

# THE THERMODYNAMIC PROPERTIES OF THE OXIDES AND THEIR VAPORIZATION PROCESSES

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## CONTENTS

I. Introduction.....	2
II. Solid-phase equilibria of binary oxide systems.....	5
A. Alkali metal oxides.....	5
B. Alkaline earth oxides.....	12
C. Boron-aluminum group oxides.....	14
D. Actinide group oxides.....	18
E. Titanium-zirconium group oxides.....	22
F. Vanadium group oxides.....	24
G. Chromium group oxides.....	27
H. Manganese group oxides.....	30
I. Iron group oxides.....	32
J. Platinum group oxides.....	35
K. Copper group oxides.....	36
L. Zinc group oxides.....	37
M. Gallium group oxides.....	38
N. Silicon group oxides.....	38
O. Nitrogen-phosphorus group oxides.....	41
P. Sulfur group oxides.....	43
Q. Halogen group oxides.....	43
R. Hydrogen oxides.....	43
III. The vaporization processes of oxides.....	44
A. Alkali metal oxides.....	46
B. Alkaline earth oxides.....	48
C. Boron-aluminum group oxides.....	51
D. Actinide group oxides.....	53
E. Titanium-zirconium group oxides.....	54
F. Vanadium group oxides.....	56
G. Chromium group oxides.....	56
H. Manganese group oxides.....	57
I. Iron group oxides.....	58
J. Platinum group oxides.....	58
K. Copper group oxides.....	60
L. Zinc group oxides.....	61
M. Gallium group oxides.....	61
N. Carbon-silicon group oxides.....	62
O. Nitrogen-phosphorus group oxides.....	63
P. Sulfur group oxides.....	64
Q. Halogen group oxides.....	64
R. Hydrogen oxides.....	64
IV. References.....	65

## I. INTRODUCTION

The primary purpose of this review is to provide the information that is necessary to carry out trustworthy thermodynamic calculations in systems involving compounds of oxygen. Very accurate thermodynamic calculations have often yielded unreliable results because the calculations were carried out without recognition of the phases or gaseous species which were most important in the system under consideration. For example, a calculation designed to determine the conditions for the reduction of  $\text{TiO}_2$  to the metal by hydrogen would be meaningless if the existence of lower oxide phases were not recognized. This review discusses for each binary system the solid phases that can exist and the gaseous oxide species that can be expected to be of chemical importance.

Many of the results of Sections II and III are summarized in table 1, which lists the following for each oxide phase:  $\Delta F$ ,  $\Delta H$ , and  $\Delta S$  of formation at  $298^\circ\text{K}$ .; the melting point in degrees Kelvin; and the temperatures in degrees Kelvin at which the total pressure of gaseous products in equilibrium with the oxide phase is equal to  $10^{-3}$  atm. in one column and 1 atm. in the other column. Whenever possible the uncertainty of all quantities given is listed. All estimated quantities are enclosed in parentheses.

References to the sources of data in table 1 are given in the text, where each system is discussed in detail. Several types of data were obtained from recent reviews; references to these data are not given in the text except where newer data have appeared since the review. Thus, unless otherwise noted, all entropy values used in this review have been taken from Kelley (246) and all high-temperature heat-capacity data have been taken from Kelley (245). These two recent excellent compilations are indispensable for any thermodynamic calculations. The second reference, which tabulates heat contents and entropy increases above  $298^\circ\text{K}$ ., is especially convenient, since it eliminates the use of involved heat-capacity equations. Any thermodynamic data required for the elements have been taken from the compilation by Brewer (54), except for a few recent data. References are not given to determinations of crystal structures when these determinations are available in *Strukturbericht* (199). Wyckoff (457) also gives a very complete listing of structures, but when the original references are not available in *Strukturbericht*, they are included here even though they may also have been given by Wyckoff. Unfortunately it has not been possible to make much use of Circular 500 of the National Bureau of Standards, *Selected Values of Chemical Thermodynamic Properties* (316), as the references to their values are not yet available. Whenever their values differ greatly from the values given here, a notation to that effect is made in the text.

The order of discussion of the oxides will be the order of the elements in the extended Periodic Table, starting at the top of each column and moving to the top of the next column to the right after reaching the bottom. Although the oxides of all elements are included for completeness, more emphasis is given to the oxides of the metallic elements. In general, the unstable peroxides are not discussed, although many metastable normal oxides are included.

The problem of nomenclature is much more difficult for the naming of the

solid compounds than for the gaseous compounds. For gaseous compounds the laws of definite combining proportions and simple integral atomic combining ratios hold exactly, since the smallest change that can be produced is to add or take away one atom. Starting with NO this process would yield  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , or N, all distinctly different substances with different names. However, if we consider a solid like TiO, we do not find any evidence of gaseous molecules in the crystal lattice. A perfect crystal of TiO weighing 64 g. is a single molecule with the formula  $\text{Ti}_{10}^{22}\text{O}_{10}^{22}$ . Removal of one atom would result in  $\text{Ti}_{10}^{22}\text{O}_{10}^{22-1}$  or a negligible change in composition. With such solid compounds one can produce essentially continuous infinitesimal changes in composition. Thus TiO crystals can be prepared with any composition varying from  $\text{TiO}_{0.7}$  to  $\text{TiO}_{1.25}$ . We find no definite combining proportions or simple integral atomic combining ratios. The only significance of the formula TiO is that the ideal crystal with all sites filled would have this formula. Often the ideal composition does not even exist. Ferrous oxide has the same sodium chloride crystal structure as TiO and also exists for a range of compositions, but the composition FeO does not exist as a stable phase. Thus, while one might refer to the range of compositions from  $\text{TiO}_{0.7}$  to  $\text{TiO}_{1.25}$  as the TiO phase region or the TiO solid-solution range, the designation of the FeO phase region to a range of compositions that does not even include the composition FeO does not seem as reasonable. It has been the practice to refer to the ferrous oxide phase region as the wustite phase region. Such a practice is not very satisfactory, since one must learn a collection of names that have no obvious relationship to the phase composition or structure. It is difficult to use the common terms such as ferrous and ferric, since the stable phases are not restricted to integral oxidation states. It proves impractical to consider the compounds as solid solutions of simple compounds, since the selection of the simple compounds often becomes very arbitrary and is especially misleading when the simple compounds do not themselves exist.

Hägg (183) has reviewed a number of possible nomenclature procedures to handle the problem of solid phases. A satisfactory nomenclature should indicate, if possible, (1) the elements involved, (2) the crystal structure of the phase region under discussion, and (3) the range in composition. The formula " $\text{TiO}_{0.7-1.25}$  (NaCl type)" meets most of these requirements. There is some difficulty in giving a definite composition range, since it varies with the temperature. Probably the best solution would be to give the maximum range. Usually the range is known only over a limited temperature range and that is what one must indicate. Hägg (183) suggests that some indication be given of the type of deviation from ideal structure. Thus, ferrous oxide is believed to deviate largely from the perfect NaCl structure by being deficient in iron atoms resulting from vacant cation sites in the lattice. He would indicate this by use of the formula " $\text{Fe}_{1-x}\text{O}$  (NaCl type)" to differentiate from a deviation due largely to anion vacancies. At any temperature above absolute zero, even for the ideal composition, there will be both cation and anion vacancies, but it is sometimes of value to indicate the predominant type of vacancy or for some compounds the type of interstitial addition. In the TiO homogeneity range either type of vacancy may predominate;

this could be indicated by the formula  $Ti_{1-x}O_{1-y}$ . However, this is somewhat cumbersome. The greatest difficulty is that usually we do not definitely know the type of deviation from ideal structure. For such situations the formula  $TiO_{0.7-1.25}$  seems most suitable. The formula  $TiO_{1\pm x}$  might also be useful. It could indicate that there is a composition range on either side of TiO of unknown extent.

The following procedure will be generally followed in this paper: " $TiO_{0.7-1.25}$  (NaCl type)" will be the usual shorthand designation to indicate the crystal type and composition range. For general discussion, when the exact composition range and crystal structure are not necessary, the term "FeO homogeneity range" or "FeO phase region" will be used to designate the range of compositions with a structure corresponding to an ideal composition FeO even when the ideal composition is not stable. Often no information is available about the composition range of a phase. Then the formula corresponding to the ideal crystal structure will be used without any commitment as to the homogeneity range. Thus, the designation of a phase as the  $Na_2O$  phase, for example, does not mean that this phase does not have a wide homogeneity range.

In Section I the order of discussion for each element is (1) the consideration of the known oxide phases, their crystal structures, and their temperature and composition ranges; (2) the heat of formation data for each phase, together with consideration of high-temperature equilibria data that relate to the thermodynamic data given in table 1.

In Section II, references will be given to the melting and vaporization data listed in table 1. The vaporization data will be analyzed in terms of the possible gaseous molecules that could be involved, and the stabilities of the various gaseous molecules will be considered. The constant-boiling compositions of each system will be considered, and the composition of the vapor in equilibrium with each phase will be discussed. A summary of the stabilities of the gaseous molecules that are known to exist is presented in table 2, where the  $D_0$  values are given in kilocalories. The term  $D_0$ , which is used by spectroscopists to represent the stability of gaseous molecules, is  $\Delta H_0$  for the reaction  $MN(g) = M(g) + N(g)$ . For polyatomic molecules,  $D_0$  is the corresponding  $\Delta H_0$  value for the molecule dissociating to the component atoms in their ground states at 0°K. These values are given in kilocalories to conform to the units used throughout the paper. They may be converted to electron volts by dividing the value in kilocalories by 23.060.

The units used in this review are consistent with the units adopted by the U. S. Bureau of Standards (316). The kilocalorie is related to the absolute joule by the expression 1 kilocalorie = 4.184 kilojoules and  $R$ , the gas constant, is taken as 1.9872 cal. per degree per mole. The use of 298°K. throughout the paper is intended as an abbreviation for 298.16°K.

It is believed that all data available in the literature up to 1951 have been considered in this review. In addition, a large fraction of the important papers up to 1952 have also been considered.

When reviews such as those of Kelley (243, 244, 245, 246), Bichowsky and

Rossini (29), etc. adequately discuss the available data, reference will be made only to the review paper and not to the original papers unless it is desired to comment specifically on these papers. When a recent paper presents a new determination along with a review of previous data, reference will be made only to the most recent paper in order to prevent the list of references from becoming unwieldy.

## II. SOLID-PHASE EQUILIBRIA OF BINARY OXIDE SYSTEMS

### A. Alkali metal oxides

All of the alkali metals have oxides approximating the formula  $M_2O$ . Except for  $Cs_2O$  ( $CdCl_2$  type) all of them have the anti- $CaF_2$  crystal structure. The alkali metals are rather unusual, in that they can form rather stable phases containing oxygen in the form of the peroxide ion,  $O_2^{--}$ , and the superoxide ion,  $O_2^-$ . Feher (137) has made x-ray studies of  $Li_2O_2$  and  $Na_2O_2$  and Aguzzi and Genoni (3) have studied  $Li_2O_2$ . They reported the oxides to be isomorphous and closely related to the  $Hg_2Cl_2$  structure. The interpretation of the structure seems questionable. Frevel (149), Templeton (406), and Margrave (291) have since reported further x-ray work on  $Na_2O_2$ . Their results do not agree with those reported by Feher, but it has not been possible to index the lines as yet. In spite of frequent claims (94, 95, 148, 207, 240) for their existence, a critical examination of all available data indicates that potassium, rubidium, and cesium probably do not form  $M_2O_2$  solid phases.

The isomorphous  $Rb_2O_3$  and  $Cs_2O_3$  (anti- $Th_3P_4$  type) have been reported by Helms and Klemm (193), but there is no definite indication that any of the other alkali metals form an  $M_2O_3$  phase. The data do not substantiate claims for  $K_2O_3$  and  $Na_2O_3$  (94, 95, 148, 207).

All of the alkali metals except lithium form  $MO_2$  superoxides. Schechter, Stephanou, and Kleinberg (254, 256, 366, 397) have only recently discovered  $NaO_2$ . X-ray studies over a range of temperatures (93, 408) and low-temperature heat-capacity measurements (415) indicate that  $NaO_2$  has at least three crystal-line modifications. Below  $196^\circ K$ . one obtains  $NaO_2$  ( $FeS_2$  marcasite type). Between  $196^\circ$  and  $223^\circ K$ . one obtains the  $FeS_2$  pyrites crystal structure and above  $223^\circ K$ . one obtains  $NaO_2$  ( $NaCl$  type). Although  $KO_2$  has been known much longer, it has not been studied as thoroughly. Above  $403^\circ K$ . it has a cubic  $NaCl$  structure (92, 93). Below  $403^\circ K$ . a tetragonal form of  $KO_2$  is formed. At lower temperatures measurements of specific heat (319, 415) indicate two further transitions. X-ray examinations confirm this, but the phases have not been characterized as yet.

In addition to the normal oxides, peroxides, and superoxides, there are reports of suboxides. The only phases definitely substantiated are  $Cs_7O_2$ ,  $Cs_4O$ , and  $Cs_3O$ , melting incongruently, and  $Cs_7O$ , melting congruently. These phases were demonstrated by Rengade (347) and verified by Brauer (49) by means of x-ray and electrical resistance measurements. The eutectic is found at  $CsO_{0.099}$ . Because complete phase diagram studies have not been made for any of the alkali metal-oxygen systems, still other phases might be demonstrated. Margrave

TABLE 1  
*Thermodynamic and physical properties of the oxides*

OXIDE	$\Delta F_{298}$	$\Delta H_{298}$	$\Delta S_{298}$	$T_M$	VAPORIZATION TEMPERATURES		
					$T_{10^{-3}\text{atm.}}$	$T_{1\text{atm.}}$	
	<i>kcal.</i>	<i>kcal.</i>	<i>e.u.</i>	$^{\circ}\text{K.}$	$^{\circ}\text{K.}$	$^{\circ}\text{K.}$	
Li <sub>2</sub> O.....	-134.0	-142.6 ± 2	-28.85	2000	1830 ± 50	2600 ± 100	
½Li <sub>2</sub> O <sub>2</sub> .....	-68.	-76. ± 2	(-26)	d. 470, 1 atm. O <sub>2</sub>			
Na <sub>2</sub> O.....	-90.	-99.4 ± 1	-31.9	1193	d. 1330 ± 20	d. 2040 ± 60	
½Na <sub>2</sub> O <sub>2</sub> .....	-53.	-61.1 ± 0.5	-25.4	948	d. 919, 1 atm. O <sub>2</sub>		
½NaO <sub>2</sub> .....	-25.9	-31.0 ± 1	-16.8	Metastable at room temperature			
K <sub>2</sub> O.....	-77.	-86.4 ± 2	(-32)	(>763)	d. 1150 ± 50	d. 1750 ± 100	
½K <sub>2</sub> O <sub>2</sub> .....	-28.7	-33.8 ± 0.5	-18.2	653	d. 760, 628 mm. O <sub>2</sub>		
Rb <sub>2</sub> O.....	-69.	-78.9 ± 3	(-32)	(>840)	d. 1100 ± 70	d. 1600 ± 100	
⅓Rb <sub>2</sub> O <sub>3</sub> .....	-36.	-42. ± 3	(-20)	762	d. 1043, 163 mm. O <sub>2</sub>		
½RbO <sub>2</sub> .....	-29.	-34. ± 3	(-18)	685	d. 1033, 225 mm. O <sub>2</sub>		
Cs <sub>7</sub> O.....	<-66.			276	d. 283 to Cs <sub>7</sub> O <sub>2</sub> + liquid		
Cs <sub>4</sub> O.....	<-66.				d. 443 to Cs <sub>2</sub> O + liquid		
Cs <sub>2</sub> O.....	<-66.				d. 323 to Cs <sub>3</sub> O + liquid		
½Cs <sub>7</sub> O <sub>2</sub> .....	<-66.						
Cs <sub>2</sub> O.....	-66.	-75.9 ± 3	(-32)	763	d. 1000 ± 70	d. 1500 ± 100	
⅓Cs <sub>2</sub> O <sub>3</sub> .....	-40.	-45. ± 5	(-20)	775	d. 1125, 108 mm. O <sub>2</sub>		
½CsO <sub>2</sub> .....	-33.	-38. ± 3	(-18)	705	d. 1153, 225 mm. O <sub>2</sub>		
BeO.....	-140.	-147. ± 5	-23.4	2820 ± 30	d. 2900 ± 50	d. 4300 ± 100	
MgO.....	-136.0	-143.7 ± 0.1	-25.7	3075 ± 30	2450 ± 100	3350 ± 300	
½MgO <sub>2</sub> .....	-68.	-74.4 ± 0.5	(-20)	d. 361, 1 atm. O <sub>2</sub> to MgO <sub>2</sub> ·3MgO			
CaO.....	-144.3	-151.7 ± 0.5	-25.0	2860 ± 25	2650 ± 50	3800 ± 200	

$\frac{1}{2}\text{CaO}_2$ .....	-72.	$-78.2 \pm 0.5$	(-20)	d. 548, 1 atm. O <sub>2</sub>		
SrO.....	-133.6	$-140.8 \pm 1$	-24.0	2730 $\pm$ 20	2400 $\pm$ 100	3500 $\pm$ 200
$\frac{1}{2}\text{SrO}_2$ .....	-70.6	$-76.6 \pm 2$	(-20)	d. 488, 1 atm. O <sub>2</sub>		
BaO.....	-126.	$-133. \pm 2$	-23.7	2196 $\pm$ 10	2120 $\pm$ 100	3000 $\pm$ 200
$\frac{1}{2}\text{BaO}_2$ .....	-70.	$-76.2 \pm 3$	(-20)	d. 1110, 1 atm. O <sub>2</sub>		
RaO.....	-123.	$(-130.) \pm 4$	(-24)			
$\frac{1}{3}\text{B}_2\text{O}_3$ (cryst.).....	-96.	$-101.8 \pm 1$	-21.3	723	1740	2520
$\frac{1}{3}\text{Al}_2\text{O}_3$ .....	-126.0	$-133.4 \pm 0.1$	-24.8	2300 $\pm$ 20	d. 2740 $\pm$ 60	d. 3800 $\pm$ 200
$\frac{1}{3}\text{Sc}_2\text{O}_3$ .....	-130.	$(-137.) \pm 3$	(-24)			
$\frac{1}{3}\text{Y}_2\text{O}_3$ .....	-134.	$(-140.) \pm 3$	(-23)	2690 $\pm$ 100		4570 $\pm$ 300
$\frac{1}{3}\text{La}_2\text{O}_3$ .....	-138.5	$-145. \pm 1$	(-22)	2590 $\pm$ 20		4470 $\pm$ 300
$\frac{1}{3}\text{Ce}_2\text{O}_3$ .....	-138.5	$(-145.) \pm 1$	(-22)			
$\frac{1}{2}\text{CeO}_2$ .....	-116.	$-122.5 \pm 2$	(-22)	3000 $\pm$ 20	under O <sub>2</sub> pressure	
$\frac{1}{3}\text{Pr}_2\text{O}_3$ .....	-138.	$-144.6 \pm 1$	(-22)			
$\frac{1}{11}\text{Pr}_6\text{O}_{11}$ .....	-117.5	$-124.0 \pm 0.5$	(-22)	d. 1340, 1 atm. O <sub>2</sub> to Pr <sub>2</sub> O <sub>3+x</sub>		
$\frac{1}{2}\text{PrO}_2$ .....	-108.5	$-115. \pm 1$	(-22)	d. 700, 1 atm. O <sub>2</sub>		
$\frac{1}{3}\text{Nd}_2\text{O}_3$ .....	-135.	$-142. \pm 1$	(-22)			
$\frac{1}{3}\text{Ac}_2\text{O}_3$ .....	-142.	$(-148.) \pm 3$	(-21)			
ThO.....	-139.	$(-145.) \pm 10$	(-21)			
$\frac{1}{2}\text{ThO}_2$ .....	-140.	$-146.6 \pm 0.5$	(-21)	3225 $\pm$ 200		4670 $\pm$ 300
$\frac{1}{5}\text{Pa}_2\text{O}_5$ .....	-100.	$(-106.) \pm 5$	(-21)			
UO.....	-123.	$(-129.) \pm 5$	(-21)			
$\frac{1}{2}\text{UO}_2$ .....	-123.3	$-129.6 \pm 0.4$	-21.2	3000 $\pm$ 200		
$\frac{1}{2.25}\text{UO}_{2.25}$ .....	-114.	$-120. \pm 1$	(-21)			
$\frac{1}{2.62}\text{UO}_{2.62}$ .....	-103.	$-109. \pm 1$	(-21)	d. 1950, 1 atm. O <sub>2</sub> to UO <sub>2.25</sub>		
$\frac{1}{8}\text{U}_3\text{O}_8$ .....	-100.5	$-106.7 \pm 4$	-20.8			
$\frac{1}{3}\text{UO}_3$ (hex.).....	-91.	$-97.3 \pm 2$	-20.7	d. 925, 1 atm. O <sub>2</sub> to U <sub>3</sub> O <sub>8</sub>		

TABLE 1—Continued

8

OXIDE	$\Delta F_{298}$	$\Delta H_{298}$	$\Delta S_{298}$	$T_M$	VAPORIZATION TEMPERATURES	
					$T_{10^{-3}\text{atm.}}$	$T_{1\text{atm.}}$
	<i>kcal.</i>	<i>kcal.</i>	<i>e.u.</i>	$^{\circ}\text{K.}$	$^{\circ}\text{K.}$	$^{\circ}\text{K.}$
$\frac{1}{2}\text{NpO}_2$ .....	-117.	(-123.) $\pm$ 5	-21			
$\frac{1}{5}\text{Np}_2\text{O}_6$ .....	-96.	(-102.) $\pm$ 5	(-21)	d. 800-900		
PuO.....	<-117.	<-123.	(-21)			
$\frac{1}{2}\text{PuO}_2$ .....	-117.	(-123.) $\pm$ 5	-21	>2200		
$\frac{1}{3}\text{Am}_2\text{O}_3$ .....	-134.	(-140.) $\pm$ 5	(-21)			
$\frac{1}{2}\text{AmO}_2$ .....	-114.	-120. $\pm$ 3	(-21)	d. 1680, 13 mm. O <sub>2</sub> to AmO <sub>1.85</sub>		
Ti <sub>1.45</sub> O.....	-118.	-125. $\pm$ 2	(-23)	Disproportionates 1198 to Ti + TiO		
TiO.....	-117.1	-123.9 $\pm$ 0.3	-22.8	d. 2010	2275 $\pm$ 50	2970 $\pm$ 100
$\frac{1}{3}\text{Ti}_2\text{O}_3$ .....	-114.2	-121.0 $\pm$ 0.1	-22.6	2400		3300 $\pm$ 300
$\frac{1}{5}\text{Ti}_3\text{O}_6$ .....	-110.6	-117.4 $\pm$ 0.1	-22.7			
$\frac{1}{2}\text{TiO}_2$ .....	-106.2	-112.8 $\pm$ 0.1	-22.1	2128 $\pm$ 20		d. 3200 $\pm$ 300
$\frac{1}{2}\text{ZrO}_2$ .....	-124.0	-130.9 $\pm$ 0.1	-23.1	2960 $\pm$ 25		4570 $\pm$ 300
$\frac{1}{2}\text{HfO}_2$ .....	-126.1	-133.0 $\pm$ 0.1	-23.1	3063 $\pm$ 25		
VO.....	-91.	-98. $\pm$ 5	-22.2			3400 $\pm$ 500
$\frac{1}{3}\text{V}_2\text{O}_3$ .....	-92.	-98.7 $\pm$ 2	-21.3	2240		d. 3300 $\pm$ 300
$\frac{1}{5}\text{V}_3\text{O}_5$ .....		<-93.5				
$\frac{1}{2}\text{VO}_2$ .....	-79.	-85.5 $\pm$ 1	-21.9	1818 $\pm$ 30		d. 3000 $\pm$ 300
$\frac{1}{13}\text{V}_8\text{O}_{13}$ .....	-75.	-81.5 $\pm$ 1	-21.2	935 $\pm$ 10		
$\frac{1}{5}\text{V}_2\text{O}_5$ .....	-68.	-74.5 $\pm$ 1	-21.1	943 $\pm$ 2	(1225)	(2100)
					In presence of high O <sub>2</sub>	
NbO.....	-90.5	-97. $\pm$ 2	(-22)			
$\frac{1}{2}\text{NbO}_2$ .....	-88.	-94.5 $\pm$ 0.5	(-22)			
$\frac{1}{5}\text{Nb}_2\text{O}_5$ .....	-84.4	-91.0 $\pm$ 0.1	(-22)	1733 $\pm$ 5		
$\frac{1}{5}\text{Ta}_2\text{O}_5$ .....	-91.3	-97.8 $\pm$ 0.1	-21.7	2150 $\pm$ 100	>2000	
$\frac{1}{3}\text{Cr}_2\text{O}_3$ .....	-83.5	-90.0 $\pm$ 0.3	-21.8	2710 $\pm$ 10		d. 3300 $\pm$ 300

LEO BREWER

$\frac{1}{2}\text{CrO}_2$ .....	-64.5	$-70.5 \pm 2$	(-20)	d. 700, 1 atm. $\text{O}_2$		
$\frac{1}{3}\text{CrO}_3$ .....	-40.0	$-45.9 \pm 1$	(-20)	460	Metastable	
$\frac{1}{2}\text{MoO}_2$ .....	-60.	$-65.5 \pm 1$	-18.3	d. $2250 \pm 50$ to Mo(s) + 1 atm. $\text{MoO}_3(\text{g})$		
$\frac{1}{11}\text{Mo}_4\text{O}_{11}$ .....	-56.	$(-61.) \pm 2$	(-20)	Disproportionates		
$\frac{1}{23}\text{Mo}_8\text{O}_{23}$ .....	-54.5	$(-60.5) \pm 2$	(-20)	Disproportionates		
$\frac{1}{26}\text{Mo}_9\text{O}_{26}$ .....	-54.5	$(-60.5) \pm 2$	(-20)	Disproportionates		
$\frac{1}{3}\text{MoO}_3$ .....	-54.0	$-60.1 \pm 0.5$	-20.5	1068	$1055 \pm 10$	$1530 \pm 50$
$\frac{1}{2}\text{WO}_2$ .....	-61.	$-67. \pm 1$	(-20.5)	d. $2125 \pm 50$ to W(s) + 1 atm. $\text{WO}_3(\text{g})$		
$\frac{1}{49}\text{W}_{18}\text{O}_{49}$ .....	-60.6	$-66.7 \pm 1$	(-20.5)	Disproportionates		
$\frac{1}{29}\text{W}_{10}\text{O}_{29}$ .....	-60.6	$(-66.7) \pm 1$	(-20.5)	Disproportionates		
$\frac{1}{3}\text{WO}_3$ .....	-60.6	$-66.7 \pm 0.1$	-20.5	$1746 \pm 1$	$1560 \pm 20$	$2100 \pm 100$
MnO.....	-86.7	$-92.0 \pm 0.1$	-17.8	2058	d. $2300 \pm 50$	d. $3400 \pm 100$
$\frac{1}{4}\text{Mn}_2\text{O}_4$ .....	-76.4	$-82.8 \pm 0.1$	-21.3	$1863 \pm 20$		
$\frac{1}{3}\text{Mn}_2\text{O}_3$ .....	-69.8	$-76.4 \pm 0.3$	-22.0	d. 1620, 1 atm. $\text{O}_2$		
$\frac{1}{2}\text{MnO}_2$ .....	-55.6	$-62.1 \pm 0.1$	-22.0	d. 1120, 1 atm. $\text{O}_2$		
$\frac{1}{2}\text{TcO}_2$ .....	-45.6	$-51.7 \pm 1$	(-20.5)			
$\frac{1}{3}\text{TcO}_3$ .....	-36.6	$-43. \pm 2$	(-21.5)	Disproportionates to $\text{TcO}_2$ and $\text{Tc}_2\text{O}_7(\text{g})$		
$\frac{1}{7}\text{Tc}_2\text{O}_7$ .....	-31.8	$-38.0 \pm 0.4$	(-21)	$392.7 \pm 0.1$	390	583
$\frac{1}{2}\text{ReO}_2$ .....	-45.1	$-51.7 \pm 7$	(-22)			
$\frac{1}{3}\text{ReO}_3$ .....	-43.	$-49 \pm 1$	(-21)	433	Disproportionates to $\text{ReO}_2$ and $\text{Re}_2\text{O}_7(\text{g})$	
$\frac{1}{7}\text{Re}_2\text{O}_7$ .....	-36.3	$-42.4 \pm 0.3$	(-20.5)	569	$483.5$	$635.5$
$\text{Fe}_{0.95}\text{O}$ .....	-58.3	$-63.2 \pm 0.5$	-16.5	d. $1644 \pm 1$	d. $2300 \pm 50$	d. $3400 \pm 100$
$\frac{1}{4}\text{Fe}_3\text{O}_4$ .....	-61.0	$-67.0 \pm 0.2$	-20.1	$1870 \pm 2$	d. $1840 \pm 10$	d. $2060 \pm 30$
$\frac{1}{3}\text{Fe}_2\text{O}_3$ .....	-59.3	$-65.7 \pm 0.2$	-21.7	d. $1730 \pm 5$ , 1 atm. $\text{O}_2$ to $\text{Fe}_3\text{O}_{4+x}$		
CoO.....	-51.	$-57. \pm 0.5$	(-19)	$2078 \pm 20$		d.
$\frac{1}{4}\text{Co}_3\text{O}_4$ .....	-45.	$-51. \pm 1$	(-20)	d. 1240, 1 atm. $\text{O}_2$		
NiO.....	-51.3	$-58.0 \pm 0.5$	-22.4	$2230 \pm 20$		d.
$\frac{1}{2}\text{RuO}_2$ .....	-20.4	$-26.3 \pm 2$	(-19.8)	>1228	d. $1400 \pm 30$ , 1 atm. $\text{O}_2$	

