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THE THERMODYNAMIC PROPERTIES OF THE OXIDES

by

Leo Brewer

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Carbide & Carbon Chemicals Corp. (Y-12 Area)	27-30
Columbia University (Failla)	31
General Electric Company	32-35
Hanford Directed Operations	36-42
Iowa State College	43
Kellex Corporation	44-45
Los Alamos	46-48
Massachusetts Institute of Technology	49
Monsanto Chemical Company, Dayton	50-51
National Bureau of Standards	52-53
Naval Radiological Defense Laboratory	54
NEPA	55
New York Directed Operations	56-57
Oak Ridge National Laboratory	58-69
Patent Advisor, Washington	70
Technical Information Division, ORDO	71-85
UCLA Medical Research Laboratory (Warren)	86
University of California Radiation Laboratory	87-91
University of Rochester	92-93
Western Reserve University (Friedell)	94
Chicago Directed Operations	95
Dr. Leo Brewer	96-155
Declassification Procedure	
Declassification Officer	156-159
Publications Officer	160
Patent Department	161-162
E. O. Lawrence	163
Area Manager	164
Information Division	165
Total	165

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Table of Contents

May 14, 1948

ABSTRACT

The thermodynamic phase relations and thermodynamic properties of the oxides are tabulated.

THE THERMODYNAMIC PROPERTIES OF THE OXIDES

By: Leo Brewer

To be declassified and made available to others for use in research, development, or manufacturing work.

May 14, 1948

THE THERMODYNAMIC PROPERTIES OF THE OXIDES

Leo Brewer

Introduction

This report is part of a more complete report which will cover the thermodynamic and physical properties of the oxides of all the elements. Since it will be some time before the remainder of the report will be completed, the portion of the report covering the thermodynamic properties of the oxides of the elements of the left hand side of the periodic table up to the iron group will be given at this time.

This portion of the report will cover the thermodynamic phase relations and the thermodynamic properties of the elements covered. It is hoped in the near future to extend this coverage to the remaining elements. A second section of the final report will cover the melting point and vaporization data and a discussion of the gaseous species present at high temperatures under various conditions as well as a discussion of the general high temperature chemistry of the oxide systems.

The work described in this paper was done under the auspices of the Atomic Energy Commission.

References to the Thermodynamic Properties of the Oxides

Three thermodynamic quantities are given in Table 1, ΔH_{298}, the heat of formation at 298°K., ΔS_{298}, the entropy of formation at 298°K., and ΔF_{298}, the free energy of formation at 298°K. ΔF_{298} was calculated by means of the relationship $\Delta F_T = \Delta H_T - \Delta S_T T$. ΔS_{298} was calculated from the entropy of the oxide and the entropies of the elements. The entropies of the elements were obtained from Brewer(31).

The discussion of the thermodynamic properties will, in general, follow the following order: (I) The known important oxide phases will be listed as reported in Strukturbericht(69). (II) The references to the heats of formation will be given together with a discussion of the reliability of the data in many cases. (III) References for entropy values will be given only for very recent determinations which are not given by Kelley(2). In some cases, the entropy values given in Table 1 have been estimated by the author. Such estimated values are given in parentheses in the table and no references are given for them. Most of the experimental values were obtained from Kelley(2) and when no note has been made of the source of an experimental entropy value, it was obtained from Kelley(2). A considerable number of entropy values were obtained from Latimer(3) which are noted in the references. (IV) Where high temperature equilibria data are available, they are discussed in relation to the thermodynamic data chosen in Table 1.

Alkali Metal Oxides - All of the alkali metals have oxides of the M_2O type, all of which have the CaF_2 type crystal structure, except Cs_2O which has the $CdCl_2$ type crystal structure. All the alkali metals form the peroxide M_2O_2 which has been shown to have a structure somewhat similar to the Hg_2Cl_2 structure in the cases of Li and Na. One might guess that K_2O_2 and Rb_2O_2 might become even more like Hg_2Cl_2 if the O_2 group is to be considered analogous to the Hg_2 group since the larger alkali metal ions would correspond more closely in size to Cl than do Li and Na. K, Rb, and Cs have M_2O_3 peroxides which are face centered cubic anti-Th_3P_4 crystal type according to Helms and Klemm(97) in the cases of Rb and Cs and peroxides of the type MO_2 which have been shown to have the CaC_2 type crystal structure. Neuman(70) reports a transition of KO_2 at 75.5°C to an unknown low temperature form. NaO_2 is apparently unstable at room temperature at one atm. oxygen. Schechter, Sisler, and Kleinberg(145) have some evidence that it can be prepared at very low temperatures. In addition to the normal oxides and the peroxides, sub-oxides have been reported for the alkali metals. For example, Rengade(63) reports the existance of compounds Cs_7O, Cs_4O and Cs_3O melting peritectically at 50°, 10° and 170°C., resectively, and the compound Cs_7O_2 melting at 3°C without disproportionation. However, no X-ray analyses have been made of these compounds. In view of the low temperatures required, it should be simple to carry out a complete investigation of these systems to clarify the situation.

Bichowsky and Rossini(4) give the heats of formation of Li_2O, LiO, Na_2O, NaO, K_2O, K_2O_3, KO_2, Rb_2O, Cs_2O, and CsO_2 from heats of solution. They also give $\Delta H_{298}=-101.6$ kcals. for the compound Na_3O. The value determined by Forcrand(5) was used for KO. The values given for RbO, Rb_2O_3, and RbO_2 were estimated by Forcrand(6) by comparison with other peroxides of the alkali metals and are rather uncertain. The values given for CsO and Cs_2O_3 were based on heats of solution determined by Forcrand(6). All the data for the alkali metal oxides and especially for the peroxides are rather uncertain. Uncertainties of ± 5 kcalories should be applied to most of the heats of formation of the peroxides.

Entropies of formation of the peroxides are not given, but they will be much less negative per atom of oxygen than the entropies of formation of the normal oxides. For example, the entropy of formation of the MO peroxides will probably be -27 e.u. per MO. The higher peroxides have even less negative entropies of formation.

