THE THERMODYNAMIC PROPERTIES OF THE OXIDES AND THEIR VAPORIZATION PROCESSES

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CONTENTS

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 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: ΔF, ΔH, and ΔS of formation at 298°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°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 NO_2, N_2O, 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 $Ti_{10^{22}}O_{10^{22}}$. Removal of one atom would result in $Ti_{10^{22}}O_{10^{22}-1}$ 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 $TiO_{0.7}$ to $TiO_{1.25}$. 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 $TiO_{0.7}$ to $TiO_{1.25}$ 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 "$TiO_{0.7\text{-}1.25}$ (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 "$Fe_{1-x}O$ (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 $TiO_{0.7\text{-}1.25}$ 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: "$TiO_{0.7\text{-}1.25}$ (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 ΔH_0 for the reaction $MN(g) = M(g) + N(g)$. For polyatomic molecules, D_0 is the corresponding ΔH_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 crystalline modifications. Below 196°K. one obtains NaO_2 (FeS_2 marcasite type). Between 196° and 223°K. one obtains the FeS_2 pyrites crystal structure and above 223°K. one obtains NaO_2 (NaCl type). Although KO_2 has been known much longer, it has not been studied as thoroughly. Above 403°K. it has a cubic NaCl structure (92, 93). Below 403°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	ΔF_{298}	ΔH_{298}	ΔS_{298}	T_M	VAPORIZATION TEMPERATURES	
					$T_{10^{-3}\text{atm.}}$	$T_{1\text{ atm.}}$
	kcal.	*kcal.*	*e.u.*	°*K.*	°*K.*	°*K.*
Li_2O	−134.0	−142.6 ± 2	−28.85	2000	1830 ± 50	2600 ± 100
½Li_2O_2	−68.	−76. ± 2	(−26)	d. 470, 1 atm. O_2		
Na_2O	−90.	−99.4 ± 1	−31.9	1193	d. 1330 ± 20	d. 2040 ± 60
½Na_2O_2	−53.	−61.1 ± 0.5	−25.4	948	d. 919, 1 atm. O_2	
½NaO_2	−25.9	−31.0 ± 1	−16.8	Metastable at room temperature		
K_2O	−77.	−86.4 ± 2	(−32)	(>763)	d. 1150 ± 50	d. 1750 ± 100
½KO_2	−28.7	−33.8 ± 0.5	−18.2	653	d. 760, 628 mm. O_2	
Rb_2O	−69.	−78.9 ± 3	(−32)	(>840)	d. 1100 ± 70	d. 1600 ± 100
⅓Rb_2O_3	−36.	−42. ± 3	(−20)	762	d. 1043, 163 mm. O_2	
½RbO_2	−29.	−34. ± 3	(−18)	685	d. 1033, 225 mm. O_2	
Cs_7O	<−66.			276		
Cs_4O	<−66.			d. 283 to Cs_7O_2 + liquid		
Cs_3O	<−66.			d. 443 to Cs_2O + liquid		
½Cs_7O_2	<−66.			d. 323 to Cs_3O + liquid		
Cs_2O	−66.	−75.9 ± 3	(−32)	763	d. 1000 ± 70	d. 1500 ± 100
⅓Cs_2O_3	−40.	−45. ± 5	(−20)	775	d. 1125, 108 mm. O_2	
½CsO_2	−33.	−38. ± 3	(−18)	705	d. 1153, 225 mm. O_2	
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_2	−68.	−74.4 ± 0.5	(−20)	d. 361, 1 atm. O_2 to $MgO_2\cdot 3MgO$		
CaO	−144.3	−151.7 ± 0.5	−25.0	2860 ± 25	2650 ± 50	3800 ± 200

$\frac{1}{2}\mathrm{CaO_2}$	−72.	−78.2 ± 0.5	(−20)	d. 548, 1 atm. O_2		
SrO	−133.6	−140.8 ± 1	−24.0	2730 ± 20	2400 ± 100	3500 ± 200
$\frac{1}{2}\mathrm{SrO_2}$	−70.6	−76.6 ± 2	(−20)	d. 488, 1 atm. O_2		
BaO	−126.	−133. ± 2	−23.7	2196 ± 10	2120 ± 100	3000 ± 200
$\frac{1}{2}\mathrm{BaO_2}$	−70.	−76.2 ± 3	(−20)	d. 1110, 1 atm. O_2		
RaO	−123.	(−130.) ± 4	(−24)			
$\frac{1}{3}\mathrm{B_2O_3}$ (cryst.)	−96.	−101.8 ± 1	−21.3	723	1740	2520
$\frac{1}{3}\mathrm{Al_2O_3}$	−126.0	−133.4 ± 0.1	−24.8	2300 ± 20	d. 2740 ± 60	d. 3800 ± 200
$\frac{1}{3}\mathrm{Sc_2O_3}$	−130.	(−137.) ± 3	(−24)			
$\frac{1}{3}\mathrm{Y_2O_3}$	−134.	(−140.) ± 3	(−23)	2690 ± 100		4570 ± 300
$\frac{1}{3}\mathrm{La_2O_3}$	−138.5	−145. ± 1	(−22)	2590 ± 20		4470 ± 300
$\frac{1}{3}\mathrm{Ce_2O_3}$	−138.5	(−145.) ± 1	(−22)			
$\frac{1}{2}\mathrm{CeO_2}$	−116.	−122.5 ± 2	(−22)	3000 ± 20 under O_2 pressure		
$\frac{1}{3}\mathrm{Pr_2O_3}$	−138.	−144.6 ± 1	(−22)			
$\frac{1}{11}\mathrm{Pr_6O_{11}}$	−117.5	−124.0 ± 0.5	(−22)	d. 1340, 1 atm. O_2 to Pr_2O_{3+x}		
$\frac{1}{2}\mathrm{PrO_2}$	−108.5	−115. ± 1	(−22)	d. 700, 1 atm. O_2		
$\frac{1}{3}\mathrm{Nd_2O_3}$	−135.	−142. ± 1	(−22)			
$\frac{1}{3}\mathrm{Ac_2O_3}$	−142.	(−148.) ± 3	(−21)			
ThO	−139.	(−145.) ± 10	(−21)			
$\frac{1}{2}\mathrm{ThO_2}$	−140.	−146.6 ± 0.5	(−21)	3225 ± 200		4670 ± 300
$\frac{1}{5}\mathrm{Pa_2O_5}$	−100.	(−106.) ± 5	(−21)			
UO	−123.	(−129.) ± 5	(−21)			
$\frac{1}{2}\mathrm{UO_2}$	−123.3	−129.6 ± 0.4	−21.2	3000 ± 200		
$\frac{1}{2.25}\mathrm{UO_{2.25}}$	−114.	−120. ± 1	(−21)			
$\frac{1}{2.62}\mathrm{UO_{2.62}}$	−103.	−109. ± 1	(−21)	d. 1950, 1 atm. O_2 to $UO_{2.25}$		
$\frac{1}{8}\mathrm{U_3O_8}$	−100.5	−106.7 ± 4	−20.8			
$\frac{1}{3}\mathrm{UO_3}$(hex.)	−91.	−97.3 ± 2	−20.7	d. 925, 1 atm. O_2 to U_3O_8		

TABLE 1—*Continued*

OXIDE	ΔF_{298}	ΔH_{298}	ΔS_{298}	T_M	VAPORIZATION TEMPERATURES	
					$T_{10^{-3}\text{atm.}}$	$T_{1\text{ atm.}}$
	kcal.	*kcal.*	*e.u.*	°*K.*	°*K.*	°*K.*
$\frac{1}{2}NpO_2$	−117.	(−123.) ± 5	−21			
$\frac{1}{5}Np_2O_5$	−96.	(−102.) ± 5	(−21)	d. 800–900		
PuO	<−117.	<−123.	(−21)			
$\frac{1}{2}PuO_2$	−117.	(−123.) ± 5	−21	>2200		
$\frac{1}{3}Am_2O_3$	−134.	(−140.) ± 5	(−21)			
$\frac{1}{2}AmO_2$	−114.	−120. ± 3	(−21)	d. 1680, 13 mm. O_2 to $AmO_{1.85}$		
$Ti_{1.43}O$	−118.	−125. ± 2	(−23)	Disproportionates 1198 to Ti + TiO		
TiO	−117.1	−123.9 ± 0.3	−22.8	d. 2010	2275 ± 50	2970 ± 100
$\frac{1}{3}Ti_2O_3$	−114.2	−121.0 ± 0.1	−22.6	2400		3300 ± 300
$\frac{1}{5}Ti_3O_5$	−110.6	−117.4 ± 0.1	−22.7			
$\frac{1}{2}TiO_2$	−106.2	−112.8 ± 0.1	−22.1	2128 ± 20		d. 3200 ± 300
$\frac{1}{2}ZrO_2$	−124.0	−130.9 ± 0.1	−23.1	2960 ± 25		4570 ± 300
$\frac{1}{2}HfO_2$	−126.1	−133.0 ± 0.1	−23.1	3063 ± 25		
VO	−91.	−98. ± 5	−22.2			3400 ± 500
$\frac{1}{3}V_2O_3$	−92.	−98.7 ± 2	−21.3	2240		d. 3300 ± 300
$\frac{1}{5}V_3O_5$		<−93.5				
$\frac{1}{2}VO_2$	−79.	−85.5 ± 1	−21.9	1818 ± 30		d. 3000 ± 300
$\frac{1}{13}V_6O_{13}$	−75.	−81.5 ± 1	−21.2	935 ± 10		
$\frac{1}{5}V_2O_5$	−68.	−74.5 ± 1	−21.1	943 ± 2	(1225) In presence of high O_2	(2100)
NbO	−90.5	−97. ± 2	(−22)			
$\frac{1}{2}NbO_2$	−88.	−94.5 ± 0.5	(−22)			
$\frac{1}{5}Nb_2O_5$	−84.4	−91.0 ± 0.1	(−22)	1733 ± 5		
$\frac{1}{5}Ta_2O_5$	−91.3	−97.8 ± 0.1	−21.7	2150 ± 100	>2000	
$\frac{1}{3}Cr_2O_3$	−83.5	−90.0 ± 0.3	−21.8	2710 ± 10		d. 3300 ± 300

