>2</sub> O <sub>3</sub> (s)	-153.17 ± 0.17	6.491 ± 0.04	1.1187
B <sub>2</sub> O <sub>3</sub> (g)	-100.5 ± 0.5	34.371 ± 0.5	1.7341
Al(s)		3.405 ± 0.01	0.5490
Al(g)	39.60 ± 0.3	19.7782 ± 0.0001	0.8322
AlO(g)	8.1 ± 1.	26.25 ± 0.01	1.0568
AlO <sub>2</sub> (g)	-10.4 ± 4.	(30.27) ± 1.	1.4483
Al <sub>2</sub> (g)	59.0 ± 2.5	28.075 ± 0.03	1.1808
Al <sub>2</sub> O(g)	-17.5 ± 2.	30.33 ± 0.4	1.5288
Al <sub>2</sub> O <sub>2</sub> (g)	-47.5 ± 4.	(33.78) ± 1.5	1.7462
Al <sub>2</sub> O <sub>3</sub> (s)	-201.54 ± 0.15	6.127 ± 0.01	1.2047
Ga(s)		4.993 ± 0.04	0.675

Table 3. Values of  $\Delta fH^{\circ}298/R$ ,  $S^{\circ}298/R$ , and  $(H^{\circ}298-H^{\circ}0)/R$  (Continued)

	$\Delta fH^{\circ}298/R$ (kK)	$S^{\circ}298/R$	$(H^{\circ}298-H^{\circ}0)/R$ (kK)
Ge(g)	32.7 ± 0.5	20.3180 ± 0.0002	0.7879
GeO(g)	17.7 ± 3.	27.749 ± 0.006	1.0734
Ge <sub>2</sub> O(g)	-11.46 ± 1.	34.21 ± 0.4	1.4712
Ge <sub>2</sub> O <sub>3</sub> (s)	-131.2 ± 0.5	10.216 ± 0.04	1.750
In(s)		6.934 ± 0.03	0.7950
In(g)	28.9 ± 0.1	20.8878 ± 0.0001	0.7455
InO(g)	20.5 ± 3.	28.76 ± 0.06	1.081
In <sub>2</sub> O(g)	-5.17 ± 2.	35.91 ± 0.4	1.5087
In <sub>2</sub> O <sub>3</sub> (s)	-111.4 ± 0.2	13.00 ± 0.4	2.0807
Tl(s)		7.734 ± 0.02	0.8217
Tl(g)	21.7 ± 0.2	21.7522 ± 0.0001	0.74538
TlO(g)	23.6 ± 5.	29.76 ± 1.	1.0904
Tl <sub>2</sub> O(s,l)	-20.1 ± 0.2	17.56 ± 1.	1.816
Tl <sub>2</sub> O(g)	3.7 ± 1.	37.85 ± 0.6	1.554
Tl <sub>2</sub> O <sub>3</sub> (s)	-46.5 ± 0.5	19.244 ± 1.	2.4295
Si(s)		2.262 ± 0.01	0.3869
Si(g)	54.2 ± 1.	20.1903 ± 0.0001	0.9081
SiO(g)	-11.9 ± 0.6	25.437 ± 0.002	1.0482
SiO <sub>2</sub> (qu)	-109.53 ± 0.1	4.99 ± 0.02	0.8318
SiO <sub>2</sub> (g)	-38.7 ± 1.	27.496 ± 0.1	1.268
Si <sub>2</sub> (g)	67.9 ± 2.	27.625 ± 0.1	1.1141
Si <sub>2</sub> O <sub>2</sub> (g)	-43.22 ± 2.	37.3 ± 3.	1.835
Si <sub>3</sub> (g)	74. ± 3.	32.3 ± 0.60	1.6783
Ge(s)		3.74 ± 0.02	0.5576
Ge(g)	44.7 ± 0.4	20.181 ± 0.001	0.8808
GeO(g)	-4.5 ± 0.5	26.915 ± 0.005	1.0562
GeO <sub>2</sub> (tet)	-69.78 ± 0.1	4.776 ± 0.02	0.8696
GeO <sub>2</sub> (g)	-13. ± 2.	29.00 ± 0.1	1.354
Ge <sub>2</sub> (g)	58. ± 1.	30.508 ± 0.001	1.3983
Ge <sub>2</sub> O <sub>2</sub> (g)	-33. ± 2.	37.6 ± 1.5	1.900
Ge <sub>3</sub> O <sub>3</sub> (g)	-59.6 ± 2.	50.2 ± 2.5	3.250
Sn(s)		6.156 ± 0.01	0.7605
Sn(g)	36.23 ± 0.1	20.2517 ± 0.0004	0.7475
SnO(s)	-33.76 ± 0.02	6.876 ± 0.035	1.0507
SnO <sub>2</sub> (g)	2.6 ± 0.6	27.904 ± 0.005	1.0663
SnO <sub>2</sub> (s)	-69.47 ± 0.02	5.895 ± 0.01	1.0084
SnO <sub>2</sub> (g)	-5. ± 6.	30.248 ± 0.5	1.4186
Sn <sub>2</sub> (g)	49.6 ± 1.	31.352 ± 0.1	1.235
Sn <sub>2</sub> O <sub>2</sub> (g)	-29. ± 2.	37.7 ± 3.	
Sn <sub>3</sub> O <sub>3</sub> (g)	-61. ± 3.	45.6 ± 4.	
Sn <sub>4</sub> O <sub>4</sub> (g)	-95. ± 3.	54.4 ± 4.	
Pb(s)		7.794 ± 0.035	0.8263
Pb(g)	23.48 ± 0.1	21.080 ± 0.001	0.74538
PbO(red)	-26.29 ± 0.06	8.16 ± 0.02	1.1095
PbO(g)	8.2 ± 1.	28.857 ± 0.003	1.0778
PbO <sub>2</sub> (g)	0.8 ± 6.	31.39 ± 0.1	1.4735
PbO <sub>2</sub> (s)	-33.1 ± 0.3	8.635 ± 0.02	1.3184
Pb <sub>2</sub> (g)	35.9 ± 0.3	33.383 ± 0.1	1.270
Pb <sub>2</sub> O <sub>2</sub> (g)	-15. ± 3.	37.3 ± 3.	
Pb <sub>2</sub> O <sub>3</sub> (s)	-59.1 ± 0.4	18.27 ± 0.25	2.5113
Pb <sub>3</sub> O <sub>3</sub> (g)	-38. ± 4.	47.5 ± 4.	
Pb <sub>3</sub> O <sub>4</sub> (g)	-66.4 ± 0.8	25.49 ± 0.3	3.6308
Pb <sub>4</sub> O <sub>4</sub> (g)	-68. ± 6.	54.2 ± 5.	
Pb <sub>5</sub> O <sub>5</sub> (g)	-93. ± 6.	58.8 ± 6.	
Pb <sub>6</sub> O <sub>6</sub> (g)	-119. ± 6.	67.8 ± 6.	

Table 3. Values of  $\Delta H^{\circ}298/R$ ,  $S^{\circ}298/R$ , and  $(H^{\circ}298-H^{\circ}0)/R$ . (Continued)

	$\Delta H^{\circ}298/R$ (kJ/K)	$S^{\circ}298/R$	$(H^{\circ}298-H^{\circ}0)/R$ (kJ/K)
Zn(s)		5.017 ± 0.02	0.6804
Zn(g)	15.69 ± 0.02	19.3494 ± 0.0002	0.74538
ZnO(s)	-42.15 ± 0.03	5.25 ± 0.05	0.8339
ZnO(g)	10.9 ± 1.	26.95 ± 0.3	1.082
Cd(s)		6.230 ± 0.02	0.7513
Cd(g)	13.45 ± 0.08	20.1623 ± 0.0001	0.74538
CdO(s)	-31.04 ± 0.1	6.59 ± 0.20	1.011
CdO(g)	15.6 ± 1.	(28.014) ± 0.1	1.104
Hg(l)		9.13 ± 0.01	1.1236
Hg(g)	7.382 ± 0.005	21.0310 ± 0.0002	0.74542
HgO(s)	-10.92 ± 0.01	8.45 ± 0.04	1.0965
HgO(g)	11.2 ± 1.0	28.86 ± 0.3	1.082

<sup>a</sup>See Table 4 for references.

included in the major compilations. In all cases, the thermodynamic values selected reproduce, within experimental uncertainty, the vapor pressure measurements considered reliable.

In reviewing the available tabulations of thermodynamic functions for gaseous atoms, it was discovered that heat capacity, Gibbs energy function, entropy, and enthalpy increment values for many elements are in error because they are based on only the observed electronic levels, e.g., as listed by Moore (1949, 1952, 1958), and do not include unobserved low-lying levels, which can contribute significantly. Although this problem was not severe for the elements covered in this paper, it should be noted that the equations for Gibbs energy functions given for gaseous atoms in Table 2 are consistent with new calculations that take into account more recent spectroscopic data and estimates of missing low-lying electronic levels (Brewer, 1983). The equations given for  $-(G^{\circ}_T - H^{\circ}_{298})/RT$  represent the tabulated values within typical limits of  $\pm 0.01$  over their applicable temperature ranges. The equations were derived by fitting tabular data and are not direct integrations of heat capacity equations. Because of the nature of the polynomial fits, values derived by differentiating these equations do not represent thermodynamic properties, e.g., heat capacities, accurately.

Data sources for each of the selected values are in any case summarized in Table 4, and more complete discussions of data sources are given below, when necessary.

The calculated partial pressures of major gaseous species in equilibrium with stable condensed oxide phases are shown below as plots of  $\log P$  vs  $1/T$  for several representative vaporization conditions. The particular conditions are 0.2 bar  $O_2$ , representing oxidizing conditions, congruent vaporization, representing neutral vaporization, and either  $10^{-15}$  bar  $O_2$  or the  $O_2$  pressure of the metal-metal oxide equilibria, representing reducing conditions. The metal-metal oxide equilibrium  $O_2$  pressure was chosen when it exceeded  $10^{-15}$  bar. The maximum vaporization rates calculated by the Hertz-Knudsen equation are also shown in plots below.

TABLE 4. Sources of data in Tables 1 through 3<sup>a</sup>

	$-(G^{\circ}_T - H^{\circ}_{298})/T$	$\Delta_f H^{\circ}_{298}$	$T_{\text{fus}}$
O(g)	6,25	7	
$O_2(g)$	6,25		
$O_3(g)$	25	25	
$Be(\alpha)$	1(2),7,8,9,14		
$Be(g)$	1,2,7,8,10,14	7,8,1,9,14	
$BeO(s)$	1,5,7(9),14	7,1,5,9,14	1
$BeO(g)$	1,5,14	1,5,14	
$Be_2O(g)$	1	1	
$Be_2O_2(g)$	1	1	
$Be_3O_3(g)$	1	1	
$Be_4O_4(g)$	1	1	
$Be_5O_5(g)$	2	b	
$Be_6O_6(g)$	2,14	b	
$Mg(s)$	2(1),7,8,14		2
$Mg(g)$	1,8,2,7,9,10,14	7,1,2(8),9,14	
$MgO(s)$	1,5,7,9,14	7,1,5,9,14	1,19
$MgO(g)$	5,1,14	5,1,14	
$Mg_2(g)$	5(1)	5(1)	
$Ca(s)$	1,7,2,8,9,14		1
$Ca(g)$	1,2,7,8,9,10,14	7,11,1,8,9,14	
$CaO(s)$	1(4),7,14	7,1,4,9,14	1
$CaO(g)$	5,1,14	5,1,14	
$CaO_2(s)$		26(9)	
$Ca_2(g)$	5(1),14	5(1),14	
$Sr(s)$	1(2),(9,14)		1
$Sr(g)$	1,3(8),9,10,14	11(1,9,14)	
$SrO(s)$	1,4(9,14)	1,4,9,14	1
$SrO(g)$	1,4,14	27,4(9),14	
$SrO_2(s)$		12(9)	
$Sr_2(g)$	1	1	
$Sr_2O(g)$		b	
$Ba(s)$	1,4,9,14		1
$Ba(g)$	10,1,4,9,10,14	8,11(1,3,9,14)	
$BaO(s)$	1,4(9,14)	1,4(9),14	1
$BaO(g)$	1,4,14	1(4),14	
$Ba_2(g)$	1	1	
$Ba_2O(g)$	b	b	
$Ba_2O_2(g)$	b	b	
$B(s)$	13,1,7,8,9,14		13
$B(g)$	13,1,7,8,9,10,14	11,1,7,9(13)	
$BO(g)$	1,2,9,14	1,2,14	
$BO_2(g)$	1,2,9,14	1	
$B_2(g)$	1,13	13,1	
$B_2O(g)$	1,2,14	1	
$B_2O_2(g)$	1(2),(9)	1,2(9)	
$B_2O_3(s)$	1,3,7,9,14	1,3,7,9,14	1
$B_2O_3(g)$	1,3(9)	1,3,7,9	
$Al(s)$	28,1,7,8,9,14,17		28
$Al(g)$	17,1,7,8,10,14	28,1,7,8,14,17	
$AlO(g)$	17(1)	17,1	
$AlO_2(g)$	17(1)	17(1)	
$Al_2(g)$	1	1	
$Al_2O(g)$	17(1)	17(1)	
$Al_2O_2(g)$	17,1	17,1	
$Al_2O_3(s)$	17,1,7,9,14	7,17,1,9,14	1,19
$Ga(s)$	1,22,8,9,14		1
$Ga(g)$	1,8(9),10,14	1,8(9),14	
$GaO(g)$	1,9	1	
$Ga_2O(g)$	1	1	
$Ga_2O_3(s)$	1,9,14	1,9,14	1
$In(s)$	1,8(9),14		1
$In(g)$	8,1,9,10,14	1,8,9,14	
$InO(g)$	1	1	
$In_2O(g)$	1	1	
$In_2O_3(s)$	1	1,9	1
$Tl(s)$	8,1,9,14		1
$Tl(g)$	8,1,9,10,14	8,11,1,9,14	
$TlO(g)$	1	1	
$Tl_2O(s)$	1	1(14)	1