Rengade(1) reports that the M_2O oxides disproportionate to M gas and MO solid. In the most favorable case for such a reaction, we calculate for $Cs_2O(s) = Cs(g) + CsO(s)$, $K =$ about 10^{-10} atmospheres at 634° K., which would indicate an extremely low reaction at this temperature. If his report of a reaction at this temperature is correct, there must be extensive solid solution formation between Cs_2O and CsO. Likewise the work of Rengade(1) and Centnerszwer and Blumenthal(1) on the dissociation pressures of the liquid peroxides give greater dissociation pressures than calculated from the heats of formations and reasonable entropies if the phases are assumed to to be immiscible. Calculations taking into account solutions are difficult because the phase relations of the oxides have not been determined and the phases in equilibrium during the decompositions are not well established. Kazarnovskii and Raikhshtein(131) have determined the equilibrium O_2 partial pressure due to decomposition of KO_2 below its melting point. Their results indicate that K_2O_3 is thermodynamically unstable and their data are in good agreement with the heats and entropies of formation given in Table 1.

Alkaline Earths - Except for BeO which has the ZnO wurtzite crystal structure, all the normal MO alkaline earths have the NaCl crystal structure. Except for Be, 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(103) discuss 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(7) was accepted as probably being more correct than the earlier lower values. The heat of formation of MgO was determined by Shomate and Huffman(8). The heats of formation of CaO, CaO_2, SrO, SrO_2, and BaO were obtained from Bichowsky and Rossini(4). 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(64) who found the heat of formation of MgO varied as much as a kilocalorie depending upon the previous heat treatment. The heat of formation of RaO was estimated.

The entropies of formation of CaO_2 and SrO_2 were estimated by Latimer(3). The entropy of BaO_2 comes from Lewis and Randall(71).

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 one atmosphere of oxygen in equilibrium with SrO_2 and SrO at 600°K while 488°K is observed. If there is no interaction between the phases, the difference must be due to an error of one kcalorie in the heat of formation of 1/2 SrO_2 or 2 e.u. in the entropy which are well within the experimental uncertainties. The oxygen partial pressures over BaO_2 measured by Hildebrand(72) 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 are reviewed by Kelley and Anderson(93). Using Bichowsky and Rossini's(4) heats of formation of the carbonates for Ca, Sr, and Ba, one obtains the following comparison of the ΔH_{298} values showing satisfactory agreement.

	From Table 1	From Carbonate Dissociation
MgO	-143.8 ± 0.5	-144.1
CaO	-151.7 ± 0.5	-152.8
SrO	-140.8 ± 1	-141.4
BaO	-133.0 ± 2	-132.0

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. Baur and Brunner(65) studied the Al-Al_2O_3 phase diagram and report a compound Al_8O_9 melting at 2323°K. with a eutectic between Al_8O_9 and Al_2O_3 at 2293°K. Brewer, Searcy, and McCullough(132) could find no new solid phase upon X-ray examination at room temperature of fused mixtures of Al + Al_2O_3. A high temperature X-ray study would be of great interest. All of the elements of this group form M_2O_3 oxides. B_2O_3 usually occurs as a glass, although Taylor and Cole(24) claim to have prepared crystalline B_2O_3. Al_2O_3 is known in at least three different crystalline forms, but the only stable form at all temperatures is the rhombohedral α-corundum form. However, the hexagonal β-Al_2O_3 can be stabilized by addition of impurities such as alkali metal oxides which form $Na_2O \cdot 11Al_2O_3$. The cubic γ-Al_2O_3 which is often formed upon oxidation of aluminum or dehydration of hydrous aluminum oxide has a structure very similar to the spinal structure of Fe_3O_4 with vacant spaces in the Al lattice. Upon heating, it 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 600°C. for La_2O_3 to 1800°C for Sm_2O_3. Goldschmidt, Ulrich, Barth and Lunde(66) and more recently Iandelli(80) have shown that as one goes from La to Sm, 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 once formed.

Oxides prepared at intermediate temperatures have a pseudo-trigonal form of unknown structure according to Goldschmidt(66). Iandelli also obtains this intermediate structure known as the B-rare earth structure but claims 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 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 350-600°C for La_2O_3 to 500-1300°C for Eu_2O_3. Thus the C form of Sm_2O_3 is prepared by ignition of the nitrate below 800°C or of the carbonate below 1100°C. The B form is prepared between 800-1800°C, and the A form is prepared above 1800°C. Lohberg(67) 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 450°C for 20 hours and $Nd(NO_3)_3$ at 700° C for 3 hours. He found that after 3 hours at 1000°C., 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 NO_3^- 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 La 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(68) has shown that

Ce_2O_2S still has the hexagonal A rare earth form even though the S anion has been inserted.

Higher oxides are known in the cases of CeO_2, Pr_6O_{11}, and Tb_4O_7, all of which have the CaF_2 crystal structure. Nd also forms a higher oxide. The tetravalent oxides with the fluorite structure form a rather wide solid solution range with the sesqui-oxides since the cubic Mn_2O_3 or C rare earth structure is the CaF_2 structure with some of the F sites vacant. Gruen and Katz(133) have by the action of atomic oxygen extended the solid solution range up to PrO_2 and TbO_2. These are probably metastable with respect to one atmosphere oxygen. One can expect in some cases to extend the solid solution range perhaps even as high as $MO_{2.2}$ by leaving vacancies in some of the metal sites of the CaF_2 structure.

The heat of formation of B_2O_3 glass was determined by Todd and Miller(17) and recalculated by Rossini(122). The heat of formation of Al_2O_3 was determined by Synder and Seltz(18) and the high temperature heat contents and entropies of Al_2O_3 are given by Ginnings and Corruccini(147). The heats of formation of Sc_2O_3 and Y_2O_3 were estimated. The heats of formation of La_2O_3, Pr_2O_3, Pr_6O_{11}, Nd_2O_3 and Sm_2O_3 were obtained by correcting Bichowsky and Rossini's(4) values to conform with the new heats of formation of the aqueous ions which were determined by Bommer and Hohmann(19). The heat of formation of Ce_2O_3 was estimated and Hirsch's(74) value for the heat of formation of CeO_2 was taken instead of smaller values by other workers. Most of the rare earth values are rather uncertain due to uncertainty as to the form of the oxide used and to the wide differences among determinations.