$\frac{1}{2}CrO_2$	−64.5	−70.5 ± 2	(−20)	d. 700, 1 atm. O_2		
$\frac{1}{3}CrO_3$	−40.0	−45.9 ± 1	(−20)	460	Metastable	
$\frac{1}{2}MoO_2$	−60.	−65.5 ± 1	−18.3	d. 2250 ± 50 to Mo(s) + 1 atm. MoO_3(g)		
$\frac{1}{11}Mo_4O_{11}$	−56.	(−61.) ± 2	(−20)	Disproportionates		
$\frac{1}{23}Mo_8O_{23}$	−54.5	(−60.5) ± 2	(−20)	Disproportionates		
$\frac{1}{26}Mo_9O_{26}$	−54.5	(−60.5) ± 2	(−20)	Disproportionates		
$\frac{1}{3}MoO_3$	−54.0	−60.1 ± 0.5	−20.5	1068	1055 ± 10	1530 ± 50
$\frac{1}{2}WO_2$	−61.	−67. ± 1	(−20.5)	d. 2125 ± 50 to W(s) + 1 atm. WO_3(g)		
$\frac{1}{49}W_{18}O_{49}$	−60.6	−66.7 ± 1	(−20.5)	Disproportionates		
$\frac{1}{29}W_{10}O_{29}$	−60.6	(−66.7) ± 1	(−20.5)	Disproportionates		
$\frac{1}{3}WO_3$	−60.6	−66.7 ± 0.1	−20.5	1746 ± 1	1560 ± 20	2100 ± 100
MnO	−86.7	−92.0 ± 0.1	−17.8	2058	d. 2300 ± 50	d. 3400 ± 100
$\frac{1}{4}Mn_3O_4$	−76.4	−82.8 ± 0.1	−21.3	1863 ± 20		
$\frac{1}{3}Mn_2O_3$	−69.8	−76.4 ± 0.3	−22.0	d. 1620, 1 atm. O_2		
$\frac{1}{2}MnO_2$	−55.6	−62.1 ± 0.1	−22.0	d. 1120, 1 atm. O_2		
$\frac{1}{2}TcO_2$	−45.6	−51.7 ± 1	(−20.5)			
$\frac{1}{3}TcO_3$	−36.6	−43. ± 2	(−21.5)	Disproportionates to TcO_2 and Tc_2O_7 (g)		
$\frac{1}{7}Tc_2O_7$	−31.8	−38.0 ± 0.4	(−21)	392.7 ± 0.1	390	583
$\frac{1}{2}ReO_2$	−45.1	−51.7 ± 7	(−22)			
$\frac{1}{3}ReO_3$	−43.	−49 ± 1	(−21)	433	Disproportionates to ReO_2 and Re_2O_7(g)	
$\frac{1}{7}Re_2O_7$	−36.3	−42.4 ± 0.3	(−20.5)	569	483.5	635.5
$Fe_{0.95}O$	−58.3	−63.2 ± 0.5	−16.5	d. 1644 ± 1	d. 2300 ± 50	d. 3400 ± 100
$\frac{1}{4}Fe_3O_4$	−61.0	−67.0 ± 0.2	−20.1	1870 ± 2	d. 1840 ± 10	d. 2060 ± 30
$\frac{1}{3}Fe_2O_3$	−59.3	−65.7 ± 0.2	−21.7	d. 1730 ± 5, 1 atm. O_2 to Fe_3O_{4+x}		
CoO	−51.	−57. ± 0.5	(−19)	2078 ± 20		d.
$\frac{1}{4}Co_3O_4$	−45.	−51. ± 1	(−20)	d. 1240, 1 atm. O_2		
NiO	−51.3	−58.0 ± 0.5	−22.4	2230 ± 20		d.
$\frac{1}{2}RuO_2$	−20.4	−26.3 ± 2	(−19.8)	>1228	d. 1400 ± 30, 1 atm. O_2	

TABLE 1—*Concluded*

OXIDE	ΔF_{298}	ΔH_{298}	ΔS_{298}	T_M	VAPORIZATION TEMPERATURES	
					$T_{10^{-3}\text{atm.}}$	$T_{1\text{ atm.}}$
	kcal.	*kcal.*	*e.u.*	°K.	°K.	°K.
$\frac{1}{4}RuO_4$	(−8.)	(−13.) ± 2	(−18)	300 (brown) metastable to $RuO_2 + O_2$		
Rh_2O	−20.	−24.0 ± 3	(−12.3)	d. 1400, 1 atm. O_2		
RhO	−18.	−23.9 ± 3	(−19)	d. 1394, 1 atm. O_2		
$\frac{1}{3}Rh_2O_3$	−17.5	−23.7 ± 3	(−20.7)	d. 1388, 1 atm. O_2		
PdO	−15.	−21. ± 2	(−20.3)	d. 1150, 1 atm. O_2		
$\frac{1}{2}OsO_2$	(−25.)	(−31.) ± 5	(−20)	Disproportionates 923, 1 atm. OsO_4(g)		
$\frac{1}{4}OsO_4$(yellow)	−17.7	−23.4 ± 3	−19.1	329	273	403
$\frac{1}{2}IrO_2$	−16.	−22. ± 3	(−20.2)	>1373	d. 1373, 1 atm. O_2	
PtO	(−11.) ± 4	(−17.) ± 5	(−20)	d. 780 ± 30, 1 atm. O_2		
$\frac{1}{4}Pt_3O_4$		(−16.) ± 6				
$\frac{1}{2}PtO_2$	(−10.) ± 10	(−16.) ± 5	(−20)	d. 750, 1 atm. O_2		
Cu_2O	−35.0	−39.8 ± 0.5	−16.3	1503		
CuO	−30.4	−37.1 ± 0.5	−22.1	1609 under oxygen pressure		
Ag_2O	−2.59	−7.31 ± 0.1	−15.8	d. 460, 1 atm. O_2		
$\frac{1}{3}Au_2O_3$			(−22.1)	Metastable		
ZnO	−76.1	−83.2 ± 0.1	−23.9	2248	d. 1600 ± 10	d. 2250 ± 25
CdO	−55.1	−62.2 ± 0.5	−23.7	>1500	d. 1240 ± 10	d. 1750 ± 20
HgO	−13.99	−21.68 ± 0.1	−26.4		d. 510 ± 10	d. 750 ± 15
Ga_2O	−75.	−82. ± 2	(−22.9)			
$\frac{1}{3}Ga_2O_3$	−79.	−86. ± 1	(−23.3)	1998		
$\frac{1}{3}In_2O_3$	−66.	−73. ± 1	(−24.0)			
Tl_2O	−33.1	−42.5 ± 1	(−31.5)			
$\frac{1}{3}Tl_2O_3$	−21.	−28. ± 2	(−24.0)	990 ± 5		
SiO	−98.	−104.6 ± 3	(−23)	>2000	1510 ± 20	
$\frac{1}{2}SiO_2$(quartz)	−98.5	−105.1 ± 0.1	−21.8	1973	d. 2250 ± 50	

GeO	−54.	−61. ± 3	(−22.5)	Metastable		
$\frac{1}{2}GeO_2$	−57.3	−64.3 ± 0.3	(−23.5)	1389 ± 4		
SnO	−62.1	−69.1 ± 0.1	−23.3	d. 660	(1300)	(1800)
$\frac{1}{2}SnO_2$	−62.1	−69.4 ± 0.05	−24.4	>2200		
PbO	−45.25	−52.4 ± 0.2	−23.4	1163	1201	1745
$\frac{1}{4}Pb_3O_4$	−36.9	−43.9 ± 1	−23.5	d.		
PbO_2	−26.2	−33.1 ± 0.5	−23.5	d.		
$\frac{1}{5}N_2O_5$	+5.0	−2.6	−26.3	>306	235	305.5
$\frac{1}{6}P_4O_6$	−83.	−90. ± 2	(−23)	297	285	449
$\frac{1}{16}P_8O_{16}$	−81.	−88. ± 2	(−23)			1700
$\frac{1}{10}P_4O_{10}$(hex.)	−67.	−73. ± 1	(−21)	695 ± 6	457	631
$\frac{1}{10}P_4O_{10}$(ortho)	−67.5	−74. ± 1	(−22)	853 ± 5	650	878
$\frac{1}{6}As_4O_6$	−46.	−52. ± 0.5	−21.6	588	493	732
$\frac{1}{5}As_2O_5$	−36.9	−43.7 ± 1	−22.8	d. > 1100		
$\frac{1}{6}Sb_4O_6$	−49.8	−55.7 ± 1	−21.7	928	841	1698
$\frac{1}{2}SbO_2$	−42.	−48. ± 3	−19.8	d. 1203, 19 mm. O_2		
$\frac{1}{13}Sb_6O_{13}$	−39.	−46. ± 3	(−22)	d. 1003, 232 mm. O_2		
$\frac{1}{5}Sb_2O_5$	−36.	−43. ± 3	(−22.7)	d. 673, 224 mm. O_2		
BiO	−43.5	−50. ± 1	(−21.1)			
Bi_2O_3	−40.	−46. ± 1	−21.5	1090 ± 2		
$\frac{1}{3}SO_3$	−29.7	−36.7 ± 0.5	−23.3	335	256	326
$\frac{1}{2}SeO_2$	−21.6	−28.2 ± 1	(−22)	613	440 ± 15	590 ± 15
$\frac{1}{3}SeO_3$			(−23)	391		
$\frac{1}{2}TeO_2$	−32.2	−38.8 ± 0.5	(−22.1)	>750	1075	
$\frac{1}{2}PoO_2$	−23.3	−30.2 ± 3	(−23.4)			
$\frac{1}{5}I_2O_5$		−11.5		d. 570		
H_2O	−56.7	−68.3	−39.0	273	253	373

(64) found no difference at room temperature between lattice constants of Na_2O samples which had been heated with excess metal and with excess Na_2O_2. Thus the homogeneity range of Na_2O 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 MO_3 containing the ozonide ion are known for sodium, potassium, and cesium (1, 16, 255).

The entropy of Li_2O was determined by Johnston and Bauer (228). Todd (415) has determined the entropies of Na_2O_2, NaO_2, and KO_2. Kelley (246) has estimated the entropy of Na_2O. The entropies of the remaining oxides were also estimated. Except for the Na_2O 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 Na_2O_2, NaO_2, and 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 Rb_2O_3 and RbO_2 were estimated by Forcrand (147) and are very uncertain. Johnston and Bauer (228) have recalculated the heat of formation of Li_2O. The heats of formation of Li_2O_2, Na_2O, K_2O, and Rb_2O 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 M_2O oxides disproportionate to M(g) and solid peroxides on the basis of attack of silver and platinum crucibles and vaporization of the alkali metal. For $Na_2O(s) = Na(g) + \frac{1}{2}Na_2O_2(s)$, the data in table 1 yield an equilibrium constant of about 10^{-9} atm. at 948°K. For $3Cs_2O(s) = 4Cs(g) + Cs_2O_3(s)$, one calculates an equilibrium constant of about 10^{-22} atm. at 763°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 M_2O 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 BeO (ZnO wurtzite structure) all the normal MO alkaline earths have the 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 ΔH 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 ΔH 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_8O_9 melting at 2323°K. with a eutectic between Al_8O_9 and Al_2O_3 at 2293°K. Beletskiĭ 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 α-corundum form. Cubic γ-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. Konig (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, γ-Al_2O_3 is converted to the stable α-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 Mn_2O_3 or C-rare earth structure by ignition of the nitrate, carbonate, or hydroxide at low temperatures ranging from 625–875°K. for La_2O_3 to 775–1600°K. for Eu_2O_3. Thus the C form of Sm_2O_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 La_2O_3 and Nd_2O_3, prepared them by heating $La(NO_3)_3$ at 725°K. for 20 hr. and $Nd(NO_3)_3$ at 1000°K. for 3 hr. He found that after 3 hr. at 1300°K. the C form of Nd_2O_3 had been converted to the A form. There is always the possibility that the forms of La_2O_3, Nd_2O_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 Ce_2O_2S 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 CeO_2, Pr_6O_{11}, and Tb_4O_{11}. Gruen, Koehler, and Katz (181) have by the action of atomic oxygen extended the homogeneity ranges to PrO_2 and TbO_2. They could not oxidize M_2O_3 oxides of yttrium, lanthanum, neodymium, samarium, europium, gadolinium, and ytterbium. All of the higher oxides have the CaF_2 crystal structure. Since the C-rare earth structure (cubic Mn_2O_3) is essentially the fluorite structure with some vacant anion sites, it is not unreasonable that wide homogeneity ranges are found between the M_2O_3 and MO_2 compositions. Thus Bruno (75) and also Rienacher and Birchenstredt (342) have prepared compositions from CeO_2 to $CeO_{1.85}$ and have found only a single phase with the CaF_2 structure. Harwood (191) has shown that ceric oxide preparations of varying colors all have the fluorite structure. McCullough (296) has shown that Y_2O_3 (Mn_2O_3 type) is completely miscible with CeO_2 (CaF_2 type). For those rare earths that do not form a stable cubic Mn_2O_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 $CeO_{1.85}$, 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 Pr_2O_3, Nd_2O_3, and Sm_2O_3 indicates a homogeneity range with oxygen uptake (312). Similar behavior is to be expected for Ce_2O_{3+x} and Tb_2O_{3+x}. The Pr_2O_3–PrO_2 system, which has been more thoroughly studied than the others, has yielded conflicting results. McCullough (298) reports a hexagonal phase around Pr_2O_3 and a cubic phase at Pr_6O_{11} and PrO_2. His results indicate that Pr_6O_{11} and 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 Y_2O_3 and CeO_2, would indicate that a complete homogeneity range should occur between Pr_6O_{11} and PrO_2. Martin (293) reports that measurements of oxygen pressure and x-ray studies show that $PrO_{1.75\text{-}2.0}$ (CaF_2 type) is a continuous-phase region. He also finds that $PrO_{1.50\text{-}1.55}$ (hexagonal) is a continuous-phase region with a two-phase region from $PrO_{1.55}$ to $PrO_{1.75}$. Thus he attributes no special significance to the composition Pr_6O_{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 $PrO_{1.715\text{-}1.83}$ (CaF_2 type) region. Their work does not definitely establish the limits of the M_2O_{3+x} phase region. For the two-phase region below $PrO_{1.715}$ they obtain about 50 mm. of oxygen at 1235–1240°K. One puzzling result is the observation of the Mn_2O_3 structure for the composition $PrO_{1.66}$ 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 $PrO_{1.83}$. Foex and Loriers (145) have also given data on this system.