TABLE 4. (continued)

	$-(G^\circ T - H_{298}^\circ)/T$	$S_{298}^\circ, H_{298}^\circ - H_0^\circ$	$\Delta_f H_{298}^\circ$	$T_{\text{fus}}$
$\text{Ti}_2\text{O(g)}$	<b>1(14)</b>		<b>1</b>	
$\text{Ti}_2\text{O}_3(\text{s})$	<b>1(14)</b>		<b>1(14)</b>	<b>1</b>
$\text{Si(s)}$	<b>21,26,8,14,16</b>			<b>21</b>
$\text{Si(g)}$	<b>16,2,7,8,9,10,14</b>		<b>2,7,16</b>	
$\text{SiO(g)}$	<b>16,2,9,14</b>		<b>16(2),9,14</b>	
$\text{SiO}_2(\text{qu})$	<sup>b</sup>		<b>7,2,9,14,16</b>	<b>19,2</b>
$\text{SiO}_2(\text{cr})$	<sup>b</sup>		<sup>b</sup>	<b>16,2</b>
$\text{SiO}_2(\text{g})$	<b>16,2,14</b>		<b>16,2,9,14,</b>	
$\text{Si}_2(\text{g})$	<b>16,2,9,14</b>		<b>16</b>	
$\text{Si}_2\text{O}_2(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Si}_3(\text{g})$	<b>23,2,14,16</b>		<b>8,2,14,16</b>	
$\text{Ge(s)}$	<b>8,16,7,9,14</b>			<b>16</b>
$\text{Ge(g)}$	<b>16,8,9,10,14</b>		<b>16(8,9,14)</b>	
$\text{GeO(g)}$	<b>12,16(9)</b>		<b>12,16(9)</b>	
$\text{GeO}_2(\text{s})$	<b>16,7,14</b>		<b>7,14,16</b>	<b>16</b>
$\text{GeO}_2(\text{g})$	<b>16</b>		<b>16</b>	
$\text{Ge}_2(\text{g})$	<b>16,9</b>		<b>16</b>	
$\text{Ge}_2\text{O}_2(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Ge}_3\text{O}_3(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Sn(s)}$	<b>8,16,7,9,14</b>			
$\text{Sn(g)}$	<b>8,16,9,10,14</b>		<b>7,16,8(9),14,16</b>	
$\text{SnO(s)}$	<b>16,7(9),14</b>		<b>16(7,9,14)</b>	<b>16</b>
$\text{SnO(g)}$	<b>16,9</b>		<b>16(9)</b>	
$\text{SnO}_2(\text{s})$	<b>16(7,9,14)</b>		<b>16(7,9,14)</b>	<b>16</b>
$\text{SnO}_2(\text{g})$	<b>16</b>		<b>16</b>	
$\text{Sn}_2(\text{g})$	<b>16,18</b>		<b>18,16</b>	
$\text{Sn}_2\text{O}_2(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Sn}_3\text{O}_3(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Sn}_4\text{O}_4(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Pb(s)}$	<b>16,7,8,9,14</b>			
$\text{Pb(g)}$	<b>16,10(2,8,9,14)</b>		<b>7,8,9,14,16</b>	
$\text{PbO(red)}$	<b>16,3,9,14</b>		<b>3,16,9,14</b>	
$\text{PbO(yel)}$	<b>16,3,14</b>		<b>16,2,20</b>	
$\text{PbO(g)}$	<b>16,3,14</b>		<b>3,16,14</b>	
$\text{PbO}_2(\text{s})$	<b>3,14,16</b>		<b>3,16,14</b>	
$\text{PbO}_2(\text{g})$	<b>16</b>		<b>16</b>	
$\text{Pb}_2(\text{g})$	<b>16,18</b>		<b>18,16</b>	
$\text{Pb}_2\text{O}_2(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Pb}_2\text{O}_3(\text{s})$	<b>16,9</b>		<b>16</b>	
$\text{Pb}_3\text{O}_3(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Pb}_3\text{O}_4(\text{s})$	<b>3,9,14,16</b>		<b>3,16,9,14</b>	
$\text{Pb}_4\text{O}_4(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Pb}_5\text{O}_5(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Pb}_6\text{O}_6(\text{g})$	<sup>b</sup>		<sup>b</sup>	
$\text{Zn(s)}$	<b>15(8),(14)</b>			
$\text{Zn(g)}$	<b>15,8,10,14</b>		<b>7,8,9,14,15</b>	<b>15</b>
$\text{ZnO(s)}$	<b>7,14</b>		<b>7(9),14</b>	<b>20</b>

<sup>a</sup> See text.

### a. Be-O System

The only high-temperature solid phase is the oxide,  $\text{BeO}$ . Under neutral and reducing conditions, vaporization takes place primarily by decomposition to  $\text{Be}$  atoms and oxygen species.  $\text{BeO}$ ,  $\text{Be}_2\text{O}_2$ ,  $\text{Be}_3\text{O}_3$ ,  $\text{Be}_4\text{O}_4$ , and  $\text{Be}_5\text{O}_5$  are the principal vapor species under oxidizing conditions. Partial pressures of major vapor species and calculated maximum vaporization rates are shown in Figs. 1–4.

$\text{Be}_5\text{O}_5(\text{g})$ ,  $\text{Be}_6\text{O}_6(\text{g})$  thermodynamic data—the enthalpy of formation was calculated by the third-law method using the mass spectrometric data of Chupka, Berkowitz, and Giese (1959) and of Theard and Hildenbrand (1964).

TABLE 4. (continued)

	$-(G^\circ T - H_{298}^\circ)/T$	$S_{298}^\circ, H_{298}^\circ - H_0^\circ$	$\Delta_f H_{298}^\circ$	$T_{\text{fus}}$
$\text{ZnO(g)}$	<sup>b</sup>			<sup>b</sup>
$\text{Cd(s)}$	<b>8,14</b>			<b>8</b>
$\text{Cd(g)}$	<b>8,7,10,14</b>			<b>8,7,14</b>
$\text{CdO(s)}$	<b>14,7</b>			<b>20</b>
$\text{CdO(g)}$	<sup>b</sup>			<sup>b</sup>
$\text{Hg(l)}$	<b>8,2,14</b>			
$\text{Hg(g)}$	<b>2,8,7,10,14</b>			<b>7,2,8,14</b>
$\text{HgO(s)}$	<b>2,7,14</b>			<b>7,2,14</b>
$\text{HgO(g)}$	<sup>b</sup>			<sup>b</sup>

### References to Table 4

- <sup>1</sup>(Glushko *et al.*, 1981).
- <sup>2</sup>(Stull *et al.*, 1971).
- <sup>3</sup>(Chase *et al.*, 1974).
- <sup>4</sup>(Chase *et al.*, 1975).
- <sup>5</sup>(Chase *et al.*, 1978).
- <sup>6</sup>(Chase *et al.*, 1982).
- <sup>7</sup>(Cox, 1978).
- <sup>8</sup>(Hultgren and Desai, 1973).
- <sup>9</sup>(Wagman *et al.*, 1982).
- <sup>10</sup>(Brewer, 1983).
- <sup>11</sup>(Brewer, 1977).
- <sup>12</sup>(Brewer and Rosenblatt, 1969).
- <sup>13</sup>(Stull *et al.*, 1971, 31 March 1979 unbound supplement).
- <sup>14</sup>(Pankratz, 1982).
- <sup>15</sup>(Stull *et al.*, 1971, 31 December 1978 unbound supplement).
- <sup>16</sup>(Glushko *et al.*, 1979a).
- <sup>17</sup>(Stull *et al.*, 1971, 31 December 1979 unbound supplement). JANAF issued two sets of supplements on Al-O species dated 1979; the later set, with references to literature as late as 1982, is cited.
- <sup>18</sup>(Balasubramanian and Pitzer, 1983).
- <sup>19</sup>(Hlavac, 1982).
- <sup>20</sup>(Shunk, 1969).
- <sup>21</sup>(Desai, 1986a).
- <sup>22</sup>(Amitin *et al.*, 1984).
- <sup>23</sup>(Brewer, 1984).
- <sup>24</sup>(Richet *et al.*, 1982).
- <sup>25</sup>(Glushko *et al.*, 1978).
- <sup>26</sup>(Glushko *et al.*, 1979b).
- <sup>27</sup>(Murad, 1981).
- <sup>28</sup>(Desai, 1986b).

<sup>a</sup> References without parentheses are in essential agreement; those in parentheses differ from the chosen value by a significant portion of the stated uncertainty. The sources of the selected data are in boldface.

<sup>b</sup> See text.

### b. Mg-O System

The only high-temperature solid phase is the oxide,  $\text{MgO}$ . In neutral and reducing atmospheres, vaporization takes place by dissociation to give gaseous oxygen species and  $\text{Mg(g)}$ ; the  $\text{MgO(g)}$  partial pressure is comparable to that of  $\text{Mg(g)}$  in oxidizing atmospheres. Partial pressures of major vapor species and calculated maximum vaporization rates are shown in Figs. 5–8. As can be seen from the graphs,  $\text{MgO}$  is especially volatile at high temperatures under reducing conditions. This has important practical consequences in pointing out the instability and limited usefulness of magnesium-based refractories in hydrogen-containing or otherwise

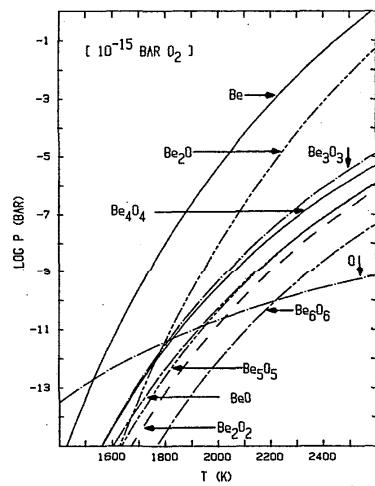
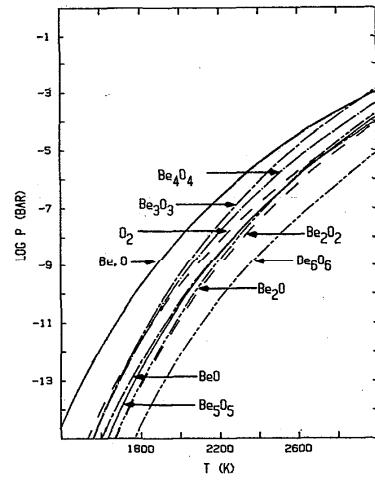
FIG. 1. BeO vaporization in  $10^{-15}$  bar  $O_2$ .

FIG. 2. BeO congruent vaporization.

