T 1018

A THERMODYNAMIC STUDY of the TITANIUM-SULFUR SYSTEM in the REGION $TiS_{0.58}$ to $TiS_{2.85}$

By

Alan Douglas Zunkel

A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering.

Signed: Alan D. Zunkel
Alan D. Zunkel
(Student)

Golden, Colorado
Date: 5 March, 1965

Approved: Andrew Larson
A. H. Larson
(Thesis Advisor)

A W Schlechten
A. W. Schlechten
(Head, Department of
Metallurgical Engineering)

Golden, Colorado
Date: 5 March, 1965

ABSTRACT

The titanium-sulfur system was studied in the disulfide-trisulfide region between 525° and 565°C by means of a static technique employing direct equilibration of the titanium sulfides with sulfur vapor in evacuated Vycor capsules which were heated in a two-furnace temperature gradient unit. The experimentally-obtained equilibrium total sulfur pressures, sulfide temperatures, and sulfide compositions were used to calculate ΔH°, ΔG° and ΔS° for the reaction $2'\mathrm{TiS}_3' \rightleftharpoons 2'\mathrm{TiS}_2' + \mathrm{S}_2$ where the equilibrium phase compositions were $\mathrm{TiS}_{1.94\pm0.01}$ in the disulfide region and $\mathrm{TiS}_{2.58\pm0.01}$ in the trisulfide region. These equilibrium compositions did not vary with temperature.

X-ray phase determinations were made on samples equilibrated at 800°C in the composition region from the disulfide phase down to metallic titanium. The phases $'\mathrm{TiS}_2'$, $'\mathrm{Ti}_2\mathrm{S}_3'$, $'\mathrm{Ti}_3\mathrm{S}_4'$, $'\mathrm{TiS}'$, and $'\mathrm{Ti}'$ were found to be the equilibrium phases present in this region.

TABLE of CONTENTS

Table of Contents (Contd.)

LIST of FIGURES

LIST of TABLES

LIST of APPENDICES

List of Appendices (Continued)

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. A. H. Larson, Associate Professor of Metallurgical Engineering, Colorado School of Mines, for his guidance throughout the course of this investigation.

The author's gratitude is also expressed to Dr. A. W. Schlechten, Professor of Metallurgical Engineering, Colorado School of Mines, for his advice and helpful suggestions in the construction of apparatus and to Dr. N. C. Schieltz and Dr. R. J. Barton, Professor and Assistant Professor of Metallurgical Engineering, respectively, Colorado School of Mines, for their assistance and counsel concerning the X-ray analyses involved in this problem.

The author would like to thank the National Science Foundation for providing him the financial support necessary to make this study possible.

INTRODUCTION

Statement of the Problem

The purpose of this investigation was to make an experimental determination of the thermodynamic properties of the titanium-sulfur system in the disulfide-trisulfide region by determining the composition, temperature, and stability of the equilibrium sulfide phases and to make a qualitative X-ray study of other phases present in the system.

Importance of the Study

To the metallurgist, thermodynamic data are essential so that he can make well-planned, intelligent experiments on any problem which might be presented to him, whether it concerns ore concentration, smelting, refining, or fabrication. Since titanium is playing a more important role each year in modern technology, the more that can be learned about titanium and its compounds, particularly in terms of thermodynamic data, the better equipped the metallurgist will be to advance titanium technology.

Previous data for the titanium-sulfur system in the disulfide-trisulfide region are open to question since equilibrium may not have been established due to improper experimental procedure and since inaccurate sulfur equilibrium data were used in the calculations. The present study was conducted using a reliable static method and accurate sulfur equilibrium data.

In the disulfide and trisulfide regions of the titanium-sulfur system, wide ranges of nonstoichiometry have been shown to exist. In other metallic sulfides such as cuprous sulfide, zinc sulfide, and lead sulfide, regions of nonstoicheiometry have given rise to semi-conducting properties. Determination of the limits of the regions of nonstoichiometry would be of value in studies of any semi-conducting properties which the titanium sulfides might have.

The titanium trisulfide phase is similar to molybdenum disulfide in its lubricating property but not in its stability. Under the proper conditions of low temperature and inert atmosphere such as exists in outer space, the titanium trisulfide phase might have some value as a lubricant.

A Survey of the Literature

Biltz and co-workers (1937, p. 97-116) studied the reaction $2TiS_3 \rightleftharpoons 2TiS_2 + S_2$ by a static method using the Bodenstein "sulfur-valve" apparatus described by Kubaschewski and Evans (1958, p. 145-147) to measure the dissociation sulfur pressure. The value of $\Delta H°$ for the reaction was found to be 38 kcal mole^{-1}. The calculations in this work were based on the data of Preuner and Schupp (1910, p. 129) for the dissociation of S_8, S_6, and S_4 to S_2. These sulfur data have been since shown to be considerably in error by Klemm and Kilian (1941, p. 279) and

Braun and co-workers (1951, p. 32). The data of Biltz (1937, p. 105) were reevaluated by Haraldsen and co-workers (1963, p. 1289) using the data of West and Menzies (1929, p. 1880) for the polyatomic sulfur equilibria. The $\Delta H°$ for the reaction was determined to be 36.6 kcal mole^{-1}. Biltz and co-workers (1937, p. 97-116) studied the above reaction in the temperature range 500°C to 551°C. The constant pressure portion of the isotherms in this temperature range terminated at about $TiS_{2.85}$ in the trisulfide region and $TiS_{2.00}$ in the disulfide region. The two-phase equilibrium total sulfur pressures were found to be between 91 and 525 mm Hg. The colors of the phases were described as graphite-black for the trisulfide phase and brassy-yellow for the disulfide phase.

Many investigations have produced X-ray and structure data for both TiS_2 and TiS_3. McTaggart and Wadsley (1958, p. 445), Jeanin and Benard (1959, p. 2875-2877), Grimmeiss and others (1961, p. 776), Oftedal (1928, p. 301), and Haag and Schonberg (1954, p. 40) give the structure of TiS_2 as hexagonal with the CdI_2 lattice. These authors vary somewhat in their values for the lattice parameters, however. Hahn and Harder (1956, p. 251-256), Haraldsen and others (1963, p. 1290), McTaggart and Wadsley (1958, p. 445), and Jeanin and Benard (1958, p. 614-617) give the structure of TiS_3 as monoclinic. Again the values for the lattice parameters vary somewhat among these authors. A table summarizing the structure and lattice parameters for TiS_2 and TiS_3 is given in Appendix I.

Abendroth and Schlechten (1959, p. 145-51) studied the titanium-sulfur system between $TiS_{0.80}$ and $TiS_{1.93}$ by the H_2- H_2S recirculation method and found a two-phase region between $TiS_{0.80}$ and $TiS_{1.30}$ and a region of solid solubility between $TiS_{1.30}$ and $TiS_{1.93}$ in the temperature range from 500°C to 1100°C.

Vermaut (1964, p. 151-153) made a cursory study of the titanium-sulfur system in the disulfide-trisulfide region and found evidence for the existence of a two-phase region with a disulfide phase of composition $TiS_{1.89}$ or $TiS_{1.91}$ and a trisulfide phase of composition $TiS_{2.85}$. He reported no data for the equilibrium sulfur pressures.

EXPERIMENTAL APPARATUS and PROCEDURE

There are two general methods used in studying metal-sulfide reactions: the dynamic method and the static method. The dynamic method is used when the sulfur pressure of the reaction is too small to be measured directly. In one technique it is necessary to determine the H_2S-H_2 ratio of the gas phase in equilibrium with the condensed phase(s) in a gas circulation system. The general reaction is as follows:

$$MeS_3 + H_2 \rightleftharpoons MeS_2 + H_2S \tag{1}$$

This method has been used by Rosenqvist (1954, p. 37), Abendroth and Schlechten (1959, p. 145-51), Larson and Schlechten (1964, p. 862-866), and Vermaut (1964, p. 1-173).

The static method is limited to studies in which the total sulfur pressure is above 10mm Hg and can be measured and controlled by the temperature of the liquid sulfur in the equilibrium apparatus. The general reaction is shown as follows:

$$2\ MeS_3 \rightleftharpoons 2\ MeS_2 + \frac{2}{X}\ S_X \tag{2}$$

This method has been used by Schaefer and co-workers (1964, p. 594-595) and Vermaut (1964, p. 1-173).

The method selected for this investigation was the static method because the approximate total sulfur pressures for the reaction $2\ TiS_3 \rightleftharpoons 2TiS_2 + S_2$ are between 97mm and 525mm Hg for sulfide temperatures between 500°C and 551°C (Biltz and co-workers, 1937, p. 102).

Apparatus:

The apparatus used in this study consisted of six separate units:

(1) A primary sulfide preparation unit;

(2) a capsule evacuation unit;

(3) an equilibration unit;

(4) a sulfide leaching unit;

(5) a sulfide drying unit; and

(6) an X-ray unit.

The first unit (Figure 1) was used to prepare the starting material. H_2S was dried by passing it through a magnesium perchlorate drying chamber. From the drying chamber, the H_2S was led through Tygon tubing into a cylindrical mullite reaction tube 1 in. in diameter and 24 in. in length containing two alundum boats filled with a mixture of TiH_2 and powdered sulfur. The smaller upstream boat acted as a "getter" to remove any oxygen from the gas. The reaction tube was heated in a "Globar" furnace. After leaving the reaction tube, the evolved H_2 and unreacted H_2S were passed through a trap, a dibutyl phthalate bubbler to prevent back-diffusion of air, and a KOH bubbler to absorb some of the H_2S before exhausting the gas to the atmosphere. All joints were sealed with "Apiezon" wax to prevent leaks.

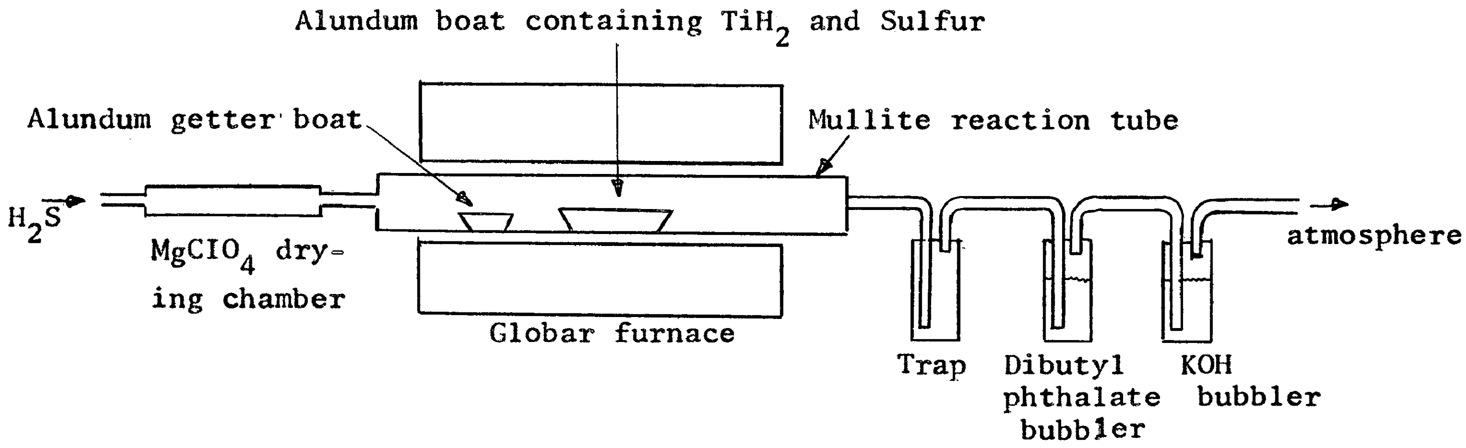
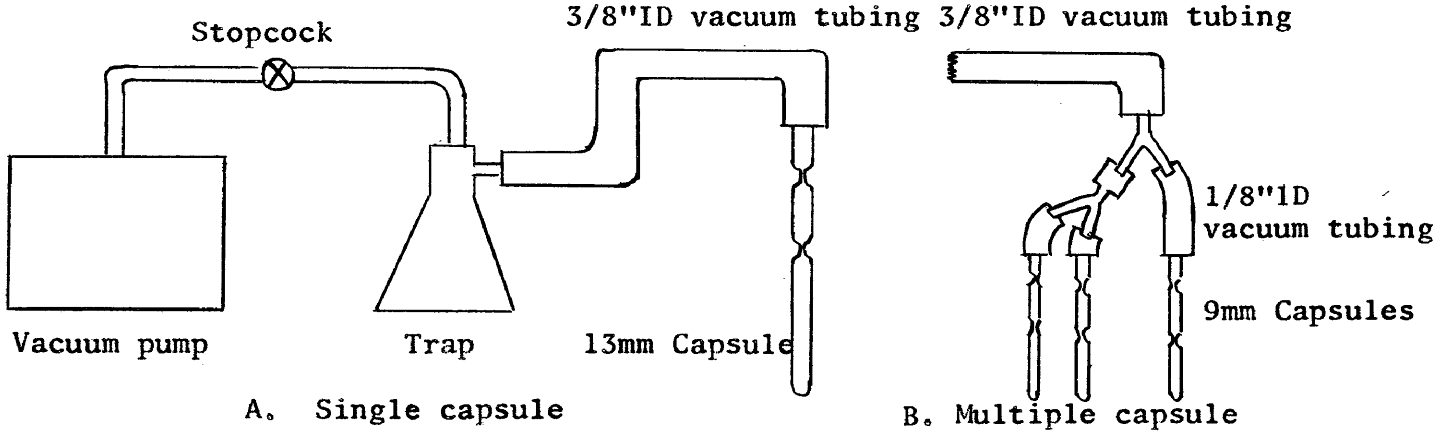


Figure 1. Primary Sulfide Preparation Unit.



A. Single capsule

B. Multiple capsule

Figure 2. Capsule Evacuation Unit.

The second unit used was the capsule evacuation system (Figure 2). This unit was used twice in the procedure. It was used once for the evacuation of the 13-mm Vycor capsules containing low-sulfur-content material, and again, later, for the evacuation of the 9-mm Vycor capsules containing the high-sulfur-content starting material which was to be equilibrated. This unit consisted of a Fisher "Duo-Seal" vacuum pump connected through a trap to a single length of 3/8-in. - ID vacuum tubing for evacuating the 13-mm capsules one at a time (Figure 2-A). Three lengths of 1/8-in.-ID vacuum tubing were connected by "Y" joints to the 3/8-in-ID tubing for the evacuation of the 9-mm capsules three at a time (Figure 2-B). The capsules were held securely in clamps attached to a ringstand during evacuation.