By the combustion of boron, Prosen, Johnson, and Yenchius (336) obtained -101 kcal. for ΔH_{298} per $\frac{1}{3}B_2O_3$, 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 Al_2O_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 Sc_2O_3 and Y_2O_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 ΔH of solution of lanthanum and praseodymium in acid solution. Spedding and Miller (392) have obtained -167.4 and -163.3 kcal., respectively, for the ΔH 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 La_2O_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 ± 1.1 kcal. $\Delta H_{298} = -435 \pm 3$ kcal. is taken as the best value for the heat of formation of La_2O_3.

The value of the heat of combustion found for Pr_2O_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 ± 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 $\frac{1}{11}Pr_6O_{11}$ yielded $\Delta H_{298} = -123.5$ kcal., in good agreement with the recent combustion value (435) of -124.6 ± 0.2 kcal. per gram-atom of oxygen for $PrO_{1.815}$. The average of -124.0 ± 0.5 kcal. is taken for ΔH_{298} of $\frac{1}{11}Pr_6O_{11}$. The data given by Bichowsky and Rossini for 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 PrO_2.

The value of the heat of combustion found for Nd_2O_3 was discarded as being too high. $\Delta H_{298} = -426 \pm 4$ kcal. is obtained from the heat of solution of Nd_2O_3. For Ce_2O_3, an estimated value of $\Delta H_{298} = -434 \pm 5$ kcal. can be given. For CeO_2, Hirsch's (205) heat of combustion was taken instead of smaller values by other workers. This value would predict that CeO_2 would be appreciably decomposed in an atmosphere of oxygen at around 2500°K. Wartenberg and Gurr (430) reported that temperatures above 2300°K. are required for the thermal decomposition of CeO_2. Thermodynamically, hydrogen should reduce 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°K. for the Pr_2O_{3+x}–$PrO_{1.715}$ region. One would calculate about 30 mm. Eyring, Lohr, and Cunningham (134) reported the formation of PrO_2 at 775°K. and 100 atm. of oxygen, while at 660°K. and 3.5 mm. of oxygen, $PrO_{1.826}$ was formed. Assuming the immiscibility of Pr_6O_{11} and PrO_2, one calculates that Pr_6O_{11} and PrO_2 would be in equilibrium with 1 atm. of oxygen at around 700°K., in reasonable agreement with the observations. Ferguson, Guth, and Eyring (139) report similar results for the Pr_2O_{3+x}–$PrO_{1.62}$ region at 1323°K. At 675°K. they found very little change beyond $PrO_{1.83}$ as the oxygen partial pressure was increased from 25 to 650 mm., indicating that the 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 La_2O_3, Pr_6O_{11}, and Nd_2O_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 Ac_2O_3 (La_2O_3 type) (461), Pu_4O_{7-x} (cubic Mn_2O_3 type) (308), and Am_2O_3 (cubic Mn_2O_3 type) (461) the actinide elements are not known to have an M_2O_3 oxide. All of the elements from thorium to americium have an MO_2 oxide with the CaF_2 structure. This phase probably has an extended homogeneity range for all of the elements. Thus $PaO_{2.0\text{-}2.5}$ (CaF_2 type) and $UO_{1.75\text{-}2.25}$ (CaF_2 type) have been reported. *N*-type semiconduction indicates the formula ThO_{2-x}. Rundle, Baenziger, Wilson, and McDonald (360) gave the lower limit of the UO_2 phase as $UO_{1.9}$, while Zachariasen (468) believes that it may extend to $UO_{1.75}$ on the basis of a sample prepared by Brewer by heating UO_2 and U together. This sample contained UO_2 with $a = 5.460$ Å. as well as the phase designated as U_4O_7 with $a = 5.477$ Å. 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 UO_{2-x} (cubic CaF_2 type) samples with $a = 5.484$ and $a = 5.47kx$. The 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 $PuO_{1.75}$. Using highly oxidizing conditions, Katz and Gruen (235) have shown that AmO_2 (fluorite) and PuO_2 (fluorite) are the highest oxides for these elements and that Np_3O_{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 PaO (NaCl type), $PaO_{2.0\text{-}2.5}$ (cubic CaF_2 type), and Pa_2O_5 (orthorhombic). Pa_2O_5 should be similar to PrO_2 in stability toward oxygen loss. Np_3O_{8-x}, Pa_2O_5 (orthorhombic), and the phase ranging from approximately U_2O_5 to U_3O_8 are all isomorphous with the orthorhombic Nb_2O_5 and Ta_2O_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), $UO_{2\pm x}$ (CaF_2 type), and the U_3O_8 (orthorhombic) homogeneity range mentioned above, a number of other phases have been reported. 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. UO_3 (hexagonal) is very closely related to U_3O_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 $UO_{2.62\text{-}3.00}$ for temperatures above 850°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 U_3O_8 and 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 $UO_{2.9}$. The relationship between the various UO_3 forms is not known. They may differ slightly in composition. UO_3 (hexagonal) is converted irreversibly to the other forms by heating in oxygen, so it may be metastable.

The behavior of compositions between UO_2 and U_3O_8 is especially complicated. The data of Biltz and Müller (32) indicated that the UO_2 homogeneity range extends to $UO_{2.25}$ with a two-phase region extending to $UO_{2.62}$ at around 1400°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 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 $UO_{2.0\text{-}2.3}$ range and report a two-phase region above $UO_{2.3}$. Alberman and Anderson (4) have reported a homogeneity range $UO_{2.0\text{-}2.2}$ below 500°K. with little change in parameter for the fluorite structure between $UO_{2.0}$ and $UO_{2.2}$ but tetragonal symmetry between $UO_{2.2}$ and $UO_{2.3}$. Above 500°K. the tetragonal range disproportionates to $UO_{2.2}$ and U_3O_8, while the fluorite range disproportionates to UO_2 (CaF_2 type) and $UO_{2.19}$ (CaF_2 type). Boullé, Jary, and Dominé-Bergès (43) reported that oxidation of UO_2 produces a homogeneity range with tetragonal symmetry which, as indicated by doubling of some of the diffraction lines, persists to $UO_{2.5}$. At the intermediate composition of $UO_{2.30\text{-}2.33}$, the double lines merge to give a single broad line and then double again at high-oxygen compositions. At $UO_{2.5}$ the orthorhombic symmetry of the U_3O_8 range is observed. Gronvøld and Haraldsen (178) have reported a tetragonal phase with a narrow homogeneity range at $UO_{2.40}$ which is stable below 543°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 $UO_{2\pm x}$ (cubic CaF_2 type) phase can be prepared between the limits $UO_{1.75\text{-}2.33}$ with lattice constants varying from 5.484 to 5.416kx. The range above $UO_{2.0}$ appears to be metastable and can be prepared only at very low temperatures. Above 500°K. for the higher oxide compositions and above 600°K. for compositions around $UO_{2.05}$, disproportionation occurs to form a two-phase mixture of $UO_{2.0}$ (cubic) and $UO_{2.25}$ (cubic CaF_2 type). Samples heated to 1200°K. still gave the two-phase mixture upon being examined at room temperature. It is possible that the homogeneity ranges of UO_2 and $UO_{2.25}$ 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 $UO_{2.25}$. The portion of the $UO_{2\pm x}$ range above $UO_{2.25}$ disproportionates above 400°K. to a two-phase mixture of $UO_{2.25}$ (cubic) and a tetragonal phase which has been shown by Hering and Perio to vary in composition with temperature between $UO_{2.42}$ and $UO_{2.29}$. This variation explains the previous discordant compositions reported for this phase. Hering and Perio, in agreement with Gronvøld 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°K., where it coexists with either a U_3O_{8-x} (orthorhombic) phase of rapidly varying composition with temperature or with the $UO_{2\pm x}$ (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°K. all compositions of the tetragonal phase are unstable with respect to $UO_{2.25}$ (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°K. they find the lowest composition of this phase to be $UO_{2.64}$. As the temperature is raised, the oxygen content decreases reaching $UO_{2.54}$ at 775°K., where it is in equilibrium with $UO_{2.25}$ (cubic). After heating to 925°K., they find $UO_{2.52}$ to consist of a single orthorhombic phase. Thus they have confirmed that the orthorhombic phase extends down to U_2O_5. It is not known whether the homogeneity range of this phase continues to expand above 925°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°K. At higher temperatures the oxygen content of the lower limit of the homogeneity range would increase to reach $UO_{2.62}$ at around 1400°K.

Hering and Perio (197) have not done any work on compositions above $UO_{2.66}$. Their work, together with the earlier work reviewed by Katz and Rabinowitch (236), would indicate that at temperatures above 775°K. $UO_{2\pm x}$ (CaF_2 type), $UO_{2.25}$ (CaF_2 type), $UO_{2.5\text{-}3.0}$ (orthorhombic to hexagonal), and the stable UO_3 phase (probably yellow UO_3(III)) are the only stable phases. At higher temperatures the two fluorite-type phases undoubtedly merge, forming a continuous-phase region. Also, UO_3 will become unstable at higher temperatures and the orthorhombic phase region will narrow. Above 1000°K. this region will not extend above $UO_{2.7}$ in an atmosphere of oxygen. With a temperature over 1515°K. and a pressure of 2×10^{-3} atm. of oxygen, no phases above the $UO_{2\pm x}$ 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°K. and 0.4 atomic per cent at 2275°K (59).