The only equilibria data available to check the thermodynamic data given in Table 1 are the oxygen dissociation pressures over the tetravalent oxides. The checks are not very good as might be expected from the uncertainties in the heats of formation. One calculates an atmosphere of O_2 over CeO_2 at 2000°K while the work of Wartenberg and Gurr(25) and others indicate that reduction does not occur until temperatures much over 2300°K are reached. Also Friedrick and Sittig(73) could reduce CeO_2 with hydrogen only above 1400°K while the calculations indicate reduction at much lower temperatures. Unless rates are extremely slow, these data indicate that the ΔH of formation of $1/2CeO_2$ should be at least 4 kilocalories more negative than given in Table 1, or else the entropies are in error. According to Foex(75), Pr_6O_{11} starts dissociating at 800-900°K. under reduced pressures. One calculates 10^{-6} atm. O_2 at 900°K. for Pr_6O_{11} decomposing to Pr_2O_3 which seems too low to correspond to the experimental data. However, the difference could be due to solid solution formation. It is most likely due to the uncertainty in the heats of formation.

Silicon, Titanium Group - SiO is known in the gaseous state but it disproportionates upon condensation to Si and SiO_2, although Inuzuka(99) claims to have found a SiO crystal form. Brewer, Edwards, and McCullough(134) could not find any new X-ray patterns upon heating Si and SiO_2 together. It may be possible to prepare a metastable SiO by rapid condensation.

The only silicon oxide definitely established in the solid state is SiO_2 which exists in at least six crystal forms. There are four stable forms. α-quartz is stable up to 575°C where there is a rapid transition to β-quartz which is stable up to 867°C.

Above 867°C, β-quartz is thermodynamically unstable with respect to β-tridymite, but the transition is very slow. β-tridymite is thermodynamically stable up to 1470°C where β-cristobalite becomes stable, but the transition is very slow. Due to the slow transitions between the quartz, tridymite, and cristobalite systems, one can obtain α-forms of both tridymite and cristobalite upon cooling, which are thermodynamically unstable with respect to α-quartz. Mosesman and Pitzer(76) review the stability and transitions of the various forms of SiO_2.

The titanium oxygen system shows a greater variety of solid oxidation states than does the silicon system. Ehrlich(77) has made an X-ray study of the Ti-O system. He found Ti dissolved up to 30 atomic percent O at 700-900°C with no phase change. He found a wide range of solid solubility around TiO from $TiO_{0.69}$ to $TiO_{1.25}$ The crystal form was the NaCl type with Ti lattice vacancies on one side and O lattice vacancies on the other side. TiO has a deep chestnut color. Ti_2O_3 which has a deep violet color, was found to have the rhombohedral α-corundum crystal type with only a limited solid solubility of less than $TiO_{1.46}$ to $TiO_{1.56}$. TiO_2 was found to have a solid solution range from $TiO_{2.0}$ to $TiO_{1.9}$ with the rutile structure while another solid solution range was found between $TiO_{1.8}$ and $TiO_{1.7}$ with a distorted rutile structure with oxygen lattice vacancies. Halla(78) claims to have prepared another unstable form of Ti_2O_3 in addition to the form with corundum structure. The structure was not determined. Chretien and Wyss(127) report Ti_3O_4 which is probably metastable similar to V_3O_4. Kelley(79) has studied the hydrogen reduction of TiO_2 and the work indicates the existence of the compound Ti_3O_5 which was also studied by

Shomate(23) and reported to be deep blue by Chretien and Wyss(127). This undoubtedly corresponds to the $TiO_{1.7}$- $TiO_{1.8}$ solid solution found by Ehrlich(77) although the compositions do not check. In addition to the tetragonal rutile form of TiO_2, a tetragonal anatase form and a rhombic 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 400-800°C with 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. Friederick and Sittig(140) review earlier attempts to prepare lower oxides of zirconium and report they obtain a lower oxide residue when ZrN containing oxide is dissolved in acid. They also tried to reduce ZrO_2 with carbon. They finally conclude that no well-defined oxide of zirconium has been prepared. Brewer, Kamm, and McCullough(135) could find no new X-ray patterns upon heating Zr and ZrO_2 together. Fast(96) and de Boer and Fast(128) found that Zr dissolves up to 40 atomic percent of oxygen without forming a new phase. Titanium metal can also dissolve a considerable amount of oxygen without a phase change. Jacobs(114) assumes the oxide coating on zirconium metal to be ZrO and obtains ΔH = -135 kilocalories per mole for the formation of ZrO which would make it stable against disproportionation. However, this is inconsistent with the X-ray evidence.

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 1000°C, the monoclinic forms of ZrO_2 and HfO_2 have a transition to a tetragonal form.

ThO_2 has the CaF_2 structure. Brewer and Zachariasen(142) have studied Th-ThO_2 mixtures. No X-ray evidence was found for a sesquioxide, although ThO with NaCl structure and a_o = 5.24-5.28 Å is found. Baenziger and Rundle(144) found a_c = 5.16 Å for ThO. Th_2O_3 should be unstable by disproportionation and ThO may be unstable thermodynamically at room temperature although it can be formed at high temperatures.

The heats of formation of SiO_2 (quartz), TiO_2 (rutile), and ZrO_2(baddeleyite) were given by Roth, Wolf, and Fritz(22). The heats of formation of HfO_2 and ThO_2 are given by Bichowsky and Rossini(4), but the ThO_2 value is believed to be in error and the value in Table 1 is based on a comparison of $ThCl_4$, UCl_4 and UO_2 heats of formation by Brewer(143). No direct determinations of the heats of formation of the lower titanium oxides are available. Nasu(45) tried to determine the equilibrium H_2O/H_2 ratio for the reduction of TiO_2 in an iron tube. The data show a distinct break and as Kelley(79) has pointed out, the high temperature data corresponds exactly to the H_2O/H_2 ratio for the FeO/Fe system as given by Darken and Gurry(108). However, 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 Ti_3O_5/Ti_2O_3 systems. In any case, these data can be used to set limits to the heats of formation of Ti_3O_5 and Ti_2O_3. The weight losses that Nasu(45) gives indicate reduction to $Ti_2O_{3.05}$. If we use the H_2O/H_2 ratio at 1022°K assuming it to apply to the reaction $3TiO_2 + H_2 = Ti_3O_5 + H_2O$, we obtain ΔH_{298}=-603k-calories for Ti_3O_5 using $\Delta H298$ = -225 kilocalories for TiO_2, the entropies given by Shomate,(23) and the high temperature heat capacity data given by Naylor(81). If one carries out the same procedure for the reaction $2Ti_3O_5 + H_2 = 3Ti_2O_3 + H_2O$ using $\Delta H_{298} = -603$ kilocalories for Ti_3O_5, one obtains $\Delta H_{298} = -380$ kilocalories for Ti_2O_3. To make these values consistent with Kelley's(79) observation that there is a break in the H_2O/H_2 ratio at Ti_3O_5, we finally choose $\Delta H_{298} = -605 \pm 10$ kilocalories for Ti_3O_5 and $\Delta H_{298} = -381 \pm 6$ kilocalories for Ti_2O_3. A value of $\Delta H_{298} = -127 \pm 3$ kilocalories is estimated for TiO on the assumption that it is just barely stable towards disproportionation at room temperature. Chretien and Wyss(127) report TiO unreduced by Mg. This is probably due to vaporization of the Mg metal.