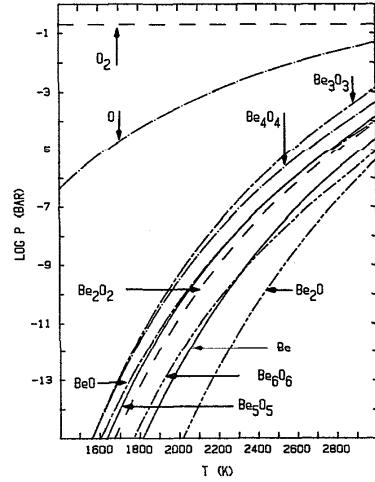
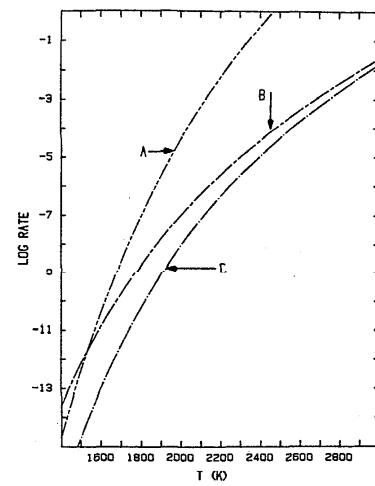
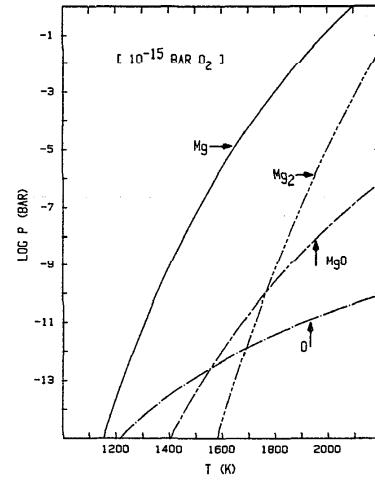
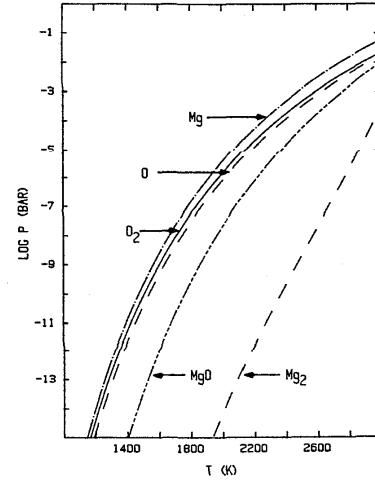
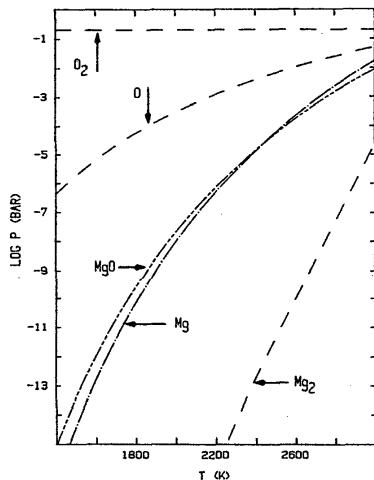
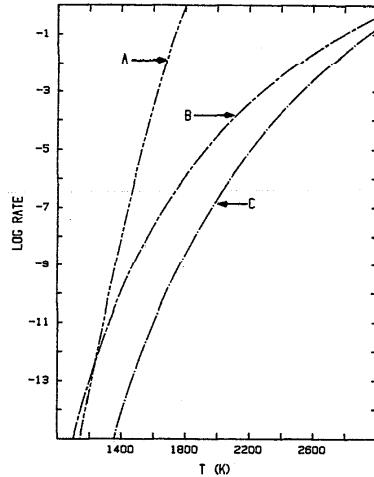
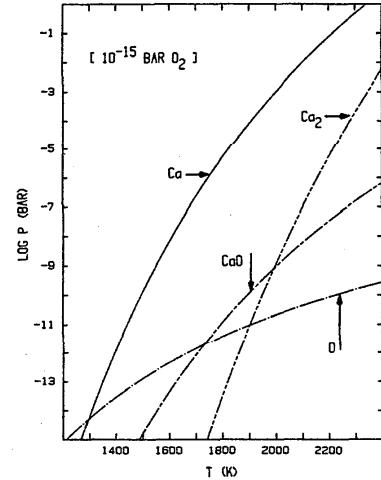
FIG. 3. BeO vaporization in 0.2 bar  $O_2$ .FIG. 4. BeO maximum vaporization rates. A— $10^{-15}$  bar  $O_2$ ; B—congruent vaporization; C—0.2 bar  $O_2$ .FIG. 5. MgO vaporization in  $10^{-15}$  bar  $O_2$ .

FIG. 6. MgO congruent vaporization.

FIG. 7. MgO vaporization in 0.2 bar  $O_2$ .FIG. 8. MgO maximum vaporization rates. A— $10^{-15}$  bar  $O_2$ ; B—congruent vaporization; C—0.2 bar  $O_2$ .FIG. 9. CaO vaporization in  $10^{-15}$  bar  $O_2$ .

reducing atmospheres. The same is true of several of the other alkaline earth oxides.

#### c. Ca-O System

The only high-temperature solid phase is the oxide, CaO. The equilibrium oxygen pressure of the peroxide,  $CaO_2$ , exceeds 0.2 bar at temperatures above about 300 K (Vannerberg, 1962). Vaporization takes place primarily by dissociation to  $Ca(g)$  and oxygen under neutral and reducing conditions;  $CaO(g)$  is the primary vapor phase product in oxidizing atmospheres. Partial pressures of major vapor species and calculated maximum vaporization rates are shown in Figs. 9–12.

#### d. Sr-O System

$SrO(s)$  is the stable high-temperature condensed phase under neutral and reducing conditions.  $SrO_2(s)$  is stable in oxidizing atmospheres at lower temperatures; the  $O_2$  pressure over  $SrO_2(s)$  reaches 0.2 bar at about 800 K (Vannerberg, 1962). Vaporization takes place primarily by dissociation to  $Sr(g)$ ,  $SrO(g)$ , and oxygen species under neutral and oxidizing conditions, while sublimation to  $SrO(g)$  dominates in oxidizing atmospheres. The calculated neutral vapor composition is consistent with the observation of Kaufman *et al.* (1965) from electric deflection experiments that the vapor at 2500 K contains about 5 mol % molecular  $SrO$ . Partial pressures of major vapor species and calculated maximum vaporization rates are shown in Figs. 13–16.

$Sr_2O(g)$  thermodynamic data—although  $Sr_2O$  is not a major species and is not listed in the IVTAN or JANAF compilations, the results of Drowart *et al.* (1964) indicate that it should be included for completeness. Therefore, their estimated molecular constants were adopted and used to evaluate thermodynamic functions:  $\angle Sr-O-Sr = 180^\circ$ ,  $r(Sr-O) = 0.192$  nm, vibrational fundamentals of 256, 233 (doubly degenerate), and  $888\text{ cm}^{-1}$ , an electronic ground state degeneracy of 3, and no excited electronic states. The enthalpy of formation of  $Sr_2O(g)$  was derived from a third-

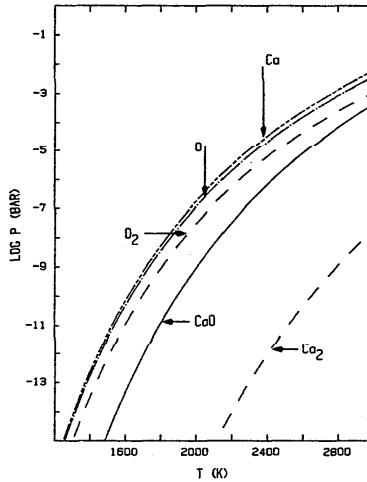


FIG. 10. CaO congruent vaporization.

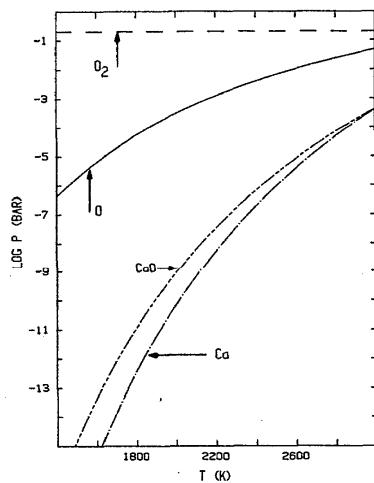
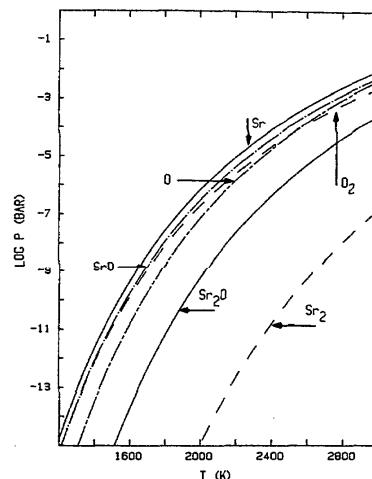
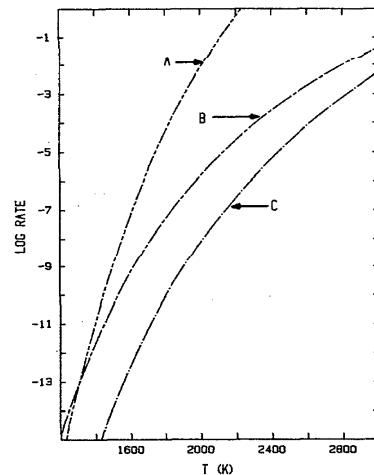
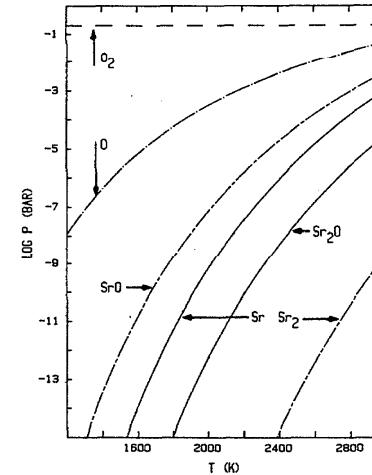
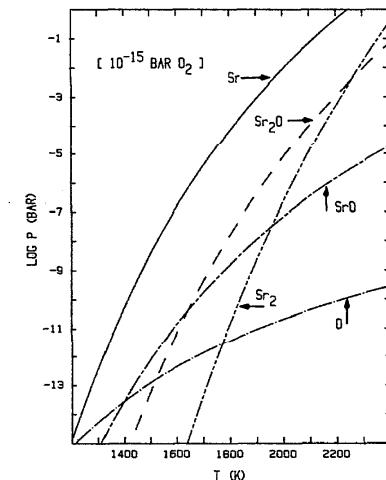
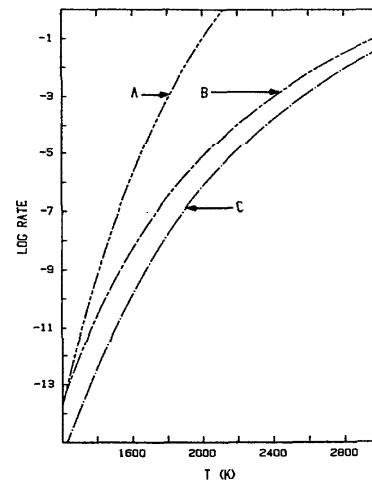
FIG. 11. CaO vaporization in 0.2 bar  $O_2$ .

FIG. 14. SrO congruent vaporization.

FIG. 12. CaO maximum vaporization rates. A— $10^{-15}$  bar  $O_2$ ; B—congruent vaporization; C—0.2 bar  $O_2$ .FIG. 15. SrO vaporization in 0.2 bar  $O_2$ .FIG. 13. SrO vaporization in  $10^{-15}$  bar  $O_2$ .FIG. 16. SrO maximum vaporization rates. A— $10^{-15}$  bar  $O_2$ ; B—congruent vaporization; C—0.2 bar  $O_2$ .

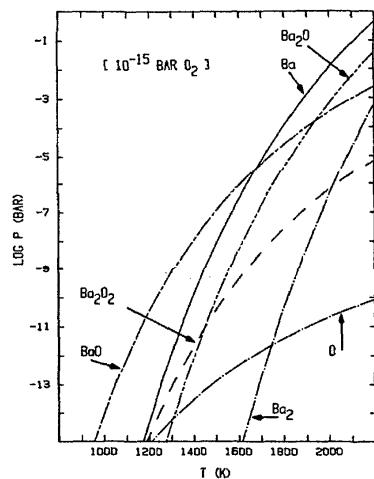
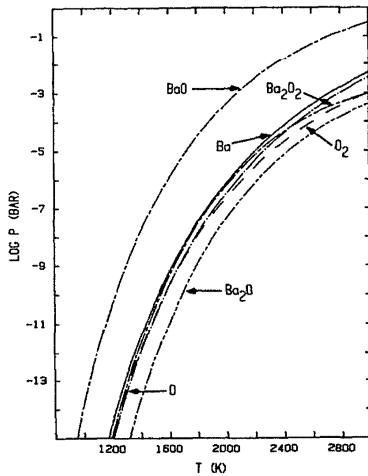
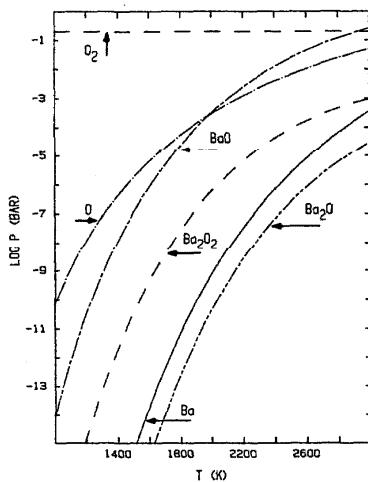
FIG. 17. BaO vaporization in  $10^{-15}$  bar  $O_2$ .