The heats of formation of ThO_2, UO_2, and U_3O_8 have been given by Huber, Holley, and Meierkord (212). The heat of formation of AmO_2 has been reported by Eyring, Lohr, and Cunningham (134). Cunningham and Asprey (105) give decomposition data for AmO_2. The heats of formation of ThO and 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 $UO_{2.62}$ and $UO_{2.25}$, one can calculate $\Delta H_{298} = 81$ kcal. for $5.4UO_{2.62} = 5.4UO_{2.25} + O_2(g)$. One measurement of oxygen pressure at 1434°K. for $UO_{2.20}$ yielded $\Delta H_{298} = 11$ kcal. for $UO_{2.25} = UO_2 + \frac{1}{8} O_2(g)$. From these results one obtains $\Delta H_{298} = -270$ kcal. for $UO_{2.25}$ and $\Delta H_{298} = -285$ for $UO_{2.62}$. As noted above, these compositions given by Biltz and Müller (32) as limits of the homogeneity ranges of the UO_2 and U_3O_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 U_3O_8–UO_3, one can, by taking into account solid-solution formation, obtain for the reaction $3UO_3 = U_3O_8 + \frac{1}{2}O_2(g)$ a value of 17.5 kcal. for ΔH_{298}. Using -853.5 kcal. for U_3O_8, one calculates $\Delta H_{298} = -290.4$ kcal. for UO_3. This undoubtedly refers to the hexagonal form of UO_3. From the data of Biltz and Fendius (30), one obtains $\Delta H_{298} = -292$ kcal. for UO_3. The heat of solution of UO_3 measured by de Forcrand (147) results in $\Delta H_{298} = -299$ kcal. for UO_3 using $\Delta H_{298} = -114.0$ kcal. for $U(s) + 2H_2O(l) + 2H^+ = UO_2^{++} + \frac{3}{2}H_2(g)$ in dilute HNO_3 (59). Mixter's (307) heat of solution of UO_3 in Na_2O_2 yields $\Delta H_{298} = -305$ kcal. when combined with the heat of solution of uranium in Na_2O_2 and $\Delta H_{298} = -290$ kcal. when combined with the heat of solution of U_3O_8 in Na_2O_2. $\Delta H_{298} = -291 \pm 3$ kcal. is taken as the best value for UO_3 (hexagonal). From the conditions of preparation and decomposition of red UO_3(II) and yellow UO_3(III), one calculates -292 kcal. for UO_3(II) and $\Delta H = -293$ kcal. for UO_3(III).

The heats of formation of NpO_2, Np_2O_5, and Am_2O_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 Ac_2O_3 is based on the Ac^{3+} potential given by Latimer (271). Brewer, Bromley, Gilles, and Lofgren (57) have given $\Delta H_{298} = -251$ kcal. for PuO_2 on the basis of high-temperature equilibria. However, this value is inconsistent with the heats of formation of ThO_2 and 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 ThO_2, UO_2, and PuO_2. An average of $\Delta H_{298} = -246 \pm 5$ kcal. will be taken for PuO_2. The heat of formation of Pu_2O_5 was estimated from the 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 UO_2 and

UO_3. Westrum, Hatcher, and Osborne (445) have determined the entropies of NpO_2 and PuO_2. 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. α-Titanium is found to dissolve a maximum of 34 atomic per cent oxygen in the range 1000–1900°K., while β-titanium dissolves 5 atomic per cent oxygen at 2010°K. The phase $TiO_{0.66\text{-}0.75}$ (tetragonal) disproportionates above 1198°K., forming the metal and TiO phases. A wide homogeneity range is found for the $TiO_{0.7\text{-}1.25}$ (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 α-titanium and liquid.

Ti_2O_3 (corundum type), which has a deep violet color, was found to have only a limited homogeneity range of less than $TiO_{1.46\text{-}1.56}$. TiO_2 (rutile) was found to have the range $TiO_{1.9\text{-}2.0}$, in agreement with its behavior as an n-type semiconductor. Another homogeneity range was found between $TiO_{1.7}$ and $TiO_{1.8}$ with a distorted rutile structure having oxygen lattice vacancies. Halla (187) claims to have prepared another unstable form of Ti_2O_3 in addition to the form with corundum structure. The structure was not determined. Foex and Loriers (144) reported a transition in Ti_2O_3 at 473°K. which was confirmed by Naylor (317). Chrétien and Wyss (96) reported Ti_3O_4, which is undoubtedly metastable, similar to V_3O_4. Kelley (247) and Wyss (458) have studied the reduction of TiO_2 by hydrogen. The work indicated the existence of the compound Ti_3O_5, which was also studied by Shomate (378) and reported by Chrétien and Wyss (96) to be deep blue. This undoubtedly corresponds to the $TiO_{1.7\text{-}1.8}$ 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_3O_5 (orthorhombic), which they relate to $TiO_2 \cdot Fe_2O_3$ (pseudobrookite). In addition to the tetragonal rutile form of TiO_2, 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_2 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_2 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°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°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°K., and that a final temperature of 1575°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°K. through a wide homogeneity range without evidence of Ti_3O_5, but he found a two-phase region at 1700°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°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. ΔH for $TiO_{0.7}$ was estimated from its observed disproportionation temperature. Latimer (271) estimated the entropy of 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 $VO_{0.4}$ at 1700–1900°K. They found $VO_{0.9-1.3}$ (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 V_3O_4 phase. Their results do not correspond to equilibrium conditions. Except at high temperatures, the lowest stable oxide phase is V_2O_3 with the α-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 V_2O_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 $VO_{1.65}$ and $VO_{1.75}$ Todd and Bonnicksen found a compound which apparently corresponds to the Ti_3O_5 of the titanium system. Between $VO_{1.8}$ and $VO_{2.0}$ they found a solid-solution range which is probably similar to the rutile solid-solution range found in the titanium system. VO_2 has the rutile crystal structure. Between $VO_{2.0}$ and $VO_{2.2}$ Hoschek and Klemm (210) found, in addition to the rutile structure, another x-ray pattern which they attributed to either another compound at about $VO_{2.1}$ or a solid-solution range above VO_2 with distortion of the rutile structure. However, Flood and Kleppa (142), who obtained the same unknown structure upon reduction of V_2O_5 by sulfur dioxide, considered that it analyzes exactly 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 VO_2 relative to VO_2 (rutile) at low temperatures, or *(3)* a compound of higher oxidation state, e.g., $VO_{2.1}$. 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 $VO_{2.1}$ and the transformation depends upon the partial pressure of the oxygen in the system. The oxygen pressure in equilibrium with V_2O_5 and the new compound is 3.5×10^{-6} atm. at 875°K. The oxygen pressure required for further reduction to 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 $VO_{2.1}$ to obtain reduction to 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 V_6O_{13}. This confirms the above interpretation of the results of the reduction by sulfur dioxide.

Above V_6O_{13}, V_2O_5 is the only other vanadium oxide. Byström, Wilhelmi, and Brotzer (91) have determined its structure. Foex (143) reported a transition for V_2O_5 at 172°K. with a 2 per cent linear contraction and a 100,000-fold increase in electrical conductivity. The behavior of V_2O_5 as an n-type semiconductor indicates the formula V_2O_{5-x} (312). Cook (102) determined the high-temperature heat contents of V_2O_3, VO_2, and V_2O_5 and reported a possible transition for 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 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, V_2O_3, and V_2O_4 to V_2O_5. Previous work on these quantities is very unreliable and is not given any consideration here. The various equilibria determinations involving the V_2O_3–V_2O_4 and V_2O_4–V_2O_5 systems are also unreliable except for the very excellent work by Flood and Kleppa (142) on the reduction of V_2O_5 to V_6O_{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 V_6O_{13}. Their results are in agreement with the heats of formation obtained from the data of Siemonsen and Ulich (381) and the stability of V_6O_{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 V_3O_5 one can set a limit to its heat of formation. ΔH_{298} of V_3O_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 V_2O_3 to VO and of VO to vanadium metal. His data yielded $\Delta H_{298} = -113$ kcal. for V_xO, where V_xO is the portion of the VO solid-solution range involved in the equilibria. In the work on the reduction of V_2O_3 he was dealing with V_yO, 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 $NbO_{2.4\text{-}2.5}$ 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 ΔF values for H_2O from Brewer (55), one may derive the following results:

$$NbO_{2.5} = NbO_{2.4} + \tfrac{1}{20}O_2(g); \qquad \Delta H_{298} = 7.66 \text{ kcal.}$$
$$NbO_{2.4} = NbO_2 + \tfrac{1}{5}O_2(g); \qquad \Delta H_{298} = 30.8 \text{ kcal.}$$

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 CrO_3 (orthorhombic) with distorted oxygen tetrahedra around each Cr (90) and Cr_2O_3 (α-corundum structure). In addition, Blanc (34) claims to have prepared two metastable forms of Cr_2O_3, one of which goes to the other upon heating at 1000°K. under reduced pressures. Greenwald and Smart (177) found Cr_2O_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 CrO_3 and Cr_2O_3. Michel and Bénard (302) prepared CrO_2 (rutile structure) and reported that Cr_2O_3 has a homogeneity range up to $CrO_{1.56}$ with a two-phase region up to CrO_2. The formula $CrO_{1.50\text{-}1.56}$ agrees with the observation of Bevan, Shelton, and Anderson (28) that it is an n-type semiconductor. Vasenin (423) reported that CrO_3 melts at 451–460°K. and starts giving off oxygen at 540°K. with precipitation of solid Cr_2O_5; the reaction goes to completion at 620°K. Milligan and Watt (303) also found x-ray evidence for such an intermediate phase. Further heating to 707–784°K. caused decomposition to Cr_2O_3. Schwartz, Fankuchen, and Ward (371) have reported the sequence of decomposition to be $CrO_3 \rightarrow Cr_3O_8 \rightarrow Cr_2O_5 \rightarrow CrO_2 \rightarrow Cr_2O_3$. Wartenberg and Reusch (431) have reported the partial decomposition of Cr_2O_3 at 2530°K. in air. This may be due to formation of Cr_3O_4 but is more probably due to an extended homogeneity range for the Cr_2O_3 phase. Lux and Proeschel (280) claimed the preparation of a red CrO (hexagonal, similar to BeO and ZnO) which has a slow rate of decomposition at 373°K. but is undoubtedly metastable at all temperatures. Kelley, Boericke, Moore, Huffman, and Bangert (249) made a careful study of the $Cr\text{–}Cr_2O_3$ system and could find no evidence for any phases below Cr_2O_3. Pascal (326) also confirmed this. Molten chromium metal dissolves 6.5 atomic per cent oxygen at 1975°K.

The value given for the heat of formation of Cr_2O_3 is an average of the values given by Kelley, Boericke, Moore, Huffman, and Bangert (249) and by Roth and Wolf (355). The CrO_2 value comes from the observation of Dominé-Bergès (115) that Cr_2O_3 goes to CrO_2 in air below 673°K. The CrO_3 value was obtained from the value given by Roth and Wolf for the heat of dissociation of CrO_3 to Cr_2O_3 and oxygen. This value indicates that CrO_3 is metastable even at room temperature.

The $H_2O{:}H_2$ 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 Cr_2O_3 to chromium metal by hydrogen agree rather well with the ratios calculated from the heat of formation shown here for Cr_2O_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 $MoO_2\text{–}MoO_3$ system. Above 1275°K. only MoO_2 and MoO_3 were found. Below 1275°K. Mo_9O_{26} and Mo_8O_{23} were found, one being prepared below 925°K. and one above. Their structures are closely related to that of $W_{10}O_{29}$ and ReO_3. Two forms of Mo_4O_{11} were also found. Glemser and Lutz (168) reported that the homogeneity range of Mo_4O_{11} is less than the range $MoO_{2.65-2.75}$ 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 MoO_2 is less than the range $MoO_{1.97-2.08}$. *Strukturbericht* (199) reports this phase as having the rutile structure, but Hägg and Magneli (184, 287) show that MoO_2 is distorted to a monoclinic structure. MoO_3 (orthorhombic) is an *n*-type semiconductor, in agreement with the homogeneity range $MoO_{2.95-3.00}$.