TABLE 1—Concluded

OXIDE	$\Delta F_{298}$	$\Delta H_{298}$	$\Delta S_{298}$	$T_M$	VAPORIZATION TEMPERATURES		
					$T_{10^{-3}\text{atm.}}$	$T_{1\text{atm.}}$	
	<i>kcal.</i>	<i>kcal.</i>	<i>e.u.</i>	$^{\circ}\text{K.}$	$^{\circ}\text{K.}$	$^{\circ}\text{K.}$	
$\frac{1}{4}\text{RuO}_4$ .....	(-8.)	(-13.) $\pm$ 2	(-18)	300 (brown) metastable to $\text{RuO}_2 + \text{O}_2$			
$\text{Rh}_2\text{O}$ .....	-20.	-24.0 $\pm$ 3	(-12.3)	d. 1400, 1 atm. $\text{O}_2$			
$\text{RhO}$ .....	-18.	-23.9 $\pm$ 3	(-19)	d. 1394, 1 atm. $\text{O}_2$			
$\frac{1}{3}\text{Rh}_2\text{O}_3$ .....	-17.5	-23.7 $\pm$ 3	(-20.7)	d. 1388, 1 atm. $\text{O}_2$			
$\text{PdO}$ .....	-15.	-21. $\pm$ 2	(-20.3)	d. 1150, 1 atm. $\text{O}_2$			
$\frac{1}{2}\text{OsO}_2$ .....	(-25.)	(-31.) $\pm$ 5	(-20)	Disproportionates 923, 1 atm. $\text{OsO}_4(\text{g})$			
$\frac{1}{4}\text{OsO}_4(\text{yellow})$ .....	-17.7	-23.4 $\pm$ 3	-19.1	329                      273                      403			
$\frac{1}{2}\text{IrO}_2$ .....	-16.	-22. $\pm$ 3	(-20.2)	>1373                      d. 1373, 1 atm. $\text{O}_2$			
$\text{PtO}$ .....	(-11.) $\pm$ 4	(-17.) $\pm$ 5	(-20)	d. 780 $\pm$ 30, 1 atm. $\text{O}_2$			
$\frac{1}{4}\text{Pt}_2\text{O}_4$ .....		(-16.) $\pm$ 6					
$\frac{1}{2}\text{PtO}_2$ .....	(-10.) $\pm$ 10	(-16.) $\pm$ 5	(-20)	d. 750, 1 atm. $\text{O}_2$			
$\text{Cu}_2\text{O}$ .....	-35.0	-39.8 $\pm$ 0.5	-16.3	1503			
$\text{CuO}$ .....	-30.4	-37.1 $\pm$ 0.5	-22.1	1609 under oxygen pressure			
$\text{Ag}_2\text{O}$ .....	-2.59	-7.31 $\pm$ 0.1	-15.8	d. 460, 1 atm. $\text{O}_2$			
$\frac{1}{3}\text{Au}_2\text{O}_3$ .....			(-22.1)	Metastable			
$\text{ZnO}$ .....	-76.1	-83.2 $\pm$ 0.1	-23.9	2248                      d. 1600 $\pm$ 10                      d. 2250 $\pm$ 25			
$\text{CdO}$ .....	-55.1	-62.2 $\pm$ 0.5	-23.7	>1500                      d. 1240 $\pm$ 10                      d. 1750 $\pm$ 20			
$\text{HgO}$ .....	-13.99	-21.68 $\pm$ 0.1	-26.4		d. 510 $\pm$ 10                      d. 750 $\pm$ 15		
$\text{Ga}_2\text{O}$ .....	-75.	-82. $\pm$ 2	(-22.9)				
$\frac{1}{3}\text{Ga}_2\text{O}_3$ .....	-79.	-86. $\pm$ 1	(-23.3)	1998			
$\frac{1}{3}\text{In}_2\text{O}_3$ .....	-66.	-73. $\pm$ 1	(-24.0)				
$\text{Tl}_2\text{O}$ .....	-33.1	-42.5 $\pm$ 1	(-31.5)				
$\frac{1}{3}\text{Tl}_2\text{O}_3$ .....	-21.	-28. $\pm$ 2	(-24.0)	990 $\pm$ 5			
$\text{SiO}$ .....	-98.	-104.6 $\pm$ 3	(-23)	>2000                      1510 $\pm$ 20			
$\frac{1}{2}\text{SiO}_2(\text{quartz})$ .....	-98.5	-105.1 $\pm$ 0.1	-21.8	1973                      d. 2250 $\pm$ 50			

GeO.....	-54.	-61. ± 3	(-22.5)	Metastable		
½GeO₂.....	-57.3	-64.3 ± 0.3	(-23.5)	1389 ± 4		
SnO.....	-62.1	-69.1 ± 0.1	-23.3	d. 660	(1300)	(1800)
½SnO₂.....	-62.1	-69.4 ± 0.05	-24.4	>2200		
PbO.....	-45.25	-52.4 ± 0.2	-23.4	1163	1201	1745
¼Pb₃O₄.....	-36.9	-43.9 ± 1	-23.5	d.		
PbO₂.....	-26.2	-33.1 ± 0.5	-23.5	d.		
½N₂O₅.....	+5.0	-2.6	-26.3	>306	235	305.5
⅙P₄O₆.....	-83.	-90. ± 2	(-23)	297	285	449
⅓P₃O₁₀.....	-81.	-88. ± 2	(-23)			1700
⅓P₄O₁₀(hex.).....	-67.	-73. ± 1	(-21)	695 ± 6	457	631
⅓P₄O₁₀(ortho).....	-67.5	-74. ± 1	(-22)	853 ± 5	650	878
⅙As₄O₆.....	-46.	-52. ± 0.5	-21.6	588	493	732
⅓As₂O₅.....	-36.9	-43.7 ± 1	-22.8	d. > 1100		
⅙Sb₄O₆.....	-49.8	-55.7 ± 1	-21.7	928	841	1698
½SbO₂.....	-42.	-48. ± 3	-19.8	d. 1203, 19 mm. O₂		
⅓Sb₆O₁₃.....	-39.	-46. ± 3	(-22)	d. 1003, 232 mm. O₂		
⅓Sb₂O₆.....	-36.	-43. ± 3	(-22.7)	d. 673, 224 mm. O₂		
BiO.....	-43.5	-50. ± 1	(-21.1)			
Bi₂O₃.....	-40.	-46. ± 1	-21.5	1090 ± 2		
⅓SO₃.....	-29.7	-36.7 ± 0.5	-23.3	335	256	326
½SeO₂.....	-21.6	-28.2 ± 1	(-22)	613	440 ± 15	590 ± 15
⅓SeO₃.....			(-23)	391		
½TeO₂.....	-32.2	-38.8 ± 0.5	(-22.1)	>750	1075	
½PoO₂.....	-23.3	-30.2 ± 3	(-23.4)			
⅓I₂O₅.....		-11.5		d. 570		
H₂O.....	-56.7	-68.3	-39.0	273	253	373

(64) found no difference at room temperature between lattice constants of  $\text{Na}_2\text{O}$  samples which had been heated with excess metal and with excess  $\text{Na}_2\text{O}_2$ . Thus the homogeneity range of  $\text{Na}_2\text{O}$  is probably small at low temperatures. For none of the other phases have the homogeneity ranges been determined, but Rengade (346) has indicated appreciable homogeneity ranges. Besides the phases discussed above, compounds of the type  $\text{MO}_3$  containing the ozonide ion are known for sodium, potassium, and cesium (1, 16, 255).

The entropy of  $\text{Li}_2\text{O}$  was determined by Johnston and Bauer (228). Todd (415) has determined the entropies of  $\text{Na}_2\text{O}_2$ ,  $\text{NaO}_2$ , and  $\text{KO}_2$ . Kelley (246) has estimated the entropy of  $\text{Na}_2\text{O}$ . The entropies of the remaining oxides were also estimated. Except for the  $\text{Na}_2\text{O}$  data estimated by Naylor (245), no high-temperature heat-content data are available for any of the oxides.

Gilles and Margrave (162) have determined the heats of formation of  $\text{Na}_2\text{O}_2$ ,  $\text{NaO}_2$ , and  $\text{KO}_2$ . The heats of formation of the cesium oxides were based on data from Forcrand (148) but are quite uncertain. The values given for  $\text{Rb}_2\text{O}_3$  and  $\text{RbO}_2$  were estimated by Forcrand (147) and are very uncertain. Johnston and Bauer (228) have recalculated the heat of formation of  $\text{Li}_2\text{O}$ . The heats of formation of  $\text{Li}_2\text{O}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Rb}_2\text{O}$  are those given by the National Bureau of Standards (316). Wallace and Ketchen (252) have obtained a new heat of solution for sodium metal which, if accepted, will make the heats of formation of all the sodium oxides 0.5 kcal. more negative per gram-atom of sodium. However, this new value is not consistent with the accepted entropy of chloride ion (426). Pending resolution of this discrepancy, the old values have been retained here. The data for the rubidium and cesium compounds are rather uncertain, and the data for the other oxides may be uncertain by as much as a kilocalorie.

Rengade (346) reports that the  $\text{M}_2\text{O}$  oxides disproportionate to  $\text{M}(\text{g})$  and solid peroxides on the basis of attack of silver and platinum crucibles and vaporization of the alkali metal. For  $\text{Na}_2\text{O}(\text{s}) = \text{Na}(\text{g}) + \frac{1}{2}\text{Na}_2\text{O}_2(\text{s})$ , the data in table 1 yield an equilibrium constant of about  $10^{-9}$  atm. at  $948^\circ\text{K}$ . For  $3\text{Cs}_2\text{O}(\text{s}) = 4\text{Cs}(\text{g}) + \text{Cs}_2\text{O}_3(\text{s})$ , one calculates an equilibrium constant of about  $10^{-22}$  atm. at  $763^\circ\text{K}$ . Thus these calculations indicate an extremely small amount of reaction. If Rengade's report of a reaction is correct, there must be wide homogeneity ranges for the  $\text{M}_2\text{O}$  phases to allow loss of the free metal vapor. He reported considerable solubility of the oxides and metals in one another, decreasing from cesium to sodium. From his method of preparation it is quite likely that his samples contained excess metal which vaporized on heating.

The extensive literature on the dissociation oxygen pressures over the various oxide phases cannot be reconciled with any reasonable thermodynamic data. Margrave and Gilles (162) have reviewed these data. Many of the studies were with liquid phases and do not give information about the solid phases. The solid-phase data are difficult to analyze, since the homogeneity ranges of the phases are not known.

### B. Alkaline earth oxides

Except for  $\text{BeO}$  ( $\text{ZnO}$  wurtzite structure) all the normal  $\text{MO}$  alkaline earths have the  $\text{NaCl}$  crystal structure. Little information about the homogeneity

ranges of the MO phases is known. The alkaline earths are *n*-type semiconductors (312). Thus the formula  $MO_{1-x}$  can be used to represent the homogeneity range. Kane (233) reports that BaO crystallized from molten barium is red and obviously has barium dissolved in it. Weber (440) reports that MgO can dissolve either magnesium or oxygen at 1500°K. Except for beryllium all the alkaline earth metals form  $MO_2$  peroxides, which have been shown to have the  $CaC_2$  crystal structure in the cases of  $SrO_2$  and  $BaO_2$ . Kotov and Raikhshtein (264) have discussed the structure of  $CaO_2$ , which apparently also has the  $CaC_2$  structure.

The heat of formation of BeO given by Roth, Borger, and Siemonsen (353) was accepted as probably being more correct than the earlier lower values. The heat of formation of MgO was determined from the heat of solution by Shomate and Huffman (379) and closely confirmed by the heat of combustion (208). The heats of formation of CaO,  $CaO_2$ , SrO,  $SrO_2$ , and BaO were obtained from Bichowsky and Rossini (29). The report of the National Bureau of Standards (316) gives  $\Delta H$  of  $MgO_2$ . The standard states of hard, high-melting oxides like MgO are difficult to define unless the thermal history has been carefully regulated. This is illustrated by the work of Taylor and Wells (403) and of Giauque (161), who found that the heat of formation of MgO varied as much as 0.9 kcal. depending upon the state of subdivision and previous heat treatment. Kobayashi (260) has reported 0.47 kcal. difference between crystalline CaO and powdered CaO. The heat of formation of RaO was estimated.

The entropies of formation of  $CaO_2$  and  $SrO_2$  were estimated. The entropy of  $BaO_2$  came from Lewis and Randall (276). Comparison with the alkali peroxides, using Latimer's rule (271), would indicate that the entropies of formation given in table 1 may be more negative by about three entropy units. Data on the dissociation oxygen pressures over  $MgO_2$  and  $CaO_2$  are not of any use for thermodynamic calculations because equilibrium conditions do not prevail and the peroxides exist at temperatures at which they are thermodynamically unstable because of slow rates of decomposition.

One calculates a pressure of 1 atm. of oxygen in equilibrium with  $SrO_2$  and SrO at 770°K., while 488°K. is the observed value. If there is no interaction between the phases, the difference must be due to an error of 2 kcal. in the heat of formation of  $\frac{1}{2}SrO_2$ , a value which is well within the experimental uncertainties. The oxygen partial pressures over  $BaO_2$  measured by Hildebrand (202) are in agreement with the thermodynamic data in table 1.

The heats of formation given in table 1 may be checked by the dissociation data of carbonates, which have been reviewed by Kelley and Anderson (248). Using Bichowsky and Rossini's (29) heats of formation of the carbonates for calcium, strontium, and barium, one obtains agreement with the  $\Delta H$  values of table 1 within 1 kcal. Lander (269) has recently obtained better data for the decomposition equilibria of  $SrCO_3$  and  $BaCO_3$ , and he determined the high-temperature heat contents of CaO, SrO, and BaO up to 1200°K. These new data also confirm the values in table 1 within 1 kcal.

*C. Boron-aluminum group oxides*

Although all of the third group elements have stable MO gases, it seems probable that the MO solids are unstable by disproportionation to M and  $M_2O_3$ , except perhaps at very high temperatures. Marsh (292) reported formation of PrO by the action of hydrogen on a  $PrO_2$ - $ThO_2$  solution but no x-ray confirmation is available. Baur and Brunner (20) studied the Al- $Al_2O_3$  phase diagram and reported a compound  $Al_3O_9$ , melting at 2323°K. with a eutectic between  $Al_3O_9$  and  $Al_2O_3$  at 2293°K. Beletskii and Rapoport (23) reported the formation of  $Al_2O$  (hexagonal) in the presence of silicon dioxide and carbon. Both reported lower oxides may be ternary aluminum-oxygen-carbon compounds. Brewer, Searcy, and McCullough (70) could find no new solid phase upon x-ray examination at room temperature of fused mixtures of aluminum and aluminum oxide ( $Al_2O_3$ ). A high-temperature x-ray study would be of great interest. The *n*-type semiconduction of  $Al_2O_3$  indicates a homogeneity range corresponding to  $Al_2O_{3-x}$  (312). All of the elements of this group form  $M_2O_3$  oxides.  $B_2O_3$  usually occurs as a glass, although Taylor and Cole (404, 405) and McCulloch (295) have prepared crystalline  $B_2O_3$ . Berger (25) has found it to be hexagonal.  $Al_2O_3$  has been reported in many different crystalline forms. Thibon, Charrier, and Tertian (409) have reviewed the various forms of  $Al_2O_3$  and reported over seven forms. All of these forms are unstable or stabilized by impurities, but the only stable pure form at all temperatures is the rhombohedral  $\alpha$ -corundum form. Cubic  $\gamma$ - $Al_2O_3$ , which is often formed upon the oxidation of aluminum or the dehydration of hydrous aluminum oxide, has a structure very similar to the spinel structure of  $Fe_3O_4$  with vacant spaces in the aluminum lattice. König (263) has shown that its lattice constant varies over a large range, indicating a wide homogeneity range. Fricke (150) has shown that the heat of formation also varies over a range of 10 kcal. Upon heating,  $\gamma$ - $Al_2O_3$  is converted to the stable  $\alpha$ -corundum.

$Sc_2O_3$ ,  $Y_2O_3$ , and the rare earths from  $Ho_2O_3$  to  $Lu_2O_3$  have the cubic  $Mn_2O_3$  structure. The other rare earths occur in three forms, depending upon the method of preparation. The hexagonal  $La_2O_3$  crystal structure or A-rare earth structure has been obtained for  $La_2O_3$ ,  $Ce_2O_3$ ,  $Pr_2O_3$ ,  $Nd_2O_3$ , and  $Sm_2O_3$  by heating the oxides to temperatures ranging from 875°K. for  $La_2O_3$  to 2100°K. for  $Sm_2O_3$ . Goldschmidt, Ulrich, and Barth (176) and more recently Iandelli (220) have shown that as one goes from lanthanum to samarium, higher and higher temperatures are required for conversion to the A structure. Either the  $La_2O_3$  structure is the thermodynamically stable form or the reconversion is very slow when this structure is once formed.

Oxides prepared at intermediate temperatures have a pseudotrigonal form of unknown structure, according to Goldschmidt (176). Iandelli also obtained this intermediate structure, known as the B-rare earth structure, but claimed it to have a different form from that reported by Goldschmidt. This B-rare earth form has been observed for  $Gd_2O_3$ ,  $Eu_2O_3$ ,  $Sm_2O_3$ , and  $Nd_2O_3$  and perhaps also for  $Pr_2O_3$  and  $Dy_2O_3$ .

Finally, all of the rare earth oxides even back to  $La_2O_3$  may be prepared in

the cubic  $\text{Mn}_2\text{O}_3$  or C-rare earth structure by ignition of the nitrate, carbonate, or hydroxide at low temperatures ranging from 625–875°K. for  $\text{La}_2\text{O}_3$  to 775–1600°K. for  $\text{Eu}_2\text{O}_3$ . Thus the C form of  $\text{Sm}_2\text{O}_3$  is prepared by ignition of the nitrate below 1100°K. or of the carbonate below 1400°K. The B form is prepared at 1100–2100°K. and the A form is prepared above 2100°K. Lohberg (278), who was the first to prepare the C forms of  $\text{La}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$ , prepared them by heating  $\text{La}(\text{NO}_3)_3$  at 725°K. for 20 hr. and  $\text{Nd}(\text{NO}_3)_3$  at 1000°K. for 3 hr. He found that after 3 hr. at 1300°K. the C form of  $\text{Nd}_2\text{O}_3$  had been converted to the A form. There is always the possibility that the forms of  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ , etc. prepared at low temperatures are stabilized by the presence of nitrate ion or other large anions which lower the cation-to-anion ratio and that the high-temperature treatment vaporizes this impurity. This would agree with the increase in temperature required as one goes from lanthanum to smaller cations. This might be checked by determining if the A form can be reconverted to the C form by heating with nitrate flux. However, it might be noted that Zachariasen (460) has shown that  $\text{Ce}_2\text{O}_2\text{S}$  still has the hexagonal A-rare earth form even though the sulfur anion has been inserted.

Higher oxides have long been known in the cases of  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ , and  $\text{Tb}_4\text{O}_{11}$ . Gruen, Koehler, and Katz (181) have by the action of atomic oxygen extended the homogeneity ranges to  $\text{PrO}_2$  and  $\text{TbO}_2$ . They could not oxidize  $\text{M}_2\text{O}_3$  oxides of yttrium, lanthanum, neodymium, samarium, europium, gadolinium, and ytterbium. All of the higher oxides have the  $\text{CaF}_2$  crystal structure. Since the C-rare earth structure (cubic  $\text{Mn}_2\text{O}_3$ ) is essentially the fluorite structure with some vacant anion sites, it is not unreasonable that wide homogeneity ranges are found between the  $\text{M}_2\text{O}_3$  and  $\text{MO}_2$  compositions. Thus Bruno (75) and also Rienacher and Birchenstredt (342) have prepared compositions from  $\text{CeO}_2$  to  $\text{CeO}_{1.85}$  and have found only a single phase with the  $\text{CaF}_2$  structure. Harwood (191) has shown that ceric oxide preparations of varying colors all have the fluorite structure. McCullough (296) has shown that  $\text{Y}_2\text{O}_3$  ( $\text{Mn}_2\text{O}_3$  type) is completely miscible with  $\text{CeO}_2$  ( $\text{CaF}_2$  type). For those rare earths that do not form a stable cubic  $\text{Mn}_2\text{O}_3$ -type phase, it can be expected that wide homogeneity ranges will exist between the three and four oxidation states but a miscibility gap is to be expected. Thus in the cerium system the fluorite phase is to be expected even below  $\text{CeO}_{1.85}$ , but at some intermediate composition a two-phase system containing a hexagonal phase and a cubic phase is to be expected. The *p*-type semiconduction of  $\text{Pr}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ , and  $\text{Sm}_2\text{O}_3$  indicates a homogeneity range with oxygen uptake (312). Similar behavior is to be expected for  $\text{Ce}_2\text{O}_{3+z}$  and  $\text{Tb}_2\text{O}_{3+z}$ . The  $\text{Pr}_2\text{O}_3$ – $\text{PrO}_2$  system, which has been more thoroughly studied than the others, has yielded conflicting results. McCullough (298) reports a hexagonal phase around  $\text{Pr}_2\text{O}_3$  and a cubic phase at  $\text{Pr}_6\text{O}_{11}$  and  $\text{PrO}_2$ . His results indicate that  $\text{Pr}_6\text{O}_{11}$  and  $\text{PrO}_2$  are distinct phases with a miscibility gap between them. This may be due to non-attainment of equilibrium. McCullough's (296) more recent results, showing the miscibility of  $\text{Y}_2\text{O}_3$  and  $\text{CeO}_2$ , would indicate that a complete homogeneity range should occur between  $\text{Pr}_6\text{O}_{11}$  and  $\text{PrO}_2$ . Martin (293) reports that measurements of oxygen pressure and x-ray studies

show that  $\text{PrO}_{1.75-2.0}$  ( $\text{CaF}_2$  type) is a continuous-phase region. He also finds that  $\text{PrO}_{1.50-1.55}$  (hexagonal) is a continuous-phase region with a two-phase region from  $\text{PrO}_{1.55}$  to  $\text{PrO}_{1.75}$ . Thus he attributes no special significance to the composition  $\text{Pr}_6\text{O}_{11}$ , which happens to be the composition in the homogeneity range in equilibrium with air at the usual ignition temperature. Cunningham and Asprey (105) have also measured oxygen pressures in this system. They obtain breaks in their pressure *versus* temperature curves which are interpreted as evidence for the existence of several phases in  $\text{PrO}_{1.715-1.83}$  ( $\text{CaF}_2$  type) region. Their work does not definitely establish the limits of the  $\text{M}_2\text{O}_{3+x}$  phase region. For the two-phase region below  $\text{PrO}_{1.715}$  they obtain about 50 mm. of oxygen at 1235–1240°K. One puzzling result is the observation of the  $\text{Mn}_2\text{O}_3$  structure for the composition  $\text{PrO}_{1.68}$  when it is cooled to room temperature, since Martin (293) does not report this structure in his studies. A study with a high-temperature x-ray camera will be necessary to clarify these observations. Ferguson, Guth, and Eyring (139) have recently reported oxygen partial pressures for the praseodymium–oxygen system which indicate a wide homogeneity range at 1325°K., in agreement with Martin (293), but with large deviations from perfect solution behavior. The deviations increase with decreasing temperature and apparently result in formation of a miscibility gap in the range of fluorite structure at 800–1200°K., in agreement with results of Cunningham and Asprey (105). The oxygen pressure appears to rise rapidly with increase of composition above  $\text{PrO}_{1.83}$ . Foex and Lories (145) have also given data on this system.

By the combustion of boron, Prosen, Johnson, and Yenchius (336) obtained  $-101$  kcal. for  $\Delta H_{298}$  per  $\frac{1}{3}\text{B}_2\text{O}_3$ , while Eggersgluess, Monroe, and Parker (122) obtained a value of  $-93.7$  kcal. Prosen, Johnson, and Pergiel (337) have obtained  $-102$  kcal. from the heat of hydrolysis of diborane, a method which appears to be reliable. The heat of formation of  $\text{Al}_2\text{O}_3$  was determined by Snyder and Seltz (388) and confirmed by Holley and Huber (208). The high-temperature heat contents and entropies have been given by Ginnings and Corruccini (164). The heats of formation of  $\text{Sc}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  are estimated. The thermodynamic data for the rare earths have been in a deplorable state. The values given by Bichowsky and Rossini (29) showed a serious discrepancy between values determined from heats of solution and those determined by combustion. It appeared that this discrepancy was somewhat resolved by the results obtained by Bommer and Hohmann (41) for the heats of solution of the rare earth metals. The values given by Brewer, Bromley, Gilles, and Lofgren (56) and in the tables of the National Bureau of Standards (316) are based on the heats of solution determined by Bommer and Hohmann. Very recent data make it clear that these heats of solution are too large by 8–10 kcal. This appears to be due to incomplete removal of potassium metal from the rare earth metals. Thus, Lohr and Cunningham (279) have obtained  $-167.5$  and  $-165.3$  kcal., respectively, for the  $\Delta H$  of solution of lanthanum and praseodymium in acid solution. Spedding and Miller (392) have obtained  $-167.4$  and  $-163.3$  kcal., respectively, for the  $\Delta H$  of solution of cerium and neodymium. These new data have been combined with the data given by Bichowsky and Rossini (29) to obtain more reliable values for the heats of formation of the oxides. In most cases it is necessary to discard heats

of formation determined by combustion. They appear to be greatly in error, because of the use of impure metal. The use of impure metal can give heats of combustion which are too high, owing to hydrogen and light metal impurities, and in a few cases give results which are too low, owing to large amounts of oxide impurities.

Thus the heats of combustion of lanthanum given by Bichowsky and Rossini (29) are all discarded as being too high. The two heats of solution of  $\text{La}_2\text{O}_3$  with the new heat of solution of lanthanum metal gave  $-431.4$  and  $-449.4$  kcal., with an average  $\Delta H_{298} = -440.4 \pm 9$  kcal. A recent determination of the heat of combustion of the metal (435) has given the value  $-433.5 \pm 1.1$  kcal.  $\Delta H_{298} = -435 \pm 3$  kcal. is taken as the best value for the heat of formation of  $\text{La}_2\text{O}_3$ .

The value of the heat of combustion found for  $\text{Pr}_2\text{O}_3$  was discarded. The heat of solution given by Bichowsky and Rossini (29) yielded  $\Delta H_{298} = -430.0$  kcal., while the data of Lohr and Cunningham (279) and of Eyring, Lohr, and Cunningham (134) yielded the value  $-437.6 \pm 1.7$  kcal. The value  $\Delta H_{298} = -433.8 \pm 4$  kcal. was taken as an average. The data given by Bichowsky and Rossini for  $\frac{1}{2}\text{Pr}_6\text{O}_{11}$  yielded  $\Delta H_{298} = -123.5$  kcal., in good agreement with the recent combustion value (435) of  $-124.6 \pm 0.2$  kcal. per gram-atom of oxygen for  $\text{PrO}_{1.815}$ . The average of  $-124.0 \pm 0.5$  kcal. is taken for  $\Delta H_{298}$  of  $\frac{1}{2}\text{Pr}_6\text{O}_{11}$ . The data given by Bichowsky and Rossini for  $\text{PrO}_2$  yield  $-229$  kcal., while the data of Lohr and Cunningham (279) and of Eyring, Lohr, and Cunningham (134) yield  $-230.6$  kcal.  $\Delta H_{298} = -230 \pm 2$  kcal. is taken as the average for  $\text{PrO}_2$ .

The value of the heat of combustion found for  $\text{Nd}_2\text{O}_3$  was discarded as being too high.  $\Delta H_{298} = -426 \pm 4$  kcal. is obtained from the heat of solution of  $\text{Nd}_2\text{O}_3$ . For  $\text{Ce}_2\text{O}_3$ , an estimated value of  $\Delta H_{298} = -434 \pm 5$  kcal. can be given. For  $\text{CeO}_2$ , Hirsch's (205) heat of combustion was taken instead of smaller values by other workers. This value would predict that  $\text{CeO}_2$  would be appreciably decomposed in an atmosphere of oxygen at around  $2500^\circ\text{K}$ . Wartenberg and Gurr (430) reported that temperatures above  $2300^\circ\text{K}$ . are required for the thermal decomposition of  $\text{CeO}_2$ . Thermodynamically, hydrogen should reduce  $\text{CeO}_2$  at all temperatures from room temperature and above. The thermodynamic data for the praseodymium oxides agree with the observation by Cunningham and Asprey (105) of 50 mm. of oxygen at  $1240^\circ\text{K}$ . for the  $\text{Pr}_2\text{O}_{3+x}$ - $\text{PrO}_{1.715}$  region. One would calculate about 30 mm. Eyring, Lohr, and Cunningham (134) reported the formation of  $\text{PrO}_2$  at  $775^\circ\text{K}$ . and 100 atm. of oxygen, while at  $660^\circ\text{K}$ . and 3.5 mm. of oxygen,  $\text{PrO}_{1.826}$  was formed. Assuming the immiscibility of  $\text{Pr}_6\text{O}_{11}$  and  $\text{PrO}_2$ , one calculates that  $\text{Pr}_6\text{O}_{11}$  and  $\text{PrO}_2$  would be in equilibrium with 1 atm. of oxygen at around  $700^\circ\text{K}$ ., in reasonable agreement with the observations. Ferguson, Guth, and Eyring (139) report similar results for the  $\text{Pr}_2\text{O}_{3+x}$ - $\text{PrO}_{1.82}$  region at  $1323^\circ\text{K}$ . At  $675^\circ\text{K}$ . they found very little change beyond  $\text{PrO}_{1.83}$  as the oxygen partial pressure was increased from 25 to 650 mm., indicating that the  $\text{PrO}_2$  phase had not yet been formed with almost an atmosphere of oxygen. Within the uncertainty due to the estimated entropies of the oxides, these results can be considered in accord with the heats of formation.