The equilibration unit (Figure 3) consisted of two multiple unit hinged resistance furnaces placed end-to-end on a slight horizontal incline. A 9-mm evacuated Vycor capsule was placed with the sulfur end in the lower furnace and the sulfide end in the higher furnace. The furnaces were inclined to insure that all of the liquid sulfur would go to the sulfur end of the capsule. Each furnace was powered by a Superior Electric Company 120-VAC powerstat and controlled by a Barber Coleman Model 293C temperature controller calibrated for chromel-alumel thermocouple wire. The powerstat and the temperature controller were connected through an Ebert Electric Company Model EM-1 Mercury plunger relay (Figure 4). A drop or rise in furnace temperature below or above that set on the temperature controller as measured by the controlling thermocouple activated or deactivated the relay and either placed the powerstat in the circuit to raise the temperature or removed it from the circuit to

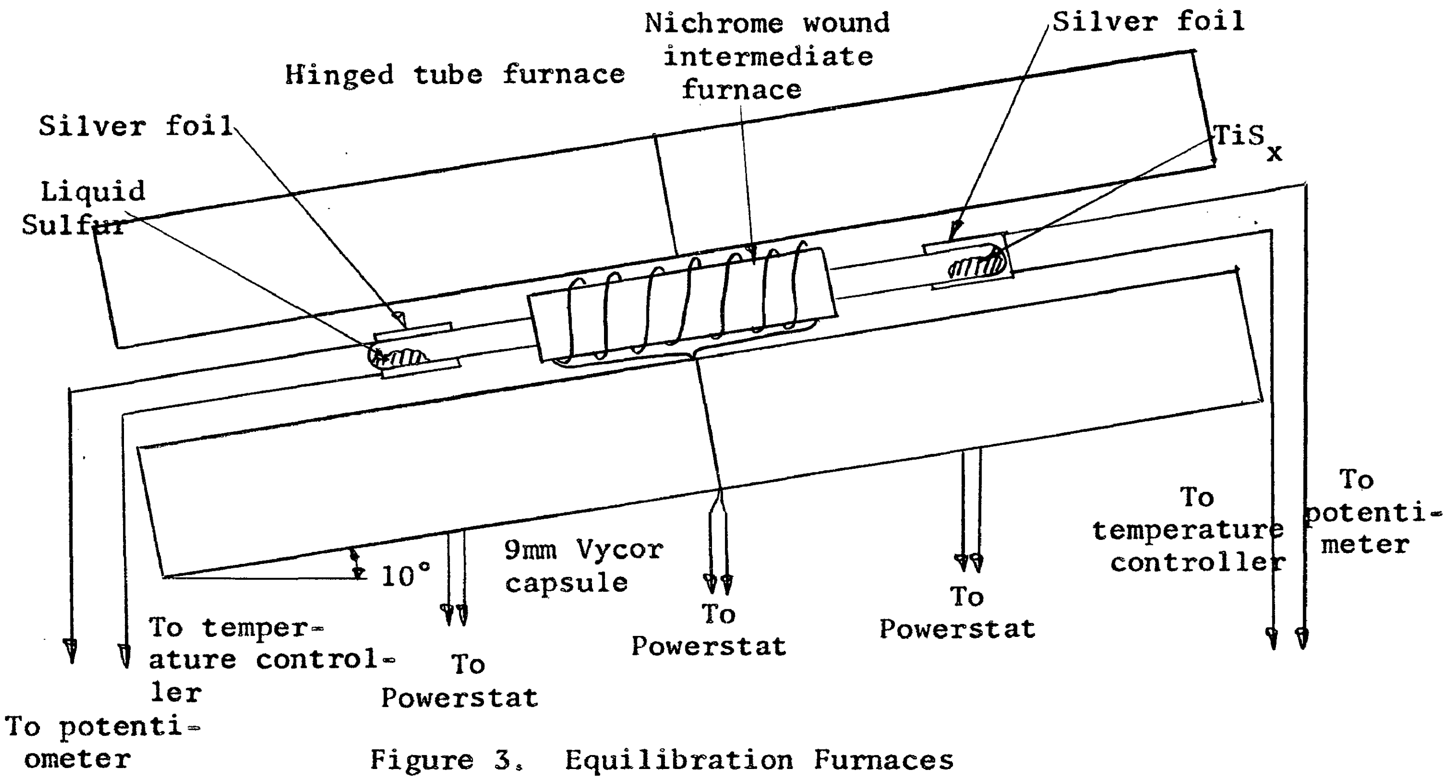


Figure 3. Equilibration Furnaces

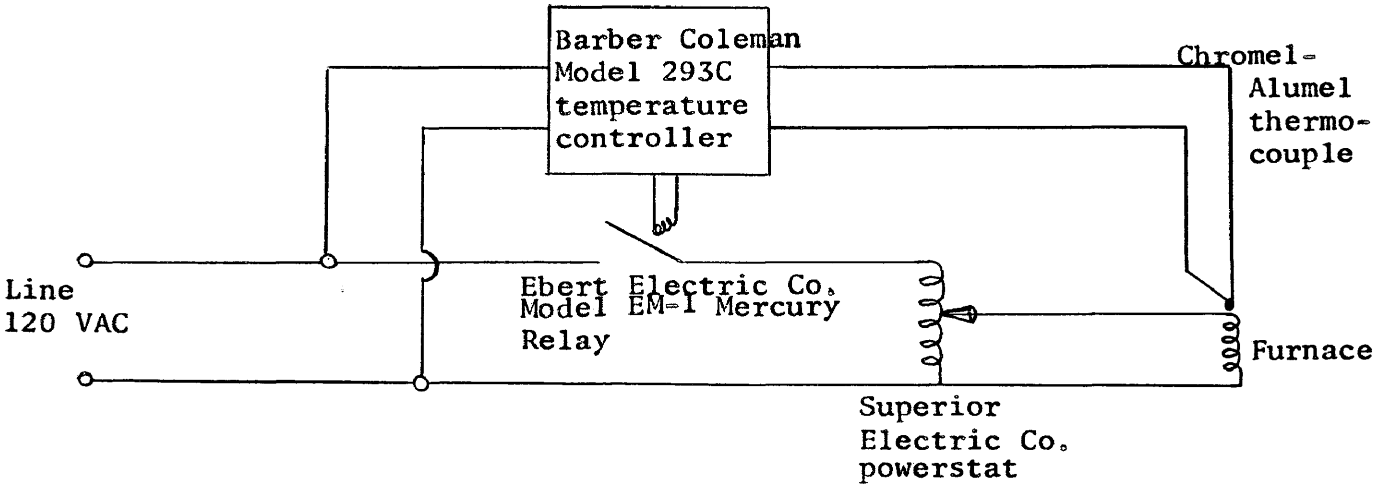


Figure 4. Temperature Controller Circuit Diagram.

lower the temperature. A temperature control of ± 1°C over a 36-hour period was accomplished by this method, (See Appendix II). Actual sulfur and sulfide temperatures were measured with a Leeds and Northrup millivolt potentiometer and a 3-foot-long chromel-alumel thermocouple which were calibrated against the melting points of 99.999% Al, 99.9% Zn, and 99.99% Pb (See Appendix III). The measuring and controlling thermocouples were placed inside and outside, respectively, of a silver foil wrapping around the ends of the capsule. Using this method temperature measurement can be considered to be accurate to ± 0.4°C. The total temperature measurement and control was then accurate to ± 1.4°C.

To prevent condensation of the sulfur vapor in the capsule at the joint between the two furnaces, a nichrome-wound intermediate furnace powered by a "Powerstat" was employed. This insured a temperature at the joint which was higher than that of the sulfur end of the capsule (See Appendix IV).

All starting materials and equilibrated samples were leached with warm CS_2 before analysis to remove any free sulfur which may have been trapped in the sample or which condensed from the gas phase on cooling. The unit used to accomplish this leaching consisted of an Erlenmeyer flask containing chemically pure CS_2 and a bent pyrex tube passing through a stopper (Figure 5). The tube supported a nichrome-wire yoke in which was placed a Gooch crucible containing the sample wrapped in filter paper. The unit was placed on a hot plate and cold tap water was allowed to flow through the tube. The CS_2 vaporized, condensed on the tube, and dripped through the sample. After passing through the sample, the CS_2 dripped

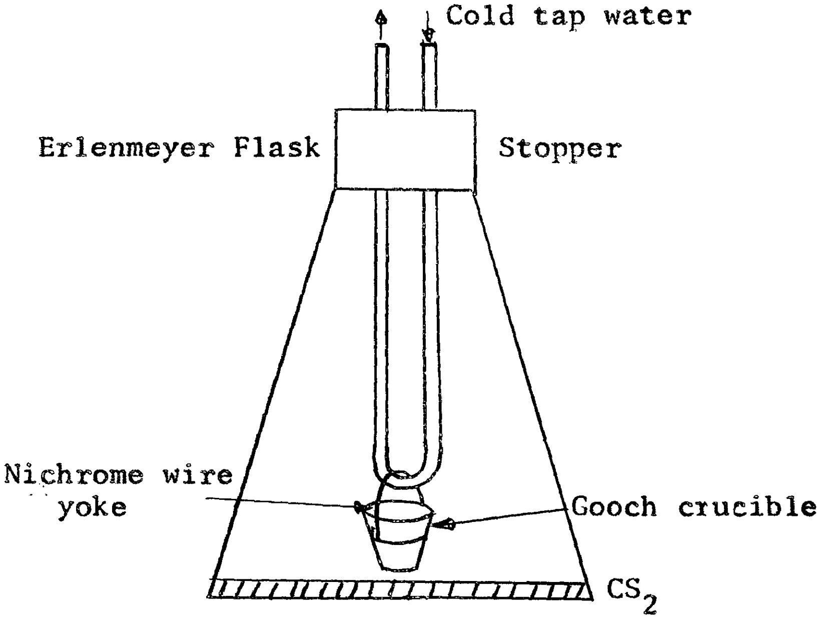


Figure 5. CS_2 Leaching Unit.

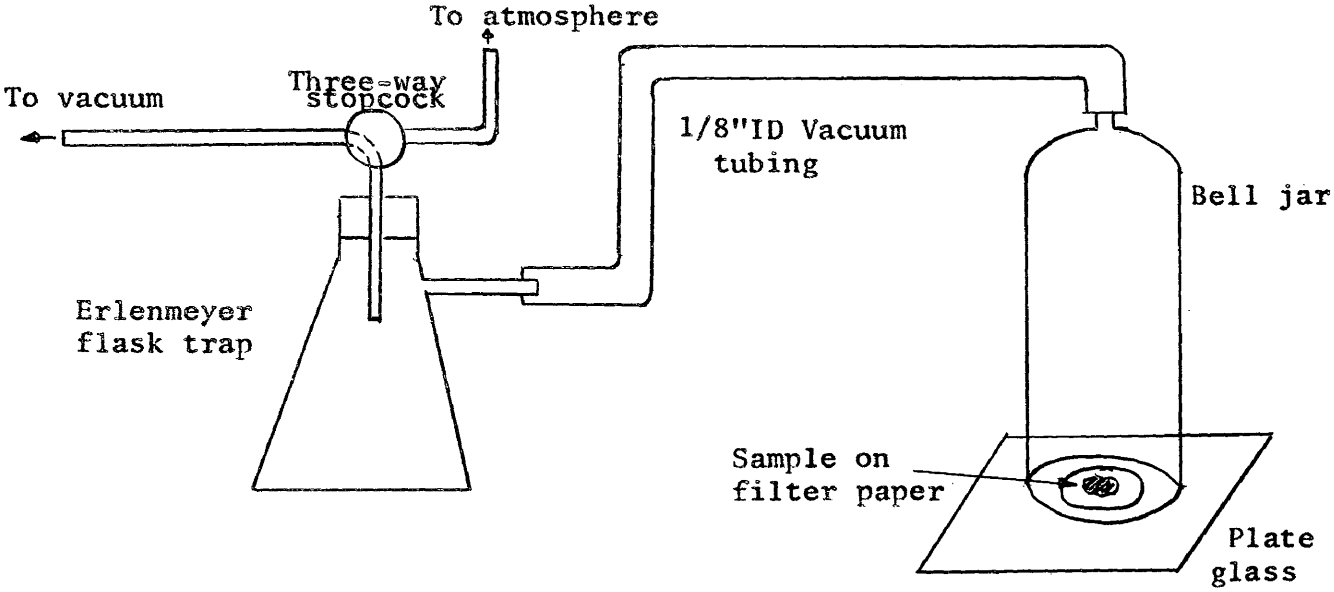


Figure 6. Vacuum Drying Unit

through the holes in the bottom of the Gooch crucible and returned to the pool of CS_2 in the bottom of the flask. A two-hour leaching period was found to be sufficient to remove all the free sulfur from the sample, (See Appendix V).

After the sample had been leached, it was dried under vacuum in the unit shown in Figure 6 to insure the vaporization of all of the CS_2. The laboratory vacuum line was connected through a three-way stopcock and trap to a bell jar placed on a square piece of plate glass. The sample was placed on a filter paper and put on the plate glass. A good seal between the bell jar and the plate glass was made by using a small amount of high-vacuum grease. After drying, the vacuum was relieved by turning the stopcock and opening the system to the atmosphere. A fifteen-minute drying time was found to be sufficient.

After the samples had been leached and analyzed, a small amount was prepared for X-ray analysis. The X-ray unit used was a Norelco Type 12045B/3 equipped to take standard powder diffraction data.

Procedure:

The procedure followed in this investigation involved eight steps:

(1) Preparation of the low-sulfur-content sulfide;
(2) preparation of the high-sulfur-content sulfide;
(3) placing the high-sulfur-content sulfide in capsules;
(4) equilibrating the samples;
(5) leaching the equilibrated samples;
(6) drying the leached samples;

(7) gravimetric analysis; and

(8) X-ray analysis.

The low-sulfur-content sulfide was prepared by mixing TiH_2 (Grade E) obtained from Metal Hydrides and enough crushed 99.999% sulfur obtained from American Smelting and Refining Company (See Appendix VI for analyses) to make TiS_2 and placing this mixture in an alundum boat. This boat was then placed in the unit shown in Figure 1. The entire system was flushed for 3 hr. with H_2S at a flow rate of 12 cc per min. to remove air. The furnace was turned on and allowed to heat up to 630°C in six hr. The furnace was maintained at 630°C for 16 hr. and then cooled to room temperature in one hr. by an air blast inside the furnace but outside the reaction tube. After the furnace had reached room temperature, the H_2S flow was stopped and the sample was removed from the reaction tube, checked for TiO_2, crushed, leached for 2 hr. with CS_2, and analyzed. If any TiO_2 was found, the sample was discarded. The product of the above procedure was difficult to predict and varied in composition between $TiS_{1.66}$ and $TiS_{1.92}$. In all cases the product was sintered, brassy-yellow in color, and very difficult to crush. Room temperature X-ray patterns showed only the disulfide phase. No TiH_2, TiO_2 or S lines were noted.

Since the combination reaction $2\,'TiS_2' + S_2 \rightleftharpoons 2\,'TiS_3'$ was found not to reach equilibrium in 48 hr. and the decomposition reaction $2\,'TiS_3' \rightleftharpoons 2\,'TiS_2' + S_2$ was found to reach equilibrium in 36 hr., the decompostition reaction was selected for study (See Appendix VII). As a result of this selection, the low-sulfur-content sulfide was then converted to a sulfide as high in sulfur composition as possible in the trisulfide region. This was accomplished by mixing the initial sulfide ($TiS_{1.66}$ to $TiS_{1.92}$) with enough powdered 99.999+% sulfur to make TiS_3 and placing this mixture in a 13-mm Vycor capsule about 4 in. long. The capsule was made by sealing the end of an 18-in. length of 13-mm Vycor and placing the sulfide-sulfur mixture in the sealed end of the tube. Four in. up from the sealed end, the tube was necked down to capillary size by heating and careful drawing. Above this neck were placed several pieces of high purity Ti sponge obtained from Titanium Corporation of America. Four in. above the first neck, another neck was made. The result was a Vycor tube with a 4-in. sulfide-sulfur section, a 4-in. titanium sponge section, and a 10-in open-ended section. The open end was then connected to the 3/8-in. vacuum tubing shown in Figure 2-A, and the vacuum pump was turned on and allowed to pump for one hr. After the one-hr. pumping period, the upper neck was sealed off by heating and drawing while the vacuum pump was still pumping. The titanium-sponge section was placed in a hinged tube furnace for 24 hr. at 700°C to allow the sponge to "getter" any O_2, H_2O, or N_2 remaining in the capsule. After "gettering", the lower neck was sealed-off leaving an evacuated capsule containing only the low-sulfur-content sulfide and sulfur. This capsule was wrapped in silver foil and heated in a hinged tube furnace for 24 hr. at 420°C and 24 hr. at 440°C. A higher temperature was not used because liquid sulfur was still present in quantity at 440°C. That liquid sulfur was still present indicated that the lower-sulfur-composition sulfide did not take up all the sulfur and TiS_3 was not formed at 440°C. After the 24-hr. heating period at 440°C, the capsule was removed from the furnace, air quenched, leached with CS_2 for 2 hr., and analyzed. In every case, the analysis before leaching was $TiS_{3.00}$ to $TiS_{3.03}$ and after leaching was $TiS_{2.64}$ to $TiS_{2.69}$. The product formed was blue-purple in color, slightly sintered, greasy to touch, and easy to crush. Room temperature X-ray patterns showed only the trisulfide phase. This product was used as the high sulfur-content starting material for the equilibration studies.

The equilibration capsules were made by placing 0.4g of the high-sulfur-content starting material ($TiS_{2.64}$ to $TiS_{2.69}$) and 0.4g of small lumps of 99.999+% sulfur in the sealed end of an 18-in. length of 9-mm Vycor tubing and making the lower neck 12 in. from the sealed end. The remainder of the capsule-making procedure was the same as for the 13-mm capsules with the exception that three capsules were evacuated at one time by modifying the apparatus shown in Figure 2A to that shown in Fig-2B. After evacuation, "gettering", and sealing, the capsule containing only the high-sulfur-content starting material and the lump sulfur was placed in the inclined equilibration furnaces with the sulfur end in the lower furnace as shown in Figure 3. Each end of the capsule was wrapped with silver foil to produce a constant temperature zone around the sulfide and the sulfur. The measuring thermocouple was placed inside the second wrap of the silver foil next to the capsule while the controlling thermocouple was held in an identical position outside of the silver foil by a ring of nichrome wire. The desired sulfur and sulfide temperatures were set on the temperature controllers, and the furnaces were allowed to come to temperature in one hr. During the heating period, the sulfur distilled from the hotter sulfide end to the cooler sulfur end of the capsule. The capsule remained in the furnaces for 36 hr., after which it was removed from the furnaces and air quenched to room temperature.

After the equilibration and air quenching, the capsule was broken open and immediately checked for H_2S or SO_2 by smelling the mouth of the open portion. An odor of H_2S or SO_2 indicated a poor seal of the capsule or the presence of TiH_2 or moisture in the starting material. If any H_2S or SO_2 was noted, the run was discarded. If no H_2S or SO_2 was found, the sample was removed from the capsule and wrapped in filter paper for leaching. The sample was then leached for 2 hr. with warm CS_2 in the apparatus shown in Figure 5.

To remove the CS_2 from the sample before analysis, the unit shown in Figure 6 was employed. The sample was removed from the leaching unit and scraped on to a clean filter paper. The sample and the filter paper were placed inside the bell jar and allowed to dry for 15 min. under vacuum. After 15 min. the sample was dry and was removed from the bell jar.