The entropies of TiO, Ti_2O_3, and Ti_3O_5 were determined by Shomate.(23) The entropy of rutile TiO_2 was determined by Shomate.(118) The entropy of ZrO_2 was determined by Kelley.(48) The entropies of HfO_2 and ThO_2 were estimated by Latimer.(3)

Vanadium Group - Hoschek and Klemm(82) and Klemm and Grimm(83) have studied the V-O system. They find evidence for considerable solubility of oxygen in the vanadium metal lattice at high temperatures which may be as high as $VO_{0.4}$ at 1450-1600°C. Between $VO_{0.9}$ and $VO_{1.3}$, they found a solid solution range with NaCl crystal structure which was 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 phases is V_2O_3 with the α-corundum crystal structure. Between the compositions

$VO_{1.65}$ and $VO_{1.75}$ they find a compound which apparently corresponds to the Ti_3O_5 of the titanium system. Between $VO_{1.8}$ and $VO_{2.0}$ they find 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(82) 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(120) who obtained the same unknown structure upon reduction of V_2O_5 by SO_2 claim that it analyzes exactly VO_2, and they believe it to be an allotropic modification.

We have 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 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 625°C and above since the unknown form is converted to the rutile form upon heating. After fourteen days at 605°C, 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(82) could prepare the unknown form by crystallization from a melt at a temperature as high as 660°C 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 oxygen partial pressure in the system. The oxygen pressure in equilibrium with V_2O_5 and the new compound is 3.5×10^{-6} atm. at 600°C. The oxygen pressure required for further reduction to VO_2(rutile) would then be even smaller. Thus it would require temperature greater than 600°C 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 two. Aebi(146) has very recently determined the structure of this unknown oxide and has found it to be monoclinic and to have the formula $V_{12}O_{26}$. This confirms the above interpretation of the SO_2 reduction work.

Above $V_{12}O_{26}$, V_2O_5 is the only other vanadium oxide. Foex(119) reports a transition for V_2O_5 at 172°K with a 2% linear contraction and a 100,000 fold increase in electrical conductivity. Cook(121) determined the high temperature heat contents of V_2O_3, VO_2 and V_2O_5 and reports a transition for VO_2 at 345°K. Hoschek and Klemm(82) found a magnetic transition at this temperature and they also determined the X-ray pattern above and below this transition and reported no change. However, Templeton(136) reports 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(28) determined the heats of combustion of V, V_2O_3, and V_2O_4 to V_2O_5. All previous work on these quantities are very unreliable and need not be given any consideration. The various equilibria determinations involving the V_2O_3/V_2O_4 and V_2O_4/V_2O_5 system are also unreliable except for the very excellent work by Flood and Kleppa(120) on the SO_2 reduction of V_2O_5 to $V_{12}O_{26}$. Recalulation of their results yields $\Delta H_{298} = -2118.8$ kilocalories and $\Delta S_{298} = -549.2$ e.u. for $V_{12}O_{26}$. Their results are in agreement with the heats of formation obtained from the data of Siemonsen and Ulich(28) and the stability of $V_{12}O_{26}$. Bichowsky and Rossini(4) give 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, we can set a limit to its heat of formation. ΔH_{298} of V_3O_5 will be more negative than -467 kilocalories.

Kobayaski(46) has studied the reduction by H_2 of V_2O_3 to VO and of VO to V metal. His data yield $\Delta H_{298} = -113$ kilocalories for V_xO where V_xO is the portion of the VO solid solution range involved in the equilibria. In the V_2O_3 reduction work, 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 his data to check the heats of formation of either VO or V_2O_3 that are given in Table 1.

Grube, Kubaschewski, and Zwiauer(84) and Brauer(100) have studied the Cb oxides by hydrogen reduction and by oxide studies. Their work indicates that CbO, CbO_2 and Cb_2O_5 are the stable oxides. They could not prepare a Cb_2O_3 phase. CbO has a NaCl cubic structure with lattice vacancies. CbO_2 has no detectable solid solution range and has a crystal structure closely related to the tetragonal rutile structure, probably the MoO_2 structure. Cb_2O_5 apparently has three forms. The low temperature form is prepared at 500-900°C and has the Ta_2O_5 crystal structure. Another form is prepared between 1000-1100°C and a high temperature form is prepared above 1100°C with all heatings in an oxygen atmosphere. There is no reversal of structure upon cooling. With longer heating times, the conversion can be made to take place at lower temperatures. Cb_2O_5 has a solid solution range from $CbO_{2.5}$ to $CbO_{2.4}$. A reported Cb_2O phase has been shown by Brauer(100) to be Cb_2N. Cb metal forms a solid solution up to almost 5 atomic percent oxygen. Zachariasen(85) has shown that Cb_2O_5 and Ta_2O_5 have almost identical orthorhombic pseudo-hexagonal crystal structures. Brewer, Edwards, McCullough and Templeton(141) studied the lower oxides of Ta. Mixtures of Ta and Ta_2O_5 which had been heated to 1600°C gave X-ray evidence for TaO_2. The structure was not worked out but is probably closely related to the monoclinic ZrO_2 and WO_2 structures. Andrews(95) found a solid solution range in Ta metal up to 2.3 atomic percent oxygen.

The heat of formation of Cb_2O_5 was determined by Becker and Roth(27). The heat of formation of Ta_2O_5 was given by Roth, Wolf and Fritz(22). Grube, Kubaschewski and Zwiauer(84) give data on the reduction of Cb_2O_5 by hydrogen and by heating in inert gas. The inert gas must have had some hydrogen or other reducing gas impurity since the degree of reduction was not consistent with the hydrogen reduction experiments. The hydrogen reduction experiments indicate that ΔH_{298} of CbO_2 is about -192 ± 4 kilocalories per mole. Taking this value for CbO_2, the data indicate that ΔH_{298} of CbO is more positive than -102 kilocalories and more negative than -98 kilocalories. $\Delta H = -100 \pm 2$ kilocalories is accepted for CbO.