Ueda and Ichinokawa (418, 419) and Sawanda, Ando, and Nomura (364) reported 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 WO_3 (tetragonal). The structure is closely related to the cubic ReO_3 structure, but no transformation to a cubic form is observed up to 1400°K. The triclinic structure of 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 $WO_{2.95-3.00}$. Hägg and Magneli (184, 287), Magneli (284, 285, 286, 287, 288), and Glemser and Sauer (171) agreed very closely on the phases of the WO_2–WO_3 system. However, Magneli (285, 286) reported $W_{10}O_{29}$ (monoclinic) to have a narrow homogeneity range, while Glemser and Sauer (171) reported $WO_{2.88-2.92}$. They also indicated $WO_{2.65-2.75}$. The phase previously called W_2O_5 is found to be $W_{18}O_{49}$ (monoclinic). WO_2 (monoclinic) has a distorted rutile structure.

Funaki and Ogawa (154) claimed the formation of Mo_2O_3 and MoO upon the reduction of MoO_2 by hydrogen at 1090–1130°K. Watt and Davies (439) reported an Mo_2O_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 Mo_2O_3, but Hägg and Magneli (184, 287) could not find any oxides below 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 Mo–MoO_2 mixtures and have found no oxides below MoO_2. Brewer, Edwards, and McCullough (61) could find no x-ray evidence for oxides below WO_2.

Neumann, Kröger, and Kunz (320) determined the heat of combustion of molybdenum to MoO_3 in fair agreement with Mixter (305). Other earlier determinations appear to be greatly in error. Mixter (305) determined the heat of formation of 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 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 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 $W(s) + 2H_2O = WO_2(s) + 2H_2(g)$.

	OBSERVED $2 \log (H_2)/(H_2O)$	CORRECTED $2 \log (H_2)/(H_2O)$
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 $2 \log (H_2)/(H_2O)$. 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 ΔH_{298} of $WO_2(s)$ a value of -133 ± 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 WO_2.

In a similar manner as above the equations given by Thompson (411) for the reaction $2WO_2 + H_2O(g) = W_2O_5 + H_2(g)$ were corrected to agree with reasonable entropies.

	OBSERVED $\log (H_2)/(H_2O)$	CORRECTED $\log (H_2)/(H_2O)$
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 $\log (H_2)/(H_2O) = 990/T - 1.1$. Using this value and -134 kcal. for ΔH_{298} of WO_2, one obtains $\Delta H_{298} = -330 \pm 3$ kcal. for W_2O_5. Using the data given by Thompson (411) for $W_2O_5(s) + H_2O(g) = 2WO_3(s) + H_2(g)$ in a similar manner as above, one obtains $\Delta H_{298} = -337 \pm 5$ kcal. for W_2O_5 using $\Delta H_{298} = -200.2$ kcal. for WO_3. This agreement is fair and the value $\Delta H_{298} = -333$ kcal. has been accepted for W_2O_5, but it should be regarded as somewhat uncertain in view of the x-ray work discussed above, which indicates a phase $WO_{2.9}$ between W_2O_5 and WO_3.

The above calculations on data which disregard the intermediate phase assume that the intermediate phase is just barely stable and that the $H_2O:H_2$ ratios are the same for the reduction step from WO_3 to $WO_{2.9}$ and from $WO_{2.9}$ to $WO_{2.75}$. If sufficient data were available to treat the two steps separately, more accurate calculations could be made. The use of W_2O_5 in the calculations instead of $W_{18}O_{49}$ does not introduce any difficulties in most calculations, as long as one formula is used consistently. For example, if instead of

$$2WO_2 + H_2O(g) = W_2O_5 + H_2(g)$$

we had considered the equilibrium to be

$$18WO_2 + 13H_2O(g) = W_{18}O_{49} + 13H_2(g)$$

we would have obtained $\Delta H_{298} = -3233$ kcal. for $W_{18}O_{49}$. From

$$W_{18}O_{49} + 5H_2O(g) = 18WO_3 + 5H_2(g)$$

we would have obtained $\Delta H_{298} = -3304$ kcal. for $W_{18}O_{49}$. $\Delta H_{298} = -3269$ kcal. may be taken as the best value for $W_{18}O_{49}$. The value per gram-atom of oxygen of -66.7 ± 1 kcal. is seen to be practically the same as the value obtained assuming W_2O_5.

The entropy of MoO_2 was obtained from the data of Tonosaki (417) on reduction by hydrogen. The entropies of WO_2 and W_2O_5 were estimated by Latimer (271).

H. Manganese group oxides

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

Mn_3O_4 (tetragonally distorted spinel structure) is found to take up oxygen to $MnO_{1.40}$ according to Rode (348) and to $MnO_{1.42}$ according to LeBlanc and Wehner (273) with no phase change. Further addition of oxygen results in the formation of $MnO_{1.50\text{-}1.6}$ (distorted spinel structure). This form of Mn_2O_3, which can also be prepared by dehydration of $Mn_2O_3 \cdot H_2O$, is closely related to the Mn_3O_4 structure, but has manganese vacancies and is metastable. McMurdie and Golovato (299) have found that Mn_3O_4 changes to the cubic spinel structure above 1433°K.

Mn_2O_3 (cubic Sc_2O_3 structure) is the stable modification of Mn_2O_3. Upon decomposition of MnO_2 (rutile structure), LeBlanc and Wehner (273) found formation of Mn_2O_3 (cubic) at $MnO_{1.95}$, a result which indicates a very narrow homogeneity range for MnO_2. The *n*-type semiconductor behavior of MnO_2 indicates the range to be MnO_{2-x} (312). The MnO_2 x-ray pattern was still obtained at $MnO_{1.8}$ but only the Mn_2O_3 pattern was obtained at $MnO_{1.6}$.

It is quite possible that the wide homogeneity ranges observed for the MnO and Mn_3O_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°C. His results checked those of LeBlanc and Wehner (273), indicating no other equilibrium phases between Mn_2O_3 and MnO_2. However, Glemser (166) has observed another phase between $MnO_{1.76}$ and $MnO_{1.93}$ 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 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 $K_2Mn_4O_8$ and $K_2Mn_8O_{16}$ each form solid-solution ranges up to MnO_2 with gradual removal of potassium. The $K_2Mn_4O_8$ series is the MnO_2 form known as ramsdellite and δ-MnO_2, while the $K_2Mn_8O_{16}$ series is the MnO_2 form known as cryptomelane. Apparently both of these forms become metastable with respect to pyrolusite, the stable form of 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 MnO_2.

Southard and Shomate (389) have determined the heat of formation of MnO. The heat of formation of Mn_3O_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° to 25°C., was made to Bichowsky and Rossini's (29) value instead of the correction in the opposite direction suggested by Shomate. The corrected ΔH_{298} for Mn_3O_4 is -330.92 ± 0.26 kcal. from the experiments with hydriodic acid and -331.64 ± 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 MnO_2 was also determined by Shomate (377) and is believed to be much more reliable than earlier work. Using the corrected Mn_3O_4 value from above, one obtains $\Delta H_{298} = -124.25 \pm 0.2$ kcal. as the heat of formation of MnO_2 by averaging the two different determinations of the MnO_2 heat by Shomate (377). Siemonsen (380) obtained $\Delta H_{298} = 25.05$ kcal. for $3Mn_2O_3 = 2Mn_3O_4 + \frac{1}{2}O_2$ by combustion of Mn_2O_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 ΔH value for Mn_3O_4, yields $\Delta H_{298} = -229.2$ kcal. for Mn_2O_3.

Todd and Bonnicksen (414) determined the entropy of MnO. Siemonsen (380) determined the entropy of Mn_2O_3 from the above dissociation data.

Aoyama and Oka (11) studied the reduction of 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 ΔH values given in table 1 is the agreement with the various determinations of the oxygen pressures due to decomposition of MnO_2. These data have been summarized by Siemonsen (380).

X-ray studies have indicated no phases below ReO_2. Both ReO_2 and TcO_2 have the monoclinic MoO_2 structure (152, 463). ReO_3 (cubic) has a structure cosely related to those of WO_3, Mo_9O_{26}, Mo_8O_{23}, and $W_{10}O_{29}$. Tc_2O_7 and Re_2O_7, the highest oxides, are not isomorphous (99a). The heats of formation of ReO_3 and Re_2O_7 were determined by Roth and Becker (352). The ReO_3 value must be greatly in error, for it indicates that ReO_3 is very unstable by disproportionation. Biltz, Lehrer, and Meisel (31) and Nechamkin, Kurtz, and Hiskey (318) have shown that ReO_3 disproportionates only when Re_2O_7 gas can escape. Cobble (99a) has recently redetermined the heats of formation of ReO_3 and Re_2O_7. He confirms the Re_2O_7 value found by Roth and Becker but obtains a much different value for ReO_3. Cobble's ΔH_{298} value of -49 ± 1 kcal. for $\frac{1}{3}ReO_3$ is in good agreement with -46 ± 5 kcal. obtained from Latimer's (271) estimate of the free energy. Cobble (99a) has also determined the heats of formation of Tc_2O_7, TcO_3, and TcO_2. The heat of formation of ReO_2 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 $Fe_{0.945}O$. 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 $Fe_{0.95}O$, while the high-oxygen side becomes higher in oxygen as the temperature is raised. At 1697°K. the range extends to $Fe_{0.835}O$. 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_3O_4 structure if carbon is present.

Liquid ferrous oxide in equilibrium with iron has the composition $Fe_{0.968}O$

at 1644°K. and $Fe_{0.992}O$ at 1797°K. The solubility of oxygen in α-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 NiO_2 to NiO with the same cubic crystal structure with lattice constants decreasing from $a = 4.620$ Å. to $a = 4.172$ Å. 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, Fe_3O_4 and Co_3O_4 are known with the cubic spinel type crystal structure. Fe_2O_3 (rhombohedral corundum type) can also be prepared as a metastable phase with the Fe_3O_4 spinel structure by oxidation of Fe_3O_4. The study of the solid solubility between Fe_3O_4 (cubic) and Fe_2O_3 (rhombohedral) is complicated by the complete solubility of Fe_3O_4 (cubic) and Fe_2O_3 (cubic) in each other. The most reliable evidence (447) indicates that Fe_3O_4 has a rather wide homogeneity range, while Fe_2O_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 Fe_3O_4 homogeneity range. Since Fe_2O_3 exhibits both *n*- and *p*-type semiconductance, it should be designated as $Fe_2O_{3\pm x}$. White (446) and Corey (103) have reviewed the preparation and properties of the iron oxides.

Co_2O_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 Co_2O_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 CoO_2 which could be detected by electron diffraction, but no 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 CoO_2, distinct oxides can be prepared as surface films. Selwood (373) reported that NiO is formed if deposited on a MgO surface, while Ni_2O_3 is formed on an Al_2O_3 surface and NiO_2 is formed on a 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 Bonnickesen (104) have given the high-temperature heat contents of the iron oxides.

Mixter (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.; Kaputinskiĭ and Gofman (234), −56.0 kcal.; and Wohler and Balz (452), −57.6 kcal. with ΔS_{298} values varying from −15.5 to −17.6. Since ΔS_{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 Co_3O_4. $\Delta H_{298} = -203 \pm 3$ kcal. was accepted for Co_3O_4.