Very few data on entropy and heat content exist for the rare earths. Blomeke

and Ziegler (36) have determined the heat contents of  $\text{La}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$ , and  $\text{Nd}_2\text{O}_3$  up to 1173°K.

#### *D. Actinide group oxides*

Except for actinium, all of the elements from thorium to americium are known to have an MO oxide with NaCl crystal structure. Except for  $\text{Ac}_2\text{O}_3$  ( $\text{La}_2\text{O}_3$  type) (461),  $\text{Pu}_4\text{O}_{7-x}$  (cubic  $\text{Mn}_2\text{O}_3$  type) (308), and  $\text{Am}_2\text{O}_3$  (cubic  $\text{Mn}_2\text{O}_3$  type) (461) the actinide elements are not known to have an  $\text{M}_2\text{O}_3$  oxide. All of the elements from thorium to americium have an  $\text{MO}_2$  oxide with the  $\text{CaF}_2$  structure. This phase probably has an extended homogeneity range for all of the elements. Thus  $\text{PaO}_{2.0-2.5}$  ( $\text{CaF}_2$  type) and  $\text{UO}_{1.75-2.25}$  ( $\text{CaF}_2$  type) have been reported. *N*-type semiconduction indicates the formula  $\text{ThO}_{2-x}$ . Rundle, Baenziger, Wilson, and McDonald (360) gave the lower limit of the  $\text{UO}_2$  phase as  $\text{UO}_{1.9}$ , while Zachariasen (468) believes that it may extend to  $\text{UO}_{1.75}$  on the basis of a sample prepared by Brewer by heating  $\text{UO}_2$  and U together. This sample contained  $\text{UO}_2$  with  $a = 5.460 \text{ \AA}$ . as well as the phase designated as  $\text{U}_4\text{O}_7$  with  $a = 5.477 \text{ \AA}$ . It is not known whether the sample had been at equilibrium. Hering and Perio (197) recently confirmed the observation of Zachariasen and Brewer by preparing  $\text{UO}_{2-x}$  (cubic  $\text{CaF}_2$  type) samples with  $a = 5.484$  and  $a = 5.47kx$ . The  $\text{PuO}_2$  phase region also extends to metal-rich concentrations. Brewer, Bromley, Gilles, and Lofgren (57) have given a summary of the evidence that it may extend to  $\text{PuO}_{1.75}$ . Using highly oxidizing conditions, Katz and Gruen (235) have shown that  $\text{AmO}_2$  (fluorite) and  $\text{PuO}_2$  (fluorite) are the highest oxides for these elements and that  $\text{Np}_3\text{O}_{8-x}$  (orthorhombic) is the highest oxide of the neptunium system. Zachariasen (461, 465) has summarized the data for the oxides of neptunium, plutonium, and americium. Zachariasen (462) and Elson, Fried, Sellers, and Zachariasen (126) have presented the evidence for  $\text{PaO}$  (NaCl type),  $\text{PaO}_{2.0-2.5}$  (cubic  $\text{CaF}_2$  type), and  $\text{Pa}_2\text{O}_5$  (orthorhombic).  $\text{Pa}_2\text{O}_5$  should be similar to  $\text{PrO}_2$  in stability toward oxygen loss.  $\text{Np}_3\text{O}_{8-x}$ ,  $\text{Pa}_2\text{O}_5$  (orthorhombic), and the phase ranging from approximately  $\text{U}_2\text{O}_5$  to  $\text{U}_3\text{O}_8$  are all isomorphous with the orthorhombic  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  phases. Zachariasen and Brewer (467) and Baenziger and Rundle (15), who have prepared ThO (NaCl type), have not been able to obtain the phase pure and it undoubtedly has only a limited temperature range of stability. The same may be true of UO (NaCl type).

The uranium system is the most complex of the actinide-oxygen systems. In addition to UO (NaCl type),  $\text{UO}_{2\pm x}$  ( $\text{CaF}_2$  type), and the  $\text{U}_3\text{O}_8$  (orthorhombic) homogeneity range mentioned above, a number of other phases have been reported.  $\text{UO}_3$  is known in at least four crystalline forms. Katz and Rabinowitch (236) have listed these forms and have given a thorough summary of the data on the uranium-oxygen system up to 1950. Rundle, Baenziger, Wilson, and McDonald (360) have earlier reviewed the uranium-oxygen system.  $\text{UO}_3$  (hexagonal) is very closely related to  $\text{U}_3\text{O}_8$  (orthorhombic). At very low temperatures there must be a miscibility gap between them, but it is likely that there is no miscibility gap between the two compositions at temperatures above room

temperature. Biltz and Müller (32) have determined the equilibrium oxygen pressures for the uranium–oxygen system. These results indicate one phase for  $\text{UO}_{2.62-3.00}$  for temperatures above  $850^\circ\text{K}$ . At lower temperatures their results indicate a miscibility gap, but true equilibrium is difficult to maintain at the lower temperatures and their results may not be reliable. Samples have been prepared between  $\text{U}_3\text{O}_8$  and  $\text{UO}_3$  which show only one phase at room temperature, but they may be due to freezing of the equilibrium corresponding to a higher temperature. Boullé and Dominé-Bergès (42) report the orthorhombic symmetry still persisting at  $\text{UO}_{2.9}$ . The relationship between the various  $\text{UO}_3$  forms is not known. They may differ slightly in composition.  $\text{UO}_3$  (hexagonal) is converted irreversibly to the other forms by heating in oxygen, so it may be metastable.

The behavior of compositions between  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  is especially complicated. The data of Biltz and Müller (32) indicated that the  $\text{UO}_2$  homogeneity range extends to  $\text{UO}_{2.25}$  with a two-phase region extending to  $\text{UO}_{2.62}$  at around  $1400^\circ\text{K}$ . Later work indicated a smaller two-phase region, and the results of Biltz and Müller may be subject to analytical errors. Recent work, which has been reviewed by Katz and Rabinowitch (236), indicates a much more complicated situation, at least at lower temperatures. Apparently  $\text{UO}_2$  can take up a good deal of oxygen at low temperature without phase change, but this wide homogeneity range is a metastable situation and annealing for a long time will cause disproportionation. Dawson and Lister (110) have recently studied the magnetic susceptibility of the  $\text{UO}_{2.0-2.3}$  range and report a two-phase region above  $\text{UO}_{2.3}$ . Alberman and Anderson (4) have reported a homogeneity range  $\text{UO}_{2.0-2.2}$  below  $500^\circ\text{K}$ . with little change in parameter for the fluorite structure between  $\text{UO}_{2.0}$  and  $\text{UO}_{2.2}$  but tetragonal symmetry between  $\text{UO}_{2.2}$  and  $\text{UO}_{2.3}$ . Above  $500^\circ\text{K}$ . the tetragonal range disproportionates to  $\text{UO}_{2.2}$  and  $\text{U}_3\text{O}_8$ , while the fluorite range disproportionates to  $\text{UO}_2$  (CaF<sub>2</sub> type) and  $\text{UO}_{2.19}$  (CaF<sub>2</sub> type). Boullé, Jary, and Dominé-Bergès (43) reported that oxidation of  $\text{UO}_2$  produces a homogeneity range with tetragonal symmetry which, as indicated by doubling of some of the diffraction lines, persists to  $\text{UO}_{2.5}$ . At the intermediate composition of  $\text{UO}_{2.30-2.33}$ , the double lines merge to give a single broad line and then double again at high-oxygen compositions. At  $\text{UO}_{2.5}$  the orthorhombic symmetry of the  $\text{U}_3\text{O}_8$  range is observed. Gronvold and Haraldsen (178) have reported a tetragonal phase with a narrow homogeneity range at  $\text{UO}_{2.40}$  which is stable below  $543^\circ\text{K}$ .

These results appear to be somewhat contradictory. Hering and Perio (197) have recently resolved the apparent discrepancies by a thorough study of the uranium–oxygen system over a range of temperatures. They find that the  $\text{UO}_{2\pm x}$  (cubic CaF<sub>2</sub> type) phase can be prepared between the limits  $\text{UO}_{1.75-2.33}$  with lattice constants varying from 5.484 to 5.416kx. The range above  $\text{UO}_{2.0}$  appears to be metastable and can be prepared only at very low temperatures. Above  $500^\circ\text{K}$ . for the higher oxide compositions and above  $600^\circ\text{K}$ . for compositions around  $\text{UO}_{2.05}$ , disproportionation occurs to form a two-phase mixture of  $\text{UO}_{2.0}$  (cubic) and  $\text{UO}_{2.25}$  (cubic CaF<sub>2</sub> type). Samples heated to  $1200^\circ\text{K}$ . still gave the two-phase mixture upon being examined at room temperature. It is possible that the homogeneity ranges of  $\text{UO}_2$  and  $\text{UO}_{2.25}$  broaden at higher

temperatures and that the two phases would separate out again. A high-temperature x-ray examination will be necessary to settle this question. All data obtained to date indicate no appreciable homogeneity range for  $\text{UO}_{2.25}$ . The portion of the  $\text{UO}_{2\pm x}$  range above  $\text{UO}_{2.25}$  disproportionates above  $400^\circ\text{K}$ . to a two-phase mixture of  $\text{UO}_{2.25}$  (cubic) and a tetragonal phase which has been shown by Hering and Perio to vary in composition with temperature between  $\text{UO}_{2.42}$  and  $\text{UO}_{2.29}$ . This variation explains the previous discordant compositions reported for this phase. Hering and Perio, in agreement with Gronvold and Haraldsen (178), find no appreciable homogeneity range for this phase at a given temperature, as indicated by the same lattice constants whether a lower or a higher oxide phase is present. Most of the variation in composition occurs at temperatures below  $500^\circ\text{K}$ ., where it coexists with either a  $\text{U}_3\text{O}_{8-x}$  (orthorhombic) phase of rapidly varying composition with temperature or with the  $\text{UO}_{2\pm x}$  (cubic) phase of very rapidly varying composition. The tetragonal homogeneity region is apparently just barely stable with respect to disproportionation to these other phases and only a narrow composition range can be prepared at any one temperature. This narrow composition range changes rapidly with temperature as the compositions of the other phases change with temperature. Above  $775^\circ\text{K}$ ., all compositions of the tetragonal phase are unstable with respect to  $\text{UO}_{2.25}$  (cubic) and the orthorhombic phase.

Hering and Perio (197) have cleared up some of the discrepancies with respect to the lower limit of the orthorhombic phase. At  $375^\circ\text{K}$ ., they find the lowest composition of this phase to be  $\text{UO}_{2.64}$ . As the temperature is raised, the oxygen content decreases reaching  $\text{UO}_{2.54}$  at  $775^\circ\text{K}$ ., where it is in equilibrium with  $\text{UO}_{2.25}$  (cubic). After heating to  $925^\circ\text{K}$ ., they find  $\text{UO}_{2.52}$  to consist of a single orthorhombic phase. Thus they have confirmed that the orthorhombic phase extends down to  $\text{U}_2\text{O}_5$ . It is not known whether the homogeneity range of this phase continues to expand above  $925^\circ\text{K}$ .. If the analyses of Biltz and Müller (32) are not in error, one would have to assume that the orthorhombic phase reaches a minimum oxygen content at about  $1000^\circ\text{K}$ .. At higher temperatures the oxygen content of the lower limit of the homogeneity range would increase to reach  $\text{UO}_{2.62}$  at around  $1400^\circ\text{K}$ ..

Hering and Perio (197) have not done any work on compositions above  $\text{UO}_{2.66}$ . Their work, together with the earlier work reviewed by Katz and Rabinowitch (236), would indicate that at temperatures above  $775^\circ\text{K}$ .,  $\text{UO}_{2\pm x}$  (CaF<sub>2</sub> type),  $\text{UO}_{2.25}$  (CaF<sub>2</sub> type),  $\text{UO}_{2.5-3.0}$  (orthorhombic to hexagonal), and the stable  $\text{UO}_3$  phase (probably yellow  $\text{UO}_3(\text{III})$ ) are the only stable phases. At higher temperatures the two fluorite-type phases undoubtedly merge, forming a continuous-phase region. Also,  $\text{UO}_3$  will become unstable at higher temperatures and the orthorhombic phase region will narrow. Above  $1000^\circ\text{K}$ ., this region will not extend above  $\text{UO}_{2.7}$  in an atmosphere of oxygen. With a temperature over  $1515^\circ\text{K}$ ., and a pressure of  $2 \times 10^{-3}$  atm. of oxygen, no phases above the  $\text{UO}_{2\pm x}$  phase region should be stable. The solubility of oxygen in uranium metal is small at all temperatures, amounting to 0.05 atomic per cent at  $1406^\circ\text{K}$ ., and 0.4 atomic per cent at  $2275^\circ\text{K}$  (59).

The heats of formation of  $\text{ThO}_2$ ,  $\text{UO}_2$ , and  $\text{U}_3\text{O}_8$  have been given by Huber, Holley, and Meierkord (212). The heat of formation of  $\text{AmO}_2$  has been reported by Eyring, Lohr, and Cunningham (134). Cunningham and Asprey (105) give decomposition data for  $\text{AmO}_2$ . The heats of formation of  $\text{ThO}$  and  $\text{UO}$  were estimated to agree with their apparent instability by disproportionation at low temperatures. From the oxygen partial pressures observed by Biltz and Müller (32) for the two-phase system containing  $\text{UO}_{2.62}$  and  $\text{UO}_{2.25}$ , one can calculate  $\Delta H_{298} = 81$  kcal. for  $5.4\text{UO}_{2.62} = 5.4\text{UO}_{2.25} + \text{O}_2(\text{g})$ . One measurement of oxygen pressure at  $1434^\circ\text{K}$ . for  $\text{UO}_{2.20}$  yielded  $\Delta H_{298} = 11$  kcal. for  $\text{UO}_{2.25} = \text{UO}_2 + \frac{1}{8}\text{O}_2(\text{g})$ . From these results one obtains  $\Delta H_{298} = -270$  kcal. for  $\text{UO}_{2.25}$  and  $\Delta H_{298} = -285$  for  $\text{UO}_{2.62}$ . As noted above, these compositions given by Biltz and Müller (32) as limits of the homogeneity ranges of the  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  phase regions may be somewhat in error. However, the heats of formation per equivalent should be applicable to the actual limiting compositions.

From the oxygen pressures determined by Biltz and Müller (32) in the range  $\text{U}_3\text{O}_8$ - $\text{UO}_3$ , one can, by taking into account solid-solution formation, obtain for the reaction  $3\text{UO}_3 = \text{U}_3\text{O}_8 + \frac{1}{2}\text{O}_2(\text{g})$  a value of 17.5 kcal. for  $\Delta H_{298}$ . Using  $-853.5$  kcal. for  $\text{U}_3\text{O}_8$ , one calculates  $\Delta H_{298} = -290.4$  kcal. for  $\text{UO}_3$ . This undoubtedly refers to the hexagonal form of  $\text{UO}_3$ . From the data of Biltz and Fendius (30), one obtains  $\Delta H_{298} = -292$  kcal. for  $\text{UO}_3$ . The heat of solution of  $\text{UO}_3$  measured by de Forcrand (147) results in  $\Delta H_{298} = -299$  kcal. for  $\text{UO}_3$  using  $\Delta H_{298} = -114.0$  kcal. for  $\text{U}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{H}^+ = \text{UO}_2^{++} + \frac{3}{2}\text{H}_2(\text{g})$  in dilute  $\text{HNO}_3$  (59). Mixer's (307) heat of solution of  $\text{UO}_3$  in  $\text{Na}_2\text{O}_2$  yields  $\Delta H_{298} = -305$  kcal. when combined with the heat of solution of uranium in  $\text{Na}_2\text{O}_2$  and  $\Delta H_{298} = -290$  kcal. when combined with the heat of solution of  $\text{U}_3\text{O}_8$  in  $\text{Na}_2\text{O}_2$ .  $\Delta H_{298} = -291 \pm 3$  kcal. is taken as the best value for  $\text{UO}_3$  (hexagonal). From the conditions of preparation and decomposition of red  $\text{UO}_3(\text{II})$  and yellow  $\text{UO}_3(\text{III})$ , one calculates  $-292$  kcal. for  $\text{UO}_3(\text{II})$  and  $\Delta H = -293$  kcal. for  $\text{UO}_3(\text{III})$ .

The heats of formation of  $\text{NpO}_2$ ,  $\text{Np}_2\text{O}_5$ , and  $\text{Am}_2\text{O}_3$  were estimated by using the heats of formation of the ions given by Westrum and Eyring (444), Brewer, Bromley, Gilles, and Lofgren (58), and Eyring, Lohr, and Cunningham (134) and estimated heats of solution by comparison with other actinide and lanthanide oxides. The heat of formation of  $\text{Ac}_2\text{O}_3$  is based on the  $\text{Ac}^{3+}$  potential given by Latimer (271). Brewer, Bromley, Gilles, and Lofgren (57) have given  $\Delta H_{298} = -251$  kcal. for  $\text{PuO}_2$  on the basis of high-temperature equilibria. However, this value is inconsistent with the heats of formation of  $\text{ThO}_2$  and  $\text{UO}_2$  determined by Huber, Holley, and Meierkord (212) and the heats of formation of the ions (56, 57, 59). One would expect  $\Delta H_{298} = -241$  kcal., assuming similar heats of solution for  $\text{ThO}_2$ ,  $\text{UO}_2$ , and  $\text{PuO}_2$ . An average of  $\Delta H_{298} = -246 \pm 5$  kcal. will be taken for  $\text{PuO}_2$ . The heat of formation of  $\text{Pu}_2\text{O}_5$  was estimated from the  $\text{PuO}_2^+$  potential given by Latimer (271). Estimated heats of formation confirm the results of Katz and Gruen (235) that no higher oxides will be found in the neptunium, plutonium, or americium system.

Jones, Gordon, and Long (231) have determined the entropies of  $\text{UO}_2$  and

UO<sub>3</sub>. Westrum, Hatcher, and Osborne (445) have determined the entropies of NpO<sub>2</sub> and PuO<sub>2</sub>. All other entropies were estimated.

### *E. Titanium-zirconium group oxides*

The titanium-oxygen system is characterized by several phase regions with appreciable homogeneity ranges. Ehrlich (124, 125) has made an x-ray study of the titanium-oxygen system. Bumps, Kessler, and Hansen (79) have recently restudied this system and have confirmed Ehrlich's results except for the discovery of a new phase between 18 and 20 weight per cent oxygen.  $\alpha$ -Titanium is found to dissolve a maximum of 34 atomic per cent oxygen in the range 1000–1900°K., while  $\beta$ -titanium dissolves 5 atomic per cent oxygen at 2010°K. The phase TiO<sub>0.66-0.76</sub> (tetragonal) disproportionates above 1198°K., forming the metal and TiO phases. A wide homogeneity range is found for the TiO<sub>0.7-1.25</sub> (NaCl type) phase. It has a deep chestnut color; Naylor (317) reported a transition at 1264°K. Bumps, Kessler, and Hansen (79) reported a peritectic reaction at 2010°K. for the TiO phase decomposing to  $\alpha$ -titanium and liquid.

Ti<sub>2</sub>O<sub>3</sub> (corundum type), which has a deep violet color, was found to have only a limited homogeneity range of less than TiO<sub>1.46-1.56</sub>. TiO<sub>2</sub> (rutile) was found to have the range TiO<sub>1.9-2.0</sub>, in agreement with its behavior as an *n*-type semiconductor. Another homogeneity range was found between TiO<sub>1.7</sub> and TiO<sub>1.8</sub> with a distorted rutile structure having oxygen lattice vacancies. Halla (187) claims to have prepared another unstable form of Ti<sub>2</sub>O<sub>3</sub> in addition to the form with corundum structure. The structure was not determined. Foex and Lories (144) reported a transition in Ti<sub>2</sub>O<sub>3</sub> at 473°K. which was confirmed by Naylor (317). Chrétien and Wyss (96) reported Ti<sub>3</sub>O<sub>4</sub>, which is undoubtedly metastable, similar to V<sub>3</sub>O<sub>4</sub>. Kelley (247) and Wyss (458) have studied the reduction of TiO<sub>2</sub> by hydrogen. The work indicated the existence of the compound Ti<sub>3</sub>O<sub>5</sub>, which was also studied by Shomate (378) and reported by Chrétien and Wyss (96) to be deep blue. This undoubtedly corresponds to the TiO<sub>1.7-1.8</sub> solid solution found by Ehrlich (124, 125), although the compositions do not check. Naylor (317) reported a transition at 450°K. with a large entropy change of 5 e.u. Rusakov and Zhdanov (361) have recently determined the structure of Ti<sub>3</sub>O<sub>5</sub> (orthorhombic), which they relate to TiO<sub>2</sub>·Fe<sub>2</sub>O<sub>3</sub> (pseudobrookite). In addition to the tetragonal rutile form of TiO<sub>2</sub>, a tetragonal anatase form and an orthorhombic brookite form are known. Anatase and brookite are both thermodynamically unstable, although they might be stabilized by impurities. The rate of conversion of both forms to rutile is slow, but conversion can be obtained above 700–1100°K. with the use of fluxes.

No oxides below MO<sub>2</sub> are definitely known for either zirconium or hafnium. It is probable that the lower oxides are unstable by disproportionation or at best only slightly stable. Friederich and Sittig (153) reviewed earlier attempts to prepare lower oxides of zirconium and reported that they obtained a lower oxide residue when very impure ZrN was dissolved in acid. They also tried to reduce ZrO<sub>2</sub> with carbon. They finally concluded that no well-defined oxide of zirconium has been prepared. Brewer, Templeton, and McCullough (71) could find no new

x-ray patterns upon heating Zr and  $ZrO_2$  together. Fast (136) and de Boer and Fast (37) found that zirconium dissolves up to 40 atomic per cent of oxygen without forming a new phase. Titanium metal can also dissolve a considerable amount of oxygen without a phase change. Jacobs (226) assumes the oxide coating on zirconium metal to be  $ZrO$  and obtains  $\Delta H = -135$  kcal. per mole for the formation of  $ZrO$ , a value which would make it appear to be stable against disproportionation. However, this is inconsistent with the x-ray evidence. Cubicciotti (106) recently made a thorough study of the  $Zr-ZrO_2$  system up to  $2988^\circ K$ . and found no intermediate phases, but both the Zr and  $ZrO_2$  phases have wide homogeneity ranges. The  $n$ -type semiconductor behavior of  $ZrO_2$  is also indicative of a homogeneity range  $ZrO_{2-x}$  (312).

The stable form of  $ZrO_2$  and  $HfO_2$  at normal temperatures is the monoclinic baddeleyite form, which has a distorted  $CaF_2$  structure. Addition of impurities such as  $MgO$  and  $CeO_2$  will convert  $ZrO_2$  and  $HfO_2$  to a cubic form with the  $CaF_2$  structure. At  $1205^\circ K$ . the monoclinic forms of  $ZrO_2$  and  $HfO_2$  have a transition to a tetragonal form. King and Coughlin (253) report an entropy change of 1.2 e.u. for  $ZrO_2$ .

Humphrey (218) has determined the heats of formation of  $TiO$ ,  $Ti_2O_3$ ,  $Ti_3O_5$ , and  $TiO_2$ . The heats of formation of  $ZrO_2$  and  $HfO_2$  have been determined by Kelley (247).

Nasu (315) tried to determine the equilibrium  $H_2O:H_2$  ratio for the reduction of  $TiO_2$  in an iron tube. The data showed a distinct break and, as Kelley (247) has pointed out, the high-temperature data correspond exactly to the  $H_2O:H_2$  ratio for the  $FeO-Fe$  system as given by Darken and Gurry (108, 109). The lower-temperature data give lower  $H_2O:H_2$  ratios than the  $FeO-Fe$  system and could correspond to either the  $TiO_2-Ti_3O_5$  or the  $Ti_3O_5-Ti_2O_3$  system. The weight losses that Nasu (315) gives indicate reduction to  $Ti_2O_{3.05}$ . Treatment of these data gave a heat of formation for  $Ti_3O_5$  considerably more negative than that determined by Humphrey (218). Wyss (458) has also studied the reduction of  $TiO_2$  by hydrogen. He found that the reaction starts rapidly at  $1165^\circ K$ ., and that a final temperature of  $1575^\circ K$ . gives  $Ti_3O_5$  with no intermediates. The lack of further reduction to  $Ti_2O_3$  seems to indicate a greater stability for  $Ti_3O_5$  than shown by Humphrey's data, which indicate that  $Ti_3O_5$  is just barely stable toward disproportionation. Kelley (247) has also observed upon reduction of  $TiO_2$  a distinct break in the  $H_2O:H_2$  ratio at the composition  $Ti_3O_5$ .

Welch (441) has found that  $TiO_2$  is reduced by hydrogen at  $1400^\circ K$ . through a wide homogeneity range without evidence of  $Ti_3O_5$ , but he found a two-phase region at  $1700^\circ K$ . corresponding to  $Ti_3O_5 + TiO_{1.82}$  (rutile). Thus he confirmed Humphrey's report that  $Ti_3O_5$  is stable only at high temperatures, although his temperatures do not quite correspond to Humphrey's data. At  $1400^\circ K$ . Humphrey's data indicate  $\Delta F = 2.8$  kcal. for  $Ti_3O_5 = TiO_2 + Ti_2O_3$ . This would correspond to a factor of 4 between the  $H_2O:H_2$  ratio for the  $TiO_2-Ti_3O_4$  system compared to the  $Ti_3O_4-Ti_2O_3$  region and would be easily detected. However, solid-solution formation in the rutile range would reduce the  $TiO_2$  activity and therefore promote the disproportionation of  $Ti_3O_5$ . Wyss (458) reported reduction

of TiO by calcium in agreement with data in table 1, but his observation that magnesium does not reduce TiO at 850°K. is not in agreement with the thermodynamic data. It is probably due to carrying out the experiment under conditions where the magnesium can escape as a gas, thus reversing the reaction. Magnesium should reduce TiO easily if pressure is maintained to keep the magnesium in the liquid state.  $\Delta H$  for  $\text{TiO}_{0.7}$  was estimated from its observed disproportionation temperature. Latimer (271) estimated the entropy of  $\text{HfO}_2$ . Naylor (317) determined the high-temperature heat contents of the titanium oxides.

#### F. Vanadium group oxides

Hoschek and Klemm (210), Klemm and Grimm (257), and Klemm and Pirscher (259) have studied the vanadium-oxygen system. They obtained evidence for considerable solubility of oxygen in the vanadium metal lattice, which may be as high as  $\text{VO}_{0.4}$  at 1700–1900°K. They found  $\text{VO}_{0.9-1.3}$  (NaCl type) to be unstable by disproportionation at lower temperatures to the vanadium metal phase and a higher oxide phase which they believe to be a metastable  $\text{V}_3\text{O}_4$  phase. Their results do not correspond to equilibrium conditions. Except at high temperatures, the lowest stable oxide phase is  $\text{V}_2\text{O}_3$  with the  $\alpha$ -corundum crystal structure. The instability of VO has been recently confirmed by Hartmann and Mässing (190) at 1225°K. However, Allen, Kubaschewski, and Goldbeck (6) have presented free-energy equations which represent VO as being stable at all temperatures. Todd and Bonnicksen (414) prepared VO from V and  $\text{V}_2\text{O}_3$  at 1625°K., indicating its stability at this temperature. The problem of the stability of VO at lower temperatures is still in question. Between the compositions  $\text{VO}_{1.65}$  and  $\text{VO}_{1.75}$  Todd and Bonnicksen found a compound which apparently corresponds to the  $\text{Ti}_3\text{O}_5$  of the titanium system. Between  $\text{VO}_{1.8}$  and  $\text{VO}_{2.0}$  they found a solid-solution range which is probably similar to the rutile solid-solution range found in the titanium system.  $\text{VO}_2$  has the rutile crystal structure. Between  $\text{VO}_{2.0}$  and  $\text{VO}_{2.2}$  Hoschek and Klemm (210) found, in addition to the rutile structure, another x-ray pattern which they attributed to either another compound at about  $\text{VO}_{2.1}$  or a solid-solution range above  $\text{VO}_2$  with distortion of the rutile structure. However, Flood and Kleppa (142), who obtained the same unknown structure upon reduction of  $\text{V}_2\text{O}_5$  by sulfur dioxide, considered that it analyzes exactly  $\text{VO}_2$ , and they believed it to be an allotropic modification.

There are three possibilities for the explanation of the formation of this new compound. It may be (1) a metastable form, (2) a stable allotropic form of  $\text{VO}_2$  relative to  $\text{VO}_2$  (rutile) at low temperatures, or (3) a compound of higher oxidation state, e.g.,  $\text{VO}_{2.1}$ . The fact that the unknown form is found together with the rutile form over a range of temperatures would indicate that rates of conversion are slow and that the compound could be a metastable form. The rutile form is definitely stable at 900°K. and above, since the unknown form is converted to the rutile form upon heating. After 14 days at 880°K. neither form had been converted to the other, so that it is not possible to establish whether the unknown structure might be a stable form at lower temperatures. Although it is possible to crystallize metastable forms, the fact that Hoschek and Klemm (210)

could prepare the unknown form by crystallization from a melt at a temperature as high as 935°K. would tend to indicate that it is probably a stable form. One possible explanation of all these observations is that the new compound is  $\text{VO}_{2.1}$  and the transformation depends upon the partial pressure of the oxygen in the system. The oxygen pressure in equilibrium with  $\text{V}_2\text{O}_5$  and the new compound is  $3.5 \times 10^{-6}$  atm. at 875°K. The oxygen pressure required for further reduction to  $\text{VO}_2$  (rutile) would then be even smaller. Thus it would require a temperature greater than 875°K. to get a high enough oxygen partial pressure over  $\text{VO}_{2.1}$  to obtain reduction to  $\text{VO}_2$ . However, this assumes that the limits of error in Flood and Kleppa's analyses are large enough to allow their compound to have an oxidation number appreciably above 2. Aebi (2) has very recently determined the structure of this unknown oxide and has found it to be monoclinic and to have the formula  $\text{V}_6\text{O}_{13}$ . This confirms the above interpretation of the results of the reduction by sulfur dioxide.

