A THERMODYNAMIC DETERMINATION OF THE DISSOCIATION ENERGY OF THE GASEOUS TIO MOLECULE

by

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A. Introduction

In recent years titanium, the earth's ninth most abundant element, has rapidly assumed a position of metallurgical importance. The slowness with which the technological aspects of the extractive metallurgy of titanium have been developed may be attributed in large measure to the dearth of knowledge of the fundamental thermodynamic properties of the element and its compounds. As the metal oxidizes rapidly above 650°C, the thermodynamic relationships in the titanium-oxygen system present a particularly fruitful field for study.

In addition to the naturally occurring dioxide, the tritapentoxide, sesquioxide and monoxide have been prepared (1). The known thermodynamic properties of these oxide phases have been summarized in a recent excellent review by Brewer (2). Thermochemical data currently available in the literature pertain principally to the solid-state reactions of interest in the titanium-oxygen system. Information on vaporization processes and equilibrium pressures of the various oxides is meager. Such data for the monoxide, TiO, would be of particular interest to astronomers and astrophysicists, for the spectrum of the TiO gaseous molecule is observed in many stars (3, 4, 5, 6, 7).

Data of the type described above may often be derived from a study of the spectra of the gaseous molecules associated with the chemical system of interest. While spectroscopy frequently yields very accurate values for the dissociation energy of diatomic molecules, as for example in the case of $I_2(g)$ (8, 9), the dissociation energy of TiO(g) has not yet been accurately determined. Two values, 159 kcal./mole (9) and 127 kcal./mole (8), respectively, have been proposed, but neither has received universal acceptance. The first of these is based on a linear Birge-Sponer extrapolation (9a) of the energy differences of the first six vibrational levels of the $^3\Pi$ ground state as observed by Christy (10) and by Lowater (11), while the latter value is obtained by applying to the value given by the linear extrapolation the plausible but uncertain correction suggested by Gaydon (8) for non-linearity of the extrapolation at high vibrational levels. The uncertainty associated with each of these proposed values is quite large, being of the order of ± 1 ev, or ± 23 kcal./mole. Although the spectrum of TiO(g) has been the subject of intense investigation (12), 13, 14), no observation of the energy separations of the higher vibrational levels has been reported. In such cases one must appeal to other methods of experimentation in order to establish a more nearly reliable value for the dissociation energy.

The available methods of determining dissociation energies of gaseous molecules have been adequately summarized by Gaydon (8) and by Herzberg (9). These approaches may conveniently be placed into three classes, *viz.*, those dependent on spectroscopic observations, those relying on thermochemical measurements, and those that utilize the observed "appearance potentials" of various ions in electron impact experiments. We have noted above that spectroscopic measurements have not proved especially fruitful in the particular case under consideration. One should, therefore, consider the types of thermochemical experiments that have proved of value for the determination of the dissociation energy of diatomic molecules.

Of the various methods that have been employed by other workers (8), most are based on a determination of the equilibrium constant for the reaction that accomplishes the dissociation of the gaseous molecule into its normal gaseous atoms, or on determinations of the equilibrium constants for various other reactions of the elements and their compounds. By the appropriate combination of the equilibrium constants for those reactions mentioned in the latter case above, one may then calculate the equilibrium constant for the dissociation reaction. Thus in the case of TiO(g), since the heat of formation of TiO(s) (15), the dissociation energy of oxygen (16, 17), and the heat of sublimation of titanium (18, 19, 20) are known, it follows that a determination of the heat of sublimation of TiO(s) will permit the calculation of the dissociation energy of TiO(g). The energy level diagram of Figure 1 depicts the pertinent relationships among those substances of interest in the present discussion.

Heats of sublimation of relatively non-volatile substances are usually derived from measurements of the equilibrium vapor pressure of the element or compound in question (21). The purpose of this investigation is, therefore, to obtain a more nearly accurate estimate of the dissociation energy of TiO(g) than has previously been available by combination of the heat of sublimation of TiO with other available thermochemical data. The heat of sublimation of TiO may be derived from determinations of the volatility of TiO by Knudsen's rate of effusion method (25).

Ditchburn and Gilmour (22) critically discussed vapor pressure data appearing in the literature in the time interval 1935-1941, and reviewed the methods of determining vapor pressures used by various workers. Methods applicable to relatively non-volatile substances that have vapor

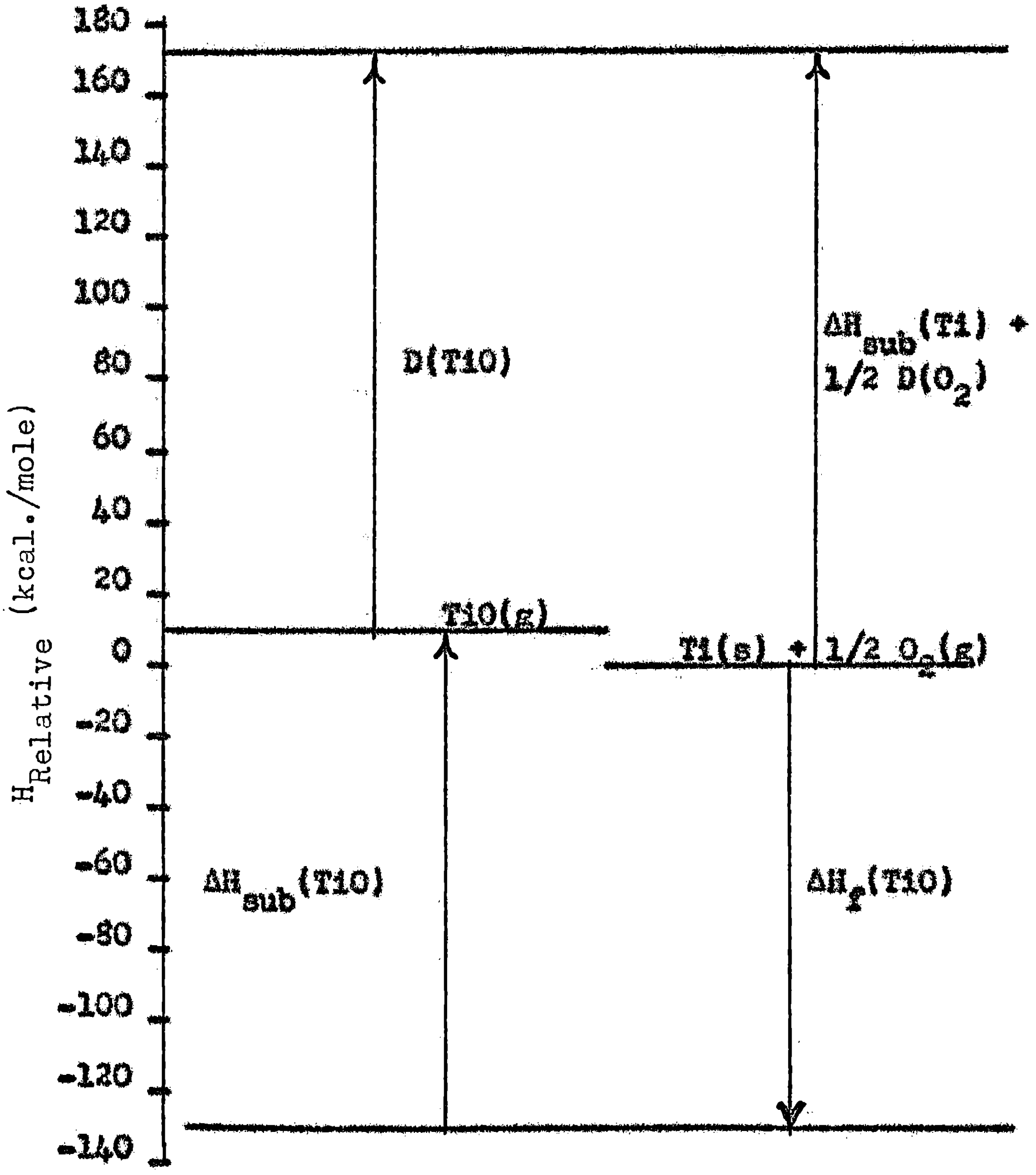


Figure 1. Relative heat contents of various species in the titanium-oxygen system.

pressures in the range 10^{-8} to 10^{-2} mm Hg have been described by Speiser and Johnston (23) with particular reference to the theory and practice of determining the vapor pressure of metals by Langmuir's rate of evaporation method (24) and by Knudsen's effusion method (25, 26, 27, 28, 29, 117, 118). In addition to the methods of Langmuir and of Knudsen, brief mention may be made of other methods such as the manometric (30), transpiration (31, 32) and electrical (33, 34, 35) techniques, as well as of those procedures utilizing the measurement of mechanical force (36, 37, 38). Very recently Honig (38a) and Chupka and Inghram (38b) have developed a method that utilizes the mass spectrograph. One distinct advantage of this new method is that, in addition to a determination of the volatility of a given material, the molecular species in the vapor phase may be identified.

Although the manometric or static methods are suitable for use at moderate temperatures, the necessary close mechanical tolerances in equipment for such experiments cannot be maintained at high temperatures. Brewer and Lofgren (32) have used the transpiration method successfully in a study of the copper-chlorine system, but as has been noted by Lepore and Van Wazer (39), this method frequently leads to erroneous results because of the uncertain effects of thermal diffusion.

The Langmuir method can be used to measure pressures that are a factor of 10^3 to 10^4 lower than those measurable by the Knudsen method because of the large evaporating surfaces employed. At a given temperature and time of run, the large weight loss obtained in a Langmuir experiment yields a calculated evaporation rate of higher percentage accuracy than that from a Knudsen experiment. As induction heating was used exclusively throughout the work reported here, it was necessary to resort to the Knudsen method of vapor pressure determination, for the conductivity of solid TiO is so low that it does not heat efficiently in the field of an induction coil. Samples of TiO were, therefore, contained in molybdenum Knudsen cells.

B. Apparatus and Materials of Construction

The design, construction, testing and application of the various items of equipment and materials employed throughout this work are described in detail in a separate report (40). The salient features of the vacuum induction furnace used for the major fraction of the research reported here are, however, outlined below.

Two distinct systems capable of producing high vacua, designated "Apparatus No. 1" and "Apparatus No. 2", respectively, were available. "Apparatus No. 1", used throughout this work, consisted of a Distillation Products VMF-100W metal diffusion pump backed by a Stokes "Microvac" fore pump, Cat. No. 212D, Ser. No. A34646. The vacuum chamber was constructed of 3" i.d., heavy-wall, flanged "Pyrex" Brand glass pipe. A glass pipe elbow was sealed to the vertically-mounted diffusion pump with Apiezon-W wax. The leg of a glass pipe "T" joined the horizontal limb of the elbow in such a manner that the axis of the arms of the "T" was vertical. The upper arm of the "T" led to an optical window which permitted observation of the sample and readings of the sample temperature, while vaporization cells of large diameter tubing could be attached to the lower arm of the "T". A magnetically operated shutter was interposed between the sample and optical window. Temperatures were determined with a Leeds and Northrup disappearing filament optical pyrometer, Cat. No. 8622-C, Ser. No. 723042, by sighting on a blackbody hole in the lid of the Knudsen cell. Of the two optical pyrometers available, that designated "No. 1" in the report cited above was used for all temperature measurements reported here. It should be noted here that pyrometer "No. 1" had been calibrated and certified by the National Bureau of Standards on the basis of the 1927 international temperature scale (41). Conversion to the 1948 international temperature scale would introduce corrections of only 3 to 4 degrees (42) in the range of temperatures encountered in this work. As these corrections are well within the absolute uncertainty of the temperature measurements, no corrections to convert temperature readings to the 1948 temperature scale have been made.

Pressures of residual gas in the vacuum system were determined with a Pirani gauge, a hot-cathode ionization gauge and a cold-cathode ionization gauge. High-frequency power for inductive heating was supplied by a 6 kva sealed-spark-gap converter manufactured by the Ajax Electrothermic Corporation. This instrument delivered 8 to 12 pulses of highly damped 16 kc current every 1/120 second with the particular charge work-coil combination used. The 32-turn water cooled 3P4 work coil supplied with the generator was used.

Although provisions for automatic temperature control were incorporated in the design of the vacuum furnace (40), this feature was not used during the latter portion of this research, for it was observed that manual control gave adequately constant temperatures. Temperature readings were estimated to be accurate to ±10°C while relative temperature readings were uncertain by no more than ±5°C.

Knudsen effusion cells and their associated supports and radiation shields were fabricated from molybdenum metal.

C. Preparation of Titanium Monoxide

All samples of TiO used in this work were taken from a larger sample of material prepared by Shomate (1) for use in the study of the low-temperature heat capacity of TiO. Portions of this same original preparation were also used by Naylor (43) in a study of the high-temperature heat capacity of TiO, and by Humphrey (15) for the determination of the heat of formation of TiO. The monoxide used in this research was furnished the author through the generosity of Dr. Leo Brewer of the University of California and Dr. K. K. Kelley of the U. S. Bureau of Mines.

Shomate prepared titanium monoxide by the reaction of equimolal quantities of titanium dioxide and titanium metal at 1350°C *in vacuo*. Analysis of the product gave 99.2 per cent TiO, 0.1 per cent TiC and 0.7 per cent SiO. Re-analysis of the same lot of material five years later gave identical results (15).

In January, 1952, approximately six months after publication of Humphrey's data (15), samples of the monoxide subsequently used in this research were submitted to the University of California Radiation Laboratory for spectrochemical analysis. The reported analysis in weight per cent follows: Si and Pb, 0.01 - 0.1 each; Al, Cu, Fe, Mg, Ni and Zr, less than 0.01 each; Ca, Cr, Mn, Mo, Sn and Zn, not detected. An analysis of the monoxide by combustion in air at 1000°C indicated a composition for the original material of $TiO_{0.997\pm0.004}$ uncorrected for silicon and carbon impurities, and $TiO_{0.999\pm0.004}$ corrected for impurities. Analyses of two samples by direct reaction with BrF_3 and measurement of the volume of oxygen released yielded calculated compositions of $TiO_{0.993\pm0.005}$ and $TiO_{0.995\pm0.005}$, respectively, uncorrected for impurities. If the data are corrected for silicon and carbon impurities, one finds $TiO_{0.989\pm0.005}$ and $TiO_{0.991\pm0.005}$. The latter two methods of analysis will be considered in more detail in the following section. No titanium assay was performed.

D. Methods of Analysis

1. Assay of TiO Samples

Sufficient amounts of monoxide material were usually available to permit the utilization of standard gravimetric and volumetric analytical procedures for the determination of sample composition. Five different methods were used to establish the composition and purity of the raw material, and of the residues obtained from various vaporization experiments.

The original monoxide sample was analysed by two methods, the first of which involved combustion in air. Specifically, 0.2462 g of TiO_y was weighed into a tared platinum dish that had been ignited previously to constant weight. The dish with oxide sample was then placed into a muffle furnace that was set at a temperature of 1000-1050°C. The combustion was allowed to proceed for eight hours. The combustion product weighed 0.3018 g. If the combustion data are taken at face value, and if no corrections are made for the supposed silicon and carbon impurities, then one finds a calculated oxide composition of $TiO_{0.997\pm0.004}$. The uncertainty limits are assigned on the assumption that weighings were accurate to ± 0.2 mg. If the analysis reported by Shomate (1) is assumed to represent correctly the percentage of silicon and carbon present in the sample, and if it is assumed further that, on ignition, the SiO is oxidized to SiO_2 and that TiC is converted to TiO_2, the combustion analysis may be corrected for the silicon and carbon impurities. One thus calculates that the composition of the original material was $TiO_{0.999\pm0.004}$.

Recently Hoekstra and Katz (43a) at Argonne National Laboratory have developed a method for the direct determination of oxygen in metallic oxides and some other oxygen-containing compounds. Samples of TiO, and of residues from various vaporization experiments were submitted to Dr. Hoekstra for analysis. A complete report of these analyses is included in a subsequent section of this thesis, while the principle of the technique is indicated below.

Metallic oxides react with bromine trifluoride as indicated by the following equation:

$$3\ TiO_y + 4\ BrF_3 = 2\ Br_2 + 3\ TiF_4 + (3y/2)\ O_2. \qquad (1)$$

If the reaction is carried out in a closed system fitted with the appropriate traps and pumps, the bromine and tetrafluoride formed as a result of the reaction may be frozen out in liquid nitrogen traps while the oxygen may be pumped off and its volume, temperature, and pressure measured. Thus if it is assumed that the sample is pure metallic oxide, the unknown parameter "y" in the above equation may be calculated. If cognisance is not taken of small amounts of impurities such as SiO, TiC and TiN, the calculated value of "y" will be slightly in error. The oxygen in SiO and the nitrogen in TiN will contribute to the volume of gas evolved from the sample. Since carbon will appear as CF_4, and will not be trapped out under the usual experimental conditions, it, too, will contribute to the measured gas volume. Not all oxygen containing compounds liberate their oxygen quantitatively on reaction with BrF_3, but form stable oxy-fluorides, or undergo no extensive reaction at all. Hoekstra and Katz (43a) found, for example, that MoO_3 formed the stable intermediate $MoOF_4$. Thus only two-thirds of the theoretical amount of oxygen is evolved.

Two analyses of the titanium monoxide used in this research were carried out by the above method. These yielded calculated compositions of $TiO_{0.993\pm0.005}$ and $TiO_{0.995\pm0.005}$, respectively. Cognisance was not taken of the silicon and carbon impurities reported present in the sample by Shomate (1). Correction of the analytical data for these reported impurities leads to calculated compositions of $TiO_{0.989\pm0.005}$ and $TiO_{0.991\pm0.005}$, respectively.

As has been noted previously, spectroscopic analyses of the same lot of material indicated only 0.1 - 0.01 per cent silicon. One is thus led to question the validity of the above corrections. The value of such corrections is further placed in doubt by virtue of the fact that there is no experimental verification of the assumption made above that solid solutions of SiO and TiC in TiO will liberate oxygen and carbon quantitatively on treatment with BrF_3. The corrected compositions should, however, fix a lower limit for the oxygen-titanium ratio in the titanium monoxide samples considered. The precision of the direct oxygen analyses is better than ±0.002, in oxygen-titanium ratio, while the estimated uncertainty (43a) is ±0.005 in terms of oxygen-titanium ratio.

In addition to the above two methods of sample analysis, limited use was made of spectroscopic and polarographic techniques. The spectroscopic analysis of TiO has been reported in a previous section, while the polarographic method of analysis for molybdenum reported by Haight (44) was used to estimate the amount of molybdenum present in the original sample material, and in the residue from a series of vaporization runs during which eight per cent of the sample was lost by sublimation and effusion from the Knudsen cell. The polarographic analysis indicated 0.5 per cent molybdenum in this residue, while a spectroscopic analysis of the same material indicated the molybdenum concentration to be over one per cent. Polarographic analysis of the original material failed to indicate the presence of molybdenum, in agreement with the spectroscopic analysis performed at the University of California, but in disagreement with a spectroscopic analysis performed at the University of Kansas that indicated about 0.1 per cent molybdenum. The polarographic method was used also to check the results of a spectrophotometric analysis for molybdenum in the sublimate collected during one vaporization experiment. The absence of molybdenum in the sublimate as indicated by the spectrophotometric analysis was confirmed by the polarographic analysis.