The method of analysis used to determine the composition of the sulfide was the combustion of the sulfide in air to TiO_2 according to the following reaction:

$$TiS_X + (X + 1)O_2 \rightleftharpoons TiO_2 + XSO_2 \qquad (3)$$

Approximately 0.3g of the sulfide was placed in a tared crucible and heated to constant weight at 900°C. After the sample was cooled to room temperature in a dessicator, the weight of the TiO_2 that was formed was determined. The value of X in TiS_X was found from the following formula (See Appendix VIII for the derivation):

$$X \text{ (in } TiS_X) = 2.49 \frac{\text{weight of } TiS_X}{\text{weight of } TiO_2} - 0.599 \qquad (4)$$

This analysis was easily and quickly performed and was reproducible with 90% confidence within X = ±0.01 (See Appendix IX). When applied to the disulfide phase ($TiS_{1.92}$), the accuracy was within 0.13% sulfur; and when applied to the trisulfide phase ($TiS_{2.60}$), the accuracy was within 0.09% sulfur. As a result then, in at least 90% of the analyses, the accuracy was always within 0.13% sulfur.

The X-ray analysis was performed using the standard powder diffraction method at room temperature. Due to the instability of the titanium sulfides in air, the samples were placed in glass capillaries immediately after drying before they were placed in the X-ray cameras. The patterns were made using Cu K_{α} radiation. The most suitable exposure times were 8 hr. for the disulfide phase and 14 hr. for the trisulfide phase at a current of 25 ma and a voltage of 35 kv. The equilibrium end compositions were checked using the diffractometer but no other compositions were checked because of the lack of enough material.

EXPERIMENTAL RESULTS

In this investigation there were three variables to consider: the temperature of the sulfide, the total pressure of the sulfur vapor in equilibrium with the sulfide, and the composition of the sulfide which was in equilibrium with the sulfur vapor. However, as a result of the method used to study the reaction $2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$, the independent experimental variables were sulfide temperature and sulfur temperature while the dependent variable was the sulfide composition. The temperature of the sulfide was controlled directly by the temperature of the sulfide furnace. The total pressure of the sulfur vapor in equilibrium with the sulfide was controlled by the temperature of the sulfur furnace. A definite composition of the sulfide then resulted in the single-phase regions by fixing the sulfur and sulfide temperatures, while in the two-phase regions a sulfide composition between the equilibrium end compositions resulted by fixing the sulfur and sulfide temperatures. The basic data then consisted of sulfide temperature, sulfur temperature, and sulfide composition. These data are given in Table 1.

TABLE 1. Equilibrium Sulfide Temperature, Sulfur Temperatures, and Sulfide Compositions Obtained for the Titanium-Sulfur System in the Disulfide-Trisulfide Region.

Experiment Number	Sulfide Temperature (°C)	Sulfur Temperature (°C)	Sulfide Composition (S/Ti)
22	525	27	1.90
33	525	302	1.92
64	525	323	1.93
53	525	328	2.10
23	525	332	2.39
52	525	336	2.57
32	525	341	2.58
24	525	364	2.60
39	525	398	2.65
68	525	425	2.66
40	525	428	2.66
61	525	460	2.85
15	540	25	1.86
42	540	326	1.91
35	540	357	1.93
51	540	362	2.01
44	540	364	2.07
50	540	366	2.22
59	540	370	2.58
34	540	373	2.61
30	540	381	2.62
43	540	409	2.64
67	540	425	2.65
41	540	433	2.66
60	540	460	2.82
10	550	25	1.85
29	550	342	1.91
19	550	377	1.90
56	550	385	1.93
49	550	387	2.17
17	550	389	2.49
48	550	390	2.27
57	550	394	2.60
28	550	402	2.60
18	550	415	2.60
66	550	425	2.63
27	550	439	2.65
58	550	460	2.78

Table 1. (Continued)

Experiment Number	Sulfide Temperature (°C)	Sulfur Temperature (°C)	Sulfide Composition (S/Ti)
20	565	27	1.85
38	565	364	1.90
21	565	400	1.91
26	565	415	1.91
47	565	417	1.96
36	565	419	2.09
45	565	420	2.08
65	565	420(Argon Tube)*	2.04
46	565	422	2.51
54	565	425	2.60
31	565	429	2.64
37	565	445	2.66
55	565	460	2.73
11	650	25	1.82
62	650	460	1.92
13	750	27	1.78
63	750	460	1.89

*Run made to show that no diffusion occurred into capsules during equilibration period.

The basic data from the X-ray analyses consisted of the sample compositions and the d values and relative intensities of the powder diffraction lines. These data are given in Table 2.

TABLE 2. X-ray Data for the Titanium-Sulfur System Between 525° and 565°C for Compositions from $TiS_{2.85}$ to $TiS_{1.93}$ and at 800°C for Compositions from $TiS_{1.78}$ to $TiS_{0.58}$.

Composition	d_{hkl} (A°)	Relative Intensity
$TiS_{2.85}$	1.096	w
	1.104	vw
	1.126	w
	1.153	vw
	1.222	m
	1.242	m
	1.299	vw
	1.339	vw
	1.362	m
	1.397	w
	1.450	w
	1.483	w
	1.56	m
	1.70	st
	1.75	vw
	1.83	m
	1.89	st
	1.99	st
	2.09	vw
	2.16	vw
	2.20	w
	2.28	st
	2.45	m
	2.67	vst
	2.89	vw
	3.22	vw
	4.10	vw
	4.30	vw
	8.76	st
$TiS_{2.60}$	1.098	w
	1.104	vw
	1.121	w
	1.153	vw
	1.222	m
	1.242	m
	1.296	vw
	1.337	vw
	1.362	m

Table 2.(Continued)

Composition	d_{hkl} (A°)	Relative Intensity
$TiS_{2.60}$ (contd)	1.400	w
	1.450	w
	1.483	w
	1.57	m
	1.70	st
	1.75	vw
	1.83	m
	1.89	st
	1.99	st
	2.09	vw
	2.16	vw
	2.20	w
	2.28	st
	2.45	m
	2.67	vst
	2.89	vw
	3.22	vw
	4.10	vw
	4.30	vw
	8.76	st
$TiS_{2.57}$	1.091	m
	1.119	vw
	1.160	vw
	1.216	vw
	1.237	vw
	1.306	vw
	1.356	m
	1.393	vw
	1.421	vw
	1.448	vw
	1.55	vw
	1.59	vw
	1.62	vw
	1.69	st
	1.74	vw
	1.82	vw
	1.89	w
	1.98	m
	2.04	m

Table 2. (Continued)

Composition	d_{hkl} (A°)	Relative Intensity
$TiS_{2.57}$(contd.)	2.20	w
	2.27	m
	2.44	w
	2.61	m
	2.67	vst
	2.88	w
	3.24	w
	5.68	w
	8.76	st
$TiS_{2.27}$	1.093	st
	1.165	w
	1.264	vw
	1.309	m
	1.364	w
	1.399	vw
	1.427	m
	1.450	vw
	1.59	m
	1.63	m
	1.70	st
	1.77	vw
	1.83	vw
	2.04	m
	2.28	w
	2.46	w
	2.62	vst
	2.68	m
	2.93	vw
	3.23	vw
	5.72	st
	8.78	st
$TiS_{1.96}$	1.091	st
	1.162	m
	1.264	w
	1.306	m
	1.425	m
	1.59	st
	1.63	m
	1.70	st

Table 2 (Continued)

Composition	d_{hkl} (A°)	Relative Intensity
$TiS_{1.96}$ (continued)	1.89	w
	2.05	vst
	2.28	vw
	2.47	vw
	2.61	vst
	2.69	vw
	2.94	vw
	3.23	vw
	5.68	st
	8.76	w
$TiS_{1.93}$	1.089	m
	1.160	w
	1.261	vw
	1.303	w
	1.421	m
	1.59	m
	1.62	w
	1.69	m
	1.89	vw
	2.03	st
	2.60	vst
	2.94	vw
	5.68	
$TiS_{1.78}$	1.089	m
	1.160	w
	1.260	vw
	1.302	w
	1.419	m
	1.59	m
	1.62	w
	1.69	m
	1.89	vw
	2.03	st
	2.59	vst
	2.94	vw
	5.68	m

Table 2. (Continued)

Composition	d_{hkl} (A°)	Relative Intensity
$TiS_{1.72}$	1.093	st
	1.164	w
	1.269	vw
	1.310	vw
	1.372	vw
	1.423	vw
	1.59	vw
	1.62	w
	1.67	vw
	1.70	vst
	1.80	vw
	1.89	vw
	1.98	vw
	2.04	vw
	2.25	vw
	2.31	m
	2.42	vw
	2.60	m
	2.78	vw
	2.97	vw
	5.68	m
$TiS_{1.54}$	1.098	m
	1.164	w
	1.272	w
	1.308	w
	1.375	vw
	1.425	m
	1.60	vw
	1.64	vw
	1.66	vw
	1.72	vst
	1.82	vw
	1.90	vw
	1.98	vw
	2.05	vw
	2.25	w
	2.35	m
	2.45	vw
	2.64	m
	2.85	vw
	2.96	vw
	5.72	m

Table 2 (Continued)

Composition	d_{hkl} (A°)	Relative Intensity
$TiS_{1.48}$	1.094	st
	1.268	vw
	1.310	vw
	1.376	vw
	1.387	vw
	1.423	m
	1.60	vw
	1.63	vw
	1.67	vw
	1.71	vst
	1.80	vw
	1.89	vw
	1.98	vw
	2.05	vw
	2.23	vw
	2.32	m
	2.42	w
	2.61	m
	2.85	vw
	2.96	vw
	5.68	m
$TiS_{1.44}$	1.098	vw
	1.175	vw
	1.250	vw
	1.275	vw
	1.315	vw
	1.374	vw
	1.385	vw
	1.428	vw
	1.439	vw
	1.60	vw
	1.65	vw
	1.67	vw
	1.72	vst
	1.81	vw
	1.89	vw
	1.98	vw
	2.06	w
	2.23	vw
	2.35	m
	2.42	w

Table 2. (Continued)

Composition	d_{hkl} (A°)	Relative Intensity
$TiS_{1.44}$ (contd.)	2.62	m
	2.78	vw
	2.98	vw
	5.68	m
$TiS_{1.40}$	1.100	m
	1.171	vw
	1.250	vw
	1.269	vw
	1.310	vw
	1.385	vw
	1.426	w
	1.439	vw
	1.60	w
	1.63	vw
	1.67	vw
	1.72	vst
	1.81	vw
	1.90	vw
	2.06	vw
	2.35	m
	2.42	w
	2.63	m
	2.78	vw
	2.97	vw
	5.68	m
$TiS_{1.33}$	1.100	m
	1.171	vw
	1.250	vw
	1.269	vw
	1.310	vw
	1.382	vw
	1.426	vw
	1.439	vw
	1.60	w
	1.63	vw
	1.71	vst
	1.81	vw

Table 2. (Contined)

Composition	d_{hkl} (A°)	Relative Intensity
$TiS_{1.33}$ (contd.)	1.90	vw
	2.06	vw
	2.34	m
	2.63	m
	2.97	vw
	5.68	m
$TiS_{1.19}$	1.094	m
	1.165	vw
	1.250	vw
	1.269	vw
	1.310	vw
	1.385	w
	1.427	w
	1.440	vw
	1.59	vw
	1.63	vw
	1.70	vst
	1.80	w
	1.90	vw
	2.05	vw
	2.32	m
	2.60	m
	2.99	vw
	5.68	m
$TiS_{1.09}$	1.094	m
	1.145	w
	1.173	vw
	1.253	vw
	1.270	vw
	1.300	vw
	1.389	vw
	1.425	vw
	1.440	vw
	1.59	w
	1.64	w
	1.71	vst
	1.80	vw

Table 2. (Continued)

Composition	d_{hkl} (A°)	Relative Intensity
$TiS_{1.09}$ (contd.)	1.90	vw
	1.99	vw
	2.05	vw
	2.11	st
	2.33	m
	2.61	w
	2.84	w
	5.68	w
$TiS_{1.05}$	1.094	m
	1.142	vw
	1.160	vw
	1.180	vw
	1.298	m
	1.386	vw
	1.430	vw
	1.48	vw
	1.58	s
	1.65	m
	1.70	m
	1.99	vw
	2.11	vst
	2.60	st
	2.83	m
$TiS_{0.66}$	1.094	m
	1.142	vw
	1.160	vw
	1.180	vw
	1.298	m
	1.389	w
	1.423	vw
	1.60	w
	1.64	m
	1.70	m
	1.99	vw
	2.11	vst
	2.58	st
	2.84	m

Table 2. (Continued)

Composition	d_{hkl} (A°)	Relative Intensity
$TiS_{0.58}$	1.095	m
	1.140	w
	1.229	w
	1.245	vw
	1.276	vw
	1.295	w
	1.333	w
	1.389	w
	1.427	vw
	1.47	m
	1.60	vw
	1.63	w
	1.70	m
	1.99	vw
	2.11	m
	2.23	vst
	2.34	vw
	2.55	w
	2.58	w
	2.84	w

CALCULATIONS and DISCUSSION

The basic reaction being studied in this investigation can be expressed as follows:

$$2\text{'}TiS_3\text{'}_{(s)} \rightleftharpoons 2\text{'}TiS_2\text{'}_{(s)} + S_{2(g)} \quad \text{where } K_{eq} = \frac{a^2_{\text{'}TiS_2\text{'}} \times P_{S_2}}{a^2_{\text{'}TiS_3\text{'}}}$$

The thermodynamic quantities to be calculated for this reaction are $\Delta H°$, $\Delta G°$, and $\Delta S°$. To calculate an equation for $\Delta G°$ as a function of temperature involves a series of calculations using the basic data of equilibrium sulfide temperature, equilibrium sulfur temperature, and equilibrium sulfide composition.

Calculations for the Disulfide-Trisulfide Region:

The static method of investigating a sulfide in equilibrium with sulfur vapor is generally superior to other methods since it involves only one gas and thus minimizes any gas segregation effects. Contained in the sulfur vapor, however, are several sulfur vapor species--S_8, S_6, S_4, S_2, and S in amounts varying with temperature and pressure. The equilibrium relationship between S_8, S_6, S_4, S, and S_2 must be considered if the reaction is to be expressed in terms of S_2 only.

The total sulfur pressure in the equilibrium capsule is fixed by the temperature of the liquid sulfur in the sulfur end of the capsule and is assumed to be constant over the entire length of the capsule. Using the data of West and Menzies (1929, p. 1880) shown in Appendix X for the total pressure of sulfur vapor above liquid sulfur, a graph of log P_T (total sulfur pressure) versus the reciprocal of the absolute temperature was made. From this graph the total sulfur pressure in the equilibrium capsule was determined from the equilibrium sulfur temperature. The data tabulated in Table 3 are the sulfur pressures corresponding to the sulfur temperatures in Table 1. The data in Table 3 are plotted in Figure 7.

The shapes of the curves in Figure 7 are dictated by Gibbs' Phase Rule:

$$F = C - P + 2 \tag{6}$$

In a two-component system involving two solid phases and one gas phase at constant temperature, the system is invariant since $F = 2 - 3 + 2 = 1$. Hence, a single sulfur pressure exists for all compositions in a two-phase region. In a single-solid-phase region, the system is univariant; hence, a unique sulfur pressure exists for each composition. Therefore on a graph of P_T versus composition, the isotherms will be parallel to the composition axis in a two-phase region and sloping in a single-phase region.

The two-phase data points in Figure 7 are tabulated in Table 4. The positions of the horizontal parts of the isotherms in Figure 7 were mathematically located by plotting log P_T versus the reciprocal of the absolute temperature using the data in Table 4. The "least squares" fit of these data is shown in Figure 8.

TABLE 3. Equilibrium Sulfide Temperatures, Total Sulfur Pressures, and Sulfide Compositions for the Titanium-Sulfur System in the Disulfide-Trisulfide Region.

Experiment Number	Sulfide Temperature (°C)	Sulfur Temperature (°C)	P_T (mm Hg)	Sulfide Composition $(\frac{S}{Ti})$
22	525	27	<1	1.90
33	525	302	50	1.92
64	525	323	86	1.93
53	525	328	95	2.10
23	525	332	104	2.39
52	525	336	110	2.57
32	525	341	127	2.58
24	525	364	198	2.60
39	525	398	367	2.65
68	525	425	560	2.66
40	525	428	595	2.66
61	525	460	946	2.85
15	540	25	<1	1.86
42	540	326	89	1.91
35	540	357	173	1.93
51	540	362	190	2.01
44	540	364	198	2.07
50	540	366	205	2.22
59	540	370	222	2.58
34	540	373	237	2.61
30	540	381	270	2.62
43	540	409	440	2.64
67	540	425	560	2.65
41	540	433	640	2.66
60	540	460	946	2.82
10	550	25	<1	1.85
29	550	342	130	1.91
19	550	377	255	1.90
56	550	385	292	1.93
49	550	387	300	2.17
17	550	389	315	2.49
48	550	390	320	2.27
57	550	394	340	2.60
28	550	402	390	2.60
18	550	415	480	2.63
66	550	425	560	2.63
27	550	439	700	2.65
58	550	460	946	2.78

Table 3. (Continued)

Experiment Number	Sulfide Temperature (°C)	Sulfur Temperature (°C)	P_T (mm Hg)	Sulfide Composition $(\frac{S}{Ti})$
20	565	27	< 1	1.85
38	565	364	198	1.90
21	565	400	380	1.91
26	565	415	490	1.91
47	565	417	510	1.96
36	565	419	520	2.09
45	565	420	530	2.08
65	565	420 (argon tube)*	530	2.04
46	565	422	545	2.51
54	565	425	560	2.60
31	565	429	605	2.64
37	565	445	765	2.66
55	565	460	946	2.73
11	650	25	< 1	1.82
62	650	460	946	1.92
13	750	27	< 1	1.78
63	750	460	946	1.89

*Run made to show that no diffusion occurred into capsules during equilibration period.