Above  $\text{V}_6\text{O}_{13}$ ,  $\text{V}_2\text{O}_5$  is the only other vanadium oxide. Byström, Wilhelmi, and Brotzer (91) have determined its structure. Foex (143) reported a transition for  $\text{V}_2\text{O}_5$  at 172°K. with a 2 per cent linear contraction and a 100,000-fold increase in electrical conductivity. The behavior of  $\text{V}_2\text{O}_5$  as an  $n$ -type semiconductor indicates the formula  $\text{V}_2\text{O}_{5-z}$  (312). Cook (102) determined the high-temperature heat contents of  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$ , and  $\text{V}_2\text{O}_5$  and reported a possible transition for  $\text{VO}_2$  at 345°K. Hoschek and Klemm (210) found a magnetic transition at this temperature. They also determined the x-ray pattern above and below this transition and reported no change. However, Templeton (406) reported that although the patterns of the  $\text{VO}_2$  forms below and above 345°K. are almost identical, there is a gradual change with temperature for high-order reflections which indicates a gradual shifting of oxygen position with temperature. All evidence therefore indicates no phase change at 345°K.

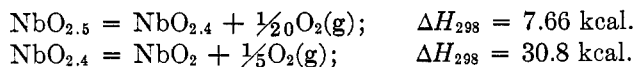
Siemonsen and Ulich (381) determined the heats of combustion of V,  $\text{V}_2\text{O}_3$ , and  $\text{V}_2\text{O}_4$  to  $\text{V}_2\text{O}_5$ . Previous work on these quantities is very unreliable and is not given any consideration here. The various equilibria determinations involving the  $\text{V}_2\text{O}_3$ - $\text{V}_2\text{O}_4$  and  $\text{V}_2\text{O}_4$ - $\text{V}_2\text{O}_5$  systems are also unreliable except for the very excellent work by Flood and Kleppa (142) on the reduction of  $\text{V}_2\text{O}_5$  to  $\text{V}_6\text{O}_{13}$  by sulfur dioxide. Recalculation of their results yields  $\Delta H_{298} = -1059.4$  kcal. and  $\Delta S_{298} = -274.6$  e.u. per mole of  $\text{V}_6\text{O}_{13}$ . Their results are in agreement with the heats of formation obtained from the data of Siemonsen and Ulich (381) and the stability of  $\text{V}_6\text{O}_{13}$ . Bichowsky and Rossini (29) gave a value for the heat of formation of VO which is accepted, since it is consistent with the disproportionation of VO at room temperature. From the stability of  $\text{V}_3\text{O}_5$  one can set a limit to its heat of formation.  $\Delta H_{298}$  of  $\text{V}_3\text{O}_5$  will be more negative than -467 kcal. Todd and Bonnicksen (414) have given the entropy of VO.

Kobayashi (261) has studied the reduction by hydrogen of  $\text{V}_2\text{O}_3$  to VO and of VO to vanadium metal. His data yielded  $\Delta H_{298} = -113$  kcal. for  $\text{V}_x\text{O}$ , where  $\text{V}_x\text{O}$  is the portion of the VO solid-solution range involved in the equilibria. In the work on the reduction of  $\text{V}_2\text{O}_3$  he was dealing with  $\text{V}_2\text{O}$ , which is at the upper end of the VO solid-solution range. Therefore until data are obtained for

the reduction of  $V_yO$  to  $V_xO$ , it will be impossible to use Kobayashi's data to check the heats of formation of either VO or  $V_2O_3$  that are given in table 1.

Grube, Kubaschewski, and Zwiauer (180) and Brauer (47, 48, 50) have studied the niobium oxides by reduction with hydrogen and by magnetic and x-ray studies. Their work indicated that NbO,  $NbO_2$ , and  $Nb_2O_5$  are the stable oxides. They could not prepare an  $Nb_2O_3$  phase. NbO (NaCl type) is reported to have considerable lattice vacancies but the homogeneity range is less than 5 atomic per cent.  $NbO_2$  has no detectable solid-solution range and has a crystal structure closely related to the tetragonal rutile structure, probably the  $MoO_2$  structure.  $Nb_2O_5$  apparently has three forms. They may have slightly different compositions. The low-temperature form is prepared at 800–1200°K. Another form is prepared at 1300–1400°K. and a high-temperature form is prepared above 1400°K. with all heatings in an atmosphere of oxygen. There is no reversal of structure upon cooling. With longer heating times, the conversion can be made to take place at lower temperatures. The observed range  $NbO_{2.4-2.5}$  is in agreement with its behavior as an  $n$ -type semiconductor (312). A reported  $Nb_2O$  phase has been shown by Brauer (46) to be  $Nb_2N$ . Niobium metal forms a solid solution up to almost 5 atomic per cent oxygen. Brauer (48) and Zachariasen (464) have shown that  $Nb_2O_5$  (low-temperature form) and  $Ta_2O_5$  have almost identical orthorhombic pseudohexagonal crystal structures. There are four reports of a high-temperature form of  $Ta_2O_5$ . Brewer and Edwards (60) have heated a mixture of Ta and  $Ta_2O_5$  to 1900°K. Brewer, Margrave, and Kane (65) have burned tantalum metal in air at 1900°K. Kelley and Humphrey (250) have burned tantalum metal in a combustion calorimeter. X-ray powder patterns were obtained of all three preparations by Templeton and Dauben (407) and found to contain a common phase which undoubtedly is a high-temperature form of  $Ta_2O_5$ . Lagergen and Magneli (267) have also reported a high-temperature modification of  $Ta_2O_5$  not isomorphous with any of the  $Nb_2O_5$  forms. Andrews (9) found a solid-solution range in tantalum metal up to 2.3 atomic per cent oxygen.

The heats of formation of  $Nb_2O_5$  (high-temperature form) and  $Ta_2O_5$  (orthorhombic) have been determined by Kelley and Humphrey (250). Grube, Kubaschewski, and Zwiauer (180), Sue (399), and Schaefer and Breil (365) have studied the reduction of  $Nb_2O_5$  by hydrogen. The data of Sue are the most complete and give very good agreement with our estimated entropies even though, as pointed out by Schaefer and Breil, the  $H_2O:H_2$  ratios given by Sue are probably slightly high, owing to thermal diffusion. Taking all the data together with  $\Delta F$  values for  $H_2O$  from Brewer (55), one may derive the following results:



Thus for  $NbO_{2.4}$ ,  $\Delta H_{298} = -219.8 \pm 0.5$  kcal. For  $NbO_2$ ,  $\Delta H_{298} = -189.0 \pm 1$  kcal. The data given by Grube, Kubaschewski, and Zwiauer (180) for the reduction to NbO by hydrogen yield  $\Delta H_{298} = -97 \pm 2$  kcal. for NbO.

*G. Chromium group oxides*

Chromium forms the oxide  $\text{CrO}_3$  (orthorhombic) with distorted oxygen tetrahedra around each Cr (90) and  $\text{Cr}_2\text{O}_3$  ( $\alpha$ -corundum structure). In addition, Blanc (34) claims to have prepared two metastable forms of  $\text{Cr}_2\text{O}_3$ , one of which goes to the other upon heating at  $1000^\circ\text{K}$ . under reduced pressures. Greenwald and Smart (177) found  $\text{Cr}_2\text{O}_3$  to be antiferromagnetic and that distortion of the structure occurs below the Curie point. Blanc (34) and Ryss and Selyanskaya (363) reported several intermediate phases between  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$ . Michel and Bénard (302) prepared  $\text{CrO}_2$  (rutile structure) and reported that  $\text{Cr}_2\text{O}_3$  has a homogeneity range up to  $\text{CrO}_{1.56}$  with a two-phase region up to  $\text{CrO}_2$ . The formula  $\text{CrO}_{1.50-1.56}$  agrees with the observation of Bevan, Shelton, and Anderson (28) that it is an  $n$ -type semiconductor. Vasenin (423) reported that  $\text{CrO}_3$  melts at  $451-460^\circ\text{K}$ . and starts giving off oxygen at  $540^\circ\text{K}$ . with precipitation of solid  $\text{Cr}_2\text{O}_5$ ; the reaction goes to completion at  $620^\circ\text{K}$ . Milligan and Watt (303) also found x-ray evidence for such an intermediate phase. Further heating to  $707-784^\circ\text{K}$ . caused decomposition to  $\text{Cr}_2\text{O}_3$ . Schwartz, Fankuchen, and Ward (371) have reported the sequence of decomposition to be  $\text{CrO}_3 \rightarrow \text{Cr}_3\text{O}_5 \rightarrow \text{Cr}_2\text{O}_5 \rightarrow \text{CrO}_2 \rightarrow \text{Cr}_2\text{O}_3$ . Wartenberg and Reusch (431) have reported the partial decomposition of  $\text{Cr}_2\text{O}_3$  at  $2530^\circ\text{K}$ . in air. This may be due to formation of  $\text{Cr}_3\text{O}_4$  but is more probably due to an extended homogeneity range for the  $\text{Cr}_2\text{O}_3$  phase. Lux and Proeschel (280) claimed the preparation of a red  $\text{CrO}$  (hexagonal, similar to  $\text{BeO}$  and  $\text{ZnO}$ ) which has a slow rate of decomposition at  $373^\circ\text{K}$ . but is undoubtedly metastable at all temperatures. Kelley, Boericke, Moore, Huffman, and Bangert (249) made a careful study of the  $\text{Cr}-\text{Cr}_2\text{O}_3$  system and could find no evidence for any phases below  $\text{Cr}_2\text{O}_3$ . Pascal (326) also confirmed this. Molten chromium metal dissolves 6.5 atomic per cent oxygen at  $1975^\circ\text{K}$ .

The value given for the heat of formation of  $\text{Cr}_2\text{O}_3$  is an average of the values given by Kelley, Boericke, Moore, Huffman, and Bangert (249) and by Roth and Wolf (355). The  $\text{CrO}_2$  value comes from the observation of Dominé-Bergès (115) that  $\text{Cr}_2\text{O}_3$  goes to  $\text{CrO}_2$  in air below  $673^\circ\text{K}$ . The  $\text{CrO}_3$  value was obtained from the value given by Roth and Wolf for the heat of dissociation of  $\text{CrO}_3$  to  $\text{Cr}_2\text{O}_3$  and oxygen. This value indicates that  $\text{CrO}_3$  is metastable even at room temperature.

The  $\text{H}_2\text{O}:\text{H}_2$  ratios obtained by Grube and Flad (179), Wartenberg and Aoyama (429), Aoyama and Kanda (10), and Okada, Kohubo, and Matsuo (322) for the reduction of  $\text{Cr}_2\text{O}_3$  to chromium metal by hydrogen agree rather well with the ratios calculated from the heat of formation shown here for  $\text{Cr}_2\text{O}_3$  and the entropies of the reactants.

Hägg and Magneli (184), Magneli (283, 287, 288), and Glemser and Lutz (168, 169) have made x-ray studies of the  $\text{MoO}_2-\text{MoO}_3$  system. Above  $1275^\circ\text{K}$ . only  $\text{MoO}_2$  and  $\text{MoO}_3$  were found. Below  $1275^\circ\text{K}$ .  $\text{Mo}_9\text{O}_{26}$  and  $\text{Mo}_8\text{O}_{23}$  were found, one being prepared below  $925^\circ\text{K}$ . and one above. Their structures are closely related to that of  $\text{W}_{10}\text{O}_{29}$  and  $\text{ReO}_3$ . Two forms of  $\text{Mo}_4\text{O}_{11}$  were also found. Glemser and Lutz (168) reported that the homogeneity range of  $\text{Mo}_4\text{O}_{11}$  is less

than the range  $\text{MoO}_2$ <sub>0.65-2.75</sub> and that this composition decomposes under reduced pressures above 925°K. At 1075°K. they reported formation of a new phase which has not been characterized as yet. The homogeneity range for  $\text{MoO}_2$  is less than the range  $\text{MoO}_1$ <sub>1.97-2.08</sub>. *Strukturbericht* (199) reports this phase as having the rutile structure, but Hägg and Magneli (184, 287) show that  $\text{MoO}_2$  is distorted to a monoclinic structure.  $\text{MoO}_3$  (orthorhombic) is an *n*-type semiconductor, in agreement with the homogeneity range  $\text{MoO}_2$ <sub>0.95-3.00</sub>.

Ueda and Ichinokawa (418, 419) and Sawanda, Ando, and Nomura (364) reported  $\text{WO}_3$  to be ferroelectric with a Curie point at 983°K. along with a change in symmetry from orthorhombic to tetragonal. Kehl, Hay, and Wahl (242) determined the structure of  $\text{WO}_3$  (tetragonal). The structure is closely related to the cubic  $\text{ReO}_3$  structure, but no transformation to a cubic form is observed up to 1400°K. The triclinic structure of  $\text{WO}_3$  reported by Bräkken (45) is really orthorhombic, according to Ueda and Ichinokawa (420, 421). Perhaps both symmetries exist at different temperatures. No transition is known between room temperature and 983°K. and the change must be gradual. Mathias and Wood (294) reported a transition below 223°K. to a form with higher symmetry. The behavior as an *n*-type semiconductor is in agreement with the homogeneity range  $\text{WO}_2$ <sub>0.95-3.00</sub>. Hägg and Magneli (184, 287), Magneli (284, 285, 286, 287, 288), and Glemser and Sauer (171) agreed very closely on the phases of the  $\text{WO}_2$ - $\text{WO}_3$  system. However, Magneli (285, 286) reported  $\text{W}_{10}\text{O}_{29}$  (monoclinic) to have a narrow homogeneity range, while Glemser and Sauer (171) reported  $\text{WO}_2$ <sub>0.88-2.92</sub>. They also indicated  $\text{WO}_2$ <sub>0.65-2.75</sub>. The phase previously called  $\text{W}_2\text{O}_5$  is found to be  $\text{W}_{18}\text{O}_{49}$  (monoclinic).  $\text{WO}_2$  (monoclinic) has a distorted rutile structure.

Funaki and Ogawa (154) claimed the formation of  $\text{Mo}_2\text{O}_3$  and  $\text{MoO}$  upon the reduction of  $\text{MoO}_2$  by hydrogen at 1090–1130°K. Watt and Davies (439) reported an  $\text{Mo}_2\text{O}_3$  phase which showed no x-ray pattern and was undoubtedly metastable. Hanawalt, Rinn, and Frevel (189) and Phelps, Gulbransen, and Hickman (331) also claimed to have found  $\text{Mo}_2\text{O}_3$ , but Hägg and Magneli (184, 287) could not find any oxides below  $\text{MoO}_2$  and Hickman and Gulbransen (201) have recently reported that they and Rinn find their earlier work to be in error. Also, Brewer, Searcy, and McCullough (70) have made x-ray studies at room temperature of heated  $\text{Mo}$ - $\text{MoO}_2$  mixtures and have found no oxides below  $\text{MoO}_2$ . Brewer, Edwards, and McCullough (61) could find no x-ray evidence for oxides below  $\text{WO}_2$ .

Neumann, Kröger, and Kunz (320) determined the heat of combustion of molybdenum to  $\text{MoO}_3$  in fair agreement with Mixer (305). Other earlier determinations appear to be greatly in error. Mixer (305) determined the heat of formation of  $\text{MoO}_2$  and obtained a value which is in close agreement with the equilibrium data for the reduction by hydrogen obtained by Tonosaki (417). The heats given for the other molybdenum oxides are consistent with their disproportionation behavior. Huff, Squitieri, and Snyder (213) have obtained a reliable value for the heat of formation of  $\text{WO}_3$ . Thompson (411) has recalculated the data of Wohler and Günther (453), Liempt (275), and Shibata (375) for reduction by hydrogen and by carbon monoxide to obtain the heat of formation

of  $\text{WO}_2$ . His calculations do not give a reasonable entropy, since he did not correct the data to be consistent with the entropies. It is very common to find that data for high-temperature equilibria often have the correct order of magnitude of equilibrium constants or free energies of reaction but incorrect temperature dependencies. This is due to the many sources of error which can vary with the temperature. The best way to treat the data is to correct the experimental data to obtain a corrected curve which goes through the center of the experimental points and has a slope consistent with the entropies. The temperature ranges of the original data were obtained and the average temperature taken as the center of the experimental data. This is illustrated by the equations given by Thompson (411) for the reaction  $\text{W}(s) + 2\text{H}_2\text{O} = \text{WO}_2(s) + 2\text{H}_2(g)$ .

	OBSERVED $2 \log (\text{H}_2)/(\text{H}_2\text{O})$	CORRECTED $2 \log (\text{H}_2)/(\text{H}_2\text{O})$
Wohler and Günther.....	$3808/T - 3.108$	$3440/T - 2.8$
Liempt.....	$2222/T - 1.169$	$4090/T - 2.8$
Shibata.....	$3146/T - 2.322$	$3700/T - 2.8$

The average for the second column of figures is  $3740/T - 2.8$  for  $2 \log (\text{H}_2)/(\text{H}_2\text{O})$ . The much better agreement in the second column than in the first shows that the three determinations agree fairly well as to the free energy of reaction, but errors in the different determinations cause different temperature dependencies. Using the corrected average, one obtains for  $\Delta H_{298}$  of  $\text{WO}_2(s)$  a value of  $-133 \pm 3$  kcal. compared to  $-135$  kcal. determined by combustion by Delépine and Hallopeau (114). The value  $\Delta H_{298} = -134 \pm 2$  kcal. was accepted for  $\text{WO}_2$ .

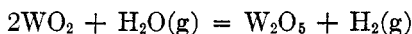
In a similar manner as above the equations given by Thompson (411) for the reaction  $2\text{WO}_2 + \text{H}_2\text{O}(g) = \text{W}_2\text{O}_5 + \text{H}_2(g)$  were corrected to agree with reasonable entropies.

	OBSERVED $\log (\text{H}_2)/(\text{H}_2\text{O})$	CORRECTED $\log (\text{H}_2)/(\text{H}_2\text{O})$
Wohler and Günther.....	$1000/T - 1.218$	$880/T - 1.1$
Liempt.....	$817/T - 0.88$	$1062/T - 1.1$
Shibata.....	$730/T - 0.807$	$1035/T - 1.1$

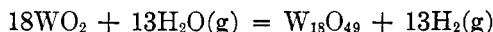
The average value for the last column is  $\log (\text{H}_2)/(\text{H}_2\text{O}) = 990/T - 1.1$ . Using this value and  $-134$  kcal. for  $\Delta H_{298}$  of  $\text{WO}_2$ , one obtains  $\Delta H_{298} = -330 \pm 3$  kcal. for  $\text{W}_2\text{O}_5$ . Using the data given by Thompson (411) for  $\text{W}_2\text{O}_5(s) + \text{H}_2\text{O}(g) = 2\text{WO}_3(s) + \text{H}_2(g)$  in a similar manner as above, one obtains  $\Delta H_{298} = -337 \pm 5$  kcal. for  $\text{W}_2\text{O}_5$  using  $\Delta H_{298} = -200.2$  kcal. for  $\text{WO}_3$ . This agreement is fair and the value  $\Delta H_{298} = -333$  kcal. has been accepted for  $\text{W}_2\text{O}_5$ , but it should be regarded as somewhat uncertain in view of the x-ray work discussed above, which indicates a phase  $\text{WO}_{2.9}$  between  $\text{W}_2\text{O}_5$  and  $\text{WO}_3$ .

The above calculations on data which disregard the intermediate phase assume

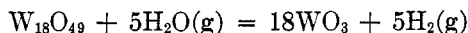
that the intermediate phase is just barely stable and that the  $\text{H}_2\text{O}:\text{H}_2$  ratios are the same for the reduction step from  $\text{WO}_3$  to  $\text{WO}_{2.9}$  and from  $\text{WO}_{2.9}$  to  $\text{WO}_{2.75}$ . If sufficient data were available to treat the two steps separately, more accurate calculations could be made. The use of  $\text{W}_2\text{O}_5$  in the calculations instead of  $\text{W}_{18}\text{O}_{49}$  does not introduce any difficulties in most calculations, as long as one formula is used consistently. For example, if instead of



we had considered the equilibrium to be



we would have obtained  $\Delta H_{298} = -3233$  kcal. for  $\text{W}_{18}\text{O}_{49}$ . From



we would have obtained  $\Delta H_{298} = -3304$  kcal. for  $\text{W}_{18}\text{O}_{49}$ .  $\Delta H_{298} = -3269$  kcal. may be taken as the best value for  $\text{W}_{18}\text{O}_{49}$ . The value per gram-atom of oxygen of  $-66.7 \pm 1$  kcal. is seen to be practically the same as the value obtained assuming  $\text{W}_2\text{O}_5$ .

The entropy of  $\text{MoO}_2$  was obtained from the data of Tonosaki (417) on reduction by hydrogen. The entropies of  $\text{WO}_2$  and  $\text{W}_2\text{O}_5$  were estimated by Latimer (271).

#### H. Manganese group oxides

$\text{MnO}$  (cubic  $\text{NaCl}$ ) undergoes a rhombohedral deformation below  $173^\circ\text{K}$ . due to antiferromagnetic forces, according to Tombs and Rooksby (416) and Greenwald and Smart (177). LeBlanc and Wehner (273) have found that  $\text{MnO}$  prepared in vacuum is especially active and can take up oxygen very readily to a composition  $\text{MnO}_{1.13}$  with no change in phase, in agreement with its behavior as a  $p$ -type semiconductor (312). Rode (348) has reported an  $\text{MnO}_{1.00-1.15}$  homogeneity range.

$\text{Mn}_3\text{O}_4$  (tetragonally distorted spinel structure) is found to take up oxygen to  $\text{MnO}_{1.40}$  according to Rode (348) and to  $\text{MnO}_{1.42}$  according to LeBlanc and Wehner (273) with no phase change. Further addition of oxygen results in the formation of  $\text{MnO}_{1.50-1.6}$  (distorted spinel structure). This form of  $\text{Mn}_2\text{O}_3$ , which can also be prepared by dehydration of  $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , is closely related to the  $\text{Mn}_3\text{O}_4$  structure, but has manganese vacancies and is metastable. McMurdie and Golovato (299) have found that  $\text{Mn}_3\text{O}_4$  changes to the cubic spinel structure above  $1433^\circ\text{K}$ .

$\text{Mn}_2\text{O}_3$  (cubic  $\text{Sc}_2\text{O}_3$  structure) is the stable modification of  $\text{Mn}_2\text{O}_3$ . Upon decomposition of  $\text{MnO}_2$  (rutile structure), LeBlanc and Wehner (273) found formation of  $\text{Mn}_2\text{O}_3$  (cubic) at  $\text{MnO}_{1.95}$ , a result which indicates a very narrow homogeneity range for  $\text{MnO}_2$ . The  $n$ -type semiconductor behavior of  $\text{MnO}_2$  indicates the range to be  $\text{MnO}_{2-x}$  (312). The  $\text{MnO}_2$  x-ray pattern was still obtained at  $\text{MnO}_{1.8}$  but only the  $\text{Mn}_2\text{O}_3$  pattern was obtained at  $\text{MnO}_{1.6}$ .

It is quite possible that the wide homogeneity ranges observed for the  $\text{MnO}$

and  $\text{Mn}_3\text{O}_4$  phases are not the equilibrium ranges and that the observed ranges extend beyond the equilibrium limits, owing to the slow rate of conversion to the stable phase. Further work at higher temperatures and with long heating times is necessary to clarify the equilibrium limits of the solid-solution ranges. Baroni (18) has studied the manganese-oxygen system up to  $900^\circ\text{C}$ . His results checked those of LeBlanc and Wehner (273), indicating no other equilibrium phases between  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$ . However, Glemser (166) has observed another phase between  $\text{MnO}_{1.76}$  and  $\text{MnO}_{1.93}$  which is unlike any of the other phases reported in the manganese oxide system and which is not the same as the unknown structure found by Ramsdell (339) and Dubois (118) in the same composition range. This phase is undoubtedly metastable. Brenet (51, 52) has presented x-ray evidence for polarization and distortion of the  $\text{MnO}_2$  lattice. Cole, Wadsley, and Walkley (101) have reviewed the various compounds reported in the literature. Many contain potassium and hydrogen. Delano (113) has shown that the compounds  $\text{K}_2\text{Mn}_4\text{O}_8$  and  $\text{K}_2\text{Mn}_8\text{O}_{16}$  each form solid-solution ranges up to  $\text{MnO}_2$  with gradual removal of potassium. The  $\text{K}_2\text{Mn}_4\text{O}_8$  series is the  $\text{MnO}_2$  form known as ramsdellite and  $\delta\text{-MnO}_2$ , while the  $\text{K}_2\text{Mn}_8\text{O}_{16}$  series is the  $\text{MnO}_2$  form known as cryptomelane. Apparently both of these forms become metastable with respect to pyrolusite, the stable form of  $\text{MnO}_2$  with rutile structure, when the potassium is completely removed. Genin (160) and Byström and Byström (89) have also done work on these compounds and have obtained results which confirm this interpretation. There are no stable oxides above  $\text{MnO}_2$ .

Southard and Shomate (389) have determined the heat of formation of  $\text{MnO}$ . The heat of formation of  $\text{Mn}_3\text{O}_4$  was determined by Shomate (377), and the value given here was obtained by correcting his value slightly. His correction of the Bichowsky and Rossini (29) value for the heat of formation of aqueous hydriodic acid was not considered warranted. In fact, a correction of 0.41 kcal., making the heat of formation more negative to correct from  $18^\circ$  to  $25^\circ\text{C}$ ., was made to Bichowsky and Rossini's (29) value instead of the correction in the opposite direction suggested by Shomate. The corrected  $\Delta H_{298}$  for  $\text{Mn}_3\text{O}_4$  is  $-330.92 \pm 0.26$  kcal. from the experiments with hydriodic acid and  $-331.64 \pm 0.3$  kcal. from the experiments with hydrogen peroxide.  $\Delta H_{298} = -331.2 \pm 0.3$  kcal. was taken as the average value. The heat of formation of  $\text{MnO}_2$  was also determined by Shomate (377) and is believed to be much more reliable than earlier work. Using the corrected  $\text{Mn}_3\text{O}_4$  value from above, one obtains  $\Delta H_{298} = -124.25 \pm 0.2$  kcal. as the heat of formation of  $\text{MnO}_2$  by averaging the two different determinations of the  $\text{MnO}_2$  heat by Shomate (377). Siemonsen (380) obtained  $\Delta H_{298} = 25.05$  kcal. for  $3\text{Mn}_2\text{O}_3 = 2\text{Mn}_3\text{O}_4 + \frac{1}{2}\text{O}_2$  by combustion of  $\text{Mn}_2\text{O}_3$ . This heat is in agreement with the oxygen partial pressures measured by Honda and Soné (209), Meyer and Rötgers (301), and Tatievskaya, Chufarov, and Antonov (401). This value, together with Shomate's  $\Delta H$  value for  $\text{Mn}_3\text{O}_4$ , yields  $\Delta H_{298} = -229.2$  kcal. for  $\text{Mn}_2\text{O}_3$ .

Todd and Bonnicksen (414) determined the entropy of  $\text{MnO}$ . Siemonsen (380) determined the entropy of  $\text{Mn}_2\text{O}_3$  from the above dissociation data.

Aoyama and Oka (11) studied the reduction of  $\text{MnO}$  by hydrogen. Their data

may be used to check the heats and entropies of formation given in table 1 for MnO. Although their data give too high a heat of formation of MnO, a plot of the free energy of reaction against temperature calculated from the thermodynamic data given in table 1 and the high-temperature specific heats determined by Southard and Shomate (389) and by Kelley, Naylor, and Shomate (251) goes directly through the experimental points of Aoyama and Oka (11) with deviations of only a few hundred calories. This is another excellent example where experimental heats of reaction at high temperatures may be in error, although the free energies are only slightly in error. An additional check of the  $\Delta H$  values given in table 1 is the agreement with the various determinations of the oxygen pressures due to decomposition of MnO<sub>2</sub>. These data have been summarized by Siemonsen (380).

X-ray studies have indicated no phases below ReO<sub>2</sub>. Both ReO<sub>2</sub> and TcO<sub>2</sub> have the monoclinic MoO<sub>2</sub> structure (152, 463). ReO<sub>3</sub> (cubic) has a structure cosely related to those of WO<sub>3</sub>, Mo<sub>9</sub>O<sub>26</sub>, Mo<sub>8</sub>O<sub>23</sub>, and W<sub>10</sub>O<sub>29</sub>. Tc<sub>2</sub>O<sub>7</sub> and Re<sub>2</sub>O<sub>7</sub>, the highest oxides, are not isomorphous (99a). The heats of formation of ReO<sub>3</sub> and Re<sub>2</sub>O<sub>7</sub> were determined by Roth and Becker (352). The ReO<sub>3</sub> value must be greatly in error, for it indicates that ReO<sub>3</sub> is very unstable by disproportionation. Biltz, Lehrer, and Meisel (31) and Nechamkin, Kurtz, and Hiskey (318) have shown that ReO<sub>3</sub> disproportionates only when Re<sub>2</sub>O<sub>7</sub> gas can escape. Cobble (99a) has recently redetermined the heats of formation of ReO<sub>3</sub> and Re<sub>2</sub>O<sub>7</sub>. He confirms the Re<sub>2</sub>O<sub>7</sub> value found by Roth and Becker but obtains a much different value for ReO<sub>3</sub>. Cobble's  $\Delta H_{298}$  value of  $-49 \pm 1$  kcal. for  $\frac{1}{3}\text{ReO}_3$  is in good agreement with  $-46 \pm 5$  kcal. obtained from Latimer's (271) estimate of the free energy. Cobble (99a) has also determined the heats of formation of Tc<sub>2</sub>O<sub>7</sub>, TcO<sub>3</sub>, and TcO<sub>2</sub>. The heat of formation of ReO<sub>2</sub> is based on the estimated free energy given by Latimer (271).

