VAPOR-SOLID EQUILIBRIA IN THE
TITANIUM-OXYGEN SYSTEM

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INTRODUCTION

The purpose of this research is to determine the nature of the vaporization processes of the titanium oxides, to measure the equilibria between the solid and the vapor, and to derive the related thermodynamic properties.

The compositions and solid-phase equilibria of the titanium oxide system together with the vaporization processes have been briefly discussed by Brewer (2) in his recent review of the thermodynamic properties of the oxides. In the past, numerous oxides of titanium have been characterized by color, composition, and methods of preparation. However, Ehrlich (13) (14) has shown by X-ray analysis that the entire system can be characterized by a series of solid solutions in several different composition ranges. Bumps, Kessler, and Hansen (3) have restudied the system using principally a micrographic analysis of arc-melted alloys. They obtained a phase diagram for the titanium-oxygen system up to an oxygen content of 36 atomic %, but were unable to extend this to compositions of higher oxygen contents due to experimental difficulties. Examination of as-cast alloys in this higher range did not quite confirm Ehrlich's results but the method was less reliable. An extension of the method of X-ray analysis to high temperatures, if successful, should be more reliable than either of these methods in establishing the nature of the solid oxides

at high temperatures.

A transition in pure titanium occurs at 882.5°K (10), but this transition temperature is increased with increasing oxygen content. The high temperature form, β -titanium, dissolves a maximum of 5 atomic % oxygen at 2010°K, α -titanium dissolves a maximum of 34 atomic % oxygen in the temperature range 1000°K - 1900°K. A new phase discovered by Bumps, Kessler, and Hansen (3), extends over the composition range, $\text{TiO}_{0.66} - 0.75$, and disproportionates at 1198°K to the α -titanium and TiO phases. The TiO phase extends over a wide homogeneity range from $\text{TiO}_{0.7}$ to $\text{TiO}_{1.25}$. The Ti_2O_3 phase has a relatively narrow homogeneity range of $\text{TiO}_{1.46} - 1.56$. Ehrlich (14) reported that the TiO_2 rutile phase extends to $\text{TiO}_{1.90}$ while Bumps, Kessler, and Hansen reported that only the rutile structure appeared in alloys of composition corresponding to $\text{TiO}_{1.84}$. Ehrlich characterized a homogeneous phase in the range, $\text{TiO}_{1.7}$ to $\text{TiO}_{1.8}$, but Bumps, Kessler, and Hansen observed that a mixture of Ti_2O_3 and TiO_2 was present in alloys of the composition range, $\text{TiO}_{1.54} - 1.76$. Rusakov and Zhdanov (35) determined the structure of substance corresponding to Ti_3O_5 which was not observed by Ehrlich. The existence of Ti_3O_5 has been indicated in studies by Wyss (46) and by Kelley, as reported by Brewer (2), on the reduction of TiO_2 by hydrogen. Shomate (36), Naylor (32) and Humphrey (22) have studied the thermodynamic properties of this compound.

Other oxides of titanium may exist but they are probably of minor importance. Halla (17) claims to have prepared an unstable form of Ti_2O_3 ; Chrétien and Wyss (4) found evidence for Ti_3O_4 which might be metastable. Two metastable form of TiO_2 , anatase and brookite, are well known.

Kubaschewski and Dench (27), by determining the equilibrium oxygen content of titanium metal in intimate contact with mixtures of the alkaline earth metals and their oxides, have obtained three points on the partial free energy of oxygen vs. composition diagram at $1000^{\circ}C$. They have drawn the complete curves at $1000^{\circ}C$ and $1200^{\circ}C$ by making use of the phase diagram of Bumps, Kessler, and Hansen (3) and the heats of formation and entropies of the oxides.

It should be possible to obtain values for the pressure of oxygen in the range of compositions below TiO_2 by measuring the equilibrium ratio of H_2O/H_2 over the oxide. However, attempts to study the equilibrium for the reduction of TiO_2 with hydrogen have lead to conflicting results. Nasu (30) measured the equilibrium ratio, H_2O/H_2 , for the reduction in an iron tube. Kelley (2) has pointed out that the high temperature data he obtained correspond exactly to the H_2O/H_2 ratio for the Fe-FeO system. The lower temperature data which might correspond to an equilibrium in the titanium-oxygen system do not agree with calculations made

using the data for the heats of formation as determined by Humphrey (22). Wyss (46), in studying the reduction, found that the reaction started at 1165°K and a final temperature of 1575°K gave Ti_3O_5 . The lack of further reduction to Ti_2O_3 would also indicate a higher stability for Ti_3O_5 than calculated from Humphrey's data. On the other hand, Welch (44) found that TiO_2 at 1400°K is reduced by hydrogen through a wide homogeneity range with no evidence of Ti_3O_5 , but that at 1700°K, a two-phase system corresponding to Ti_3O_5 - $TiO_{1.82}$ was found.

No direct determinations of any of the vapor pressures or dissociation pressures have been published except that of TiO by Gilles and Wheatley, reported by Brewer (2) and Skinner (39c). Starodubtsev and Timokhina (42), using a mass spectrometer, observed Ti^+ , TiO^+ , Ti , TiO and TiO_2 ions and molecules in the vapor of TiO_2 heated in vacuum.

Brewer (2) discusses the criterion for evaluating the vaporization data of oxides. In general, the vapor in equilibrium with a solid oxide consists predominantly either of the dissociation products, atoms of metal and oxygen, or gaseous oxide molecules. Since, in general, the pressure to be expected from the dissociation products can be calculated from thermodynamic data, a distinction can be made between the two cases on the basis of whether the observed vapor pressure is of the same order of magnitude as the calculated pressure or greater. If the vapor pressure

of the undissociated molecule is very much less than the dissociation pressure, it will of course not be observed.

In addition, the solid phase must be characterized as to whether or not it can form an invariant system with the gas. If no invariant system can be formed, the composition of the solid will change continuously as vaporization proceeds, and the vapor pressure will decrease until a two-phase system is formed. On the other hand, if an invariant system can be formed, the vapor composition and the solid composition will remain equal and the pressure will remain constant at constant temperature as vaporization proceeds. In general, if the dissociation pressure is high compared with the vapor pressure of the metal, an invariant system will not be formed in an oxide phase.

As we have seen, the solid phases in the titanium oxide system are characterized by wide homogeneity ranges. Thermodynamic calculations show that in the range of compositions from pure titanium to Ti_2O_3 , the partial pressure of titanium gas must be considerably higher than that of oxygen. The exact relation is of course unknown because of the lack of knowledge of the heats and entropies of solution in the solid solution ranges. However, by assuming stability for the compounds which have been indicated, the approximate limits of the partial pressures may be calculated. If the vapor pressure of $\text{TiO}(\text{g})$ and $\text{TiO}_2(\text{g})$ are low enough to be neglected (that is, the dissociation energies

are so low that the molecules may be considered to be almost completely dissociated at high temperatures and low pressures), we would expect to find an invariant system between the compositions Ti_2O_3 and Ti_3O_5 , since it is in this range that the partial pressures of oxygen and titanium will be in the same ratio as the composition of the solid. The situation is complicated by the possibility, as indicated by the spectroscopic dissociation energy of $TiO(g)$, that $TiO(g)$ will be an important species in the vapor. If the pressures measured over TiO solid are higher than expected for the partial pressure of Ti , then the presence of TiO gas will be confirmed. The possibility arises that for the range of compositions of smaller oxygen content than TiO , a composition will exist at which the partial pressures of Ti and TiO are in such ratio that an invariant system is formed. At the stoichiometric composition TiO , however, the system cannot be invariant because even a small pressure of Ti will cause the vapor to be richer in Ti than the solid. We should again find an invariant system in the neighborhood of Ti_2O_3 or Ti_3O_5 . This situation will not be altered by the presence of TiO_2 gas except that the rate at which the invariant system is approached will be decreased because of the decreased rate of change of the composition of the solid. In fact, the rate of change may be so slow as to be imperceptible within experimental error. In this case, we may find a whole

range of compositions which are effectively invariant with respect to the change in vapor pressure during evaporation.

X-RAY DIFFRACTION STUDIES OF THE SOLID PHASE

In this section we shall discuss the information obtained from X-ray diffraction studies of the oxides of titanium at room temperature and at high temperatures. This study was undertaken in an attempt to clarify the nature of the solid phases at high temperature in relation to the solid-vapor equilibria.

Experimental:

Materials:

The titanium dioxide used in this research was "Baker's Analyzed", C.P. grade, the following analysis being given:

Water Soluble Salts	0.04%
Arsenic	0.000000%
Iron	0.0003%
Lead	0.001%
Zinc	0.002%

The titanium metal used in the preparation of the lower oxides of titanium was from the sample used by C.W. Kothen (26) for low temperature heat capacity measurements. The iodide process titanium had been donated by the New Jersey Zinc Company, Palmerton, Pennsylvania. Its analysis follows:

Manganese	0.0082%
Silicon	0.007%
Aluminum	0.0066%
Nitrogen, Tellurium, Lead, and Copper	0.02%

Intermediate oxides of titanium were prepared by heating together equivalent amounts of titanium and titanium dioxide in molybdenum or tantalum crucibles, the reaction being carried out under high vacuum in the vapor pressure apparatus. Weighed amounts of the oxide and metal were intimately mixed, placed in the crucible and heated to 1500°C in vacuum for one hour. The sample was then removed, reground in a mortar and replaced in the crucible for a further heating period of several hours at 1500°C. Following this treatment, the samples appeared homogeneous, but to insure complete reaction, the regrinding and heating process was repeated. At this temperature the reaction of any of the oxides with the crucible appeared to be negligible, although the dioxide and the sesquioxide attacked tantalum at 1700°C. If any tantalum or molybdenum oxides had been formed they should have been volatile.

Analysis of the oxides were carried out by igniting samples in air at 800°C to 900°C in a platinum crucible. Assuming that the oxides were pure titanium and oxygen, and that the oxidation product was pure titanium dioxide, the following mole ratios of oxygen to titanium were obtained.

Oxide	Batch	Mole Ratio O/Ti
TiO	1	1.075
	2	1.029
Ti ₂ O ₃	1	1.503
	2	1.491
Ti ₃ O ₅	1	1.667

Apparatus:

Heating and temperature control: All heating was done by induction, using G.E. Electronic heaters. The temperature was controlled with a motor driven variometer (41) in series with the work coil, the variometer being operated manually.

All temperatures were measured with a Leeds and Northrup disappearing filament optical pyrometer, the pyrometer being calibrated periodically against a standard tungsten filament lamp calibrated at the National Bureau of Standards. The calibrations were made with the optical window in the line of sight so that only one correction, including both the pyrometer correction and the correction for light absorbed by the optical window, was necessary.

High temperature X-ray diffraction camera: The X-ray diffraction camera used to obtain diffraction patterns of the oxides at high temperatures was designed by Edwards (11). It had since been modified by Skinner (37) and Hoch (20). A schematic diagram appears in Figure 1, showing the arrangement of the furnace elements, induction coil, and sample. A 3/8 inch slot in the water-cooled copper jacket is covered with aluminum foil to protect the film from heat radiation while allowing passage of the diffracted X-ray beam. The film is wrapped in aluminum foil before loading in the film holder to prevent exposure by light. The copper X-radiation before entering the collimator is filtered by passing through nickel foil which also serves as a vacuum seal.

FIG. 1 HIGH TEMPERATURE X-RAY CAMERA

Procedure:

The samples for the high temperature work were prepared by forming a thick paste of the powdered material with General Electric Radio Service Cement and extruding this through a 1/32 inch hole. After drying for a few minutes, the extruded samples were baked out in an electric furnace for a few minutes at 400°C. X-ray powder patterns were taken in the room temperature camera, before and after firing, to insure that the samples were not oxidized during the process. The samples used in the low temperature camera (North American Phillips) were generally small amounts of powder cemented to a thin glass rod. In this manner, a very small amount of material was necessary to obtain the diffraction pattern.

The camera was loaded with film, (which had been degassed by keeping under vacuum for at least three days), the sample put in place in the sample holder within the furnace elements, and the vacuum pumps turned on. Following overnight pumping, liquid nitrogen was put in the trap and the heating begun at a low rate to maintain a vacuum of better than 5×10^{-4} mm. Hg as degassing of the various parts proceeded. When the desired temperature had been reached, the temperature was maintained for an hour to allow equilibrium to be attained. Following this equilibration period, the X-ray was turned on for a one hour exposure during which time the temperature was held constant.

After shutting off the X-ray, the heating was discontinued, the furnace allowed to cool, and the film removed and developed.

The films were measured with a General Electric XRD Film Scale, and visually compared with patterns of the oxide obtained at room temperature.

Results:

Titanium Monoxide: The X-ray diffraction patterns of titanium monoxide at room temperature showed rather broad diffuse lines, no sharp back reflections being obtained. In order to obtain sharp well-defined lines, it is necessary to treat the sample with a long heating period at a temperature near the transition temperature (3). The lattice constant obtained from nine reflections, $a = 4.16 \text{ \AA}$ as compared with $a = 4.171 \text{ \AA}$ reported by Rostoker (34) for pure TiO and $a = 4.162$ for $\text{TiO}_{1.17}$.

The results of the high temperature work are not too conclusive. Five patterns were obtained at high temperature in two series with slightly differing results. The first pattern obtained at 1600°K contained three distinct sets of lines which could be identified as:

(1) TiO , face centered cubic, $a = 4.19 \text{ \AA}$, slightly spotted diffuse lines of medium intensity with no back reflections.

(2) Ta (or possibly β -Ti) body centered cubic, $a = 3.30 \text{ \AA}$, spotted but sharp lines giving well-defined back reflections.