X-ray diffraction techniques were used extensively throughout this research, and have proved to be a valuable tool for the elucidation of the composition and phase relationships of crystalline solid substances. X-ray diffraction techniques were used to obtain an estimate of the purity, nature and number of solid phases present in a given sample, and to determine the composition of various $TiO_{1\pm x}$ preparations obtained during the course of this work.

Numerous workers have studied the phase relationships in the titanium-oxygen system by means of X-ray diffraction techniques (45, 46, 47, 48, 49, 50, 51, 52), but only Ehrlich (46, 47), Bumps, _et alii_ (51) and Rostoker (52) have investigated extensive ranges of composition by this method. For our purposes, we need consider only the lattice parameter _vs._ composition relationships throughout the $TiO_{1\pm x}$ (NaCl-type) homogeneity range. General phase relationships in the titanium-oxygen system are discussed in more detail in the following section of this thesis.

The X-ray diffraction data reported by Bumps, _et alii_ (51) are due to Rostoker (52). Both Rostoker and Ehrlich (46) report determinations of the variation of the size of the unit cell of cubic $TiO_{1\pm x}$ as a function of composition. Similar data were obtained in this research. These data are collected for the purpose of comparison in Figure 2.

It is important to note that while both Ehrlich and Rostoker report their lattice parameter values in Angstrom units, they actually used kX units. As neither Rostoker nor Ehrlich report the wave-length of the radiation used in their work, there is some uncertainty involved in the conversion of their data to Angstrom units. In this research all X-ray data were obtained with filtered characteristic copper $K\alpha_1$ and $K\alpha_2$ radiation, of wave-length 1.54050 A and 1.54434 A, respectively, or with filtered molybdenum $K\alpha_1$ and $K\alpha_2$ radiation of wave-length 0.70926 A and 0.71354 A, respectively.

All data shown in Figure 2 have, where necessary, been converted to Angstrom units as internationally agreed upon in 1946 (53). Since the kX unit is larger than the Angstrom unit by a factor of 1.00202 (53), the data of Ehrlich and of Rostoker were converted to Angstroms on this basis.

Ehrlich makes no estimate of the uncertainty limits of either his lattice parameter data or of his chemical analyses, so no attempt has been made to indicate such limits for those points that represent his data in Figure 2. The range of uncertainty in composition ascribed to the data of Rostoker is that given by Bumps, et alii (51), while the composition limits for the data obtained in this research were estimated as described previously. Analyses of samples for which X-ray data were obtained during the course of this work were performed by Hoekstra (43a).

Rostoker reports the uncertainty of his lattice parameters to be about ±0.005 A. As Cohen's method (54, 55, 56, 57) was used to derive the lattice constants, it is the opinion of the author that Rostoker's estimates are decidedly pessimistic. Rostoker did not undertake a least-squares treatment of his data to establish an estimated uncertainty for his lattice parameter measurements, but set the quoted limits from a knowledge of the fact that values of the lattice parameter derived from measurements of a given film, repeated by the same observer at intervals of about two weeks, were in agreement to about ±0.005 A (57a). He was unable to give an estimate of the uncertainty to be assigned to the chemical analyses of his samples, for he did not perform the analyses, and had no information other than that of the samples were assayed for titanium, and that oxygen was calculated by difference. It is perhaps pertinent to note that it has been found possible at the University of Kansas for different observers to derive lattice parameter values that are in agreement to within about one part in 40,000 from measurements of a given film repeated at an interval of about six months. Rostoker's estimates have, however, been taken at face value and are so indicated in Figure 2.

A comprehensive survey and bibliography of the subjects of systematic errors in X-ray cameras and the precision measurement of lattice constants has been given by Buerger (58), while contributions of more recent date have been made by Warren (59), Thomas (60), Ekstein and Siegel (61) and Straumanis (62). Cohen's method of analytical extrapolation, to eliminate the effect of the systematic errors inherent in all present types of precision cameras, is now firmly established as probably the most generally useful technique available for the precision determination of lattice constants, and was, therefore, employed throughout this work. One of its chief advantages lies in the fact that the basic analytical extrapolation can be extended to a least-squares treatment to reduce the effect of random errors in the initial data, and to estimate the precision of the calculated parameters from the criterion of external consistency (63). Hess (64) has criticised certain aspects of Cohen's treatment, and suggests a modified method. Hess points out, however, that unless some diffration lines occur in the region of the film 90° > θ > 75° the two methods give almost identical results. Following the method of Jette and Foote (63), the probable error of lattice constants determined for samples used in this research was found to vary from about one to two parts in 40,000. In Figure 2, the size of the rectangle surrounding each datum obtained during this work indicates the uncertainty in both composition and lattice constant. In view of the uncertainties as to the effect of sample purity, analytical errors and X-ray diffraction techniques on the data of various workers, it is difficult to assign a specific reason for the differences among the lattice parameter *vs.* composition data for the TiO phase shown in Figure 2. While all the data are in fair agreement in view of the assigned uncertainties, it will be noted that the data of Rostoker yield consistently higher lattice parameters than those found by Ehrlich or in this research. This is the type of deviation to be expected if Rostoker's samples contained TiC in solid solution to the extent of two or three mole per cent.

2. Analysis of Sublimates

During the latter portion of this research, collections of the material that effused from the Knudsen cells were obtained by condensation on platinum or quartz targets. In general, the mass of material collected during a given experiment was of the order of a milligram, so methods suitable for the analysis of small amounts of material had to be devised.

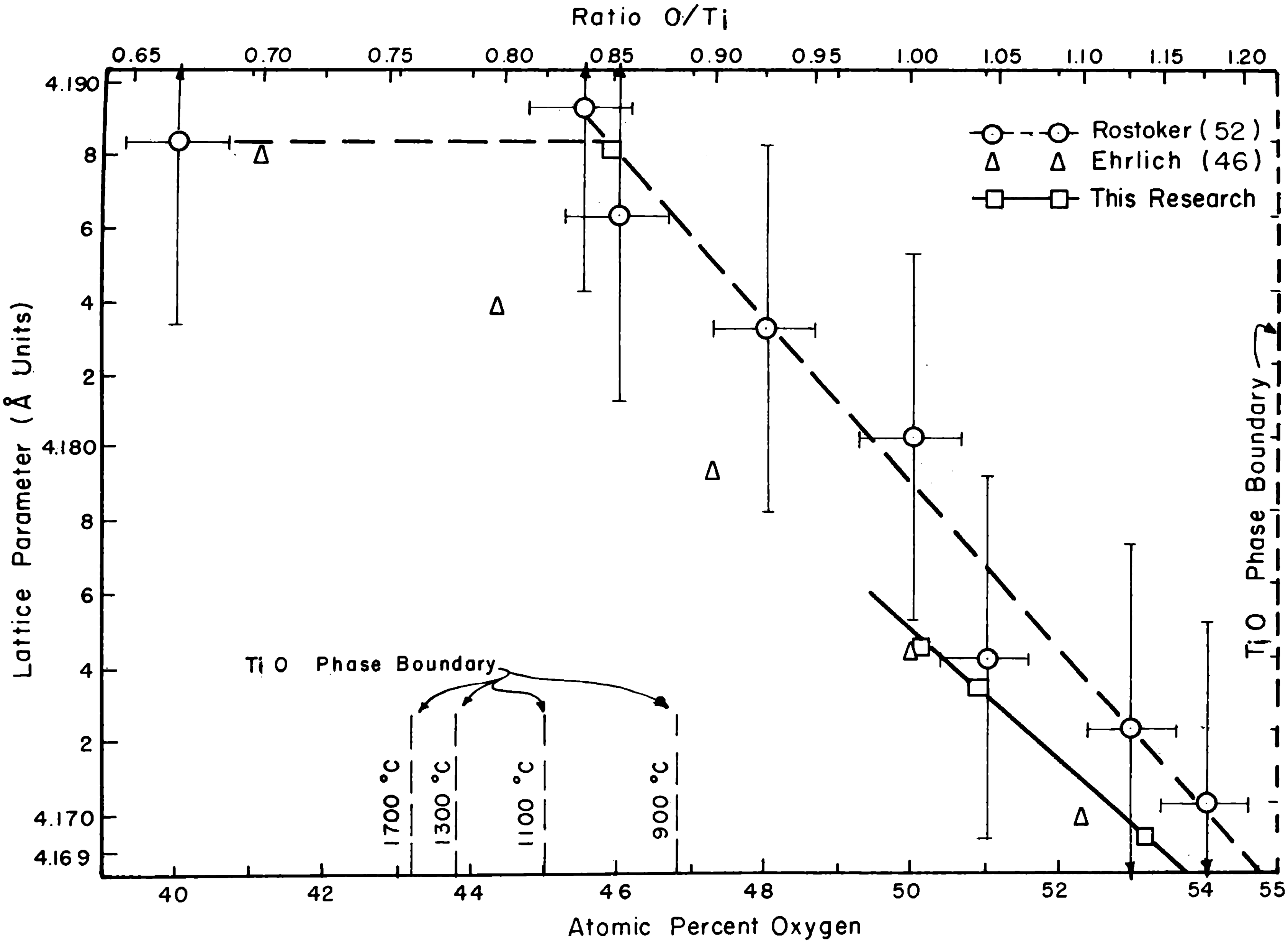
The polarographic method of analysis for molybdenum (44) was, as previously noted, used only once for sublimates. X-ray diffraction techniques were tried, but unfortunately sublimates do not often give satisfactory diffraction patterns. Substances condensed from the vapor phase on a relatively cool surface usually deposit in a highly oriented manner.

Hence the random orientation of crystallites necessary for the production of suitable X-ray diffraction patterns does not obtain in such deposits. If the layer of condensed material is sufficiently massive, it may often be removed from the supporting substrate by mechanical means, ground to fine powder, and then subjected to the usual X-ray powder techniques. This latter procedure proved possible in only three instances during the course of this work, but information of value was obtained in these cases.

Platinum was employed as a condensation target in the first three vaporization experiments. Since X-ray diffraction studies revealed that the sublimate had reacted with the platinum collector, all subsequent experiments were performed with quartz targets.

Titanium was determined by the well-known colorimetric procedure in which hydrogen peroxide is used as the color developer (65). Weissler (66) has extended the method to permit the simultaneous spectrophotometric determination of titanium, vanadium and molybdenum, or of titanium and vanadium (67). Weissler's method was used with only slight modifications in all analyses of sublimates for titanium and molybdenum reported in a subsequent section of this thesis.

Figure 2. Lattice Parameter of the TiO Phase
as a Function of Composition


Ratio O/Ti
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
1.10
1.15
1.20
4.190
8
6
4
2
4.180
8
6
4
2
4.170
4.169
Lattice Parameter (Å Units)
40
42
44
46
48
50
52
54
55
Atomic Percent Oxygen
Rostoker (52)
Ehrlich (46)
This Research
Ti O Phase Boundary
1700 °C
1300 °C
1100 °C
900 °C
Ti O Phase Boundary

Those sublimates collected on platinum were brought into solution by fusion with potassium pyrosulfate. The melt was dissolved in 3.6 N H_2SO_4, and transferred quantitatively to a 100 ml volumetric flask. Hydrogen peroxide was then added to give a final concentration of one per cent peroxide, and the solution was made to volume at 20°C with 3.6 N H_2SO_4. During the early part of this work, the blank solution used was 3.6 N H_2SO_4. Optical densities of the solution at 330 mμ and 410 mμ were then determined with a Beckman Model "DU" quartz spectrophotometer, and the concentration of molybdenum and titanium in the solution determined by solution of appropriate simultaneous equations. Coefficients of the terms in the simultaneous equations had been determined previously from measurements of the optical density of standard solutions of molybdenum and of titanium as a function of wave-length and concentration.

It was noted early in this work that the optical density <u>vs</u>. wave-length plots of peroxidized solutions of sublimates were of an unusual shape in the region 300-360 mμ relative to similar curves obtained with standard solutions of molybdenum, titanium, or mixtures of these. This puzzling behavior was first attributed to the presence of molybdenum in the sublimates. The subsequent change to quartz targets necessitated a change in procedure to bring the sublimates into solution. It was found that a mixture of concentrated sulfuric and hydrofluoric acids serves admirably. While silicon is volatilized during this process, titanium is retained in solution if sulfuric acid is present in excess. Residual amounts of fluoride were removed by repeated fuming of the sulfuric acid. The remainder of the procedure was then completed as described above.

Just as in the previous method, only 3.6 N H_2SO_4 was used as a blank solution for the spectrophotometric determination of titanium and molybdenum in the unknown. Again the unusual curvature of the plots in the region 300-360 mμ was noted. As various considerations led to the conclusion that an entirely insignificant amount of molybdenum could have reached the collector plate during any given vaporization experiment, the entire analytical procedure was re-examined.

This was deemed necessary for two reasons. First, it was desirable to establish whether the observed high values of optical density in the region 300-360 mμ were owing to the presence of molybdenum in the solutions, or to improper analytical procedures. Large amounts of molybdenum in the sublimates might indicate reaction of the molybdenum crucible with the TiO sample to form volatile molybdenum oxides. Second, it was observed that, according to the analyses, more titanium was found in the sublimates than was theoretically possible from a consideration of the crucible weight loss and the geometry of the system. Pressures of TiO calculated from collector plate data were a factor of two higher than pressures calculated from the weight loss of the crucible. It was suspected that some error in analytical procedure had introduced a substance into the solutions that not only absorbed strongly at 330 mμ, thus making it appear that molybdenum was present in the solutions, but also had an appreciable absorption at 410 mμ, thus leading to apparent titanium concentrations higher than the actual titanium concentrations in the various solutions.

Fresh standard solutions of molybdenum and of titanium were carefully prepared from materials of high purity. The concentration of the various solutions was checked by both volumetric and gravimetric methods of analysis. Precise agreement was found between the two check methods in every case. Most important of all, the blank solution was prepared in parallel with the standard solutions. That is, the blank was carried through every step of the procedure in a manner identical to that used for the standards; hydrogen peroxide was included in the blank. A new series of standard curves was then established, and new simultaneous equations derived for the determination of molybdenum and titanium in mixtures of the two.

Subsequent analysis of a sublimate by the modified procedure described above gave a curve of optical density *vs.* wave-length identical in all respects to similar curves obtained with solutions containing titanium alone. Curves were also determined for solutions free of titanium and molybdenum, and that had been carried through the pyrosulfate fusion method and the modified method, respectively. In these latter two cases, only 3.6 N H_2SO_4 was used as a blank; no peroxide was added to the blank solutions. As had been suspected earlier, the curves rose sharply to higher values of optical density in the region 300-360 mμ. The optical density values for these latter solutions do not fall to zero in the region of maximum absorption of peroxidized titanium solutions, *viz.*, in the region of 410 mμ.

The above considerations are of importance for the following reasons. First, one may conclude from the above that molybdenum was not present in any of the sublimates. Partial additional confirmation of this conclusion was obtained by polarographic analysis, as mentioned previously. Secondly, the titanium determinations carried out prior to the time that blank solutions were prepared in parallel with the unknowns should all yield results that are too high by an indeterminate amount. The effect on the determination of titanium is slight, but nevertheless present.

While the standard curves for titanium found in this work indicate a precision of about ±2 per cent relative to total titanium, it is well known that precision and accuracy are quite different matters in spectrophotometric work (68). It is generally conceded that errors of ±10 per cent are common. In view of what has been said above, the estimated uncertainty in the spectrophotometric determinations of titanium reported in a later section of this thesis is at least ±10 per cent relative to total titanium, and all determinations except those for vaporization experiments labeled No. 11 and No. A-4, respectively, are probably high by an indeterminate amount.

3. Analysis of Residues

During the course of this work, residues were obtained from vaporization experiments during which approximately 8, 14 and 27 per cent, respectively, of the original sample material had sublimed. In addition to the residues, a deposit that formed on the under side of the crucible lid during the course of experiments that yielded a total weight loss of about eight per cent was obtained. These four samples were analyzed by direct determination of oxygen by the BrF_3 method (43a), and were also subjected to analysis by X-ray diffraction techniques. These data are presented in graphical form in Figure 2, while a tabular summary is deferred until a later section of this thesis in order to facilitate the collation of these data with other data.

No chemical analysis of residue composition other than the direct determination of oxygen was undertaken. That residue obtained from the series of experiments that yielded a total weight loss of eight per cent was, however, submitted to spectrographic analysis, and was also analyzed polarographicly (44) for molybdenum.

The spectrographic analysis was reported on a semi-quantitative basis, and was based on the assumption that the original, unheated monoxide sample contained 0.7 per cent silicon. That is, the silicon content of the original material was taken as an internal standard. The reported analysis of the original material, in weight per cent, is, Si 0.7, B 0.15, Mg 0.29, Fe 0.15, Mo 0.2. Analysis of the same material at the University of California gave, Si 0.1 - 0.01, B not reported, Mg 0.01, Fe 0.01, Mo not detected. The residue analysis performed at the University of Kansas gave, Si 0.14, B 0.53, Mg 0.33, Fe 0.7, Mo over 1 per cent. By polarographic analysis, the molybdenum content of the residue was estimated to be 0.5 per cent.

E. The Titanium-Oxygen System

1. Phase Relationships in the Titanium-Oxygen System

Many of the binary phase diagrams and some of the ternary diagrams of titanium systems have been determined. A recent excellent compilation of binary and ternary titanium phase diagrams has been published by Hansen, McPherson and Rostoker (68a). As has been noted by Rostoker and Kessler (69) and by Hansen and Kessler (70), the solid phase relationships observed in titanium binary systems are of four basic types. These are classified principally as to the effect the alloying element has on either raising or lowering the transformation temperature of the pure metal, and on the phase changes that immediately follow at the titanium-rich end of the systems. The pure metal undergoes an isothermal transformation at 882.5°C (71, 72) from the low-temperature, hexagonal close packed α form to the high-temperature, body centered cubic β modification.

The first type of system is represented by Figure 3. The binary systems of titanium with molybdenum (73, 74), niobium (73), vanadium (75, 76, 77), and tantalum (78) are known to belong to this group. The phase diagram is characterized by terminal α and β solid solutions with the formation of an $\alpha+\beta$ field that grows wider with decreasing temperature. The continuous series of β solid solutions is stabilised to low temperatures by increasing percentages of alloying element.

The second type of system as represented by Figure 4, is typical of the binary systems of titanium with chromium (77, 79, 80, 81, 82, 83), iron (79), silicon (84), nickel (85), copper (86, 87, 88), and with hydrogen (89, 90, 91, 92). The phase relationships are similar to those shown in Figure 3, but here the β phase decomposes below the eutectoid temperature into α plus an intermediate compound.

A third type of behavior is depicted in the diagram of the titanium-aluminum system, Figure 5. Here the addition of alloying element raises the α-β transformation temperature, and thus restricts the β field while the α solid solution is stabilized to high temperatures. The known members of this group include aluminum (93, 94), and carbon (48, 95). Whereas aluminum shows extensive solubility in α-titanium, the maximum solubility of carbon is less than 0.5 per cent. Aluminum, the only metal in this group, forms substitutional solid solutions; carbon is dissolved interstitially.

The binary systems of titanium with nitrogen (48, 95) and with oxygen (46, 47, 51, 95, 96) have equilibrium diagrams similar in most respects to those systems included in type three above. The feature that distinguishes this fourth class of titanium systems from the third type is the formation of the β phase by the peritectic reaction of the liquid with the α phase, as shown in Figure 6.