There have been a number of equilibria determinations involving reduction of NiO to nickel. Fricke and Weitbrecht (151) studied the $CO–CO_2$ equilibrium from 1044° to 1289°K. Watanabe and Ishikawa and Watanabe (224, 438) reported data from 980–1110°K. which give virtually the same ΔH 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 ΔF. Bogatskiĭ (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 ΔH 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 ΔH_{298} were calculated from the experimental ΔF values. The equilibrium data of Fricke and Weitbrecht (1044–1289°K.) for reduction with carbon monoxide and the data of Bogatskiĭ (940–1400°K.) gave essentially the same value of $\Delta H_{298} = -57.12$ kcal., although Bogatskiĭ's data showed more variation in ΔH_{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 ΔH_{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 RuO_2 (rutile structure) and RuO_4 have been definitely shown to exist. 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 RuO_4 and RuO_2. Although RuO_4 vaporizes undecomposed at room temperature, it decomposes at slightly higher temperatures to RuO_2. Latimer (271) gives the free energy of formation of RuO_4, from which one may obtain a heat of formation by means of an estimated entropy. These data indicate that RuO_4 is thermodynamically unstable even at room temperature. The heat of formation of 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 RuO_2. Latimer (271) has estimated the entropy of RuO_2.

Rhodium: The only definitely determined phase is Rh_2O_3 (corundum structure). Wohler and Muller (455) have reported the existence of Rh_2O and RhO, since these compositions have smaller oxygen decomposition pressures than Rh_2O_3, but their data do not distinguish between distinct phases and an extended homogeneity range. Also, if Rh_2O and RhO do exist, they are on the verge of being unstable by disproportionation to Rh and Rh_2O_3 and probably have only limited temperature ranges of stability, for the decomposition temperatures at 760 mm. of oxygen are 1400°, 1394°, and 1388°K. for Rh_2O, RhO, and Rh_2O_3, respectively. From the decomposition pressures over a range of temperatures, one can obtain $\Delta H = -27.8$ kcal. for Rh_2O. 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 RhO and Rh_2O_3. Latimer (271) has estimated the entropies. Latimer (271) has given data from which one obtains $\Delta F_{298} = -14$ kcal. for RhO_2; this value makes RhO_2 thermodynamically unstable with respect to Rh_2O_3.

Palladium: PdO (tetragonal) is the only stable anhydrous phase. Its *p*-type semiconduction fixes it as PdO_{1+x} (312). Latimer (271) gives data for PdO_2 which fix $\Delta F_{298} = 0$ and for PdO_3 which fix ΔF_{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: OsO_2 (rutile structure) and OsO_4 are the only known oxides of osmium. Wartenberg (427) has determined the heat of formation of OsO_4 (gas), and Kelley (243) has summarized the vapor-pressure data for OsO_4; from these values one can calculate the heats of formation of the two forms of solid 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 OsO_2 disproportionates to solid osmium and 1 atm. of OsO_4 gas at 923°K., Latimer has estimated the free energy of 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 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 IrO_2 by hydrogen. $\Delta H = -44$ kcal. is taken as a weighted average. Latimer has estimated the entropy. IrO_2 (rutile structure) is the only pure phase in the iridium–oxygen system. The data quoted by Latimer (271) for Ir_2O_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 PtO (tetragonal), Pt_3O_4 (cubic), and PtO_2 (hexagonal) have been reported. Waser and McClanahan (433, 434) have reported $Na_xPt_3O_4$ (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 $Pt(OH)_2$, one can estimate $\Delta F_{298} = -11 \pm 4$ kcal. for PtO. From Latimer's data on PtO_2, one can calculate $\Delta F_{298} = -17 \pm 10$ kcal., a value which appears too positive; hence -20 ± 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 Pt_3O_4 and PtO_2 at 823°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 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 Cu_2O (cubic) and CuO (monoclinic) are known. Cu_2O_{1+x} is a p-type semiconductor, while $CuO_{1\pm x}$ is both an n- and a p-type semiconductor (312). Faivre (135) has reported no appreciable solubility of copper metal in Cu_2O. Okada (323) believed that the reported structure for Cu_2O (cubic) is wrong and that a different cubic structure is necessary. Auwers (14) has reported a transition for Cu_2O at 329°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 Cu–Cu_2O equilibrium from 1365° to 1575°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 Cu_2O.

In addition to Ag_2O (cubic), AgO and Ag_2O_3 have been reported. The thermodynamic data given by Latimer (271) demonstrate that the higher oxides are metastable at 1 atm. of oxygen. Ag_2O 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°K. Pavlyuchenko and Gurevich (328) and Iijima (221) have studied the Ag–Ag_2O 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 Ag_2O 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.

Au_2O and Au_2O_3 are known, but Au_2O is thermodynamically unstable by disproportionation to Au and Au_2O_3, while Au_2O_3 is metastable with respect to the metal and oxygen. Latimer (271) and the National Bureau of Standards (316) have given data for Au_2O_3.

L. Zinc group oxides

ZnO_{1-x} (hexagonal) is an *n*-type semiconductor (312). Ehret and Greenstone (123) have confirmed this homogeneity range directly by demonstrating that red ZnO is 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 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 ΔH for 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 ZnO. These different determinations by different methods yield $\Delta H_{298} = -83.2 \pm 0.2$ kcal.

Hedger and Terrey (192) have demonstrated that CdO is the only cadmium oxide phase. CdO_{1-x} (NaCl type) is an *n*-type semiconductor (312). Faivre (135) found the homogeneity range to extend to $CdO_{0.996}$ at 975°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 $CdO(s) = Cd(g) + \frac{1}{2}O_2(g)$ 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 Hg_2O. Lamure (268) has shown that Hg_2O disproportionates. Garrett and Hirschler (157) have shown that red 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_2O and Ga_2O_3. Brukl and Ortner (74) reported that Ga_2O disproportionates at an appreciable rate to Ga_2O_3 and Ga at 1075°K. The available thermodynamic data indicate that solid Ga_2O is unstable at all temperatures. Ga_2O_3 has many metastable modifications and thus shows a behavior similar to that of Al_2O_3. The only thermodynamically stable form at all temperatures is β-Ga_2O_3 ($Na_2O \cdot 11Al_2O_3$ type). Roy, Hill, and Osborn (356) have reviewed the preparation and properties of the other forms of Ga_2O_3. Klemm and Schnick (258) have measured the heats of formation of Ga_2O and Ga_2O_3 by combustion calorimetry and have obtained fair agreement with Roth and Becker's (352) Ga_2O_3 value of -255.8 kcal. Latimer (271) has estimated the entropies.

Thiel and Luckmann (410) claimed the preparation of In_2O and InO and x-ray evidence of which they give no details. Stubbs, Schufle, and Thompson (398) have recently studied the In–In_2O_3 system and found only In_2O_3 (cubic Mn_2O_3 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_2O and InO are either mixtures or metastable phases.

Tl_2O (Pb_2O structure) and Tl_2O_3 (cubic Mn_2O_3 type) are the only definitely established oxides of thallium. $\Delta H_{298} = -43.2$ kcal. for Tl_2O 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_2O–Tl_2O_3 liquid solutions. His treatment of his data is incorrect. Recalculation of the data assuming Raoult's law and using an estimated ΔS yields $\Delta H_{298} = 42$ kcal. for $Tl_2O_3(s) = Tl_2O(s) + O_2(s)$ and $\Delta H_{298} = -84.5$ kcal. for $Tl_2O_3(s)$.

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_2 exists in at least six crystalline modifications, of which four have stable temperature ranges. α-Quartz (hexagonal) is stable up to 848°K. where it is transformed readily to β-quartz (hexagonal), which is stable up to 1140°K. Above this temperature, β-quartz is thermodynamically unstable with respect to β-tridymite (hexagonal) but the transition is very slow. β-Tridymite is stable up to 1743°K. where β-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 α-forms of both tridymite and cristobalite which are thermodynamically unstable with respect to α-quartz. Mosesman and Pitzer (313) have reviewed the stability and transitions of the various forms of SiO_2. Buerger (76) has discussed the changes in structure upon transformation and the reasons for the greatly varying rates of transformation. Above 1200°K. an excellent catalysis for the transformation is elemental silicon, which apparently is effective through the intermediate SiO gas. Ewles and Youell (133) have reported that hydrogen at 1025°K. for 2 hr. reduces SiO_2 to $SiO_{1.999}$. The *n*-type semiconduction also indicates SiO_{2-x} (312).

There have been many reports of the formation of an SiO phase which is most easily prepared by condensation of 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 SiO does not exist as a stable solid phase at temperatures below 1300°K. The SiO solid samples that can be obtained at room temperature by the quenching of SiO gas produced by the reduction of 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 SiO is stable above 1450°K. This is similar to the behavior of the FeO phase, which is unstable at low temperatures but which becomes stable at higher temperatures. Although most 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 SiO.

Until recently, it has been difficult to obtain pure silicon metal, and previous determinations of the heats of formation of the 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 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 SiO at low temperatures as well as its stability above 1450°K.

The question of the stability of solid GeO is similar to that of SiO discussed above. Bues and Wartenberg (78) presented calorimetric and vapor-pressure data which indicate that 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 GeO than over Ge + GeO_2; this certainly fixes GeO as being unstable with respect to Ge and GeO_2. By the heat of combustion of GeO, prepared by rapid condensation of 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 $GeO_2(s) + Ge(s) = 2GeO(s)$, ΔH_{298} is about +7 kcal. and that GeO solid is certainly thermodynamically unstable at all temperatures below 1000°K.

Laubengayer and Morton (262) have discussed the transformation at 1306°K. ± 10° from GeO_2 (tetragonal rutile type) to GeO_2 (hexagonal α-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, SnO and SnO_2. Veselovskiĭ (424), Spandau (390), and Spandau and Kohlmeyer (391) have reviewed the properties of SnO. Veselovskiĭ (424) has reported that SnO is unstable at low temperatures, stable at 320–650°K., and unstable at higher temperatures with respect to disproportionation to tin metal and SnO_2. Spandau (390) finds SnO unstable from 673°K. to 1313°K. but claims that it is stable above 1313°K. as a liquid phase. He reports that SnO dissolves SnO_2 but not tin metal. SnO is commonly known as a tetragonal form, isomorphous with red PbO (311). Partington and Moser (325) have prepared a red SnO which is different from the tetragonal form. Kelley (247) has determined the heat of formation of SnO_2 (tetragonal type). As Veselovskiĭ (424) has pointed out, the heat of formation of SnO can be very accurately related to that of SnO_2 from the fact that SnO is just barely stable. He gives $\Delta H_{298} = -0.652 \pm 0.1$ kcal. for $2SnO = SnO_2 + Sn$, from which the heat of formation of 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 PbO exist. The phase Pb_2O reported by Ferrari (140) has been shown to be $PbO_{1.33\text{-}1.57}$ (orthorhombic pseudocubic). Above 762°K., yellow PbO (orthorhombic) is the stable phase and exhibits no detectable homogeneity range. Below 762°K. red PbO (tetragonal) is the stable phase, and when prepared at high temperatures, this phase has no detectable homogeneity range. However, when red PbO is prepared at low temperatures by decomposition of yellow PbO, it can exist as $PbO_{1.00\text{-}1.02}$ (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 PbO (312).