(3) Five lines of weak to medium intensity, not belonging to either of the above systems, but similar in appearance to the Ta lines, could be indexed in the hexagonal system with constants $a = 4.03 \text{ \AA}$ and $c = 6.32 \text{ \AA}$.

The second pattern, obtained after heating the sample at 1600°K for two hours rather than one hour prior to exposure to X-radiation, was identical with the first.

A pattern obtained after quenching the sample (by turning off the power and allowing the sample and furnace elements to cool by radiation) did not have any of the lines of the third set, and the lines of the second set were much weaker, only the alternate strong lines appearing at all. A pattern obtained by long exposure in the low temperature camera showed an extremely faint pattern resembling that obtained in the next series.

At 1250°K the only lines developed were the broad diffuse lines of the TiO , NaCl type pattern.

The next pattern was obtained at 1800°K . In reaching this temperature the tantalum furnace elements were overheated with the result that a slight deposit of tantalum formed on the sample. Again three sets of lines were obtained; a NaCl type pattern of medium intensity for TiO , a strong body centered cubic pattern for Ta, and a third

hexagonal pattern. In this pattern however, while the TiO lines are spotted and diffuse as before, the other lines are all smooth and diffuse, indicating a very small crystal size.

The pattern obtained after quenching is identical and since more accurate diffraction angles could be obtained from the room temperature pattern, it was used in determination of the lattice constants. These were: for TiO , $a = 3.16 \text{ \AA}$; for Ta , $a = 3.28 \text{ \AA}$; and for the hexagonal pattern $a = 3.09$ and $c = 4.91$.

A pattern obtained at 1650°K proved to be identical. An attempt to restore the sample to its original condition by heating below the transition temperature at 1264°K for several hours failed. The pattern obtained following this treatment was identical.

Titanium Sesquioxide: The X-ray diffraction patterns obtained from titanium sesquioxide at room temperature showed clear well-defined lines with sharp back reflections. All of the lines present could be indexed in the rhombohedral system, corundum-type lattice, giving lattice constants $a = 5.42 \text{ \AA}$, $\alpha = 56^\circ 48'$ as compared with the value reported by Skinner (39b), $a = 5.415$, $\alpha = 56^\circ 42'$.

The patterns taken at high temperatures showed very sparsely spotted lines which were difficult to measure or identify. However, it was possible to make fairly accurate measurements on one pattern obtained at 1600°K . Indexing the spots, with the help of the room temperature pattern

already worked out, it was possible to determine the lattice constants, $a = 5.72 \text{ \AA}$ and $\alpha = 54^\circ 55'$. One pattern, obtained at 1250°K , another at 1750°K , and two at 1800°K were entirely similar except for the degree of expansion of the lattice. The patterns at the higher temperatures also contained the diffuse Ta lines obtained previously.

The patterns obtained at room temperature, following quenching, were not distinguishable from the original Ti_2O_3 pattern except for the inclusion of the tantalum lines.

Following this series, the furnace elements in the camera were readjusted to permit attainment of high temperatures without vaporizing tantalum. A sample of Ti_2O_3 was heated until melting just began. Then the power was reduced and the exposure to X-radiation made at about 2100°K . There were very few spots on the developed film, but they occupied positions expected for Ti_2O_3 lines.

The pattern of the quenched sample indicated considerable non-homogeneity, the lines being spotted and rather diffuse. There were six lines which did not belong to the Ti_2O_3 system, but all six did correspond to weak lines found in a pattern to be discussed in the next section.

Titanium Pentoxide: The only structure determination of titanium pentoxide reported has been by Rusakov and Zhdanov (35), who obtained a structure belonging to the rhombic system with constants $a = 3.747 \text{ \AA}$, $b = 9.465 \text{ \AA}$,

and $c = 9.715 \text{ \AA}$. The pattern we obtained for Ti_3O_5 does not correspond to this system, nor apparently to any simple system. While some lines appear at the same angles as in Ti_2O_3 , rutile or anatase, there is no correspondence as would be expected for a mixture. If the material does consist of a two-phase mixture, the phases are certainly other than the normal Ti_2O_3 or rutile. In general appearance, the pattern might be considered as that of a very distorted rutile lattice. This would agree with that reported by Ehrlich (14) for the range $\text{TiO}_{1.70} - 1.80$.

Five patterns were obtained in the high temperature camera, three of which, obtained at 1600°K , were burned in the center but did show the low angle reflection. These three patterns all showed fairly strong rutile lines which were probably due to oxidation of the sample. In addition, there were some very weak spots which did not correspond to any of the known oxides but did match quite well the lines on a pattern obtained from material collected from the vapor of the oxides.

A fourth pattern obtained with a new sample at 1750°K showed no traces of rutile lines at all. The pattern was extremely spotted but the spots could be matched with the lines on the pattern mentioned above.

A fifth pattern was obtained with a partially melted sample using the same procedure as in the case of Ti_2O_3 . This pattern contained very few spots but most of the ones

present matched Ti_3O_5 . The pattern obtained after quenching showed a large number of fairly intense spots which corresponded to lines of the Ti_3O_5 pattern. The pattern obtained in the room temperature camera contained only one line not found in the Ti_3O_5 system, and this corresponded to one in the pattern of the vaporized material.

Since this pattern appears to correspond to a high temperature form of Ti_3O_5 , the lines will be listed here giving the relative intensities and values of $1/d^2$, the reciprocal of the square of the interplanar distances.

1	strong	0.0413
2	very strong	0.0807
3	strong	0.0921
4	strong	0.1301
5	strong	0.1344
6	medium	0.1550
7	medium	0.1640
8	medium	0.1713
9	weak diffuse	0.2053
10	weak	0.2527
11	weak	0.2630
12	strong	0.2802
13	weak	0.3209
14	medium	0.3401
15	medium	0.3645
16	weak	0.3742
17	medium	0.4129

These values were read from a pattern obtained using material collected during the progress of vapor pressure run No. 17 of TiO . Of three patterns, this was the clearest. Of the other two, one was obtained using material collected during the last vapor pressure runs on TiO_2 and one was obtained using material collected during the first stages of evaporation of Ti_3O_5 from a molybdenum crucible. These

other two patterns showed differences which might indicate that this material is not homogeneous, or that the compositions do not correspond exactly. Line 3 is weak, lines 4 and 5 form a single diffuse line, line 6 is missing, line 9 is stronger and sharper, lines 10 and 11 are weaker and closer together, the relative intensities of lines 13 and 14 are reversed and line 15 is stronger. Since no lines appear on the high temperature Ti_3O_5 patterns, it is impossible to make an accurate comparison in this case.

Titanium Dioxide, Rutile: The X-ray diffraction patterns of rutile obtained from three different sources proved to be identical. These were:

1. From a sample of anatase heated to 1400°C for three hours.
2. From the oxidation of Ti_3O_5 to constant weight at 900°C in air.
3. From the oxidation in air of a sample of rutile which had previously been partially reduced by heating near the melting point in vacuum.

The lattice constants obtained from wide angle reflections were $a = 4.58 \text{ \AA}$ and $c = 2.95 \text{ \AA}$, in good agreement with the reported values (39a), $a = 4.57$, and $c = 2.95$.

Two X-ray diffraction patterns obtained at high temperatures confirm results obtained by Dr. Michael Hoch in this laboratory. Up to 1800°K , the pattern is simply that of expanded rutile.

In addition to the patterns of pure rutile mentioned, in the course of the vaporization experiments, a series of patterns of oxygen-deficient rutile were obtained. Patterns were obtained corresponding to the compositions $\text{TiO}_{1.493}$, $\text{TiO}_{1.91}$, $\text{TiO}_{1.847}$, and $\text{TiO}_{1.822}$. The next lowest composition was that of Ti_3O_5 , $\text{TiO}_{1.667}$. As found by Ehrlich (14), these patterns may be characterized as distorted rutile, the degree of distortion depending on the oxygen deficiency.

Discussion of Results:

On the basis of the evidence obtained in this work, the nature of the transitions which occur in the lower oxides and the nature of the solid phases cannot be very well defined.

Titanium Monoxide: The transition observed in TiO at 1264°K does not involve a very large amount of energy, 0.82 kcal./mole , (32) and in view of the simple structure of the low temperature phase, it seems extremely unlikely that the transition involved a structural change. This is confirmed by our high temperature X-ray patterns which show the NaCl type lattice as high as 1800°K . The extra lines appearing in the two series of patterns raise more questions. The smooth, diffuse, body centered cubic lines in the second series can definitely be assigned to tantalum for it is known that the furnace elements were heated near

their melting point. The spotted appearance of the extra cubic lines in the first series cannot be explained. If these are due to β -titanium which has the same structure and very nearly the same lattice constant as tantalum, they naturally would be obscured by the tantalum lines in the second series. The presence of β -titanium would be difficult to account for on the basis of the phase diagram determined by Bumps, Kessler, and Hansen (3) even if the TiO did partially dissociate. The nature of the two hexagonal patterns obtained in the two series is also difficult to account for. In the first series these lines did not appear at room temperature, indicating that the phase transforms into, or is soluble in, TiO at lower temperature. These lines did not appear in the second series at all. The new set has lattice constants similar to α -titanium but higher than those expected for α -titanium saturated with oxygen (34), $a = 2.955 \text{ \AA}$, $c = 4.82 \text{ \AA}$.

It may be that all of these extra lines are due to contaminations and do not represent phase changes or dissociations at all.

Rostoker (34) has measured the change in lattice constant with oxygen content of both α -titanium and TiO. He concludes from a study of the interatomic distances compared with the ionic radii of titanium and oxygen and from the electrical resistivity that the forces in the TiO lattice are metallic rather than ionic or covalent.

Perhaps some light could be shed on this problem and the nature of the transition at 1264°K , which is probably related, if accurate lattice constant measurements could be made over the temperature range of the transitions. However, such a problem is beyond the scope of this research.

Titanium Sesquioxide: No evidence was found for a structural change in titanium sesquioxide at high temperatures, the only changes being in the expansion of the lattice and slight decrease in the lattice angle. The transition near 473°K was found by Naylor (32) to involve a relatively small enthalpy change, 0.215 kcal./mole . Foex and Loriaers (15) studied the transition by observing a sharp drop in the resistivity and an equally abrupt rise in the thermal expansion coefficient. They surmised that the transition was of second order and involved the magnetic properties of the sesquioxide.

The diffuseness of the pattern obtained on quenching the sample that had partially melted, together with the six lines corresponding to what may possibly be a high temperature form of Ti_3O_5 , indicate that at the melting point there may be a tendency to disproportionate to the higher oxide and titanium monoxide gas.

Titanium Pentoxide: Titanium pentoxide does seem to give evidence of undergoing a structural change at high temperature. Naylor reported a rather large enthalpy (32) change of 2.26 kcal./mole at the transition at 450°K .

In addition, he reported a rather peculiar behavior of his samples in that, once the material was heated above the transition, it would no longer reproduce that portion of the enthalpy curve below the transition temperature.

The patterns obtained for the high temperature form of the oxide are not clear enough to indicate definitely what the high temperature form is. Of all the known titanium oxide patterns available for comparison, the one described previously gives the best agreement. This is the only conclusion that can be drawn. There is a definite change in the structure as evidenced in the X-ray diffraction patterns on cooling to room temperature. There remains the possibility that at high temperature the oxide is amorphous and perhaps this extends to some extent to room temperature. Ehrlich (14) noticed on his patterns a decrease in the intensity of the lines and a general increase in the background darkening starting at about the composition $\text{TiO}_{1.80}$.

Titanium Dioxide, Rutile: On the basis of patterns obtained for the compositions TiO_2 , $\text{TiO}_{1.95}$, $\text{TiO}_{1.90}$, $\text{TiO}_{1.80}$, and $\text{TiO}_{1.60}$, Ehrlich (14) reported that the rutile phase extended to about the composition $\text{TiO}_{1.90}$ and that another homogeneity range extended from $\text{TiO}_{1.80}$ to about $\text{TiO}_{1.70}$. He apparently based his estimate for the lower limit of the second phase on the intensity of the Ti_2O_3 , corundum-type, lines in the pattern corresponding to

$\text{TiO}_{1.60}$. Due to the similarity of the patterns obtained for $\text{TiO}_{1.90}$ and $\text{TiO}_{1.80}$, he avoided mention of a two-phase system between these compositions. The series of patterns obtained here give no indication of a two-phase system between TiO_2 and $\text{TiO}_{1.80}$, but rather a continuing series of solid solutions in which the rutile lattice is gradually distorted almost beyond recognition.

VAPOR PRESSURE AND VAPORIZATION PROCESSES

In this section we shall discuss the experimental determination of the vapor pressures and the vaporization processes of the titanium oxides, and derive the related thermodynamic properties.

Experimental:

Materials:

The materials are the same as those described in the previous section; the titanium oxides, TiO , Ti_2O_3 , Ti_3O_5 , and TiO_2 .

Apparatus:

Vapor Pressure Cells: The pyrex vapor pressure cell was essentially the same as described by Edwards, Johnston and Ditmars (9) and is shown schematically in Figure 2. To avoid cutting open the cell after each run, a vacuum seal is formed with a dry "O" ring placed between flat ground surfaces in the position indicated. Satisfactory vacuums of better than 1×10^{-5} mm. Hg, as measured by a hot cathode ionization gauge, could be maintained during a run with this arrangement.

The tripod for supporting the Knudsen cell consisted of three tungsten rods fixed in a holder which was in turn supported by three molybdenum rods running up the length of the cell. These molybdenum rods, besides giving

PYREX GLASS FURNACE
FIGURE 2

stability to the tripod, served to shield the pyrex cell wall from the sample, (preventing the formation of a continuous conducting film) and, supported a magnetically operated shutter.