### *I. Iron group oxides*

The lowest oxide for iron, cobalt, and nickel is the MO phase (cubic NaCl type), which becomes slightly deformed to rhombohedral symmetry because of antiferromagnetic bonding at low temperatures. Tombs and Rooksby (416), Rooksby (350), and Smart and Greenwald (177, 387) have discussed this distortion. CoO apparently becomes tetragonal because of antiferromagnetism.

According to Darken and Gurry (108, 109), the FeO phase, which is unstable by disproportionation at room temperature, becomes stable at 833°K. with a composition of Fe<sub>0.945</sub>O. Gulbransen and Ruka (182) report that this phase may be stable at even lower temperatures in the form of thin films on a metal surface. As the temperature is raised, the homogeneity range increases. The low-oxygen side remains almost constant at about Fe<sub>0.95</sub>O, while the high-oxygen side becomes higher in oxygen as the temperature is raised. At 1697°K. the range extends to Fe<sub>0.835</sub>O. Bénard (26) has also studied the FeO phase in detail and has presented additional data. Lihl (277) has reported that FeO is found with the Fe<sub>3</sub>O<sub>4</sub> structure if carbon is present.

Liquid ferrous oxide in equilibrium with iron has the composition Fe<sub>0.968</sub>O

at 1644°K. and  $\text{Fe}_{0.992}\text{O}$  at 1797°K. The solubility of oxygen in  $\alpha$ -iron is 0.01–0.02 atomic per cent at room temperature, according to Sloman (385). Vogel and Martin (425) give data on the solubilities in the various forms of iron at higher temperatures, but their measurements are apparently too high. According to Darken and Gurry (108, 109), the solubility is not over 0.04 atomic per cent of oxygen even at 1775°K. Fischer and von Ende (141) also give solubility data. Ralston (338) and Taylor and Chipman (402) give data on the solubility of FeO in liquid iron. The solubility is 0.5 atomic per cent at the eutectic point of 1797°K., 1.05 atomic per cent at 1875°K., and 2.1 atomic per cent at 2075°K.

The homogeneity range of the CoO phase is not known, although apparently considerable amounts of oxygen can be taken up by CoO without a phase change and CoO is a *p*-type semiconductor (312). The extent of solubility of CoO in cobalt is not known, although it is small enough so that no change in the cobalt lattice constant is observed upon adding CoO at 775°K.

The homogeneity range of the NiO phase is not known quantitatively, although considerable amounts of oxygen can be taken up without a phase change and NiO is a *p*-type semiconductor. Chufarov, Zhuravleva, and Tatievskaya (97) and Bogatskiĭ (38, 39, 40) have reported that heating nickelous nitrate in air at temperatures from 775°K. to 1300°K. will produce compositions from  $\text{NiO}_2$  to NiO with the same cubic crystal structure with lattice constants decreasing from  $a = 4.620 \text{ \AA}$ . to  $a = 4.172 \text{ \AA}$ . as the oxygen content decreases. Brewer and Mastick (67) reported that nickel dissolves in NiO at 1800°K. and that the solubility decreases with decrease in temperature. Shimomura and Nishiyama (376) found that NiO saturated with nickel has the sodium chloride structure instead of the usual rhombohedrally deformed sodium chloride structure. Bennett, Cairns, and Ott (24) reported a different cubic form (not face centered) of NiO when prepared below 385°K.

According to Hensel and Scott (195), molten nickel dissolves 0.785 atomic per cent of oxygen at the eutectic temperature of 1708°K. At 1738°K. 1.08 atomic per cent is dissolved and 1.93 atomic per cent of oxygen is dissolved in molten nickel at 1925°K.

Of the higher oxides,  $\text{Fe}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4$  are known with the cubic spinel type crystal structure.  $\text{Fe}_2\text{O}_3$  (rhombohedral corundum type) can also be prepared as a metastable phase with the  $\text{Fe}_3\text{O}_4$  spinel structure by oxidation of  $\text{Fe}_3\text{O}_4$ . The study of the solid solubility between  $\text{Fe}_3\text{O}_4$  (cubic) and  $\text{Fe}_2\text{O}_3$  (rhombohedral) is complicated by the complete solubility of  $\text{Fe}_3\text{O}_4$  (cubic) and  $\text{Fe}_2\text{O}_3$  (cubic) in each other. The most reliable evidence (447) indicates that  $\text{Fe}_3\text{O}_4$  has a rather wide homogeneity range, while  $\text{Fe}_2\text{O}_3$  (rhombohedral) has only a very narrow homogeneity range even at 1725°K., where it is in equilibrium with 1 atm. of oxygen and the high-oxygen end of the  $\text{Fe}_3\text{O}_4$  homogeneity range. Since  $\text{Fe}_2\text{O}_3$  exhibits both *n*- and *p*-type semiconductance, it should be designated as  $\text{Fe}_2\text{O}_{3\pm x}$ . White (446) and Corey (103) have reviewed the preparation and properties of the iron oxides.

$\text{Co}_2\text{O}_3$  has never been prepared in the pure state, but traces of a phase which may have the rhombohedral corundum structure have been reported for samples

of CoO heated in oxygen. Baroni (18) claims to have prepared  $\text{Co}_2\text{O}_3$  with a structure that is probably tetragonal. At 400–1100°K. with 50–100 atm. of oxygen he has reported the formation of a surface layer of  $\text{CoO}_2$  which could be detected by electron diffraction, but no  $\text{CoO}_2$  could be prepared in the bulk. No nickel oxide phases above the NiO phase have been prepared and identified as a distinct phase although, as noted above, the cubic NiO phase can apparently take up considerable oxygen without a phase change. However, as in the case of  $\text{CoO}_2$ , distinct oxides can be prepared as surface films. Selwood (373) reported that NiO is formed if deposited on a MgO surface, while  $\text{Ni}_2\text{O}_3$  is formed on an  $\text{Al}_2\text{O}_3$  surface and  $\text{NiO}_2$  is formed on a  $\text{TiO}_2$  surface.

Darken and Gurry (108, 109) have made a very thorough study of the iron-oxygen system, and their results are generally accepted as being the most reliable. The thermodynamic data given in table 1 are based on their data. Todd and Bonnicksen (414) have given the entropy of FeO. Coughlin, King, and Bonnicksen (104) have given the high-temperature heat contents of the iron oxides.

Mixer (306) obtained  $\Delta H_{298} = -57.5$  kcal. for CoO from the heat of combustion. Equilibrium studies with hydrogen or carbon monoxide gave the following values: Emmett and Shultz (127),  $-56.3$  kcal.; Watanabe (436),  $-54.5$  kcal.; Kaputinskii and Gofman (234),  $-56.0$  kcal.; and Wohler and Balz (452),  $-57.6$  kcal. with  $\Delta S_{298}$  values varying from  $-15.5$  to  $-17.6$ . Since  $\Delta S_{298}$  should be somewhat more negative than reported, the heats obtained from equilibrium measurements should probably be more negative. Considering this,  $\Delta H_{298} = -57 \pm 0.5$  kcal. was accepted as the best value for CoO. Foote and Smith (146), Watanabe (437), and Chufarov, Zhuravleva, and Tatevskaya (97) are in good agreement in regard to the partial pressure of the oxygen in equilibrium with CoO and  $\text{Co}_3\text{O}_4$ .  $\Delta H_{298} = -203 \pm 3$  kcal. was accepted for  $\text{Co}_3\text{O}_4$ .

There have been a number of equilibria determinations involving reduction of NiO to nickel. Fricke and Weitbrecht (151) studied the CO– $\text{CO}_2$  equilibrium from 1044° to 1289°K. Watanabe and Ishikawa and Watanabe (224, 438) reported data from 980–1110°K. which give virtually the same  $\Delta H$  from a plot of  $\log K$  against  $1/T$ , but the  $\log K$  values are uniformly displaced by about 0.25 unit or about 1 kcal. in  $\Delta F$ . Bogatskii (38, 39) has made a complete study of the system and has obtained values of  $\log K$  almost identical with those of Fricke and Weitbrecht but with a slightly smaller  $\Delta H$  from a plot of  $\log K$  against  $1/T$ . Pease and Cook (330) have studied the reduction by hydrogen and have obtained results in close agreement with those of Fricke and Weitbrecht. Using  $(\Delta F - \Delta H_{298})/T$  values, the following  $\Delta H_{298}$  were calculated from the experimental  $\Delta F$  values. The equilibrium data of Fricke and Weitbrecht (1044–1289°K.) for reduction with carbon monoxide and the data of Bogatskii (940–1400°K.) gave essentially the same value of  $\Delta H_{298} = -57.12$  kcal., although Bogatskii's data showed more variation in  $\Delta H_{298}$ . The equilibrium data of Pease and Cook (758–873°K.) for reduction by hydrogen gave  $\Delta H_{298} = -57.45$  kcal. The data of Watanabe (980–1110°K.) for reduction by carbon dioxide gave  $\Delta H_{298} = -58.0$  kcal., although  $\Delta H_{298}$  from the  $\log K$  versus  $1/T$  plot was closer to  $-57.1$  kcal.

For comparison with these data, we have the calorimetric determinations of Roth of  $\Delta H_{298} = -58.9$  kcal. and of Mixter of  $\Delta H_{298} = -57.9$  kcal. Brewer and Mastick (67) have obtained  $\Delta H_{298} = -59.9$  kcal. from Johnston and Marshall's (229) vapor-pressure data for a nickel-saturated NiO phase. The value of  $\Delta H_{298} = -58.0 \pm 0.4$  kcal. was accepted as the best value.

### *J. Platinum group oxides*

Many of these oxides have low decomposition temperatures and their study must be carried out at temperatures where equilibrium conditions are difficult to obtain. Most of the work has been done without the aid of x-ray analysis and many phases have been reported which do not exist. Many of the oxides have been prepared from aqueous solutions and some of the reported oxide phases appear not to exist when anhydrous.

*Ruthenium:* Although many oxide phases have been reported for the ruthenium-oxygen system, only the oxides  $\text{RuO}_2$  (rutile structure) and  $\text{RuO}_4$  have been definitely shown to exist.  $\text{RuO}_4$  exists as a yellow form when freshly sublimed and as the stable brown form. Debray and Joly (111) and Remy and Kohn (343) have investigated the decomposition of  $\text{RuO}_4$  and  $\text{RuO}_2$ . Although  $\text{RuO}_4$  vaporizes undecomposed at room temperature, it decomposes at slightly higher temperatures to  $\text{RuO}_2$ . Latimer (271) gives the free energy of formation of  $\text{RuO}_4$ , from which one may obtain a heat of formation by means of an estimated entropy. These data indicate that  $\text{RuO}_4$  is thermodynamically unstable even at room temperature. The heat of formation of  $\text{RuO}_2$  is based on the measurements by Remy and Kohn (343) of the oxygen partial pressure. Their observation that addition of metal reduces the oxygen would indicate an appreciable homogeneity range for  $\text{RuO}_2$ . Latimer (271) has estimated the entropy of  $\text{RuO}_2$ .

*Rhodium:* The only definitely determined phase is  $\text{Rh}_2\text{O}_3$  (corundum structure). Wohler and Muller (455) have reported the existence of  $\text{Rh}_2\text{O}$  and  $\text{RhO}$ , since these compositions have smaller oxygen decomposition pressures than  $\text{Rh}_2\text{O}_3$ , but their data do not distinguish between distinct phases and an extended homogeneity range. Also, if  $\text{Rh}_2\text{O}$  and  $\text{RhO}$  do exist, they are on the verge of being unstable by disproportionation to  $\text{Rh}$  and  $\text{Rh}_2\text{O}_3$  and probably have only limited temperature ranges of stability, for the decomposition temperatures at 760 mm. of oxygen are  $1400^\circ$ ,  $1394^\circ$ , and  $1388^\circ\text{K}$ . for  $\text{Rh}_2\text{O}$ ,  $\text{RhO}$ , and  $\text{Rh}_2\text{O}_3$ , respectively. From the decomposition pressures over a range of temperatures, one can obtain  $\Delta H = -27.8$  kcal. for  $\text{Rh}_2\text{O}$ . Wohler and Jockum (454) gave  $\Delta H = -22.7$  kcal. from a calorimetric determination of the heat of reduction by hydrogen. A weighted average of  $\Delta H = -24.0 \pm 3$  kcal. is taken. Similar averages are taken for  $\text{RhO}$  and  $\text{Rh}_2\text{O}_3$ . Latimer (271) has estimated the entropies. Latimer (271) has given data from which one obtains  $\Delta F_{298} = -14$  kcal. for  $\text{RhO}_2$ ; this value makes  $\text{RhO}_2$  thermodynamically unstable with respect to  $\text{Rh}_2\text{O}_3$ .

*Palladium:*  $\text{PdO}$  (tetragonal) is the only stable anhydrous phase. Its  $p$ -type semiconduction fixes it as  $\text{PdO}_{1+x}$  (312). Latimer (271) gives data for  $\text{PdO}_2$  which fix  $\Delta F_{298} = 0$  and for  $\text{PdO}_3$  which fix  $\Delta F_{298}$  as much greater than zero. These phases are thus thermodynamically unstable, and they have not been observed in pure

form. Wohler (451) determined the oxygen decomposition pressure from which the heat of formation can be obtained. It was averaged with Wohler and Jockum's (454) calorimetric value. Latimer (271) estimated the entropy.

*Osmium:*  $\text{OsO}_2$  (rutile structure) and  $\text{OsO}_4$  are the only known oxides of osmium. Wartenberg (427) has determined the heat of formation of  $\text{OsO}_4$  (gas), and Kelley (243) has summarized the vapor-pressure data for  $\text{OsO}_4$ ; from these values one can calculate the heats of formation of the two forms of solid  $\text{OsO}_4$ . The yellow solid is the stable form. For the metastable white form,  $\Delta H_{298} = -93.4$  kcal. and  $\Delta F_{298} = -70.7$  kcal. From the fact that  $\text{OsO}_2$  disproportionates to solid osmium and 1 atm. of  $\text{OsO}_4$  gas at  $923^\circ\text{K}$ ., Latimer has estimated the free energy of  $\text{OsO}_2$ , which can then be used with an estimated entropy to obtain the heat of formation.

*Iridium:* Wohler and Witzman (456) have given oxygen decomposition pressures for  $\text{IrO}_2$  from which one can obtain  $\Delta H = -50$  kcal. Wohler and Jockum (454) gave  $\Delta H = -40.2$  kcal. from calorimetric determination of the heat of reduction of  $\text{IrO}_2$  by hydrogen.  $\Delta H = -44$  kcal. is taken as a weighted average. Latimer has estimated the entropy.  $\text{IrO}_2$  (rutile structure) is the only pure phase in the iridium-oxygen system. The data quoted by Latimer (271) for  $\text{Ir}_2\text{O}_3$  show that it is thermodynamically unstable.

*Platinum:* Baroni (17), Galloni and Raflo (156), Busch (83), and Galloni and Busch (155) have studied the platinum-oxygen system. The oxides  $\text{PtO}$  (tetragonal),  $\text{Pt}_3\text{O}_4$  (cubic), and  $\text{PtO}_2$  (hexagonal) have been reported. Waser and McClanahan (433, 434) have reported  $\text{Na}_x\text{Pt}_3\text{O}_4$  (cubic), which they suggest can occur for  $x$  from zero to 1 and is the same as the phase reported by Busch (83). From the data given by Latimer (271) for  $\text{Pt}(\text{OH})_2$ , one can estimate  $\Delta F_{298} = -11 \pm 4$  kcal. for  $\text{PtO}$ . From Latimer's data on  $\text{PtO}_2$ , one can calculate  $\Delta F_{298} = -17 \pm 10$  kcal., a value which appears too positive; hence  $-20 \pm 10$  is used here. These values are in reasonable agreement with the partial pressure of oxygen required to form these phases. The report of formation of  $\text{Pt}_3\text{O}_4$  and  $\text{PtO}_2$  at  $823^\circ\text{K}$ . and 1 atm. of oxygen by Busch (83) is difficult to explain unless one assumes that these phases were formed upon cooling. Galloni and Busch (155) believe that  $\text{PtO}$  may not be stable as an anhydrous phase, but Latimer's data would indicate that it should be formed.

### K. Copper group oxides

The oxides  $\text{Cu}_2\text{O}$  (cubic) and  $\text{CuO}$  (monoclinic) are known.  $\text{Cu}_2\text{O}_{1+x}$  is a  $p$ -type semiconductor, while  $\text{CuO}_{1+x}$  is both an  $n$ - and a  $p$ -type semiconductor (312). Faivre (135) has reported no appreciable solubility of copper metal in  $\text{Cu}_2\text{O}$ . Okada (323) believed that the reported structure for  $\text{Cu}_2\text{O}$  (cubic) is wrong and that a different cubic structure is necessary. Auwers (14) has reported a transition for  $\text{Cu}_2\text{O}$  at  $329^\circ\text{K}$ ., a result which has not been verified. Randall, Nielsen, and West (340) have carefully reviewed the thermodynamic data for the copper-oxygen system and more recent work has been in agreement with their final values. The latest new work reported is that of Girardi and Siebert (165), who studied the  $\text{Cu-Cu}_2\text{O}$  equilibrium from  $1365^\circ$  to  $1575^\circ\text{K}$ . The values of the

National Bureau of Standards (316), which differed only slightly from those of Randall, Nielsen, and West (340), are used here. Hu and Johnston (211) have determined the entropy of  $\text{Cu}_2\text{O}$ .

In addition to  $\text{Ag}_2\text{O}$  (cubic),  $\text{AgO}$  and  $\text{Ag}_2\text{O}_3$  have been reported. The thermodynamic data given by Latimer (271) demonstrate that the higher oxides are metastable at 1 atm. of oxygen.  $\text{Ag}_2\text{O}$  is reported to be a  $p$ -type semiconductor, but Faivre (135) reports that it takes up 4 mole per cent of silver metal at  $475^\circ\text{K}$ . Pavlyuchenko and Gurevich (328) and Iijima (221) have studied the  $\text{Ag-Ag}_2\text{O}$  equilibrium and find that no oxidation of silver by oxygen takes place at any temperature with an oxygen pressure less than 1 atm. and that the decomposition of  $\text{Ag}_2\text{O}$  is independent of oxygen partial pressures below 1 atm. Previous measurements of the oxygen dissociation pressure have not been for an equilibrium system or have been measurements of absorption phenomena. The heat of formation, as determined from cell measurements and calorimetric measurements, is given by the National Bureau of Standards (316) and has been accepted here.

$\text{Au}_2\text{O}$  and  $\text{Au}_2\text{O}_3$  are known, but  $\text{Au}_2\text{O}$  is thermodynamically unstable by disproportionation to  $\text{Au}$  and  $\text{Au}_2\text{O}_3$ , while  $\text{Au}_2\text{O}_3$  is metastable with respect to the metal and oxygen. Latimer (271) and the National Bureau of Standards (316) have given data for  $\text{Au}_2\text{O}_3$ .

#### L. Zinc group oxides

$\text{ZnO}_{1-x}$  (hexagonal) is an  $n$ -type semiconductor (312). Ehret and Greenstone (123) have confirmed this homogeneity range directly by demonstrating that red  $\text{ZnO}$  is  $\text{ZnO}$  with up to 0.02 per cent excess zinc dissolved in it. Rees and Spink (341) also found evidence for an appreciable homogeneity range in  $\text{ZnO}$  dust, since broad lines due to variation in lattice parameters are observed. No other oxides of zinc are known. Becker and Roth (22) have obtained good agreement between combustion and solution methods of determining  $\Delta H$  for  $\text{ZnO}$  and very close agreement with the value obtained from older data by Bichowsky and Rossini (29). The cell measurements of Makolkin (290) also agree after correction to conform to the known entropy of  $\text{ZnO}$ . These different determinations by different methods yield  $\Delta H_{298} = -83.2 \pm 0.2$  kcal.

Hedger and Terrey (192) have demonstrated that  $\text{CdO}$  is the only cadmium oxide phase.  $\text{CdO}_{1-x}$  (NaCl type) is an  $n$ -type semiconductor (312). Faivre (135) found the homogeneity range to extend to  $\text{CdO}_{0.996}$  at  $975^\circ\text{K}$ . Becker and Roth's (22) combustion value of  $-62.36$  kcal. and Makolkin's (290) cell value of  $-62.15$  kcal. are in good agreement. Becker and Roth discarded their solution value of  $-61.04$  kcal. Their values can be compared with  $-64.2$  kcal., obtained from the excellent equilibrium measurements for the reaction  $\text{CdO(s)} = \text{Cd(g)} + \frac{1}{2}\text{O}_2\text{(g)}$  by Hincke (204), and  $-65.9$  kcal. obtained from similar measurements by Ueno (422). There appears to be no basis in the published literature for the value of  $-60.86$  kcal. given by the National Bureau of Standards (316).

There is no evidence for a stable  $\text{Hg}_2\text{O}$ . Lamure (268) has shown that  $\text{Hg}_2\text{O}$  disproportionates. Garrett and Hirschler (157) have shown that red  $\text{HgO}$  is the

stable form of HgO at room temperature. Zachariasen (466) has confirmed that yellow and red HgO give the same x-ray pattern, and that the difference between red and yellow HgO is probably one of particle size or slight difference in composition. HgO (orthorhombic) is pseudotetragonal and may be a distortion of PbO (tetragonal). The National Bureau of Standards (316) gives  $\Delta H_{298} = -21.68$  kcal. and  $\Delta S_{298} = -26.4$  e.u. for HgO (red).

#### *M. Gallium group oxides*

The only known solid oxides are Ga<sub>2</sub>O and Ga<sub>2</sub>O<sub>3</sub>. Brukl and Ortner (74) reported that Ga<sub>2</sub>O disproportionates at an appreciable rate to Ga<sub>2</sub>O<sub>3</sub> and Ga at 1075°K. The available thermodynamic data indicate that solid Ga<sub>2</sub>O is unstable at all temperatures. Ga<sub>2</sub>O<sub>3</sub> has many metastable modifications and thus shows a behavior similar to that of Al<sub>2</sub>O<sub>3</sub>. The only thermodynamically stable form at all temperatures is  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (Na<sub>2</sub>O · 11Al<sub>2</sub>O<sub>3</sub> type). Roy, Hill, and Osborn (356) have reviewed the preparation and properties of the other forms of Ga<sub>2</sub>O<sub>3</sub>. Klemm and Schnick (258) have measured the heats of formation of Ga<sub>2</sub>O and Ga<sub>2</sub>O<sub>3</sub> by combustion calorimetry and have obtained fair agreement with Roth and Becker's (352) Ga<sub>2</sub>O<sub>3</sub> value of  $-255.8$  kcal. Latimer (271) has estimated the entropies.

Thiel and Luckmann (410) claimed the preparation of In<sub>2</sub>O and InO and x-ray evidence of which they give no details. Stubbs, Schufle, and Thompson (398) have recently studied the In-In<sub>2</sub>O<sub>3</sub> system and found only In<sub>2</sub>O<sub>3</sub> (cubic Mn<sub>2</sub>O<sub>3</sub> type). They gave the heat and free energy of formation. Their value agrees well with the value  $\Delta H_{298} = -222.5$  kcal. given by Becker and Roth (21). It would appear that any preparations of In<sub>2</sub>O and InO are either mixtures or metastable phases.

Tl<sub>2</sub>O (Pb<sub>2</sub>O structure) and Tl<sub>2</sub>O<sub>3</sub> (cubic Mn<sub>2</sub>O<sub>3</sub> type) are the only definitely established oxides of thallium.  $\Delta H_{298} = -43.2$  kcal. for Tl<sub>2</sub>O is given by Roth and Meichsner (354). Recalculation of the data listed by Bichowsky and Rossini (29) gives a value 1-2 kcal. less negative.  $\Delta H_{298} = -42.5 \pm 1$  kcal. is taken as the best value. Duncan (120) has determined the oxygen partial pressures for the Tl<sub>2</sub>O-Tl<sub>2</sub>O<sub>3</sub> liquid solutions. His treatment of his data is incorrect. Recalculation of the data assuming Raoult's law and using an estimated  $\Delta S$  yields  $\Delta H_{298} = 42$  kcal. for Tl<sub>2</sub>O<sub>3</sub>(s) = Tl<sub>2</sub>O(s) + O<sub>2</sub>(s) and  $\Delta H_{298} = -84.5$  kcal. for Tl<sub>2</sub>O<sub>3</sub>(s).

#### *N. Silicon group oxides*

There are no solid oxides of carbon at room temperature. The gaseous oxides will be considered in the section dealing with gaseous species.

SiO<sub>2</sub> exists in at least six crystalline modifications, of which four have stable temperature ranges.  $\alpha$ -Quartz (hexagonal) is stable up to 848°K. where it is transformed readily to  $\beta$ -quartz (hexagonal), which is stable up to 1140°K. Above this temperature,  $\beta$ -quartz is thermodynamically unstable with respect to  $\beta$ -tridymite (hexagonal) but the transition is very slow.  $\beta$ -Tridymite is stable up to 1743°K. where  $\beta$ -cristobalite (cubic) becomes stable, but this transition

is also very slow. Owing to the slow transitions between the quartz, tridymite, and cristobalite systems, one can obtain upon cooling  $\alpha$ -forms of both tridymite and cristobalite which are thermodynamically unstable with respect to  $\alpha$ -quartz. Mosesman and Pitzer (313) have reviewed the stability and transitions of the various forms of  $\text{SiO}_2$ . Buerger (76) has discussed the changes in structure upon transformation and the reasons for the greatly varying rates of transformation. Above  $1200^\circ\text{K}$ . an excellent catalysis for the transformation is elemental silicon, which apparently is effective through the intermediate  $\text{SiO}$  gas. Ewles and Youell (133) have reported that hydrogen at  $1025^\circ\text{K}$ . for 2 hr. reduces  $\text{SiO}_2$  to  $\text{SiO}_{1.999}$ . The  $n$ -type semiconduction also indicates  $\text{SiO}_{2-z}$  (312).

There have been many reports of the formation of an  $\text{SiO}$  phase which is most easily prepared by condensation of  $\text{SiO}$  gas. Edwards (121) has made a thorough review of the available data and has also carried out examinations with a high-temperature x-ray camera. He has demonstrated that  $\text{SiO}$  does not exist as a stable solid phase at temperatures below  $1300^\circ\text{K}$ . The  $\text{SiO}$  solid samples that can be obtained at room temperature by the quenching of  $\text{SiO}$  gas produced by the reduction of  $\text{SiO}_2$  are metastable and will disproportionate if heated to a temperature where the rate of disproportionation is sufficiently rapid. However, Edwards has presented evidence that solid  $\text{SiO}$  is stable above  $1450^\circ\text{K}$ . This is similar to the behavior of the  $\text{FeO}$  phase, which is unstable at low temperatures but which becomes stable at higher temperatures. Although most  $\text{SiO}$  samples prepared by quenching the vapor are amorphous, Inuzuka (223) has prepared some samples with sufficient structure to give x-ray diffraction patterns and has obtained a cubic lattice for  $\text{SiO}$ .

Until recently, it has been difficult to obtain pure silicon metal, and previous determinations of the heats of formation of the  $\text{SiO}_2$  forms do not appear to be very accurate. Humphrey and King (219) have recently determined the heats of formation of quartz and cristobalite. The quartz value is given in table 1. For cristobalite,  $\Delta H_{298} = -209.33$  kcal. Wartenberg (428) has measured the heat of solution of amorphous  $\text{SiO}$  in hydrofluoric acid, from which Edwards (121) has calculated  $\Delta H_{298} = -104.6 \pm 3$  kcal. This value is consistent with the thermodynamic instability of  $\text{SiO}$  at low temperatures as well as its stability above  $1450^\circ\text{K}$ .

The question of the stability of solid  $\text{GeO}$  is similar to that of  $\text{SiO}$  discussed above. Bues and Wartenberg (78) presented calorimetric and vapor-pressure data which indicate that  $\text{GeO}$  is a stable solid at low temperatures. Jolly and Latimer (230) have repeated this work recently and have obtained results which indicate that Bues and Wartenberg are in error. For one thing, Bues and Wartenberg (78) obtain a higher pressure over  $\text{GeO}$  than over  $\text{Ge} + \text{GeO}_2$ ; this certainly fixes  $\text{GeO}$  as being unstable with respect to  $\text{Ge}$  and  $\text{GeO}_2$ . By the heat of combustion of  $\text{GeO}$ , prepared by rapid condensation of  $\text{GeO}$  vapor, Jolly and Latimer (230) have obtained  $\Delta H_{298} = -61 \pm 4$  kcal. This is in agreement with their conclusions based on the x-ray studies and vapor-pressure measurements that for  $\text{GeO}_2(\text{s}) + \text{Ge}(\text{s}) = 2\text{GeO}(\text{s})$ ,  $\Delta H_{298}$  is about  $+7$  kcal. and that  $\text{GeO}$  solid is certainly thermodynamically unstable at all temperatures below  $1000^\circ\text{K}$ .

Laubengayer and Morton (262) have discussed the transformation at  $1306^\circ\text{K.} \pm 10^\circ$  from  $\text{GeO}_2$  (tetragonal rutile type) to  $\text{GeO}_2$  (hexagonal  $\alpha$ -quartz type). The transformation is slow and each form has a distinct melting point. Jolly and Latimer (230) have determined the heat of formation, obtaining  $\Delta H_{298} = -128.5 \pm 0.5$  kcal. in good agreement with Becker and Roth (21) and Hahn and Juza (185).