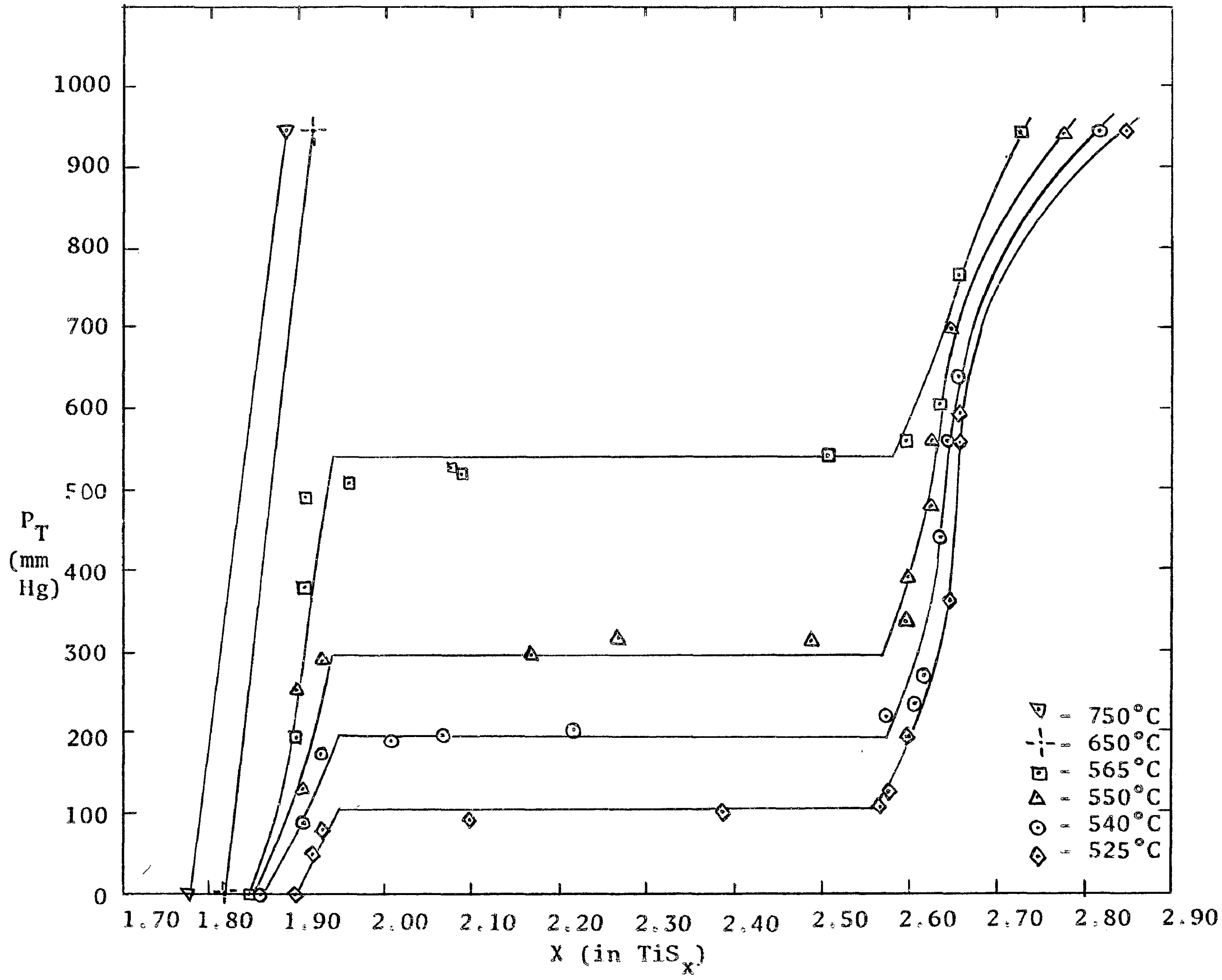


Figure 7. Equilibrium Total Sulfur Pressures for the Titanium-Sulfur System in the Region from $TiS_{1.78}$ to $TiS_{2.90}$

TABLE 4. Equilibrium P_T for the Reaction $2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$.

Sulfide Temperature (°K)	P_T (mm Hg)	P_T (atm)	P_T (mm Hg) From Equation 7	P_T (atm) From Equation 7
798	95	0.125		
	104	0.137	104	0.137
	110	0.145		
813	190	0.250		
	198	0.261	197	0.259
	205	0.270		
823	300	0.395		
	315	0.414	297	0.391
	320	0.421		
838	510	0.671		
	520	0.684	541	0.713
	530	0.697		
	545	0.717		

The equation of this straight line is:

$$\log P_T \text{ (atm)} = -\frac{11993}{T} + 14.165 \qquad (7)$$

The standard deviation of the data is 8.47mm but a rigorous statistical analysis of the data to determine the variation of this line is not meaningful due to the small number of data points. Thus no confidence limits for the equations derived in the remainder of this discussion are given.

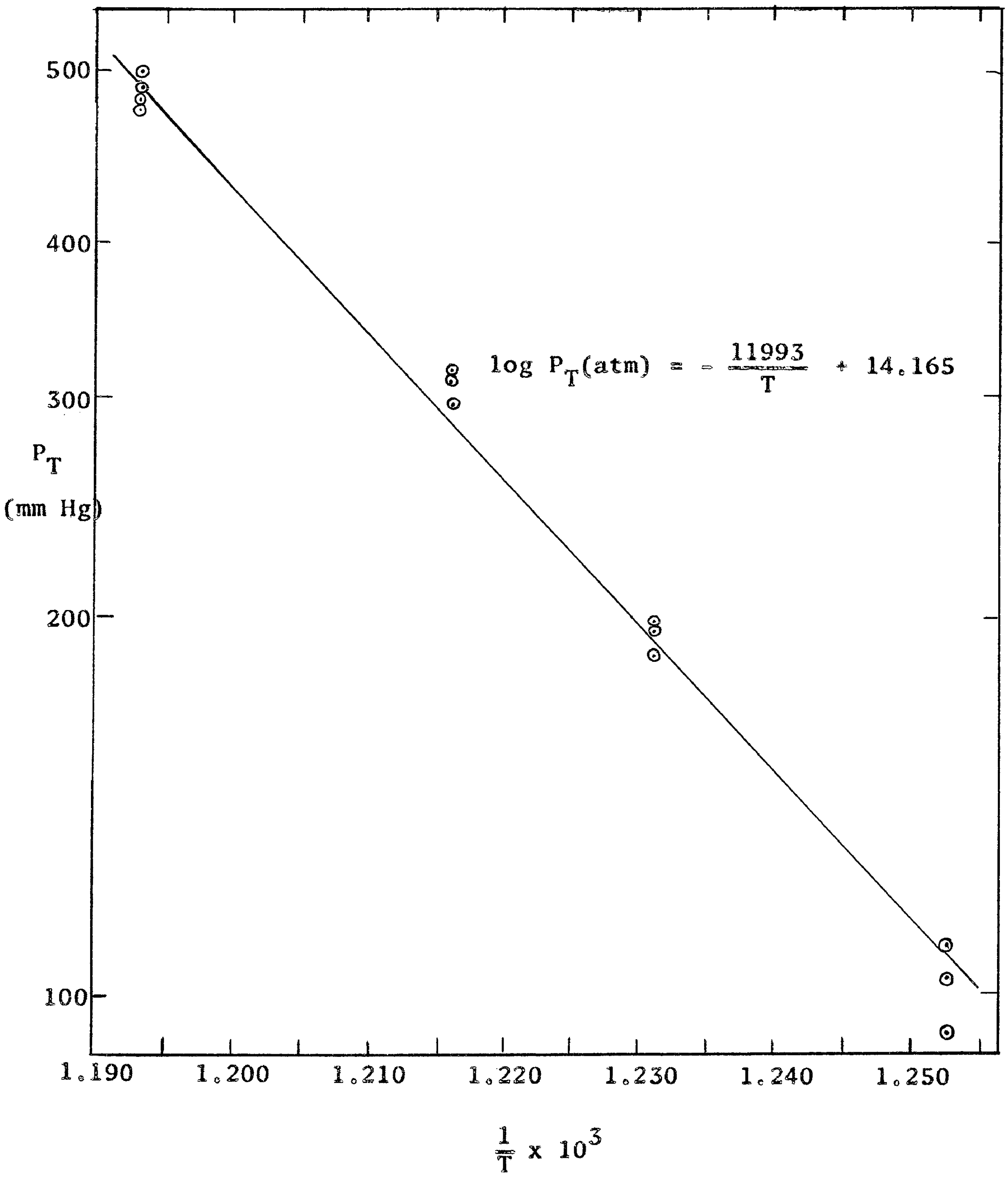


Figure 8. Log P_T versus $\frac{1}{T} \times 10^3$ for the Mathematical Determination of the Equilibrium P_T.

Since the equilibrium total pressures have been determined, the equilibrium P_{S_2} can be found by considering the polyatomic sulfur equilibria. Kubaschewski and Evans (1958, p. 342) and Freeman (1962, p. 24) give the following data for the polyatomic sulfur equilibria:

$$2S_2 \rightleftharpoons S_4 \qquad K_1 = \frac{P_{S_4}}{P_{S_2}^2}$$

$$\Delta G° = -28,400 + 31.88\ T = -RT\ \ell n\ K_1 \tag{8}$$

$$3S_2 \rightleftharpoons S_6 \qquad K_2 = \frac{P_{S_6}}{P_{S_2}^3}$$

$$\Delta G° = -63,720 + 69.3\ T = -RT\ \ell n\ K_2 \tag{9}$$

$$4S_2 \rightleftharpoons S_8 \qquad K_3 = \frac{P_{S_8}}{P_{S_2}^4}$$

$$\Delta G° = -92,160 + 101.2T = -RT\ \ell n\ K_3 \tag{10}$$

$$S_2 \rightleftharpoons 2S \qquad K_4 = \frac{P_S^2}{P_{S_2}}$$

$$K_4 \text{ at } 798°K = 3 \times 10^{-22}, \quad K_4 \text{ at } 838°K = 7 \times 10^{-21} \tag{11}$$

Since the total pressure is the sum of the pressures of the individual species, the following equation is applicable:

$$P_T = P_S + P_{S_2} + P_{S_4} + P_{S_6} + P_{S_8} \tag{12}$$

As can be seen from equations (8)-(11), the pressures of the various sulfur species are temperature dependent. Even though the total sulfur pressure and the pressures of the various sulfur species in the sulfur end of the reaction capsule are fixed by the temperature of the sulfur in that end of the capsule, the pressure of the sulfur species is variable in the hotter sulfide end of the capsule. In the sulfide end, the S_8, S_6 and S_4 decompose giving more S_2 and thus a higher P_{S_2}. By solving equations (8) - (12) simultaneously where T is the absolute temperature of the sulfide end of the capsule, an equation giving P_T as a function of P_{S_2} is obtained for a given sulfur and sulfide temperature. This equation has the form:

$$P_T = P_{S_2} + K_1 P_{S_2}^2 + K_2 P_{S_2}^3 + K_3 P_{S_2}^4 + K_4^{1/2} \; P_{S_2}^{1/2} \qquad (13)$$

where K_1, K_2, K_3 and K_4 are the equilibrium constants for the polyatomic sulfur equilibria at the sulfide temperature. For the sulfide temperatures used in the work, the pressure of the monatomic species is negligible as shown in Equation (11), so by dropping the last term in Equation (13), the final equation is:

$$P_T = P_{S_2} + K_1 P_{S_2}^2 + K_2 P_{S_2}^3 + K_3 P_{S_2}^4 \qquad (14)$$

By solving Equation (14) using the equilibrium P_T in the reaction capsule as fixed by the temperature of the sulfur end, the pressure of the diatomic sulfur vapor in equilibrium with the sulfide can be determined (See Appendix XI for a sample calculation). Table 5 gives the equilibrium P_T and the equilibrium P_{S_2} for the reaction:

$$2\text{'}TiS_3\text{'} \rightleftharpoons 2\text{'}TiS_2\text{'} + S_2.$$

TABLE 5. Equilibrium P_T and P_{S_2} for the Reaction $2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$.

Sulfide Temperature (°K)	P_T (atm)	P_{S_2} (atm)
798	0.137	0.060
813	0.259	0.095
823	0.391	0.130
838	0.713	0.204

The Clausius-Clapeyron equation is the most convenient relationship to use in beginning the evaluation of the thermodynamic quantities $\Delta H°$, $\Delta G°$, and $\Delta S°$ for the reaction being studied. The most useful form of the equation for thermodynamic calculations is as follows:

$$\frac{d(\log K_p)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H°}{2.303R} \tag{15}$$

The equilibrium constant for the reaction $2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$ is as follows:

$$K_{eq} = \frac{a^2{'TiS_2'} \times P_{S_2}}{a^2{'TiS_3'}} \tag{16}$$

It can be assumed that the activities of both $'TiS_3'$ and $'TiS_2'$ are unity at all temperatures since the sulfides are involved in the reaction as pure solids with no appreciable composition change with temperature. Therefore the equilibrium constant for the reaction becomes:

$$K_{eq} = K_p = P_{S_2} \tag{17}$$

From equation (15) then, the slope of a plot of log P_{S_2} versus the reciprocal of the absolute temperature is $-\frac{\Delta H^\circ}{2.303R}$. From this slope, ΔH° for the reaction can be readily calculated. The data in Table 6 are presented in a form suitable for making a log P_{S_2} versus the reciprocal of the absolute temperature plot. This plot is shown in Figure 9 for the reaction $2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$.

TABLE 6. Equilibrium log P_{S_2} and $\frac{1}{T} \times 10^3$ for the Reaction
$2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$

Sulfide Temperature (°K)	$\frac{1}{T} \times 10^3$ $(\frac{1}{°K} \times 10^3)$	P_{S_2} (atm)	log P_{S_2}
798	1.253	0.060	-1.222
813	1.230	0.095	-1.022
823	1.215	0.130	-0.886
838	1.193	0.204	-0.696

From the slope of the straight line plot in Figure 9, ΔH° is found to be 40,200 cal mole^{-1}.

The standard Gibbs free energy change, ΔG°, for the reaction was evaluated from the following equation:

$$\Delta G^\circ = -2.303 \, RT \log K_{eq} \tag{18}$$

Since $K_{eq} = K_p = P_{S_2}$, equation (18) becomes:

$$\Delta G^\circ = -2.303 \, RT \log P_{S_2} \tag{19}$$

The values of ΔG° for the reaction $2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$ at the experimental sulfide temperatures are tabulated in Table 7.