Bumps, Kessler and Hansen (51) have recently reported a study of the titanium-oxygen system up to a composition of 30 weight per cent oxygen, and the equilibrium lines of Figure 6 from pure metal through the TiO phase region are based on their data. As pointed out by these authors, the difficulty of accurate temperature measurement renders the precise determination of the solidus and liquidus lines of the TiO homogeneity range extremely difficult. Their data do not, therefore, definitely exclude the possibility that stoichiometric TiO melts congruently as shown in the insert of Figure 6.

Brewer (2), in a recent excellent review of the thermodynamic properties of the oxides, has summarized most of the data employed in the construction of the phase diagram for compositions richer in oxygen than $TiO_{1.2}$. No thorough investigation of this portion of the titanium-oxygen system has been reported; the equilibrium lines shown must, therefore, be regarded as very approximate.

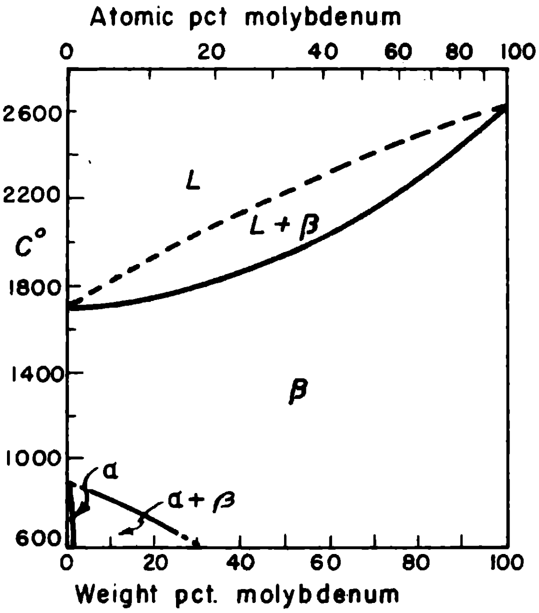
The melting point of TiO_2 has been determined by Bunting (97), von Wartenberg _et alii_ (98, 99, 100) and by St. Pierre (101). Bunting's value of 1850°C was used in the construction of the phase diagram. St. Pierre used pyrometric cones for temperature measurement. The melting point of Ti_2O_3 given by Junker (102) is based on very uncertain extrapolation techniques that omitted consideration of the Ti_3O_5 phase. The disproportionation temperature of Ti_3O_5 was estimated from the observations of Welch (103) on the reduction of TiO_2 by hydrogen. The homogeneity ranges of the solid phases correspond approximately to those found by Ehrlich (46, 47).

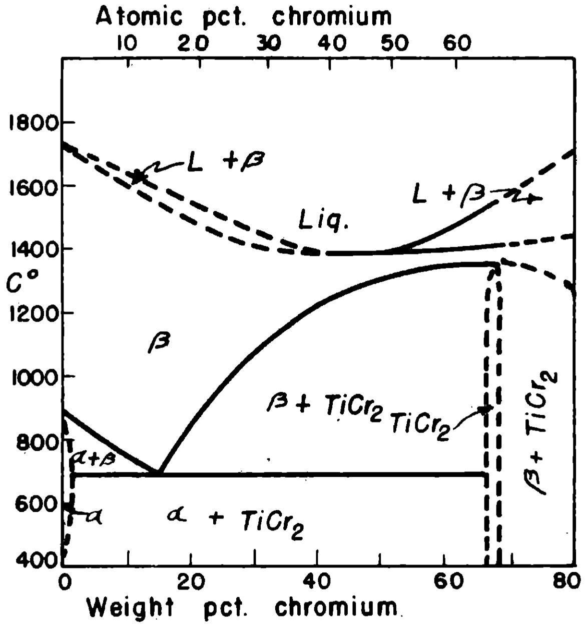
The structures of the solid phases found in the titanium-oxygen system have been summarized by Brewer (2). In addition to the tetragonal rutile form of TiO_2, a tetragonal anatase and an orthorhombic brookite modification, both unstable at low temperatures with respect to rutile, are known. Rusakov and Zhdanov (104) report Ti_3O_5 to be orthorhombic, while Ti_2O_3 crystallises in the rhombohedral corundum structure. The cubic (NaCl-type) TiO phase is found to have a wide homogeneity range extending from about $TiO_{0.75}$ to $TiO_{1.25}$ at 1600°C.

Figure 3 (Upper left). Phase Diagram of the Titanium-Molybdenum System (73, 74).

Figure 4 (Upper right). Phase Diagram of the Titanium-Chromium System (79).

Figure 5 (Lower). Phase Diagram of the Titanium-Aluminum System (93).


Atomic pct molybdenum
0
20
40
60
80
100
2600
2200
1800
1400
1000
600
C°
L
L + β
β
α
α + β
0
20
40
60
80
100
Weight pct. molybdenum


Atomic pct. chromium
10
20
30
40
50
60
1800
1600
1400
1200
1000
800
600
400
C°
L + β
Liq.
L + β
β
β + TiCr₂
TiCr₂
β + TiCr₂
α+β
α
α + TiCr₂
0
20
40
60
80
Weight pct. chromium

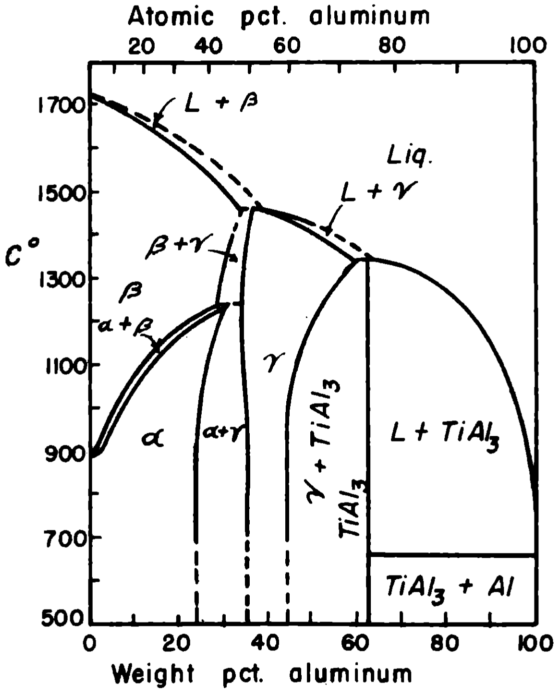
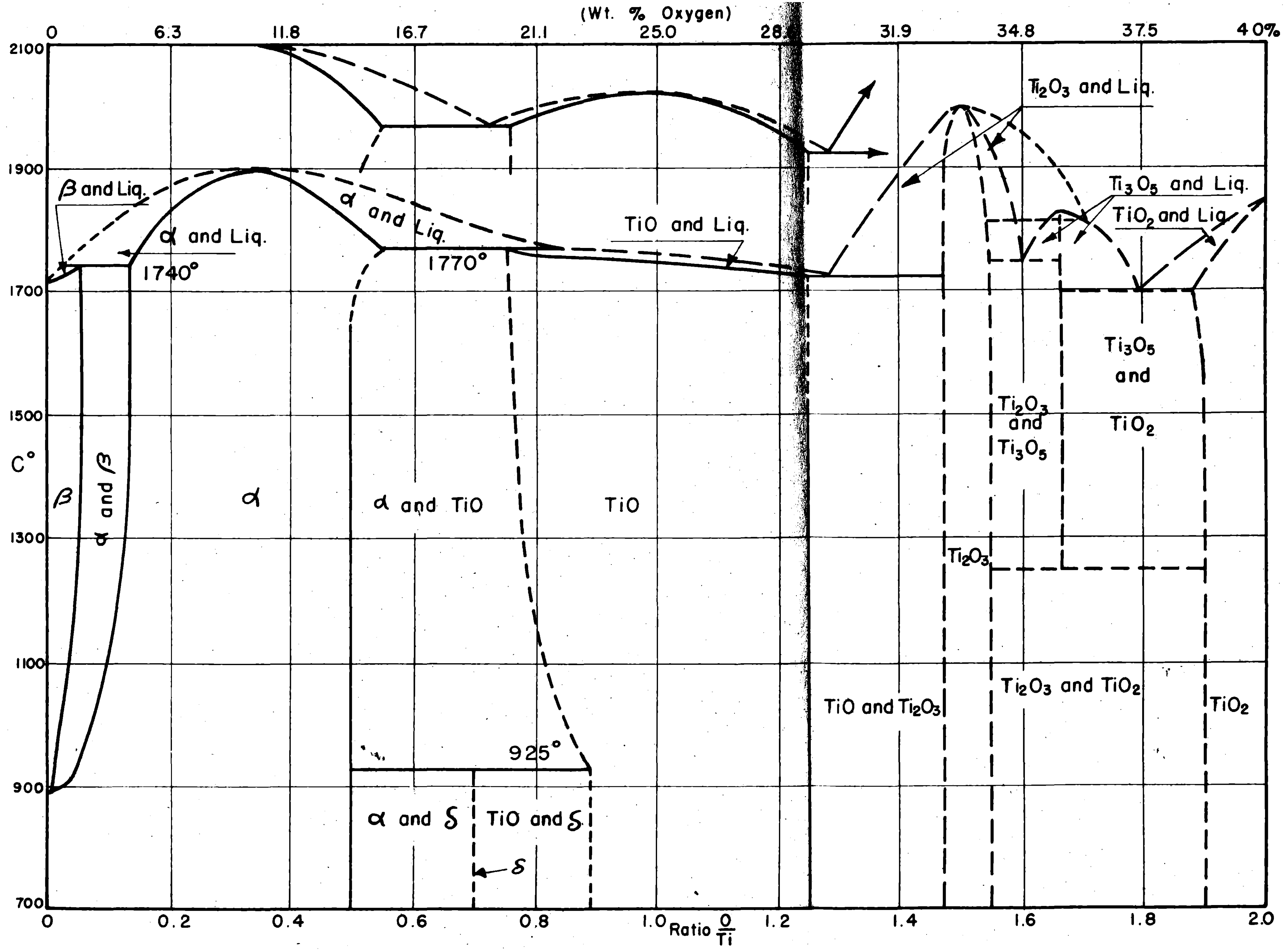

Atomic pct. aluminum
20
40
60
80
100
1700
1500
1300
1100
900
700
500
C°
L + β
Liq.
L + γ
β+γ
β
α + β
α
α+γ
γ
γ + TiAl₃
TiAl₃
L + TiAl₃
TiAl₃ + Al
0
20
40
60
80
100
Weight pct. aluminum

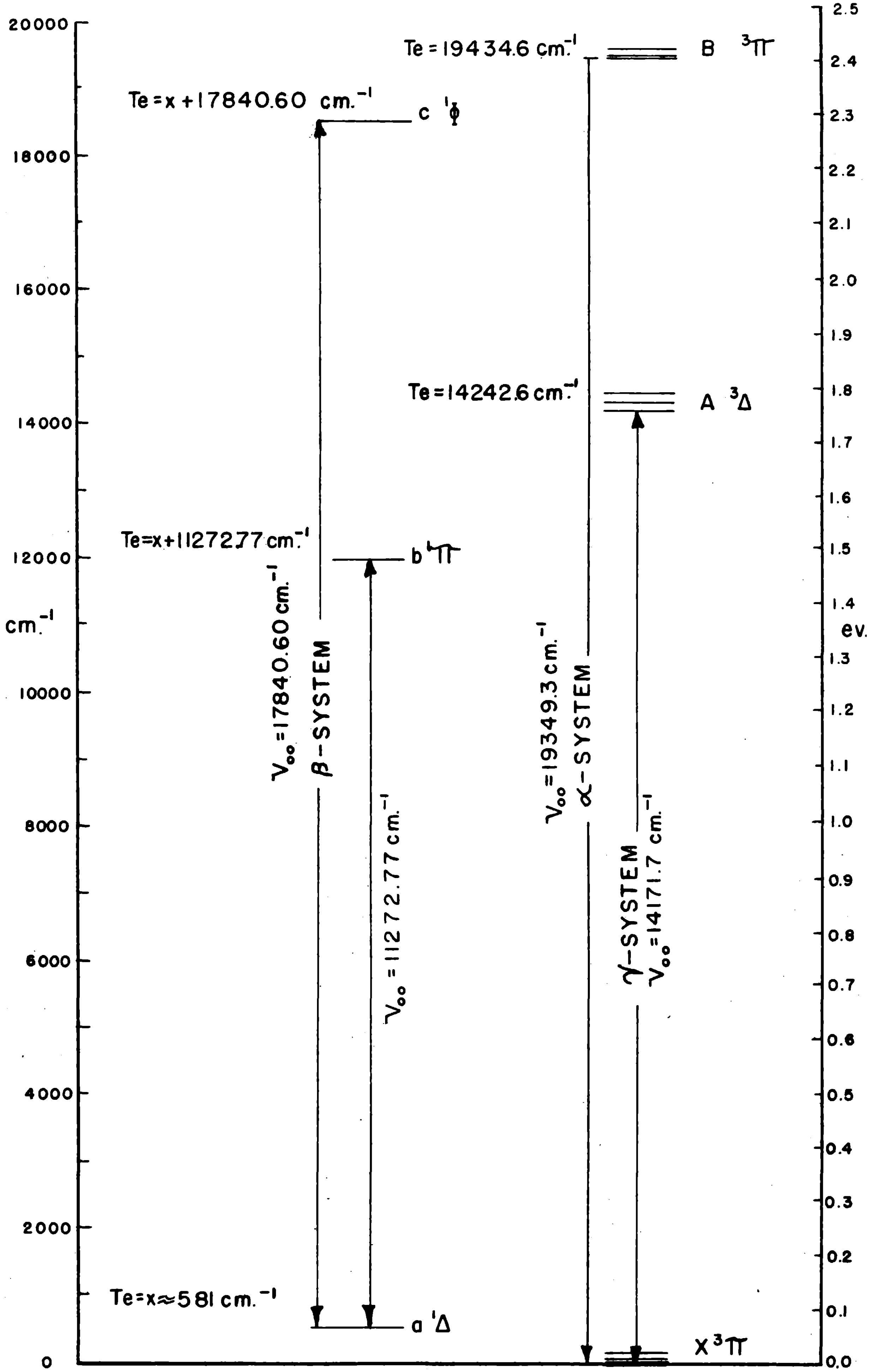
Figure 6. The Phase Diagram of the Titanium-Oxygen System (51).


(Wt. % Oxygen)
0
6.3
11.8
16.7
21.1
25.0
28.
31.9
34.8
37.5
40%
2100
1900
1700
1500
1300
1100
900
700
C°
β and Liq.
α and Liq.
1740°
α and Liq.
1770°
TiO and Liq.
Ti2O3 and Liq.
Ti3O5 and Liq.
TiO2 and Liq.
β
α and β
α
α and TiO
TiO
Ti2O3
Ti2O3 and Ti3O5
Ti3O5 and TiO2
925°
α and δ
TiO and δ
δ
TiO and Ti2O3
Ti2O3 and TiO2
TiO2
0
0.2
0.4
0.6
0.8
1.0
Ratio O/Ti
1.2
1.4
1.6
1.8
2.0

2. Spectroscopy of Gaseous TiO

It has been pointed out in the introduction that considerable work on the spectrum of TiO(g) has been accomplished. The molecular energy level diagram is shown in Figure 7. Phillips (7, 12, 13, 14) has recently continued the study of the spectrum, and has determined the molecular constants of the $^3\Pi$, $^3\Delta$. $^1\Phi$, $^1\Pi$ and $^1\Delta$ states. He has also shown that the $^3\Pi$ is the ground state with the $^1\Delta$ state only about 500 cm^{-1} higher.

Figure 7. Molecular Energy Level Diagram for the TiO Molecule.



20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
$cm.^{-1}$
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
ev.
$Te = 19434.6\ cm.^{-1}$
$B\ ^3\Pi$
$Te = x + 17840.60\ cm.^{-1}$
$c\ ^1\Phi$
$Te = 14242.6\ cm.^{-1}$
$A\ ^3\Delta$
$Te = x + 11272.77\ cm.^{-1}$
$b\ ^1\Pi$
$\nu_{oo} = 17840.60\ cm.^{-1}$
β-SYSTEM
$\nu_{oo} = 11272.77\ cm.^{-1}$
$\nu_{oo} = 19349.3\ cm.^{-1}$
α-SYSTEM
γ-SYSTEM
$\nu_{oo} = 14171.7\ cm.^{-1}$
$Te = x \approx 581\ cm.^{-1}$
$a\ ^1\Delta$
$X\ ^3\Pi$

F. Vaporization Phenomena of the TiO Phase

1. Vaporization Processes of Oxides

The nature of the phase diagram is of importance in the consideration of all equilibrium measurements for, as is clear from the phase law, one may obtain unique values of the pressure at given temperatures only in systems possessing a single degree of freedom. For simple binary systems, the above requirement may be satisfied in a number of ways. At a given temperature, one may obtain a unique value of the pressure in a system composed of three phases, as for example two condensed phases and the equilibrium vapor phase. The condensed phases may both be solids or liquids, or may consist of one solid and one liquid. The foregoing requirement may also be satisfied by systems containing a single condensed phase, solid or liquid, and the equilibrium vapor phase if one variable in addition to the temperature is fixed. This additional variable to be fixed may be the pressure, the composition of one of the variable composition phases or the relationship between the compositions of the different phases. If, in the binary system of pure elements A and B, a compound AB is formed that is infinitely stable as a gaseous species, then the composition AB will behave as a unary system, and will be a constant subliming composition in the same sense as pure A or pure B. Even if AB is not infinitely stable as a gaseous species, but decomposes partially or completely to the constituent gaseous atoms upon vaporization, the system will still be unary if the vapor phase has the same composition as the condensed phase. At a given temperature, therefore, the equilibrium pressure in such systems is unique. In either event, the compound is known as a congruently subliming one. A phase diagram for such a system is given by Ricci (132) on page 128 as Figure 7-5.

Frequently, however, it is found that vaporization produces a vapor phase whose composition is different from that of the single condensed phase. The system is then one of two components in which, at constant temperature, the equilibrium pressure varies with the composition of the vapor phase. The composition of the condensed phase, solid or liquid, may or may not vary depending on whether it is a solution or an incongruently vaporizing compound. A phase diagram showing both possibilities is given by Ricci (132) on page 133 as Figure 7-15. Since in such systems continued vaporization produces a change in the composition of the vapor phase, the pressure will change with the extent of vaporization.

Meaningful vapor pressure measurements may, therefore, be obtained only under the following conditions: (1) use of a constant-composition vaporization process as in the case of a congruently subliming compound, or in the case of an azeotrope; (2) use of a two-phase solid or liquid system; or (3) use of a single-phase solid or liquid system under experimental conditions such that only a very small quantity of sample is vaporized during the course of a single measurement. Experiments of this latter type may be conducted at a variety of compositions to obtain the pressure-composition relationship.

In order to evaluate the vaporization data of oxides, one must establish the nature of the gaseous species associated with the system being considered. Brewer (2) has given an excellent summary of the vaporization processes for oxide systems, and suggests simple experimental criteria to be used in distinguishing among the various possibilities. It is desirable, however, to consider the several possible vaporization mechanisms with particular reference to the titanium-oxygen system.