Tin forms two oxides,  $\text{SnO}$  and  $\text{SnO}_2$ . Veselovskii (424), Spandau (390), and Spandau and Kohlmeyer (391) have reviewed the properties of  $\text{SnO}$ . Veselovskii (424) has reported that  $\text{SnO}$  is unstable at low temperatures, stable at  $320$ – $650^\circ\text{K.}$ , and unstable at higher temperatures with respect to disproportionation to tin metal and  $\text{SnO}_2$ . Spandau (390) finds  $\text{SnO}$  unstable from  $673^\circ\text{K.}$  to  $1313^\circ\text{K.}$  but claims that it is stable above  $1313^\circ\text{K.}$  as a liquid phase. He reports that  $\text{SnO}$  dissolves  $\text{SnO}_2$  but not tin metal.  $\text{SnO}$  is commonly known as a tetragonal form, isomorphous with red  $\text{PbO}$  (311). Partington and Moser (325) have prepared a red  $\text{SnO}$  which is different from the tetragonal form. Kelley (247) has determined the heat of formation of  $\text{SnO}_2$  (tetragonal type). As Veselovskii (424) has pointed out, the heat of formation of  $\text{SnO}$  can be very accurately related to that of  $\text{SnO}_2$  from the fact that  $\text{SnO}$  is just barely stable. He gives  $\Delta H_{298} = -0.652 \pm 0.1$  kcal. for  $2\text{SnO} = \text{SnO}_2 + \text{Sn}$ , from which the heat of formation of  $\text{SnO}$  is obtained.

The lead oxide system is a rather complicated one, and the literature indicates conflicting results. Byström (84, 85, 86, 87) has carried out very accurate x-ray work to fix the structures and homogeneity ranges of the phases. Katz (237, 239) and Katz and Faivre (238) have reviewed the information available on the lead-oxygen system and have carried out experiments to clarify the behavior of this system. By use of the Chevenard thermal balance, very precise x-ray analyses, and chemical studies, they have made a classical study of this difficult system which has resolved many of the previous discrepancies. Their conclusions may be summarized as follows:

No oxides below  $\text{PbO}$  exist. The phase  $\text{Pb}_2\text{O}$  reported by Ferrari (140) has been shown to be  $\text{PbO}_{1.33-1.57}$  (orthorhombic pseudocubic). Above  $762^\circ\text{K.}$ , yellow  $\text{PbO}$  (orthorhombic) is the stable phase and exhibits no detectable homogeneity range. Below  $762^\circ\text{K.}$  red  $\text{PbO}$  (tetragonal) is the stable phase, and when prepared at high temperatures, this phase has no detectable homogeneity range. However, when red  $\text{PbO}$  is prepared at low temperatures by decomposition of yellow  $\text{PbO}$ , it can exist as  $\text{PbO}_{1.00-1.02}$  (orthorhombic pseudotetragonal), owing to slight distortion of the lattice as indicated by slight broadening of some of the x-ray diffraction lines. This range is in agreement with the  $p$ -type semiconductivity of  $\text{PbO}$  (312).

$\text{Pb}_3\text{O}_4$  (tetragonal) also has no detectable homogeneity range, but certain preparations of this phase are found to be orthorhombic pseudotetragonal, owing to a slight distortion, and this distorted phase can probably lose a little oxygen.  $\text{PbO}_{1.33-1.57}$  (orthorhombic pseudocubic) is a homogeneity range with very interesting behavior. For part of this range, from  $\text{PbO}_{1.4}$  to  $\text{PbO}_{1.55}$ , there is a tendency for an order-disorder transformation with the maximum ordering

occurring at the composition  $\text{Pb}_2\text{O}_3$ . From Byström's (86, 87) work one would conclude that the  $\text{PbO}_{1.33-1.57}$  phase is not truly orthorhombic for the entire range but is distorted to monoclinic symmetry. Byström reports two closely related structures derived from the cubic  $\text{CaF}_2$  structure, one orthorhombic and one monoclinic. Katz's work would fix these as part of the same phase region, with the monoclinic symmetry perhaps associated with the superlattice due to ordering. For the most ordered composition,  $\text{Pb}_2\text{O}_3$ , Byström (85) has recently reported a monoclinic structure. This ordering produces a most unusual behavior upon oxidation and reduction through this phase region. If one oxidizes  $\text{PbO}_{1.33}$ , one obtains a continuous change in composition through the phase region  $\text{PbO}_{1.33-1.57}$ . If the oxidation is stopped at an intermediate point in the partially ordered range, e.g.,  $\text{PbO}_{1.52}$ , reduction back to  $\text{PbO}_{1.33}$  will proceed with a continuous change in composition. However, if the oxidation proceeds beyond  $\text{PbO}_{1.55}$  into the completely disordered range, then reduction will proceed in such a manner as to avoid the ordered region. When the composition  $\text{PbO}_{1.55}$  is reached, further reduction produces the composition  $\text{PbO}_{1.4}$  with no intermediate composition appearing. Further reduction proceeds with continuous composition change through the completely disordered region  $\text{PbO}_{1.33-1.40}$ . Thus we have a remarkable situation where under certain types of transformations, a homogeneous-phase region behaves as if it were a two-phase region because the order required in the intermediate region offers too much resistance to the change taking place. Phenomena of this type may well be the explanation of the contradictory results that have been obtained for the praseodymium-oxygen and uranium-oxygen systems, where phases of the same or similar crystal structure appear to have miscibility gaps between them when one would expect none. The extraordinarily skillful resolution of the lead-oxygen system by Katz and Faivre (238) will serve as a model for those working on other complex systems.

The  $\text{PbO}_{1.87-2.0}$  (tetragonal rutile type) homogeneity range was worked out by Katz (239) in agreement with its  $n$ -type semiconductivity. He also found a  $\text{PbO}_{1.93}$  phase that does not have the structure of any other lead oxide. It is not known whether this new phase has an extended homogeneity range. Kamayama and Fukumoto (232) and Zaslavskii, Kondrashev, and Tolkachev (469) have recently reported a new orthorhombic form of  $\text{PbO}_2$  formed by anodic oxidation of lead solutions. The heats of formation of the lead oxides have been given by the National Bureau of Standards (316).

#### *O. Nitrogen-phosphorus group oxides*

None of the nitrogen oxides are stable in an atmosphere of oxygen at room temperature. The gaseous oxides will be discussed in Section III of this paper. The thermodynamic data for  $\text{N}_2\text{O}_5$ , the only solid oxide at room temperature, have been given by Yost and Russell (459) and Latimer (271). Eriks (129) has determined the structure of  $\text{N}_2\text{O}_5$  as being  $\text{NO}_2^+\text{NO}_3^-$ . Broadley and Monteath (73) have determined the structure of  $\text{N}_2\text{O}_4$  (cubic). The  $\text{N}_2\text{O}_4$  molecule is all in one plane. Dulmage, Meyers, and Lipscomb (119) have determined the structure of  $\text{N}_2\text{O}_2$  (monoclinic).

No oxides below  $P_2O_3$  have been definitely established.  $PO_2$  (cubic) (442) is best prepared by disproportionation of  $P_2O_3$  at  $500^\circ K$ . Hill, Faust, and Hendricks (186) reported  $P_2O_5$  existing in three crystalline modifications. They found the stable solid form to be possibly of tetragonal structure with hexagonal and orthorhombic metastable phases. The metastable hexagonal form is formed by condensation of  $P_4O_{10}$  vapor and is essentially a molecular lattice, according to Decker and MacGillavry (112). It has a triple point at  $693^\circ K$ . with  $P_4O_{10}$  gas at 4.75 atm. The liquid form is also metastable and polymerizes readily to the metastable orthorhombic solid, which has a triple point at  $835^\circ K$ . and 0.58 atm. In this case the liquid is the stable form. The orthorhombic form can be converted to the stable form, which has a triple point at  $853^\circ K$ . and 0.73 atm. MacGillavry, Decker, and Nijland (281) reported that the thermodynamically stable form, called possibly tetragonal by Hill, Faust, and Hendricks, is really orthorhombic and has the same general type of linkages as  $V_2O_5$ .

Koerner and Daniels (262) have recently determined the heat of formation of  $P_2O_3$ . Yost and Russell (459) have given the thermodynamic data for  $P_2O_5$ . White phosphorus is conveniently taken as the standard state of phosphorus, although it is not the stable form. From the disproportionation of  $P_2O_3$  to red phosphorus and  $PO_2$  (cubic), one can fix the heat of formation of  $PO_2$ .

Schulman and Schumb (369) reported that  $As_2O_3$  (cubic) is stable only below  $260^\circ K$ ., while  $As_2O_3$  (monoclinic) is stable above  $260^\circ K$ . Their results indicated that  $0.45 \pm 0.1$  kcal. is absorbed upon conversion to the monoclinic form. Stranski, Korb, and Decker (400) have reported yet a third modification prepared by quenching  $As_2O_3$  vapor from  $1700^\circ K$ . A number of intermediate phases between  $As_2O_3$  and  $As_2O_5$  have been reported, but there are no conclusive data establishing any of these as stable. The heats of formation of  $As_2O_5$  and  $As_2O_3$  have been determined by de Passille (327) by combustion. The values given for  $As_2O_3$  by Maier (289) and Berthelot (27) have been given greater weight.

No oxides below  $Sb_2O_3$  have been established. Byström (87, 88) and Buerger and Hendricks (77) agree that  $Sb_2O_3$  (orthorhombic), which is formed by condensation of the gas, consists of infinite double chains rather than finite molecules of  $Sb_2O_3$ .  $Sb_2O_3$  (cubic) is stable up to  $846^\circ K$ . and  $Sb_2O_3$  (orthorhombic) is stable above  $846^\circ K$ .  $Sb_2O_5$  decomposes on heating to  $Sb_6O_{13}$  (tetragonal pseudocubic), which decomposes in turn to  $SbO_2$ , which is orthorhombic when pure and dry.  $SbO_2$  decomposes to  $Sb_2O_3$  upon heating. The  $\Delta H$  values of the National Bureau of Standards are obviously based on the calorimetric data of Mixter (304), which are incompatible with the chemical behavior. The values given by Maier (289), largely based on the data of Simon and Thaler (384), have been used here.

Sillén (382, 383) and Aurivillius and Sillén (13) have studied the forms of  $Bi_2O_3$ . A complex structure is found for a low-temperature form.  $Bi_2O_3$  (monoclinic) is stable from room temperature to  $980^\circ K$ .  $Bi_2O_3$  (cubic  $Mn_2O_3$  type) is prepared by heating at  $1000^\circ K$ . in the presence of certain impurities. Silicon appears to be the most important impurity for stabilizing this structure. In addition,  $Bi_2O_3$  (tetragonal pseudocubic) is obtained by condensation of the vapor at  $1075^\circ K$ . The formula  $Bi_2O_{3+x}$  is indicated by the  $p$ -type semiconductiv-

ity of  $\text{Bi}_2\text{O}_3$  (312). Scholder and Strobbel (368) have discussed the  $\text{BiO}_2$ - $\text{Bi}_2\text{O}_3$  phase region. This phase region is probably never prepared free of alkali or water. The  $\Delta H$  value given by Latimer (271) for  $\text{BiO}_2$  indicates that all phases above  $\text{Bi}_2\text{O}_3$  are metastable in 1 atm. of oxygen. The  $\Delta H$  values for  $\text{BiO}$  and  $\text{Bi}_2\text{O}_3$  of the National Bureau of Standards (63) are accepted here. Glemser and Filcek (167) present data that indicate the non-existence of stable solid  $\text{BiO}$ .

#### *P. Sulfur group oxides*

The only stable solid oxide of sulfur at room temperature and 1 atm. of oxygen is  $\text{SO}_3$ , which exhibits a very complex behavior because of slow attainment of equilibrium among various possible molecular species. Yost and Russell (459) have reviewed the behavior of  $\text{SO}_3$ . The solid form designated as  $\gamma$ - $\text{SO}_3$  has the lowest vapor pressure and is thus the most stable modification. The properties of  $\text{SO}_3$  given in table 1 are those of  $\gamma$ - $\text{SO}_3$  as tabulated by Yost and Russell (459). Solid or liquid  $\text{SO}_3$  is very stable toward decomposition to  $\text{SO}_2$  and oxygen. Westrik and MacGillavry (443) have shown that  $\gamma$ - $\text{SO}_3$  consists of  $\text{S}_3\text{O}_9$  puckered rings in a molecular lattice.  $\text{S}_2\text{O}_8$ , reported by Appel and Goehring (12), is very unstable and decomposes at room temperature in a few hours.

$\text{SeO}_2$  and  $\text{TeO}_2$  are the only stable solid oxide phases that have been demonstrated conclusively for these elements. Glemser and Porscher (170) have shown that the reported  $\text{TeO}$  has no stable existence. Yost and Russell (459) have reviewed the preparation of  $\text{SeO}_3$  and  $\text{TeO}_3$ , but it is not known whether these phases are stable or metastable at room temperature and 1 atm. of oxygen. Lehmann and Kröger (274) found two forms of  $\text{SeO}_3$ , and they reported that  $\text{SeO}_3$  decomposes to  $\text{SeO}_2$  at 453°K.  $\text{SeO}_2$  (tetragonal) consists of endless chains, according to McCullough (297). In addition to the well-known  $\alpha$ - $\text{TeO}_2$  (tetragonal rutile type), Ito and Sawada (225) have reported  $\beta$ - $\text{TeO}_2$  (brookite-like structure) and Stehlik and Baluk (395, 396) have reported  $\gamma$ - $\text{TeO}_2$  (tetragonal). The stability relationships are not known. Yost and Russell (459) have given the heats of formation of  $\text{SeO}_2$  and  $\alpha$ - $\text{TeO}_2$ .

Rollier (349) has stated that  $\text{Po}_2\text{O}_3$  should be similar to the cubic  $\text{Mn}_2\text{O}_3$  type and that  $\text{PoO}_2$  should be similar to the tetragonal rutile type. The thermodynamic data given by Latimer (271) for  $\text{PoO}_2$  and  $\text{PoO}_3$  demonstrate that  $\text{PoO}_3$  is thermodynamically unstable.

#### *Q. Halogen group oxides*

All of the oxides of the halogens except  $\text{I}_2\text{O}_5$  are thermodynamically unstable (56).

#### *R. Hydrogen oxides*

The only thermodynamically stable oxide of hydrogen is water,  $\text{H}_2\text{O}$ , which has a solid form that can exist at room temperature at very high pressures. Altogether six solid modifications of ice have been reported by Bridgman (72) in his high-pressure studies.  $\text{H}_2\text{O}_2$  is thermodynamically unstable and will decompose with explosive violence at 425°K. Latimer (271) and Yost and Russell (459) have given the thermodynamic properties of the hydrogen oxides.

## III. THE VAPORIZATION PROCESSES OF OXIDES

For evaluation of the vaporization data of oxides, there are several useful procedures which allow one to characterize the system being considered. The first fact which should be established is whether any important gaseous oxide molecules exist. It will be found that most oxides vaporize exclusively by decomposition to the gaseous elements. However, there will be a considerable number of oxides which will vaporize to an appreciable extent to form gaseous oxide molecules. A simple experimental criterion can be used to distinguish between these two types of behavior. For any oxide one can calculate the partial pressures of the elements in equilibrium with the oxide phase by use of the thermodynamic data for the oxide and for the elements. If this decomposition partial pressure is compared with the total observed pressure in equilibrium with the oxide, one can readily distinguish between the two types. When there are important gaseous oxide molecules, the total observed pressure will be considerably greater than the pressure due to decomposition to the elements. When the total pressure is the same within experimental errors as the pressure due to the elements, one can conclude that gaseous oxide molecules are not important. There are sufficient data for most oxides to allow this criterion to be used. In addition, there are spectroscopic data available which can also be used to determine if gaseous oxide molecules can be expected to be of importance. However, one must use the spectroscopic data with considerable caution, as the ground states for many gaseous oxides have not been fixed with certainty as yet and often the spectroscopic data will apply to excited states and will give erroneous conclusions about chemical systems which include all states of the molecule. In addition, the use of spectroscopic data to fix the heats of formation of gaseous molecules is still a rather uncertain process and does not often yield unambiguous results. However, the tabulation of dissociation energies of gaseous oxides by Gaydon (158), which is largely based on spectroscopic data, has been very useful for fixing the gaseous oxide molecules which can be expected to be important.

In addition to characterization of the gaseous phase, one must distinguish between two types of solid phases. There is the solid phase which can never form an invariant system with the gaseous phase in equilibrium with it and there is the solid phase which has one composition which does form an invariant system with the gaseous phase. Silver oxide is an example of the first. As vaporization proceeds, more oxygen than silver vaporizes and the silver oxide phase becomes poorer in oxygen and moves toward the silver-rich end of its homogeneity range until it becomes saturated with respect to silver. Then further vaporization results in formation of a silver metal phase. Then the system consisting of two components and three phases becomes invariant and the compositions of all phases are uniquely fixed at any temperature. Before the appearance of the silver metal phase, no vapor pressure characteristic of the silver oxide phase can be measured by conventional methods, since the pressure varies greatly from one end of the homogeneity range to the other. Calcium oxide is an example of an oxide of the second type. If one starts with calcium oxide at the calcium-rich end of its homogeneity range, it will lose more calcium than oxygen as it vapor-

izes. If one starts at the oxygen-rich end of its homogeneity range, it will lose more oxygen than calcium. Therefore, no matter where one starts, one will reach a constant-boiling mixture for which the composition of the vapor will be the same as the composition of the solid phase. One will have an invariant system at a given temperature with the compositions of all phases fixed even though there are only two phases present. Normally such a system would not be invariant, as reference to the phase rule will show, but the additional restriction that the composition of the solid phase be equal to that of the gaseous phase removes all remaining degrees of freedom if the temperature has already been fixed. For all compositions other than the constant-boiling system, the composition and therefore the vapor pressure will change during the vaporization process. For those phases for which no constant-boiling composition exists, no characteristic vapor pressure can be determined. Many workers have mistakenly tried to obtain pure one-phase systems for their vapor-pressure measurements when they should have used two-phase systems. Thus it would be meaningless to determine the vapor pressure of silver oxide by the usual methods, since one would never know to which composition in the homogeneity range the vapor pressure corresponds and since the composition and vapor pressure would change during the determination, one would not even get a definite vapor pressure. Only some method that would allow the determination of the vapor pressure without causing any appreciable vaporization and one which would fix the exact composition of the solid phase would give a result of any meaning if pure silver oxide were used. To get a vapor-pressure measurement of any meaning by conventional methods, one would have to use a mixture of silver and silver oxide. If one were measuring the decomposition vapor pressure by determining the concentration of silver in the gas phase, then one would get a result essentially the same as for pure silver, since the reduction of the activity of silver by the very small solubility of oxygen in silver metal is negligible. However, the oxygen partial pressure would be of interest and since it is so much larger than the silver partial pressure, it could be measured by determination of the total pressure.

For any metal-oxygen system there is, usually, only one composition which is constant-boiling. If there is more than one oxide phase in the system and if there are important gaseous oxide species, then more than one constant-boiling composition can be obtained. However, this is a very uncommon situation for oxides. Since there are a considerable number of metal-oxygen systems which have no oxide phases with constant-boiling compositions, there are actually only a few phases which have constant-boiling compositions. They are believed to be the following: All the alkali  $M_2O$  phases, all the alkaline earth  $MO$  phases, all the  $M_2O_3$  phases of the boron-aluminum group including all the rare earths,  $TiO$ ,  $TiO_{2-z}$ ,  $ZrO_2$ ,  $HfO_2$ ,  $ThO_2$ ,  $UO$ ,  $UO_2$ ,  $NpO_2$ ,  $Pu_4O_{7-z}$ ,  $Am_2O_3$ ,  $V_2O_3$ ,  $NbO$ ,  $TaO_2$ ,  $PaO_2$ ,  $Cr_2O_3$ ,  $MnO$ ,  $FeO$ ,  $CoO$ ,  $NiO$ ,  $CuO$ ,  $ZnO$ ,  $CdO$ ,  $HgO$ ,  $Ga_2O_3$ ,  $In_2O_3$ ,  $Tl_2O$ ,  $SiO$ ,  $SiO_2$ ,  $GeO_2$ ,  $SnO_2$ ,  $PbO$ ,  $PO_2$ ,  $P_2O_5$ ,  $As_2O_3$ ,  $Sb_2O_3$ ,  $Bi_2O_3$ ,  $SeO_2$ ,  $TeO_2$ ,  $PoO_2$ , and  $I_2O_5$ . Except for the phases listed above, oxide phases will be found to lose either oxygen or a higher oxide molecule or metal vapor or a lower oxide molecule without reaching any constant-boiling composition for which the vapor

and condensed phase have the same composition. The vaporization will proceed until a new phase has formed. The two-phase mixture will, of course, be invariant at constant temperature or constant pressure until all of the original phase has disappeared. There are a few oxide phases of highest oxidation number, such as  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{Re}_2\text{O}_7$ ,  $\text{OsO}_4$ , etc., for which the vapor will always have a slightly higher oxygen-to-metal ratio than the condensed phase and thus there will be no constant-boiling composition. However, the difference between the compositions of the vapor and the condensed phase is so small at lower temperatures that for practical purposes they may be considered as constant-boiling compositions.

In the following discussion, spectroscopic evidence will often be used to establish the existence of gaseous oxide molecules. Since several excellent recent reviews of the spectroscopic data exist, in particular those by Gaydon (158), Herzberg (200), Pearse and Gaydon (329), and Rosen (351), references will not, in general, be given for the source of the spectroscopic data.

#### A. Alkali metal oxides

The melting points and dissociation pressures of the alkali metal oxides and peroxides have been determined by Rengade (344, 345) and Centnerszwer and Blumenthal (94). *Gmelin's Handbuch* (172, 173) contains a review of these data. At high temperatures some of the intermediate peroxides appear to undergo disproportionation but all of the peroxides eventually lose oxygen gas by decomposition by successive steps to the  $\text{M}_2\text{O}$  phase at high enough temperatures. The decomposition pressures given in table 1 are for the highest measured oxygen pressures. Bunzel and Kohlmeyer (82) have determined the melting points of  $\text{Na}_2\text{O}$  and  $\text{Na}_2\text{O}_2$ . Todd (413) has obtained  $803^\circ\text{K}$ . for the melting point of  $\text{KO}_2$ . Margrave (64) has confirmed the values for  $\text{Na}_2\text{O}$ , but he obtained  $653^\circ\text{K} \pm 20^\circ$  for  $\text{KO}_2$ .

All available data indicate that there are no important alkali metal oxide gaseous molecules except possibly  $\text{Li}_2\text{O}$  and  $\text{LiO}$ . Brewer and Mastick (66) have carried out theoretical calculations to demonstrate that  $\text{Cs}_2\text{O}$ ,  $\text{Rb}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Na}_2\text{O}$  vaporize by decomposition to the metal gases and  $\text{O}_2$  with no appreciable contribution due to an  $\text{M}_2\text{O}$  molecule. Their calculations indicate that  $\text{Li}_2\text{O}$  could possibly be important, but the uncertainty of the calculations was large. Brewer and Margrave (64) have experimentally determined the vapor pressures of  $\text{Li}_2\text{O}$  and  $\text{Na}_2\text{O}$  by the Knudsen effusion method. Both observed pressures agreed with the pressures expected due to simple decomposition to the gaseous elements. However, as theoretical calculations indicated that  $\text{LiO}$  as well as  $\text{LiO}_2$  could be stable enough to be as important as the elemental species, Brewer, Margrave, and Kane (65) measured the volatility of  $\text{Li}_2\text{O}$  in streams of argon and oxygen. If the oxide molecules were unimportant, the volatility in oxygen should be much smaller than in argon. No decrease in volatility upon changing from argon to oxygen at 1 atm. was observed, thus demonstrating that the  $\text{Li}_2\text{O}$  molecule was comparable to the elements in the saturated vapor of  $\text{Li}_2\text{O}$ . In some experiments higher volatilities were observed in oxygen than in argon,

TABLE 2  
*Energies of dissociation of gaseous oxides to the atoms at 0°K.*

	$D_0$		$D_0$
	<i>kcal.</i>		<i>kcal.</i>
Li <sub>2</sub> O.....	270 ± 6	CdO.....	<88
LiO.....	< 92	GaO ( <sup>2</sup> Σ?).....	58 ± 12
BeO ( <sup>2</sup> Σ?).....	97 ± 28	InO ( <sup>2</sup> Σ?).....	25 ± 5
MgO ( <sup>2</sup> Σ?).....	<100	CO ( <sup>1</sup> Σ).....	256.2
CaO ( <sup>2</sup> Σ?).....	103 ± 8	CO <sub>2</sub> ( <sup>1</sup> Σ).....	381.5
SrO ( <sup>2</sup> Σ?).....	111 ± 4	SiO ( <sup>1</sup> Σ).....	169 ± 3
BaO ( <sup>2</sup> Σ?).....	126 ± 4	GeO ( <sup>1</sup> Σ).....	155 ± 4
BO ( <sup>2</sup> Σ <sup>+</sup> ).....	126 ± 4	SnO ( <sup>1</sup> Σ).....	132 ± 2
B <sub>2</sub> O <sub>3</sub> .....	655 ± 10	PbO ( <sup>1</sup> Σ).....	98 ± 2
Al <sub>2</sub> O (?). . . . .	246 ± 7	N <sub>2</sub> O.....	263 ± 1
AlO ( <sup>4</sup> ?).....	137 ± 8	NO ( <sup>2</sup> π).....	149 ± 1
ScO ( <sup>2</sup> Σ).....	138 ± 23	N <sub>2</sub> O <sub>3</sub> .....	379 ± 1
YO ( <sup>2</sup> Σ?).....	161 ± 46	NO <sub>2</sub> .....	221 ± 1
LaO ( <sup>2</sup> Σ?).....	161 ± 46	N <sub>2</sub> O <sub>4</sub> .....	454 ± 1
CeO.....	149 ± 46	N <sub>2</sub> O <sub>5</sub> .....	512 ± 4
PrO.....	142 ± 12	PO ( <sup>2</sup> π).....	142 ± 12
GdO.....	115 ± 46	P <sub>4</sub> O <sub>6</sub> .....	1180 ± 15
LuO.....	99 ± 35	P <sub>4</sub> O <sub>10</sub> .....	1588 ± 15
ThO <sub>2</sub> .....	>410	AsO ( <sup>2</sup> π).....	114 ± 3
UO.....	198 ± 10	As <sub>4</sub> O <sub>6</sub> .....	864 ± 20
UO <sub>2</sub> .....	>355	SbO ( <sup>2</sup> π).....	74 ± 9
UO <sub>3</sub> .....	508 ± 10	Sb <sub>4</sub> O <sub>6</sub> .....	886 ± 15
TiO ( <sup>2</sup> π).....	160 ± 2	BiO ( <sup>2</sup> π?).....	92 ± 23
ZrO ( <sup>2</sup> π?).....	170 ± 20	O <sub>2</sub> ( <sup>2</sup> Σ).....	117.2
ZrO <sub>2</sub> .....	360 ± 20	O <sub>3</sub> .....	142 ± 1
VO ( <sup>2</sup> Δ?).....	126 ± 23	SO ( <sup>2</sup> Σ?).....	92 or 118
V <sub>2</sub> O <sub>5</sub> .....	725 ± 15	SO <sub>2</sub> .....	241 ± 7
CrO ( <sup>2</sup> ?).....	124 ± 11	SO <sub>3</sub> .....	322 ± 7
MoO <sub>3</sub> .....	445 ± 5	SeO.....	81 ± 23
WO <sub>3</sub> .....	465 ± 7	SeO <sub>2</sub> .....	201 ± 5
MnO.....	92 ± 9	TeO.....	63 or 79
Re <sub>2</sub> O <sub>7</sub> .....	860 ± 10	TeO <sub>2</sub> .....	215 ± 7
FeO.....	<98	F <sub>2</sub> O.....	84 ± 3
NiO.....	<99	Cl <sub>2</sub> O.....	94 ± 2
RuO <sub>2</sub> .....	238 ± 20	ClO.....	44 ± 5
RuO <sub>4</sub> .....	352 ± 30	ClO <sub>2</sub> .....	120 ± 2
OsO <sub>2</sub> .....	263 ± 40	ClO <sub>3</sub> .....	157 ± 3
OsO <sub>4</sub> .....	406 ± 30	Cl <sub>2</sub> O <sub>7</sub> .....	400 ± 5
RhO <sub>2</sub> .....	193 ± 30	BrO.....	51?
IrO <sub>2</sub> .....	242 ± 20	IO.....	44?
PtO <sub>2</sub> .....	198 ± 10	OH ( <sup>2</sup> Σ).....	101 ± 1
CuO ( <sup>2</sup> Σ?).....	113?	H <sub>2</sub> O.....	218.3
AgO ( <sup>2</sup> Σ).....	32 ± 9	H <sub>2</sub> O <sub>2</sub> .....	251 ± 1
ZnO.....	<92		

a result which would tend to indicate that LiO can be important under oxidizing conditions. However, these results were not consistently reproducible. Since traces of water could also give high volatilities, owing to formation of the stable LiOH gaseous molecule, no conclusive results could be obtained concerning LiO.

To illustrate how unimportant gaseous oxide molecules are in the vapors of the other alkalis, one can calculate that saturated  $K_2O$  vapor at  $1000^\circ K$ . contains  $1 \times 10^{-5}$  atm.  $O_2(g)$ ,  $4 \times 10^{-5}$  atm.  $K(g)$ , and  $10^{-16}$  atm.  $K_2O(g)$ . The total pressure of all species in equilibrium with liquid  $K_2O$  should reach 1 atm. at  $1740^\circ K. \pm 120^\circ$  with 0.2 atm.  $O_2(g)$ , 0.8 atm.  $K(g)$ , and probably about  $10^{-4}$  atm.  $K_2O(g)$  in addition to minor amounts of  $O(g)$  and  $K_2(g)$ . In table 1 the calculated temperatures are given at which the total pressures in equilibrium with the condensed oxides are  $10^{-3}$  atm. and 1 atm. For  $K_2O$  the atmospheric temperature is given as  $d.1740 \pm 120$  to indicate that vaporization takes place by decomposition to  $M(g)$  and  $O_2(g)$ .