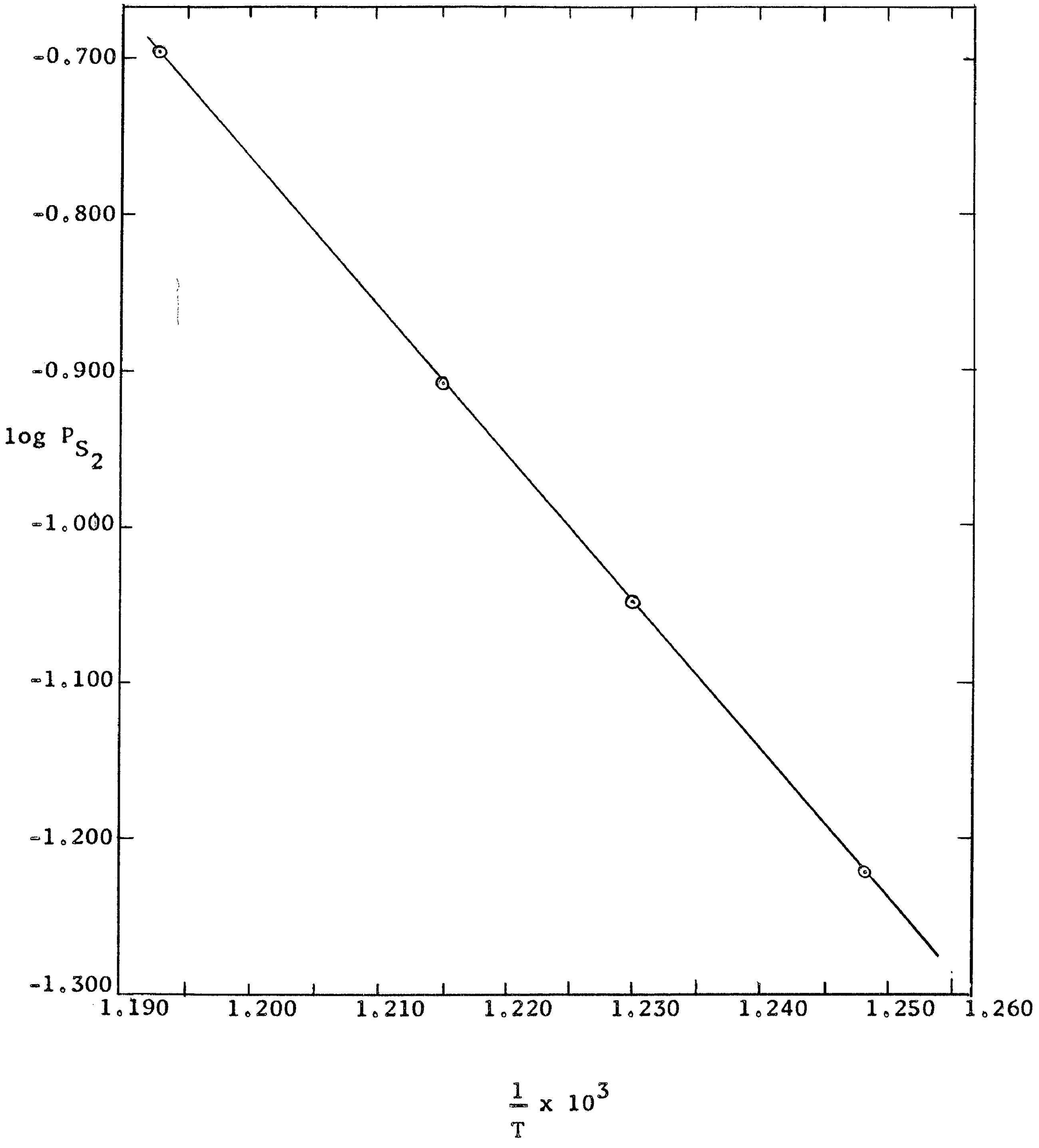


Figure 9. Log P_{S_2} versus $\frac{1}{T} \times 10^3$ for Reaction $2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$.

TABLE 7. ΔG° for the Reaction $2\text{'TiS}_3\text{'} \rightleftharpoons 2\text{'TiS}_2\text{'} + S_2$ for the Experimental Sulfide Temperatures.

Sulfide Temperature (°K)	$\log P_{S_2}$	ΔG° (cal mole^{-1})
798	-1.222	4460
813	-1.022	3800
823	-0.886	3340
838	-0.696	2670

To find ΔS° for the reaction $2\text{'TiS}_3\text{'} \rightleftharpoons 2\text{'TiS}_2\text{'} + S_2$, the following free energy equation was used:

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \qquad (20)$$

It can be seen that the slope of a graph of ΔG° versus absolute temperature is $-\Delta S^\circ$ for the reaction if $C_p = 0$ for the reaction; i.e., $\Delta H^\circ \neq f(T)$ and $\Delta S^\circ \neq f(T)$.

From the slope of the graph in Figure 10, ΔS° is found to be 44.8 cal deg^{-1} mole^{-1}.

The equation for ΔG° as a linear function of temperature is as follows:

$$\Delta G^\circ = 40200 - 44.8T \qquad (21)$$

Table 8 summarizes all the data used in the preceding calculations. No calculations were involved in determining the d values for the diffraction lines present on the x-ray powder patterns. The distances to the lines on the patterns were measured and converted directly to d values using standard tables based on Cu K_α radiation and a 10-cm camera diameter.

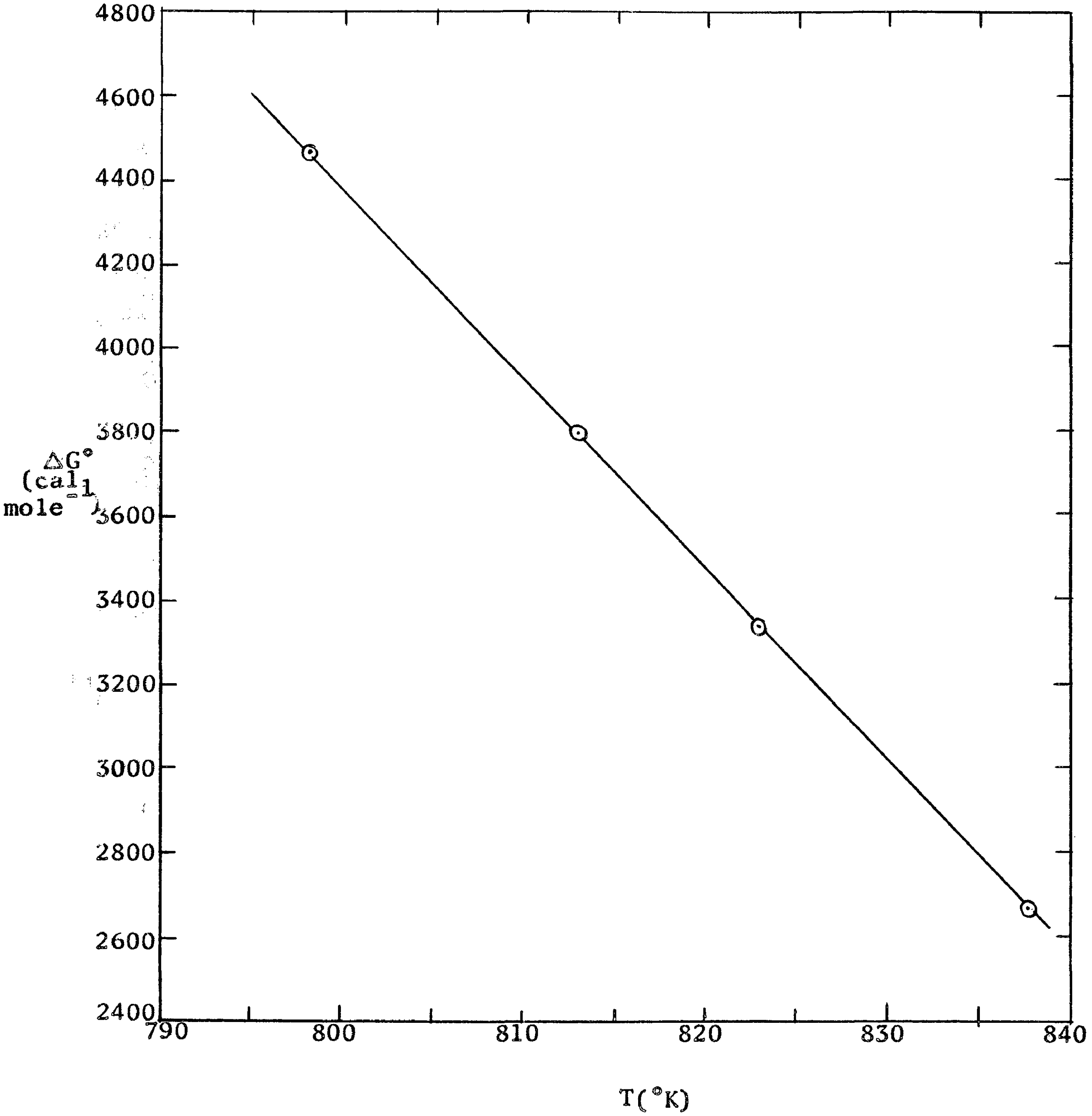


Figure 10. ΔG° versus T for Reaction $2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$.

TABLE 8. Equilibrium Data for the Reaction 2'TiS_3' $\rightleftharpoons$ 2 'TiS_2' + S_2.

Sulfide Temperature (°K)	Sulfur Temperature (°K)	P_T (mm)	P_T (atm)	$P_{T(average)}$ (atm)	P_{S_2} (atm)	$\frac{1}{T} \times 10^{-3}$ $(\frac{1}{°K} \times 10^{-3})$	log P_{S_2}	ΔG° (cal $mole^{-1}$)
798	328	95	0.125					
	332	104	0.137	0.137	0.060	1.253	-1.222	4460
	336	110	0.145					
813	362	190	0.250					
	364	198	0.261	0.259	0.095	1.230	-1.022	3800
	366	205	0.270					
823	387	300	0.395					
	389	315	0.414	0.391	0.130	1.215	-0.886	3440
	390	320	0.421					
838	417	510	0.671					
	419	520	0.684	0.713	0.204	1.193	-0.696	2670
	420	530	0.697					
	422	545	0.717					

Discussion of Results in the Region 'TiS_2' to 'TiS_3':

The two primary purposes of this investigation were to determine the thermodynamic properties of the titanium-sulfur system in the disulfide-trisulfide region and to determine the composition of the phases which are present at equilibrium. These two objectives were fulfilled, and the following paragraphs are devoted to discussion of the results obtained.

This study of the titanium-sulfur system was limited to the sulfide temperature range from 525°C to 565°C with the exception of two experiments at 650°C and 750°C. This temperature range was chosen because the total pressure of the sulfur in equilibrium with the phases present in this temperature range was easily controlled and did not exceed the capability of the capsules to resist exploding. Above sulfide temperatures of 565°C, the equilibrium total sulfur pressures approach 1000mm Hg and below sulfide temperatures of 525°C, the sulfur pressures fall below 90mm Hg. Also in this temperature range, there is no diffusion of atmospheric gases into the capsule as shown by an experimental run at 565°C using an argon-filled protection tube around the equilibrium capsule. The analysis of this sample was the same as the analysis for a sample run under the same conditions without the protection tube.

The equilibrium trisulfide composition which was found in the two-phase mixtures was $TiS_{2.58 \pm 0.01}$ for all temperatures investigated. This composition was determined from X-ray patterns: $TiS_{2.57}$ was a two-phase mixture and $TiS_{2.58}$ was single-phase. Also, extrapolation of the isotherms in the single-phase regions to the isotherms in the two-phase regions showed that the end compositions did not vary significantly with temperature.

The composition $TiS_{2.58}$ is the lower limit of a wide region of trisulfide solid solution which, according to this study, extends at least to $TiS_{2.85}$. The composition $TiS_{3.00}$ was never obtained due to the very high sulfur pressure involved. Room-temperature X-ray powder patterns of quenched samples were identical for compositions between $TiS_{2.58}$ and $TiS_{2.85}$, and the d values obtained from these patterns were in good agreement with the d values found by Haraldsen and co-workers (1963, p. 1290) for a composition TiS_3 with the monoclinic lattice parameters a = 4.793A°, b = 3.433A°, c = 8.714A°, and $\beta = 97.74°$ (See Appendix XII for comparison). A reciprocal lattice construction using the previously mentioned parameters was attempted but was found to be too complex to be of practical value. See Figure 11 for graphical comparison of d values from $TiS_{2.85}$ to $TiS_{1.78}$.

From the d values then, the conclusion can be reached that the lattice parameters change very little as the $\frac{S}{Ti}$ ratio changes in the trisulfide region. Precise lattice parameter determinations with varying composition would have to be made to show this conclusively, however.

Biltz and co-workers (1937, p. 102) did not explicity give a lower composition limit of the trisulfide region, but their P_T versus composition curves did begin to slope upward beyond $TiS_{2.85}$, indicating the beginning of a single phase region.

As the total sulfur pressure increases in the trisulfide region, the isotherms tend to spread apart, the lower temperature isotherms going to higher $\frac{S}{Ti}$ ratios. If TiS_3 were to be made, it should be done in an evacuated capsule at a sulfide temperature lower than 525°C and at a total sulfur pressure above 1000 mm Hg.

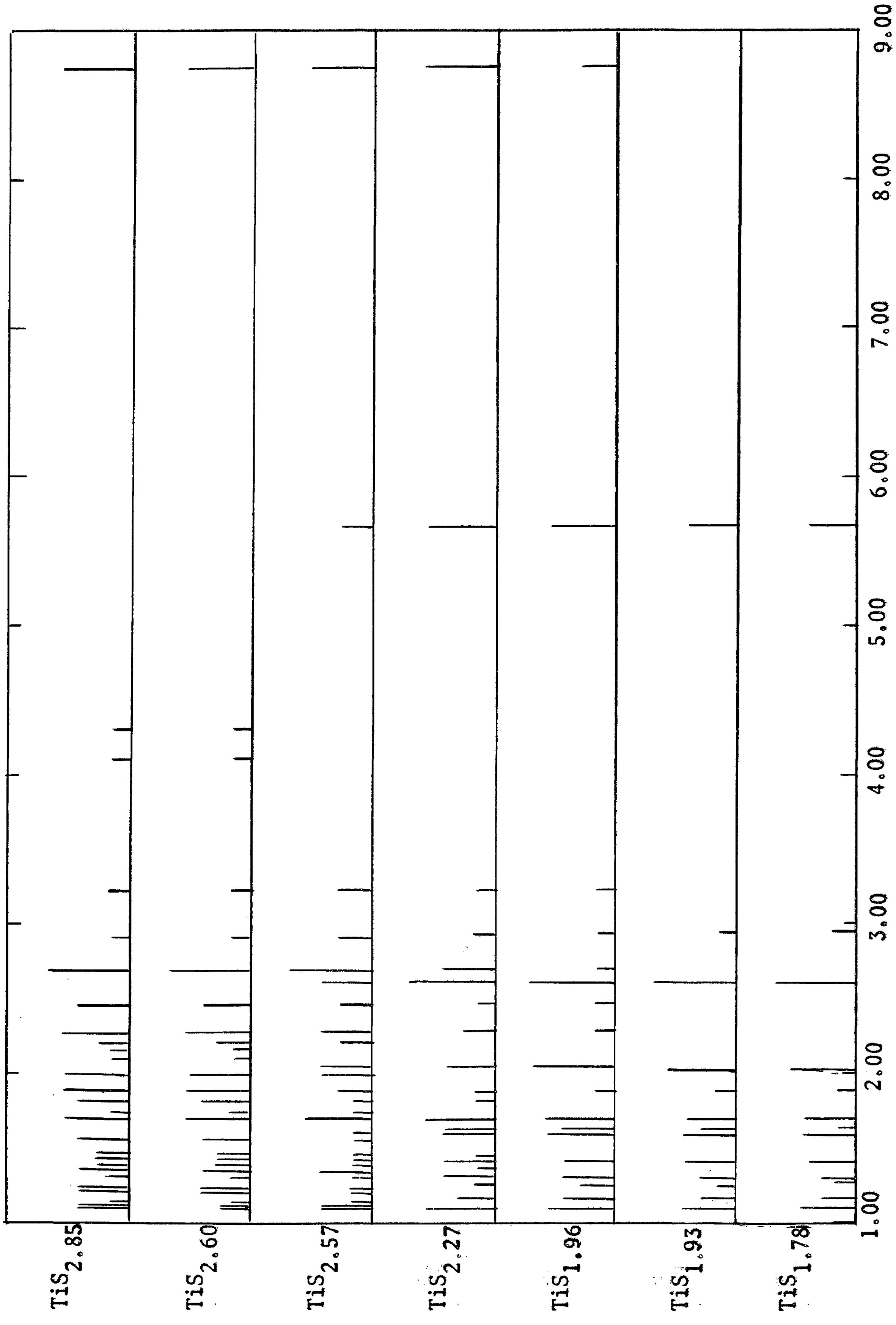


Figure 11. X-ray Data for TiS$_x$ from TiS$_{2.85}$ to TiS$_{1.78}$.

The trisulfide phase showed a very slight amount of vaporization over a 36-hr. period. This vaporization occurred more noticeably at lower temperatures. The vapor pressure of the trisulfide, however, was assumed to be small and thus made no significant contribution to the total pressure in the equilibrium capsule. An X-ray pattern of the volatile substance was identical to that of the residue and the starting material, thus showing that no decomposition occurred during vaporization.

In the disulfide region, the maximum equilibrium composition was determined to be $TiS_{1.94\pm0.01}$ by the same method employed in the trisulfide region. In the X-ray patterns, however, $TiS_{1.93}$ was single-phase and $TiS_{1.96}$ was a two-phase mixture. The limiting composition again did not vary significantly with temperature.

The composition $TiS_{1.94}$ is the upper limit of a region of disulfide solid solution which, according to this investigation, extends at least down to a composition of $TiS_{1.77}$. Abendroth and Schlechten (1959, p. 148) state that this solid solution region extends down to $TiS_{1.30}$. Some X-ray work was done in this investigation in the region below $TiS_{1.77}$, but the results will be discussed in a later section. Abendroth's and Schlechten's work (1959, p. 145-151) is at this point, however, verified down to $TiS_{1.77}$. Room-temperature X-ray powder patterns were identical for compositions between $TiS_{1.93}$ and $TiS_{1.77}$, and the d values from these patterns showed very good agreement with those d values found by Abendroth (1957, p. 69-70). A reciprocal lattice construction using the hexagonal lattice parameters a = 3.408A° and c = 5.702A° given by Jeanin and Benard (1959, p. 2876) for $TiS_{1.92}$ produced a theoretical powder pattern also in very good agreement with the experimental pattern (See Appendix XII for d value comparisons and Appendix XIII for the reciprocal lattice construction).