The metal vapor pressure cell has also been described previously (40). However, several modifications were made to improve its operation as indicated in Figure 3. A VMF-260 oil diffusion pump, pumping through a large liquid nitrogen trap, was connected directly to the main chamber as was the ionization gauge tube. All gaskets were replaced by "O" rings, and the copper to glass seals of the work coil inlets were replaced by the "O" ring and glass plate arrangement described by Hoch (19). A simplified tripod of tungsten rods was used to support the Knudsen cell containing the sample.

Knudsen cells: Knudsen cells were either drawn from .010 inch tantalum or molybdenum sheet by the method described by Ziegler, Speiser and Johnston (47), or were constructed of seamless tubing, the tops and bottoms being drawn. The cells used in the measurement of the vapor pressure of TiO were drawn from tantalum, 1 inch in diameter and 1/2 to 3/4 inches high. A 1/16 inch hole was drilled in the center of the top. These cells, when heated in the pyrex vapor pressure apparatus, showed rather large temperature gradients across the top, a reading taken at the edge being about 130° higher than one taken near the

METAL VAPOR PRESSURE CELL

FIGURE 3

edge of the effusion hole at 1770°K, and about 200° higher at 2050°K. This large gradient caused a deposit of material to build up around the hole in the center, which, while not blocking it, would cause a decrease in effusion rate due to the increased depth of the orifice. Therefore, for the last series of runs, a hole was drilled near the side where no deposit could form.

For the first two series of vapor pressure measurements on Ti_2O_3 , the Knudsen cells were drawn from .010 inch molybdenum. Since the molybdenum is tougher and more brittle than tantalum, some difficulty was had in drawing cells of sufficient length. After much difficulty, three cells 1/2 inch in length and 3/4 inch in diameter were obtained. However, it was discovered later that there were cracks in the walls of each of these cells through which molten Ti_2O_3 could penetrate. These cracks developed either during the drawing operation or resulted from strains when the cell was heated to high temperature. It seems doubtful that an appreciable amount of vapor could effuse through these cracks during a run, but some doubt is nevertheless cast on the results of the vapor pressure measurements made using these cells.

A third type of Knudsen cell was used for the experiments with rutile and for the third series with Ti_2O_3 . The molybdenum cell was made from 1/4 inch O.D. molybdenum tubing with a 1/32 inch wall, and 1 1/16 inches in length.

This was enclosed in a 1/2 inch diameter, .020 inch wall tantalum tube closed at both ends except for a 1/4 inch diameter hole in the top through which the molybdenum cell just projected. With this design, the rate of weight loss of the cell at elevated temperatures was considerably reduced, as was the temperature gradient. The temperature observed in the effusion hole was within just a few degrees of the surface temperature at the edge of the hole when this was corrected for the emissivity of molybdenum. These surface readings, however, may have been slightly high due to the proximity of the edge of the cell. There was some condensation on the under side of the lid. In the case of the Ti_2O_3 runs, the molybdenum cell projected just a fraction more and there was considerable condensation on the under side of the lid, besides an observable temperature difference.

For the fourth series of experiments on Ti_2O_3 , the third 3/4 inch molybdenum cell, mentioned above, was enclosed in a 3/4 inch diameter, .020 inch wall, tantalum tube 1 1/8 inches long. The top of the molybdenum cell was flush with the upper shield of tantalum containing a 3/8 inch hole to allow passage of the effusing vapor. There remained a space between the bottom of the molybdenum cell and the lower tantalum shield in which a 1/32 inch hole was drilled to allow ready evacuation of this space. It was hoped that this design would reduce the radial

temperature gradient where the sample itself was located if not eliminating the gradient between the sample and the top of the cell. Again some material deposited on the top, but considerably less than in the unshielded cells.

The last and most successful Knudsen cell design, in so far as it removed the temperature gradient problem, was used for the vapor pressure measurements of Ti_3O_5 . The molybdenum cell was formed from 1/2 inch O.D. 1/16 inch wall seamless molybdenum tubing, the top and bottom drawn from .010 inch molybdenum sheet. The bottom was fitted inside the tube and welded as usual, but the top was made to fit over the outside of the tube and the weld made around the outside wall. This placement of the weld allowed the top of the cell to be fitted flush with a tantalum shield. The cell was placed within a 3/4 inch tantalum tube and held firmly against shields closing the ends. Although the corrected surface temperatures registered from 20° to 41° lower than the temperature observed in the effusion hole, a relatively small amount of material was condensed at the top of the cell.

Procedure:

Vapor Pressure Measurement: Before filling the Knudsen cells with the sample, they were either heated in vacuum to a constant weight (at a temperature above the highest run temperature), or in the case of the molybdenum cells, the rate of weight loss at the high temperatures was determined

using the same procedure as used in measuring vapor pressures.

The 0.5 to 2 gram powdered samples were put into the Knudsen cells through the effusion hole. In the case of the double walled cells, where it was important not to spill any material into the space between the molybdenum and tantalum, a small funnel was used. After filling, the diameter of the effusion hole was measured using an optical micrometer, the diameter being measured in four directions.

The times at high temperature were measured to one second with an ordinary wrist watch. The temperature was measured with an optical pyrometer as previously mentioned. Readings were taken at regular intervals, usually fifteen minutes for a four hour to eight hour run, but at five or ten minute intervals for the shorter runs and thirty minute intervals for the longer runs.

The weight loss was determined directly by weighing the cell before and after each run. On several runs a small quartz collector disk was placed in the path of the effusing vapor. The weight gained by the collector was in general too small to measure, but, after several runs, enough material could be collected in this manner for an X-ray diffraction pattern of the material condensed from the effusing vapor.

In order to determine the composition of the effusing vapor and the composition of the solid from which it

evaporated, experiments were carried out in which the oxide was vaporized at a relatively rapid rate from an uncovered molybdenum crucible, a portion of the vapor being condensed on a quartz collector disk. A portion of the solid was analyzed before and after each vaporization, and an X-ray diffraction pattern taken of the material collected.

Calculations:

The method of obtaining the various quantities was discussed in the previous section. The mathematical treatment of these quantities will be discussed here.

The expression derived from kinetic theory relating the rate of effusion of a gas through an orifice into a vacuum and the pressure of that gas is

$$P = m \sqrt{\frac{2 \pi R T}{M}}$$

where m is the effusion rate, R is the universal gas constant, T is the absolute temperature, and M , the molecular weight of the effusing gas. If more than one species of molecule is effusing, then P is the partial pressure of this species, m is the effusion rate of this species alone and M is its molecular weight. On substituting the appropriate constants, taking pressure in atmospheres, and rate of effusion in grams/cm.²/sec, this expression becomes

$$P_{\text{atm.}} = m \sqrt{\frac{T}{M}} \times 22.557 \times 10^{-3}$$

If several species of molecule A,B,... are present in the vapor, the total effusion rate will be the sum of the individual effusion rates.

$$m = m_A + m_B + \dots$$

If $N_A, N_B, \dots$ are the mole fraction of the species, A,B,... in the effusing vapor, and $M_A, M_B, \dots$ are their molecular weights, the individual effusion rates are obtained from the total effusion rate using the expression

$$m_A = \frac{N_A M_A}{N_A M_A + N_B M_B + \dots} \times m$$

$$m_B = \frac{N_B M_B}{N_A M_A + N_B M_B + \dots} \times m$$

The total pressure, of course, will be given as the sum of the partial pressures calculated individually

$$P = P_A + P_B + \dots$$

Since molecular weights are of roughly the same order of magnitude, the total pressure will bear approximately the same relation to the effusion rate as if only a single species of a given molecular weight were effusing. Therefore, the total rate of effusion will give a rough estimate of the total pressure even when more than one species is involved.

Of more interest thermodynamically is the equilibrium constant for the vaporization process which, for one mole of gas formed, is given as

$$K = P_A^{N_A} P_B^{N_B} \dots$$

Under the conditions in the Knudsen cell, this is an approximation that involves the following assumptions:

1. The mechanism of vaporization is such that the ratios of the molecular effusion rates are the same as the ratios of the partial pressures under true equilibrium conditions.
2. The condition that the ratio of the area of the effusion hole to the effective area of evaporation is much smaller than the effective accommodation coefficients is satisfied.
3. All reaction rates involved are rapid so that the steady state assumed approaches equilibrium.
4. The solid consists of a single phase only.

An alternative expression for the equilibrium constant would be

$$K = P_A^{P_A/P} P_B^{P_B/P} \dots$$

This expression is an approximation involving the assumptions:

1. The mechanism of the vaporization is such that the ratio of steady state pressures assumed are the same as the ratio of the partial pressures

under true equilibrium conditions.

2. Same as 2 and 3 above.

For our purposes, since the possibility of a two-phase solid system arises, the second expression is perhaps the preferred one. However, since the ratios of the molecular rates of effusion are not known accurately and the differences between N_A , N_B ,... and P_A/P , P_B/P ,... respectively do not affect the calculated equilibrium constant greatly, the first expression has been used in our calculation.

The effusion rate, m , in grams/cm.²/sec. is calculated from the relation

$$m = \frac{w}{t_{\text{eff}} A_{\text{eff}}}$$

Here w is the weight, in grams, of material lost during the run, t_{eff} is the effective duration of the run in seconds and A_{eff} is the effective orifice area through which effusion takes place.

The quantity, w , was obtained by correcting the actually measured weight loss for that due to evaporation of the cell itself. No correction was made for the runs in the tantalum cells. For the runs made in the shielded molybdenum cells, the weight loss was calculated using Blackburn's (8) expression for the vapor pressure of molybdenum and the measured area of molybdenum surface exposed.

The expressions used were

$$\log P = - \frac{34.008}{T} - 0.7547 \times 10^{-3} T + 9.095$$

and

$$w_{\text{Mo}} = \frac{P t_{\text{eff}} A \sqrt{M}}{22.557 \times 10^{-3} \sqrt{T}}$$

Where P is the vapor pressure of molybdenum at $T^{\circ}\text{K}$, A is the area of the molybdenum exposed, and M is the atomic weight of molybdenum, 95.95 gm./mole. T was taken as T_{Av} for the run and t_{eff} the effective time for the run.

The weight loss of the unshielded molybdenum cells was determined in the following manner. A series of runs was made with the empty cells. From the measured rate of evaporation, assuming the expression for the vapor pressure of molybdenum, an effective area was calculated for each run. These effective areas were in general greater than the actual area of the cell, indicating that the surface temperature from which evaporation took place was higher than the assumed temperature which was read in the effusion hole. This temperature gradient increased with temperature, so that the logarithm of the effective area, $\log A_{\text{eff}}$, decreased almost linearly with the reciprocal temperature $1/T$ in the range where measurements were taken. Assuming that at 1000°K the gradient would have disappeared and the effective area would equal the true area, the following expression was found to fit the experimental data.

$$\text{Log } A_{\text{eff}} = \text{Log } A_{10000\text{K}} + 12.3 \times 10^{-14} T^4.$$

Combining this expression with that for the vapor pressure of molybdenum, the rate of evaporation of the cells could be extrapolated to lower temperatures. The standard deviation of w_M , calculated by this method for seven runs on the second cell, was 6%.

The effective time, t_{eff} , was calculated by the averaging method which has been described previously (7) (38) to account for temperature fluctuations during the run as well as the initial heating period. A quantity $m(T)$, proportional to the rate of evaporation could be expressed by the relation

$$\log m'(T) = A/T$$

"A" being the slope of a plot of $\log m(T)$ vs. $1/T$ obtained from a preliminary calculation.

Then

$$t_{\text{eff}} = \int m'(T) dt / m'(T_{\text{Av}})$$

where T_{Av} is the arithmetic average of the temperature over the run. The integration is performed numerically.

The effective orifice area was obtained by correcting the measured area for thermal expansion and for the effect of the non-ideal conditions, finite size and finite depth. The thermal expansion data for tantalum and molybdenum obtained in this laboratory (12) were used, the function A_T/A_R being calculated from the linear expansion data and

plotted in the desired temperature range. For tantalum this is

$$A_T/A_R = 1 + 1.216 \times 10^{-5} (T-291) + 1.537 \times 10^{-9} (T-291)^2$$

For molybdenum it is,

$$A_T/A_R = 1.00197 + 4.80 \times 10^{-6} (T-273) + 4.41 \times 10^{-9} (T-273)^2$$

A_T/A_R is the ratio of the area at temperature, T , to that at room temperature.

The correction for the non-idealized effusion conditions was applied according to the equation derived by Whitman (45). This is

$$K = W_A W_B / [1 - (1-fW_B)(1-W_A)],$$

where K is the factor by which the actual orifice area must be multiplied in order to obtain the area of the idealized orifice in an idealized cell, (an orifice in an infinitesimally thin wall of an infinite chamber containing an infinitely large evaporating surface). W_A is the probability that molecules evaporating from the effective surface area will reach the top of the cylindrical cell and W_B is the probability that molecules entering the effusion orifice will pass through without being reflected. These are approximated by the ordinary Clausing correction (6). The factor, f , is the ratio of the cross sectional areas of the effusion orifice and of the cell itself. The effective accommodation coefficient is assumed to be unity.