The first fact that should be established is whether gaseous oxide molecules can be of importance in the vaporization process. Brewer points out that while most oxides vaporize exclusively by decomposition to the gaseous elements, an appreciable number of oxide phases vaporize to form stable gaseous oxide molecules. In favorable instances, one may distinguish between these two cases rather easily. For example, one may calculate the partial pressures of the elements in equilibrium with a given oxide phase at a given temperature by use of the thermodynamic data for the oxide and for the elements. If the calculated decomposition partial pressure is much less than the experimentally observed total pressure in equilibrium with the oxide, one may conclude that gaseous oxide molecules are of importance in the vaporization process. Conversely, if the observed pressure is the same within experimental errors as the decomposition pressure, one may conclude that gaseous oxide molecules are not important. In the case of the titanium-oxygen system, the thermodynamic data required for the above calculations are available.

In addition, one may often make use of spectroscopic data to determine whether gaseous oxide molecules can be expected to be of importance. In view of the fact that chemical systems will include all states of the molecule, care must be exercised in formulating conclusions about chemical systems from a consideration of spectroscopic data, for the available spectroscopic data frequently apply only to excited states of the molecule. The work of Phillips (12, 13, 14) has definitely established that the spectroscopic data for TiO(g) apply to the ground state of the molecule, yet the dissociation energy of TiO(g) is uncertain by about ± 1 ev because insufficient data are available to fix the nature of the long extrapolation to the convergence limit. Hence we see that not only must the nature of the gaseous phase be established in order to evaluate vaporization data, but one must also establish that the composition of the solid phase does not change as vaporization progresses. In the above discussion of the criterion to be used to characterize the vapor phase, the qualification "In favorable instances" is carefully chosen, for that criterion will in general fail or lead to erroneous conclusions unless the solid phase under consideration is a constant-subliming composition.

Prior to the present work, there were no data concerning TiO that would indicate whether the vapor had the same composition as the condensed phase, nor whether decomposition to the gaseous elements accompanies vaporization. At least four possibilities for vaporization of stoichiometric liquid or solid TiO exist: (1) pure TiO(g) alone is formed; (2) Ti(g), and O (g) or 1/2 O_2(g) are formed in equivalent proportions; (3) TiO(g) is formed together with excess Ti(g), O(g) or 1/2 O_2(g); or (4) Ti(g), and O(g) or 1/2 O_2(g) are formed in non-equivalent proportions. All four of the possible gaseous species will of course be present, but except for an unusual coincidence only two of these, at most, would be of much importance.

Processes (1) and (2) fall into the category of congruently subliming compositions which have phase diagrams similar to that given by Ricci (132) on page 54 as Figure 3-4. Processes (3) and (4) are examples of incongruently subliming compositions which have phase diagrams similar to that given by Ricci (132) on page 50 as Figure 3-3. Let us consider the above possibilities in some detail.

If process (1) above describes the manner in which stoichiometric TiO vaporizes, one may use the available thermodynamic and spectroscopic data to calculate the partial pressure of TiO(g) in equilibrium with solid TiO. It is to be emphasized that process (1) implies that TiO(s) is a constant vaporizing composition. Since two different values for the dissociation energy of TiO(g) have been proposed, the problem may be divided into two cases. We shall consider both cases as follows:

Case I. Let us assume that the dissociation energy of TiO(g) is given correctly by the linear Birge-Sponer extrapolation. Herzberg (9) reports a value of 6.9 ev at 0°K. The heat of formation of TiO(s) has been determined by Humphrey (15) to be $\Delta H^\circ_{298} = -123.91 \pm 0.28$ kcal./mole; the dissociation energy of oxygen has been determined by Brix and Herzberg (17) to be $41{,}261 \pm 15$ cm^{-1} at 0°K; Edwards, Johnston and Ditmars (20) have determined the heat of sublimation of titanium to be $\Delta H^\circ_0 = 112.763 \pm 0.153$ kcal./mole. It is convenient to choose a reference temperature of 298°K, and the values given at 0°K may be changed by use of the heat content functions for O_2, O, Ti(s), Ti(g) and TiO(s) given in the National Bureau of Standards Tables (16), and similar values for TiO(g) given by Gilles, Filson, Gallup and Wheatley (106). Conversion factors were taken from the 1947 values of the National Bureau of Standards.

The relationships among these quantities may be seen clearly by reference to Figure 1, and they may be expressed in the following equations:

$Ti(g) + O(g) = TiO(g)$, $\Delta H^\circ_{298} = -160.2_{55}$ kcal./mole, (2)

$TiO(s) = Ti(s) + 1/2\ O_2(g)$, $\Delta H^\circ_{298} = 123.9_1$ kcal./mole, (3)

$1/2\ O_2(g) = O(g)$, $\Delta H^\circ_{298} = 59.55_8$ kcal./mole, (4)

and $Ti(s) = Ti(g)$, $\Delta H^\circ_{298} = 113.4_{21}$ kcal./mole. (5)

Summation of the above equations yields the equation for the process under consideration, while summation of the heats of reaction gives the heat of sublimation of TiO. Thus we find for

$TiO(s) = TiO\ (g)$, $\Delta H^\circ_{298} = 136.634$ kcal./mole. (6)

The heat of sublimation of TiO may be combined with the free energy functions for the solid state, as calculated from the data given by Kelley (43, 105), and the free energy functions for the gaseous molecule given by Gilles, Filson, Gallup and Wheatley (106) to formulate an equation for the vapor pressure of TiO(s),

$$\log P_{TiO} = \frac{-1}{4.576}\left(\frac{\Delta F^\circ - \Delta H^\circ_{298}}{T}\right) - \frac{\Delta H^\circ_{298}}{4.576T}. \qquad (7)$$

The vapor pressure of TiO as calculated in the above manner is indicated as a function of temperature by curve 2 of Figure 8. The vapor pressure of titanium metal (20), curve 1 of the same Figure, is included for reference purposes.

Case II. If one assumes that the dissociation energy of TiO is 126.8_{47} kcal./mole, as suggested by Gaydon (8), we then find in precisely the same manner as before,

$TiO(s) = TiO(g)$, $\Delta H^{\circ}_{298} = 168.922$ kcal./mole. (8)

The vapor pressure of TiO derived from this heat of sublimation and the free energy functions for the solid and vapor is illustrated in Figure 8 by curve 6.

The second process suggested to describe the vaporization of stoichiometric TiO was process (2), above, and it also may be considered in two separate cases. In the first instance, we may consider the important gaseous species to be Ti(g) and O(g). Alternatively, Ti(g) and $O_2(g)$ may be taken as the species that characterise the vaporization process.

If the assumption that stoichiometric TiO is an azeotrope is retained, one may calculate from the data given previously that, for

$TiO(s) = Ti(g) + O(g)$, $\Delta H^{\circ}_{298} = 296.889$ kcal./mole. (9)

Since in this case the partial pressure of Ti is equal to the partial pressure of O, the equilibrium constant is given by

$$K_p = P_{Ti}P_O = P^2_{Ti} = P^2_O. \qquad (10)$$

The free energy functions of Ti(g) have been computed by Gilles and Wheatley (107) and by Kolsky and Gilles (107a), while the free energy functions for O(g) are given in the

National Bureau of Standards Tables (16). Curve 3 of Figure 8 gives the partial pressure of titanium and of oxygen as derived from the above data.

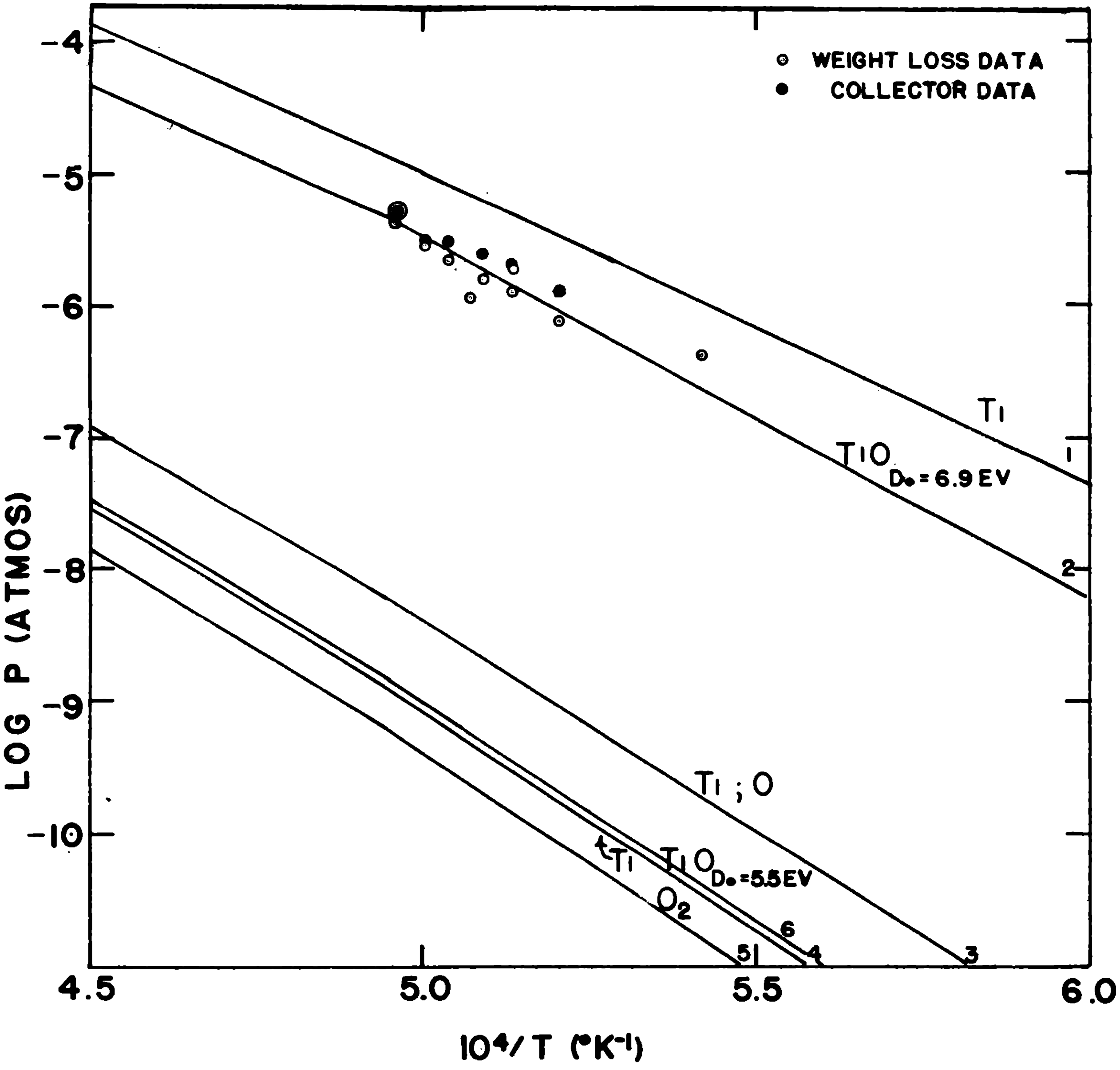
Similarly, for the reaction

$$TiO(s) = Ti(g) + 1/2\ O_2(g), \qquad (11)$$

one calculates $\Delta H^{\circ}_{298} = 237.331$ kcal./mole. The equilibrium constant is now given by $K_p = P_{Ti}P_{O_2}^{1/2}$, while the titanium partial pressure is now twice the oxygen partial pressure. The heat of reaction derived above has been combined with free energy functions in the usual manner to calculate the equilibrium partial pressure of Ti(g) and of $O_2(g)$, as shown by curves 4 and 5, respectively, of Figure 8.

It is emphasized again that stoichiometric TiO(s) must be a constant-subliming composition if either possibility (1) or (2) describes the vaporization phenomena. If such is indeed the case, reference to Figure 8 shows clearly that TiO(g) will be the important species in the vapor phase if the dissociation energy of TiO(g) is as high as 6.9 ev, while the elements will predominate in the gas if the dissociation energy is of the order of 5.5 ev. Experimentally, the distinction between these two possibilities may be made easily, for it will be noted from Figure 8 that, if TiO(g)

Figure 8. Partial Pressures of Various Gaseous Species in Equilibrium with Solid TiO.


WEIGHT LOSS DATA
COLLECTOR DATA
LOG P (ATMOS)
-4
-5
-6
-7
-8
-9
-10
4.5
5.0
5.5
6.0
10⁴/T (°K⁻¹)
Ti
1
TiO D₀ = 6.9 EV
2
Ti ; O
3
TiO D₀ = 5.5 EV
4
6
tTi
O₂
5

is quite stable, the volatility of solid TiO will be approximately 10^3 times that to be expected if decomposition to the elements accompanies vaporization.

One further point deserves mention. It will be noted from what has been said above that the thermodynamic data employed in the calculation of the equilibrium partial pressure of the elements over solid TiO do not contain information derived from spectroscopic sources other than the dissociation energy of O_2, which is accurately known. The uncertainties frequently introduced by the use of spectroscopic data are not, therefore, present in the calculated partial pressures due to the elements. The accuracy of the data is such that the equilibrium constant for such reactions as

$$TiO(s) = Ti(g) + O(g) \qquad (9)$$

is firmly established.

It is interesting to note that if it could be established by independent means, such as a molecular weight determination or a mass spectrographic determination, that a compound vaporizes by decomposition to the elements and that no change in the composition of the solid accompanies this process, vaporization studies would yield a value for the equilibrium constant for the reaction, which could be used to obtain a heat of formation. Suppose, for example, the heat of formation of TiO(s) were unknown. A determination of the concentration of titanium in the vapor phase would permit the calculation of the titanium partial pressure. Since the oxygen pressure is equal to the titanium pressure under the conditions outlined above. the equilibrium constant is given simply by $K_p = P_{Ti}^2$. Once the equilibrium constant is established, it may be combined with the appropriate free energy functions and the thermodynamic data for the elements to calculate the heat of formation of TiO(s). Similar considerations apply if the predominant oxygen species in the vapor is O_2(g) rather than O(g).

If possibility (3) or (4) describes the action of the system, the quantitative interpretation of vaporization data is vastly more complicated. To distinguish between a congruently subliming (process (1) and (2)) and an incongruently subliming (process (3) and (4)) substance, one notices that in the former the solid composition does not change on extensive vaporization, whereas in the latter it does.

Chemical analysis of the residual solid material after a vaporization experiment during which an appreciable fraction of the original sample has sublimed would establish, first, whether or not the solid had changed in composition during the course of vaporization. If a change in solid composition is noted, one may immediately reject possibilities (1) and (2). Second, the direction of change in solid composition would permit a decision as to whether titanium or oxygen was the predominant elementary species in the vapor.

A distinction between processes (3) and (4) may usually be made from a consideration of the original and final composition of the solid phase, and a knowledge of the total weight loss. It is not always possible to distinguish between (3) and (4) from vaporization data alone, for it is conceivable that, if the system departs sufficiently from ideality, the partial pressure of titanium or of oxygen associated with possibility (4) might be of the same order of magnitude as the total pressure to be expected in case process (3) or (1) describes the system. The reason for the difficulty in distinguishing between processes (3) and (4) may be seen from the following considerations. The equilibrium constant for the reaction

$$TiO(s) = Ti(g) + O(g) \qquad (9)$$

is about 10^{-18} in the neighborhood of 2000°K. Thus process

(4) may lead to appreciable weight losses because the value of the equilibrium constant may be satisfied when the titanium partial pressure is quite high, say 10^{-6} atmosphere, if the oxygen partial pressure is about 10^{-12} atmosphere. Hence a vaporization mechanism such as process (4) could conceivably yield weight loss comparable with those to be expected for a process such as possibility (3), in which oxide molecules are important. The composition of the residue would be expected to change more rapidly for a given percentage weight loss for a mechanism such as (4) than would be observed for a process such as (3), and it might be possible to make the distinction.

One further factor of great importance has been ignored throughout the above discussion, namely, the activity of TiO in the $TiO_{1\pm x}$ solid solution (Fig. 6), and the variation of a_{TiO} with temperature and composition. In the case of possibility (1), TiO is assumed infinitely stable as a gaseous molecule and there is no change in solid composition as vaporization occurs. One may, therefore, take a_{TiO} as unity at all temperatures in the solid solution of composition $N_2/N_1 = 1$, that is, in stoichiometric TiO. Under such circumstances, the titanium-oxygen system may conveniently be considered in terms of the two quasi-binary systems Ti-TiO and TiO-O_2, respectively.

In the event that stoichiometric TiO is an azeotrope and vaporizes by decomposition to the elements, the standard state of TiO in $TiO_{1\pm x}$ is again conveniently taken as unity at the composition $N_2/N_1 = 1$. In general, the composition of an azeotropic mixture is a function of temperature and pressure. One might, therefore, desire to choose the standard state as the azeotropic composition at each temperature and pressure of interest. For solid-vapor equilibria, and in the range of temperatures and pressures readily amenable to experiment, the composition of a constant-subliming mixture does not usually vary rapidly with temperature, nor with pressure. It is likely, therefore, that the same standard state could be chosen at all temperatures of interest without incurring serious error.

If stoichiometric TiO is not an azeotrope, but vaporizes according to possibility (3) or (4), and if there is no constant-subliming composition anywhere within the $TiO_{1\pm x}$ homogeneity range, the best choice of a standard state is perhaps not so clear as in the previous cases discussed. That composition corresponding to the titanium-rich edge of the $TiO_{1\pm x}$ solid solution might be chosen as standard state, but the composition, that is, the value of the parameter "x" in the isothermal equilibrium,

$$Ti(\alpha,\ cryst.) + \frac{(1-x)}{2} O_2(g) = TiO_{1-x}(cryst.), \qquad (12)$$

is a function of temperature as shown in Figure 6. Hence one would have to choose a different standard state at each temperature. A better choice would be to take the standard state as some composition within the homogeneity range, or at the oxygen-rich edge of the solid solution. The composition of the oxygen-rich edge is, as shown in Figure 6, essentially independent of temperature. In any event, the choice of a standard state is purely arbitrary, and may be fixed at whatever composition is convenient for the particular problem under consideration.

From the above it is clear that, in considering vaporization processes such as (3) or (4), one may no longer write the equilibrium constant in terms of the partial pressures alone; the activity of the solid phase must appear in the equilibrium constant expression. Even if one starts with stoichiometric TiO, and assigns that composition unit activity, the activity of the solid will change during the course of a simple vaporization experiment as the composition of the solid changes. If only a very small percentage of the sample is vaporized during a given experiment, thus keeping the change in solid composition to a minimum, one may study the composition-total pressure relationship. While simple vapor-pressure measurements by the Knudsen or Langmuir techniques will yield information of value for such systems, utilization of other experimental methods to characterize the system is clearly desirable.

Reference to the phase rule shows that a binary system existing in two phases, say solid of variable composition and gas, at constant temperature is univariant. One more variable must be fixed for the system to be invariant. The only variables at our disposal are the pressure and the composition of one of the phases. It is not usually experimentally possible to fix the composition of a phase of variable composition arbitrarily, nor is it convenient to fix the pressure of the equilibrium gas phase at any particular value of interest for a given experiment. It is, however, quite easy to fix the pressure of the gas phase at one atmosphere. In metal oxide systems the oxygen partial pressure varies markedly over the range of compositions usually of interest. Hence restriction of experiments to equilibria involving oxygen at a partial pressure of one atmosphere drasticly limits the range of compositions that can be investigated. While it is possible to lower the oxygen partial pressure somewhat by admixture with some inert gas, the practical limit to such a procedure is rapidly reached.