Chromium Group - Cr forms an oxide CrO_3 with rhombic crystal structure and Cr_2O_3 with the α-corundum crystal structure. In addition Blanc(86) claims to have prepared two forms of Cr_2O_3, one of which goes to the other upon heating at 700°C under reduced pressures. Blanc(86) and Ryss and Selyanskaya(87) claim that there are several intermediate oxide phases between CrO_3 and Cr_2O_3. It is not likely that all of the reported compounds correspond to equilibrium phases. Michel and Benard(98) prepared CrO_2 with the tetragonal rutile type structure and they report that Cr_2O_3 can form a solid solution up to $CrO_{1.56}$ with a two phase region up to CrO_2. Vasonin(130) reports that CrO_3 melts at 460°K and starts giving off oxygen at 540°K with precipitation of a solid lower oxide. The reaction is complete at 620°K and Vasonin claims the solid formed is Cr_2O_5. X-ray patterns indicated a phase which was not Cr_2O_3 nor CrO_3. Further heating to 707-784°K causes decomposition to Cr_2O_3. Wartenberg and Reusch(21) report that Cr_2O_3 partially decomposes at 2260°C and 0.2 atm. O_2 partial pressure. This may be due to the formation of Cr_3O_4 but is probably due to solid solution formation. There have been some claims of the existence of a CrO phase, but Kelley, Boericke, Moore, Huffman and Bangert(59) have made a careful study of the Cr-O system below Cr_2O_3 and they could find no evidence for the formation of any phases below Cr_2O_3. Pascal(117) also confirms this. Molten Cr metal dissolves 6.5 atomic percent oxygen at 1700°C.

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(59) and Roth and Wolf(53).

The value for CrO_3 was obtained from the value given by Roth and Wolf for the heat of dissociation of CrO_3 to Cr_2O_3 and oxygen.

The H_2O/H_2 ratios obtained by Grube and Flad(60), Wartenberg and Aoyama(61), and Aoyama and Kanda(62) for the hydrogen reduction of Cr_2O_3 to Cr metal agree rather well with the ratios calculated from the heat of formation chosen here for Cr_2O_3 and the entropies of the reactants.

Hagg and Magneli(51) have made an X-ray study of the molybdenum oxides in the range MoO_2 to MoO_3. Above 1275°K. only MoO_2 and MoO_3 phases were found, but below 1275°K. two forms of $Mo_{18}O_{52}$ were found, one being prepared below 925°K. and one above. A Mo_4O_{11} phase and one other phase were also found in addition to MoO_2 and MoO_3. MoO_2 has the tetragonal rutile type structure according to Strukturbericht(69), but Hagg and Magneli(51) show that MoO_2 is monoclinic instead of tetragonal. MoO_3 has a rhombic type structure. Hagg and Magneli(51) also studied the tungsten oxides between WO_2 and WO_3. They find WO_2 to be isomorphous with the monoclinic MoO_2 instead of the tetragonal form reported in Strukturbericht(69). WO_3 has a rhombic structure. Hagg and Magneli(51) report that WO_3 tends to loose oxygen to form a solid solution with slightly less oxygen. A compound at $WO_{2.90}$ is also reported which has a narrow range of homogeneity. Another phase of approximate composition $WO_{2.75}$ was also found. Glemser and Sauer(102) have also studied the phases between WO_2 and WO_3. They report that the solid solution $WO_{2.95-3.0}$ has the ReO_3 type structure. A complex phase was found at $WO_{2.88-2.92}$ and another phase of low symmetry was found at $WO_{2.65-2.76}$ which was tentatively taken as W_4O_{11}. The WO_2 phase occurred at $WO_{2.00-2.03}$. The agreement between the work of Glemser and Sauer(102) and Hagg and Magneli(51) is very close. The compound which is reported as W_2O_5 in the literature evidently should be W_4O_{11}.

Hanawalt, Rinn and Frevel(123) and Phelps, Gulbransen and Hickman(124) have claimed to have found Mo_2O_3 but Hagg and Magneli(51) could not find any oxides below MoO_2 and Hickman and Gulbransen(125) have recently reported that they and Rinn find their earlier work to be in error. Also Brewer, Searcy and McCullough(126) have made x-ray studies of Mo-MoO_2 mixtures and have found no oxides below MoO_2. At high temperatures it appears that MoO_2 and MoO_3 are the only stable molybdenum oxide phases. Brewer, Edwards, McCullough and Templeton(141) could find no x-ray evidence for oxides below WO_2, but the oxides between WO_2 and WO_3, such as W_4O_{11}, are probably stable up to high temperatures.

Bichowsky and Rossini(4) give the heat of formation of MoO_3 which is rather uncertain and they also give a heat of formation of MoO_2 which agrees closely with the value accepted which was determined by Tonosaki(49) from hydrogen reduction equilibria data. The heat of formation given for WO_2 was obtained from Bichowsky and Rossini(4). Thompson(16) has recalculated the hydrogen reduction data and CO reduction data of Wohler and Gunther, Liempt and Shibata(105) and obtains a good check with the heat given by Bichowski and Rossini(4). However, his calculations do not give a reasonable entropy value since he did not correct the data to be consistent with the entropies. It is very common to find that high temperature equilibria data often have the correct order of magnitude of equilibrium constants or free energies of reaction but have incorrect temperature dependences or heats of reaction. This is due to the many sources of error which can vary with the temperature and 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 looked up and the average temperature taken as the center of the experimental data. This is illustrated by the equations given by Thompson(16) for the reaction $W(s) + 2H_2O \doteq WO_2(s) + 2H_2(g)$.

	Observed $2\log(H_2)/(H_2O)$	Corrected $2\log(H_2)/(H_2O)$
Wohler and Gunther's data	$3808/T - 3.108$	$3440/T - 2.8$
Liempt's data	$2222/T - 1.169$	$4090/T - 2.8$
Shibata's data(105)	$3146/T - 2.322$	$3700/T - 2.8$

The average for the last column is $3740/T - 2.8$ for $2\log(H_2)/(H_2O)$. The much better agreement in the last column than in the first shows that the three determinations agree fairly well as to the free energy of reaction, but different 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 kilocalories compared to -130.5 kilocalories given by Bichowsky and Rossini(4). $\Delta H_{298} = -131 \pm 2$ kilocalories was accepted as the heat of formation of WO_2.