That the d values obtained from the powder patterns of compositions between $TiS_{1.93}$ and $TiS_{1.77}$ did not change measurably would indicate that the lattice parameters do not change appreciably with changing $\frac{S}{Ti}$ ratios. Jeanin and Benard (1959, p. 2875-2877), however, made very accurate lattice parameter measurements in the region between $TiS_{1.92}$ and $TiS_{1.81}$ and found that the a and c values did increase slightly with decreasing $\frac{S}{Ti}$ ratios. This, they postulated, was evidence that the nonstoichiometry of the disulfide phase is a result of interstitial titanium atoms. This same lattice parameter variation probably occurs similarly in the trisulfide region, but as stated previously, a precise lattice parameter study would be necessary to show this variation.

Jeanin and Benard (1959, p. 2876) also stated that the lower limit of the disulfide phase was $TiS_{1.81}$. Below this composition, they said, new lines appeared in the X-ray patterns possibly indicating the formation of a new phase or the change of the disulfide lattice into a closely related structure. The X-ray patterns of $TiS_{1.78}$ obtained by both Abendroth (1957, p. 69-70) and this investigator did not show the appearance of these new lines. This indicates that the phase limit is at least below $TiS_{1.78}$.

Biltz and co-workers (1937, p. 102) found the maximum limit of the composition in the disulfide region to be $TiS_{2.00}$ in the temperature range from 500°C to 551°C. The composition $TiS_{2.01}$ was obtained in this investigation in one of the experimental runs and was found to definitely be a two-phase mixture. That $TiS_{2.00}$ is not an equilibrium single-phase composition at higher temperatures is verified by the fact that Jeanin and Benard (1959, p. 2875) were not able to produce this composition in any of their experiments at 1000°C. The highest composition that they were able to obtain was $TiS_{1.92}$. In this work the composition that was the highest in sulfur content and still single-phase was $TiS_{1.93}$. Since $TiS_{1.96}$ was a two-phase mixture, the equilibrium single-phase composition is $TiS_{1.94}$ or $TiS_{1.95}$. This shows that the end composition does change slightly over wide temperature ranges. If single-phase $TiS_{2.00}$ were to be attempted, a sulfide temperature lower than 525°C would have to be used.

For compositions between and including $TiS_{1.96}$ and $TiS_{2.57}$, room temperature X-ray patterns of quenched samples showed a two-phase mixture (See Appendix XIV), the two phases present being $TiS_{1.94 \pm 0.01}$ and $TiS_{2.58 \pm 0.01}$.

Biltz and co-workers (1937, p. 102-105) found the compositions in equilibrium in the disulfide and trisulfide regions to be consistently higher in sulfur composition than the compositions found in this investigation. Biltz's data (1937, p. 103-104) may have shown higher sulfur composition due to his method and apparatus. He employed the Bodenstein condensed sulfur valve technique which consisted of removal of sulfur fractions from his equilibrium system. Any sulfur in the gas phase when he condensed the sulfur valve would have given him a valve lower in weight than the actual weight of sulfur removed from his sample and thus given him a higher apparent sulfur analysis for his remaining sample. Biltz also may not have allowed enough time for equilibrium to be attained.

Since he was studying the decomposition reaction, too short a time allowed for equilibrium would lead to results too high in sulfur composition.

The value of $\Delta H°$ for the reaction $2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$ was found to be 40200 cal mole^{-1} in this investigation. The $\Delta H°$ for the same reaction as determined by Biltz and co-workers (1937, p. 105) and corrected by Haraldsen and co-workers (1963, p. 1288-1289) was found to be 36600 cal mole^{-1}. The $\Delta S°$ for the same reaction was found to be 44.8 cal mole^{-1} °K^{-1} in this investigation. Biltz and co-workers (1937, p. 97-116) did not give a value of $\Delta S°$; but when his data are calculated and plotted suitably, the value obtained is 42.7 cal mole^{-1}°K^{-1}. Thus the values of $\Delta H°$ and $\Delta S°$ found in this investigation are more positive than the values found by Biltz. The reason for this difference in the values of $\Delta H°$ and $\Delta S°$ lies in the fact that Biltz's total sulfur pressure data are from 78 to 113% higher than the data of present study and his diatomic sulfur pressure data are correspondingly 75% to 82% higher (Biltz and co-workers, 1937, p. 105). Shown in Tables 9 and 10 and Figure 12 are the comparisons between the two sets of data.

The equation for $\Delta G°$ as a function of temperature from Biltz's corrected data is $\Delta G° = 36{,}600 - 42.7T$. It is felt that from the results of this investigation a more accurate and reliable equation, $\Delta G° = 40{,}200 - 44.8T$, can be given.

Discussion of Results for Compositions in the Region $'TiS_{0.5}'$ to $'TiS_2'$:

The extent of the region of the solid solution in the disulfide region and the phases present in the region around TiS are still open to

TABLE 9. Comparison of Biltz's Data and Present Investigation Data for Equilibrium Sulfide Temperature, Total Sulfur Pressures, and Sulfide Compositions

PRESENT STUDY			BILTZ		
Sulfide Temperature (°C)	P_T (mm Hg)	Sulfide Composition ($\frac{S}{Ti}$)	Sulfide Temperature (°C)	P_T (mmHg)	Sulfide Composition ($\frac{S}{Ti}$)
525	946	2.85	525	267	2.87
	595	2.66		232	2.77
	560	2.66		225	2.65
	367	2.65		226	2.60
	198	2.60		220	2.53
	127	2.58		225	2.46
	110	2.57		224	2.38
	104	2.39		222	2.27
	95	2.10		218	2.21
	86	1.93		221	2.13
	50	1.92		217	2.05
	< 1	1.90		181	1.95
				0	1.93
550	946	2.78	551	550	2.92
	700	2.65		536	2.88
	560	2.63		536	2.85
	480	2.63		529	2.57
	390	2.60		528	2.32
	340	2.60		531	2.30
	320	2.27		529	2.25
	315	2.49		526	2.20
	300	2.17		528	2.18
	292	1.93		526	2.10
	255	1.90		515	2.05
	130	1.91		489	2.02
	1	1.85		413	1.99
				1	1.98

TABLE 10. Comparison of Thermodynamic Data of Biltz and Present Investigation for the Reaction 2'TiS_3' ⇌ 2'TiS_2' + S_2.

PRESENT STUDY					BILTZ				
Sulfide Temperature (°K)	P_T (atm)	P_{S_2} (atm)	log P_{S_2}	ΔG° (cal/mole^{-1})	Sulfide Temperature (°K)	P_T (atm)	P_{S_2} (atm)	log P_{S_2}	ΔG° (cal/mole^{-1})
838	0.713	0.204	-0.696	2760	824	0.695	0.228	-0.647	2420
823	0.391	0.130	-0.886	3340	811	0.458	0.161	-0.793	2940
813	0.259	0.095	-1.022	3800	798	0.294	0.109	-0.963	3520
798	0.137	0.060	-1.222	4460	773	0.120	0.050	-1.301	4600

question. Abendroth and Schlechten (1959, p. 148) claim that this solid solution region extends from $TiS_{1.92}$ to $TiS_{1.30}$ in the temperature range from 800°C to 1100°C with a two-phase region extending from $TiS_{1.30}$ to $TiS_{0.80}$. Jeanin and Benard (1959, p. 2876) postulate the limit of the disulfide to be $TiS_{1.81}$ with either a new phase forming or a structure modification occurring below this composition. Hahn (1958, p. 275) gives compositions of $TiS_{3.00}$, $TiS_{2.00}$, $TiS_{1.33}$, $TiS_{1.00}$, and $TiS_{0.66}$ as single phases with the appropriate two-phase regions between these end phases.

X-ray phase determinations were made in this investigation at 800°C to help clarify these questions. The samples for the X-ray determinations were prepared by mixing various compositions in the proper proportions to obtain the desired compositions. These finely ground samples were placed in evacuated capsules and heated at 800°C for 36 hr. After equilibration, the samples were gravimetrically analyzed by oxidation in air to TiO_2 and

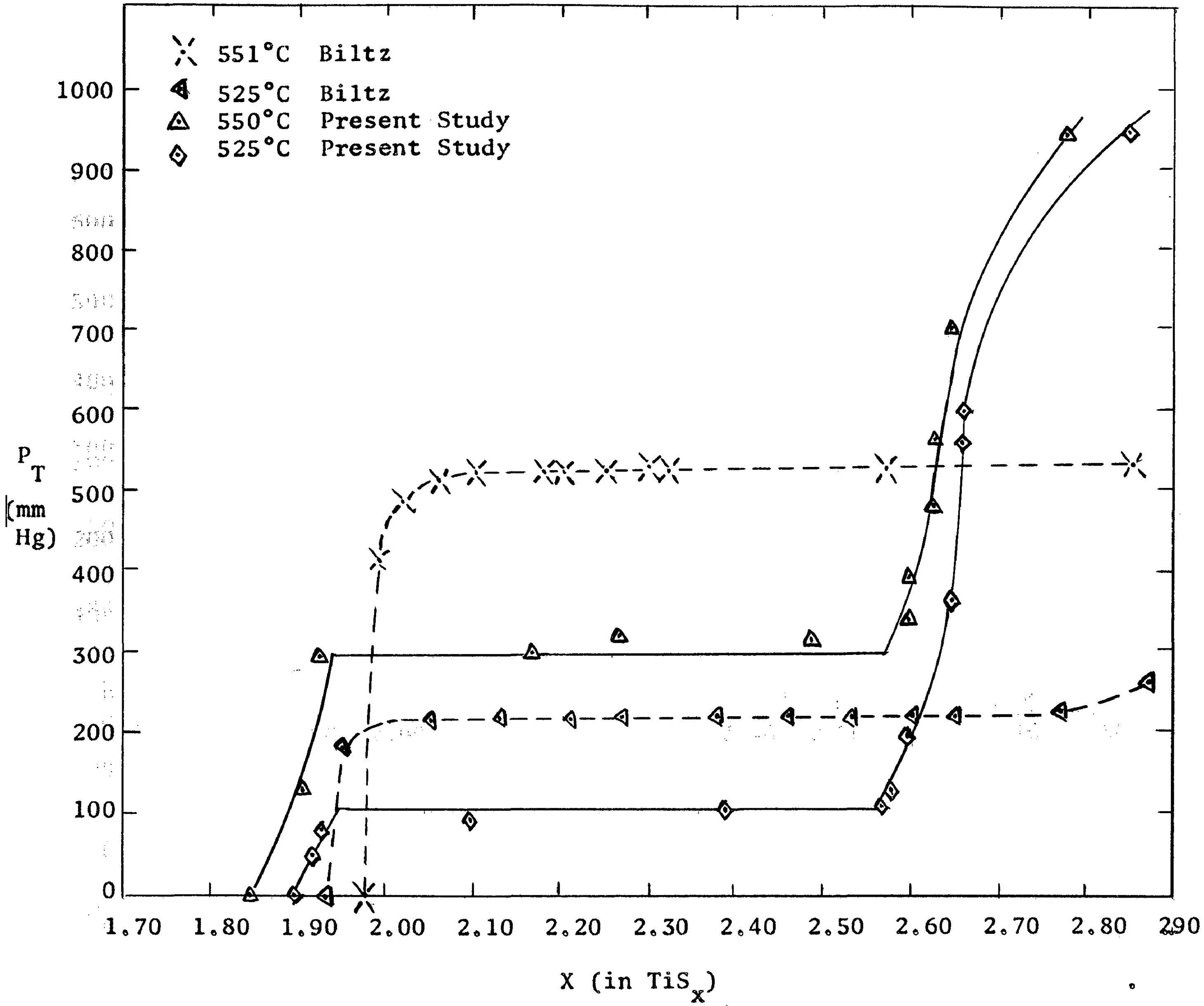


Figure 12. Equilibrium Total Sulfur Pressures for the Titanium-Sulfur System in the Region from $TiS_{1.78}$ to $TiS_{2.90}$ Comparing the Data of the Present Study and the Data of Biltz.

placed in thin-walled capillaries for X-ray analysis.

The results of these x-ray studies were as follows: A single-phase region showing the disulfide phase from $TiS_{1.94\pm0.01}$ to $TiS_{1.74\pm0.02}$, a two-phase region showing the disulfide phase and 'Ti_2S_3' phase from $TiS_{1.74\pm0.02}$ to $TiS_{1.52\pm0.02}$, a single-phase region ('Ti_2S_3') from $TiS_{1.52\pm0.02}$ to $TiS_{1.48\pm0.02}$, a two-phase region showing 'Ti_2S_3' and 'Ti_3S_4' phases from $TiS_{1.48\pm0.02}$ to $TiS_{1.37\pm0.03}$, a single-phase region ('Ti_3S_4') from $TiS_{1.37\pm0.03}$ to $TiS_{1.17\pm0.02}$, a two-phase region showing 'Ti_3S_4' and low temperature 'TiS' phases from $TiS_{1.17\pm0.02}$ to $TiS_{1.07\pm0.02}$, a single-phase region ('TiS') from $TiS_{1.07\pm0.02}$ to $TiS_{0.68\pm0.02}$, and a two-phase region from $TiS_{0.68\pm0.02}$ to $TiS_{0.30}$, which, according to Hahn and Ness (1957, p. 581), is the limit of solubility of sulfur in metallic titanium. These results are shown graphically in Figure 13. Each of the single-phase regions with the exception of the 'Ti_2S_3' region showed a rather wide range of solid solubility. The two-phase regions varied

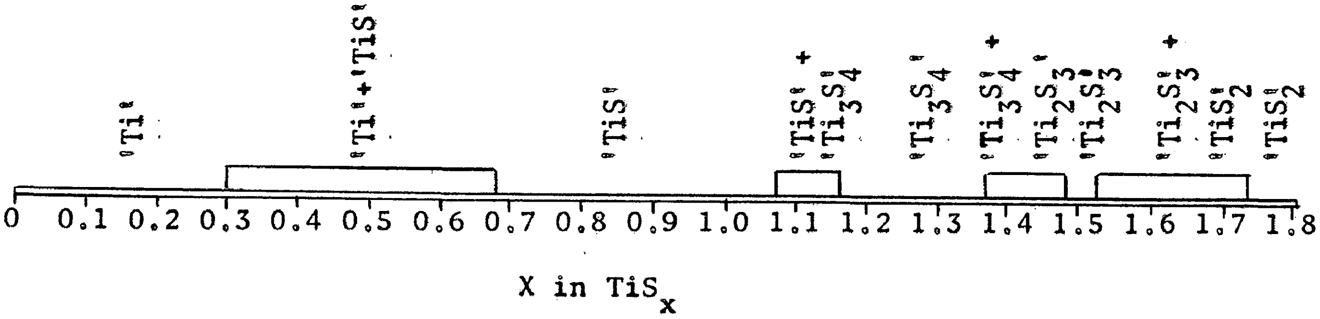


Figure 13. Phases Present in the Titanium-Sulfur System Below $TiS_{1.85}$ at 800°C.

in extent (See Appendix XII for comparisons of the single-phase d values with published data and Appendix IV for the determinations of the sources

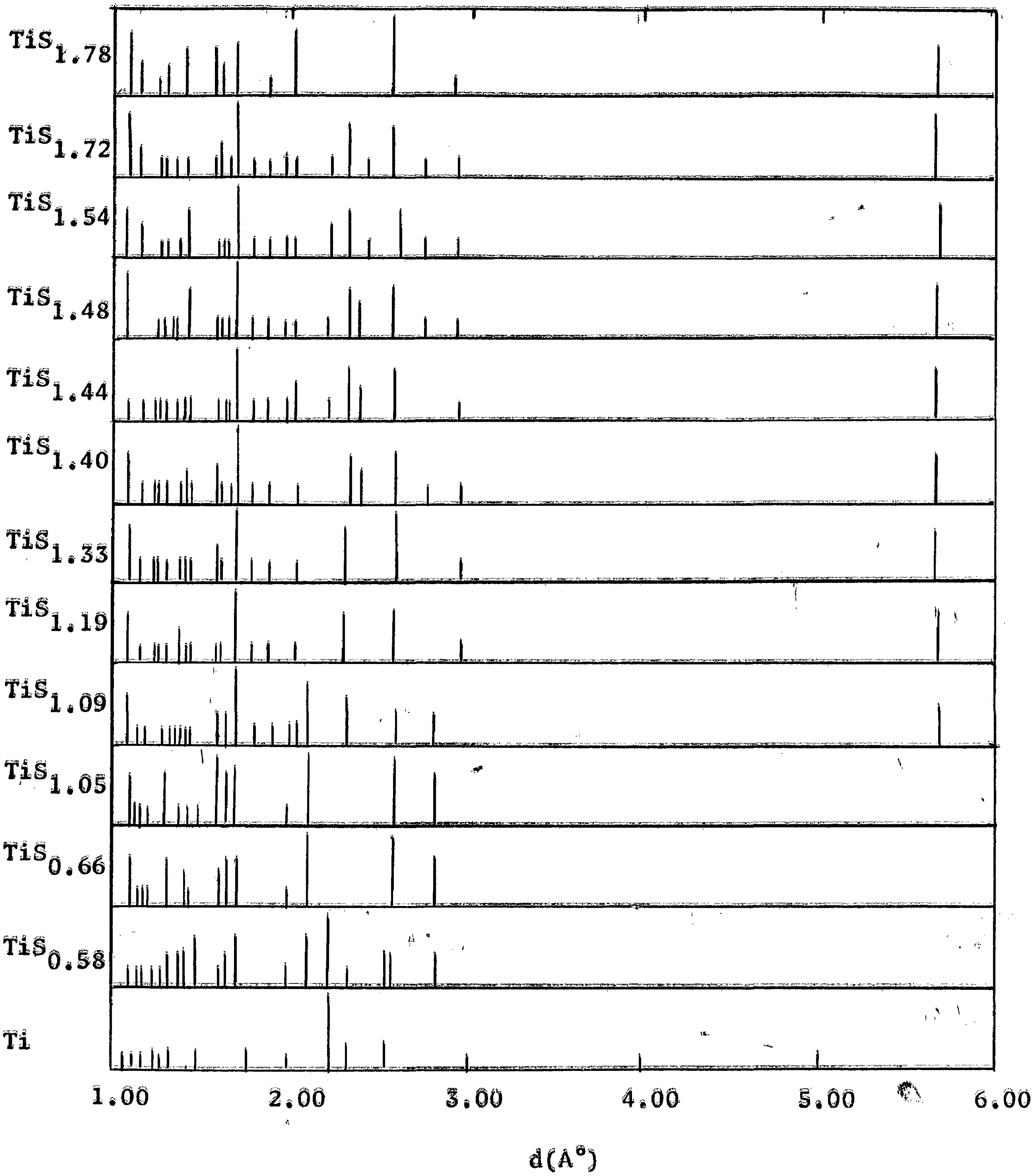


Figure 14. X-ray Data for TiS_x from $TiS_{1.78}$ to Ti.

of the lines in the two-phase regions). Figure 14 shows the comparisons of the d values for the titanium-sulfur system from $TiS_{1.78}$ to metallic Ti.