An experimental check of the Clausing factor has been

made recently by McKinley and Vance (29). It may be instructive to compare this equation derived by Whitman with the simpler one derived by Speiser and Johnston (40), which may be written

$$K' = \frac{1}{1 + f}$$

Here the accommodation coefficient is assumed to be unity and the effective surface area of the sample is assumed to be the cross-sectional area of the cylindrical cell. If a knife-edged orifice is used, W_B becomes unity and Whitman's expression reduces to

$$K = \frac{1}{1 + f\left(\frac{1}{W_A} - 1\right)}$$

Thus, for a cell with a depth to radius ratio of $(l/a) \approx 2.2$, so that $W_A = 0.5$, the two expressions are identical. For shorter cells, Whitman's correction becomes slightly smaller while for larger ones it becomes greater. With cells of ordinary design the difference is negligible, particularly for very small values of f . The difficulty with the Speiser, Johnston "correction" is that its derivation assumes a uniform, steady, state pressure within the cell. This assumption becomes invalid as soon as the correction term is no longer negligible. Its virtue lies in that it does give the theoretical conditions under which equilibrium is approached in a simple straight-

forward manner. The actual conditions must be determined experimentally since the effective accommodation coefficient is never actually known. If cells must be used which do have a large f value, the Whitman correction is better than none at all. Whitman discusses the approximations made in the derivation and the errors to be expected in its application.

Results:

The results of all of the vapor pressure experiments are summarized in Tables I through IV and plotted in Figures 4 through 7. In Figure 8, the vapor equilibrium curves are plotted together for comparison. However, the values tabulated require some additional explanation.

As has already been mentioned, the temperature gradients observed in these cells present a rather serious problem in the determination of the temperature. In addition, due to these gradients, black body conditions were not always attained when sighting in the effusion hole. This became apparent in the course of making runs No. 1 through No. 11 on TiO (Table I). During two runs, No. 1 and No. 7, two regions could be observed in the effusion hole which gave temperature readings differing by as much as 60° . During run Nos. 4, 5, and 6, a few readings were taken on the tantalum surface for comparison and during all subsequent runs surface readings were taken regularly along with the

TABLE I
PRESSURE ABOVE TiO

Run	Temp. °K	Effective Time Sec.	Effective Orifice Area Cm. ²	Weight Loss Gms. X 10 ³	Total Evaporation Rate gm./cm. ² /sec. X 10 ⁵	Pressure atm. X 10 ⁶ (calculated as TiO)	-Log ₁₀ P _{atm.}
14	1847	109080	0.1524	2.79	0.1678	0.2035	6.691
9	1880	57694	0.01709	3.85	0.3905	0.4778	6.321
11	1908	36875	0.01710	3.91	0.6201	0.7643	6.117
16	1913	29275	0.01525	3.17	0.7101	0.876	6.058
17	1920	117378	0.01526	13.04	0.7280	0.900	6.046
4	1930	21712	0.01708	3.85	1.038	1.287	5.890
7	1930	28980	0.01710	6.83	1.378	1.708	5.768
8	1934	28721	0.01710	5.27	1.073	1.332	5.876
13	1942	28800	0.01526	7.33	1.668	2.074	5.683
5	1960	28868	0.01709	8.03	1.628	2.034	5.692
10	1968	14382	0.01711	5.38	2.186	2.736	5.563
1	1981	14400	0.0429	18.4	2.978	3.740	5.427
2	2003	14627	0.01653	25.19	10.42	13.16	4.881

TABLE II
VAPOR PRESSURE OVER Ti_2O_3

Series No.	Run	Temp. °K	Effective Time Sec.	Effective Orifice Area Cm. ²
1	1	1933	14760	0.004540
	2	1969	8680	0.004543
	3	2043	14900	0.004549
	4	2116	13950	0.004556
	5	2011	9842	0.04032
	6	2113	6959	0.04040
	7	2085	6998	0.04038
	8	2008	13380	0.04031
	9	2010	37400	0.04031
2	10	2022	10800	0.04354
	11	2029	7441	0.04354
	12	2023	7301	0.04354
	13	2059	7409	0.04357
	14	2064	19770	0.04357
	15	1990	25030	0.04351
	16	2035	15930	0.04355
	17	2106	6545	0.04361
	18	2045	8273	0.04356
3	19	1982	14400	0.01401
	20	2090	14520	0.01404
	21	2101	14400	0.01404
	22	2106	14400	0.01404
	23	2097	20040	0.01404
	24	2151	10860	0.01405
	25	2100	9000	0.02136
		2136		0.01405
	26	2102	14400	0.02136
		2138		0.01405
4	27	2108	25200	0.02136
		2146		0.02136
	28	2109	10140	0.055
		2147		0.055
	29	2120	14040	0.01754
	30	2102	12600	0.01754
	31	2122	41400	0.01754
	32	2116	13740	0.01754
	33	2108	14400	0.01754
	34	1971	14400	0.01749
	35	1992	21600	0.01750
	36	2017	29220	0.01751
	37	2076	14760	0.01753
	38	2030	28560	0.01751
	39	2131	14400	0.01755

TABLE II (Cont'd)
VAPOR PRESSURE OVER Ti_2O_3

Series No.	Run	Total Weight Loss X 10 ³	Weight Loss of Mo cell	Net Weight Loss
1	1	1.80	0.22	1.58
	2	1.22	0.25	0.97
	3	4.51	1.70	2.81
	4	10.08	5.57	4.51
	5	3.36	0.64	2.72
	6	7.86	2.70	5.16
	7	5.07	1.66	3.41
	8	2.63	0.81	1.82
	9	8.15	2.35	5.80
2	10	7.10	1.04	6.06
	11	5.12	0.82	4.30
	12	4.39	0.72	3.67
	13	6.80	1.38	5.42
	14	17.93	4.02	13.91
	15	7.09	1.34	5.75
	16	8.55	1.94	6.61
	17	17.01	2.73	14.28
	18	4.55	1.20	3.35
3	19	2.35	0.01	2.34
	20	3.53	0.08	3.45
	21	2.19	0.10	2.09
	22	2.57	0.11	2.46
	23	2.86	0.13	2.73
	24	3.20	0.16	3.04
	25	1.60	0.10	1.50
	26	2.50	0.17	2.33
	27	3.71	0.34	3.37
4	28	4.49	0.14	4.35
	29	6.14	0.05	6.09
	30	3.34	0.03	3.31
	31	18.99	0.15	18.84
	32	6.58	0.05	6.53
	33	6.29	0.04	6.25
	34	0.66	0.00	0.66
	35	1.22	0.01	1.21
	36	3.51	0.02	3.49
	37	4.10	0.03	4.07
	38	4.19	0.02	4.17
	39	26.31	0.06	26.05

TABLE II (Cont'd)
VAPOR PRESSURE OVER Ti_2O_3

Series No.	Run	Evaporation Rate gm./cm. ² /sec. X 10 ⁵	$\sqrt{K} = \sqrt{\bar{P}_{TiO} \bar{P}_{TiO_2}}$ X 10 ⁶	$-\frac{1}{2} \log K$
1	1	2.358	1.375	5.862
	2	2.460	1.447	5.840
	3	4.146	2.485	5.605
	4	7.096	4.328	5.364
	5	0.685	0.407	6.390
	6	1.835	1.119	5.951
	7	1.207	0.731	6.136
	8	0.337	0.200	6.699
	9	0.385	0.229	6.640
2	10	1.289	0.769	6.114
	11	1.327	0.793	6.101
	12	1.155	0.689	6.162
	13	1.679	1.010	5.996
	14	1.615	0.973	6.012
	15	0.528	0.312	6.506
	16	0.953	0.570	6.244
	17	5.003	3.044	5.516
	18	0.930	0.558	6.253
3	19	1.160	0.685	6.164
	20	1.692	1.026	5.989
	21	1.034	0.629	6.201
	22	1.217	0.741	6.130
	23	0.970	0.589	6.230
	24	1.992	1.225	5.911
	25	0.780	0.474	6.324
		1.186	0.727	6.138
	26	0.758	0.461	6.336
4		1.152	0.706	6.151
	27	0.626	0.381	6.419
		0.626	0.385	6.414
	28	0.780	0.475	6.323
		0.780	0.479	6.320
	29	2.473	1.510	5.821
	30	1.498	0.911	6.040
	31	2.594	1.585	5.800
	32	2.710	1.653	5.782
	33	2.475	1.507	5.822
	34	0.262	0.154	6.812
	35	0.320	0.189	6.724
	36	0.682	0.406	6.392
	37	1.573	0.950	6.022
	38	0.834	0.498	6.303
	39	10.308	6.309	5.200

TABLE III

VAPOR PRESSURE OVER Ti_3O_5

Run	Temp. °K	Effective Time Sec.	Effective Orifice Area Cm. ²	Total Weight Loss X 10 ³	Weight Loss of Mo cell
1	1940	7450	0.01762	2.69	0.00
2	1952	14400	0.01763	2.69	0.01
3	1947	24360	0.01763	3.19	0.01
4	1947	26160	0.01763	3.40	0.01
5	2001	14700	0.01764	3.49	0.01
6	2009	14520	0.01764	1.16	0.02
7	2079	14400	0.01767	2.87	0.05
8	2166	14400	0.01771	27.19	0.20
9	2122	14400	0.01769	5.06	0.10
10	2009	11820	0.01768	1.73	0.06
11	2070	14340	0.01767	1.58	0.04
12	2078	14460	0.01767	1.72	0.05
13	2088	6660	0.01768	1.19	0.03
14	2078	29020	0.01767	3.08	0.10
15	2076	28660	0.01767	3.73	0.10
16	2068	59260	0.01767	6.90	0.18

TABLE III (Cont'd)

VAPOR PRESSURE OVER Ti_3O_5

Run	Weight Loss of Ti_3O_5 $\times 10^3$	Total Evaporation Rate $\text{gm./cm.}^2/\text{sec.}$ $\times 10^5$	$\sqrt[3]{K} = \sqrt[3]{P_{\text{TiO}} P_{\text{TiO}_2}^2}$ Atm. $\times 10^6$	$- 1/3 \log K$
1	2.69	2.049	1.244	5.905
2	2.68	1.056	0.643	6.192
3	3.18	0.740	0.450	6.347
4	3.39	0.735	0.447	6.350
5	3.48	1.342	0.827	6.082
6	1.14	0.445	0.275	6.561
7	2.82	1.108	0.696	6.157
8	26.99	10.583	6.790	5.168
9	4.96	1.947	1.236	5.908
10	1.67	0.799	0.505	6.297
11	1.54	0.608	0.381	6.419
12	1.67	0.654	0.411	6.386
13	1.16	0.985	0.620	6.208
14	2.98	0.581	0.365	6.438
15	3.63	0.717	0.450	6.347
16	6.72	0.642	0.403	6.395

TABLE IV
VAPOR PRESSURE OVER TiO₂-x

Run	Temp. °K	Effective Time Sec.	Effective Orifice Area Cm. ²	Weight Loss Gms. X 10 ³	Total Evaporation Rate gm./cm. ² /sec. X 10 ⁵	Pressure Atm. X 10 ⁶ (calculated as TiO ₂)	- log P
*33	1849	28872	0.01379	1.45	0.364	0.395	6.403
*30	1867	28800	0.01379	1.94	0.488	0.533	6.273
*29	1916	12960	0.01380	1.98	1.107	1.223	5.913
*32	1918	14400	0.01381	2.45	1.232	1.362	5.866
14	1936	14400	0.01353	3.33	1.709	1.899	5.721
*31	1943	10800	0.01381	2.96	1.985	2.207	5.656
25	1949	28800	0.01381	11.06	2.808	3.098	5.509
*28	1954	18072	0.01382	6.03	2.414	2.693	5.570
27	1956	14472	0.01382	5.29	2.645	2.953	5.530
26	1958	14400	0.01382	6.29	3.161	3.529	5.452
15	1966	14400	0.01353	4.93	2.530	2.831	5.548
16	1972	14400	0.01353	4.67	2.397	2.686	5.571
17	1982	14400	0.01354	5.98	3.067	3.446	5.463
18	2010	14400	0.01354	8.90	4.565	5.164	5.287

*Used in calculating equation.

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

effusion hole readings. When the effusion hole temperatures were plotted vs. the surface temperature, (the surface temperature being taken on the edge of the effusion hole), the points fell near two different curves corresponding to a high reading and to a low reading. Following run No. 11, a 1/32 inch hole was drilled in the top of the cell near the edge and a series of temperature comparisons made between the surface readings and the two "black body" readings. On plotting these temperatures, the same two curves mentioned above were obtained. Letting T_s be the surface temperature obtained by correcting the observed brightness temperature for the emissivity of Tantalum (23), T_L the temperature in the center hole, and T_H the temperature in the outer hole, the following relations were obtained in the temperature range covered.

$$T_H = 1.243 T_s - 376 \quad (a)$$

$$T_L = 1.126 T_s - 209 \quad (b)$$

$$T_L = 0.9061 T_H + 132 \quad (c)$$

The following conclusions were drawn:

1. The high readings were due to reflection from the walls of the cell which were considerably hotter than the bottom of the cell or the material contained therein. They occurred when the bare surface of the tantalum appeared in the field of view or when the titanium oxide had sintered or melted to produce a surface of high reflectivity.

2. The low readings occurred when the powdered oxide came into the field of view. Due to its low reflectivity and high emissivity, it should give more nearly the correct temperature.
3. Material evaporated away from the edges of the cell and deposited in the center so that, except for the initial run, no material should be at the temperature of the wall.

It is obvious that under these conditions it would be impossible to determine an "average" temperature unambiguously. The temperatures listed in Table I were obtained by assuming that T_L is the true temperature. For run Nos. 1 through 5 this is taken as the temperature observed in the effusion hole. For run Nos. 8 through 11, a value for T_L was calculated from the observed surface temperature, using equation (b) above. This was averaged with either the temperature observed in the effusion hole or calculated from the temperature observed in the effusion hole using equation (c) above. Run Nos. 13 through 17 were made in a cell with a hole drilled near the edge, the center hole being plugged. The temperatures listed were calculated from the observed effusion hole temperatures using equation (c).