In a similar manner as above the equations given by Thompson(16) 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 Gunther's data	$1000/T - 1.218$	$880/T - 1.1$
Liempt's data	$817/T - 0.88$	$1062/T - 1.1$
Shibata's data	$730/T - 0.807$	$1035/T - 1.1$

The average value for the last column is $\log(H_2)/(H_2O) = 990/T - 1.1$

Using this value and -131 kilocalories for ΔH_{298} of WO_2, one obtains ΔH_{298} = -324 ± 3 kilocalories for W_2O_5. Using the data given by Thompson(16) for $W_2O_5(s) + H_2O(g) = 2WO_3(s) + H_2(g)$ in a similar manner as above, one obtains ΔH_{298} = - 328 ± 5 kilocalories for W_2O_5 using ΔH_{298} = - 195.7 kilocalories for WO_3 from Bichowsky and Rossini(4). This agreement is fairly good and ΔH_{298} = -325 kilocalories has been accepted for W_2O_5, but it should be regarded as somewhat uncertain in view of the x-ray work discussed above that indicates a phase $WO_{2.9}$ between W_2O_5 and WO_3 and in view of the fact that Shibata(105) reports considerable solid solution formation 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 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_4O_{11} 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 $4WO_2 + 3H_2O(g) = W_4O_{11} + 3H_2(g)$, we would have obtained ΔH_{298}= -711 k-calories for W_4O_{11}. From $W_4O_{11} + H_2O(g) = 4WO_3 + H_2(g)$, we would have obtained ΔH_{298} = -719 kilocalories for W_4O_{11}. ΔH_{298} = - 715 ± 7 kilocalories may be taken as the best value for W_4O_{11}. A more complete x-ray study in conjunction with the reduction work is necessary here. The heat of formation of WO_3 given by Bichowsky and Rossini(4) appears to be reliable as two different determinations agreed closely.

The entropy of formation of MoO_2 was obtained from the hydrogen reduction data of Tonosaki(49) while the entropies of MoO_3 and WoO_3 were determined by Seltz, Dunkerly and DeWitt(50). The entropies of WO_2 and W_2O_5 were estimated by Latimer(3).

All data given for uranium were obtained from Brewer, Bromley, Gilles and Lofgren(52), who discuss the uranium oxides in detail.

Manganese Group - MnO has the cubic NaCl structure. Mn_2O_3 has the cubic Sc_2O_3 structure which is closely related to the CaF_2 structure. Mn_3O_4 has a tetragonally distorted spinel structure and it can be oxidized to another form of Mn_2O_3 with a similar distorted spinel structure with Mn lattice vacancies. The spinel type Mn_2O_3, which can also be prepared by dehydration of $Mn_2O_3 \cdot H_2O$, is unstable with respect to the normal form of Mn_2O_3. Le Blanc and Wehner(88) have found that MnO prepared in vacuum is especially active and can take up oxygen very readily. It takes up oxygen up to $MnO_{1.13}$ with no change in phase. Similarly they found that Mn_3O_4 can take up oxygen forming a solid solution up to $MnO_{1.42}$. Above $MnO_{1.42}$, the unstable distorted spinel type of Mn_2O_3 was formed which had a solid solution range up to $MnO_{1.58}$. Upon decomposition of MnO_2, which has the tetragonal rutile structure, they found formation of cubic Mn_2O_3 at $MnO_{1.95}$ which indicates a very small solid solution range for MnO_2. The MnO_2 lines were still obtained at $MnO_{1.8}$, but at $MnO_{1.6}$ only the cubic Mn_2O_3 structure was observed. It is quite possible that the wide solid solution ranges observed for the MnO phase and the Mn_3O_4 are not the equilibrium ranges and that the observed ranges extend beyond the equilibrium limits due to the low rate of conversion to the stable phase. Further work at higher temperatures and longer heating times is necessary to clarify the equilibrium limits of the solid solution ranges. Baroni(101) has studied the Mn-O system up to 900°C and checks the results of Le Blanc and Wehner(88), that there are no other equilibrium phases between M_2O_3 and MnO_2. However, Glemser (89) 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(90) and Dubois(91) in the same composition range. These phases are undoubtedly metastable. Cole, Wadsley and Walkley(148) reviewed the various compounds reported in the literature. Many contain potassium and hydrogen. Delano(137) has shown that 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(138) has also done work on these compounds which confirms this interpretation. There are no stable oxides above MnO_2.

Southard and Shomate(54) determined the heat of formation of MnO. The heat of formation of Mn_3O_4 was determined by Shomate(56) and the value given here was obtained by correcting his value slightly. His correction of the Bichowsky and Rossini(4) value for the heat of formation of aqueous HI was not considered warranted. In fact, a correction of 410 calories making the heat of formation more negative to correct from 18° to 25°C was made to Bichowsky and Rossini's(4) value instead of the correction in the opposite direction suggested by Shomate. The corrected ΔH_{298} for Mn_3O_4 is -330,920 ± 260 calories from the HI experiments and -331,640±300 calories from the H_2O_2 experiments. ΔH_{298} = - 331,000 ± 300 calories was taken as the average value. The heat of formation of MnO_2 was also determined by Shomate(56) and is believed to be much more reliable than earlier work. Using the corrected Mn_3O_4 value from above, one obtains ΔH_{298} = - 124,250 ± 200 calories as the heat of formation of MnO_2 by averaging the two different determinations of the MnO_2 heat by Shomate(56). Siemonsen(58) reviewed data on the dissociation pressures of MnO_2 and Mn_2O_3. He obtained ΔH = 50.1 kilocalories for $6Mn_2O_3 = 4Mn_3O_4 + O_2$ and ΔH_{298} = 36.2 k-cals. for $4MnO_2 = 2Mn_2O_3 + O_2$. Using the heats of formation of Mn_3O_4 and MnO_2 from above, we obtain ΔH_{298} = -229 kilocalories for Mn_2O_3 from the first reaction and -231 kilocalories from the second reaction. ΔH_{298} = -230 ± 1 kilocalories was taken as the best value.

Kelley and Moore(57) determined the entropy of MnO_2. Kelley(2) gives the entropies of MnO and Mn_3O_4. Siemonsen(58) determined the entropy of Mn_2O_3 from the above dissociation data.