For all phases other than the  $M_2O$  phases it is believed that the equilibrium oxygen pressure exceeds the metal partial pressure and that all of these phases will lose oxygen continuously without formation of any constant-boiling compositions. For each  $M_2O$  phase, the metal-rich end of the homogeneity range will be in equilibrium with a much higher metal pressure than oxygen pressure, while the metal-poor end will be in equilibrium with a higher oxygen pressure than metal pressure. There is an intermediate composition, which has as yet not been determined for any of these phases, that will be constant-boiling. Among the lighter elements this composition will probably be on the metal-rich side of  $M_2O$  but it may be on the metal-poor side for the heavier elements.

### B. Alkaline earth oxides

The melting points of BeO and MgO have been given by Wartenberg, Reusch, and Saran (432) and those of BeO and CaO have recently been redetermined by Ol'shanskil (324). The melting points of CaO, SrO, and BaO are given by Schumacher (370). The melting and decomposition temperatures of  $MgO_2$  and  $BaO_2$  were obtained from *Gmelin's Handbuch* (174, 175). Mellor (300) has given the data for  $CaO_2$ , and Centnerszwer and Blumenthal (95) have given the data for  $SrO_2$ .

Erdway and Seifert (130) have determined the vapor pressure of BeO. Their results agree closely with those expected on the basis of decomposition to the elements. Using the entropy data given by Kelley (246) and the spectroscopic heat of dissociation of  $BeO(g)$ , one calculates that BeO is unimportant. However, the spectroscopic heats appear to be much too low for MgO, CaO, and SrO. To obtain an upper limit to  $D_0$  of BeO, we can assume that BeO is almost as important as the elements. This yields  $D_0 = 125$  kcal., compared to the spectroscopic values of 69 and 85 kcal. given by Herzberg (200) and 101 kcal. given by Gaydon (158).

The best treatment of the BeO data is to consider the vaporization to be exclusively to beryllium and oxygen atoms. The atmospheric boiling point calcu-

lated on this basis agrees very closely with the boiling point of BeO determined by Mott (314).

The situation regarding the saturated vapors of MgO, CaO, SrO, and BaO is somewhat uncertain at present. Spectral bands are known for MO gaseous molecules in  $^1\Sigma$  states for all the alkaline earths. Derivation of  $D_0$  values from the spectroscopic data yield values that indicate this molecule to be rather unstable. Using these values, one would calculate that MgO, CaO, and possibly SrO vaporize predominantly by decomposing to the gaseous elements. The alkaline earth solids are stable enough so that atomic oxygen will be more important than O<sub>2</sub> except for MgO, where they will be of equal importance. On the other hand, Classen and Veenemans (98) and Moore, Allison, and Struthers (310) agree well on the direct determination of the vapor pressure of SrO. Their vapor pressures are distinctly higher than the pressures expected on the basis of simple decomposition, and there must be a stable gaseous strontium oxide species. Likewise the BaO vapor-pressure determinations by Classen and Veenemans (98), Hermann (196), and Blewett, Liebhafsky, and Hennelly (35) definitely establish the existence of a stable BaO species. Huldt and Lagerqvist (214, 215) have used a very useful method of confirming the stability of these oxides. They have injected the alkaline earth into a flame of known temperature and known partial pressure of oxygen. By measuring the absorption due to the free atoms, they were able to determine the extent of dissociation of the gaseous molecules to the elements. This method does not identify the molecule, but the stabilities which they have determined are in excellent agreement with the vapor-pressure measurements.

Thus, as Huldt and Lagerqvist (215), Brewer and Mastick (66), and Drummond and Barrow (116) have pointed out, there is a real discrepancy between the chemical evidence and the spectroscopic evidence on the stability of the alkaline earth oxides. A number of possible explanations of this discrepancy can be given. The most likely explanation is that the spectroscopic data do not refer to the ground state of the molecule. For example, it may be that the lowest singlet state of the observed bands is an excited state and that the true ground state, which lies much lower in energy and therefore is much more populated, may be a triplet state. Some support for this is offered by the calculations of Brewer and Mastick (66). They found that a model assuming doubly charged ions in the gaseous alkaline earth molecule could not give the correct heat of formation, while a model involving singly charged ions, and thus presumably unpaired electrons, did give much better agreement with the observed chemical stability of these molecules. This latter model could well correspond to a triplet ground state for the alkaline earths. Some unresolved bands of MgO have been reported (19, 351) which might be due to a triplet system. Further work may disclose band systems involving the true ground state of these molecules or the ground state may be like the ground state of F<sub>2</sub>, which does not combine with any excited states to give a band spectrum but only produces a continuum. This same uncertainty about the true ground state exists for many other molecules, and it will be hazardous to use the spectroscopic data for chemical calcu-

lations until it has been established that the data do apply to the ground state of the molecule. If the lowest observed state is not the ground state and is excited by as much as 1 e.v., the calculated concentrations will be in error by several hundred fold at 2000°K.

Another possible explanation is that the molecule observed in the vapor pressure and flame experiments is an  $M_2O_2$  molecule. It would be difficult to give a satisfactory picture of the bonding in such a molecule, but it might be noted that Aldrich (5) has recently reported evidence for  $Ba_2O_2$  by observation of  $Ba_2O_2^+$  ions in a mass spectrograph. Brewer and Mastick (66) were able to eliminate the possibility of the importance of an  $M_2O$  species.

For the time being, it will be assumed that the main oxide species is the MO molecule in a triplet state. The heats of formation of the MO molecules can be derived from the vapor-pressure data and the data of Huldtt and Lagerqvist. Drummond and Barrow (171) have evaluated the data in terms of  $^1\Sigma_1$ ,  $^3\Sigma_1$ , or  $^3\pi$  states. The heats of formation of the solid oxides given in table 1 are used together with the heats of sublimation of the metals given by Brewer (54). For BaO ( $^3\Sigma$ ), one obtains  $D_0$  or  $\Delta H_0$  for  $BaO(g, ^3\Sigma) = Ba(g, ^1S) + O(g, ^3P)$  at 0°K. equal to  $127 \pm 4$  kcal. from the vapor-pressure data and  $122 \pm 6$  kcal. from the flame data. If the results were calculated on the basis of a singlet state, the  $D_0$  from the vapor-pressure measurements would be 3 kcal. larger and the flame value would be 5 kcal. larger. For SrO ( $^3\Sigma$ ), the vapor-pressure data give  $D_0 = 110 \pm 4$  kcal. Huldtt and Lagerqvist (215) appear to have made an error in calculating  $D_0$  from the equilibrium data given by Huldtt (214). Recalculation gives  $D_0 = 117 \pm 7$  kcal. for SrO ( $^3\Sigma$ ) from the flame data. These may be compared with  $D_0 = 30-35$  kcal. from spectroscopic data (200) for SrO ( $^1\Sigma$ ). There is only the vapor-pressure determination by Classen and Veenemans (98) for CaO. Their data agree very closely with the pressure that would be expected for decomposition to the gaseous elements. Huldtt and Lagerqvist (215) give a  $D_0$  value for CaO which does not agree with the equilibrium Ca and CaO concentrations that they report in their flame. Assuming that the reported concentrations are correct and that an error has been made in calculating the  $D_0$  value, one obtains  $D_0 = 103 \pm 8$  kcal. for CaO ( $^3\Sigma$ ). This value is in agreement with the conclusion that the vapor-pressure determinations correspond to vaporization by decomposition to the elements. Thus at 1700°K. one calculates  $6 \times 10^{-10}$  atm. Ca(g),  $6 \times 10^{-10}$  atm. O(g), and  $1 \times 10^{-10}$  atm CaO (g,  $^3\Sigma$ ) in equilibrium with solid CaO. At 2700°K. one calculates approximately the same partial pressure of  $5 \times 10^{-3}$  atm. for all three species. The spectroscopic value of  $D_0 = 35$  kcal. for CaO ( $^1\Sigma$ ) would lead one to expect a negligible amount of the CaO gas. The calculated boiling point of 3800°K. agrees well with Mott's (314) observed value of 3900°K.

There are no accurate measurements of the vapor pressure of MgO. Mott (314) gave a boiling point of 3900°K.; this would indicate that MgO must vaporize by decomposition to the gaseous elements. Ruff and Schmidt (359) gave some rough vapor-pressure measurements that are surely much too high, as they were carried out in a graphite system that causes reduction of the oxide.

Thus their reported pressures for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and the other alkali oxides have been shown to be much too high.

The value of  $D_0 = 112$  kcal. for  $\text{MgO}$  ( $^3\Sigma$ ) from the flame data of Huld and Lagerqvist (215) must be in error, since this value would indicate a rather high volatility for  $\text{MgO}$  as the molecule. One can set an upper limit to the  $\text{MgO}$  partial pressure from the data of Moore (309). He studied the reduction of  $\text{MgO}$  by tungsten metal to produce solid  $\text{WO}_2$  and  $\text{Mg}$  gas. His observed vapor pressures, which should include both the  $\text{Mg}$  and  $\text{MgO}$  partial pressures, were about one-tenth as large as the partial pressure for  $\text{MgO}$  which one calculates from the value of  $D_0 = 112$  which yields  $\Delta H_{298} = 126$  kcal. for  $\text{MgO}(s) = \text{MgO}$  ( $^3\Sigma$ ). In addition, he was able to account for all the volatility on the basis of the partial pressure of magnesium to be expected from the known thermodynamic data for  $\text{MgO}$  and  $\text{WO}_2$  solids. Since he observed a pressure of  $10^{-7}$  atm. at  $1800^\circ\text{K}$ ., the partial pressure of  $\text{MgO}$  must be less than this at  $1800^\circ\text{K}$ . The heat of sublimation at  $298^\circ\text{K}$ . must be greater than 138 kcal. This gives, as an upper limit,  $D_0 \leq 100$  kcal. Thus the total pressure in equilibrium with  $\text{MgO}$  will be somewhere between the lower limit calculated on the basis of decomposition to the elements and the upper limit based on this  $D_0$  value. The temperature at which the total pressure will be  $10^{-3}$  atm. will be between  $2400^\circ\text{K}$ . and  $2520^\circ\text{K}$ . The atmospheric boiling point will be between  $3300^\circ\text{K}$ . and  $3430^\circ\text{K}$ . As averages  $2450^\circ\text{K} \pm 100^\circ$  and  $3350^\circ\text{K} \pm 200^\circ$  will be taken.

Under highly oxidizing conditions to almost neutral conditions, the  $\text{MO}$  molecule is the main vaporizing species for all of the alkaline earth oxides except  $\text{BeO}$ .  $\text{SrO}$  and  $\text{BaO}$  are more important than the elements even under neutral conditions, and under reducing conditions all of the alkaline earth oxides vaporize predominantly to the metal atom vapor.

In summary the following  $\Delta H_{298}$  values are given for  $\text{MO}(s) = \text{MO}(g, ^3\Sigma)$ :  $\text{MgO}$ ,  $\geq 138$  kcal.;  $\text{CaO}$ ,  $149.5 \pm 8$  kcal.;  $\text{SrO}$ ,  $127.6 \pm 4$  kcal.;  $\text{BaO}$ ,  $107.7 \pm 4$  kcal. These are consistent with the  $D_0$  values given in table 2.

### C. Boron-aluminum group oxides

The melting points were determined as follows:  $\text{B}_2\text{O}_3$ , Kracek, Morey, and Merwin (265);  $\text{Al}_2\text{O}_3$ , Geller and Yavorsky (159);  $\text{Y}_2\text{O}_3$ , *International Critical Tables* (222);  $\text{La}_2\text{O}_3$ , Wartenberg and Reusch (431). The melting point of  $\text{CeO}_2$  is an estimate based on the observation of Wartenberg and Gurr (430) that the melting point is over  $2900^\circ\text{K}$ .

Spectroscopic evidence has established the existence of  $\text{BO}$ ,  $\text{AlO}$ ,  $\text{ScO}$ ,  $\text{YO}$ , and  $\text{LaO}$  molecules in the  $^2\Sigma$  state. Linear Birge-Sponer (33) extrapolations indicate heats of dissociation of 160–210 kcal. In addition,  $\text{CeO}$ ,  $\text{PrO}$ ,  $\text{GdO}$ , and  $\text{LuO}$  are known but the electronic states have not been established. Heats of dissociation of 120–150 kcal. are indicated. Bands have also been reported for  $\text{NdO}$ ,  $\text{SmO}$ ,  $\text{DyO}$ ,  $\text{HoO}$ , and  $\text{YbO}$ . In no case has the ground electronic state been conclusively established.

Speiser, Naiditch, and Johnston (393) have determined the vapor pressure of  $\text{B}_2\text{O}_3$ , but the exact molecular species has not been determined. Using the

spectroscopic  $D_0$  value for BO, one can show that  $B_2O_3$  could not be vaporizing as BO and oxygen. Assuming  $B_2O_3$ , their data give  $\Delta H_{1500} = 669$  kcal. for  $B_2O_3(g) = 2B(g) + 3O(g)$  at  $1500^\circ K$ . However, under reducing conditions  $B_2O_3$  will vaporize as BO. For example, a mixture of B and  $B_2O_3$  should produce 1 atm. partial pressure of BO at about  $1100^\circ K$ . BO is stable enough so that even the most stable oxides can be reduced by boron under vacuum conditions. Zintl, Morawietz, and Gastinger (470) have demonstrated that boron reduces  $ZrO_2$  to form BO gas, and Searcy (372) has demonstrated the reduction of BeO by boron to form BO gas. Searcy has taken the data for the two reactions to calculate  $\Delta H_{298} = 4.5 \pm 3$  kcal. for  $B(s) + \frac{1}{2}O_2(g) = BO(g)$ , which yields a  $D_0$  value of  $182 \pm 5$  kcal. using 133 kcal. as the heat of sublimation of boron as determined by Searcy (372). This value is in fair agreement with the spectroscopic value of  $161 \pm 23$  kcal., obtained by Gaydon (158) by correcting the linear Birge-Sponer extrapolated value of 209 kcal.

Brewer and Searcy (69) have reviewed the previous studies of the gaseous oxide species of aluminum and have carried out further studies. The various experimental data point to the existence of two stable gaseous oxide molecules which appear to be  $Al_2O$  and AlO. Under neutral or oxidizing conditions, AlO is the important species, while under reducing conditions  $Al_2O$  becomes more important. Although two species must exist, it is not possible to fix them unambiguously from the available data. The species designated as AlO could actually be  $Al_2O_2$ .

As for the alkaline earths, there is a serious discrepancy between the  $D_0$  value of 137 kcal. obtained from the chemical studies and the spectroscopic  $D_0$  values of  $-21$  to  $-87$  kcal. (158, 200). The low values appear quite inconsistent with the high stabilities of related oxide molecules. It is possible that the true ground state is not the  $^2\Sigma$  state, which is the one observed in the spectra, but is a quartet state considerably lower in energy than the  $^2\Sigma$  state. Although AlO bands can be observed in burning aluminum, which probably attains a temperature of  $3800^\circ K$ . at 1 atm., they cannot be observed in thermally excited sources at lower temperatures. Russell and Foster (362) reported no signs of AlO absorption bands when a mixture of Al and  $Al_2O_3$  was heated to  $2700^\circ K$ . away from air, but they have observed AlO bands in burning aluminum. Also Allen, Rinehart, and White (7, 448) reported AlO bands emitted by supersonic projectiles burning in air. Owing to the high pressure around these projectiles, they attain a temperature of  $4100^\circ K$ . The high temperature required to obtain the doublet AlO bands would also indicate that the lowest doublet state is an excited state.

The situation in regard to the other oxides of this group is still somewhat obscure. If the  $D_0$  values given by Herzberg (200), which are obtained from a linear Birge-Sponer extrapolation, are used, one would calculate that reactions of the type  $M(s) + M_2O_3(s) = 3MO(g)$  are important for yttrium, lanthanum, and cerium. However, if the values given by Gaydon (158), which are about 50 kcal. smaller, are used, then the above reaction would not be important. There are no reliable chemical data to settle this matter. Likewise one cannot say whether the  $M_2O_3$  oxides vaporize undecomposed, vaporize to MO molecules, or vaporize to the elements. Even very rough vapor-pressure determinations would

be of value here. The only data that exist are the boiling points of 4570°K. and 4470°K. for  $\text{Y}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$ , respectively, given by Mott (314) and the observation of Wartenberg (430) that  $\text{Ce}_2\text{O}_3$  vaporizes appreciably at 2600°K. If these values are reliable, stable gaseous molecules are indicated. All of the oxides of this group are so stable that monatomic oxygen is much more important a species than molecular oxygen in the saturated vapor of these oxides.

#### *D. Actinide group oxides*

The melting point of  $\text{ThO}_2$  has been given by Ruff, Ebert, and Woitinek (357) and accepted by Wartenberg and Reusch (431). The melting point of  $\text{UO}_2$  was determined by Friederich and Sittig (153) as 2500–2600°C. but was erroneously reported in their summary table as 2500–2600°K. Brewer (59) has found no evidence of melting and only partial sintering at 2700°K., and 3000°K. is taken as the most probable melting point. Phipps, Seifert, and Simpson (333, 334) have studied the thermal decomposition of  $\text{PuO}_2$  and have reported a melting point for the decomposed mixture. Their results indicate that pure  $\text{PuO}_2$  melts above 2200°K.

Mott (314) reported a boiling point of 4670°K. for  $\text{ThO}_2$  in a carbon system. Brewer (53) found the vapor pressure to be less than  $10^{-7}$  atm. at 2200°K., and Shapiro (374) found  $10^{-8}$  atm. at 2200°K., a value which is consistent with that of Mott. Since the boiling point calculated on the basis of decomposition to the gaseous atoms would be much higher, there must be a stable gaseous molecule.  $\text{ThO}$  bands have been reported by Krishnamurty (266) but no  $D_0$  value can be given. Thus it is not possible to decide if  $\text{ThO}$  or  $\text{ThO}_2$  is the more important gaseous molecule. In view of the formation of solid  $\text{ThO}$ , it would seem that gaseous  $\text{ThO}$  should be of chemical importance. Comparison with the zirconium system would indicate that both  $\text{ThO}$  and  $\text{ThO}_2$  will be of importance in the gaseous state.

Uranium is a rather unique element in the number of oxidation states that are found among its oxide phases. Thus there are oxide phases containing uranium of oxidation number 2, 4, 5, and 6. Likewise among the gaseous species, uranium appears to be unique in having three important oxide molecules in the same temperature range. Even though solid  $\text{UO}_3$  loses oxygen at rather low temperatures, where there is no appreciable volatility of oxide molecules,  $\text{UO}_3$  gas does become important at very high temperatures. Biltz and Müller (32) have observed volatility in the two-phase region between  $\text{UO}_{2.25}$  and  $\text{UO}_{2.62}$  at temperatures above 1430°K. due to disproportionation of the  $\text{UO}_{2.62}$  phase to  $\text{UO}_{2.25}$  solid and  $\text{UO}_3$  gas. The volatility is not observed for compositions above  $\text{UO}_{2.62}$  even though the equilibrium partial pressure of  $\text{UO}_3$  is higher, because the higher oxygen partial pressure above such samples reduces the rate of vaporization so much. For the  $\text{UO}_{2.25}$ – $\text{UO}_{2.62}$  region at 1430°K., the oxygen pressure is only  $4 \times 10^{-4}$  atm. and would not interfere with the vaporization of  $\text{UO}_3$ . Below the composition  $\text{UO}_{2.25}$  the  $\text{UO}_{2.62}$  phase disappears and the  $\text{UO}_3$  activity, and therefore the  $\text{UO}_3$  partial pressure, rapidly becomes quite small. From the sublimation data given by Biltz and Müller (32), a partial pressure of  $10^{-5}$  atm. of  $\text{UO}_3$  in equilibrium with  $\text{UO}_{2.62}$  at 1600°K. can be estimated. From this and the ther-

modynamic data for solid  $\text{UO}_3$ , one can calculate  $10^{-4}$  atm.  $\text{UO}_3$  gas in equilibrium with solid  $\text{UO}_3$  at  $1600^\circ\text{K}$ . and  $10^{-5}$  atm.  $\text{UO}_3$  gas in equilibrium with solid  $\text{UO}_3$  at  $1450^\circ\text{K}$ . Of course, an oxygen pressure of many atmospheres would be required to maintain solid  $\text{UO}_3$  at these temperatures and to get such a high  $\text{UO}_3$  partial pressure. If oxygen gas at 1 atm. were passed over  $\text{UO}_{2.62}$  at  $1950^\circ\text{K}$ ., it is calculated to be in equilibrium with  $10^{-3}$  atm.  $\text{UO}_3$  gas. At  $1773^\circ\text{K}$ . the solid phase would be  $\text{UO}_{2.7}$  and there would be  $10^{-4}$  atm.  $\text{UO}_3$  gas.

That this volatility must be due to the  $\text{UO}_3$  molecule is demonstrated by considering that no other oxide molecule could be responsible for so high a volatility and that the vapor pressure is what one would expect by comparison with the vapor pressure of  $\text{WO}_3$ . Alberman and Anderson (4) comment that the vaporizing species could not be  $\text{UO}_3$ , since it should precipitate  $\text{U}_3\text{O}_8$  upon condensation, while condensates of much lower oxygen composition are observed. This reasoning is obviously incorrect. No matter what the gaseous species is, the solid phase that will condense will be the solid phase in equilibrium with the oxygen partial pressure at the temperature conditions of the condensing surface. Thus when the oxygen pressure is low, the condensate will be low in oxygen.

If one were to measure the volatility in the  $\text{UO}_{2\pm x}$  phase region as a function of composition at a fixed temperature, e.g.,  $2000^\circ\text{K}$ ., the volatility at the high-oxygen end of the region would be large, corresponding to about  $10^{-3}$  atm.  $\text{UO}_3$ . Reducing the oxygen composition would rapidly reduce the  $\text{UO}_3$  partial pressure until it became negligible, but the total volatility would reach an approximately constant value corresponding to the  $\text{UO}_2$  vapor pressure. By comparison with the  $\text{ZrO}_2$  and  $\text{ThO}_2$  vapor pressures the  $\text{UO}_2$  partial pressure would be around  $10^{-3}$  atm. at  $2000^\circ\text{K}$ . Even further reduction of the oxygen composition toward the metal-rich end of the  $\text{UO}_{2\pm x}$  phase region would result again in an increase in volatility due to the  $\text{UO}$  partial pressure. The composition in equilibrium with the  $\text{UO}$  phase is estimated to have a partial  $\text{UO}$  pressure of  $10^{-6}$  atm. at  $2000^\circ\text{K}$ . Thus at a fixed temperature, one can expect three different important gaseous oxide species for the  $\text{UO}_{2\pm x}$  phase region. There is no other phase in any oxide system for which such behavior could be expected. There should be two constant-boiling compositions, one in the  $\text{UO}$  and one in the  $\text{UO}_2$  phase region. For the other actinides, both the  $\text{MO}$  and the  $\text{MO}_2$  gaseous molecules can be expected to be important up to americium. At americium and beyond, the  $\text{MO}_2$  molecule will be unimportant. The  $\text{M}_2\text{O}_3$  molecule may become important. Phipps, Seifert, and Simpson (333, 334) have studied the volatility of  $\text{PuO}_2$ . Under the conditions of their experiment the  $\text{PuO}_2$  was partially reduced and the main gaseous species was  $\text{PuO}$ . From their data, one can estimate a vapor pressure of  $10^{-6}$  atm. for pure  $\text{PuO}$  at  $1850^\circ\text{K}$ . The partial pressure of  $\text{PuO}_2$  is much less than  $10^{-5}$  atm. at  $2200^\circ\text{K}$ .

#### *E. Titanium-zirconium group oxides*

The melting points were determined as follows:  $\text{TiO}$ , Bumps, Kessler, and Hansen (79);  $\text{Ti}_2\text{O}_3$ , *International Critical Tables* (222);  $\text{TiO}_2$ , Wartenberg,

Reusch, and Saran (432);  $ZrO_2$ , Clausing (99), Hennings (194), and Zirnowa (471);  $HfO_2$ , Clausing (99) and Hennings (194).

The vapor pressure of TiO has been reported by Gilles and Wheatley (163). They obtained  $\Delta H_{298} = 135 \pm 1$  kcal. for  $TiO(s) = TiO(g, {}^3\pi)$  or  $D_0 = 160 \pm 2$  kcal. The results agreed with the  $D_0$  obtained by a linear Birge-Sponer extrapolation, thus establishing TiO as a more important species than titanium and oxygen atoms in the saturated vapor. Phillips (332) has established the relative positions of the singlet and triplet systems of TiO. The  ${}^3\pi_r$  state is found to be the ground state, although the lowest singlet level is only slightly above the ground state.

Mott (314) has reported 3300°K. as the boiling point of  $Ti_2O_3$ . No other data are available. The assumption that  $Ti_2O_3$  vaporizes by decomposing to TiO and O gases gives only a slightly higher boiling point. The oxygen partial pressure for  $TiO_{2-x}$  decomposing to  $Ti_2O_3$  solid is smaller than the oxygen pressure for  $TiO_{2-x}$  decomposing to TiO gas. Thus, under conditions where TiO gas can escape, it seems likely that  $Ti_2O_3$  and  $Ti_3O_5$  will disproportionate to TiO gas and  $TiO_{2-x}$  solid. Thus the only two constant-boiling compositions are in the  $TiO_{1-x}$  and  $TiO_{2-x}$  phase regions. Wartenberg (430) reports that  $TiO_2$  is not volatile at 2100°K. but vaporizes extensively at 2300°K. This would be consistent with  $TiO_2$  vaporizing to TiO and O gases.

Data are available for us to make at least a tentative assignment of important gaseous species in the zirconium-oxygen system. Skinner, Edwards, and Johnston (386) report that zirconium metal coated with  $ZrO_2$  was very much less volatile than pure zirconium metal. This would indicate that  $ZrO_2$  has a smaller vapor pressure than zirconium and that the reaction  $Zr(s) + ZrO_2(s) = 2ZrO(g)$  results in a lower partial pressure of ZrO than the partial pressure of zirconium. Searcy (372) has recalculated the data of Zintl, Moravietz, and Gastingier (470) to obtain a  $ZrO_2$  vapor pressure of  $1.5 \times 10^{-7}$  atm. at 2073°K. This is higher than the vapor pressure of zirconium metal determined by Skinner, Edwards, and Johnston (386), so it will certainly serve as an upper limit for the vapor pressure of  $ZrO_2$ . Brewer (53) has reported a  $ZrO_2$  vapor pressure of  $10^{-6}$  atm. at 2000°K. Mott (314) has given a boiling point of 4570°K. for  $ZrO_2$  which is in good agreement with Searcy's value, but it was determined in a carbon system and thus should be too low. These vapor pressures are much higher than the vapor pressure due to decomposition to zirconium and oxygen atoms. Thus they indicate the existence of a stable gaseous oxide molecule. If the  $D_0$  value of 181 kcal. for ZrO obtained by a linear Birge-Sponer extrapolation (33, 200) is used, one calculates  $2 \times 10^{-10}$  atm. at 2073°K. for the vapor pressure of  $ZrO_2$  decomposing to ZrO and O gases. This would seem to indicate that  $ZrO_2$  must vaporize directly to a  $ZrO_2$  molecule. Starodubtsev (394) has observed  $ZrO_2^+$  in a mass spectrograph, a result which tends to confirm the existence of the  $ZrO_2$  molecule, but the ion may have been formed by secondary collisions rather than from a  $ZrO_2$  molecule. Searcy's value for the vapor pressure of  $ZrO_2$  would yield 370 kcal. for the  $D_0$  of  $ZrO_2$ . To make  $ZrO_2$  less volatile than zirconium metal, this should be reduced at least to 360 kcal. To make the partial pressure of ZrO

in equilibrium with a mixture of Zr and  $ZrO_2$  less than the vapor pressure of zirconium, the  $D_0$  value of  $ZrO$  would have to be reduced to 170 kcal. It is assumed that this applies to the  ${}^3\pi$  state of  $ZrO$ , which by comparison with  $TiO$  should be the ground state instead of a singlet state.

Although  $HfO$  bands are known (266), no data are available for them. It is likely that the hafnium-oxygen system will be very similar to the zirconium-oxygen system and that  $HfO_2$  will be an important species.

#### *F. Vanadium group oxides*

The melting points were determined as follows:  $V_2O_3$ , Friederich and Sittig (153);  $VO_2$  and  $V_2O_5$ , Cook (102);  $V_6O_{13}$ , Hoschek and Klemm (210);  $Nb_2O_5$ , Brauer (48, 50);  $Ta_2O_5$ , Ruff, Seiferhild, and Suda (358) and Tiede and Birnbauer (412).

The only vapor-pressure determination recorded is that of  $V_2O_5$  by Polyakov (335). These data indicate a high enough vapor pressure so that it must be due to a stable gaseous molecule such as  $V_2O_5$ . Correcting Polyakov's data to give a reasonable entropy yields  $\Delta H_{298} = 65 \pm 10$  kcal. for the sublimation of  $V_2O_5(s)$ . Although there are no data to confirm this, it is likely that  $Nb_2O_5$  and  $Ta_2O_5$  molecules are of chemical importance. Bands attributed to  $NbO$  are known, and it is believed that  $TaO$  bands may have been observed. Nothing can be said of their stability.  $VO$  ( ${}^2\Delta$ ) is known, but whether this is the true ground state has not been established. Mott (314) has reported a boiling point of 3300°K. for  $V_2O_3$ , but this was determined in a carbon system and may be low. The boiling point calculated on the basis of decomposition to vanadium and oxygen atoms would be much higher. If one took the  $D_0$  of  $VO$  given by Herzberg (200) from a linear Birge-Sponer extrapolation, one would calculate a boiling point not much higher than those observed by Mott (314). This would seem to establish the importance of the  $VO$  molecule, but there are insufficient data to reach any conclusive result. The boiling of  $VO_2$  is undoubtedly due to evolution of oxygen and  $V_2O_5$  gas, leaving  $V_2O_3$  liquid.  $V_2O_5$ ,  $V_6O_{13}$ ,  $VO_2$ , and  $V_3O_5$  should lose oxygen and decompose to  $V_2O_3$ , which will have a constant-boiling composition. The  $VO$  phases also will have a constant-boiling composition if the  $VO$  molecule is important. Heating  $V_2O_3$  in oxygen will produce a large partial pressure of  $V_2O_5$  even when solids of higher oxidation number are unstable.