Besides heating by radiation and conduction, the tops of the cells were heated partially by induction. The bottoms, being slightly recessed within the walls of the cells, would

not be heated as effectively by induction. Therefore, there is a possibility that the center of the bottom might be cooler than the top. However, the bottom would be more effectively heated by radiation, so the difference would be slight. In the range of temperatures covered, the difference between the assumed temperature and the observed temperature of the coolest portion of the cell, (the center of the top) is about 30° . The difference between the high and the low readings is about 55° . It would seem reasonable to assume, therefore, that the uncertainty of the temperature is $\pm 30^{\circ}$. This will be a systematic error, and, since it may vary considerably with temperature, will have a tendency to introduce an error in the slope of the curve, $-\log P$ as a function of $1/T$, obtained by plotting the points.

The temperature gradients in the other types of Knudsen cells also presented a rather serious problem due to the higher temperatures involved. The effusion holes of the unshielded molybdenum cells were drilled near the side so that the temperatures observed may have been too high. On the other hand, the material in the cells, Ti_2O_3 , did not seem to show such a marked tendency to distill away from the walls so that perhaps more material was at this high temperature. Due to the necessity of reading the effusion hole temperature at the low end of the "X High" scale of the pyrometer, considerable difficulty was had in obtaining

good precision in the temperature measurement. Since the precision in reading the surface temperature was much better, a plot of effusion hole temperature vs. corrected surface temperature was drawn up as before, and the temperature was obtained from this plot using the corrected surface temperatures (Table II, series 1 and 2).

This same method was used to obtain the temperatures of all other runs. Where the precision in the effusion hole readings and surface readings was comparable, an average was used as the true temperature.

The column "Effective Time" needs no further explanation.

The cell dimensions and orifice dimensions used in calculating the effective orifice area are listed in Table IX of the appendix. The remaining columns are self-explanatory, the calculations carried forward in a straightforward manner as described in the preceding section. For the calculation of the pressure over TiO , the vapor has been assumed to consist predominantly of TiO molecules. In calculating the equilibrium constant for the vaporization of Ti_2O_3 (Table II) the equilibrium

has been assumed, while for the vaporization of Ti_3O_5 (Table III) the equilibrium

has been assumed.

The vapor over the solid, rutile, in the runs listed in Table IV has been assumed to consist predominantly of TiO_2 molecules. The reasons for making these assumptions will now be discussed.

As has already been mentioned, the titanium-oxygen system is characterized by a system of solid solutions which extend over considerable composition ranges. Therefore, any free energy calculations made using the thermodynamic functions of the pure compounds cannot be expected to give very accurate results. However, they may be used to set certain limits. For example, the titanium gas pressure over TiO must be less than it is over pure titanium, but it must be more than that calculated for the equilibrium

Otherwise TiO would not be stable but would disproportionate. Since TiO is found to be stable up to about 2010°K where it melts peritectically (3) we may assume that it does not disproportionate.

Using the vapor pressure of titanium measured by Ditmars (10), and the free energy functions listed by the National Bureau of Standards (31), (extrapolated where necessary) we may calculate that at 2000°K the vapor pressure of titanium is given by $\log P = -4.983$ while the hypothetical pressure over TiO and Ti_2O_3 is given by $\log P = -5.461$. Our measured pressure over TiO is of the

order of $\log P = -5.445$. Thus, we might expect titanium atoms to be of major importance in the vapor of TiO . However, the uncertainties in the terms used to calculate the pressure of Ti , together with the uncertainty in the experimental determination are just enough to allow Ti atoms to be a minor constituent in the vapor at 2000°K .

Experimentally, while some evidence of disproportionation was found, it seems hardly likely that more than a maximum of 10% of the vapor could have been titanium atoms. Following Run No. 17 (Table I) the cell was cut open and the contents analyzed. Some loose material, which apparently was a residue that had never entered the vapor, contained a considerable amount of Ti_2O_3 as determined by X-ray analysis. An analysis of 0.1970₇ grams of this material showed it to have the average composition $\text{TiO}_{1.311}$. The remainder of the material in the cell had condensed from the vapor and crystallized on the top and the bottom of the cell. About 80% of the material on the top was removed and found to have the composition $\text{TiO}_{0.982}$. Assuming that all of the condensed material was of the same composition, from the initial amount and composition of material placed in the cell (1.3244₃ grams of $\text{TiO}_{1.029}$), and the total weight lost (0.04631 grams) the average composition of the vapor was calculated as $\text{TiO}_{1.029}$, the same as the initial composition! However, this analysis is subject to considerable error because of the assumptions involved.

That the vapor must have actually consisted of a relatively small proportion of titanium atoms may be shown by the following argument. The presence of the loose material, consisting in good proportion of Ti_2O_3 , shows that a residue was left and that a distinction can be made between the relatively large fraction of material that passed through the vapor state, and the small fraction that did not. Actually, loose material must have consisted at least in part of recondensed molecules, so that the actual residue is smaller than the one observed. It can be calculated that if 1.32443 grams of oxide, having the composition $TiO_{1.029}$ (0.020577 moles of Ti, 0.021174 moles of O), vaporize in the molecular ratio $Ti/TiO = 1/10$, the residue of pure Ti_2O_3 remaining will contain 0.00209 moles. Since this is considerably in excess of the amount of residue found which contained a maximum of 0.00089 moles of Ti_2O_3 , it may be assumed that the molecular ratio Ti/TiO is less than 1/10. The additional assumptions must be made that no residue was lost by melting and that the accommodation coefficient for Ti atoms on TiO solid is about the same as that for TiO molecules on TiO solid. The amount of melting, if any, appeared to be very slight. In view of the simple structure of TiO, the second assumption seems to be a reasonable one also.

No definite conclusions could be drawn from the X-ray analysis of material collected from the effusing beam.

The material collected in two separate experiments apparently was oxidized in the air or during a recrystallization in vacuum. Both patterns were identical with the rutile pattern. A third collection, made during the progress of run No. 17, gave the same pattern as obtained from the vaporization of rutile and from one experiment with Ti_3O_5 . The significance of these results is not clear but it does cast some doubt on the reliability of this technique when applied to the other oxides.

During the rate of effusion experiments with titanium dioxide, it was observed that an appreciable weight loss was obtained far below the temperature at which dissociation could be expected to take place. Therefore, during the initial runs of the second series, a collector disk was placed above the effusion hole. A deposit, formed on the collector, showed that the effusing vapor contained condensable material. Although no analysis was made of this material, X-ray analysis of material, collected during an initial evaporation from an open molybdenum crucible, showed the presence of molybdenum dioxide. A second evaporation from the same crucible produced a deposit whose X-ray diffraction pattern showed weaker MoO_2 lines together with rutile lines, while the analysis of a third deposit showed only rutile lines. Analysis of the residue after the first evaporation showed the average composition $TiO_{1.943}$. No analysis was made after the second evaporation, but the final

residue had the average composition $\text{TiO}_{1.847}$. The X-ray patterns of these residues were similar to those reported by Ehnlich (14) for compositions in this range as has been mentioned. Unfortunately, these data cannot be used to obtain, even approximately, the composition of the normal vapor over oxygen deficient rutile since the weight losses due to evaporation of Mo, MoO_2 , and the titanium oxides cannot be separated. However, certain conclusions may be drawn. Under conditions where MoO_2 gas can escape, molybdenum will partially reduce TiO_2 . The amount of reduction is limited because the partial free energy of oxygen rises rapidly with decreasing oxygen content in oxygen deficient rutile. Since no MoO_2 was observed in the deposit obtained on the collector disk during the final runs of a series, in spite of the much greater intensity of MoO_2 diffraction lines compared with titanium oxide diffraction lines, it may be assumed that the amount of MoO_2 in the vapor was indeed small. Yet the observed effusion rates correspond to pressures considerably higher than expected for dissociation of solid TiO_2 . Thus, the observed effusion rates for the final runs in the series, must correspond to vaporization of TiO_2 molecules. The results of Table IV are calculated on this basis. The data obtained during the initial runs are listed in Table VIII and will be discussed later.

The material collected from vaporization of Ti_2O_3

gave the same X-ray diffraction pattern as Ti_2O_3 . Within experimental error no change could be observed in the composition of Ti_2O_3 following vaporization of a portion, and the X-ray diffraction patterns were identical. Thermodynamic calculations, using the data obtained for the vapor pressures of TiO and TiO_2 , indicate that the predominant species in the vapor over Ti_2O_3 will be TiO and TiO_2 , and, that a "constant boiling" composition should be obtained very close to the composition $TiO_{1.5}$. Therefore, in our calculations, the effusion rates of TiO and TiO_2 have been assumed equal. A slight variation in the relative proportions of TiO and TiO_2 in either direction will not affect, within experimental error, the calculated equilibrium constant for the equilibria

For example, the assumption that the partial pressures of TiO and TiO_2 are equal, rather than the effusion rates, results in a change of only 0.47% in the calculated value of $\sqrt{K}$.

The assumed species in the vapor of Ti_3O_5 were derived in a similar manner. However, in this case, the X-ray diffraction patterns of the collected material correspond to that of an oxide of composition $TiO_{1.82}$, and the thermodynamic calculations indicated that the molecular ratio of TiO_2 to TiO in the vapor should be about 10/1. However,

this calculation is subject to considerable error and very slight changes in the free energy function used could lead to an entirely different result. Evaporation from a molybdenum crucible with a total weight loss corresponding to 27.7% of the original material resulted in no significant change in the analysis. Hence, the ratio of TiO_2 molecules to TiO molecules evaporating must have been of the order of 2/1. Therefore the molecular rates of effusion of TiO_2 and TiO were assumed to be in the ratio 2/1 in calculating the equilibrium constant for the reaction

Discussion of Results and Thermodynamic Treatment:

Due to the low vapor pressures over the titanium oxides at their melting points it has not been possible to extend the measurements over a very wide range. Neither was it found possible to extend them into the liquid range. Molten titanium monoxide was found to soak through the walls of the tantalum crucible at a rapid rate and also to react slightly with the tantalum. The other oxides showed a strong tendency to wet molybdenum and were able to creep out of the effusion hole of the Knudsen cells when molten.

Because of this short temperature range the data where-ever possible have been treated using the relation

$$- R \ln K = \frac{\Delta F^\circ}{T} = \Delta \left(\frac{F^\circ - H^\circ_0}{T} \right) + \frac{\Delta H^\circ_0}{T}$$

Since there are no free energy functions for titanium dioxide gas and no data available to estimate them, the TiO_2 data were treated using a " Σ " function (24) and an estimated value for the heat capacity of titanium dioxide gas.

Titanium Monoxide: The calculation of the heat of sublimation of $\text{TiO}_{(s)}$ is listed in Table V. The relation applying to the equilibrium, $\text{TiO}_{(s)} = \text{TiO}_{(g)}$, is

$$\frac{\Delta H_0^0}{T} = -R \ln P - \left(\frac{F^0 - H_0^0}{T} \right)_{(g)} + \left(\frac{F^0 - H_0^0}{T} \right)_{(s)}$$

The free energy functions for titanium monoxide, solid, and gas were taken from the National Bureau of Standards' tabulation (31), as were all others used in this work. The values were extrapolated where necessary. The five runs indicated in Table V as "not included in the average" were initial runs during which excessive weight losses were observed due to degassing. The average value for ΔH_0^0 from eight runs is

$$\Delta H_0^0 = 134.55 \text{ kcal./mole.}$$

from which $\Delta H_{298} = 135.32 \text{ kcal./mole.}$

This value is in excellent agreement with the value $\Delta H_{298} = 135 \pm 1 \text{ kcal./mole}$ reported by Brewer (2) to have been obtained by Gilles and Wheatley using a molybdenum Knudsen cell.

Expanding the term, $\Delta(F^0 - H_0^0/T)$, as a linear function of the temperature we obtain the equation

TABLE V
HEAT OF SUBLIMATION OF T10

Run	T °K	- RlnP atm.	$-\left(\frac{F^O - H_0^O}{T}\right)_g$	$-\left(\frac{F^O - H_0^O}{T}\right)_s$	$\frac{\Delta H_0^O}{T}$	ΔH_0^O kcal./mole
14	1847	30.605	62.647	19.87	73.382	135.54
9	1880	28.912	62.798	20.11	71.600	134.61
11	1908	27.979	62.924	20.31	70.593	134.69
16	1913	27.709	62.945	20.34	70.314	134.51
17	1920	27.655	62.975	20.39	70.240	134.86
* 4	1930	26.941	63.019	20.46	69.500	134.14
* 7	1930	26.383	63.019	20.46	68.942	133.06
8	1934	26.877	63.036	20.49	69.423	134.26
* 13	1942	25.994	63.070	20.54	68.524	133.07
5	1960	26.035	63.148	20.67	68.513	134.28
10	1968	25.445	63.183	20.73	67.898	133.62
* 1	1981	24.823	63.239	20.82	67.242	133.20
* 2	2003	22.326	63.334	20.97	64.690	129.57
* Not included in average.					Average = 134.55 ± .52	

$$\log P_{\text{TiO}} = - \frac{29,420}{T} + 10.441 - 0.583 \times 10^{-3}T$$

The curve in Figure 4 is drawn using this equation.

The value for the heat of sublimation of titanium monoxide may be used in conjunction with values for the heat of formation of titanium monoxide, heat of sublimation of titanium, and dissociation energy of oxygen to calculate the dissociation energy of TiO in the gaseous state. Thus, for the reaction

we may sum the reaction equations

This value for the dissociation energy is in good agreement with that obtained by Christy (5) from a linear Birge-Sponer extrapolation of the vibrational levels of the lower $^3\Pi$ state. The value of 6.88 electron volts corresponding to 158.8 kcal./mole is quoted by Herzberg (18).