The problem of obtaining known oxygen pressures of the order of 10^{-6} to 10^{-12} atmosphere or lower is usually circumvented in the following manner. The solid phase is equilibrated with a gas mixture such as carbon monoxide-carbon dioxide of known initial composition. The equilibrium constant for the homogeneous gas reaction

$$CO_2 = CO + 1/2\ O_2 \tag{13}$$

is known as a function of temperature. At fixed temperature and total pressure, therefore, the partial pressure of oxygen in such a mixture may be calculated from a knowledge of the equilibrium constant, the total pressure and the P_{CO_2}/P_{CO} ratio in the mixture at room temperature by virtue of the additional requirement of conservation of mass. Other mixtures such as H_2-H_2O, H_2-CH_4 and H_2-NH_3 may be used when appropriate to the system under consideration.

In a strict sense, the equilibration of metal oxides with carbon monoxide-dioxide mixtures makes the system ternary. It is frequently found, however, that the solubility of carbon in the condensed phases is negligibly small; hence the reactions of interest simply involve the transfer of oxygen from the gas mixture to the solid phases, and the system may be considered binary for all practical purposes. Darken and Gurry (108, 109) have used the method indicated above in an excellent study of the iron-oxygen system.

If such studies could be successfully performed on the titanium-oxygen system, the activity of oxygen as a function of composition and temperature throughout the $TiO_{1\pm x}$ range could be established. By virtue of the Gibbs-Duhem equation, the corresponding activity of titanium may be derived. Knowing a_{Ti} and a_O, the activity of TiO, or in fact any titanium-oxygen complex, in the $TiO_{1\pm x}$ solid solution may be established. In this instance, by application of the isothermal proportionality $a_{TiO} = k a_{Ti} a_O$, where k is a constant, the Gibbs-Duhem equation reduces to

$$\log a_{TiO} = -\int \left[(N_2/N_1) - 1 \right] (d \log P_{O_2}^{1/2}). \qquad (14)$$

The limits of integration will depend on the particular choice of standard state for TiO and the composition of interest.

In practice, however, the method indicated above probably will not prove fruitful for a study of the TiO solid solution range, for the available thermodynamic data indicate that the equilibrium oxygen pressure over TiO is very low. Reference to the equilibrium constant for the homogeneous gas reaction given in equation (13) shows that, at a temperature of 2000°K, the experimentally practical lower limit to the oxygen pressure attainable with such a system is of the order of 10^{-10} atmosphere (16). Hence it probably will not be possible to study compositions as stable as TiO. Welch's observations (103) on the reduction of TiO_2 by hydrogen indicate, however, that compositions down to Ti_2O_3 could probably be studied by the above method.

2. Previous Work

No equilibrium studies with the $TiO_{1\pm x}$ phase of the last type considered above have been reported in the literature. The only datum as to the volatility of TiO is the rough observation by Ehrlich (46) that about one per cent of a sample of TiO vaporized in about 15 minutes at approximately 1600°C. From this information and the dimensions of the containing vessel, Brewer and Mastick (110) have calculated an approximate vapor pressure of TiO at 1873°K:

$P_{TiO} = 1.1 \times 10^{-5}$ atmosphere. Using an estimated value for the heat of formation of TiO(s) that would make TiO(s) just barely stable with respect to disproportionation, Brewer and Mastick (110) were able to calculate the equilibrium constant for the vaporization of TiO to the gaseous elements. They then assumed that the heat of formation of TiO(s) is constant throughout its entire homogeneity range, and assumed further that the partial pressure of titanium over the titanium metal phase in equilibrium with the TiO phase, that is, metal containing 33 atomic per cent dissolved oxygen, is the same as the vapor pressure of pure titanium metal. From these data they were able to calculate $P_{Ti} = 2.5 \times 10^{-6}$ atmosphere and $P_O = 10^{-14}$ atmosphere at 1873°K for the TiO phase saturated with titanium metal. From similar considerations for the $TiO_{1\pm x}$ composition saturated by Ti_2O_3, they conclude that the oxygen partial pressure will not change rapidly across the TiO range, and that TiO must therefore lose more Ti atoms than O atoms. It would appear from the above calculations that there could be no invariant vaporizing composition within the $TiO_{1\pm x}$ homogeneity range. As Brewer points out (111), however, the new data (15) for the stabilities of the various phases of the titanium-oxygen system indicate that TiO is quite stable with respect to disproportionation. Thus one might expect quite a large change in oxygen pressure across the $TiO_{1\pm x}$ range, and the possibility of finding a constant subliming mixture within the range seems not so remote. We shall have occasion to reconsider the above arguments in light of the experimental evidence presented below.

3. The Volatility of TiO

(a) Theory of the effusion method. The determination of the vapor pressure of solids and liquids from the rate of effusion of a vapor through an orifice was first suggested by Knudsen (25, 26, 27, 28). In this method the vapor flows from a space, where it is in equilibrium at some given temperature with a solid or liquid, through an orifice into a high vacuum. The phenomenon varies greatly as the hole is large or small. For a sufficiently large hole, the flow can be treated theoretically by the methods of hydrodynamics. At the other extreme, where the hole is small compared with the molecular mean free path, the molecules issue independently of each other. Only a trace of mass motion towards the hole develops. If the dimensions of the hole are comparable with the mean free path, an intermediate type of flow occurs.

In the case of the very small hole the outflow of molecules through it should be the same as their flow across any small plane area of equal size drawn in the body of the gas. It can be shown from the kinetic theory of gases (112) that the total number of molecules that cross unit area in unit time toward one side is given by $N = 1/4\ (n\bar{v})$, where n is the number of molecules in unit volume of the gas phase and $\bar{v}$ is the mean velocity of the molecules. For practical applications it is convenient to replace $n\bar{v}$ by immediately observable quantities such as the mass m, the volume V or the quantity of gas in terms of the pV product. The mass of gas is just $nm = pM/RT$, and $\bar{v} = (8RT/\pi M)^{1/2}$. Hence we have

$$m = p(M/2\pi RT)^{1/2} \qquad (15)$$

as the mass of gas crossing unit area in unit time. This formula should apply not only in the interior of the gas but also to effusion through a hole in the wall of a containing vessel, provided its diameter is small compared with the molecular mean free path, and provided further that the aperture is infinitely thin. In Equation (15), "p", then, stands for the pressure on the side from which the gas comes. If there is a gas on both sides of the hole, effusion will obviously occur in both directions independently.

Strictly, the value of p calculated from the above equation is not the same as the true equilibrium pressure p°, for the opening in the wall disturbs the equilibrium of the vapor in the Knudsen cell. Let us consider first a closed cell in which, at constant temperature, equilibrium is established at the true vapor pressure p°. In this instance, the number of atoms that escape from the surface of the solid in unit time is equal to the number that strike the surface per second _and_ _condense_. Not every atom that strikes the solid surface condenses, but a fraction β may bounce off. The number that strike and condense per unit time is then proportional to αp°, where $\alpha = 1 - \beta$ is the condensation coefficient.

If a hole is now opened in the Knudsen cell, as in effusion experiments, a steady state will be established at a lower pressure such that the rate of effusion of atoms from the hole is just balanced by the _net_ rate of evaporation from the surface of the condensed phase. From these considerations it may be shown (23) that the pressure p, as established from the measured weight loss of the cell, is related to the equilibrium pressure p° by $p^\circ/p = 1 + a/\alpha A$ (16) where a is the area of the orifice and A is the effective area for evaporation of the condensed phase. It is evident that when $a/A \ll \alpha$, $p \approx p°$. Thus the condition for the equilibrium determination of the vapor pressure may be tested by using cells of various a/A values. If the effusion rate is independent of these ratios, the measured pressure may be taken as the equilibrium pressure within the errors of the measurements.

While measurement of the loss in weight of the sample for a given time of evaporation yields the data for calculating the rate of vaporization unambiguously, it is frequently desirable to obtain information as to the molecular species present in the effusive beam. To this end, condensation targets have been very frequently used (113) to measure the rate of effusion from a Knudsen cell. It follows from the kinetic theory (112) that the mass of gas crossing unit area of the aperture in the Knudsen cell in unit time at an angle θ from the normal to the plane of the orifice, and lying within an element dω of solid angle is

$$m = p(M/2\pi RT)^{1/2} f(\underbrace{\cos}_{\pi}\ \theta/\pi)\ d\omega. \tag{17}$$

It is thus seen that the intensity of the beam at any angle θ is proportional to cos θ. This proportionality is strictly true only if the orifice is infinitely thin and if it may be considered to be a point source.

If a target of radius R is placed over the Knudsen cell at a distance l from the orifice, and on the assumption that the orifice may be considered a point source, integration of the above equation shows that the fraction of the total effusing vapor intercepted by the target is

$$k = R^2/(R^2 + l^2). \qquad (18)$$

If all the vapor striking the target condenses, the weight of condensate should be mk, where m is the weight loss of the Knudsen cell. In case thermal dissociation of a molecule into non-condensible products takes place, a mass balance may not be obtained. For example, if TiO(s) vaporizes to Ti(g) and O(g), perhaps only the titanium may condense on the collector plate. Since a mass balance would not be obtained in this instance, one would be led to suspect that the vapor species were Ti(g) and O(g) rather than TiO(g). Collector plate data are thus clearly of great value for the elucidation of the vaporization mechanism.

As has been noted above, it has been assumed that the effusion aperture is infinitely thin and that it may be considered a point source. In the usual experimental arrangement, these conditions may be adequately satisfied by reaming the edge of the effusion hole to knife-edge thinness and by employing small apertures. The problem of effusion through cylindrical apertures of arbitrary dimensions has been studied in great detail by Clausing (114, 115, 116), while contributions of more recent date have been made by Whitman (29, 117) and by Rossman and Yarwood (118). Clausing finds that the effect of a tubular orifice on the effusing molecular beam is twofold. First the rate of effusion is less than that to be expected from a knife-edged aperture, for some of the molecules are reflected at the walls of the tube and find their way back into the Knudsen cell. Second, the molecules no longer issue from the orifice with the usual cosine distribution of directions; a larger fraction of the total number of molecules escape in the forward direction than is the case with an infinitely thin orifice. Clausing represents the intensity of the effusing beam in any direction θ, as proportional to $T \cos \theta$, where T is a rather complicated function of θ and the tube dimensions. If the geometry of the system comprised of Knudsen cell and collector plate is known, the effect of the geometry on the total effusion rate and on the fraction of the effusate intercepted by the collector may be calculated in a straightforward manner from the equations given by Clausing. Clausing (116) lists values of the percentage reduction in total effusion rate as a function of the orifice dimensions, while values of the fraction of the total effusate collected as a function of the orifice dimensions and the solid angle of collection have been calculated by Gilles, et alii (119). As has been noted by Whitman (29), the validity of calculations based on Clausing's equations is dependent on four fundamental conditions:

(1) The molecules collide only with the walls of the tube (free molecule flow).

(2) The reflection of molecules after such collisions is diffuse.

(3) The molecules enter the orifice with the usual cosine distribution of directions.

(4) The molecules enter uniformly over the face of the orifice.

Condition (1) requires that the mean free path of the molecules be at least ten times the order of the dimensions of the apparatus (120). Plausible arguments (121, 27, 122, 123) have been offered in support of condition (2), but insufficient experimental evidence is available to give it general validity. Condition (3) will not be precisely fulfilled at the orifice owing to the distortion of the cosine distribution by the Knudsen cell itself (115), while condition (4) will not be satisfied by those molecules reflected by the lid on the Knudsen cell. Whitman (29) estimates the maximum error in Clausing's correction factors resulting from these last two effects to be less than ten per cent, while it may be much less.

In view of the above discussion. the equation relating vapor pressure to the rate of vaporization from a Knudsen cell may be written

$$P_{atmos} = (m/44.331\ Kat)\ (T/M)^{1/2}, \tag{19}$$

where m is the mass of gas effusing through the area a in time t, and the constant 44.331 arises from the combination of the constants in the original equation with the factor converting pressure to units of atmospheres. Clausing's factor, K, corrects the observed weight loss for the attenuation occasioned by using an orifice of finite length. If the pressure is calculated from the observed mass of material condensed on a collector plate, the equation becomes

$$P_{atmos} = (m_c/44.331\ Kkat)\ (T/M)^{1/2}, \tag{20}$$

where m_c is the mass of condensate on the collector, $k = k(\Theta, L/r)$ is the fraction of the total effusate intercepted by the target, L is the length and r the radius of the orifice. The quantities p, m, m_c and M must, of course, all refer to the same molecular species. If more than one species is present in the vapor, a similar equation will apply to each such species. The total pressure is of course the sum of the partial pressures, while the observed weight loss is the sum of the individual weight losses.

In general it is not at all easy to assign a specific fraction of the total weight loss to a given molecular species in effusion experiments involving more than one molecular or atomic substance in the gas. It is in fact impossible to make such an assignment from weight loss data alone. If of N species, N - 1 can be collected on a condensation target, and if the mass of each of these N - 1 species can be determined by suitable analytical procedures, the mass of the other species may be determined by difference if the total weight loss is known. Frequently, however, not all the N - 1 species are chemically distinguishable. For example, in a condensate of Ti and $TiO_{1\pm x}$, one may determine only total titanium. Even if the weight gain of the collector is known and it is assumed that this weight gain is due to Ti and $TiO_{1\pm x}$ alone, the relative proportions of the two in the condensate cannot be fixed, for "x" is not known. In this instance, X-ray diffraction data would help to establish the composition of the oxide phase (Fig. 2).

The case of a constant vaporizing mixture is of special interest. Let us assume that stoichiometric TiO is a constant vaporizing composition, but vaporizes by decomposition to the gaseous elements (process 2). In an effusion experiment, the requirement that TiO be constant vaporizing means that the moles of Ti(g) effusing in unit time must equal the moles of O(g) effusing in unit time. If z_i represents the rate of effusion of species "i", the vapor pressure equation takes the form

$$z_i = p_i \;/(2\pi M_i RT)^{1/2}. \tag{21}$$

Since we require $z_{Ti} = z_O$, we find that

$$p_{Ti} = p_O \;(M_{Ti}/M_O)^{1/2} \tag{22}$$

in this special case. Hence one need determine only the rate of effusion of Ti(g), say from collector plate data, to establish the partial pressures of both Ti(g) and O(g) <u>inside</u> the Knudsen cell. It should be noted that in such a case $p_{Ti} \neq p_O$ inside the Knudsen cell, yet the product of the partial pressures may still be equated to the equilibrium constant for the reaction.

(b) The effusion assembly. Throughout the work reported here, molybdenum metal was used as the primary material of construction. The Knudsen effusion cells were fabricated from molybdenum crucibles 1/2" in diameter by 1" in height, and having the laboratory designation "Type A". The wall thickness was 0.060", while the bottom was 1/8" thick. A snugly fitting lid was formed from 0.060" molybdenum sheet. A small, knife-edged effusion hole was formed in the center of the lid by cutting a 30° bevel on the under side of the lid. The Knudsen cell and a 10-turn spiral of 1 mil molybdenum sheet rested on a stack of ten 1-3/8" diameter 0.030" thick molybdenum radiation shields which were separated by 0.060" molybdenum spacers. A similar stack of molybdenum radiation shields surmounted the Knudsen cell, except that in this latter case each shield was pierced by a centrally bored hole whose diameter increased linearly with the distance of a given shield from the effusion chamber. The diameter of the central hole in the shield farthest from the crucible subtended an angle of about 30° at the orifice. The assembly of crucible and shields was surrounded by a 5-turn spiral of 1 mil molybdenum sheet which was dimpled on one-inch centers to afford slight but positive separation of the turns. Three 0.080" molybdenum rods, equally spaced on a 1" circle, traversed the entire assembly to maintain the relative orientation of the various components. Molybdenum tube spacers, placed over the rods, supported a molybdenum collimator and a platinum or quartz collector plate above the Knudsen cell. The orifice-collector distance was about five centimeters. The geometry of the design was such that approximately 6 per cent of the total effusate was intercepted by the target. This assembly rested on a molybdenum stand which rested, in turn, on a one centimeter thick zircon plate in the bottom of the pyrex vacuum chamber.

Detailed descriptions of the effusion assembly, vacuum induction furnace and associated equipment have been reported elsewhere (40).

(c) Experimental procedure. Reference to the equation given previously relating vapor pressure to rate of effusion discloses that the quantities that must be established experimentally to permit calculation of a pressure are the weight loss of the sample, the elapsed time, the temperature, the dimensions of the orifice and the geometry of the collector plate relative to the orifice. It is assumed that the molecular weight of the gaseous species is known. The usual procedure was, therefore, as follows: The initial mass of sample, Knudsen cell, lid and collector plate were determined by weighing on a standard analytical balance. The weights used had been calibrated by the shorter method of Pienkowsky

(124) against a standard set of weights bearing a National Bureau of Standards Certificate. The diameters of the effusion hole, collimator and central hole in the collector, respectively, were measured to the nearest micron with a Gaertner micrometer slide comparator, Cat. No. M342, Ser. No. 2943, while the thickness of the orifice was established by measurement with a standard microscope that was fitted with a micrometer fine-adjustment screw. The thickness of the collector plate was measured with an ordinary screw micrometer, while the collimator-orifice and collector-orifice distances were established by means of a screw micrometer depth gauge. The orifice diameter at the high temperature of a given experiment was obtained by correcting the room-temperature value for the thermal expansion of molybdenum. The thermal expansion of molybdenum has been determined by Michel (125), Demarquay (126), Edwards, *et alii* (127) and by Worthing (128). The data of Demarquay, which are in excellent agreement with those of Edwards, *et alii*, were used throughout this work, and may be represented by the equation

$$l_t = l_o\,(1 + 6.8 \times 10^{-3} - 5 \times 10^{-6}\,t + 4.4 \times 10^{-9}t^2). \qquad (23)$$

The effusion assembly was placed in the pyrex vaporization cell and the entire unit was then attached to the vacuum system. The water jacket that surrounded the vaporization cell was so designed that the water level rose to approximately one inch above the top of the ground-glass joint at the juncture of vaporization cell and vacuum manifold. A 32-turn, water cooled induction coil, designated 3P4 by the manufacturer, supplying high-frequency power was placed around the water jacket in such a position that the Knudsen cell would be at the center of the coil.

Power was not supplied to the system until the residual gas pressure, as read from an ionization gauge, had fallen to about 5×10^{-6} mm Hg. After some experience had been gained in the manipulation of high vacuum systems, it was found that the rate of power input required to reach the desired ultimate operating temperature for a given run could be applied from the beginning of the experiment. In such cases the pressure would rise rapidly to about 10^{-5} mm Hg, and then fall slowly to 5×10^{-6} mm Hg or less over a period of about thirty minutes. During the latter portion of this work, the residual gas pressure in the vacuum system never rose above 10^{-4} mm Hg in any given experiment, and was usually less than 5×10^{-6} mm Hg throughout the high-temperature portion of a given run.