FIG. 18. BaO congruent vaporization.

FIG. 19. BaO vaporization in 0.2 bar  $O_2$ .

law treatment of the equilibrium data of Drowart *et al.* (1964) using these calculated functions. As can be seen in the graphs,  $Sr_2O$  is a minor feature of the vaporization chemistry under each of the environmental conditions.

$CaO_2(s)$  thermodynamic data—the enthalpy of formation was recalculated by (Garvin *et al.*, 1987) from the experimental data cited by Glushko *et al.* (1979b).

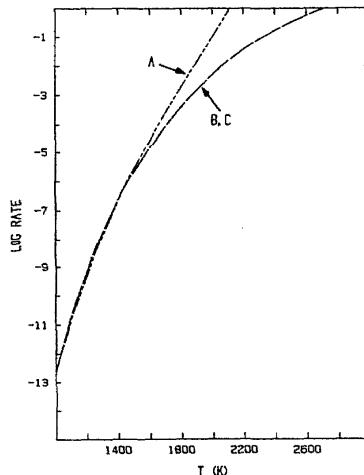
#### e. Ba-O System

$BaO(s)$  is the condensed phase stable at high temperatures under neutral and reducing conditions. In oxidizing atmospheres  $BaO_2(s)$  is stable at low temperatures; the  $O_2$  pressure over  $BaO_2(s)$  reaches 0.2 bar at about 1000 K (Vannerberg, 1962; Kedrovskii *et al.*, 1967).

The calculated vaporization equilibria shown in Figs. 17–19 indicate that  $BaO(g)$  is the principal product for vaporization under oxidizing and neutral conditions, but that  $Ba(g)$  becomes important at high temperatures under reducing conditions. It should be pointed out that our calculated neutral vapor composition differs appreciably from the reported results of four separate mass spectrometric studies (Inghram *et al.*, 1955; Newbury *et al.*, 1968; Semenov *et al.*, 1972; Hilpert and Gerads, 1975) in that the latter indicate almost comparable  $BaO$  and  $Ba$  partial pressures at 1500 to 1800 K. Recent mass spectrometric investigation in our own laboratory (Lamoreaux and Hildenbrand, 1983), however, show that under neutral conditions the ratio  $p(BaO)/p(Ba) > 100$ , so that, as suspected, some reduction of  $BaO$  was occurring in the earlier work. The calculated maximum vaporization rate is shown in Fig. 20.

Here again, the major compilations do not include data for the species  $Ba_2O_2$  and  $Ba_2O$ , but they are included here for completeness since they have been observed; molecular constants were selected as noted below. The enthalpies of formation for these species were chosen so as to be consistent with the neutral composition inferred from our mass spectra at low ionizing energy.

$Ba_2O(g)$  thermodynamic data—the Gibbs energy functions were calculated using the approximate molecular

FIG. 20. BaO maximum vaporization rates. A— $10^{-15}$  bar  $O_2$ ; B—congruent vaporization; C—0.2 bar  $O_2$ .

constants of Kudin (1981):  $r(\text{Ba-O}) = 0.231 \text{ nm}$ ,  $\angle \text{Ba-O-Ba} = 180^\circ$ , electronic ground state degeneracy = 3, no excited electronic states, and vibrational fundamentals of 500, 280(2), and  $720 \text{ cm}^{-1}$ .

$\text{Ba}_2\text{O}_2$  thermodynamic data—the Gibbs energy functions were calculated using the matrix isolation spectroscopy results of Ault and Andrews (1975) for the planar rhombic molecule with a derived O–Ba–O angle of  $102^\circ$  and observed vibrational fundamentals at 402 and  $501 \text{ cm}^{-1}$ , and the estimated molecular constants of Kudin (1981):  $r(\text{Ba-O}) = 0.21 \text{ nm}$ , vibrational fundamentals 470, 330, 270, and  $200 \text{ cm}^{-1}$ , electronic ground state degeneracy = 1, and no excited electronic states.

#### f. B–O System

The stable solid phase is  $\text{B}_2\text{O}_3$ , with a melting point of 723 K. Vaporization takes place primarily by evolution of  $\text{B}_2\text{O}_3(\text{g})$ , except that  $\text{B}_2\text{O}_2(\text{g})$  becomes important at high temperatures under reducing conditions and  $\text{BO}_2(\text{g})$  is important at low temperatures under oxidizing conditions. The calculated vaporization equilibria and vaporization rates are shown in Figs. 21–24. Partial pressures under reducing conditions were calculated for an  $\text{O}_2$  partial pressure of  $10^{-15} \text{ bar}$  up to 1923 K, where the calculated  $\text{O}_2$  pressure of the B– $\text{B}_2\text{O}_3$  equilibrium reaches this value, and for the  $\text{O}_2$  pressure of the B– $\text{B}_2\text{O}_3$  equilibrium at higher temperatures. If liquid  $\text{B}_2\text{O}_3$  is the only condensed phase present, its composition will change during vaporization unless  $\text{B}_2\text{O}_3(\text{g})$  evolution dominates; if the liquid composition is changing, the partial pressures indicated are thus strictly applicable only at the start of vaporization.

#### g. Al–O System

$\text{Al}_2\text{O}_3$  is the stable solid phase in this system. The major gaseous aluminum species are Al,  $\text{AlO}$ , and  $\text{Al}_2\text{O}$ , depending on conditions. Some earlier reviews selected data that indicated a much higher thermodynamic stability for  $\text{AlO}_2(\text{g})$ , such that this species dominated the vaporization chemistry under oxidizing conditions. We agree with the recent

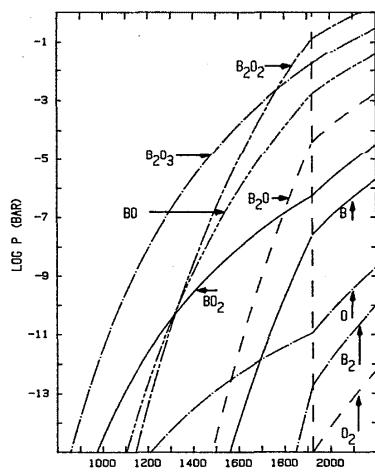


FIG. 21.  $\text{B}_2\text{O}_3$  vaporization in  $10^{-15} \text{ bar O}_2$  below 1923 K and vaporization of B– $\text{B}_2\text{O}_3$  mixture above 1923 K.

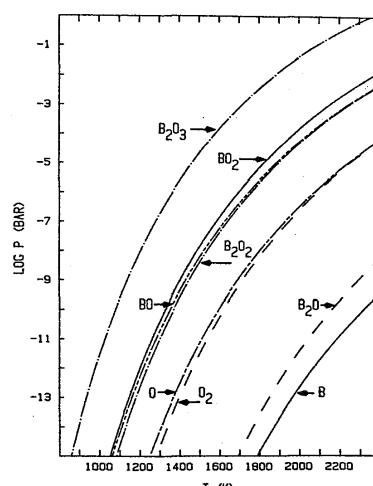


FIG. 22.  $\text{B}_2\text{O}_3$  congruent vaporization.

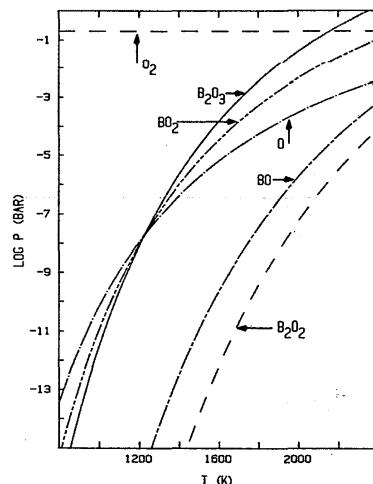


FIG. 23.  $\text{B}_2\text{O}_3$  vaporization in 0.2 bar  $\text{O}_2$ .

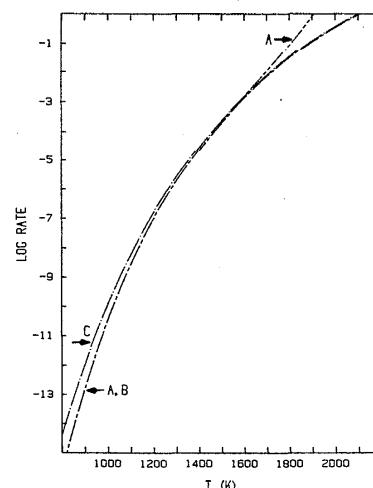


FIG. 24.  $\text{B}_2\text{O}_3$  maximum vaporization rates. A— $10^{-15} \text{ bar O}_2$ ; B—congruent vaporization; C—0.2 bar  $\text{O}_2$ .

IVTAN (Glushko *et al.*, 1981) and JANAF table (Stull *et al.*, 1971, December 31, 1979 unbound supplement) publications that assign a significantly lower stability to  $\text{AlO}_2(\text{g})$ , based primarily on the studies of Ho and Burns (1980). The calculated vaporization equilibria and maximum vaporization rates are shown in Figs. 25–28. Vaporization under reducing conditions was calculated for an  $\text{O}_2$  pressure of  $10^{-15}$  bar of  $\text{O}_2$  up to 2230 K, where the calculated  $\text{O}_2$  pressure of the  $\text{Al}-\text{Al}_2\text{O}_3$  equilibrium reaches  $10^{-15}$  bar, and for the  $\text{O}_2$  pressure of the  $\text{Al}-\text{Al}_2\text{O}_3$  equilibrium above this temperature.

#### **h. Ga-O System**

The stable solid phase is  $\text{Ga}_2\text{O}_3$ . The calculated vaporization equilibria and maximum vaporization rates are shown in Figs. 29–32. Vaporization under reducing conditions was calculated for an  $\text{O}_2$  pressure of  $10^{-15}$  bar up to 1446 K, where the  $\text{O}_2$  pressure of the  $\text{Ga}-\text{Ga}_2\text{O}_3$  equilibrium reaches this value, and for the  $\text{O}_2$  pressure of the  $\text{Ga}-\text{Ga}_2\text{O}_3$  equilibrium at higher temperatures.

#### **i. In-O System**

The stable solid phase is  $\text{In}_2\text{O}_3$ . The calculated vaporization partial pressures and maximum vaporization rates are shown in Figs. 33–36. Partial pressures under reducing conditions were calculated for an  $\text{O}_2$  pressure of  $10^{-15}$  bar up to 1239 K, where the  $\text{O}_2$  pressure of the  $\text{In}-\text{In}_2\text{O}_3$  equilibrium reaches this value, and for the  $\text{O}_2$  pressure of the  $\text{In}-\text{In}_2\text{O}_3$  equilibrium at higher temperatures.

#### **j. Tl-O System**

The stable solid oxide phase under neutral and reducing conditions, and in 0.2 atm of  $\text{O}_2$  above about 1060 K, is  $\text{Tl}_2\text{O}$ .  $\text{Tl}_2\text{O}_3$  is the stable phase at lower temperatures under oxidizing conditions. Calculated partial pressures and maximum rates for vaporization processes are shown in Figs. 37–40. Partial pressures over  $\text{Tl}_2\text{O}$  under reducing conditions were calculated for an  $\text{O}_2$  pressure of  $10^{-15}$  bar up to 731 K, where the  $\text{O}_2$  partial pressure of the  $\text{Tl}-\text{Tl}_2\text{O}$  equilibrium

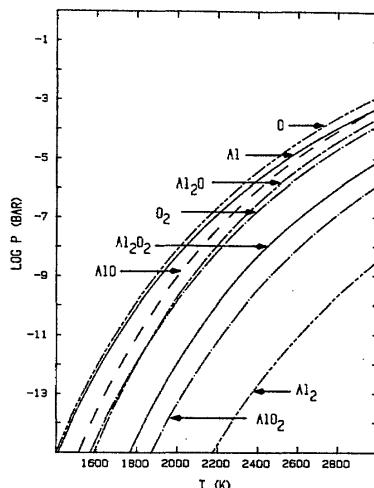


FIG. 26.  $\text{Al}_2\text{O}_3$  congruent vaporization.

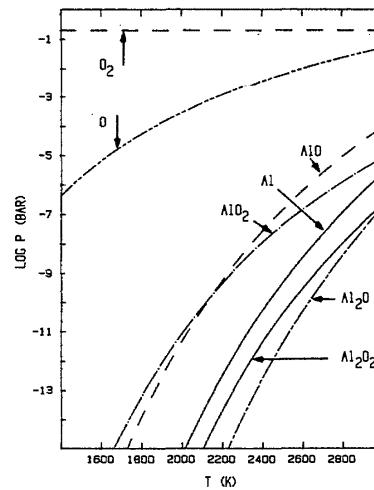


FIG. 27.  $\text{Al}_2\text{O}_3$  vaporization in 0.2 bar  $\text{O}_2$ .