#### *G. Chromium group oxides*

The melting point of  $Cr_2O_3$  is not well established. Buntings (81) obtained 2548°K. but Wartenberg, Reusch, and Saran (432) claim that this is low, owing to partial production of  $Cr_2O_3$ . They prefer a value of around 2675°K. The value 2600°K.  $\pm 50^\circ$  is taken as an average. The melting point of  $CrO_3$  is based on the determinations of Jaeger and Germs (227) and Vasenin (423). The melting point of  $WO_3$  has been given by Jaeger and Germs (226). The melting point of  $MoO_3$  and the vaporization data of  $MoO_3$  and  $WO_3$  were obtained from Kelley (243) and Ueno (422).

The higher oxides of chromium all lose oxygen without appreciable loss of

chromium to form  $\text{Cr}_2\text{O}_3$ . If  $\text{Cr}_2\text{O}_3$  vaporized by decomposition to the gaseous elements, its atmospheric boiling point would be around  $3750^\circ\text{K}$ .  $\text{Cr}_2\text{O}_3(\text{s})$  is so stable that monatomic oxygen would be as important as molecular oxygen in the equilibrium vapor. There are no reliable vapor-pressure determinations for  $\text{Cr}_2\text{O}_3$ . On the basis of work by Mott (314), a boiling point of  $3300^\circ\text{K}$ . can be assigned. If this is reliable, a stable gaseous molecule would be indicated. The spectrum of  $\text{CrO}$  is known; the lowest observed state is probably a triplet, but it is not known whether this state is the ground state. Gaydon (158) gives  $D_0 = 74$  kcal. for this state; this value is considerably low and thus this state may not be the ground state. Huldt and Lagerqvist (216) have used their flame method to obtain  $D_0$  of  $\text{CrO}$  by observing absorption of atomic chromium as a function of temperature. They obtain  $D_0 = 103.5 \pm 11$  kcal. assuming a  $^3\Sigma$  ground state. However, the transition probabilities calculated by Huldt and Lagerqvist (217) from these data for chromium atoms are too low by a factor of about 90 when compared to the data of Estabrook (131). Therefore their partial pressures should be one-ninetieth as large as those calculated. Thus their  $D_0$  should be larger by 20.5 kcal., resulting in  $D_0 = 124 \pm 11$  kcal. for  $\text{CrO}$ . This value would yield a calculated boiling point for  $\text{Cr}_2\text{O}_3$  vaporizing to  $\text{CrO}$  and  $\text{O}_2$  of around  $3000^\circ\text{K}$ ., in fair agreement with Mott's value. Thus  $\text{CrO}$  seems definitely substantiated as an important gaseous species under neutral or oxidizing conditions. The species  $\text{Cr}_x\text{O}_2$  and  $\text{Cr}_x\text{O}_3$  might be of importance. At very high temperatures and oxidizing conditions even  $\text{CrO}_3$  ( $x = 1$ ) could be of importance, since it is formed endothermally from solid  $\text{Cr}_2\text{O}_3$  with an increase in entropy and might have sufficient stability.

Both  $\text{MoO}_3$  and  $\text{WO}_3$  vaporize essentially undecomposed, and lower oxides disproportionate to the metal and the  $\text{MO}_3$  molecule. Vapor-density measurements by Brewer and Elliott (62) have indicated that the molybdenum oxide species is the monomer  $\text{MoO}_3$ . As the temperature is raised above the temperature at which the solid oxide phases can exist, leaving only the solid metal, the  $\text{MO}_3$  molecule will diminish in stability but can be expected to still be of importance in an oxygen atmosphere well above  $2000^\circ\text{K}$ . At very high temperatures the  $\text{M}_x\text{O}$  and  $\text{M}_x\text{O}_2$  molecules may become important.  $\text{WO}$  bands have been reported but have not been analyzed.

The stability of the  $\text{MoO}_3$  and  $\text{WO}_3$  molecules is fixed by the vapor-pressure measurements of Ueno (422). Earlier work on the vapor pressure of these oxides is in error, owing to the presence of water. In the presence of water, increased volatility is obtained, owing to the molecules  $\text{MoO}_3 \cdot \text{H}_2\text{O}$  and  $\text{WO}_3 \cdot \text{H}_2\text{O}$  (62). The data of Moore (309) on the volatility of tungsten from a mixture of  $\text{WO}_2$  and  $\text{MgO}$  also helps to fix the stability of  $\text{WO}_3$  gas and possible lower oxide species. Lower oxide species are quite unimportant compared to  $\text{MoO}_3$  and  $\text{WO}_3$  under most conditions.

#### H. Manganese group oxides

The melting point of  $\text{MnO}$  has been given by White, Howat, and Hay (448). Wartenberg, Reusch, and Saran (432) have given the melting point of  $\text{Mn}_3\text{O}_4$ .

Boyd, Cobble, Nelson, and Smith (44, 100) reported the melting point of  $Tc_2O_7$ , and Kelley (243) has given the melting and vaporization data for the rhenium oxides. Cobble (99a) reported the vapor-pressure data for  $Tc_2O_7$ .

The higher manganese oxides lose oxygen without appreciable vaporization. Brewer and Mastick (67) have shown that the observed volatility of  $MnO$  agrees with the calculated decomposition pressure, thus showing that no gaseous oxide molecules are important under neutral conditions. This fixes  $D_0$  at less than 106 kcal. Huldt and Lagerqvist (218) have obtained  $D_0 = 92 \pm 9$  kcal. from their flame studies.  $MnO$  is observed spectroscopically but the ground state is not definitely established. Herzberg (200) gives  $D_0 = 101$  kcal. from a linear extrapolation. Gaydon (158) had corrected this to 92 kcal. Thus the lowest observed state of  $MnO$  is undoubtedly the ground state and Gaydon's method of correcting the Birge-Sponer extrapolation is justified.

$Re_2O_7$  and probably  $Tc_2O_7$  vaporize to a stable  $M_2O_7$  molecule and lower oxides disproportionate to the metal and the  $M_2O_7$  molecule. However, this molecule is formed exothermally and rapidly becomes unstable when the metal is the only solid phase. The situation becomes the same as that described for the platinum group metals, and only  $M_xO$  and  $M_xO_2$  gaseous molecules can be important at higher temperatures. As long as the  $MO_2$  phase still exists,  $MO_3$  is also a possibly important molecule but it, like  $M_2O_7$ , becomes unimportant at high temperatures. No information is available on possible  $M_xO$  and  $M_xO_2$  molecules.

### *I. Iron group oxides*

Melting points of the iron oxides have been given by Darken and Gurry (108, 109). The melting points of  $CoO$  and  $NiO$  have been reported by Wartenberg, Reusch, and Saran (432). Brewer and Mastick (67) have reviewed the vaporization data for  $NiO$  and the iron oxides. The observed volatilities have agreed with those calculated on the basis of decomposition to the metal atoms and oxygen molecules; this demonstrates that no oxide molecules are of importance under neutral conditions. The same can be expected for  $CoO$ . Spectral bands are known for  $FeO$ ,  $CoO$ , and  $NiO$ , but the states have not been established and it is not known if the ground states have been observed. If the very uncertain data derived from these spectroscopic observations can be taken at their face value, the diatomic molecules can be expected to be of some chemical importance at moderate temperatures under highly oxidizing conditions. The constant-boiling compositions will be in the  $FeO$ ,  $CoO$ , and  $NiO$  phase regions. Darken and Gurry (109) have determined the constant-boiling composition at 1873°K. for the  $FeO$  phase region to be  $FeO_{1.116}$ . Brewer and Mastick (67) have found the constant-boiling composition for the  $NiO$  phase region to be on the nickel-rich side of  $NiO_{0.995}$ .

### *J. Platinum group oxides*

The melting and vaporization data for  $OsO_4$  have been given by Kelley (243). All of the oxides of the metals of this group decompose to the metal even in an atmosphere of oxygen without any extensive vaporization except for  $OsO_4$ ,

which vaporizes undecomposed, and for  $\text{OsO}_2$ , which disproportionates to osmium metal and  $\text{OsO}_4$  gas.  $\text{RuO}_4$  can also vaporize at room temperature to give an appreciable partial pressure of  $\text{RuO}_4$  gas, but both the solid and the gas are metastable under those conditions.  $\text{RuO}_4$  gas is formed endothermically from  $\text{RuO}_2$  solid and oxygen gas and reaches its maximum equilibrium partial pressure at  $1400^\circ\text{K}$ ., where  $\text{RuO}_2$  solid becomes unstable with respect to the metal and 1 atm. of oxygen. The  $\text{RuO}_4$  partial pressure under these conditions is about  $10^{-6}$  atm. Both  $\text{RuO}_4$  and  $\text{OsO}_4$  gases are formed exothermally from the metal and oxygen gas; at higher temperatures, where the metal is the only solid phase, these molecules rapidly become unstable. Above  $1400^\circ\text{K}$ . no solid oxide phases can exist even in an atmosphere of oxygen, and all the metals except osmium can exist in an atmosphere of oxygen. Osmium can exist in an atmosphere of oxygen at temperatures somewhat above  $1500^\circ\text{K}$ ., where  $\text{OsO}_4$  gas is not so stable. At these higher temperatures, where the metal phase exists in contact with an atmosphere of oxygen, one can show that the only metal oxide species that can be of importance are the  $\text{M}_x\text{O}$  and  $\text{M}_x\text{O}_2$  gaseous molecules. The reason that the molecules can have one or two but no more oxygen atoms per molecule is that all these oxides are formed endothermally or only slightly exothermally from the solid metal and oxygen gas. A molecule formed endothermally can be of chemical importance only if it has a positive entropy of formation. Any molecule with more than two atoms of oxygen per molecule would have a negative entropy of formation. Thus at high temperatures, the platinum metals can react with oxygen to form only  $\text{M}_x\text{O}$  and  $\text{M}_x\text{O}_2$  molecules in appreciable concentration.

Quantitative data are available only for platinum in oxygen. Schneider and Esch (367) have reported the extent of vaporization of platinum in a stream of oxygen as a function of oxygen pressure. They claim to have demonstrated the formation of several gaseous species. However, replotting of their data shows that a single  $\text{Pt}_x\text{O}_2$  species will account for the results quite satisfactorily within their experimental error. Brewer and Elliott (62) have obtained similar data. It is likely that the molecule is  $\text{PtO}_2$ , but no data are available to allow one to fix the number of platinum atoms per molecule. Platinum metal at  $1773^\circ\text{K}$ . in an atmosphere of oxygen is in equilibrium with  $3 \times 10^{-5}$  atm. of  $\text{PtO}_2$  gas. There are no spectroscopic data to serve as a guide as to possible molecules. A band spectrum is known which has been attributed to  $\text{PtO}$  but there is no definite identification of the spectrum. There are some rough data on the volatilities of the platinum metals in oxygen from which one can obtain possible heats of formation by assigning the vaporizing species to either  $\text{M}_x\text{O}$  or  $\text{M}_x\text{O}_2$ . One would judge that  $\text{M}_x\text{O}_2$  would be the reasonable choice up to about  $2000^\circ\text{K}$ . Iridium vaporizes about one hundred times more rapidly in air than platinum and ruthenium vaporizes about two hundred times more rapidly at  $1500^\circ\text{K}$ . (450). The molecules are undoubtedly  $\text{IrO}_2$  and  $\text{RuO}_2$ . For  $\text{MO}_2(\text{s}) = \text{MO}_2(\text{g})$ ,  $\Delta H_{298} = 87 \pm 5$ ,  $85 \pm 7$ , and  $93 \pm 8$  kcal. for platinum, iridium, and ruthenium, respectively. Holborn and Austin (206) reported that at  $1943^\circ\text{K}$ . the volatility of iridium in air increases less rapidly than the first power of the oxygen pressure,

a result which indicates an important contribution at this temperature by an  $\text{Ir}_x\text{O}$  species. Under conditions of low pressures or very high temperatures, where oxygen is present as monatomic oxygen,  $\text{M}_2\text{O}$  is the only choice, as it is the only molecule that could have a positive entropy of formation from atomic oxygen. Thus at a fixed pressure, increasing the temperature will increase the attack of a platinum metal by oxygen with formation of a  $\text{M}_2\text{O}_2$  molecule with the maximum attack due to this molecule at the temperature where  $\text{O}_2$  and  $\text{O}$  are equally important. Above this temperature attack will decrease if the  $\text{M}_2\text{O}_2$  molecule is the main species. However, attack due to an  $\text{M}_2\text{O}$  molecule will still increase with increasing temperature, and at high enough temperatures, one could be sure that there will be extensive attack. Since  $\text{PdO}_2$  is unimportant for palladium, the  $\text{PdO}$  molecule is probably solely responsible for attack of palladium. Thus it is only at intermediate temperatures that the platinum metals are relatively inert under equilibrium conditions toward oxygen gas. Assuming that the  $\text{M}_2\text{O}_2$  species is  $\text{MO}_2$ , one can summarize the data for the reaction  $\text{M}(\text{s}) + \text{O}_2(\text{g}) = \text{MO}_2(\text{g})$  by the values of  $\Delta H_{298} = 40, 63, 64, 28, 41,$  and  $55$  kcal. for ruthenium, rhodium, palladium, osmium, iridium, and platinum, respectively. The values for osmium, rhodium, and palladium were estimated assuming heats of sublimation for  $\text{MO}_2$  similar to those reported above for the other platinum metals. All these values except the one for platinum are uncertain by at least 10 kcal.  $\Delta S$  for this reaction can be expected to be between +5 and +9 entropy units. At  $3500^\circ\text{K}$ ., where the  $\text{MO}_2$  partial pressure in an atmosphere of oxygen reaches its maximum because of conversion of  $\text{O}_2$  to  $\text{O}$  at higher temperatures, the pressures will be approximately  $10^{-1}, 10^{-2.5}, 10^{-2.5}, 0.5, 10^{-1},$  and  $10^{-2}$  atm. for ruthenium, rhodium, palladium, osmium, iridium, and platinum, respectively. Since the heats of formation of these  $\text{MO}_2$  molecules are less endothermic than the heats of sublimation of the metals, the vapor pressure of the metal will rise more rapidly than the  $\text{MO}_2$  partial pressure and at  $3500^\circ\text{K}$ . only  $\text{RuO}_2, \text{OsO}_2,$  and  $\text{IrO}_2$  have larger pressures than the metal atoms.  $\text{PdO}_2$  is so unstable and palladium metal so volatile that the palladium pressure will be higher than the  $\text{PdO}_2$  pressure in any measurable range. The only oxide phase among the platinum metal oxides that has essentially a constant-boiling composition is the  $\text{OsO}_4$  phase region. To calculate the  $D_0$  values given in table 2, the heats of sublimation of the platinum metals were obtained from Brewer (54).

#### *K. Copper group oxides*

Randall, Nielson, and West (340) have given the melting points of the copper oxides. Wartenberg, Reusch, and Saran (432) have redetermined the melting point of  $\text{Cu}_2\text{O}$ . Mack, Osterhof, and Kraner (282) have determined the vapor pressure of  $\text{CuO}$  by a rather uncertain method, but their vapor pressures are higher by a factor of  $10^6$ – $10^8$  than the pressure expected on the basis of decomposition to the gaseous elements. Thus a stable gaseous oxide molecule is clearly indicated. Spectroscopic data are not of use in identifying the molecule. Spectral bands of  $\text{CuO}$  are known. The lowest state is probably  ${}^2\Sigma^+$  but it has not definitely been established as the ground state.  $\text{AgO}$  is known as a  ${}^2\Sigma$  state.

If the spectroscopic  $D_0$  value obtained for CuO can be used, one can obtain a reasonable agreement with the vapor-pressure data for CuO. It seems rather unlikely that any  $M_2O$  molecules would be of importance. In view of the molecule  $Cu_3Cl_3$ , reported by Brewer and Lofgren (63), a polymerized cupric oxide molecule is a definite possibility. The silver and gold oxides decompose directly to solid metal and oxygen upon heating. There will be some vaporization of silver metal as AgO in oxygen at high temperatures. AgO will reach a maximum concentration at the boiling point of silver metal, but it can never be expected to be very large. The only constant-boiling compositions will be in the copper system. It is possible that both the  $Cu_2O$  and CuO phase regions have constant-boiling compositions.

#### *L. Zinc group oxides*

The melting point of ZnO has been determined by Bunting (80). All oxides of this group vaporize by decomposition to the gaseous elements. No gaseous oxide molecules are believed to be of any chemical importance. This was demonstrated by Brewer and Mastick (67) for ZnO and CdO by showing that the experimental vapor pressures agreed with the decomposition pressures calculated from the thermodynamic data. Spectroscopic observations have never indicated any ZnO bands. Bands have been attributed to CdO and HgO, but they are of uncertain assignment. The ZnO, CdO, and HgO phase regions each have a constant-boiling composition for which the ratio of oxygen to metal in the vapor phase is the same as the ratio of oxygen to metal in the condensed phase. The boiling points given in table 1 are those temperatures where the sum of the  $M(g)$  and  $O_2(g)$  partial pressures in equilibrium with the condensed oxide phase is equal to 1 atm. It was assumed that the constant-boiling compositions were reasonably close to the stoichiometric composition, even though they are surely on the metal-rich side.

#### *M. Gallium group oxides*

Hill, Roy, and Osborn (203) reported the melting point of  $Ga_2O_3$ , and Duncan (120) has given the melting point of  $Tl_2O_3$ . No vaporization data are available except the qualitative observation that  $Ga_2O$  is quite volatile at 1300°K. It is very unlikely that any species other than  $M_2O$  or MO molecules are of importance. GaO has been observed spectroscopically with a  $^2\Sigma$  state as the lowest state, but it is uncertain whether this state is the ground state. InO has been observed spectroscopically. The lowest state is probably  $^2\Sigma$ , but it is not known whether the ground state has been observed.

$Tl_2O_3$  loses oxygen to form  $Tl_2O$  without appreciable vaporization.  $Ga_2O_3$  probably decomposes predominantly to GaO gas under oxidizing or neutral conditions, and to  $Ga_2O$  gas under highly reducing conditions. In this respect its behavior is analogous to that of  $Al_2O_3$ .  $In_2O_3$  and  $Tl_2O$  probably vaporize predominantly by decomposition to the gaseous elements, although some rough data indicate  $In_2O$  and  $Tl_2O$  as possible important species. Thus Thiel and Luckman (410) report the sublimation of  $In_2O$  from a mixture of In and  $In_2O_3$  at

950°K. at reduced pressures, and Halla, Tompa, and Zimmerman (188) report appreciable volatility of  $Tl_2O$  at 573°K. The constant-boiling compositions of this group will be found in the  $Tl_2O$ ,  $In_2O_3$ , and  $Ga_2O_3$  phase regions.

#### *N. Carbon-silicon group oxides*

The melting points given in table 1 were obtained as follows:  $SiO$ , Edwards (121);  $SiO_2$ , Mosesman and Pitzer (313);  $GeO_2$ , Laubengayer and Morton (272);  $SnO_2$ , Wartenberg and Gurr (430);  $PbO$ , Kelley (244).

All elements of this group have  $MO$  gaseous oxides, in a  ${}^1\Sigma^+$  state, which are of chemical importance. Excellent agreement has been obtained between spectroscopic and chemical determinations of the heat of formation of the oxides. The oxides of this group are unique in that the linear Birge-Sponer extrapolation (33) to the ground-state atoms yields a  $D_0$  value very close to the true value. For most other diatomic molecules, Gaydon (158) has shown that the linear extrapolation yields too high a  $D_0$  value. Except for  $CO_2$ , which is of chemical importance only at low temperatures, there is no evidence for  $MO_2$  gaseous molecules in this group. The volatilities of the  $MO_2$  solids are consistent with the reaction  $MO_2(s) = MO(g) + \frac{1}{2}O_2(g)$ . All of the  $MO$  solids vaporize predominantly by the reaction  $MO(s) = MO(g)$  with only a very small partial pressure of oxygen. When the  $MO$  solid is not stable, as for  $SnO$ ,  $GeO$ , and  $SiO$ , except perhaps for limited temperature ranges, the reaction  $M(s) + MO_2(s) = 2MO(g)$  produces the maximum partial pressure of  $MO$  gas, and this reaction has been used to obtain the  $D_0$  values of  $SiO$ ,  $GeO$ , and  $SnO$ . Brewer and Mastick (67) have reviewed the data available for these compounds. Since then, Bues and Wartenberg (78) and Jolly and Latimer (230) have obtained new data on  $GeO$ , and Edwards (121) has made a more recent survey of the data available for  $SiO$ . Drummond and Barrow (117) have recently recalculated the  $SnO$  data determined by Vesselovskii (424) and have claimed that the linear Birge-Sponer extrapolation does not go to the ground-state atoms. Their results differ from the conclusions of Brewer and Mastick (67), owing to the use of a different heat of sublimation of tin in the thermochemical calculations. However, Brewer and Porter (68) have since then determined the heat of sublimation of tin and have confirmed the value used by Brewer and Mastick. Thus the validity of the linear extrapolation of vibration levels to convergence has been confirmed for all the oxides of group IV elements. It is of interest to note that, as discussed in the titanium group section, the linear extrapolation has been shown to hold for  $TiO$  also. The  $D_0$  value given for  $PbO$  is based on the vapor-pressure determination by Feiser (138).

In summary, the vapor composition over the oxides of this group may be summarized as follows: Both  $CO(s)$  and  $CO_2(s)$  vaporize to  $CO$  and  $CO_2$  molecules, respectively, although  $CO$  is thermodynamically unstable at low temperatures but its rate of disproportionation is very small. At high temperatures,  $CO$  is the only important molecule.  $SiO$  or  $Si + SiO_2$  solids, depending upon the temperature range, vaporize almost exclusively to  $SiO$  gas.  $SiO_2(s)$  vaporizes to  $SiO(g)$  and  $O_2(g)$ . Both the  $SiO$  and  $SiO_2$  phase regions have constant-boiling

compositions which probably lie reasonably close to the stoichiometric compositions. The germanium-oxygen and tin-oxygen systems show the same behavior as the silicon-oxygen system, except that it has not been established yet whether  $\text{GeO}(s)$  has any temperature range of stability. The higher lead oxides will all lose oxygen without any appreciable vaporization of  $\text{PbO}$ . Thus only the  $\text{PbO}$  phase has a constant-boiling composition. The  $\text{SnO}$  vaporization temperatures given in table 1 are for a mixture of  $\text{Sn}$  and  $\text{SnO}_2$ .

#### *O. Nitrogen-phosphorus group oxides*

None of the nitrogen oxide gaseous molecules are thermodynamically stable, even though the  $D_0$  values are large. This is due to the extraordinary stability of the nitrogen molecule, which makes all nitrogen compounds relatively unstable. The molecules  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ , and  $\text{N}_2\text{O}_5$  have been discussed by Yost and Russell (459), who have given the thermodynamic properties. Koerner and Daniels (262) have recently determined  $\Delta H$  of  $\text{NO}_2$ . Daniels and Bright (107) have given the vapor pressure of  $\text{N}_2\text{O}_5$ . Since all of these compounds are formed endothermically from the elements, their equilibrium concentration in a mixture of nitrogen and oxygen will increase with temperature, but only  $\text{NO}$  can reach any appreciable equilibrium concentration. At a total pressure of 1 atm. the maximum concentration of  $\text{NO}$  will be 0.1 atm. at about  $3700^\circ\text{K}$ ., where monatomic oxygen becomes important. At higher temperatures,  $\text{NO}$  will decrease in importance, since it is formed exothermically from monatomic oxygen.

The condensed phases  $\text{P}_2\text{O}_3$ ,  $\text{PO}_2$ , and  $\text{P}_2\text{O}_5$  vaporize to form, respectively,  $\text{P}_4\text{O}_6$ ,  $\text{P}_8\text{O}_{16}$ , and  $\text{P}_4\text{O}_{10}$ . Yost and Russell (459) have discussed these molecules and have pointed out that the formula  $\text{P}_8\text{O}_{16}$  is in some doubt and may be  $\text{P}_4\text{O}_8$ , according to the data of Emmett and Shultz (128). Hill, Faust, and Hendricks (186) have given the melting points and vapor-pressure data for the various forms of  $\text{P}_2\text{O}_5$ . Kelley (243) and Yost and Russell (459) have reported fusion and vaporization data for the other oxides of phosphorus.

As  $\text{P}_2\text{O}_3$  appears to be thermodynamically unstable with respect to red phosphorus and  $\text{PO}_2$ , it does not have a stable constant-boiling composition, but the  $\text{PO}_2$  and  $\text{P}_2\text{O}_5$  phase regions will have constant-boiling compositions. At high temperatures the complex molecules must break down to simpler molecules. It is not known whether  $\text{P}_2\text{O}_3$ ,  $\text{PO}_2$ , and  $\text{P}_2\text{O}_5$  molecules are important intermediates or whether the complex molecules break down directly to  $\text{PO}$  gas. In view of the compact nature of  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$  and the high stability of  $\text{PO}$  gas, one might guess that the decomposition would proceed from  $\text{P}_4\text{O}_{10}$  through  $\text{P}_4\text{O}_8$  to  $\text{P}_4\text{O}_6$  by loss of oxygen molecules and then would proceed directly from  $\text{P}_4\text{O}_6$  to  $\text{PO}$  upon breakdown of the phosphorus framework. However, the complex molecules are extremely stable and temperatures as high as  $3000^\circ\text{K}$ . would be required to convert  $\text{P}_4\text{O}_{10}$  to  $\text{P}_4\text{O}_6$  at atmospheric pressure. Under those conditions,  $\text{PO}$  would probably also be quite important and  $\text{P}_4\text{O}_{10}$  would probably go all the way to  $\text{PO}$  and  $\text{O}_2$  when it started decomposing. The  $D_0$  values given for the phosphorus compounds are very uncertain, because the  $D_0$  of  $\text{P}_2$  is not definitely known and one cannot convert heats of formation from solid phosphorus to

heats of formation from gaseous monatomic phosphorus without introducing a large uncertainty. The spectroscopic determination of the  $D_0$  of PO, which has a  ${}^2\pi$  ground state, is also highly uncertain.

Little is known about the gaseous species of the arsenic, antimony, and bismuth systems. The molecules of the  $M_4O_{10}$  type undoubtedly become less important. Vapor-density measurements (270) have established the stability of  $Sb_4O_6$  at  $1833^\circ K.$  and of  $As_4O_6$  up to  $1100^\circ K.$ , above which it starts decomposing to simpler molecules. Judging from the spectroscopic data,  $AsO$  ( ${}^2\pi$ ) will be of more importance than  $SbO$  ( ${}^2\pi$ ), but both will be of chemical importance at very high temperature. Schulman and Schumb (369) have given the melting points and vapor-pressure data for the  $As_2O_3$  forms. Kelley (243, 244) reported the melting point and vapor pressures of  $Sb_2O_3$  (243) and the melting point of  $Bi_2O_3$ .

#### *P. Sulfur group oxides*

Yost and Russell (459) have given the melting points and vapor-pressure data for  $SO_3$ ,  $SeO_2$ , and  $TeO_2$ . Lehmann and Kruger (274) reported the melting point of  $SeO_3$ . Amelin and Beljakov (8) have recently determined new vapor-pressure data for  $SeO_2$ . Kelley (243) has presented earlier sublimation data for  $SeO_2$ .  $SO_3$  is a fairly stable molecule, which is half-decomposed to  $SO_2$  in an atmosphere of oxygen at  $1058^\circ K.$  Vapor-density measurements (270) show that  $SO_2$  is undecomposed at  $2223^\circ K.$  and that  $SeO_2$  is undecomposed at  $773^\circ K.$  Evans (132) has demonstrated the partial decomposition of  $SeO_2$  gas at  $823^\circ K.$  by the appearance of  $Se_2$  bands which can be suppressed even at  $1300^\circ K.$  by as much as 1 mm. of oxygen. The extent of decomposition is thus very small. At very high temperatures  $SO$ ,  $SeO$ , and  $TeO$  are probably of chemical importance. All have been observed spectroscopically. The lowest known  $SO$  state is a  ${}^3\Sigma^-$  state, but it is not known if it is the ground state.  $SO$  may be condensed but is then believed to be  $S_2O_2$ , an unstable molecule. The lowest states of the  $SeO$  and  $TeO$  band systems have not been characterized and it is not known if the ground state has been observed. This, together with the uncertainties in the  $D_0$  values of  $S_2$ ,  $Se_2$ , and  $Te_2$ , makes it difficult to predict the importance of these species. The constant-boiling compositions will be found in the  $TeO_2$ ,  $SeO_2$ ,  $SO_3$ , and, at very low temperatures, in the  $SO_2$  phase regions. Nothing is known about the gaseous oxides of polonium. They will probably behave like the tellurium oxides.

#### *Q. Halogen group oxides*

All of the halogen oxides are thermodynamically stable. The  $D_0$  values were calculated from the thermodynamic data given by Brewer, Bromley, Gilles, and Lofgren (56).

#### *R. Hydrogen oxides*

Yost and Russell (459) have reported melting points and vapor-pressure data for  $H_2O$  and  $H_2O_2$ .  $H_2O_2$  may be vaporized to a  $H_2O_2$  molecule which is, however, thermodynamically unstable.  $H_2O$  is the only important species up to very high temperatures, where  $OH$  becomes important under oxidizing conditions.

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