Aoyama and Oka(55) studied the reduction of MnO by hydrogen and 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(54) and Kelley, Naylor and Shomate(92) goes directly through the experimental points of Aoyama and Oka(55) 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.

ReO_3 has a cubic structure somewhat similar to the rhombic WO_3 structure. There are also the oxides Re_2O_7 and ReO_2. ReO_2 and TcO_2 have the monoclinic MoO_2 structure(129) with densities of 11.2 and 6.9, respectively. X-ray work has indicated that there are no stable oxides below ReO_2.

The heats of formation of ReO_3 and Re_2O_7 were determined by Roth and Becker(94), but they must be greatly in error; for they indicate that ReO_3 is very unstable by disproportionation to solid Re_2O_7 and Re metal. The heat of formation of ReO_2 was calculated from the free energy of formation given by Latimer(3).

Iron, Nickel and Cobalt Group - The lowest oxide for this group is the MO oxide with the NaCl type crystal structure. According to Darken and Gurry(108), the FeO phase which is unstable by disproportionation at room temperature becomes stable at 833°K with a composition of $Fe_{0.945}O$. As the temperature is raised the solid solution region becomes wider. 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 solid solution extends to $Fe_{0.835}O$. Bernard(111) has also studied the FeO solid solution in detail. 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 the Fe metal phase is small. According to Sloman(104), the solid solubility of oxygen in α-iron is 0.01 to 0.02 atomic percent at room temperature. Vogel and Martel(106) give data on the high temperature solid solubilities in the various forms of iron, but their solubilities are apparently too high. According to Darken and Gurry(108), the solubility is not over 0.04 atomic percent of oxygen even at 1500°C. Ralston(107) and Taylor and Chipman(110) give data on the solubility of FeO in liquid iron. The solubility is 0.5 atomic percent of oxygen at the eutectic point of 1524°C, 1.05 atomic percent at 1600°C, and 2.1 atomic percent at 1800°C.

The extent of solubility of CoO in Co is not known although it is small enough so that no change in the Co lattice constant can be observed at 500°C upon addition of CoO. The extent of the solid solution range of the CoO phase similar to that of the FeO phase is not known although apparently considerable amounts of oxygen can be taken up by CoO without a phase change.

According to Hensel and Scott(109), molten Ni dissolves 0.785 atomic percent of oxygen at the eutectic temperature of 1435°C. 1.08 atomic percent are dissolved at 1465°, 1.55 atomic percent of oxygen are dissolved at 1550°C, and 1.93 atomic percent of oxygen are dissolved in molten nickel at 1650°C. The solubility range of the NiO phase is not known although considerable amounts of oxygen can be taken up by NiO without a phase change. Bogatskii(115) claims that heating $Ni(NO_3)_2$ in air at temperatures from 500°C to 1000°C will produce compositions from NiO_2 to NiO with the same cubic crystal structure except that the lower temperature preparations of higher oxygen composition have larger lattice constants. Bennett, Cairns, and Ott(116) report a different cubic form (not face centered) of NiO when prepared below 110°C.

Of the higher oxides, Fe_3O_4 and Co_3O_4 are known with the spinel type crystal structure. Fe_2O_3 is known in the rhombohedral

α-corundum form and in a cubic form which can be obtained by oxidation of Fe_3O_4 and has the same spinel type structure with vacancies in the Fe lattice. There is definitely some solid solution formation between Fe_3O_4 and α-Fe_2O_3, but the extent has not been clarified. It is complicated by the fact that a complete solid solution exists between Fe_3O_4 and the metastable cubic γ-Fe_2O_3, and unless rates of conversion are rapid, equilibrium conditions will not be maintained between the Fe_3O_4 and α-Fe_2O_3. White(112) and Corey(113) review the preparations 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 α-corundum structure have been reported for samples of CoO heated in oxygen. Baroni(101) claims to have prepared Co_2O_3 with a structure which is probably tetragonal. He also claims that CoO will react with 50-100 atmospheres O_2 at 100-800°C to form a surface layer of CoO_2 which could be detected by electron diffraction, but no CoO_2 can be prepared in the bulk. No nickel oxides above NiO have been definitely prepared or 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 a surface film. For example, Selwood(139) reports that NiO is formed if deposited on a MgO surface while Ni_2O_3 is formed on a Al_2O_3 surface and NiO_2 is formed on a TiO_2 surface. All evidences indicate that these higher oxides are unstable as pure phases.

TABLE 1

Thermodynamic and Physical Properties of the Oxides

The heats and free energies of formation are given in k-calories per atom of oxygen. The entropy of formation is given in calories per degree per atom of oxygen.

Oxide	ΔF_{298}	ΔH_{298}	ΔS_{298}	T_M °K	$T_{10^{-3}\text{atm}}$	T_1 °K
Li_2O	-134.	-142.3±2	(-28.)	2000	volatile at 1200 °K as Li_2O gas	
$1/2Li_2O_2$		-76.		d.470 °K	at 1 atm O_2	
Na_2O	-90.	-99.5±.2	-31.9	1000	vaporizes by dissociation to Na and O_2 gases	
$1/2Na_2O_2$		-59.6		733	d.919, 1 atm O_2	
K_2O	-77.	-86.2±3	(-32.)		dissociates to K and O_2 gases	
$1/2K_2O_2$	-46.	-54.	(-27.)	763	the peroxides decompose giving off O_2 gas	
$1/3K_2O_3$		-42.		703		
$1/2KO_2$		-34.		653		
Rb_2O	-73.	-82.9±3	(-32.)		dissociates to Rb and O_2 gases	
$1/2Rb_2O_2$		-54.		840	77mmO_2	1156°
$1/3Rb_2O_3$		-42.		762	163mmO_2	1043°
$1/2RbO_2$		-34.		685	225mmO_2	1033°
Cs_2O	-73.	-82.1±3	(-32.)	763	dissociates to Cs and O_2 gases	
$1/2Cs_2O_3$		-60.		867	73mmO_2	1187°