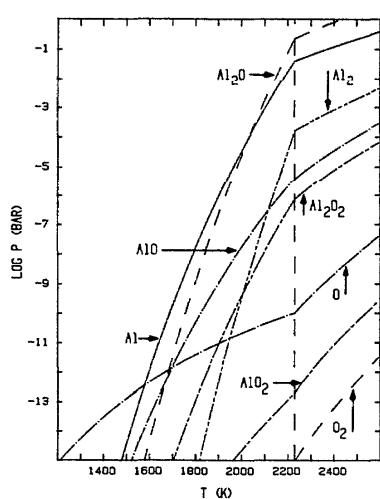


FIG. 25.  $\text{Al}_2\text{O}_3$  vaporization in  $10^{-15}$  bar  $\text{O}_2$  below 2230 K and vaporization of  $\text{Al}-\text{Al}_2\text{O}_3$  mixture above 2230 K.

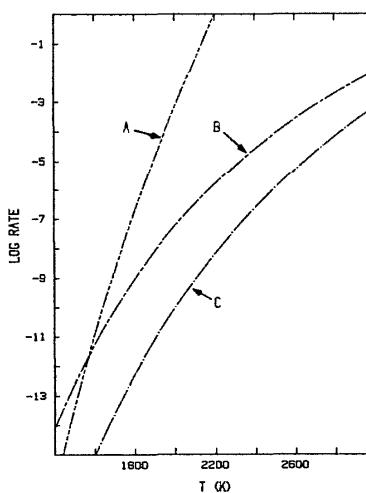


FIG. 28.  $\text{Al}_2\text{O}_3$  maximum vaporization rates. A— $10^{-15}$  bar  $\text{O}_2$ ; B—congruent vaporization; C—0.2 bar  $\text{O}_2$ .

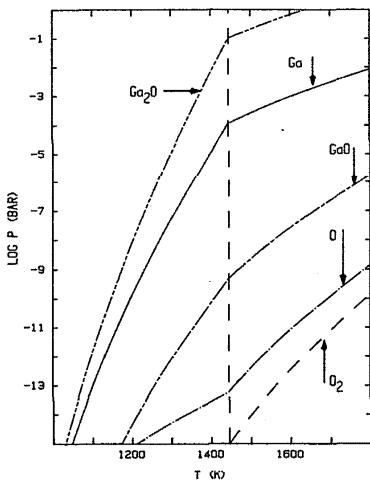


FIG. 29.  $\text{Ga}_2\text{O}_3$  vaporization in  $10^{-15}$  bar  $\text{O}_2$  below 1446 K and vaporization of  $\text{Ga}-\text{Ga}_2\text{O}_3$  mixture above 1446 K.

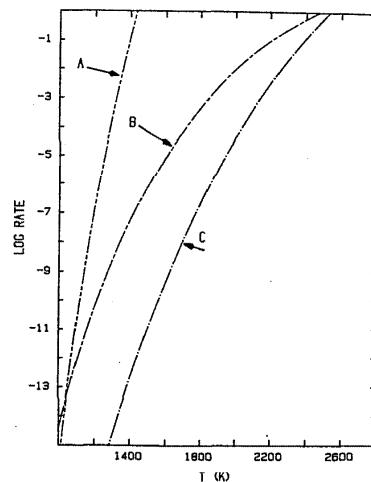


FIG. 32.  $\text{Ga}_2\text{O}_3$  maximum vaporization rates. A— $10^{-15}$  bar  $\text{O}_2$ ; B—congruent vaporization; C—0.2 bar  $\text{O}_2$ .

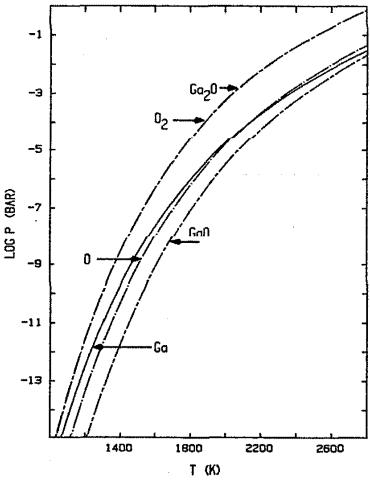


FIG. 30.  $\text{Ga}_2\text{O}_3$  congruent vaporization.

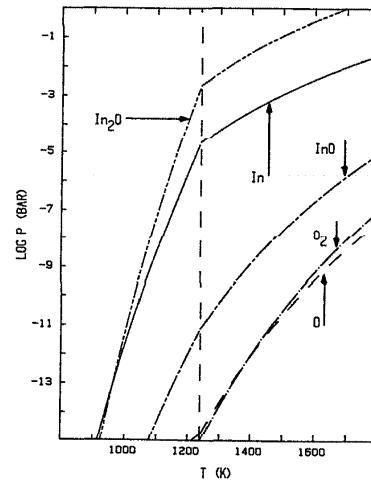


FIG. 33.  $\text{In}_2\text{O}_3$  vaporization in  $10^{-15}$  bar  $\text{O}_2$  below 1239 K and vaporization of  $\text{In}-\text{In}_2\text{O}_3$  mixture above 1239 K.

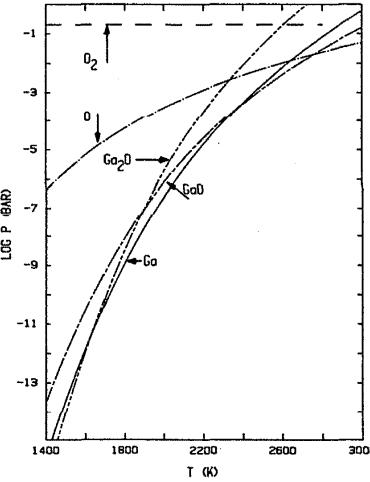


FIG. 31.  $\text{Ga}_2\text{O}_3$  vaporization in 0.2 bar  $\text{O}_2$ .

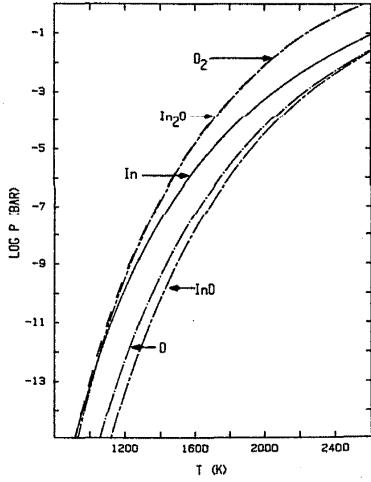
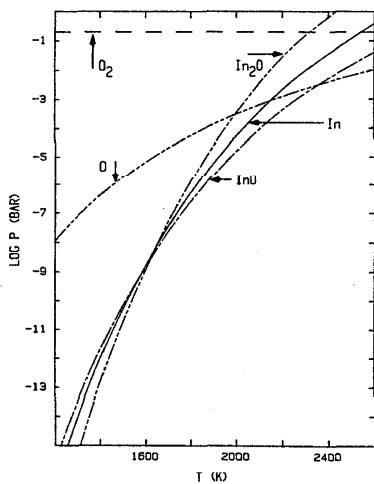
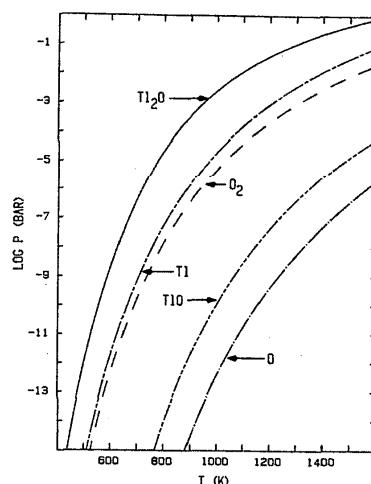
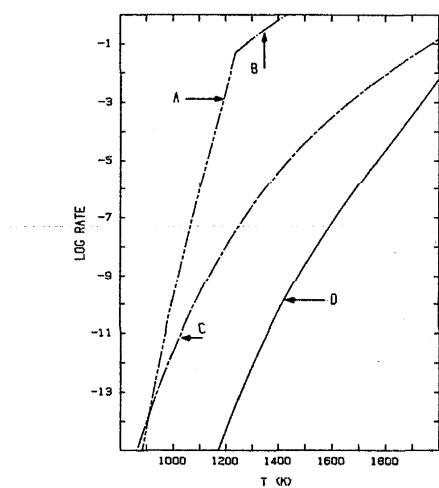
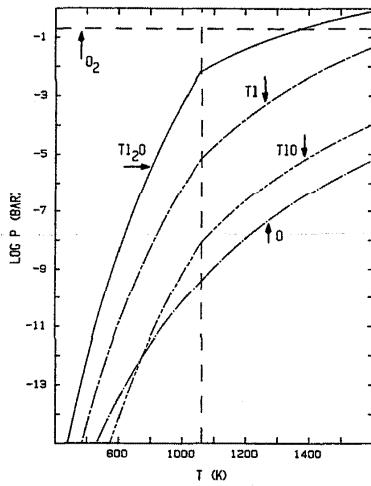
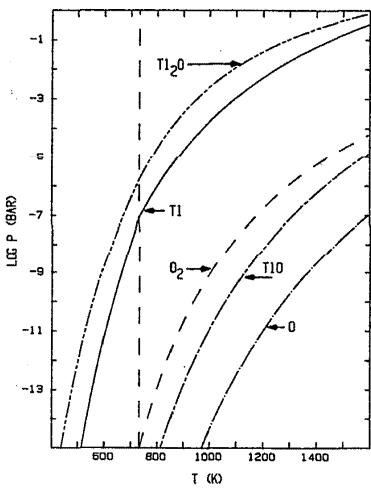
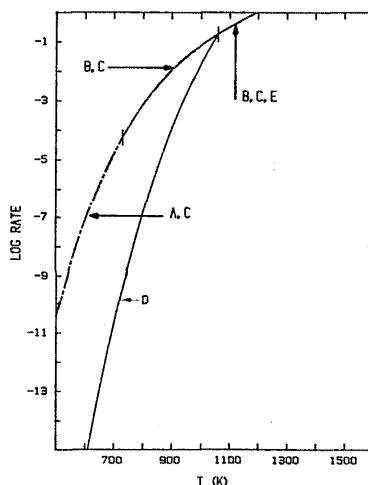


FIG. 34.  $\text{In}_2\text{O}_3$  congruent vaporization.

FIG. 35.  $\text{In}_2\text{O}_3$  vaporization in 0.2 bar  $\text{O}_2$ .FIG. 38.  $\text{Tl}_2\text{O}$  congruent vaporization.FIG. 36.  $\text{In}_2\text{O}_3$  maximum vaporization rates. A— $10^{-15}$  bar  $\text{O}_2$ ; B— $\text{In}-\text{In}_2\text{O}_3$ ; C—congruent vaporization; D—0.2 bar  $\text{O}_2$ .FIG. 39.  $\text{Ti}_2\text{O}_3$  vaporization below 1060 K and  $\text{TlO}$  vaporization above 1060 K in 0.2 bar  $\text{O}_2$ .FIG. 37.  $\text{Tl}_2\text{O}$  vaporization in  $10^{-15}$  bar  $\text{O}_2$  below 731 K and vaporization of  $\text{Tl}-\text{Tl}_2\text{O}$  mixture above 731 K.FIG. 40. Maximum vaporization rates of thallium oxides. A— $\text{Tl}_2\text{O}$  in  $10^{-15}$  bar  $\text{O}_2$ ; B— $\text{Tl}-\text{Tl}_2\text{O}$  equilibrium vaporization; C— $\text{Tl}_2\text{O}$  congruent vaporization; D— $\text{Tl}_2\text{O}_3$  vaporization in 0.2 bar  $\text{O}_2$ ; E— $\text{Tl}_2\text{O}$  vaporization in 0.2 bar  $\text{O}_2$ .

reaches this value, and for the  $O_2$  pressure of the  $Tl-Tl_2O$  equilibrium at higher temperatures. Partial pressures for vaporization in 0.2 bar of  $O_2$  were calculated for  $Tl_2O_3$  up to 1060 K, and for  $Tl_2O$  at higher temperatures.

#### k. Si-O System

Calculated partial pressures for vaporization of  $SiO_2$  are shown in Figs. 41–44.  $SiO(g)$  is the principal silicon-containing vaporization product under neutral and reducing conditions, while  $Si_2O_2(g)$  is favored under oxidizing conditions below about 2500 K.