The elapsed time at any instant during a given experiment was read from a synchronous motor-driven dial-type timer readable to the nearest 0.01 minute. The temperature was read by sighting through an optical window onto the orifice of the effusion cell with a Leeds and Northrup disappearing filament type optical pyrometer, having the laboratory designation "Pyrometer No. 1". Window corrections and pyrometer calibration corrections were applied in the usual manner. The total time of a run varied from about one hour to over thirty hours depending on the temperature and the weight loss desired. Temperature was recorded at frequent intervals as a function of the elapsed time.

In order to correct the temperature readings for the effect of slight temperature variations during the run, and particularly for the "heating up" and "cooling down" portions of a given experiment, the method suggested by Johnston and coworkers (129) was used. The assumption was made that the rate of effusion, m(T), could be expressed as a function of temperature by an equation of the form

$$\log m(T) = A/T + C, \qquad (24)$$

where A and C are constants determined from observed weight losses and times at high temperatures. An "effective time" of run at "constant" temperature is then calculated by graphical integration in the equation

$$t_{eff} = \int_0^t \left[m(T)/m(T_{ave}) \right] dt, \qquad (25)$$

where m(T) is evaluated at each observed temperature during a given run from the equation given above, and $m(T_{ave})$ is the rate of effusion at the arithmetic average temperature for the high-temperature portion of the run. The quantities t_{eff} and T_{ave} were then inserted into the Knudsen equation to obtain a calculated pressure at the temperature T_{ave}.

At the conclusion of a given heating period, the effusion assembly was left in the high-vacuum system until the temperature of the Knudsen cell had fallen to about 100°C. The diffusion pump was then turned off and allowed to cool down to room temperature. The vacuum was then broken by admitting air to the system, and the Knudsen cell and collector plate were then removed for weighing. After the collector plate had been weighed, the sublimate was dissolved and analyzed for titanium according to the procedures given previously.

It was found that some of the effusate from the Knudsen cell that condensed on the under side of the upper radiation shields revaporized and eventually found its way to the collector plate, thus giving a greater amount of condensate on the target than was to be expected from the total weight loss and the geometry of the system. In order to correct for this effect, two "blank" runs were carried out. These were accomplished by replacing the Knudsen cell that contained the sample with an empty cell, and carrying the system through the same procedure as for a vapor pressure determination. The time of run and temperature were made as nearly the same as possible with those of the vapor pressure run that immediately preceded the blank run. As no sample was present in the Knudsen cell, any titanium that reached the collector plate must have come from material revaporized from the hot radiation shields.

In this manner it was found that from 11 to 16 per cent of the total titanium collected during a vapor pressure run could be accounted for by material revaporized from the shields. Where no direct experimental data are available, the pressures calculated from collector plate data are, therefore, lowered by 14 per cent to correct for revaporization from the shields. It should be noted that the above correction will give only a lower limit to the actual error incurred from this source, for in a vapor pressure run material is being deposited on the shields continuously, thus replacing some of the material that revaporizes. It is also possible that the condensation coefficient of the vapor on the hot molybdenum shields is far from unity. Thus all the factors that one might consider lead to the conclusion that the error due to revaporization is greater than the correction estimated by means of a blank run.

(d) The experimental data. Both quantitative and qualitative data were obtained during the course of this investigation. While emphasis was placed upon the determination of the volatility of TiO, it became evident during the latter part of this work that information of a confirmatory or supplementary nature was desirable. Various experiments other than those concerned directly with the determination of the vapor pressure of TiO were, therefore, conducted. In view of the necessarily complex arguments to be presented in a subsequent section of this thesis, the data are presented in the approximate chronological order in which they were obtained, and are, wherever practicable, summarized in tabular form for convenience of reference.

The primary data from which the volatility of TiO may be calculated are summarized in Table I, while additional data of interest and some quantities derived from the

Table I

Vaporization Data for TiO(s)

Run	Sample wt. (g)	Effective time (sec.)	T_{ave} (°K)	Orifice area at T°K (cm^2)	L/2r	Weight Loss (mg)	Wt. gain of Collector (mg)	Total Titanium Collected (mg)	Titanium Blank (mg)
2	—	4168	1845	0.09671	0.00732	1.4	—	—	—
4	—	5015	2016	0.09224	(0.000)	15.2_7	—	—	—
5	—	7499	1946	0.09208	(0.000)	10.4	—	—	—
6	—	5876	1970	0.09213	(0.000)	4.9	—	—	—
7	1.2717	14707	2014	0.04611	0.049	26.9	2.7[(a)]	1.2789	(0.1790)
8	1.2448	13969	1964	0.04438	0.113	6.9	0.9[(a)]	0.5694	(0.0797)
9	1.2379	10743	1984	0.04438	0.140	7.2	1.0[(a)]	0.5373	0.0860
10	1.2307	14687	1947	0.04434	0.164	5.7	-1.2[(b)]	0.5423	(0.0759)
11	1.2250	110921	1921	0.04433	0.220	24.5	3.4[(b)]	2.3423	0.2479
A-4	1.2005	40511	1998	0.04441	0.322	30.3	2.5[(b)]	1.733	—

(a) Platinum collector. (b) Quartz collector.

information given in Table I are tabulated in Table II. Run No. 1 is not recorded, as it was a rough preliminary experiment and the data obtained are not of sufficient accuracy to warrant inclusion in the table. Run No. 3 is omitted because the vacuum system cracked during operation; the sample was, therefore, destroyed. The effective time and average temperature of a given run were calculated as described previously, while the orifice area was calculated from the diameter of the effusion hole at the temperature of the run.

Column 6 of Table I lists the various values of orifice length to diameter for each run. In run No. 2, the crucible lid was a piece of 5 mil molybdenum sheet. The effusion hole was drilled in the center of this sheet, and no attempt to ream the hole to knife-edge thinness was made. As runs 4, 5, and 6 employed an orifice reamed to knife-edge thinness, the ratio of length to diameter is assumed to be zero. In runs 7 through A-4, a knife-edged orifice was also employed. It was found, however, that at the conclusion of run No. 7 the crucible lid had become welded tightly to the crucible. The crucible was not opened for examination until run A-4 had been completed. Examination of the lid then showed that an even deposit of material had accumulated on the lid during

Table II

Vaporization Data for TiO(s)

Run	K(L/2r)	Net Titanium Collected (mg)	Calculated Net TiO (mg)	k(L/2r, θ)	Mean Free Path, TiO (cm)	Residual Gas Pressure (mm Hg)
2	0.9929	---	---	---	54.	7×10^{-5}
4	(1.000)	---	---	---	5.9	4×10^{-5}
5	(1.000)	---	---	---	12.8	5×10^{-5}
6	(1.000)	---	---	---	19.8	7×10^{-5}
7	0.9534	1.099_9	1.467_3	0.05424	4.9	6×10^{-6}
8	0.8990	0.489_7	0.653_3	0.06026	17.3	3×10^{-6}
9	0.8778	0.451_3	0.602_1	0.06141	12.8	1×10^{-5}
10	0.8599	0.466_4	0.622_2	0.06343	22.	2×10^{-5}
11	0.8210	2.094_4	2.793_9	0.06615	38.	2×10^{-6}
A-4	0.7600	1.73_3	2.31_2	0.07132	11.6	1×10^{-6}

the course of runs 7 through A-4. The orifice was, therefore, no longer knife-edged but was a short tube. While the diameter of the orifice had not changed, it was found that the thickness of the orifice was now 0.90 ± 0.05 mm. Since no direct knowledge of the orifice thickness, other than the initial and final thickness, during the course of runs 7 through A-4 was available, it has been assumed that the increase in orifice thickness during a given experiment was proportional to the weight loss for that run. This assumption permits the calculation of an "average" hole thickness for any given run, and it is this "average" value of L/2r that is tabulated in column 6 of Table I.

Column 8 of Table I lists the observed weight gain of the condensation target for each run. Platinum targets were used for runs 7 through 9, while quartz was the collector material in subsequent experiments. It will be noted that in run 10, the first use of a quartz collector, the target lost weight despite the fact that a sublimate was clearly visible. This anomaly is believed to be the result of loss of adsorbed water vapor and gases from the quartz when it was warmed by radiation from the effusion assembly in the high vacuum system. In all subsequent runs, the cleaned quartz collector was heated in the flame of a Meeker burner, and was cooled in a desiccator before weighing.

Column 9 tabulates the total mass of titanium found in the sublimate, as determined spectrophotometricly by the procedures described previously. As pointed out earlier, these values are uncertain by ± 10 per cent, and all but the last two may be high by an indeterminate amount. Column 10 gives the correction to be applied for revaporization of material from the radiation shields. As noted previously, the third and fifth corrections were determined by "blank" runs, and those in parentheses are 14 per cent of the titanium collected. No correction is given for experiment A-4 because there were no shields in the apparatus. It is important to note that the total mass of titanium collected is, in every case except for run 10, less than the weight gain of the collector. Since the discrepancy is greater than can be accounted for on the basis of analytical errors, it is clear that some species other than titanium is contributing to the sublimate.

The factors calculated by Clausing (116) to correct vaporization data for the effect of using a tubular orifice rather than a knife-edged orifice are given in column 2 of Table II, while the fraction of the effluent intercepted by the collector plate, as derived from the work of Gilles, *et alii* (119), is tabulated in column 5. Column 3 is simply the difference of columns 9 and 10 of Table I, while the data of column 4 are derived by application of the appropriate gravimetric factor to the data of column 3. The mean free path of a TiO molecule *inside* the Knudsen cell was calculated from the measured vapor pressure, the temperature of the crucible and an assumed generous upper limit of 5 A for the TiO molecular diameter. The mean free path thus calculated will be a lower limit. These values, tabulated in column 6 of Table II, are not only larger than the orifice by a factor of 10 or more, but are with two exceptions larger than the dimensions of the effusion cell by a factor of 10. Hence "free molecule" flow may be expected to occur within the crucible as well as through the orifice.

From the data in Table II, one may calculate the vapor pressure of TiO at each experimental temperature. Combination of the vapor pressure data with the free energy functions for solid and gas yield a value for the heat of sublimation of TiO at 298°K for each experimental temperature. The free energy functions used are listed in Table III.

It is of interest to comment briefly on the free energy functions used for TiO(g) as tabulated in Table III. Available tabulations (16, 130) of the free energy functions for TiO(g)

Table III

Free Energy Functions for Various Substances

$$\left|\frac{F^\circ - H^\circ_{298}}{T}\right| \quad \text{(e.u.)}$$

T(°K)	Ti(s)(16)	TiO(s)(43)	Ti(g)(107)	O(g)(16)	1/2 O_2(g)(16)	TiO(g)(106)
1800	14.03	20.35	48.223	43.3608	28.202	64.112
1850	14.17	20.69	48.344	43.4740	28.295	64.311
1900	14.32	21.03	48.463	43.5884	28.389	64.507
1950	14.45	21.36	48.580	43.6969	28.479	64.698
2000	14.58	21.69	48.694	43.8064	28.569	64.887
$\Delta H^\circ_{f,298}$ (Kcal.)	0	-123.91(15)	113.421(20)	59.558(17)	0	---

are slightly in error for two reasons. Firstly, the earlier tabulations were derived by treating the molecule as a harmonic oscillator, rigid rotator, and used values of the molecular constants less precise than those currently available. Secondly, only the ground electronic state was considered in the calculations.

It will be noted in Figure 7 that the $^1\Delta$ state lies only about 500 wave numbers above the $^3\Pi$ ground state, and will, therefore, make a significant contribution to the free energy functions for TiO(g) at the temperatures of interest in this work.

In view of the uncertainties in the tabulations noted above, the free energy functions of TiO(g) were recalculated. The details of the calculations appear in a separate report (106), but it may be noted here that the molecule was treated as an anharmonic oscillator, non-rigid rotator; terms to account for the interaction of vibration and rotation were included, as was the contribution of the $^1\Delta$ state. The resulting functions are only about two per cent larger in absolute value than those given in previous tabulations.

Table IV contains the results of the calculations of the vapor pressure and heat of sublimation of TiO from the data in Tables I and II, and the free energy functions in Table III. The values in the third column of Table IV were obtained by assuming that the total weight loss of the sample arose from loss of TiO(g) alone, *i.e.*, by using the values in the seventh column of Table I. The values in the fifth column of Table IV were obtained by assuming that all the titanium on the collector plate, as found by the analysis, was deposited by the TiO(g) that had effused in the direction of the collector, *i.e.*, by using the values in the fourth column of Table II.

The experimental data for the vapor pressure of TiO that are listed in Table IV are plotted in Figure 8. The excellent agreement of the experimental data with the vapor pressure curve for TiO calculated from available thermodynamic data and an assumed dissociation energy of about 159 kcal./mole lends strong support to the thesis that TiO(g) is the important species in the vapor, and that the dissociation energy of TiO(g) is given correctly by the linear Birge-Sponer extrapolation. We shall, however, have occasion to re-examine the validity of this conclusion in the light of data to be presented shortly.

The data of Table IV are presented in the order of increasing temperature in order to facilitate the examination of the ΔH°_{298} values for systematic errors. If the free energy functions are correct, and if there are no systematic errors in the measurements, the ΔH°_{298} values should show no

Table IV

The Vapor Pressure of TiO

Run	T (°K)	P(TiO) (Units: 10^{-6} atmos) Wt. Loss Data	P(TiO) (Units: 10^{-6} atmos) Collector Data	ΔH°_{298} (Kcal.) Wt. Loss	ΔH°_{298} (Kcal.) Collector
2	1845	0.42_{399}	----------	134.3_{0}	----------
11	1921	0.750_{61}	1.294_{0}	137.2_{4}	135.16
5	1946	1.87_{49}	----------	135.3_{5}	----------
10	1947	1.26_{74}	2.181_{0}	136.9_{3}	134.83
8	1964	1.54_{83}	2.432_{7}	137.2_{5}	135.49
6	1970	1.13_{37}	----------	138.8_{6}	----------
9	1984	2.16_{24}	2.944_{6}	137.2_{2}	136.01
A-4	1998	2.79_{52}	2.990_{5}	137.0_{9}	136.82
7	2014	5.26_{91}	5.299_{0}	135.5_{6}	135.54
4	2016	4.18_{25}	----------	136.6_{0}	----------
			Average =	136.64	135.64
			P. E. of Average =	±0.27	±0.19

Average of all data = 136.27 ± 0.20 Kcal./mole trend with temperature, and should be constant within the precision of the measurements. This is seen to be the case.

It is of interest to note that the data as presented in Table IV do not give a just impression of the precision attainable by the Knudsen method of vapor pressure measurement. If the data in column 5 of Table IV are examined closely, it will be observed that the scatter from the mean of those values obtained early in this work is much greater than that for those values derived from the last five experiments. Hence if runs 2, 4, 5, 6, and 7 were omitted from consideration, the markedly reduced scatter of runs 8, 9, 10, 11 and A-4 from their mean would be immediately apparent. One is thus led to consider whether the unweighted mean of all available data, as presented in Table IV, represents the "best" value for the heat of sublimation of TiO.

Reference to Table IV discloses that, while all the data yield about the same calculated heat of sublimation, the collector plate data yield heats that are consistently lower than those obtained from weight-loss data. It has been emphasized previously that the collector plate data are considered to be quite uncertain for at least two reasons. These are, (1) the chemical analyses of sublimates for titanium are uncertain by at least ten per cent while all except for runs

11 and A-4 are probably high by an unknown amount, and (2) the correction applied for revaporization of material from the shields represents only a lower limit to the true correction factor. All the collector plate data will, therefore, be rejected in the calculation of the "best" value for the heat of sublimation of TiO.

Heats of vaporization calculated from weight-loss data obtained early in this work are also considered unreliable relative to later results because (1) experience in the operation of the high-vacuum furnace had not yet been gained; hence temperature control and measurement was not as good as in later runs, and the residual gas pressure in the system was higher than in the final series of experiments, (2) the geometry of the effusion assembly was not as well defined and reproducible as in later runs, and (3) each of the early experiments involved relatively short periods of time at high temperature, thus leading to relatively large percentage errors in the time and weight-loss data. Further, runs 2, 4, and 7 are believed to have yielded high weight losses, for the samples used had not been degassed at high temperature prior to use while the weight loss for run 6 is believed to be low, because it was found at the conclusion of the run that practically all the sample had been vaporized. Only traces of the sample material remained on the wall of the crucible and in a small cup-shaped crucible insert. Thus it is doubtful that the vapor was saturated with respect to the solid throughout run 6.

It is the opinion of the author that, in view of the above discussion, the "best" value for the heat of sublimation of TiO on the assumption that process (1) is the only important one is given by the mean the values calculated from the weight-loss data for runs 8, 9, 10, 11 and A-4. The mean of these data yield a value of 137.15±0.04 kcal./mole, where the uncertainty limits are the probable error of the mean as calculated on the basis of the criterion of external consistency. If uncertainty limits are assigned on the basis of the criterion of internal consistency, the uncertainty of ± 8°K in the temperature is far more important than the uncertainty in any of the other quantities involved in the calculation. The quoted temperature uncertainty leads to an uncertainty of ± 0.6 kcal./mole in ΔH°_{298}.

While the data of Table IV indicate that TiO(s) vaporizes to give TiO molecules, process (1), it is of interest to examine the other possibilities for the vaporization of TiO discussed in section F, above. A comparison of the net Ti or calculated net TiO found on the collector plate with the mass of material to be expected on the basis of the crucible weight loss and the geometry of the system is given in Table V. Column 2 of Table V lists values of the quantity mk, calculated from the observed weight loss of the crucible, m (column 7, Table I), and the geometry factor, k (column 5, Table II). These are the masses that should be collected, and they are not dependent on any assumption regarding the effusing species. Columns 3 and 4 tabulate the net mass of titanium or of TiO, respectively, found on the target by chemical analysis of the sublimate for titanium. These values are uncertain by at least ten per cent with the first four likely too high. Because they have been corrected for revaporization, one set of these should check the values in column 2. Column 5 tabulates the weight gain of the collector corrected for revaporization from the shields in the same manner as the deposit weights were corrected. These weight gains of the collector are subject to relatively large errors because of their small absolute values. They, too, should check the values in column 2.

It is clear from Table V that the collector gain is greater than that to be expected from the sample weight loss

Table V

Comparison of Weight Loss and Collector Data

Run	mk(mg)	Net Ti Collected(mg)	Net TiO Collected(mg)	Net Wt. gain Collector(mg)
7	1.459	1.100	1.467	2.3
8	0.415	0.490	0.653	0.8
9	0.442	0.451	0.602	0.8_4
10	0.362	0.466	0.622	-1.4
11	1.620	2.094	2.794	3.0
A-4	2.160	1.733	2.312	2.5

and from the net metal collected. The mass of metal collected is in reasonably good agreement with the weight loss data, and the collector weight gain is in reasonably good agreement with the calculated net mass of TiO collected, i.e., columns 2 and 3 agree reasonably well, as do columns 4 and 5.

The higher vapor pressures and lower heats of vaporization obtained from the collector data indicate that probably too small a revaporization correction was made. If a much larger correction were made, the values in columns 4 and 5 of Table V could be made to agree with those in column 2. Since the values in Table V suggest that the effusing species is Ti(g), and that residual pressure in the system oxidizes the metal to TiO on the collector, it is instructive to follow, for a moment, a different line of argument.