Titanium Dioxide: The titanium dioxide originally placed in the Knudsen cells was anatase, but at the tempera-

ture of the initial run, 1647°K, it rapidly changed to the rutile form. The total rate of evaporation dropped during a long series of runs until finally a condition was reached in which the rate of evaporation remained essentially constant with temperature. As will be shown presently the composition of the solid had dropped to between $\text{TiO}_{1.9}$ and $\text{TiO}_{1.95}$ when this stage was reached. It has been assumed that the vapor consists predominantly of TiO_2 molecules and that the pressure of TiO_2 vapor is essentially the same as it would have been over pure TiO_2 solid. A value of 13 cal./mole/deg. has been estimated for the heat capacity, C_p , of TiO_2 gas. The heat capacity of the solid has been taken from Kelley (25).

$$C_p = 17.97 + 0.28 \times 10^{-3} T - 4.35 \times 10^5 T^{-2}$$

This equation is also in good agreement with the values listed by the National Bureau of Standards (31). The final six runs of the second series of experiments were used in a " Σ " calculation (24). As may be seen in Table IV and Figure 5 the pressures during the runs preceding No. 28 in the second series are higher than average. The temperature range could have been extended by including the final three runs of the first series. However, it is probable that a slight discrepancy in the temperature measurement caused the vapor pressures in the first series to appear lower than in the second. Including these runs, all made at a higher tempera-

ture, might not give the true slope for $\log P$ vs. $1/T$.

Using these data in the relations

$$- R \ln P = 4.97 \ln T - 0.14 \times 10^{-3} T + 2.175 \times 10^5 T^{-2}$$

$$= \sum = \frac{\Delta H_0}{T} + I$$

we obtained $\Delta H_0 = 141,680$

and

$$I = - 84.83 \pm .09$$

Thus,

$$- \log P_{\text{TiO}_2} = \frac{30,975}{T} + 2.502 \log T - 18.545$$

$$+ 0.031 \times 10^{-3} T - 0.48 \times 10^5 T^{-2}$$

The curve plotted in Figure 5 is drawn from this equation.

$$\Delta H = 141,680 - 4.77 T - 0.14 \times 10^{-3} T^2 \\ - 4.35 \times 10^5 T^{-1}$$

$$\Delta H_{298} = 138.79 \text{ kcal./mole}$$

$$\Delta S_{298} = 49.01 \text{ E.U.}$$

We may now calculate the dissociation energy of TiO_2 gas at 298.16°K using the following data

$\text{TiO}_2(\text{g}) = \text{TiO}_2(\text{s})$	$\Delta H_{298} = - 138.79$
$\text{Ti}(\text{s}) = \text{Ti}(\text{g})$	$\Delta H_{298} = 113.33$
$\text{O}_2(\text{g}) = 2 \text{ O}(\text{g})$	$\Delta H_{298} = 116.25$
$\text{TiO}_2(\text{s}) = \text{Ti}(\text{s}) + \text{O}_2(\text{g})$	$\Delta H_{298} = 225.52$
<hr/>	
$\text{TiO}_2(\text{g}) = \text{Ti}(\text{g}) + 2 \text{ O}(\text{g})$	$\Delta H_{298} = 316.31 \text{ kcal./mole.}$

This value is 1.81% less than twice the dissociation energy of TiO at 298.16°K and therefore of the correct order of magnitude, although we might have estimated a value 10% lower.

We may also check the reliability of our extrapolation by comparing the calculated entropy for the vaporization with an estimated entropy. Using a relation given by Kubaschewski and Evans (28), we may estimate the entropy of TiO₂ gas as $S_{298} = 62.2$. For the sublimation at 298.16°K, $\Delta S_{298} = 50.1$. This is in good agreement with our calculated value of $\Delta S_{298} = 49.01$.

Titanium Sesquioxide: The thermodynamic calculations for Ti₂O₃ are listed in Table VI. In the absence of free energy functions for titanium dioxide gas, the data have been treated using the relation

$$-R \ln K = \frac{\Delta F^{\circ}}{T} = \Delta \left(\frac{F^{\circ} - H_0^{\circ}}{T} \right) + \left(\frac{\Delta F^{\circ}}{T} \right)_{\text{TiO}_2 \text{ Sub.}} + \frac{\Delta H_0^{\circ}}{T}$$

$$\text{Where } \Delta \left(\frac{F^{\circ} - H_0^{\circ}}{T} \right) = \left(\frac{F^{\circ} - H_0^{\circ}}{T} \right)_{\text{TiO(g)}} + \left(\frac{F^{\circ} - H_0^{\circ}}{T} \right)_{\text{TiO}_2(s)} - \left(\frac{F^{\circ} - H_0^{\circ}}{T} \right)_{\text{Ti}_2\text{O}_3(s)}$$

TABLE VI
THERMODYNAMIC CALCULATIONS FOR Ti_2O_3

Series No.	Run	T	-RlnK	$-\Delta\left(\frac{F^\circ - H^\circ_0}{T}\right)$	$\left(\frac{\Delta F}{T}\right)$ Sublimation of TiO_2	$\frac{\Delta H^\circ_0}{T}$	ΔH°_0
1	1	1933	53.626	41.137	26.290	68.473	132.36
	2	1969	53.425	41.016	25.056	69.385	136.62
	3	2043	51.275	40.762	22.646	69.391	141.77
	4	2116	49.070	40.510	20.439	69.141	146.30
	5	2011	58.456	40.873	23.665	75.664	152.16
	* 6	2113	54.440	40.520	20.531	74.429	157.27
	* 7	2085	56.132	40.617	21.352	75.397	157.20
	* 8	2008	61.283	40.883	23.757	78.409	157.45
	* 9	2010	60.743	40.876	23.691	77.928	156.64

* Included in average.

Average = $157.14 \pm .30$

TABLE VI (Cont'd)
THERMODYNAMIC CALCULATIONS FOR Ti_2O_3

Series No.	Run	T	-RlnK	$-\Delta\left(\frac{F^\circ - H^\circ}{T}\right)$	$\left(\frac{\Delta F}{T}\right)$ Sublimation of TiO_2	$\frac{\Delta H^\circ}{T}$	ΔH°
2	10	2022	55.931	40.835	23.312	73.454	148.52
	11	2029	55.812	40.811	23.090	73.533	149.20
	12	2023	56.370	40.831	23.273	73.928	149.56
	* 13	2059	54.852	40.707	22.149	73.410	151.15
	* 14	2064	54.998	40.690	21.993	73.695	152.11
	* 15	1990	59.517	40.945	24.346	76.116	151.47
	* 16	2035	57.120	40.790	22.894	75.016	152.66
	17	2106	50.461	40.544	20.726	70.279	148.01
	* 18	2045	57.203	40.755	22.581	75.377	154.15

* Included in average.

Average = 152.31 ± 1.06

TABLE VI (Cont'd)
THERMODYNAMIC CALCULATIONS FOR Ti_2O_3

Series No.	Run	T	-RlnK	$-\Delta\left(\frac{F^\circ - H_0^\circ}{T}\right)$	$\left(\frac{\Delta F}{T}\right)$ Sublimation of TiO_2	$\frac{\Delta H_0^\circ}{T}$	ΔH_0°
3	19	1982	56.389	40.972	24.609	72.752	144.19
	20	2090	54.788	40.600	21.209	74.179	155.03
	* 21	2101	56.727	40.562	20.882	76.407	160.54
	* 22	2106	56.077	40.544	20.726	75.895	159.84
	* 23	2097	56.992	40.575	21.000	76.567	160.56
	* 24	2151	54.074	40.389	19.436	75.027	161.37
	25	2100	57.852	40.565	20.908	77.509	162.77
		2136	56.151	40.441	19.866	76.726	163.89
	26	2102	57.962	40.558	20.843	77.677	163.28
		2138	56.270	40.434	19.801	76.903	164.42
	27	2108	58.721	40.537	20.674	78.584	165.66
		2146	58.676	40.406	19.579	79.503	170.61
	28	2109	57.843	40.534	20.648	77.729	163.93
		2147	57.816	40.403	19.553	78.666	168.90

* Included in average.

Average = 160.58 ± 0.54

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TABLE VI (Cont'd)
THERMODYNAMIC CALCULATIONS FOR Ti_2O_3

Series No.	Run	T	-Rlnk	$-\Delta \left(\frac{F_o - H_o}{T} \right)$	$\left(\frac{\Delta F}{T} \right)$ Sublimation of TiO_2	$\frac{\Delta H_o}{T}$	ΔH_o
4	* 29	2120	53.251	40.496	20.322	73.425	155.66
	* 30	2102	55.254	40.558	20.843	74.969	157.58
	* 31	2122	53.059	40.489	20.270	73.278	155.50
	* 32	2116	52.894	40.510	20.439	72.965	154.39
	* 33	2108	53.260	40.537	20.674	73.123	154.14
	* 34	1971	62.316	41.009	24.990	78.335	154.40
	* 35	1992	61.511	40.938	24.281	78.168	155.71
	* 36	2017	58.474	40.852	23.469	75.857	153.00
	* 37	2076	55.089	40.648	21.627	74.110	153.85
	* 38	2030	57.660	40.807	23.051	75.416	153.09
	39	2131	47.570	40.458	20.009	68.019	144.95

* Included in average.

Average = 154.73 ± 1.33

and $\frac{\Delta H_0^0}{T}$ refer to the reaction

and
$$\left(\frac{\Delta F}{T}\right)_{\text{TiO}_2 \text{ Sub.}} = - R \ln P_{\text{TiO}_2}$$

refers to the equilibrium $\text{TiO}_2(\text{s}) = \text{TiO}_2(\text{g})$.

$\frac{\Delta H_0^0}{T}$ has been calculated for each run according to the relation

$$\frac{\Delta H_0^0}{T} = - R \ln K - \left(\frac{F^0 - H_0^0}{T}\right) - \left(\frac{\Delta F}{T}\right)_{\text{TiO}_2 \text{ Sub.}}$$

The average values of ΔH_0^0 calculated for each series of runs are

Series No. 1	157.14
Series No. 2	152.31
Series No. 3	160.58
Series No. 4	154.73

These values for ΔH_0^0 are not in good agreement with that calculated directly from the heats of formation of the oxides which is,

$$\Delta H_0^0 = 147.93 .$$

We may calculate the total heat of sublimation using the value derived for the heat of sublimation of TiO_2 .

Thus, using ΔH_0^0 from Series No. 3

In Figure 6 the curve labeled "calculated" was drawn using the value of ΔH_0^0 from the heats of formation of the oxides together with the values obtained here for the heat of sublimation of TiO and vapor pressure of TiO_2 . The other curve was drawn using the value for ΔH_0^6 obtained from the average of four runs in Series No. 3. There is a possibility that the experimental pressures obtained in this series are too low but there is a greater probability that the values obtained in the other series are too high as has been mentioned.

In Series No. 1, after degassing has been completed, there seems to be no significant change in the value of ΔH_0^0 nor trend with temperature. The weight losses during the first runs were low due to the small effusion hole used, so that a total of only 1.7% of the material had evaporated at the end of run No. 5. The run following No. 9 in the first series was made above the melting point allowing some of the liquid to flow through a crack thus ending the series. In Series No. 2, a long degassing period before starting the series evaporated about 4.6% of the original material. Nevertheless, the observed vapor

pressures in Series No. 2 are considerably higher than in the other and in addition the ΔH_8 values show a trend towards higher values except for run Nos. 15 and 17. Some melting probably occurred during run No. 17 and material escaped from a crack in the cell wall.

The runs of Series No. 3 were made in the small bore Knudsen cell described previously. The relatively large uncertainty due to temperature gradient, non-equilibrium conditions, and neglect of accommodation coefficient may have affected the results of this series, but the results are probably still more reliable than in the other series. Because of the narrowness of the cell and the temperature gradient, a considerable amount of material collected at the top of the cell. Because of this material the effusion hole became effectively blocked, so that for run Nos. 25 and 26, calculations were made assuming Langmuir evaporation from an area the size of the orifice at the observed surface temperature. During the early part of run No. 27, the material melted and completely blocked the hole. For run No. 28, the material was melted (at $2137 \pm 10^\circ\text{K}$) and since it overflowed the effusion hole, the area of overflow was estimated and used in the calculation. In this manner, a very rough estimate of the accommodation coefficient might be made (21). The average, for runs Nos. 27 and 28, is about 0.60. The temperatures in these runs were obtained directly from the surface readings and there-

fore are possibly subject to error, being too high. Therefore, our accommodation coefficient may actually be closer to unity than indicated.

Unfortunately, the initial runs of Series No. 4 were made near the melting point of Ti_2O_3 so that if any material passed through a crack in the cell, it would have been in contact with the tantalum shield throughout the course of the series. This undoubtedly accounts for the scatter and generally high values for the pressure and low values for ΔH_0^0 .