$SiO_2$  (quartz, cristobalite, liquid) thermodynamic data—the CODATA (Cox, 1978) value of the enthalpy of formation of quartz was accepted. Other data were taken from the recent article of Richet *et al.* (1982), which reviewed the available literature.

$Si_2O_2(g)$  thermodynamic data—Gibbs energy functions were calculated using the molecular constants of Khanna *et al.* (1981) for a planar  $Si-O-Si-O$  molecule with the terminal atoms lying on opposite sides of the central  $O-Si$  bond axis:  $\angle Si-O-Si = \angle O-Si-O = 109.5^\circ$ ,  $r(Si-O, \text{terminal}) = 0.174 \text{ nm}$ ,  $r(Si-O, \text{central}) = 0.151 \text{ nm}$ , ground electronic state degeneracy = 1, and no excited electronic states. The vibrational fundamentals as measured by infrared and Raman matrix isolation spectroscopy were 1222, 804, 766, 252, and  $79 \text{ cm}^{-1}$ ; the remaining fundamental at  $180 \text{ cm}^{-1}$  was calculated by force constant calculations (Khanna *et al.*, 1981). The Gibbs energy functions calculated using these constants are 2.8 K greater than those calculated using the data of Anderson and Ogden (1969) for a molecule with  $D_{2h}$  symmetry. The enthalpy of formation was then calculated by the third-law method from the mass spectrometric data of Porter *et al.* (1955) and of Zmbov *et al.* (1973).

#### I. Ge-O System

The stable condensed phase below 1308 K is tetragonal  $GeO_2$ ; the hexagonal crystal structure is stable from 1308 K to the melting temperature, 1388 K (Glushko *et al.*, 1979a). Calculated partial pressures for vaporization of  $GeO_2$  are shown in Figs. 45–48.  $GeO$  is the major germanium-contain-

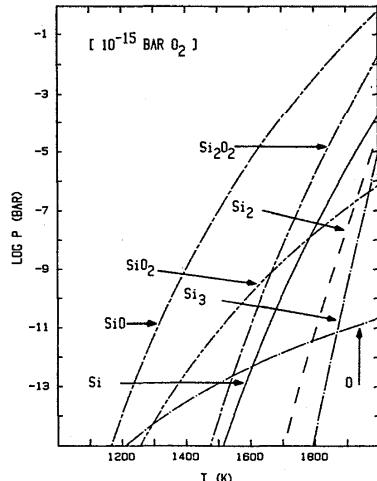


FIG. 41.  $SiO_2$  vaporization in  $10^{-15} \text{ bar } O_2$ .

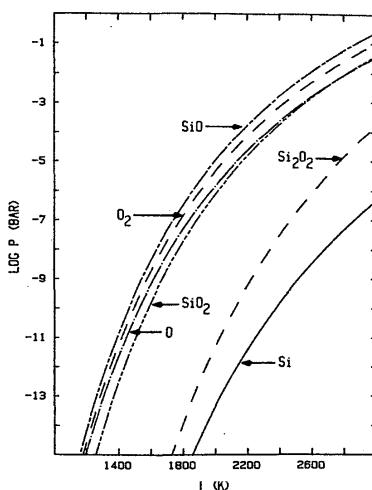


FIG. 42.  $SiO_2$  congruent vaporization.

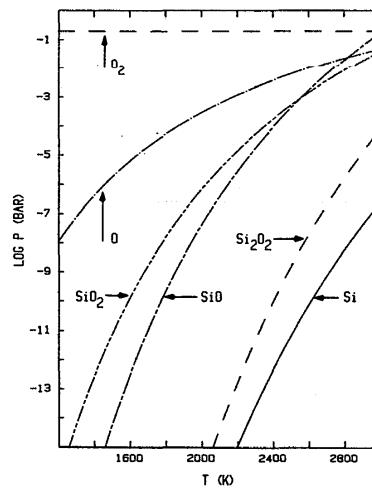


FIG. 43.  $SiO_2$  vaporization in 0.2 bar  $O_2$ .

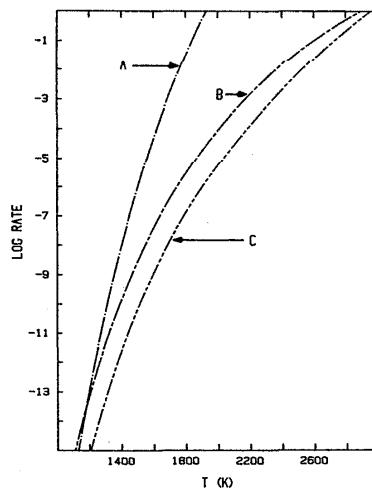


FIG. 44.  $SiO_2$  maximum vaporization rates. A— $10^{-15} \text{ bar } O_2$ ; B—congruent vaporization; C—0.2 bar  $O_2$ .

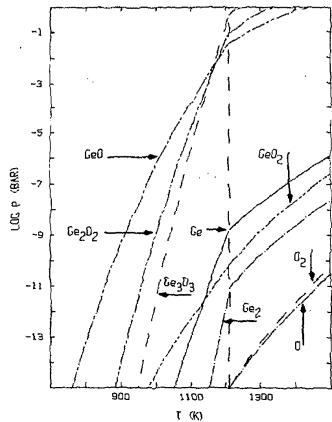


FIG. 45.  $\text{GeO}_2$  vaporization in  $10^{-15}$  bar  $\text{O}_2$  below 1210 K and vaporization of  $\text{Ge}-\text{GeO}_2$  mixture above 1210 K.

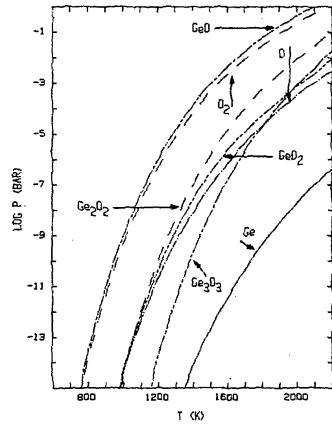


FIG. 46.  $\text{GeO}_2$  congruent vaporization.

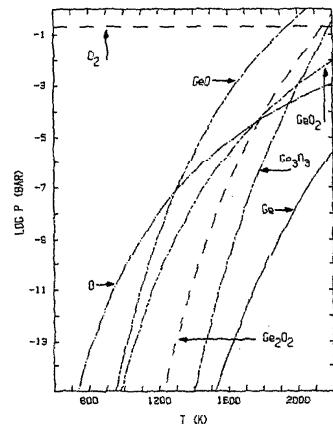


FIG. 47.  $\text{GeO}_2$  vaporization in 0.2 bar  $\text{O}_2$ .

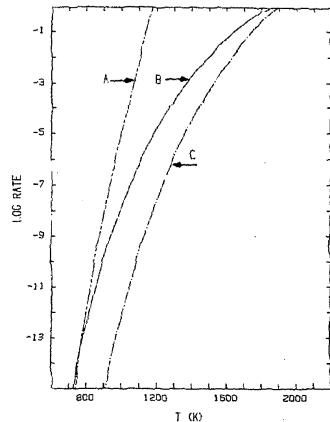


FIG. 48.  $\text{GeO}_2$  maximum vaporization rates. A— $10^{-15}$  bar  $\text{O}_2$ ; B—congruent vaporization; C—0.2 bar  $\text{O}_2$ .

ing vapor species under most conditions, with the polymeric species  $\text{Ge}_2\text{O}_2$  and  $\text{Ge}_3\text{O}_3$  becoming important at higher temperatures under reducing conditions.

$\text{Ge}_2\text{O}_2(\text{g})$  thermodynamic data—Gibbs energy functions were calculated using the molecular data of Ogden and Ricks (1970) which were estimated except for the observed vibrational fundamentals at 601 and 666  $\text{cm}^{-1}$ :  $D_{2h}$  symmetry, symmetry number = 4,  $r(\text{Ge}-\text{O}) = 0.187 \text{ nm}$ ,  $\angle \text{O}-\text{Ge}-\text{O} = 83^\circ$ . The electronic ground state degeneracy was taken as unity, no excited electronic states were considered, and the remaining vibrational fundamentals of 120, 500, 450, and 80  $\text{cm}^{-1}$  were estimated by analogy with the alkali metal  $\text{M}_2\text{O}_2$  species (Lamoreaux and Hildenbrand, 1984). The enthalpy of vaporization was chosen to yield calculated vaporization equilibria consistent with the mass spectrometric data of Drowart *et al.* (1965).

$\text{Ge}_3\text{O}_3(\text{g})$  thermodynamic data—Gibbs energy functions were calculated using the molecular data of Ogden and Ricks (1970), which were estimated except for doubly degenerate vibrational fundamentals at 824 and 438  $\text{cm}^{-1}$ :  $D_{3h}$  symmetry, symmetry number = 6,  $r(\text{Ge}-\text{O}) = 0.185 \text{ nm}$ ,  $\angle \text{O}-\text{Ge}-\text{O} = 100^\circ$ ,  $\angle \text{Ge}-\text{O}-\text{Ge} = 140^\circ$ . The electronic ground state degeneracy was taken to be 1, no excited electronic states were considered, and the remaining vibrational fundamentals were estimated by analogy to  $\text{Be}_3\text{O}_3$ ; 159(2), 70(2), 150, 70(2), and 90  $\text{cm}^{-1}$ . The enthalpy of formation was chosen to yield calculated vaporization equilibria in agreement with the mass spectrometric studies of Drowart *et al.* (1965).

#### m. Sn-O System

The stable condensed phase is  $\text{SnO}_2$ . Calculated partial pressures for vaporization of  $\text{SnO}_2$  are shown in Figs. 49–52.  $\text{SnO}(\text{g})$  is the principal tin-containing vaporization species, with the polymeric species  $\text{Sn}_2\text{O}_2$ ,  $\text{Sn}_3\text{O}_3$ , and  $\text{Sn}_4\text{O}_4$  becoming important at higher temperatures under reducing conditions.

$\text{Sn}_2\text{O}_2(\text{g})$  thermodynamic data—because the existing spectroscopic data are insufficient to adequately determine

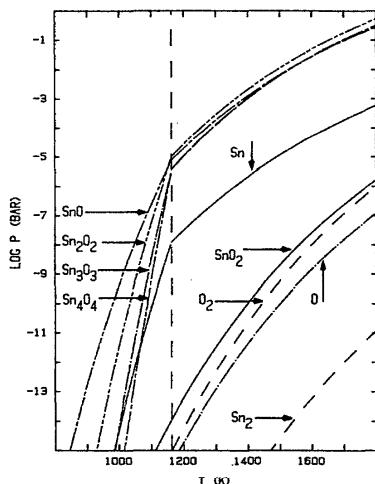


FIG. 49.  $\text{SnO}_2$  vaporization in  $10^{-15}$  bar  $\text{O}_2$  below 1163 K and vaporization of  $\text{Sn}-\text{SnO}_2$  mixture above 1163 K.

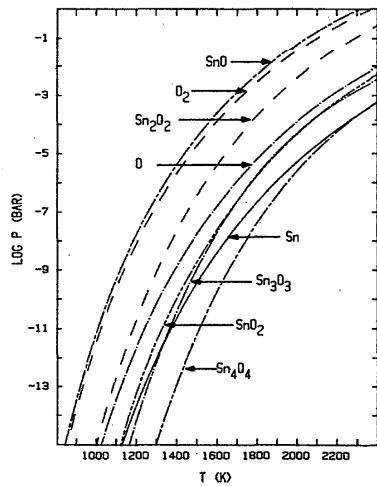


FIG. 50.  $\text{SnO}_2$  congruent vaporization.

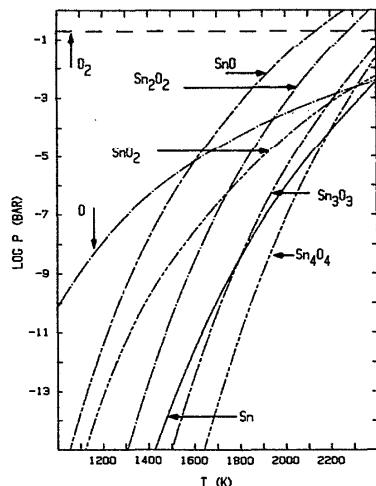


FIG. 51.  $\text{SnO}_2$  vaporization in 0.2 bar  $\text{O}_2$ .