Let us assume that process (2) occurs, i.e., TiO(s) vaporizes congruently and exclusively by decomposition to the gaseous elements.

We shall calculate on the basis of this assumption and the data in Tables I and II, the equilibrium constant for process (2). Since we have assumed TiO to be a constant vaporizing composition, the oxygen partial pressure is calculable from the titanium pressure. The product of these partial pressures is the equilibrium constant for the reaction

$$TiO(s) = Ti(g) + O(g). \qquad (9)$$

In Table VI, this equilibrium constant is tabulated and compared with its value calculated from the known thermodynamic data for the oxide and for the elements. The third column contains values of the partial pressure of Ti(g) obtained from the Knudsen equation and column 3 of Table II. This procedure is based on the assumption that Ti(g) is the only species transporting titanium. Values in column 4 of Table VI were calculated from column 3 and equation (22). Values in the next column were obtained from the two previous, and values in the last column have been obtained from the known thermodynamic data.

As Table VI shows clearly, the experimental data, when treated according to the assumed vaporization mechanism, cannot be brought into accord with the known thermodynamic properties of the system. The equilibrium constant calculated from the titanium and oxygen partial pressures is larger than the equilibrium constant established by reliable thermodynamic data by a factor of 10^6. Thus, in agreement with the conclusion reached earlier, process (2) cannot account for the vaporization of TiO.

Table VI

The Equilibrium Constant for the Reaction $TiO(s) = Ti(g) + O(g)$

Run	T°K.	P_{Ti} (atmos.) (Units; 10^{-6})	P_O (atmos.) = $(M_O/M_{Ti})^{1/2}P_{Ti}$ (Units: 10^{-6})	$K = P_{Ti}P_O$ Experimental (Units: 10^{-12})	K Thermal Data (Units: 10^{-18})
11	1921	1.1203	0.64748	0.7254	0.5439
10	1947	1.8883	1.0913	2.0607	1.496
8	1964	2.1062	1.2173	2.5639	2.858
9	1984	2.5494	1.4734	3.7563	6.014
A-4	1998	2.5892	1.4964	3.8745	10.04
7	2014	4.5879	2.6516	12.1653	16.94

Let us now examine the data to see if process (4) can be the mechanism of the vaporization. Thus, if one drops the assumption that TiO is a constant vaporizing composition, yet retains the hypothesis that vaporization occurs by decomposition to the elements, it is then clear from a consideration of the titanium pressures given in column 3 of Table VI and the known equilibrium constant for the vaporization of TiO to the elements that the partial pressure of oxygen over TiO(s) at the experimental temperatures reported in Table VI must be of the order of 10^{-12} atmosphere. If such were indeed the case, the observed volatility of TiO could be explained on the basis of vaporization of titanium alone, and the composition of the solid would change rapidly toward an oxide of greater oxygen content as vaporization progressed. The failure to obtain a satisfactory mass balance in the case of collector plate data, and the possibility that TiO might vaporize incongruently by decomposition to the elements led to several experiments designed to clarify these points.

(e) Supplementary experiments. All experiments performed during the course of this work other than those intended primarily to establish the vapor pressure of TiO have been given the prefix letter "A". Experiment A-3 is not included here, for it merely involved a test of the heating efficiency of a modified effusion assembly and is not relevant to this discussion.

Two experiments, designated A-1 and A-2, respectively, were performed to obtain an evaporated titanium metal film on a quartz collector plate. An effusion assembly essentially the same as that employed for the determination of the volatility of TiO was used. The Knudsen cell was in this case a graphite crucible.

Both experiments yielded an even, tightly adherent film of titanium on the quartz collector. In the case of run A-1, the film had the characteristic bright metallic luster of a front-surface mirror, and was thick enough to prevent light transmission. The film surface as viewed from the back, through the quartz plate, had a deep golden color. The same description applies to the titanium film obtained in run A-2, except that the film was much thinner and had the appearance of a half-silvered mirror. In neither case had visible oxidation of the films taken place as a result of being subjected to the temperatures and pressures prevalent in the vacuum furnace during their preparation.

Both deposits were allowed to stand exposed to the laboratory atmosphere for a period of 24 hours without visible signs of oxidation. The thinner of the two films has been retained for a period of over a year, yet shows no visible trace of oxidation to the chestnut-brown to golden colored TiO phase. The thicker of the two films was placed in an ordinary laboratory drying oven for successive 24-hour periods at temperatures of 105°C, 165°C and 200°C, respectively. No sign of oxidation was evident after the treatments at 105 and 165°C, but a slight tarnishing of part of the film was discernible after the period at 200°C. The above observations, although of a rough qualitative nature, suggest that a titanium metal film would not be oxidized rapidly at the low oxygen pressures encountered in the vacuum furnace. While it is true that the oxygen pressure in the vacuum furnace is very low during a typical vapor pressure run, it is probable that the temperature of the target, which is heated by the high intensity radiation from the effusion crucible, is much higher than 200°C. A reasonable estimate would place the temperature of the collector at roughly 500 - 600°C. It is conceivable that at these temperatures a film of titanium metal, or of TiO, might pick up an appreciable quantity of oxygen even at the low pressure existing during normal operation of the vacuum furnace.

A fourth experiment, designated run No. A-4, was conducted to test the hypothesis that the abnormally large amount of titanium found on the collector plate relative to the crucible weight loss for a given vapor pressure run was the result of revaporization of material from the hot molybdenum radiation shields. The effusion assembly employed was precisely the same as that used for vapor pressure runs 7 through 11 with one important exception. In this instance, all the radiation shields that normally lay between the effusion cell and the collector plate were removed from the assembly. A vapor pressure determination was then made by exactly the same procedure as described previously. No blank run was made, for it was assumed that revaporization from the three molybdenum rods that supported the collector and collimator would be negligible.

Reference to Table IV shows the marked improvement in the agreement of the vapor pressure and heat of vaporization of TiO calculated from the weight loss data and from the collector data, respectively, for run A-4 as compared with similar quantities for the other runs. Reference to Table V illustrates the agreement obtained in this case among the collector weight gain, TiO found on the collector by chemical analysis and the crucible weight loss. While the agreement is much better than for the other runs, it still leaves something to be desired. It is possible, however, that the discrepancies that still exist may be within the combined analytical and weighing errors. In any event, the data of run A-4 strongly indicate that the presence of radiation shields between the crucible and collector leads to abnormally large amounts of sublimate on the target.

One quite anomalous observation relevant to run A-4 deserves mention. It was found at the completion of the run that the sublimate on the quartz collector plate did not have the deep chestnut brown color characteristic of finely divided TiO as did all other sublimates obtained throughout the course of this investigation. The tightly adherent film of sublimate exhibited a greyish metallic luster when viewed from the front surface, yet appeared deep golden yellow in color when viewed from the back of and through the quartz plate. Every other deposit observed throughout this work, whether it occurred on platinum targets, quartz targets, molybdenum radiation shielding, the under side of crucible lids or on the water-cooled pyrex wall of the vacuum chamber, was without exception either golden yellow in color like TiO in massive form, or deep chestnut brown as is finely divided TiO. An attempt to identify the sublimate by X-ray diffraction techniques failed, for sublimates rarely yield satisfactory diffraction patterns. The deep brown sublimate that condensed on the water cooled wall of the vacuum chamber gave a weak diffraction pattern of poor quality, but the lines characteristic of the NaCl-type TiO phase could be identified. No explanation for the above anomaly is immediately forthcoming.

One further series of vaporization experiments was concluded. This final series was intended to yield large percentage weight losses in order that any change in composition of the solid that took place as vaporization progressed might be easily detected. To obtain large fractional weight losses in a reasonable time the lid was removed from the effusion cell, and the temperature of the sample was held just below the melting point. Accurate temperature measurements could not be made because blackbody conditions did not obtain. The design of the assembly was in all other respects the same as that used in the vapor pressure experiments described previously. The effusion cell was, therefore, an open crucible surmounted by a stack of ten radiation shields. The lowest of these shields rested on the top of the crucible, and had a centrally bored 1/4" diameter hole. A quartz collector plate was placed above the assembly as in the case of vapor pressure runs.

Three runs were completed and were given the designations A-5.1, A-5.2 and A-5.3, respectively. Runs A-5.1 and A-5.2 are to be considered a single experiment, for no definitive data were taken between the two runs. It was noted during the course of run A-5.1 that the sublimate was not forming a tightly adherent deposit on the collector plate, but was flaking off. The run was therefore terminated and the collector plate was thoroughly cleaned. The experiment was subsequently resumed under the designation A-5.2. In this latter instance, the sublimate condensed on the target in an even, tightly adherent film. When viewed from the front surface, the sublimate had a black color with slight metallic lustre. When viewed from the back of and through the quartz plate, the brownish color characteristic of TiO could be observed. An attempt to identify the sublimate by direct recording X-ray diffraction techniques failed for, as is frequently the case with sublimates, the deposit was so thin and the structure so highly oriented with respect to the substrate that only one broad, illy defined diffraction maximum was observed. An interpretation of the pattern was therefore impossible.

The sample material had not been molten at any time during runs A-5.1 or A-5.2, but remained as a sintered button on the bottom of the molybdenum crucible. The entire sample button was removed from the crucible and ground in an Al_2O_3 mortar to pass a 200 mesh screen. Portions of the powdered residue were then removed for X-ray and chemical analysis, while the remainder was reserved for run A-5.3. It was found that 13.73 per cent of the sample had vaporized during runs A-5.1 and A-5.2.

Run A-5.3 was performed in precisely the same manner as A-5.1 and A-5.2, except that the sample material was the residue from the previous two runs. The sublimate again flaked off the quartz condensation target, but a sufficient quantity of sublimate was obtained for examination by X-ray diffraction techniques. The weight loss during run A-5.3 alone was found to be 15.99 per cent of the material present at the start of the run, while the total equivalent weight loss for the series of three runs was 27.50 per cent of the original sample.

The residue and sublimate from run A-5.3 were ground in an Al_2O_3 mortar to pass 200 mesh, and portions were reserved for chemical and X-ray examination. In addition to these two samples, it was found that a deposit had formed on the radiation shield that rested on the top of the molybdenum crucible during run A-5.3. This deposit, which had the characteristic golden yellow color of TiO in massive form, was mechanically removed from the molybdenum shield and retained for X-ray analysis. The observational data for runs A-5.1 through A-5.3 are presented in Table VII, while a summary of samples obtained during this work, sample composition and lattice parameters of the various materials is given in Table VIII.

Table VII

Vaporization Data for Runs A-5.1 through A-5.3

Run	Sample	Sample Weight (g)	T (°K)	Time (sec.)	Orifice Area (cm^2)	Weight Loss (g)	Weight Loss (%)
A-5.1 through A-5.2	$TiO_{0.993}$ First use	0.4451	2000	34,800	0.32	0.0611	13.73
A-5.3	$TiO_{1.038}$ Residue from A-5.2	0.2926(a)	2000	45,000	0.32	0.0468(b)	15.99(b) 27.50(c)

(a) A portion of the residue from run A-5.2 was removed for X-ray and chemical analysis. The remainder was used as starting material for run A-5.3

(b) For run A-5.3 alone

(c) Total equivalent percentage weight loss for runs A-5.1 through A-5.3

Table VIII

Summary of Samples and of Lattice Parameter *versus* Composition Data

Sample Description	Sample[(a)] Composition	Lattice Parameter[(c)] (23 ± 3) °C (A)
Original Bur. of Mines "TiO"	$TiO_{0.993}$	----
Residue from Runs 7 through A-4. 7.98% wt. loss Sample had melted.	$TiO_{1.006}$	$4.1745_8 \pm 0.0001_3$ Film 571; Sharp intense lines; few weak lines.
Deposit on crucible lid after Runs 7 through A-4	$TiO_{0.847}$(d)	$4.1862_6 \pm 0.0002_2$ Films 524 and 525; Sharp intense lines; Eight extra lines
Residue from Runs A-5.1 through A-5.2. 13.73% wt. loss.	$TiO_{1.038}$	$4.1735_4 \pm 0.0001_3$ Film 572; sharp intense lines; Several extra lines.
Residue from Run A-5.3. 15.99% wt. loss. Starting material $TiO_{1.038}$. Total eq. wt. loss for A-5.1 through A-5.3 is 27.50%	$TiO_{1.137}$	$4.1693_6 \pm 0.0001_3$ Films 529 and 530; Sharp intense lines. Ten extra lines.
Deposit on shield after Run A-5.3	$TiO_{1.105}$(b)	$4.1704_8 \pm 0.0002_6$ Film 532; Sharp intense lines. Al_2O_3, Mo included
Sublimate on collector, Run A-5.3	$TiO_{1.132}$(b)	$4.1695_6 \pm 0.0001_8$ Film 534; Sharp intense lines; Al_2O_3 included.

(a) Analyzed by direct determination of oxygen.
(b) Estimated from lattice parameter and Fig. 2.
(c) λ (Cu Kα) = 1.54050 A; λ (Mo Kα) = 0.70926 A.
(d) After run A-4 the sublimate on the collector plate had the anomalous metallic-like appearance.

An examination of the data presented in Table VIII makes it quite clear that the composition of the residue from a given vaporization experiment is richer in oxygen than the starting material. It may also be noted that the oxygen enrichment increases as the percentage weight loss increases.

There are three possibilities that might explain this change in the residue composition. Process (1), the congruent sublimation for form TiO(g), may have associated with it a contamination of the residue by the residual oxygen and/or nitrogen in the vacuum system. They may enter the crucible and react with the sample to such an extent as to account for the observed oxygen enrichment of the residue.

Process (3), the incongruent sublimation with incomplete dissociation, may produce TiO(g) and Ti(g) in such proportions as to explain the change in composition of the residue.

Process (4), the incongruent sublimation with complete dissociation, may produce a much higher pressure of Ti(g) than O(g), thus leaving an oxygen rich residue.

Let us treat the last of these first. We have noted previously in the discussion of the data presented in Table VI that, if the volatility data are to be explained on the basis of a mechanism involving vaporization by decomposition to the elements, consideration of the observed titanium pressures and the known equilibrium constant for the dissociation reaction (Eq. 9) leads to the conclusion that the titanium pressure must be of the order of 10^{-6} atmosphere and that the oxygen pressure must be of the order of 10^{-12} atmosphere. Thus the volatility of TiO might be explained on the basis of vaporization of titanium alone. From an examination of the weight loss and residue composition data given in Tables VII and VIII it is seen that the various samples can not have lost titanium alone, for if such had been the case the residues would be much richer in oxygen than is observed. In the case of the sample that underwent a 27.50 per cent weight loss, one calculates that if only titanium vaporized the composition of the residue should lie within the two-phase field between Ti_2O_3 and Ti_3O_5. Examination of the residues from vaporization experiments by X-ray diffraction techniques failed to disclose the presence of any phase other than the TiO phase, while chemical analysis of the residues established that all had compositions that lay well within the TiO field.

It may be argued that as vaporization proceeds to give a residue of higher oxygen content the oxygen partial pressure will increase while that of titanium will decrease, thus preventing a change in composition so great that a new oxide phase is formed. In view of the factor of 10^6 between the titanium and oxygen pressures at the composition $TiO_{1.000}$, the above argument cannot be maintained, for even if the oxygen pressure increases extremely rapidly as one proceeds to compositions richer in oxygen, the titanium pressure must then fall equally rapidly. Hence when the oxygen pressure has risen to 10^{-11} atmosphere, the titanium pressure will have decreased to 10^{-7} atmosphere. When this latter situation obtains, the volatility of the sample will still be due to the loss of titanium alone. The important point is, however, that the total volatility will have decreased by a factor of 10, while the total pressure is still essentially that due to titanium. No such marked decrease in total pressure was observed to accompany extensive changes in sample composition. While the relation between titanium pressure and oxygen pressure may not be precisely reciprocal as has been assumed above, the assumption seems not unreasonable by analogy with Darken and Gurry's observations (108, 109) on the $Fe_{1-x}O$ (NaCl-type) phase in the iron-oxygen system.

We conclude, therefore, that the volatility of TiO and the change in sample composition with the extent of vaporization cannot be explained on the basis of vaporization of titanium alone, and hence reject process (4).

Let us now examine process (3), which was the third mechanism of vaporization suggested as an explanation of the change in residue composition with the extent of vaporization. That is, we shall assume that solid TiO vaporizes to give both TiO(g) and Ti(g), and that these gaseous species are present in such proportions as to account for the observed change in residue composition. The sublimate resulting from such a process would be expected to be titanium rich. Table IX gives data concerning these sublimates.

The final column of Table IX lists the masses of the sublimates for the various experiments and their compositions as calculated by performing a mass balance or as estimated from the observed lattice parameter and the curve of Figure 2.

The deposits on the under side of the lid after run A-4, and on the under side of the first radiation shield after run A-5.3 present a difficulty, for the visual examination did not reveal definitely whether they appeared because of spattering, creeping, or sublimation. It is not clear, then, whether they should be considered as part of the residue or the sublimate.

Further, it will be noted that the data for runs 7 through A-4 apply to the total series of experiments. Each experiment within the group was conducted at a different temperature. In general, one would expect the ratio

Table IX

Summary of Sample Mass and Composition Data

Runs 7 through A-4

	Starting-Material	Residue	Deposit on Crucible Lid	Sublimate
Mass (g) :	1.2717	1.0448	0.1254	0.1015(a)
Composition:	$TiO_{0.993}$	$TiO_{1.006}$	$TiO_{0.847}$	$TiO_{1.044}$(c) $TiO_{0.934}$(d)

Runs A-5.1 through A-5.2

	Starting Material	Residue	Deposit on Shield	Sublimate
Mass (g) :	0.4451	0.3840	---	0.0611(a)
Composition:	$TiO_{0.993}$	$TiO_{1.038}$	---	$TiO_{0.732}$

Run A-5.3

	Starting Material	Residue	Deposit on Shield	Sublimate
Mass (g) :	0.2926	0.2448	0.0010	0.0468(a)
Composition:	$TiO_{1.038}$	$TiO_{1.137}$	$TiO_{1.105}$(b)	$TiO_{1.132}$(b) $TiO_{0.588}$(c) $TiO_{0.597}$(d)

(a) Wt. loss; (b) From lattice parameter and Fig. 2;
(c) From mass balance. Deposit considered part of residue;
(d) From mass balance. Deposit considered part of sublimate.

P(TiO)/P(Ti) to be a function of temperature as well as of sample composition. While the composition change was slight for this series of runs, the temperature range was about 100°C. The temperature during runs A-5.1 to A-5.2, and run A-5.3 was the same in each case, but the sample composition changed markedly. We thus conclude that calculations of the type suggested above will, at best, yield only a rough estimate of the "average" ratio P(TiO)/P(Ti) in each case for which data are available.

If the deposit is considered part of the residue for runs 7 through A-4, one calculates a sublimate composition that is richer in oxygen than in titanium. This is inconsistent with the original premise that Ti(g) and TiO(g) are the only species in the vapor phase. If the deposit is considered to be a part of the sublimate, one calculates a gross sublimate composition of $TiO_{0.934}$. This latter result is consistent with the assumption of Ti(g) and TiO(g) as vapor species.