Titanium Pentoxide: The thermodynamic calculations for Ti_3O_5 are listed in Table VII. The data have been treated in a manner exactly analogous to that used for Ti_2O_3 . Values of ΔH_0^0 for each run were calculated using the relation

$$\frac{\Delta H_0^0}{T} = -R \ln K - \Delta \left(\frac{F^0 - H_0^0}{T} \right) - 2 \left(\frac{\Delta F}{T} \right)_{TiO_2 \text{ Sub.}}$$

$$\text{Here, } \Delta \left(\frac{F^0 - H_0^0}{T} \right) = \left(\frac{F^0 - H_0^0}{T} \right)_{TiO(g)} + 2 \left(\frac{F^0 - H_0^0}{T} \right)_{TiO_2(s)} - \left(\frac{F^0 - H_0^0}{T} \right)_{Ti_3O_5(s)}$$

and ΔH_0^0 refers to the reactions

TABLE VII
THERMODYNAMIC CALCULATIONS FOR Ti_3O_5

Run	T	-RlnK	$-\Delta \left(\frac{F^\circ - H^\circ}{T} \right)$	$\left(\frac{\Delta F}{T} \right)$ Sublimation of TiO_2	$\frac{\Delta H^\circ}{T}$	ΔH°
1	1940	81.056	38.262	26.054	67.210	130.39
2	1952	84.967	38.218	25.633	71.919	140.39
3	1947	87.094	38.236	25.804	73.722	143.54
4	1947	87.135	38.236	25.804	73.763	143.62
5	2001	83.458	38.037	23.992	73.511	147.10
6	2009	90.017	38.007	23.731	80.562	161.85
7	2079	84.487	37.728	21.535	79.145	164.54
8	2166	70.916	37.378	19.019	70.256	152.17
9	2122	81.070	37.556	20.270	78.086	165.70
* 10	2099	86.408	37.649	20.934	82.189	172.51
* 11	2070	88.082	37.764	21.810	82.226	170.21
* 12	2078	87.643	37.732	21.561	82.253	170.92
* 13	2088	85.173	37.693	21.261	80.344	167.76
* 14	2078	88.343	37.732	21.561	82.953	172.38
* 15	2076	87.094	37.740	21.627	81.580	169.36
* 16	2068	87.753	37.772	21.875	81.775	169.11

* Included in average.

Average = 170.32 ± 1.62

$$\text{and } \frac{\Delta F}{T} = -R \ln P_{\text{TiO}_2} \text{ Sub.}$$

again refers to the equilibrium $\text{TiO}_2(\text{s}) = \text{TiO}_2(\text{g})$.

The average value is

$$\Delta H_0^\circ = 170.32 \text{ kcal./mole}$$

The value of ΔH_0° for this reaction calculated from the heats of formation is 146.45 kcal./mole, so again the agreement is not very good. Since the discrepancy between the "observed" and the calculated values for the reaction involving Ti_3O_5 is almost twice that for the Ti_2O_3 reaction, we might expect to find an error in the values for the TiO_2 functions. However, it must be remembered that a long extrapolation was necessary to obtain free energy functions for solid Ti_3O_5 .

The total heat of sublimation may be obtained as in the previous case.

Figure 7, the curve marked calculated is drawn using the value $\Delta H_0^\circ = 146.45 \text{ kcal./mole}$. The experimental curve is drawn using the average value of $\Delta H_0^\circ = 170.32 \text{ kcal./mole}$.

In the single series of runs made with Ti_3O_5 the values calculated for ΔH_0° are seen to rise continuously through

run No. 7. Melting occurred during run No. 8, allowing a small amount of material, condensed on the lid, to flow through the effusion hole and evaporate from a larger area. Thus, the rate of evaporation is relatively too high and the value calculated for ΔH_0^0 has dropped. The rise continues with run Nos. 9 and 10 until a relatively constant value of ΔH_0^0 is obtained, although the scatter seems unusually large. Of the initial material, 8.65% evaporated before the constant ΔH_0^0 value was attained. (All but 4.07% evaporated during run No. 8.) This may indicate an initial loss of an excess TiO_2 but the composition would not be changed appreciably before the "constant boiling" state is reached.

Accuracy of the Data:

The accuracy of the experimental data has been estimated in the following manner:

Weight Loss: With two weighings made for each determination, the uncertainty is estimated at 0.1 milligrams, the percent uncertainty from this source depending on the total weight loss. The uncertainty in the correction for evaporation by the molybdenum cells is estimated at 20% for the unshielded cells and 40% for the shielded cells.

Effective orifice area: The standard deviation in the measurement of the orifice area was determined to be 2%. The error in the Clausing correction has been es-

estimated assuming a 20% error in the depth to radius ratio and a 20% error in the constant in the equation (6)

$$K = \frac{1}{1 + 0.5 (1/a)}$$

to be of the order of 4%. The total uncertainty in the effective orifice area is then 5%.

Effective time: There is no significant error in the effective time, because of the length of the runs.

Temperature: The serious problem arising from the presence of rather large temperature gradients has been discussed. The uncertainty arising from this source has been estimated as follows. For each series of runs the standard deviation of the temperature observed in the effusion hole from the temperature of the run and from the surface temperature was determined. Taking the uncertainty arising from the gradient to be one half of the latter, the total uncertainty was determined by combining these two errors with the normal uncertainty of the temperature measurement in the usual manner. The normal uncertainty (arising from errors in calibration of the standard lamp, $\pm 5^\circ$; error in calibrating pyrometer, $\pm 2^\circ$; error in reading temperature $\pm 2^\circ$; and error due to fluctuation, $\pm 2^\circ$) is determined to be $\pm 6^\circ$.

Pressure: Combining these errors in accordance with the relations

$$P = (w/t_{\text{eff}}A_{\text{eff}}) \sqrt{2\pi RT/M}$$

and $\log P = -A/T - B$

the total uncertainty in P (or K) is determined for each series of runs.

Thermodynamic functions: The estimated uncertainty in the experimentally determined pressures is extended to the thermodynamic calculations. The high temperature enthalpy data on which the free energy functions of the solids are based were obtained by Naylor (32) who reports the following as the deviation of a smooth curve from the experimental points: for TiO , 0.3% to 1800°K; for Ti_2O_3 and rutile, 0.2% to 1800°K; and for Ti_3O_5 , 0.2% to 1400°K. Assuming that the uncertainty will be the greatest at the extreme end of the temperature range and allowing for systematic errors, we may estimate an uncertainty of 2% at the highest temperature. We may estimate a 20% uncertainty in extrapolation beyond the limit of the data. There is an uncertainty in the free energy functions of gaseous TiO due to the uncertainty in the relative positions of low-lying triplet and singlet electronic states (33), but this is a maximum of 0.4% in our temperature range. Uncertainties in the free energy functions of other gaseous species are negligible.

In the absence of free energy functions for TiO_2 gas, the data have been treated using the " Σ " function,

$$\begin{aligned}\Sigma &= -R \ln P + (C_{pTiO_2(g)} - a) \ln T - \frac{b}{2} T + \frac{c}{2} T^{-2} \\ &= \frac{\Delta H_0}{T} + I\end{aligned}$$

values of ΔH_0 and I being obtained by a least squares fit. The coefficients, a, b, and c are the coefficients in the expression

$$C_{pTiO_2(s)} = a + bT - cT^{-2}$$

The function, $a \ln T + \frac{b}{2} T - \frac{c}{2} T^{-2}$, bears about the

same relation to the enthalpy data as the free energy function so we may estimate the same error for it.

$C_{pTiO_2(g)}$ is estimated as 13 ± 3 cal./mole/deg.

Summary: The following uncertainties are derived:

For the heat of sublimation of TiO:

Equilibrium reaction	$TiO(s) = TiO(g)$
Uncertainty in P_{TiO} ,	49. %
Uncertainty in $\log P_{TiO}$,	3.5%
$\Delta H_0^\circ = 134.55 \pm 2.7$ kcal./mole	

For the heat of sublimation of TiO_2 :

Equilibrium reaction	$TiO_2(s) = TiO_2(g)$
Uncertainty in P_{TiO_2} ,	16. %
Uncertainty in $\log P_{TiO_2}$,	1.2%
Uncertainty in the slope, $\log P_{TiO_2}$ vs. $\frac{1}{T}$,	

which is approximately ΔH_T in the temperature range of the data, 9.6%.

This high uncertainty in the heat of sublimation arises from the necessity of calculating ΔH_0 by the method of least squares in a short temperature interval, the square root of the sum of the squares of the reciprocal temperatures about their mean being $0.257 \times 10^{-4} \text{ deg}^{-1}$. The uncertainty in $\log P$ used in the calculation included systematic deviations. The experimental standard deviation was smaller, 2.7%.

The uncertainty in extrapolated values is correspondingly greater. On extrapolating $(-R \ln P)$ from the mean of the observed data the sources of error may be listed with the deviation in units of cal/deg/mole.

Uncertainty of $R \ln P$, 0.32

Uncertainty of slope,

$$1.26 \times 10^4 \times \left(\frac{1}{T} - 5.244 \times 10^{-4} \right)$$

Uncertainty in $C_{p\text{TiO}_2(g)}$

$$3(\ln T - 7.5535) - 0.52 \times 10^4 \left(\frac{1}{T} - 5.244 \times 10^{-4} \right)$$

Uncertainty in $C_{p\text{TiO}_2(s)}$

$$\begin{aligned} & 6(17.97 \ln T + 0.14 \times 10^{-3} T - 2.175 \times 10^5 T^{-2}) - 2.91 \\ & - 0.70 \times 10^4 \left(\frac{1}{T} - 5.244 \times 10^{-4} \right) \end{aligned}$$

Because of the method used to calculate ΔH_0 and I , the deviation of the "slope" in the temperature range of

the data is sensibly independent of the error in the choice of the sigma function. However, the deviation of extrapolated values depends on the choice of the sigma function as indicated in the relations listed above.

The uncertainty in ΔH_{298} is found to be 10.8%

$$\Delta H_{298} = 138.79 \pm 15 \text{ kcal./mole.}$$

The uncertainty in ΔS_{298} calculated from the data is ± 6.9 E.U.

The experimental value of $S_{298} = 49.01 \pm 6.9$ E.U. may be compared with the estimated value of 50.12 E.U. Perhaps the calculated uncertainty is slightly large.

For the dissociation energy of Ti_2O_3 :

Uncertainty of $\sqrt[2]{K_{Ti_2O_3}}$

Series No. 1	39%
Series No. 2	30%
Series No. 3	52%
Series No. 4	28%

Uncertainty of $\frac{1}{2} \log K_{Ti_2O_3}$

Series No. 1	2.7%
Series No. 2	2.1%
Series No. 3	3.8%
Series No. 4	1.9%

Uncertainty of $\frac{\Delta F}{T}$ for the sublimation of TiO_2 , extrapolated, 3.6 cal/deg./mole.

Series No. 1	$\Delta H_0^0 = 157.14 \pm 8.4$ kcal./mole
Series No. 2	$\Delta H_0^0 = 152.31 \pm 8.4$
Series No. 3	$\Delta H_0^0 = 160.58 \pm 8.4$
Series No. 4	$\Delta H_0^0 = 154.73 \pm 8.4$
<hr/>	
Average	$\Delta H_0^0 = 156.19 \pm 8.4$ kcal./mole.

ΔH_0^0 may also be calculated directly from the heats of formation of the oxides. Recalling that the heats of formation were obtained from heat of combustion measurements (22)

$$\Delta H_0^0 = \Delta H_{0c}^0 (\text{Ti}_2\text{O}_3)_s - \Delta H_{0c}^0 (\text{TiO})_s - \Delta H_{\text{sub}}^0 (\text{TiO})$$

$$\Delta H_0^0 = 147.93 \pm 2.7 \text{ kcal./mole.}$$

For the dissociation energy of Ti_2O_3 :

$$\text{Uncertainty of } \sqrt[3]{K_{\text{Ti}_3\text{O}_5}} \quad ; \quad 24\%$$

$$\text{Uncertainty of } 1/3 \log K_{\text{Ti}_3\text{O}_5} \quad ; \quad 1.7\%$$

$$\text{Uncertainty of } \left(\frac{\Delta F}{T} \right)_{\text{sub. TiO}_2} \quad ; \quad 3.6 \text{ cal./deg./mole.}$$

$$\Delta H_0^0 = 170.32 \pm 18.7 \text{ kcal./mole}$$

From heats of formation,

$$\Delta H_0^\circ = 146.45 \pm 2.7 \text{ kcal./mole.}$$

It may be observed that the discrepancies between the "observed" and calculated values for ΔH_0° are larger than the calculated uncertainties, but not larger than the maximum uncertainty (probability of 1 in 25 that value lies outside limits) (37) which may be taken as twice the calculated uncertainty.

Dissociation Pressure of Titanium Dioxide:

Results:

The data given here were obtained during the series of vapor pressure runs on rutile and consist of all of the runs made prior to the attainment of a constant rate of weight loss. As has been explained this constant rate of weight loss at a given temperature was taken to indicate the effective limit beyond which vaporization of TiO_2 molecules predominated over the dissociation to oxygen gas.