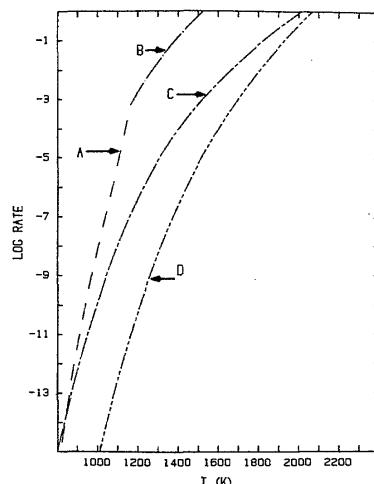


FIG. 52.  $\text{SnO}_2$  maximum vaporization rates. A— $10^{-15}$  bar  $\text{O}_2$ ; B— $\text{Sn}-\text{SnO}_2$  equilibrium; C—congruent vaporization; D—0.2 bar  $\text{O}_2$ .

the molecular constants of  $\text{Sn}_2\text{O}_2(\text{g})$ , the estimated  $S_{298}^{\circ}/R$  value of Colin *et al.* (1965) was used along with the estimated value  $C_p^{\circ}/R = 2.3 \text{ g-at.}$  derived by analogy to other gaseous compounds to calculate the Gibbs energy functions shown in Table 2. The enthalpy of formation was selected to yield calculated equilibria in agreement with the results of Colin *et al.*; the thermodynamic data presented in Tables 2 and 3 are consistent with observed partial pressures over the temperature range of the mass spectrometer studies.

$\text{Sn}_3\text{O}_3(\text{g})$  thermodynamic data—the data were derived as for  $\text{Sn}_2\text{O}_2(\text{g})$ , except that the value of  $C_p^{\circ}/R$  was estimated as  $2.5/\text{g-at.}$

$\text{Sn}_4\text{O}_4(\text{g})$  thermodynamic data—the data were derived as for  $\text{Sn}_3\text{O}_3(\text{g})$ .

#### n. Pb-O System

The stable condensed oxide phase under neutral and reducing conditions, and in 0.2 atm of  $\text{O}_2$  at temperatures above about 800 K, is  $\text{PbO}$ . Calculated partial pressures for vaporization of  $\text{PbO}$  are shown in Figs. 53–56. The predominant vapor phase species under neutral and oxidizing conditions are  $\text{PbO}$  and its polymers  $\text{Pb}_2\text{O}_2$ ,  $\text{Pb}_3\text{O}_3$ ,  $\text{Pb}_4\text{O}_4$ ,  $\text{Pb}_5\text{O}_5$ , and  $\text{Pb}_6\text{O}_6$ ; under reducing conditions the predominant vapor species is atomic lead.

$\text{Pb}_2\text{O}_2$ ,  $\text{Pb}_3\text{O}_3$ ,  $\text{Pb}_4\text{O}_4$ ,  $\text{Pb}_5\text{O}_5$ , and  $\text{Pb}_6\text{O}_6$  thermodynamic data—Drowart, Colin, and Exsteen (1965) and Kazenas, Chizhikov, and Tsvetkov (1968) analyzed the vapors over  $\text{PbO}$  by mass spectroscopy. The thermodynamic properties of the gaseous  $\text{PbO}$  polymers given in Tables 2 and 3 were derived from the results of Drowart and co-workers, who made measurements to 1200 K and observed all five of these species. Kazenas *et al.* made measurements at temperatures up to 950 K and did not observe the pentamer or hexamer. The enthalpies of formation and entropies at 298 K selected by Drowart *et al.* were accepted for the dimer, trimer, and tetramer; the Gibbs energy functions for these species were derived by assuming that  $C_p^{\circ}/R = 3.0/\text{g-at.}$  at all temperatures above 298 K. Although this heat capacity

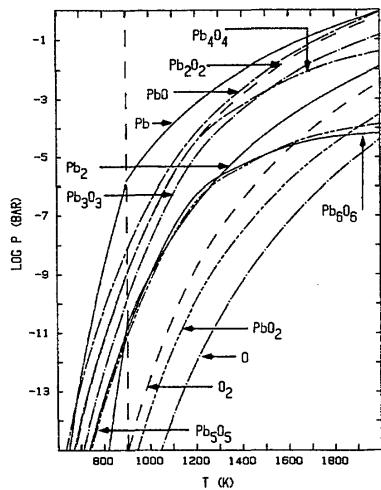


FIG. 53. PbO vaporization in  $10^{-15}$  bar  $O_2$  below 905 K and vaporization of Pb-PbO mixture above 905 K.

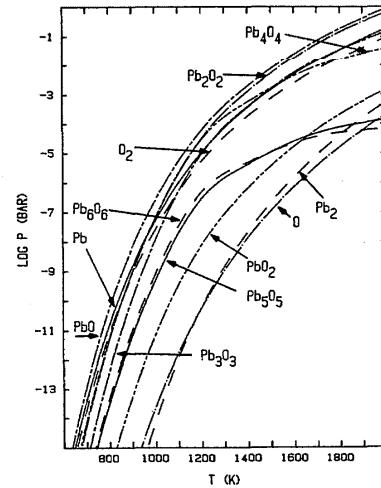


FIG. 54. PbO congruent vaporization.

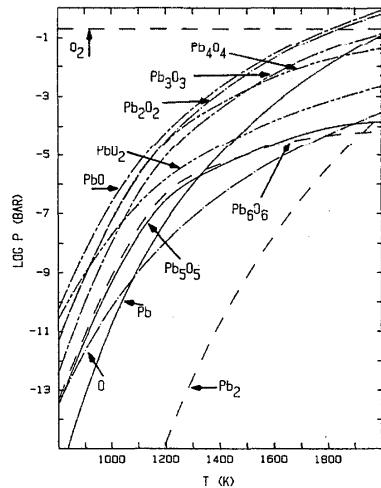


FIG. 55. PbO vaporization in 0.2 bar  $O_2$ .

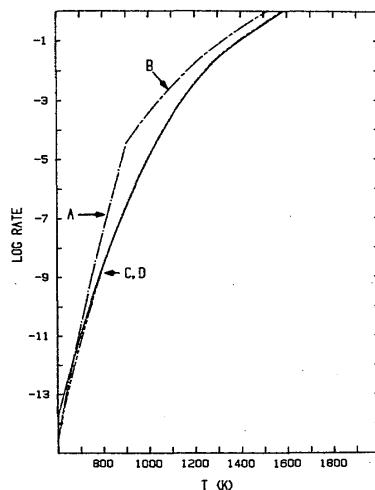


FIG. 56. PbO maximum vaporization rates. A— $10^{-15}$  bar  $O_2$ ; B—Pb-PbO equilibrium; C—congruent vaporization; D—0.2 bar  $O_2$ .

value seems somewhat large, calculations using the resulting thermodynamic properties are in excellent agreement with Drowart's gas phase equilibria over the temperature range of measurements. Equilibrium data are available for  $Pb_5O_5$  and  $Pb_6O_6$  at only one temperature, 1200 K. The entropy at 298 K for these two species was estimated by extrapolating the values for the monomeric through tetrameric species, and the estimated value  $C_p^o/R = 3.0$  was used to calculate values of the Gibbs energy functions. The gas phase equilibria at 1200 K were then used to derive values of the enthalpies of formation.

#### **o. Zn-O System**

The stable solid phase is  $ZnO$ . Vaporization takes place predominantly by dissociation into gaseous  $Zn$  and  $O_2$ , and a much smaller amount of  $ZnO(g)$ . Figures 57-60 show calculated partial pressures for vaporization of  $ZnO$ . The Gibbs energy function of gaseous  $ZnO$  was calculated using the estimated internuclear distance of Brewer and Rosenb-

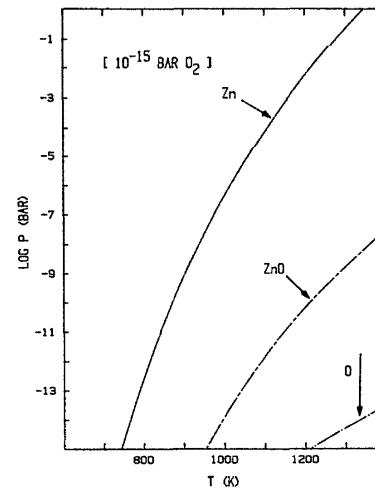


FIG. 57.  $ZnO$  vaporization in  $10^{-15}$  bar  $O_2$ .

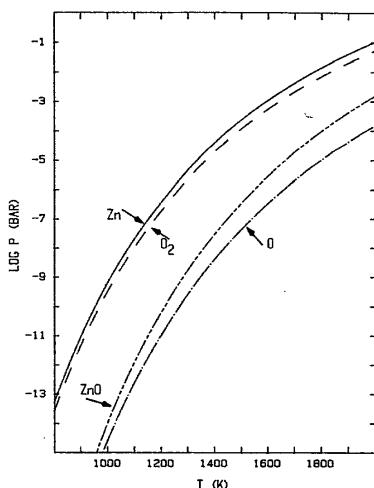
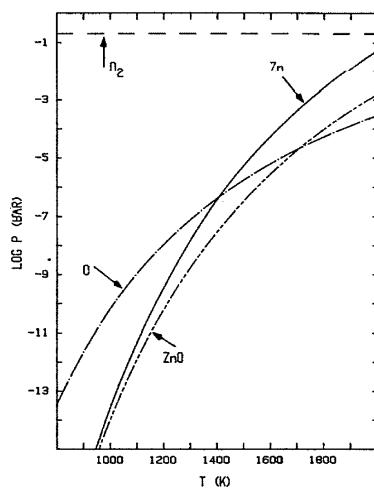
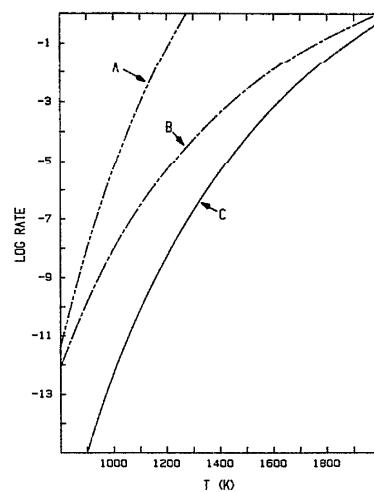


FIG. 58. ZnO congruent vaporization.

FIG. 59. ZnO vaporization in 0.2 bar O<sub>2</sub>.FIG. 60. ZnO maximum vaporization rates. A— $10^{-15}$  bar O<sub>2</sub>; B—congruent vaporization; C—0.2 bar O<sub>2</sub>.

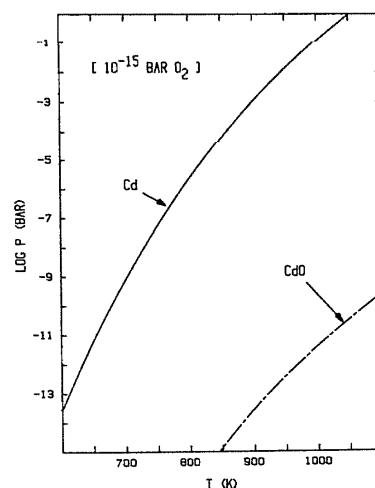
latt (1969) for the nondegenerate electronic ground state,  $r(\text{Zn}-\text{O}) = 0.174 \text{ nm}$  and the value of the vibrational fundamental,  $810 \text{ cm}^{-1}$ , from the matrix-isolation study of Prochaska and Andrews (1980). The selected value of  $\Delta_f H_{298}^\circ/R$  for ZnO(g),  $10.9 \pm 1 \text{ kK}$ , was derived using the mass spectrometric relative intensity measurements of Grade *et al.* (1982) for the vaporization of ZnO(s), and is in reasonable accord with the selected value of Pedley and Marshall (1983),  $13.1 \pm 5 \text{ kK}$ .

#### p. Cd-O System

The stable solid phase is CdO. Vaporization takes place predominantly by dissociation into gaseous Cd and O<sub>2</sub> and a much smaller amount of CdO(g). Figures 61–64 show calculated partial pressures for vaporization of CdO. The Gibbs energy function of CdO(g) was calculated using the estimated internuclear distance of Brewer and Rosenblatt (1969) for the nondegenerate electronic ground state,  $r(\text{Cd}-\text{O}) = 0.185 \text{ nm}$ . The vibrational fundamental,  $719 \text{ cm}^{-1}$ , was taken from the matrix-isolation study of Prochaska and Andrews (1980). The selected value of  $\Delta_f H_{298}^\circ/R$  for CdO(g),  $15.6 \pm 1 \text{ kK}$ , was derived from the mass spectrometric relative intensity measurements of Grade and Hirschwald (1982) for the vaporization of CdO(s), and is in good accord with the selected value of Pedley and Marshall (1983),  $15.1 \pm 10 \text{ kK}$ , and the lower limit found by Behrens and Mason (1981),  $13.7 \text{ kK}$ .

#### q. Hg-O System

The stable solid phase is HgO. Vaporization takes place primarily by dissociation into gaseous Hg and O<sub>2</sub> and a smaller amount of HgO(g). Figures 65–68 show calculated partial pressures for vaporization of HgO. The Gibbs energy function of HgO(g) was calculated using the estimated internuclear distance of Brewer and Rosenblatt (1969),  $0.195 \text{ nm}$ , for the nondegenerate electronic ground state and the vibrational fundamental,  $676 \text{ cm}^{-1}$ , of Butler *et al.* (1979) determined by matrix-isolation spectroscopy. The calculated values of  $-(G_T^\circ - H_{298}^\circ)/RT$  are about 0.1 greater

FIG. 61. CdO vaporization in  $10^{-15}$  bar O<sub>2</sub>.