In the disulfide region, the lower limit of the 'TiS_2' phase appears to be between $TiS_{1.72}$ and $TiS_{1.77}$. This limit agrees somewhat with the limit of $TiS_{1.81}$ proposed by Jeanin and Benard (1959, p. 2876). At $TiS_{1.81}$ they found new lines appearing in the X-ray patterns and said that these new lines were due to another phase or a structure modification. In this investigation, these new lines were not observed in the $TiS_{1.77}$ pattern but were seen in the $TiS_{1.72}$ pattern. Abendroth (1957, p. 70) noticed these new lines at $TiS_{1.62}$. These new lines can be attributed to the phase 'Ti_2S_3' which has a very narrow homogeneity range, extending from $TiS_{1.48 \pm 0.02}$ to $TiS_{1.52 \pm 0.02}$. Thus the region between $TiS_{1.52 \pm 0.02}$ and $TiS_{1.74 \pm 0.02}$ would be a two-phase region between the 'TiS_2' and 'Ti_2S_3' phases. In this region at 800°C, Abendroth and Schlechten (1959, p. 148) showed that the H_2S/H_2 ratios are increasing with increasing sulfur content of the condensed phase. This indicates a single-phase region; however, their data points are far enough apart that they may have missed the two-phase horizontal. The above authors suggest a miscibility gap below 500°C in which the high temperature compounds disproportionate into 'Ti_2S_3' and 'TiS_2'. Two samples of $TiS_{1.60}$ were heated to 800°C for 48 hr. One sample was water-quenched before X-ray analysis and the other was furnace-cooled to room temperature in 12 hr. before X-ray analysis. Room temperature X-ray patterns taken immediately after the samples reached room temperature showed no disproportionation. That 'Ti_2S_3' is probably a stable equilibrium phase at 800°C is further substantiated by the fact that

Abendroth and Schlechten's isotherm becomes almost vertical at $TiS_{1.50}$. This is typical behavior around the ends of a two-phase region when the equilibrium compound has a very narrow homogeneity range.

In this study, X-ray patterns between $TiS_{1.48\pm0.02}$ and $TiS_{1.37\pm0.03}$ showed a two-phase region at 800°C, the two phases in equilibrium being 'Ti_2S_3' and 'Ti_3S_4'. The d values obtained from the 'Ti_3S_4' phase patterns were in good agreement with the d values obtained for the same composition by Hahn and Harder (1956, p. 249) (See Appendix XII). The characteristic lines of the 'Ti_2S_3' phase were also present in these patterns. In this composition range at 800°C, Abendroth and Schlechten (1959, p. 148) found increasing H_2S/H_2 ratios with increasing sulfur content, again indicating a single-phase region. If 'Ti_2S_3' is a stable phase in this system, however, there must be a two-phase region between the 'Ti_2S_3' and 'Ti_3S_4' phases. However, in Abendroth and Schlechten's curves, there is a change of slope in the composition range $TiS_{1.40}$ to $TiS_{1.45}$ which may have been the two-phase region attempting to show up but not being allowed enough time to reach equilibrium.

The 'Ti_3S_4' phase extends from $TiS_{1.37\pm0.03}$ to $TiS_{1.17\pm0.02}$ at 800°C according to X-ray patterns from compositions in this range. Abendroth and Schlechten (1959, p. 148) show that the 'Ti_3S_4' phase terminates at $TiS_{1.33}$ at 800°C. They give no points, however, between $TiS_{1.33}$ and $TiS_{1.09}$, the $TiS_{1.09}$ being in the two-phase region between $TiS_{1.33}$ and $TiS_{0.80}$. That $TiS_{1.33}$ is the equilibrium single-phase composition at the upper end of the two-phase region was determined by them from extrapolation of the sloping isotherm in the single-phase region to the horizontal isotherm in the two-phase region. Due to the low H_2S/H_2 ratio (4×10^{-4}) in equilibrium with 'Ti_3S_4' at 800°C, difficulty was no doubt encountered by Abendroth in differentiating between small changes in the H_2S/H_2 ratio. It would then be difficult to determine the lower composition limit of the 'Ti_3S_4' phase accurately. A more accurately determined isotherm would probably slope until it reached $TiS_{1.17 \pm 0.02}$ and then become horizontal. The H_2S/H_2 ratio in equilibrium with the $TiS_{1.33}$ was checked in this investigation and found to be 4×10^{-4}, which is in good agreement with Abendroth and Schlechten's data.

At 800°C, the two-phase region below and including the 'Ti_3S_4' phase extends from $TiS_{1.17 \pm 0.02}$ to $TiS_{1.07 \pm 0.02}$, the other phase present being the low-temperature form of 'TiS'. An X-ray diffraction pattern of a single-phase composition in the 'TiS' region was in very good agreement with the pattern for low-temperature 'TiS' obtained by Bartram (1959, p. 94), (See Appendix XII). Abendroth and Schlechten (1959, p. 148) proposed a two-phase region extending from $TiS_{1.33}$ to $TiS_{0.80}$. The X-ray pattern they obtained for $TiS_{0.80}$, however, does not agree with either the high-temperature TiS pattern given by Hahn (1956, p. 243), the low-temperature TiS given by Bartram, (1959, p. 94) or the TiS found in this investigation. Abendroth and Schlechten give the H_2S/H_2 ratio in equilibrium with $TiS_{0.80}$ as 4×10^{-4}. This point was checked in this investigation and the H_2S/H_2 ratio was undetectable, indicating that the composition $TiS_{0.80}$ was no longer in a two-phase region but was in the next lower single-phase region. From these data it can be concluded that at 800°C, $TiS_{0.80}$ is not the equilibrium composition of the phase present near TiS, but that this composition is within the 'TiS' homogeneity region.

The extent of the 'TiS' phase is from $TiS_{1.07 \pm 0.02}$ to $TiS_{0.68 \pm 0.02}$. All X-ray patterns in this region agreed with the pattern for low-temperature 'TiS'. Below $TiS_{0.68 \pm 0.02}$ lies a two-phase region extending down to the limit of solubility of sulfur in titanium which is near $TiS_{0.30}$. All X-ray patterns in this region showed the presence of the 'TiS' phase and metallic titanium solid solution.

CONCLUSIONS

On the basis of the experimental results obtained in this investigation for the titanium-sulfur system in the disulfide-trisulfide region, several conclusions can be reached, and several bases for further investigation can be proposed.

The equilibrium phase compositions in a disulfide-trisulfide two-phase mixture in the temperature range from 525°C to 565°C are $TiS_{1.94 \pm 0.01}$ and $TiS_{2.58 \pm 0.01}$. These equilibrium compositions do not vary appreciably with temperature. The extent of the trisulfide-phase solid solution is from $TiS_{2.58 \pm 0.01}$ to at least $TiS_{2.85}$. Additional experimental work should be done in this region both to determine the upper limit of this solid solution and to determine the type of defect responsible for the wide range of nonstoichiometry. It would also be interesting to find out how the lattice parameters vary with composition in this region. In the disulfide region, the solid solution extends from $TiS_{1.94 \pm 0.01}$ to $TiS_{1.74 \pm 0.02}$ with a new phase, probably 'Ti_2S_3', appearing below this composition. A redetermination of the H_2S/H_2 ratios at closer composition intervals in this region would be necessary to find out for sure if the 'Ti_2S_3' phase is present below $TiS_{1.74\pm0.02}$ and to determine more accurately the lower limit of the disulfide phase.

In the temperature range from 525° to 565°C the equation for $\Delta G°$ as a function of temperature is:

$$2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$$

$$\Delta G° = 40,200 - 44.8T$$

This temperature range is narrow, however, and a determination of the accuracy of the equation was not significant due to the small number of data points obtained in the two-phase region. A determination of the H_2S/H_2 ratios above the sulfides at temperatures below 525°C should be made in order to more fully describe the system in the disulfide-trisulfide region. From these proposed data and the data from this investigation then, a more accurate expression for $\Delta G°$ as a function of temperature could be determined due to the increased number of data points over a wider temperature range. This would allow a better statistical treatment of the data and thus give a better idea of the accuracy of the expression.

The most work, however, needs to be done in the region below $TiS_{1.80}$ in sulfur content. The literature is still very confusing and lacking in agreement in the region near $TiS_{1.50}$ and literature for the system below $TiS_{0.80}$ is almost completely lacking. From the cursory X-ray study conducted in this investigation below $TiS_{1.80}$, it appears that 2 two-phase regions exist between $TiS_{1.77}$ and $TiS_{1.33}$. As stated previously, a redetermination of the H_2S/H_2 ratios along with extensive X-ray study are necessary in this region to resolve these questions finally. The extents of the 'Ti_3S_4' and 'TiS' solid solutions need to be determined more accurately, but due to the low H_2S/H_2 ratios above these compositions at 800° to 900°C, an extensive X-ray treatment will have to be relied upon. The 'Ti_3S_4' phase, which has been found by other investigators but which did not appear in this study, should also be the object of further experimental work. Investigations of the region from $TiS_{1.00}$ to Ti would be of value in the steel industry since compounds and solid solutions in this region are stable at high temperatures and would appear in iron or steel in which fairly large amounts of titanium and sulfur are present.

SUMMARY

The single-phase regions which exist in the titanium-sulfur system at 800°C between TiS_2 and metallic titanium are 'TiS_2' from $TiS_{1.94 \pm 0.01}$ to $TiS_{1.74 \pm 0.02}$, 'Ti_2S_3' from $TiS_{1.52 \pm 0.02}$ to $TiS_{1.46 \pm 0.02}$, 'Ti_3S_4' from $TiS_{1.37 \pm 0.03}$ to $TiS_{1.17 \pm 0.02}$, 'TiS' from $TiS_{1.07 \pm 0.02}$ to $TiS_{0.68 \pm 0.02}$ and 'Ti' from approximately $TiS_{0.30}$ to metallic titanium. Between these single-phase solid solutions lie the appropriate two-phase regions. The limits of these phases were determined by X-ray diffraction patterns of samples equilibrated at 800°C in Vycor capsules for 36 hr. These patterns were taken at intervals of $X = 0.04$ in TiS_x except in the 'TiS_3' and 'TiS_2' regions where patterns were taken for every $X = 0.02$. The upper composition limit of the disulfide region was $TiS_{1.94 \pm 0.01}$ and did not vary in composition from 525° to 750°C and the lower composition limit of the trisulfide region was $TiS_{2.58-0.01}$ and did not vary between 525° and 565°C.

The free energy equation for the reaction $2\text{'}TiS_3\text{'} \rightleftharpoons 2\text{'}TiS_2\text{'} + S_2$ is $\Delta G° = 40200 - 44.8T$ in the temperature range from 525 to 565°C as determined by a static method. This method involved sealing a mixture of high-purity sulfur and an arbitrary sulfide in an evacuated Vycor capsule and equilibrating the sample at known but different sulfur and sulfide temperatures for 36 hr. After equilibration the samples were analyzed by oxidation in air to TiO_2 at 900°C. By use of the data of equilibrium sulfur temperature, sulfide temperature, and sulfide composition, the above equation was determined from a log P_{S_2} versus the reciprocal of the absolute temperature plot. A precise determination of the accuracy of the above equation was not significant due to the small number of data points obtained in the two-phase region.

PPENDIX I. Crystallographic Data for Titanium Disulfide and Titanium Trisulfide

Compound	Structure	Lattice Parameters (A°) a	b	c	$\frac{c}{a}$	B	Investigator	Date
TiS_2	Hexagonal; CdI_2 Lattice	3.39	-	5.70	1.68	-	Grimmeis	1961
TiS_2	Hexagonal; CdI_2 Lattice	3.4049	-	5.6912	1.662	-	Jeanin & Benard	1959
TiS_2	Hexagonal; CdI_2 Lattice	3.397	-	5.691	1.675	-	Oftedal	1928
TiS_2	Hexagonal; CdI_2 Lattice	3.39	-	5.70	1.68	-	McTaggart & Wadsley	1958
TiS_2	Hexagonal; CdI_2 Lattice	3.39	-	5.70	1.68	-	Haag & Schonberg	1954
TiS_3	Monoclinic	4.99	3.38	17.6	-	97.5°	Hahn & Harder	1956
TiS_3	Monoclinic	4.97	3.42	8.78	-	97.17°	Jeanin & Benard	1958
TiS_3	Monoclinic $P2_1/m$	4.973	3.433	8.714	-	97.74°	Haraldsen et al	1963
TiS_3	Monoclinic	5.01	3.40	8.80	-	98.4°	McTaggart & Wadsley	1958
TiS_3	Monoclinic	5.01	3.40	8.80	-	98.4°	Grimmeis	1961

APPENDIX II. Determination of Temperature Control of Sulfide and Sulfur Furnaces.

Hour	Sulfur Furnace (°C)	Sulfide Furnace (°C)
0	350	550
1	350	550.5
2	350	550
3	349.5	550
4	349	550.5
5	350	550
6	350	550
7	349.5	549.5
8	349	549
9	350	549
10	350.5	549
11	351	549.5
12	350	550
13	350	550.5
14	349.5	550.5
15	350	551
16	351	550
17	350	550
18	350	550
19	350	550
20	349	549.5
21	350	550
22	350.5	550
23	350.5	550
24	351	550.5
25	351	550.5
26	350.5	550.5
27	350	550
28	350	550
29	349.5	550
30	349.5	550
31	350	549.5
32	350	550
33	351	549
34	350.5	550
35	350	549.5
36	350.5	549.5

From these data, the temperature control on each furnace can be said to be ±1°C.