Pb_3O_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. $PbO_{1.33\text{-}1.57}$ (orthorhombic pseudocubic) is a homogeneity range with very interesting behavior. For part of this range, from $PbO_{1.4}$ to $PbO_{1.55}$, there is a tendency for an order-disorder transformation with the maximum ordering occurring at the composition Pb_2O_3. From Byström's (86, 87) work one would conclude that the $PbO_{1.33-1.57}$ 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 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, Pb_2O_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 $PbO_{1.33}$, one obtains a continuous change in composition through the phase region $PbO_{1.33-1.57}$. If the oxidation is stopped at an intermediate point in the partially ordered range, e.g., $PbO_{1.52}$, reduction back to $PbO_{1.33}$ will proceed with a continuous change in composition. However, if the oxidation proceeds beyond $PbO_{1.55}$ into the completely disordered range, then reduction will proceed in such a manner as to avoid the ordered region. When the composition $PbO_{1.55}$ is reached, further reduction produces the composition $PbO_{1.4}$ with no intermediate composition appearing. Further reduction proceeds with continuous composition change through the completely disordered region $PbO_{1.33-1.40}$. 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 $PbO_{1.87-2.0}$ (tetragonal rutile type) homogeneity range was worked out by Katz (239) in agreement with its *n*-type semiconductivity. He also found a $PbO_{1.98}$ 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 Zaslavskiĭ, Kondrashev, and Tolkachev (469) have recently reported a new orthorhombic form of 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 N_2O_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 N_2O_5 as being $NO_2^+NO_3^-$. Broadley and Monteath (73) have determined the structure of N_2O_4 (cubic). The N_2O_4 molecule is all in one plane. Dulmage, Meyers, and Lipscomb (119) have determined the structure of N_2O_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°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°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°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°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°K., while As_2O_3 (monoclinic) is stable above 260°K. Their results indicated that 0.45 ± 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°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°K. and Sb_2O_3 (orthorhombic) is stable above 846°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 ΔH 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°K. Bi_2O_3 (cubic Mn_2O_3 type) is prepared by heating at 1000°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°K. The formula Bi_2O_{3+x} is indicated by the *p*-type semiconductivity of Bi_2O_3 (312). Scholder and Strobble (368) have discussed the BiO_2–Bi_2O_5 phase region. This phase region is probably never prepared free of alkali or water. The ΔH value given by Latimer (271) for BiO_2 indicates that all phases above Bi_2O_3 are metastable in 1 atm. of oxygen. The ΔH values for BiO and Bi_2O_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 BiO.

P. Sulfur group oxides

The only stable solid oxide of sulfur at room temperature and 1 atm. of oxygen is 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 SO_3. The solid form designated as γ-SO_3 has the lowest vapor pressure and is thus the most stable modification. The properties of SO_3 given in table 1 are those of γ-SO_3 as tabulated by Yost and Russell (459). Solid or liquid SO_3 is very stable toward decomposition to SO_2 and oxygen. Westrik and MacGillavry (443) have shown that γ-SO_3 consists of S_3O_9 puckered rings in a molecular lattice. S_2O_3, reported by Appel and Goehring (12), is very unstable and decomposes at room temperature in a few hours.

SeO_2 and 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 TeO has no stable existence. Yost and Russell (459) have reviewed the preparation of SeO_3 and 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 SeO_3, and they reported that SeO_3 decomposes to SeO_2 at 453°K. SeO_2 (tetragonal) consists of endless chains, according to McCullough (297). In addition to the well-known α-TeO_2 (tetragonal rutile type), Ito and Sawada (225) have reported β-TeO_2 (brookite-like structure) and Stehlik and Baluk (395, 396) have reported γ-TeO_2 (tetragonal). The stability relationships are not known. Yost and Russell (459) have given the heats of formation of SeO_2 and α-TeO_2.

Rollier (349) has stated that Po_2O_3 should be similar to the cubic Mn_2O_3 type and that PoO_2 should be similar to the tetragonal rutile type. The thermodynamic data given by Latimer (271) for PoO_2 and PoO_3 demonstrate that PoO_3 is thermodynamically unstable.

Q. Halogen group oxides

All of the oxides of the halogens except I_2O_5 are thermodynamically unstable (56).

R. Hydrogen oxides

The only thermodynamically stable oxide of hydrogen is water, H_2O, 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. H_2O_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 vaporizes. 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-x}, ZrO_2, HfO_2, ThO_2, UO, UO_2, NpO_2, Pu_4O_{7-x}, 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 MoO_3, WO_3, Re_2O_7, 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 M_2O 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 Na_2O and Na_2O_2. Todd (413) has obtained 803°K. for the melting point of KO_2. Margrave (64) has confirmed the values for Na_2O, but he obtained 653°K. ± 20° for KO_2.

All available data indicate that there are no important alkali metal oxide gaseous molecules except possibly Li_2O and LiO. Brewer and Mastick (66) have carried out theoretical calculations to demonstrate that Cs_2O, Rb_2O, K_2O, and Na_2O vaporize by decomposition to the metal gases and O_2 with no appreciable contribution due to an M_2O molecule. Their calculations indicate that Li_2O could possibly be important, but the uncertainty of the calculations was large. Brewer and Margrave (64) have experimentally determined the vapor pressures of Li_2O and Na_2O 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 LiO as well as LiO_2 could be stable enough to be as important as the elemental species, Brewer, Margrave, and Kane (65) measured the volatility of Li_2O 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 Li_2O molecule was comparable to the elements in the saturated vapor of Li_2O. 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
	kcal.		*kcal.*
Li_2O	270 ± 6	CdO	<88
LiO	≮ 92		
		GaO $(^2\Sigma?)$	58 ± 12
BeO $(^3\Sigma?)$	97 ± 28	InO $(^2\Sigma?)$	25 ± 5
MgO $(^3\Sigma?)$	<100		
CaO $(^3\Sigma?)$	103 ± 8	CO $(^1\Sigma)$	256.2
SrO $(^3\Sigma?)$	111 ± 4	CO_2 $(^1\Sigma)$	381.5
BaO $(^3\Sigma?)$	126 ± 4	SiO $(^1\Sigma)$	169 ± 3
		GeO $(^1\Sigma)$	155 ± 4
BO $(^2\Sigma^+)$	126 ± 4	SnO $(^1\Sigma)$	132 ± 2
B_2O_3	655 ± 10	PbO $(^1\Sigma)$	98 ± 2
Al_2O (?)	246 ± 7		
AlO $(^4?)$	137 ± 8	N_2O	263 ± 1
ScO $(^2\Sigma)$	138 ± 23	NO $(^2\pi)$	149 ± 1
YO $(^2\Sigma?)$	161 ± 46	N_2O_3	379 ± 1
LaO $(^2\Sigma?)$	161 ± 46	NO_2	221 ± 1
CeO	149 ± 46	N_2O_4	454 ± 1
PrO	142 ± 12	N_2O_5	512 ± 4
GdO	115 ± 46		
LuO	99 ± 35	PO $(^2\pi)$	142 ± 12
		P_4O_6	1180 ± 15
ThO_2	>410	P_4O_{10}	1588 ± 15
UO	198 ± 10		
UO_2	>355	AsO $(^2\pi)$	114 ± 3
UO_3	508 ± 10	As_4O_6	864 ± 20
		SbO $(^2\pi)$	74 ± 9
TiO $(^3\pi)$	160 ± 2	Sb_4O_6	886 ± 15
ZrO $(^3\pi?)$	170 ± 20	BiO $(^2\pi?)$	92 ± 23
ZrO_2	360 ± 20		
		O_2 $(^3\Sigma)$	117.2
VO $(^2\Delta?)$	126 ± 23	O_3	142 ± 1
V_2O_5	725 ± 15	SO $(^3\Sigma?)$	92 or 118
		SO_2	241 ± 7
CrO $(^3?)$	124 ± 11	SO_3	322 ± 7
MoO_3	445 ± 5	SeO	81 ± 23
WO_3	465 ± 7	SeO_2	201 ± 5
		TeO	63 or 79
MnO	92 ± 9	TeO_2	215 ± 7
Re_2O_7	860 ± 10		
		F_2O	84 ± 3
FeO	<98	Cl_2O	94 ± 2
NiO	<99	ClO	44 ± 5
		ClO_2	120 ± 2
RuO_2	238 ± 20	ClO_3	157 ± 3
RuO_4	352 ± 30	Cl_2O_7	400 ± 5
OsO_2	263 ± 40		
OsO_4	406 ± 30	BrO	51?
RhO_2	193 ± 30		
IrO_2	242 ± 20	IO	44?
PtO_2	198 ± 10		
		OH $(^2\Sigma)$	101 ± 1
CuO $(^2\Sigma?)$	113?	H_2O	218.3
AgO $(^2\Sigma)$	32 ± 9	H_2O_2	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°K. contains 1×10^{-5} atm. $O_2(g)$, 4×10^{-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°K. ± 120° 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 ± 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'shanskiĭ (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 calculated 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_2 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_2, 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 calculations 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 Huldt 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 ΔH_0 for BaO(g, $^3\Sigma$) = Ba(g, ^1S) + O(g, ^3P) at 0°K. equal to 127 ± 4 kcal. from the vapor-pressure data and 122 ± 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. Huldt and Lagerqvist (215) appear to have made an error in calculating D_0 from the equilibrium data given by Huldt (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. Huldt 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 6×10^{-10} atm. Ca(g), 6×10^{-10} atm. O(g), and 1×10^{-10} atm CaO (g, $^3\Sigma$) in equilibrium with solid CaO. At 2700°K. one calculates approximately the same partial pressure of 5×10^{-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 SiO_2, Al_2O_3, and the other alkali oxides have been shown to be much too high.

The value of $D_0 = 112$ kcal. for MgO ($^3\Sigma$) from the flame data of Huldt and Lagerqvist (215) must be in error, since this value would indicate a rather high volatility for MgO as the molecule. One can set an upper limit to the MgO partial pressure from the data of Moore (309). He studied the reduction of MgO by tungsten metal to produce solid WO_2 and Mg gas. His observed vapor pressures, which should include both the Mg and MgO partial pressures, were about one-tenth as large as the partial pressure for MgO which one calculates from the value of $D_0 = 112$ which yields $\Delta H_{298} = 126$ kcal. for $MgO(s) = MgO$ ($^3\Sigma$). 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 MgO and WO_2 solids. Since he observed a pressure of 10^{-7} atm. at 1800°K., the partial pressure of MgO must be less than this at 1800°K. The heat of sublimation at 298°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 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°K. and 2520°K. The atmospheric boiling point will be between 3300°K. and 3430°K. As averages 2450°K. ± 100° and 3350°K. ± 200° will be taken.

Under highly oxidizing conditions to almost neutral conditions, the MO molecule is the main vaporizing species for all of the alkaline earth oxides except BeO. SrO and 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 ΔH_{298} values are given for $MO(s) = MO(g, {}^3\Sigma)$: MgO, ≥ 138 kcal.; CaO, 149.5 ± 8 kcal.; SrO, 127.6 ± 4 kcal.; BaO, 107.7 ± 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: B_2O_3, Kracek, Morey, and Merwin (265); Al_2O_3, Geller and Yavorsky (159); Y_2O_3, *International Critical Tables* (222); La_2O_3, Wartenberg and Reusch (431). The melting point of CeO_2 is an estimate based on the observation of Wartenberg and Gurr (430) that the melting point is over 2900°K.

Spectroscopic evidence has established the existence of BO, AlO, ScO, YO, and LaO molecules in the $^2\Sigma$ state. Linear Birge–Sponer (33) extrapolations indicate heats of dissociation of 160–210 kcal. In addition, CeO, PrO, GdO, and 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 NdO, SmO, DyO, HoO, and YbO. In no case has the ground electronic state been conclusively established.