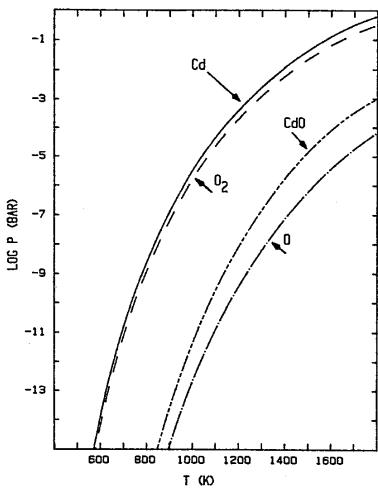


FIG. 62. CdO congruent vaporization.

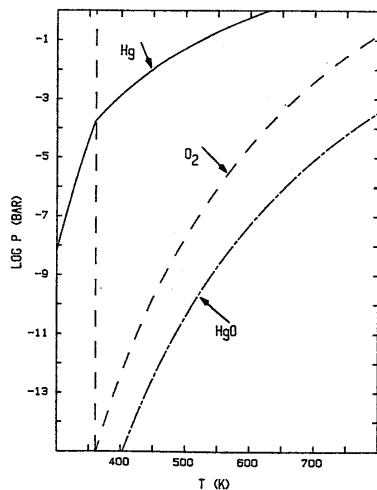
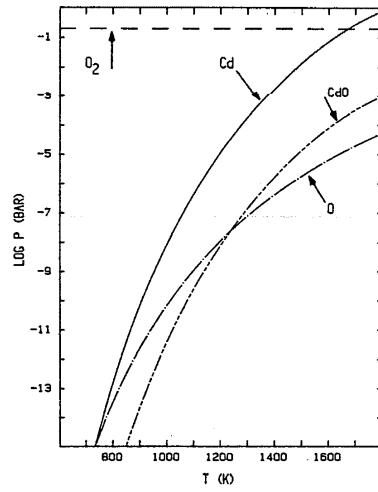
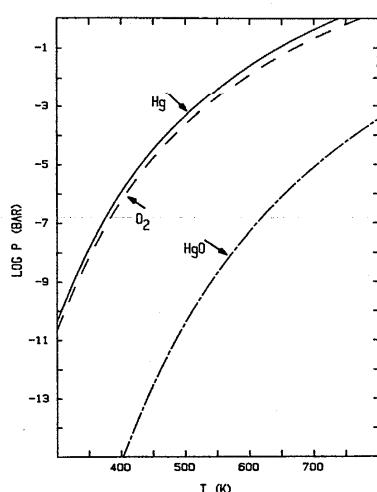
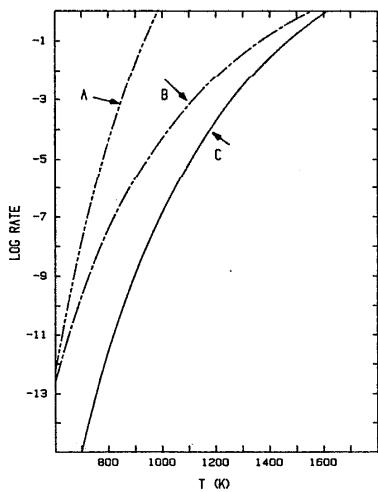
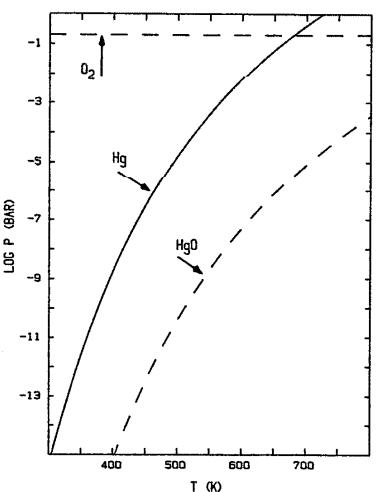
FIG. 65. HgO vaporization in  $10^{-15}$  bar  $O_2$  below 361 K and vaporization of Hg-HgO mixture above 361 K.FIG. 63. CdO vaporization in 0.2 bar  $O_2$ .

FIG. 66. HgO congruent vaporization.

FIG. 64. CdO maximum vaporization rates. A— $10^{-15}$  bar  $O_2$ ; B—congruent vaporization; C—0.2 bar  $O_2$ .FIG. 67. HgO vaporization in 0.2 bar  $O_2$ .

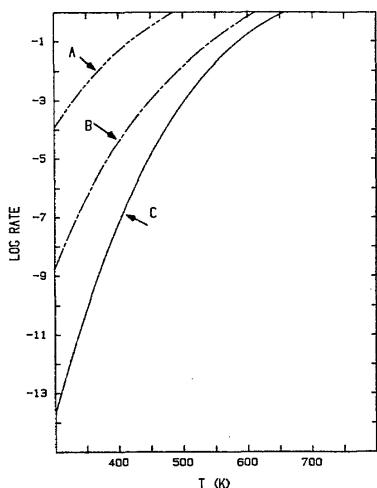


FIG. 68. HgO maximum vaporization rates. A— $10^{-15}$  bar O<sub>2</sub>; B—congruent vaporization; C—0.2 bar O<sub>2</sub>.

than those of JANAF (Stull *et al.*, 1971) from 298 to 2000 K. The selected value of  $\Delta_f H_{298}^\circ / R$  for HgO(g),  $11.2 \pm 1$  kK, was derived from the mass spectrometric ion intensity ratio measurements of Grade and Hirschwald (1982). JANAF (Stull *et al.*, 1971), and Pankratz (1982) had selected the estimated value  $5 \pm 8$  kK.

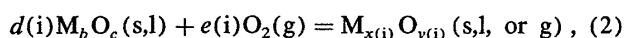
### 3. High-Temperature Equilibria and Reaction Rates

Calculations using the selected thermochemical data were discussed in the previous paper (Lamoreaux and Hildenbrand, 1984). The basic equations are presented here so that species partial pressures and maximum vaporization rates can be calculated for specific temperatures and oxidation conditions.

#### 3.1. Mathematics of Vaporization Calculations

For many vaporization conditions one or two vapor species are predominant, and calculation of the chemical equilibrium from thermodynamic data is straightforward. Calculations can be more complicated when several species are present in significant quantities. The following procedure is a general method for calculating the equilibrium pressures of vapor species in equilibrium with a condensed phase of known composition.

The chemical species present at equilibrium in the vaporization of a condensed binary oxide can be described mathematically as being formed by linear combination of the vaporizing oxide M<sub>b</sub>O<sub>c</sub> and oxygen O<sub>2</sub> according to the general reaction for the production of species i,



where  $e(i)$  may be zero, negative, or positive. Possible species include the vaporizing phase M<sub>b</sub>O<sub>c</sub> (s or l), considered to be species 1, and O<sub>2</sub>(g) as well as the species produced by their linear combination. From mass balance,

$$d(i) = x(i)/b \quad (3)$$

and

$$e(i) = [by(i) - cx(i)]/2b. \quad (4)$$

We define the Gibbs energy of species i at temperature T as

$$G_T^\circ(i)/RT = (G_T^\circ - H_{298}^\circ)/RT + \Delta_f H_{298}^\circ(i)/RT. \quad (5)$$

The Gibbs energy change for the reaction producing species i from M<sub>b</sub>O<sub>c</sub> (s or l) and O<sub>2</sub>(g),  $\Delta_r G_T^\circ(i)$ , is given by

$$\begin{aligned} \Delta_r G_T^\circ(i)/RT &= G_T^\circ(i)/RT - d(i) \\ &\times G_T^\circ[M_bO_c(s \text{ or } l)]/RT \\ &- e(i)G_T^\circ[O_2(g)]/RT, \end{aligned} \quad (6)$$

and the equilibrium constant for producing gas species i is

$$\begin{aligned} K(i) &= \exp[-\Delta_r G_T^\circ(i)/RT] \\ &= p(i)/\{a(1)^{d(i)}p[O_2(g)]^{e(i)}\}, \end{aligned} \quad (7)$$

where the pressures  $p(i)$  are considered low enough that they are equal to fugacities, and  $a(1)$  is the activity of M<sub>b</sub>O<sub>c</sub>. If M<sub>b</sub>O<sub>c</sub> is a pure condensed phase, its activity is unity, and

$$p(i) = k(i)p(O_2)^{e(i)} \quad (8)$$

for the gas species. If the oxygen pressure is known, the pressure of each species i can be calculated from this equation.

For congruent vaporization, the vapor composition is the same as the condensed phase, and

$$\frac{\sum[p(i)x(i)]}{\sum[p(i)y(i)]} = \frac{b}{c}. \quad (9)$$

This leads to the expression

$$\sum\{K(i)p(O_2)^{e(i)}[cx(i) - by(i)]\} = 0, \quad (10)$$

where summation is over the gaseous species present. In practice, this equation is solved for  $p(O_2)$  by graphical interpolation or by numerical methods. The value found for  $p(O_2)$  is then used in Eq. (8) to find the other partial pressures.

For the above calculations to correspond to equilibrium vaporization, they must be used for vaporization of the condensed oxide phases or phases stable under the particular vaporization conditions. Where more than one oxide phase is a possibility, the stable phase or phases must be determined. Two condensed oxide phases of fixed composition at a given temperature are related by the equilibrium

$$\text{Oxide}(1) = \text{Oxide}(2) + fO_2(g). \quad (11)$$

Oxide(1) is assumed to have the greater oxygen activity. The equilibrium constant for this reaction is

$$K_{eq} = a(2)p(O_2)^f/a(1). \quad (12)$$

If both condensed phases are at equilibrium, their activities are unity, and the pressure of O<sub>2</sub> is given by the equation

$$p_{eq}(O_2) = K_{eq}^{(1/f)}. \quad (13)$$

Oxide (1) is the stable phase for O<sub>2</sub> pressures greater than  $p_{eq}(O_2)$ , and oxide (2) is stable for O<sub>2</sub> pressures less than  $p_{eq}(O_2)$  at the given temperature.

### 3.2. Vaporization Rate Calculations

Maximum vaporization rates are calculated using the Hertz-Knudsen equation of classical kinetic theory, which applies to free vaporization from an uncontaminated surface at low pressures. For gas species *i* evolving from the surface, the maximum vaporization rate  $dn(i)/dt$  in mol cm<sup>-2</sup> s<sup>-1</sup> is

$$\frac{dn(i)}{dt} = \frac{p(i)}{[2\pi M(i)RT]^{1/2}}, \quad (14)$$

where  $M(i)$  and  $p(i)$  are the gram molecular weight and equilibrium partial pressure of vapor species *i*, and  $R$  and  $T$  are the molar gas constant and absolute temperature. Since 1 bar is  $10^6$  dyn cm<sup>-2</sup> and  $R$  is  $8.3144 \times 10^6$  erg mol<sup>-1</sup> deg<sup>-1</sup>, for pressures in bar, this is equivalent to

$$\frac{dn(i)}{dt} = 43.8 \left( \frac{p(i)}{[M(i)T]^{1/2}} \right) \text{ mol cm}^{-2} \text{ s}^{-1}. \quad (15)$$

Calculation of maximum vaporization rates is more difficult for incongruent than for congruent processes. In general, solid-phase activities during the vaporization process are not known, and calculated maximum vaporization rates of oxides that deviate from their original stoichiometry should be considered indicative rather than exact (Beruto *et al.*, 1981). In the present work, maximum vaporization rates have been calculated for incongruent, as well as congruent vaporization. Only initial vaporization rates, for which no condensed phase composition changes have taken place, are considered. Vaporization rates are expressed in terms of the mass of originally present oxide  $M_b O_c$  lost as measured by the volatility of metal atoms. The total mass loss thus calculated is

$$\frac{dm}{dt} = 44.3 \left( \frac{M(M_b O_c)}{b} \right) \sum \left( \frac{p(i)x(i)}{[M(i)T]^{1/2}} \right), \quad (16)$$

where  $dm/dt$  is the mass loss rate in g cm<sup>-2</sup> s<sup>-1</sup>,  $M_b O_c$  is the formula of the condensed oxide, and  $x(i)$  and  $M(i)$  are the number of gram atoms of metal per mole and gram molecular weight of gas species *i*.

Although actual vaporization rates may be lower because of kinetic factors, the calculated maximum vaporization rate is useful as a rough guide to material loss rates. Recent references on maximum vaporization rates include works by Turkdogan (1980) and Beruto *et al.* (1981).

### 4. Acknowledgments

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