Oxide	ΔF_{298}	ΔH_{298}	ΔS_{298}	T_M °K	$T_{10^{-3}\,atm}$	T_1 °K
$1/3Cs_2O_3$		-47		775	108mmO_2	1125°
$1/2CsO_2$		-41		705	225mmO_2	1153°
BeO	-140.	-147±5	-23.4	2795±30	2900±50	4300±100
MgO	-136.	-143.8±.5	-25.7	3075±30	vaporizes by dissociation to Mg and O gases	
$1/2MgO_2$				d.361 at	1 atm.O_2 to $MgO_2.3MgO$	
CaO	-144.3	-151.7±.5	-25.0	2845±20	vaporizes by dissociation to Ca and O gases	
$1/2CaO_2$	-71.0	-78.2	-23.	d. 548 °K	in 1 atm. O_2	
SrO	-133.	-140.8±1	-24.8	2730±20	2400±100	3400±200
$1/2SrO_2$	-70.	-76.6±2	-23	d. 488,	1 atm. O_2	
BaO	-126.	-133±2	-22.8	2196±10	2100±100	2900±200
$1/2BaO_2$	-70.	-76.2±3	-20	1070±50	d.1110 ,	1 atm. O_2
RaO	-123.	(-130)±4	(-23.)			
$1/3B_2O_3$ gls.	-104.	-112.8±.3	(-26)	567		>1770
$1/3Al_2O_3$	-125.6	-133.0±.1	-24.9	2300±20	2395	3250
$1/3Sc_2O_3$	-140.	-147.±3	(-24.)			
$1/3Y_2O_3$	-143.	(-150)±2	(-23)	2690±100		4570
$1/3La_2O_3$	-145.	-152.±2	(-22)	2590±20		4470
$1/3Ce_2O_3$	-142.	-149.±2	(-22)			
$1/2CeO_2$	-116.	-123.±4	(-22)	3000±200	under O_2 pressure	
$1/3Pr_2O_3$	-141.	-148.±2	(-22)			
1/11 Pr_6O_{11}	-120.	-127.±4	(-22)	d. losing O_2		
1/3 Nd_2O_3	-140.	-147.±2	(-22)			
$1/3Sm_2O_3$	-136.	-143.±4	(-22)			
$1/2SiO_2$	-96.	-104.±2	-26.7	1973		2500
TiO	-120.	(-127)±3	-22.8			

Oxide	ΔF_{298}	ΔH_{298}	ΔS_{298}	T_m °K	$T_{10^{-3}}$ atm	T_1 °K
$1/3Ti_2O_3$	-120.	-127±2	-22.6	2400		3300
$1/5Ti_3O_5$	-114.	-121±2	-22.3			
$1/2TiO_2$	-106.	-112.5±1	-22.1	2130±20		<3270
$1/2ZrO_2$	-122.5	-129.5±.5	-23.3	2988		4570
$1/2HfO_2$	-129.5	-135.8±1	-21.2	3053±20		
ThO		(-150)±10				
$1/2ThO_2$	-148.	-155±10	-21.5	3225±200		4670
VO	-91.	-98±5	(-22)	2323		
$1/3V_2O_3$	-92.	-98.7±2	-21.3	2250		3300
$1/5V_3O_5$		<-93.5				
$1/2VO_2$	-79.	-85.5±1	-21.9	1818±80		3000
$1/26V_{12}O_{26}$	-75.	-81,5±1	-21.2			
$1/5V_2O_5$	-68.	-74.5±1	-21.1	943±3		
CbO		<-96				
$1/2CbO_2$	-89.	-96±2	(-22)			
$1/5Cb_2O_5$	-86.	-92.5± 1	(-22)	1795±100	under O_2 pressure	
$1/2TaO_2$		<-100				
$1/5Ta_2O_5$	-94 .	-100±1	-21.7	2150±100		
$1/3Cr_2O_3$	-83.5	-90,0±.3	-21.8	2710±10		3300
$1/3CrO_3$	-40.	-46.3±1	(-21.)	460	decomposes 540	
$1/2MoO_2$	-60.5	-66±1	-18.3			
$1/11Mo_4O_{11}$					disproportionates	
$1/52Mo_{18}O_{52}$					disproportionates	
$1/3MoO_3$	-53.	-59±2	-20.6	1068	1055	1424
$1/2WO_2$	-59.5	-65.5±1	-20.5	1850	d.1900 to $W+WO_3$ (g)	
$1/11W_4O_{11}$	-59.	-65±1	-20.5			

Oxide	ΔF_{298}	ΔH_{298}	ΔS_{298}	T_M °K	$T_{10^{-3}\text{atm}}$	T_1 °K
$1/2.9WO_{2.9}$		(-65±1)				
$1/3WO_3$	-59.	-65±.1	-20.5		1560	
UO	-130.	-136±5	(-20.)			
$1/2UO_2$	-129.	-135±2	-21.2	3000±200		
$1/2.25UO_{2.25}$		-125±2	(-20)			
$1/2.62UO_{2.62}$		-113.5±2	(-20)			
$1/8U_3O_8$	-106.	-112±2	-20.8	d. 1950, 1 atm. O_2 to $UO_{2.25}$		
$1/3UO_3$	-96.	-102±2	-20.7	d. 925, 1 atm. O_2 to U_3O_8		
MnO	-86.7	-92.0±.1	-17.7	2070		
$1/4Mn_3O_4$	-76.4	-82.8±.1	-21.4	1865±20	WRS	
$1/3Mn_2O_3$	-70.3	-76.7±.3	-21.5	d.		
$1/2MnO_2$	-55.6	-62.1±.1	-22.0	d.		
$1/2ReO_2$		-70±7	(-22)			
$1/3ReO_3$		-27.5±15	(-21)			
$1/7Re_2O_7$		-42.5±5	(-20.5)			
$Fe_{0.95}O$	-59.1	-64.3±.5	-17.6	1644±1		
$1/4Fe_3O_4$	-60.8	-66.8±.1	-20.1	1870±2 under 0.0575 atm. O_2		
$1/3Fe_2O_3$	-59.4	-65.8±.7	-21.7	d.1730 to Fe_3O_4 at 1 atm. O_2		
CoO				2075±20		
$1/4Co_3O_4$						
NiO	-50.8	-57.5±.4	-22.4	2230±20		
RuO_2						
RuO_4						
Rh_2O						
RhO						
Rh_2O_3						

Oxide	ΔF_{298}	ΔH_{298}	ΔS_{298}	T_M °K	$T_{10^{-3}atm}$	T_1 °K
PdO						
PdO_2						
PdO_3						
OsO_2						
OsO_4						
IrO_2						
PtO						
PtO_2						
Cu_2O						
CuO						
Ag_2O						
AgO						
Au_2O						
Au_2O_3						

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