The data and calculations are listed in Table VIII for both series of runs. The temperature, effective time, effective orifice area, total weight loss corrected for evaporation of molybdenum, and total evaporation rate were determined in the manner previously described. The pressure of TiO_2 gas was calculated at each temperature using the equation derived from the data obtained in the final runs of the second series. In applying this equation to the runs of the first series all of the calculated pressures were

TABLE VIII
DISSOCIATION PRESSURE OF TiO_2

Run	Temp. °K	Effective Time Sec.	Effective Orifice Area Cm. ²	Total Weight Loss Gms. X 10 ³
1	1647	3600	0.01345	4.19
2	1647	14400	0.01345	1.50
3	1677	14400	0.01346	1.15
4	1668	14400	0.01346	0.45
5	1771	14400	0.01348	2.62
6	1762	14640	0.01348	0.90
7	1771	14400	0.01348	1.13
8	1772	14400	0.01348	0.78
9	1856	14400	0.01350	4.46
10	1848	14400	0.01350	3.18
11	1854	13140	0.01350	2.01
12	1923	14400	0.01352	4.43
13	1928	14400	0.01352	3.42
14	1936	14400	0.01352	3.33
15	1966	14400	0.01353	4.93
19 (a)	1670	420	0.01374	3.33
19 (b)	1764	10080	0.01377	7.30
20	1856	13320	0.01379	7.38
21	1917	5400	0.01381	6.80
22	1922	10860	0.01381	7.61
23	1945	14520	0.01381	7.83
24	1946	14400	0.01381	5.95
25	1949	28800	0.01381	11.06
26	1958	14400	0.01382	6.29
27	1956	14460	0.01382	5.29

TABLE VIII (Cont'd)
DISSOCIATION PRESSURE OF TiO_2

Run	Total Evaporation Rate gm./cm. ² /sec. $\times 10^5$	Pressure of TiO_2 (calculated) atm. $\times 10^6$	Evaporation Rate of TiO_2 (calculated) gm./cm. ² /sec. $\times 10^6$
1	8.653	0.00364	0.004
2	0.774	0.00364	0.004
3	0.593	0.00752	0.007
4	0.232	0.00608	0.006
5	1.350	0.0611	0.058
6	0.456	0.0508	0.048
7	0.582	0.0611	0.058
8	0.402	0.0625	0.059
9	2.294	0.342	0.315
10	1.595	0.294	0.271
11	1.183	0.378	0.348
12	2.275	1.189	1.074
13	1.757	1.294	1.168
14	1.709	1.496	1.347
15	2.530	2.518	2.250
19 (a)	57.70	0.00794	0.008
19 (b)	5.259	0.0659	0.062
20	4.018	0.442	0.407
21	9.119	1.380	1.249
22	5.074	1.503	1.359
23	3.905	2.265	2.035
24	2.992	2.291	2.058
25	2.781	2.415	2.168
26	3.161	2.811	2.535
27	2.645	2.742	2.457

TABLE VIII (Cont'd)
DISSOCIATION PRESSURE OF TiO_2

Run	Evaporation Rate of MoO_2 gm./cm. ² /sec. $\times 10^6$	Average Mole Ratio O/Ti in Solid	Pressure of MoO_2 atm. $\times 10^6$
1	8.649	1.9947	7.00
2	0.770	1.9874	0.623
3	0.586	1.9840	0.479
4	0.226	1.9820	0.184
5	1.292	1.9782	1.084
6	0.408	1.9740	0.342
7	0.524	1.9716	0.440
8	0.343	1.9694	0.288
9	1.979	1.9636	1.700
10	1.324	1.9552	1.135
11	0.785	1.9500	0.674
12	1.201	1.9450	1.050
13	0.589	1.9402	0.516
14	0.362	1.9375	0.318
15	0.280	1.9355	0.248
19 (a)	57.69	1.9965	47.02
19 (b)	5.197	1.9852	4.353
20	3.611	1.9704	3.102
21	7.870	1.9570	6.871
22	3.715	1.9446	3.248
23	1.870	1.9342	1.645
24	0.934	1.9277	0.822
25	0.613	1.9221	0.540
26	0.626	1.9171	0.552
27	0.188	1.9145	0.104

TABLE VIII (Cont'd)
DISSOCIATION PRESSURE OF TiO_2

Run	Pressure of O_2 atm. $\times 10^{10}$	Temp. at $P_{\text{O}_2} = 3.5$ $\times 10^{10}$	Pressure of O_2 at 1850°K atm. $\times 10^{10}$
1	4.82	1639	7550.
2	0.428	1702	671.
3	0.436	1725	206.
4	0.154	1754	104.
5	2.24	1784	32.3
6	0.658	1812	12.9
7	0.910	1811	13.1
8	0.600	1815	8.28
9	6.86	1835	5.69
10	4.70	1839	5.02
11	2.82	1866	2.00
12	6.89	1901	0.718
13	3.50	1928	0.316
14	2.28	1951	0.161
15	2.18	1983	0.0647
19 (a)	40.2	1611	24950.
19 (b)	8.49	1739	156.
20	12.5	1817	10.4
21	43.2	1837	5.38
22	21.2	1863	2.28
23	12.6	1902	0.684
24	6.31	1926	0.336
25	4.23	1942	0.206
26	4.60	1948	0.172
27	0.857	1989	0.0541

multiplied by the factor 0.8 in order that the calculated pressure for this series should agree with the measured pressure of the final three runs. We have assumed that the discrepancy between the two runs has arisen from a systematic error in the temperature measurement causing the errors for the two series to be shifted parallel to each other. The evaporation rate of TiO_2 was then calculated using the relation

$$m = P \sqrt{2 \pi R T / M}$$

The evaporation rate of MoO_2 was then obtained by subtracting the evaporation rate of TiO_2 from the total evaporation rate, making the assumption that the species predominating in the effusing vapor are TiO_2 and MoO_2 . The basis for these assumptions will be discussed presently. The average mole ratio of oxygen to titanium in the solid was then calculated with the assumption that starting with pure TiO_2 the only changes in composition were due to loss of TiO_2 and oxygen in the form of the reaction product MoO_2 . The total weight loss of TiO_2 and MoO_2 was determined at the midpoint of each run, and the molar ratio calculated. The initial amount of TiO_2 placed in the cell was corrected for a 0.3% loss on ignition determined separately. The pressure of MoO_2 was then calculated in the usual manner and the pressure of O_2 calculated from the assumed equilibrium

This equilibrium was calculated using the expression for the free energy of formation of molybdenum dioxide solid given by Thompson (43) and the vapor pressure of molybdenum dioxide gas over molybdenum dioxide solid obtained in this laboratory recently by Blackburn (1). These are:

For $\text{Mo(s)} + \text{O}_2(\text{g}) = \text{MoO}_2(\text{s})$ in the range 918°K to 1096°K

$$\Delta F^\circ = -130,884 - 4.304 T \ln T + 2.21 \times 10^{-3} T^2 \\ - 2.515 \times 10^4 T^{-1} + 67.57 T$$

and for $\text{MoO}_2(\text{s}) = \text{MoO}_2(\text{g})$

$$\log P_{\text{MoO}_2} = - \frac{17.873}{T} + 6.035$$

or

$$\Delta F^\circ = 81,751 - 27.60 T$$

Combining these two relations, extrapolating to the range 1600°K to 2000°K, and simplifying, results in the expression for

$$\Delta F^\circ = -48.551 + 11.38 T$$

or

$$-\log K = -\log P_{\text{MoO}_2} + \log P_{\text{O}_2} \\ = - \frac{11,231}{T} + 2.657$$

The extrapolation of the observed temperatures and pressures for each run to the average pressure of oxygen, $P_{\text{O}_2} = 3.5$

$\times 10^{10}$ atm., was performed in the following manner. First the temperature of each run was plotted vs. the average composition. This corresponds to an extrapolation assuming infinite heat of solution of O_2 in TiO_{2-x} . Then the extrapolation was performed using an assumed low heat of solution and another set of points plotted vs. average composition. For runs made at widely different temperatures the extrapolations were in opposite directions, and for many of the runs the extrapolation was short. The position of the true curve of temperature vs. composition between these two sets of points could readily be determined. Having drawn the best smooth curve between the points the actual slope of $-\log P_{O_2}$ vs. $\frac{1}{T}$ could be estimated and this estimate used for the extrapolation of the $-\log P_{O_2}$ values to the average temperature, 1850°K. The data so calculated are plotted in Figures 9 and 10.

Discussion of Results:

Because of the assumptions and approximations made, no great degree of accuracy can be assigned to these calculations. However, the curves obtained do show a reasonable form and the magnitude of the calculated oxygen partial pressures is not inconsistent with the free energies of formation of the oxides of titanium, taking into consideration the formation of solid solutions.

The assumptions involved in this calculation will be discussed in more detail. The assumption that the

FIGURE 9

FIGURE 10

partial pressure of titanium dioxide may be considered as essentially constant over a short range of composition is admittedly an approximation but may be within the experimental error. The error introduced by this assumption should be evident as a discrepancy between the two series of runs in the composition of the solid calculated at equal pressure and temperature. Such a discrepancy does exist since the composition at which the O_2 pressure becomes negligible in the first series is considerably higher in oxygen content than in the second series made at higher average temperatures. However, the calculated pressure of TiO_2 would have to be raised 45% in order to bring the two series into line so there must be other errors influencing the results.

The assumption has also been made that the pressure of MoO_2 gas in the system is much greater than the pressure of $O_2(g)$ or $O(g)$. According to the calculations the molybdenum dioxide gas pressure should be 1000 times greater than the O_2 gas pressure at equilibrium and 10 to 100 times greater than the O gas pressure. Due to the uncertainty in the data used to calculate the equilibrium, a very large error could be introduced by this assumption. However, the pressures of O_2 calculated from the pressures attributed to molybdenum dioxide, assuming equilibrium, are not inconsistent with the assumption.

The assumption that equilibrium is attained between

the various gaseous species and the solids Mo and TiO_{2-x} is also subject to considerable error. If the oxidation of molybdenum by titanium dioxide is considered as a gas phase reaction, depending on the dissociation of titanium dioxide to oxygen, the rate will be slow due to the very low pressure of oxygen and this will strongly affect the attainment of equilibrium. If the reaction occurs at a solid-solid interface we might expect the reaction to be more rapid and the attainment of equilibrium more likely. The error introduced if equilibrium is not attained would tend to lower $\text{MoO}_2(\text{g})$ pressures and hence the calculated oxygen pressures. This affect could be tested by measuring the vapor pressure over an intimate mixture of powdered molybdenum and titanium dioxide in which the area of the solid-solid interface would be greatly increased.

The assumption has also been made that the diffusion of oxygen through the titanium oxide is rapid so that the concentration at the surface where the reaction or vaporization takes place is essentially that of the bulk oxide. This assumption is supported by work on the kinetics of the reaction between titanium and oxygen (16) which involves the reverse reaction, but the rate determining step is the diffusion of oxygen into titanium. The diffusion of oxygen through TiO_{2-x} must be even more rapid.

Unfortunately, the material in the cell was not analyzed as a check on the calculation of the composition. Therefore,

the calculated compositions cannot be considered as being very reliable. The calculated composition depends very strongly on the assumed compositions of the vapor. As we have seen, this is subject to considerable error particularly as the ratio of MoO_2 to TiO_2 decreases.

SUMMARY AND CONCLUSIONS

Powder X-ray diffraction patterns taken at elevated temperatures indicate that there is no structural change in the oxides, TiO , Ti_2O_3 , and rutile at temperatures near their respective melting points. The case with Ti_3O_5 is not yet clear. It apparently exists as a compound in a limited homogeneity range, distinct from that of Ti_2O_3 or rutile and may undergo a structural transformation. The structures of neither the high temperature form nor the low temperature form have been determined. The rutile phase extends over a wide homogeneity range from the composition TiO_2 to about $\text{TiO}_{1.8}$, though the original structure becomes extremely distorted.

Measurement of vapor pressures by the rate of effusion method has indicated that the important species in the vapor of the titanium oxides near their melting points are Ti , TiO , and TiO_2 except in the case of pure TiO_2 . This undergoes dissociation, evolving oxygen and forming an oxygen-deficient rutile phase. The predominating gaseous species over $\text{TiO}(\text{s})$ is $\text{TiO}(\text{g})$ but there is evidence that $\text{Ti}(\text{g})$ is present also. A relatively wide range of very nearly "constant boiling" compositions is found near Ti_2O_3 and Ti_3O_5 .

The heats of sublimation of TiO at 0°K and 298°K and of TiO_2 at 298°K have been calculated as well as the heats

of dissociation at 298°K of Ti_2O_3 and Ti_3O_5 dissociating to form TiO gas and TiO_2 gas.

Equations for the vapor pressure of TiO solid and the partial pressure of TiO_2 gas over TiO_2 solid have been obtained.

The dissociation energies of TiO gas at 0°K and TiO_2 gas at 298°K have been calculated.

An approximate calculation has been made to obtain the partial pressure of O_2 versus composition in the oxygen-deficient rutile phase region.

APPENDIX

APPENDIX

TABLE IX

EFFUSION CELL DIMENSIONS AND CORRECTION

Table No.	Run Nos.	Depth of Cell Cm.	Radius of Cell Cm.	Depth of Orifice Cm.	Radius of Orifice Cm.	Area of Orifice Cm. ²	K
I	1	1.9	1.2	0.0254	0.1219	0.0467	0.896
	2	1.5	1.2	0.0254	0.0775	0.01885	0.855
	4-5	1.5	1.2	0.0254	0.0787	0.01946	0.857
	7-11	1.5	1.2	0.0254	0.0788	0.01949	0.857
	13-17	1.2	1.2	0.0254	0.0747	0.01751	0.851
II	1-4	1.0	0.96	0.0254	0.0428	0.005767	0.760
	5-9	1.0	0.96	0.0254	0.1187	0.04425	0.890
	10-18	1.0	0.96	0.0254	0.1232	0.04767	0.892
	19-26	1.8	0.24	0.0254	0.0814	0.02082	0.658
	29-39	1.1	0.89	0.0254	0.0799	0.02004	0.862
III	1-16	1.8	0.50	0.0254	0.0811	0.02068	0.834
IV	14-18	1.75	0.24	0.0254	0.0792	0.01973	0.671
	25.33	1.90	0.24	0.0254	0.0811	0.02068	0.653

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AUTOBIOGRAPHY

I, Warren Olley Groves, was born in Teheran, Iran, November 8, 1928, my parents being Presbyterian missionaries to Iran. I received my elementary education at the mission school in Teheran and on our return to the United States, attended schools in Danville, Kentucky, and later at duPont Manual Training High School in Louisville, Kentucky. My undergraduate training was obtained at Lafayette College, in Easton, Pennsylvania, from which I received the degree Bachelor of Arts in 1948. At The Ohio State University, I have held graduate teaching assistantships in general chemistry and quantitative analysis, also a research fellowship under The Ohio State University Research Foundation, and, for the academic year 1953-1954, the General Electric Fellowship. During the year 1952, I was employed by Dr. Herrick L. Johnston as a cryogenic engineer, taking part in the Atomic Energy Commission project at Eniwetok Atoll. The following year I returned to The Ohio State University to complete work for the degree Doctor of Philosophy.