Speiser, Naiditch, and Johnston (393) have determined the vapor pressure of B_2O_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°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°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 ± 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 ± 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°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°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°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 Y_2O_3 and La_2O_3, respectively, given by Mott (314) and the observation of Wartenberg (430) that Ce_2O_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 ThO_2 has been given by Ruff, Ebert, and Woitinek (357) and accepted by Wartenberg and Reusch (431). The melting point of 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 PuO_2 and have reported a melting point for the decomposed mixture. Their results indicate that pure PuO_2 melts above 2200°K.

Mott (314) reported a boiling point of 4670°K. for 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. ThO bands have been reported by Krishnamurty (266) but no D_0 value can be given. Thus it is not possible to decide if ThO or ThO_2 is the more important gaseous molecule. In view of the formation of solid ThO, it would seem that gaseous ThO should be of chemical importance. Comparison with the zirconium system would indicate that both ThO and 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 UO_3 loses oxygen at rather low temperatures, where there is no appreciable volatility of oxide molecules, UO_3 gas does become important at very high temperatures. Biltz and Müller (32) have observed volatility in the two-phase region between $UO_{2.25}$ and $UO_{2.62}$ at temperatures above 1430°K. due to disproportionation of the $UO_{2.62}$ phase to $UO_{2.25}$ solid and UO_3 gas. The volatility is not observed for compositions above $UO_{2.62}$ even though the equilibrium partial pressure of UO_3 is higher, because the higher oxygen partial pressure above such samples reduces the rate of vaporization so much. For the $UO_{2.25}$–$UO_{2.62}$ region at 1430°K., the oxygen pressure is only 4×10^{-4} atm. and would not interfere with the vaporization of UO_3. Below the composition $UO_{2.25}$ the $UO_{2.62}$ phase disappears and the UO_3 activity, and therefore the 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 UO_3 in equilibrium with $UO_{2.62}$ at 1600°K. can be estimated. From this and the thermodynamic data for solid UO_3, one can calculate 10^{-4} atm. UO_3 gas in equilibrium with solid UO_3 at 1600°K. and 10^{-5} atm. UO_3 gas in equilibrium with solid UO_3 at 1450°K. Of course, an oxygen pressure of many atmospheres would be required to maintain solid UO_3 at these temperatures and to get such a high UO_3 partial pressure. If oxygen gas at 1 atm. were passed over $UO_{2.62}$ at 1950°K., it is calculated to be in equilibrium with 10^{-3} atm. UO_3 gas. At 1773°K. the solid phase would be $UO_{2.7}$ and there would be 10^{-4} atm. UO_3 gas.

That this volatility must be due to the 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 WO_3. Alberman and Anderson (4) comment that the vaporizing species could not be UO_3, since it should precipitate U_3O_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 $UO_{2\pm x}$ phase region as a function of composition at a fixed temperature, e.g., 2000°K., the volatility at the high-oxygen end of the region would be large, corresponding to about 10^{-3} atm. UO_3. Reducing the oxygen composition would rapidly reduce the UO_3 partial pressure until it became negligible, but the total volatility would reach an approximately constant value corresponding to the UO_2 vapor pressure. By comparison with the ZrO_2 and ThO_2 vapor pressures the UO_2 partial pressure would be around 10^{-8} atm. at 2000°K. Even further reduction of the oxygen composition toward the metal-rich end of the $UO_{2\pm x}$ phase region would result again in an increase in volatility due to the UO partial pressure. The composition in equilibrium with the UO phase is estimated to have a partial UO pressure of 10^{-6} atm. at 2000°K. Thus at a fixed temperature, one can expect three different important gaseous oxide species for the $UO_{2\pm x}$ 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 UO and one in the UO_2 phase region. For the other actinides, both the MO and the MO_2 gaseous molecules can be expected to be important up to americium. At americium and beyond, the MO_2 molecule will be unimportant. The M_2O_3 molecule may become important. Phipps, Seifert, and Simpson (333, 334) have studied the volatility of PuO_2. Under the conditions of their experiment the PuO_2 was partially reduced and the main gaseous species was PuO. From their data, one can estimate a vapor pressure of 10^{-6} atm. for pure PuO at 1850°K. The partial pressure of PuO_2 is much less than 10^{-5} atm. at 2200°K.

E. Titanium–zirconium group oxides

The melting points were determined as follows: TiO, Bumps, Kessler, and Hansen (79); Ti_2O_3, *International Critical Tables* (222); 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 Gastinger (470) to obtain a ZrO_2 vapor pressure of 1.5×10^{-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 ozygen 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 2×10^{-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. ± 50° 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 Cr_2O_3. If Cr_2O_3 vaporized by decomposition to the gaseous elements, its atmospheric boiling point would be around 3750°K. $Cr_2O_3(s)$ 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 Cr_2O_3. On the basis of work by Mott (314), a boiling point of 3300°K. can be assigned. If this is reliable, a stable gaseous molecule would be indicated. The spectrum of 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 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 CrO. This value would yield a calculated boiling point for Cr_2O_3 vaporizing to CrO and O_2 of around 3000°K., in fair agreement with Mott's value. Thus CrO seems definitely substantiated as an important gaseous species under neutral or oxidizing conditions. The species Cr_xO_2 and Cr_xO_3 might be of importance. At very high temperatures and oxidizing conditions even CrO_3 ($x = 1$) could be of importance, since it is formed endothermally from solid Cr_2O_3 with an increase in entropy and might have sufficient stability.

Both MoO_3 and WO_3 vaporize essentially undecomposed, and lower oxides disproportionate to the metal and the MO_3 molecule. Vapor-density measurements by Brewer and Elliott (62) have indicated that the molybdenum oxide species is the monomer MoO_3. As the temperature is raised above the temperature at which the solid oxide phases can exist, leaving only the solid metal, the MO_3 molecule will diminish in stability but can be expected to still be of importance in an oxygen atmosphere well above 2000°K. At very high temperatures the M_xO and M_xO_2 molecules may become important. WO bands have been reported but have not been analyzed.

The stability of the MoO_3 and 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 $MoO_3 \cdot H_2O$ and $WO_3 \cdot H_2O$ (62). The data of Moore (309) on the volatility of tungsten from a mixture of WO_2 and MgO also helps to fix the stability of WO_3 gas and possible lower oxide species. Lower oxide species are quite unimportant compared to MoO_3 and WO_3 under most conditions.

H. Manganese group oxides

The melting point of MnO has been given by White, Howat, and Hay (448). Wartenberg, Reusch, and Saran (432) have given the melting point of Mn_3O_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 OsO_2, which disproportionates to osmium metal and OsO_4 gas. RuO_4 can also vaporize at room temperature to give an appreciable partial pressure of RuO_4 gas, but both the solid and the gas are metastable under those conditions. RuO_4 gas is formed endothermically from RuO_2 solid and oxygen gas and reaches its maximum equilibrium partial pressure at 1400°K., where RuO_2 solid becomes unstable with respect to the metal and 1 atm. of oxygen. The RuO_4 partial pressure under these conditions is about 10^{-6} atm. Both RuO_4 and 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°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°K., where 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 M_xO and M_xO_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 M_xO and M_xO_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 Pt_xO_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 PtO_2, but no data are available to allow one to fix the number of platinum atoms per molecule. Platinum metal at 1773°K. in an atmosphere of oxygen is in equilibrium with 3×10^{-5} atm. of 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 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 M_xO or M_xO_2. One would judge that M_xO_2 would be the reasonable choice up to about 2000°K. Iridium vaporizes about one hundred times more rapidly in air than platinum and ruthenium vaporizes about two hundred times more rapidly at 1500°K. (450). The molecules are undoubtedly IrO_2 and RuO_2. For $MO_2(s) = MO_2(g)$, $\Delta H_{298} = 87 \pm 5, 85 \pm 7$, and 93 ± 8 kcal. for platinum, iridium, and ruthenium, respectively. Holborn and Austin (206) reported that at 1943°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 Ir_xO species. Under conditions of low pressures or very high temperatures, where oxygen is present as monatomic oxygen, M_xO 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 M_xO_2 molecule with the maximum attack due to this molecule at the temperature where O_2 and O are equally important. Above this temperature attack will decrease if the M_xO_2 molecule is the main species. However, attack due to an M_xO molecule will still increase with increasing temperature, and at high enough temperatures, one could be sure that there will be extensive attack. Since PdO_2 is unimportant for palladium, the 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 M_xO_2 species is MO_2, one can summarize the data for the reaction $M(s) + O_2(g) = MO_2(g)$ 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 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. ΔS for this reaction can be expected to be between +5 and +9 entropy units. At 3500°K., where the MO_2 partial pressure in an atmosphere of oxygen reaches its maximum because of conversion of O_2 to 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 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 MO_2 partial pressure and at 3500°K. only RuO_2, OsO_2, and IrO_2 have larger pressures than the metal atoms. PdO_2 is so unstable and palladium metal so volatile that the palladium pressure will be higher than the 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 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 Cu_2O. Mack, Osterhof, and Kraner (282) have determined the vapor pressure of 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 CuO are known. The lowest state is probably $^2\Sigma^+$ but it has not definitely been established as the ground state. 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 Vesselovskiĭ (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 GeO(s) has any temperature range of stability. The higher lead oxides will all lose oxygen without any appreciable vaporization of PbO. Thus only the PbO phase has a constant-boiling composition. The SnO vaporization temperatures given in table 1 are for a mixture of Sn and 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 N_2O, NO, NO_2, N_2O_3, N_2O_4, and N_2O_5 have been discussed by Yost and Russell (459), who have given the thermodynamic properties. Koerner and Daniels (262) have recently determined ΔH of NO_2. Daniels and Bright (107) have given the vapor pressure of N_2O_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 NO can reach any appreciable equilibrium concentration. At a total pressure of 1 atm. the maximum concentration of NO will be 0.1 atm. at about 3700°K., where monatomic oxygen becomes important. At higher temperatures, NO will decrease in importance, since it is formed exothermically from monatomic oxygen.

The condensed phases P_2O_3, PO_2, and P_2O_5 vaporize to form, respectively, P_4O_6, P_8O_{16}, and P_4O_{10}. Yost and Russell (459) have discussed these molecules and have pointed out that the formula P_8O_{16} is in some doubt and may be P_4O_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 P_2O_5. Kelley (243) and Yost and Russell (459) have reported fusion and vaporization data for the other oxides of phosphorus.

As P_2O_3 appears to be thermodynamically unstable with respect to red phosphorus and PO_2, it does not have a stable constant-boiling composition, but the PO_2 and P_2O_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 P_2O_3, PO_2, and P_2O_5 molecules are important intermediates or whether the complex molecules break down directly to PO gas. In view of the compact nature of P_4O_6 and P_4O_{10} and the high stability of PO gas, one might guess that the decomposition would proceed from P_4O_{10} through P_4O_8 to P_4O_6 by loss of oxygen molecules and then would proceed directly from P_4O_6 to PO upon breakdown of the phosphorus framework. However, the complex molecules are extremely stable and temperatures as high as 3000°K. would be required to convert P_4O_{10} to P_4O_6 at atmospheric pressure. Under those conditions, PO would probably also be quite important and P_4O_{10} would probably go all the way to PO and O_2 when it started decomposing. The D_0 values given for the phosphorus compounds are very uncertain, because the D_0 of 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 ${}^2\pi_r$ 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°K. and of As_4O_6 up to 1100°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°K. Vapor-density measurements (270) show that SO_2 is undecomposed at 2223°K. and that SeO_2 is undecomposed at 773°K. Evans (132) has demonstrated the partial decomposition of SeO_2 gas at 823°K. by the appearance of Se_2 bands which can be suppressed even at 1300°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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