Examination of the data for the succeeding two experiments discloses that the apparent gross sublimate composition, as calculated from a mass balance, becomes increasingly rich in titanium relative to oxygen, or to TiO, as the solid becomes richer in oxygen. Such a trend in vapor composition with solid composition is unreasonable. One would expect, rather, that as the solid became richer in oxygen the partial pressure of titanium would fall while that of oxygen and of TiO(g) would rise, thus giving a vapor phase also richer in oxygen than the initial vapor.

One additional noteworthy fact appears in Table IX. It will be noted that, in the case of run A-5.3, while a mass balance yields a calculated sublimate composition of about $TiO_{0.59}$, direct establishment of the sublimate composition from measurements of the lattice parameter of the TiO phase found in the sublimate and interpolation in Figure 2 yields a composition of $TiO_{1.13}$. In view of the high reliability of the chemical analyses and of the lattice parameter determinations, this gross disagreement is certainly real and, therefore, in the opinion of the author, necessitates the rejection of process (3). It is the writer's opinion that the only virtue of the assumption that both Ti(g) and TiO(g) are important species in the vaporization process is that one might then have a plausible explanation for the appearance of the deposit of composition $TiO_{0.847}$ in runs 7 through A-4. For this reason, and for the sake of exhaustive treatment of the available experimental data, the discussion of this latter hypothesis will be continued a bit further.

The data of Tables I and II, when treated on the assumption of process (1), that TiO(g) is the only important species in the vapor, will clearly give an upper limit to the vapor pressure of TiO, and hence an upper limit to the dissociation energy of TiO(g). It is desirable to establish from the available data, if possible, a lower limit for the vapor pressure of TiO, and hence a lower limit for the dissociation energy of TiO(g). If one is willing to assume for the moment, despite how unlikely it may appear, that both Ti(g) and TiO(g) are important species in the vaporization of TiO(s), the data of Table IX may be used as follows to make a rough estimate of the lower limit for the vapor pressure of TiO.

Let us consider the data for runs 7 through A-4 presented in Table IX. The first sublimate composition tabulated obviously has no meaning for this discussion, as the composition is inconsistent with the assumption of Ti(g) and TiO(g) as the only vapor species. The second sublimate composition, $TiO_{0.934}$, may be used to calculate the ratio of Ti to TiO in the sublimate. It may be argued, however, that the vapor phase must have been at least as rich in titanium as the deposit on the underside of the crucible lid for runs 7 through A-4. The occurrence of this deposit, of composition $TiO_{0.847}$, might thus be explained. It may be argued further that the vapor phase must have been even richer in titanium than the deposit, for under the assumption that Ti(g) and TiO(g) are the vapor species the first trace of deposit that forms must be richer in titanium than the original solid. This deposit will then partially revaporize to give a vapor phase still richer in titanium. Hence the remaining deposit must change in composition toward an oxide richer in oxygen. That is to say, the deposit of composition $TiO_{0.847}$ has undergone continual fractional sublimation during the series of runs, and therefore represents only an upper limit to the proportion of TiO(g) in the vapor phase. In order that we might have a generous lower limit for the TiO pressure, it is assumed that the sublimate for runs A-5.1 through A-5.2, whose composition as calculated from a mass balance is $TiO_{0.732}$, represents a generous lower limit to the TiO pressure for runs 7 through A-4. Hence we find that, for the vapor phase during runs 7 through A-4,

$$z(TiO)/z(Ti) = 0.732/0.268 = (P_{TiO}/P_{Ti})(M_{Ti}/M_{TiO})^{1/2}, \qquad (26)$$

or $P_{TiO}/P_{Ti} = 2.36$. Thus, under the foregoing assumptions, we find that the partial pressure of TiO(g) is roughly twice the partial pressure of titanium. For simplicity of calculation, and to get an even more generous lower limit to the TiO partial pressure, let us assume that the pressure of TiO(g) is equal to that of titanium. If the factors in molecular weight are neglected, the above assumption means that the pressures of TiO reported in Table III are high by about a factor or two. This is an error of 0.301 in log P, which when multiplied by 4.576 T leads to a calculated error in ΔH°_{298} for the vaporization of TiO to TiO(g) of only 2.76 Kcal./mole, where T has been taken as 2000°K.

We have concluded that process (3) alone cannot account for the change in the composition of the residue. Because of the slight possibility that this process may occur along with others, we have shown that only a small error will be introduced in the calculation of the dissociation energy of TiO(g).

Let us turn our attention to the remaining possibility proposed to account for the oxygen enrichment of residues from vaporization experiments. Let us assume that, although TiO(s) vaporizes congruently to give TiO(g) alone, oxygen and/or nitrogen effuse into the orifice from the vacuum system in sufficient quantities to produce the composition changes.

Both oxygen and nitrogen must be considered as possible sources of contamination in the residues for no distinction is made between oxygen and nitrogen in the chemical analyses. Further, since TiO and TiN are isomorphous and form a continuous series of solid solutions, the addition of small amounts of nitrogen to a given TiO_x solution will have approximately the same effect on lattice parameters as the addition of an equal amount of oxygen.

Table X contains data that will enable an evaluation of this possibility. Column 2 of Table X lists, for each run, the oxygen found in the residue in excess of that to be expected if vaporization is to TiO(g) exclusively. The mass and composition data in Table IX were used with weight losses in Table I. In column 3 are tabulated the mass of oxygen and nitrogen, respectively, that could have entered the crucible and reacted with the sample during the course of a given experiment.

These values have been calculated by use of Knudsen's equation (Eq. 15) from a knowledge of the pressure and temperature of the gas at the crucible orifice. These latter two quantities are not subject to direct measurement in the usual experimental arrangements used, but it has been estimated that the gas temperature was about 1000°K at the crucible aperture and that the total pressure was about ten times the residual gas pressure indicated by the pressure gauge situated near the diffusion pump. The required residual gas pressure and geometry data have been given previously in Tables I, II and VII.

Table X

Comparison of Excess Oxygen in Residues with Oxygen Entering Crucible

Run	Excess oxygen remaining in residue. (g)	Oxygen and nitrogen entering crucible during run. (g)
7 through A-4	$-0.0011_1^{(a)}$ $+0.0028_4^{(b)}$	0.00072 O_2 0.00290 N_2
A-5.1 through A-5.2	0.0032_9	0.00088 O_2 0.00350 N_2
A-5.3	$0.0040_2^{(b)}$	0.00113 O_2 0.00452 N_2

(a) Deposit considered part of residue.
(b) Deposit considered part of sublimate.

In the case of experiments 7 through A-4, two values for "excess" oxygen are listed. These arise because of the uncertainty as to how to treat the deposit of composition $TiO_{0.847}$ found on the under side of the crucible lid at the conclusion of the series of runs. If the deposit is considered part of the residue one calculates that there is in fact a deficiency rather than an excess of oxygen in the residue. The magnitude of the deficiency is perhaps within the experimental error.

If the deposit is considered to be a "sublimate" rather than a "residue", it is found that there is an excess of oxygen in the residue over that to be expected if TiO(g) alone is lost from the crucible. In this latter instance, reference to column 3 of Table X discloses that sufficient oxygen and nitrogen could have entered the crucible during the course of the experiment to account for the observed change in residue composition. In the other two runs for which data are available, it is again seen that the change in composition of the residues can be explained on the assumption that TiO(g) alone is vaporized, and that oxygen and nitrogen enter the crucible and react with the sample.

Perhaps the most conclusive evidence favoring the contamination mechanism is to be seen in Table IX. Every recovered material from run A-5.3, residue, deposit, and sublimate showed an oxygen content greater than the original sample.

G. Conclusions

The foregoing sections of this thesis have presented the experimental details and results of an investigation of the volatility of TiO(s) by Knudsen's effusion method at several temperatures from 1845°K to 2014°K. Four different vaporization mechanisms were originally proposed to explain the observed vaporization phenomena.

Process (2), in which TiO is assumed to vaporize congruently by complete decomposition to the elements, was rejected because the observed volatility is a factor of 10^3 greater than that to be expected for such a process on the basis of the known thermodynamic properties of the system. The equilibrium constant calculated from the experimental data is a factor of 10^6 larger than the equilibrium constant established by reliable thermodynamic data for the reaction in question.

A vaporization mechanism in which TiO is assumed to sublime incongruently by complete decomposition to the elements was designated Process (4). It was found that the titanium partial pressures, as calculated from the amount of metal found in the sublimate by chemical analysis and on the assumption that Ti(g) is the only metal-bearing species in the vapor, are high enough to account for the observed volatility of TiO. Consideration of the known equilibrium constant for the reaction described by Process (4) leads to the conclusion that the oxygen partial pressure must then be so low that the contribution of oxygen to the volatility of TiO must be entirely negligible. Under such conditions the composition of the solid must change very rapidly to an oxide of higher oxygen content, and should in one instance during this work have yielded an entirely different oxide phase. Since X-ray and chemical analyses of residues from vaporization experiments disclosed no such very rapid change in composition nor any phase other than the TiO phase, Process (4) cannot be a valid explanation of the experimental facts.

The simplest vaporization mechanism considered was Process (1), in which TiO is assumed to vaporize congruently to give TiO(g) molecules. The weight-loss and collector-plate data treated according to this process yield a value for the dissociation energy of TiO(g) in excellent agreement with the value suggested by Herzberg (9) from spectroscopic observations. While analyses disclosed that the residues from vaporization experiments were somewhat richer in oxygen than the original sample material, it has been shown that this change in sample composition could have been occasioned by contamination of the sample with oxygen and nitrogen from the atmosphere in the vacuum furnace. Such an explanation of the change in sample composition is given further strong support from the observation that, for one experiment, all materials such as residue, deposit on radiation shield and sublimate on quartz collector that were recovered at the end of the experiment were shown by analysis to be richer in oxygen than the original sample material.

In view of the fact that a change in sample composition with extent of vaporization was noted, Process (3), in which TiO is assumed to vaporize incongruently by partial decomposition to give both TiO(g) and Ti(g), was examined. Since the change in solid composition is toward an oxide of higher oxygen content, Ti(g) must, for the process under consideration, be the most important elementary species in the vapor. An appropriate ratio of TiO(g) and Ti(g) partial pressures would explain the change in sample composition, the volatility data, and the observation that a titanium-rich deposit formed on the underside of the crucible lid in one series of experiments. In all other experiments, however, the deposits and residues obtained were oxygen-rich. This single observation of a titanium-rich product is anomalous.

In any event, it has been shown that even if the TiO(g) pressure is only half that calculated on the assumption that Process (1) is the correct vaporization mechanism, one thereby incurs an error of only 2.7 kcal./mole in the calculated dissociation energy of TiO(g).

We conclude, therefore, that the volatility of TiO can best be explained on the assumption that TiO is a congruently subliming composition and that TiO(g) is the only important species in the vapor. The assumption that both TiO(g) and Ti(g) are important vapor species leads to a lower limit for the dissociation energy of TiO(g) while a definite upper limit, if not the true value, for the dissociation energy is given by the assumption that TiO(g) alone is important.

Hence, we conclude from the above discussion that a generous upper limit to the heat of vaporization of TiO to TiO(g) is $\Delta H^{\circ}_{298,\ v} \leq 139.03$ Kcal./mole, and that a generous lower limit to the dissociation energy of TiO(g) is, therefore, $D^{\circ}_{0}(\mathrm{TiO}) \geq 156.74$ Kcal./mole. It is the opinion of the author, however, that the change in solid composition with the extent of vaporization is adequately explained on the basis of contamination by the atmosphere in the vacuum furnace, and that Process (1) actually describes the vaporization phenomena of TiO. Hence, the "best" value for the heat of sublimation of TiO is, in this writer's opinion, $\Delta H^{\circ}_{298,v} = 137.15 \pm 0.60$ Kcal./mole. The dissociation energy of TiO(g) is, therefore, $D^{\circ}_{0}(\mathrm{TiO}) = 158.62 \pm 0.60$ Kcal./mole. In any event, the vapor pressure data as treated on the assumption that TiO(g) is the only important species in the vapor yield, at worst, a lower limit to the heat of vaporization of TiO of $\Delta H^{\circ}_{298,v} \geq 137.15$ Kcal./mole, and thus an upper limit to the dissociation energy of TiO(g) of $D^{\circ}_{o}(TiO) \leq 158.62$ Kcal./mole.

H. Suggestions for Future Work.

The present work has yielded a value for the dissociation energy of TiO(g) of a much higher order of accuracy than has previously been available. While the vapor pressure experiments strongly indicate that TiO vaporizes to TiO molecules, the data do not permit an unequivocal choice between this vaporization mechanism and one in which both Ti(g) and TiO(g) are considered important vapor species. Further experiments to clarify this point would be desirable, and several procedures that would yield the necessary information are listed below:

(a) A sample of stoichiometric TiO may be heated in an open crucible to a temperature well below that at which appreciable volatilization occurs. Under such conditions, very little sample would be lost by sublimation, yet the sample temperature would be high enough so that oxygen and nitrogen entering the crucible from the furnace atmosphere would react with the sample. If such an experiment were continued for a sufficiently long time, the sample should gain weight if there is oxygen and nitrogen pick-up. Analysis of the sample would further establish whether a change in composition had occurred.

(b) The gas evolved from samples of TiO_x on treatment with BrF_3 could be subjected to analysis by the usual methods to establish whether the gas consisted entirely of oxygen or whether nitrogen was also present. Analysis of the evolved gas by mass spectrometer techniques would be extremely valuable. The presence of nitrogen in the gas would confirm the hypothesis that TiO vaporizes to TiO(g), and that the change in sample composition with extent of vaporization, as noted in this work, is due to contamination of the sample by the residual gas in the vacuum system.

(c) Direct determination of the species present in the vapor phase above TiO(s) by the mass spectrometer techniques developed by Honig (38a) and Inghram and Chupka (38b) would allow one to make a definite choice between the two possible vaporization mechanisms suggested in this present work.

(d) Samples of TiO could be heated in a very high vacuum, say about 10^{-7} atmosphere, to establish whether oxygen and nitrogen contamination occurred at such reduced pressures.

Our present knowledge of the titanium-oxygen phase diagram at compositions richer in oxygen than $TiO_{1.25}$ is in a deplorable state. Completion of the phase diagram up to the composition TiO_2 would be a valuable addition to our knowledge of this system. The methods of thermal analysis, high-temperature X-ray diffraction techniques, metallographic analysis, electrical resistivity measurements and equilibration with appropriate gas mixtures would prove valuable. The method of equilibration with various gas mixtures, such as CO-CO_2 and H_2-H_2O, has been discussed previously. Darken and Gurry (108, 109) have used such a method in a complete study of the iron-oxygen system, while Welch (103) has made a partial study of the titanium-oxygen system by equilibrating oxide samples with H_2-H_2O mixtures. The expansion of Welch's work to include greater temperature ranges and different gas mixtures would not only help to establish the nature of the phase diagram at the high oxygen end of the Ti-O system, but would also yield valuable information as to the activity of oxygen and titanium in compositions down to about Ti_2O_3.

The low oxygen side of the phase diagram might be investigated by the method of Kubaschewski and Dench (131), in which titanium-oxygen alloys of various compositions were equilibrated in bombs at a known temperature with calcium, magnesium or barium mixed with its respective oxide. After quenching, the excess alkaline earth metal and its oxide were leached out of the residue and the concentration of oxygen in the titanium determined by the vacuum fusion method.

The method has several serious limitations in that it is difficult to find structural materials for the bomb that will not react with the charge, and that will withstand temperatures above 1000°C. Further, the active metal employed must be insoluble in the titanium charge and in the bomb material at the temperature of the experiment. Yet another serious limitation to the method is that the equilibrium oxygen pressure in the bomb cannot be varied continuously at a given temperature. One may thus obtain only one oxygen pressure at a given temperature for each active metal used. Despite the serious limitations, it is believed that the method merits further study.

The phase diagram studies indicated above should be supplemented by vapor pressure studies of the other oxides of titanium such as Ti_2O_3, Ti_3O_5 and TiO_2. Any such studies should include experiments in which the volatility of mixtures of each pair of oxide phases is established. With two solid phases at fixed temperature, the pressure of the vapor phase is unique. Thus the pressure at the edges of the homogeneous field of each oxide phase could be established.

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APPENDIX I

Relation Among Atomic Per Cent, Weight Per Cent and Atomic Ratio in the Titanium-Oxygen System

O/Ti	At. % O	Wt. % O	O/Ti	At. % O	Wt. % O
0.00	0.000	0.000	1.02	50.49	25.41
0.02	1.961	0.664	1.04	50.98	25.78
0.04	3.846	1.318	1.06	51.46	26.15
0.06	5.660	1.965	1.08	51.92	26.51
0.08	7.407	2.603	1.10	52.38	26.87
0.10	9.090	3.232	1.12	52.83	27.23
0.12	10.714	3.854	1.14	53.27	27.59
0.14	12.28	4.467	1.16	53.70	27.93
0.16	13.79	5.073	1.18	54.13	28.28
0.18	15.25	5.672	1.20	54.54	28.62
0.20	16.67	6.262	1.22	54.95	28.96
0.22	18.03	6.846	1.24	55.36	29.30
0.24	19.35	7.422	1.26	55.75	29.63
0.26	20.63	7.991	1.28	56.14	29.96
0.28	21.88	8.553	1.30	56.52	30.29
0.30	23.08	9.108	1.32	56.90	30.61
0.32	24.24	9.657	1.34	57.26	30.93
0.34	25.37	10.199	1.36	57.63	31.25
0.36	26.47	10.73	1.38	57.98	31.56
0.38	27.54	11.26	1.40	58.33	31.87
0.40	28.57	11.79	1.42	58.68	32.18
0.42	29.58	12.30	1.44	59.02	32.49
0.44	30.56	12.81	1.46	59.35	32.79
0.46	31.51	13.32	1.48	59.68	33.09
0.48	32.43	13.82	1.50	60.00	33.39
0.50	33.33	14.31	1.52	60.32	33.68
0.52	34.21	14.80	1.54	60.63	33.98
0.54	35.06	15.28	1.56	60.94	34.27
0.56	35.90	15.76	1.58	61.24	34.55
0.58	36.71	16.23	1.60	61.54	34.83
0.60	37.50	16.70	1.62	61.83	35.11
0.62	38.27	17.16	1.64	62.12	35.39
0.64	39.02	17.61	1.66	62.41	35.67
0.66	39.76	18.06	1.68	62.69	35.95
0.68	40.48	18.51	1.70	62.96	36.22
0.70	41.18	18.95	1.72	63.24	36.49
0.72	41.86	19.39	1.74	63.50	36.76
0.74	42.53	19.82	1.76	63.77	37.02
0.76	43.18	20.25	1.78	64.03	37.29
0.78	43.82	20.67	1.80	64.28	37.55
0.80	44.44	21.09	1.82	64.54	37.81
0.82	45.05	21.50	1.84	64.79	38.07
0.84	45.65	21.91	1.86	65.03	38.32

(Cont'd)

(Appendix I Cont'd)

O/Ti	At. % O	Wt. % O	O/Ti	At. % O	W. % O
0.86	46.24	22.32	1.88	65.28	38.57
0.88	46.81	22.72	1.90	65.52	38.82
0.90	47.37	23.11	1.92	65.75	39.07
0.92	47.92	23.51	1.94	65.99	39.32
0.94	48.45	23.90	1.96	66.22	39.57
0.96	48.98	24.28	1.98	66.44	39.81
0.98	49.49	24.66	2.00	66.67	40.05
1.00	50.00	25.04			