APPENDIX III. Calibration of Leeds and Northrup Potentiometer

Thermocouple: Chromel-Alumel Room Temperature: 30°C=1.20mv

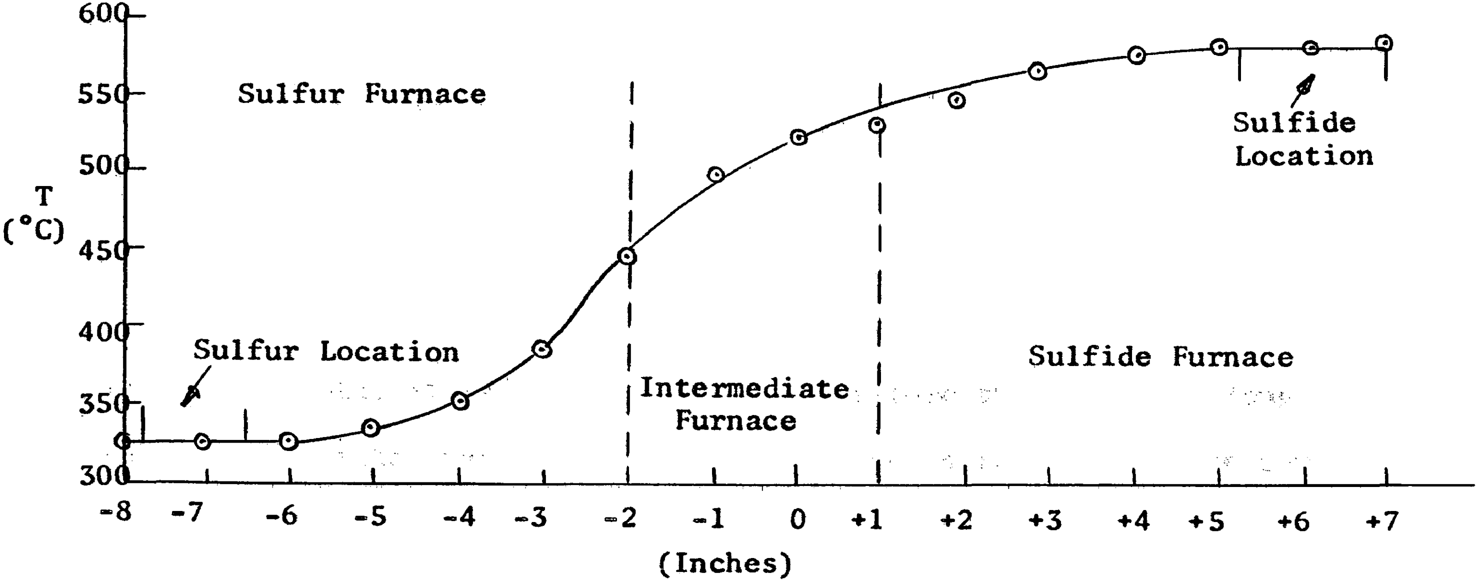
Metal	Melting Temperature (°C)	Corrected Millivolt Reading (mv)	Measured Temperature (°C)	Difference (°C)
99.999% Al	659.7	27.45	659.75	+ 0.05
99.9% Zn	419.47	17.21	419.5	+ 0.03
99.99% Pb	327.43	13.36	327.3	- 0.13

As a result of these data, no correction was applied to the potentiometer readings.

APPENDIX IV. Determination of the Temperature Gradient in the Equilibration Furnaces.

Initial Sulfur End Temperature: 322°C-Initial Sulfide End Temperature: 570°C

Inches from Joint	Temperature (°C)
-8	322
-7	322
-6	322
-5	336
-4	354
-3	380
-2	449
-1	504
0	522
+1	531
+2	541
+3	557
+4	565
+5	570
+6	570
+7	570



From these data, it is seen that the temperature at any point along the capsule was higher than the temperature of the sulfur end of the capsule.

APPENDIX V. Determination of CS_2 Leaching Time for Equilibrated Samples.

Leaching Time (Hours)	Composition after Leaching
0	$TiS_{3.03}$
1	$TiS_{2.44}$
2	$TiS_{2.35}$
3	$TiS_{2.35}$

From these data, a two-hour leaching time was selected for removal of free sulfur.

APPENDIX VI. Chemical Analysis of Metal Hydrides, Grade E TiH_2

Element	Percentage
Ti	95 - 96
H_2	3.5 - 3.8
N_2	0.2 max
Ca	0.05 max
Mg	0.05 max
C	0.1 max
Fe	0.1 max
Al	0.1 - 0.3 max
Si	0.1 max
Zr	0.1 max

Spectrographic Analysis of American Smelting and Refining Company's 99.999+% Sulfur (Lot 103):

Element	Percentage
Sb	N.D.*
Tl	N.D.
Mg	N.D.
Mn	N.D.
Pb	N.D.
Sn	N.D.
Si	N.D.
Cr	N.D.
Fe	N.D.
Ni	N.D.
Bi	N.D.
Al	N.D.
Ca	N.D.
Cu	N.D.
In	N.D.
Cd	N.D.
Zn	N.D.
Ag	N.D.
Na	1 ppm**
Cl	1 ppm

---

*N.D. denotes "none detected by standard spectrographic method."

**Denotes chemical analysis.

APPENDIX VII. Determination of the Equilibrium Times for the Reaction $2'TiS_3' \rightleftharpoons 2'TiS_2' + S_2$.

Experiment Number	Starting Material	Sulfide Temperature (°C)	Sulfur Temperature (°C)	Reaction Time (hrs.)	Final Product
1	$TiS_{1.22}$	540	460	24	$TiS_{2.58}$
2	$TiS_{1.22}$	540	460	48	$TiS_{2.61}$
8A	$TiS_{2.72}$	540	460	18	$TiS_{2.75}$
8B	$TiS_{2.72}$	540	460	36	$TiS_{2.83}$
8C	$TiS_{2.72}$	540	460	54	$TiS_{2.83}$

From these data, the decomposition reaction was chosen and a reaction time of 36 hours was selected.

APPENDIX VIII. Derivation of the Equation for X in TiS_x where $X = \frac{\text{moles S}}{\text{moles Ti}}$

1. The weight of TiS_x and the weight of TiO_2 are obtained from weighing a tared crucible and contents before and after ignition.

2. $$\text{Moles Ti} = \text{Moles } TiO_2 = \frac{\text{weight } TiO_2}{79.90}$$

3. $$\text{Moles S} = \frac{\text{weight } TiS_x - \text{weight Ti}}{32.07} \text{ where weight Ti} = \text{wt } TiO_2 \left(\frac{47.90}{79.90}\right)$$
$$= 0.599 \text{ wt } TiO_2$$

4. $$\text{Therefore moles S} = \frac{\text{weight } TiS_x - 0.599 \text{ weight } TiO_2}{32.07}$$

5. $$\text{Therefore } X = \frac{\text{moles S}}{\text{moles Ti}} = \frac{\dfrac{\text{weight } TiS_x - 0.599 \text{ weight } TiO_2}{32.07}}{\dfrac{\text{weight } TiO_2}{79.90}}$$

6. Simplifying (5) $$X = 2.49 \left(\frac{\text{weight } TiS_x}{\text{weight } TiO_2} - 0.599\right)$$

APPENDIX IX. Determination of Analysis Accuracy and Confidence Limit

Experiment Number	Analysis
A	$TiS_{2.56}$
B	$TiS_{2.56}$
C	$TiS_{2.57}$
D	$TiS_{2.58}$
E	$TiS_{2.58}$
F	$TiS_{2.60}$
G	$TiS_{2.57}$
H	$TiS_{2.58}$
I	$TiS_{2.56}$
J	$TiS_{2.56}$

Average Analysis: $TiS_{2.57}$

From these data, since the analysis of Experiment Number F is the only analysis which varies more than ± 0.01 from the average analysis, the accuracy of the analysis is $\pm$ 0.01 with 90% confidence.

APPENDIX X. Total Sulfur Pressure of Sulfur Vapor above Liquid Sulfur Between 120°C and 540°C. (From West and Menzies).

Liquid Sulfur Temperature (°C)	Total Sulfur Vapor Pressure (mm Hg)
120	0.0304
140	0.109
160	0.332
180	0.888
200	2.12
220	4.60
240	9.19
260	17.2
280	30.2
300	50.4
320	80.7
350	152.5
380	268.5
420	524.4
460	946.5
500	1605
540	2583

APPENDIX XI. Calculation of P_{S_2} from P_T Using Polyatomic Sulfur Data at 838°K.

$$2\,S_2 \rightleftharpoons S_4 \qquad K_1 = \frac{P_{S_4}}{P^2_{S_2}} \qquad \Delta G^\circ = -28400 + 31.88T = -RT\ \ln K_1$$

$$\ln K_1 = \frac{-28{,}400 + 21.88\ (838)}{-1.987\ (838)} = 1.012$$

$$K_1 = 2.75$$

$$\text{Therefore}\quad P_{S_4} = 2.75\ P^2_{S_2}$$

$$3S_2 \rightleftharpoons S_6 \qquad K_2 = \frac{P_{S_2}}{P^3_{S_2}} \qquad \Delta G^\circ = -63720 + 69.3T = -RT\ \ln K_2$$

$$\ln K_2 = \frac{-63720 + 69.3\ (838)}{-1.987\ (838)} = 3.392$$

$$K_2 = 30$$

$$\text{Therefore}\quad P_{S_6} = 30\ P^3_{S_2}$$

$$4S_2 \rightleftharpoons S_8 \qquad K_3 = \frac{P_{S_8}}{P^4_{S_2}} \qquad \Delta G^\circ = -92160 + 101.2T = -RT\ \ln K_3$$

$$\ln K_3 = \frac{-92160 + 101.2\ (838)}{-1.987\ (838)} = 4.417$$

$$K_3 = 83$$

$$\text{Therefore}\quad P_{S_8} = 83\ P^4_{S_2}$$

Now $P_T = P_{S_2} + P_{S_4} + P_{S_6} + P_{S_8} = P_{S_2} + 2.75\ P_{S_2}^2 + 30\ P^3_{S_2} + 83\ P^4_{S_2}$

APPENDIX XI. (Continued)

Now letting $f(P_{S_2}) = P_{S_2} + 2.75\ P_{S_2}^2 + 30\ P_{S_2}^3 + 83\ P_{S_2}^4 - P_T$ and plotting $f(P_{S_2})$ against P_{S_2} for $P_T = 0.713$ atm and $P_{S_2} = 0.100$ atm, 0.200 atm, and 0.250 atm, $P_{S_2} = 0.204$ atm is found from the graph when $f(P_{S_2}) = 0$.

Therefore $P_{S_2} = 0.204$ atm when $P_T = 0.713$ atm at 838°K.

APPENDIX XII. Comparison of the X-ray Data from the Present Study with Published Data for 'TiS_3', 'TiS_2', 'Ti_2S_3', 'Ti_3S_4' and 'TiS'.

Compound	Present Study Data			Published Data		Source
	X-ray Pattern d_{hkl} (A°)	Relative Intensity	Reciprocal Lattice Construction d_{hkl} (A°)	d_{hkl} (A°)	Relative Intensity	
'TiS_3'	1.70	st		1.70	st	Haraldsen
	1.75	vw		--		
	1.83	m		1.83	vw	
	1.90	st		1.90	w	
	1.99	st		1.99	st	
	2.09	vw		--		
	2.16	vw		--		
	2.20	w		2.22	vw	
	2.28	st		2.28	w	
	2.45	m		2.47	w	
	2.67	vst		2.69	vst	
	2.89	vw		2.91	vw	
	3.22	vw		--		
	4.10	vw		4.06	vw	
	4.30	vw		4.38	w	
	--			4.57	vw	
	--			4.94	vw	
	8.76	m		8.73	m	
'TiS_2'	1.089	m	1.095	1.095	0.35	Abendroth
	1.160	w	1.162	1.165	0.10	
	1.261	vw	1.261	1.270	0.05	
	1.303	w	1.300	1.310	0.16	
	1.421	m	1.427	1.425	0.36	
	1.59	m	1.60	1.60	0.40	
	1.62	w	1.62	1.63	0.14	
	1.69	m	1.69	1.70	0.35	
	1.89	vw	1.90	1.90	0.09	
	2.03	st	2.04	2.05	0.80	
	2.60	vst	2.59	2.63	1.00	
	2.94	vw	2.94	--	--	
	5.68	m	5.68	5.70	0.60	
'Ti_2S_3'	1.094	st		1.097	s	
	--			1.170	w	
	--			1.243	w-m	
	1.268	vw		1.273	w	

APPENDIX XII. (Contd.) Comparison of the X-ray Data from the Present Study with Published Data for 'TiS_3', 'TiS_2', 'Ti_2S_3', 'Ti_3S_4' and 'TiS'

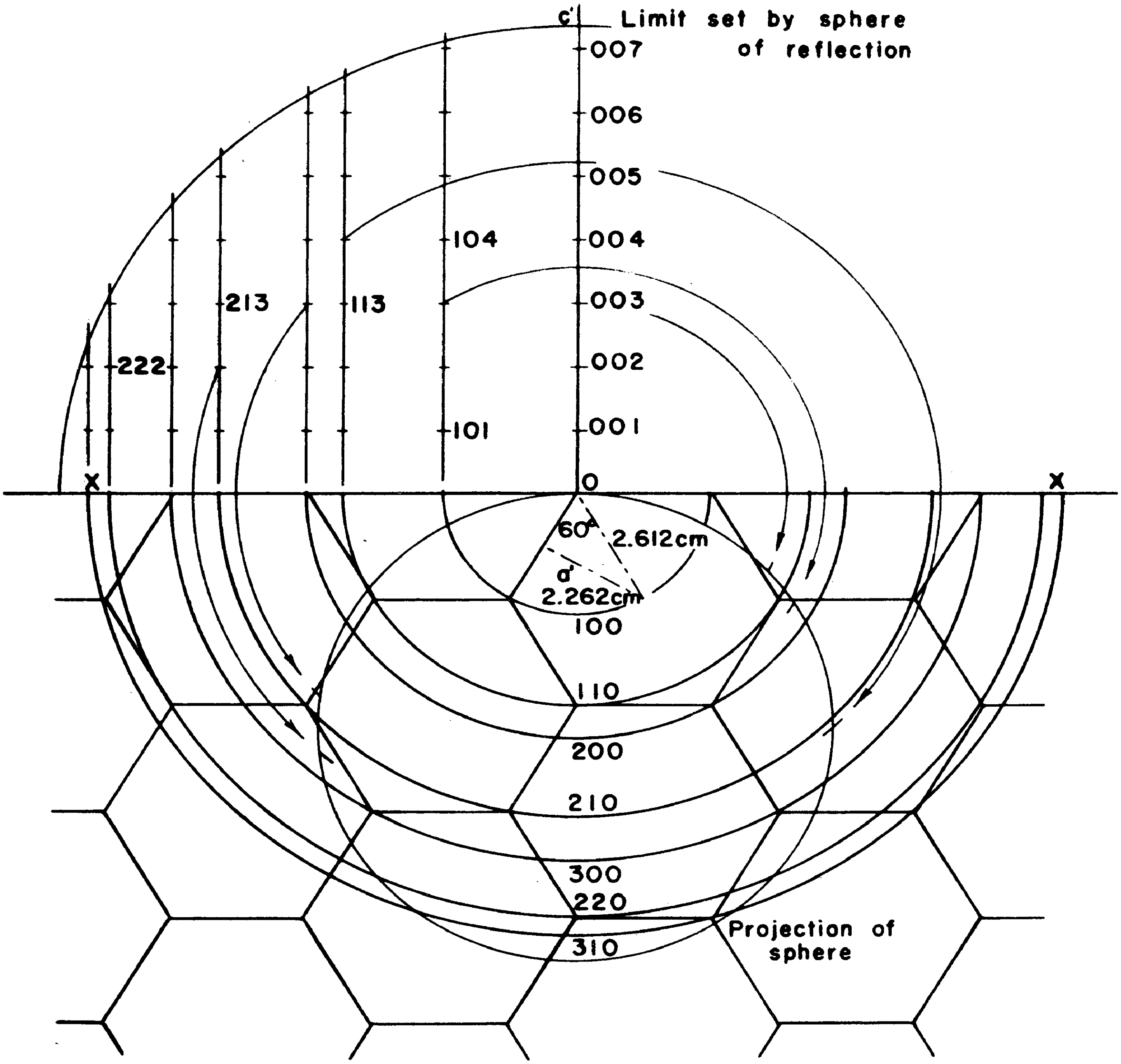
Compound	Present Study Data			Published Data		Source
	X-ray Pattern d_{hkl} (A°)	Relative Intensity	Reciprocal Lattice Construction d_{hkl} (A°)	d_{hkl} (A°)	Relative Intensity	
'Ti_2S_3' (contd.)	1.310	vw		1.317	w	Bartram
	1.376	vw		--		
	1.387	vw		1.382	m	
	--			1.426	m	
	1.423	m		1.435	w	
	1.60	vw		1.601	m	
	1.63	vw		1.640	w	
	1.67	vw		--		
	1.71	vst		1.711	s	
	1.80	vw		1.806	m-s	
	1.89	vw		1.900	w	
	1.98	vw		--		
	2.05	vw		2.052	s	
	2.23	vw		--		
	2.32	m		2.33	vs	
	2.42	vw		--		
	2.61	m		2.624	s	
	2.85	vw		2.865	w-m	
	2.97	vw		2.953	vw	
	5.68	m		5.61	s	
'Ti_3S_4'	1.100	w		1.100	st/sst	Hahn & Harder
	--			1.124	ss	
	1.171	vw		1.172	s	
	1.250	vw		1.248	s/m	
	1.269	vw		1.274	ss	
	1.310	vw		1.318	s	
	1.382	vw		1.384	m	
	1.426	vw		1.430	s/m	
	1.439	vw		1.44	s	
	--			1.47	sss	
	1.60	w		1.60	m	
	1.63	vw		1.64	sss	
	1.71	vst		1.71	st/sst	
	1.81	vw		1.81	m/st	
	1.90	vw		1.90	sss	

APPENDIX XII. Comparison of the X-ray Data from the Present Study with
(Contd.) Published Data for 'TiS$_3$', 'TiS$_2$', 'Ti$_2$S$_3$', 'Ti$_3$S$_4$' and 'TiS'.

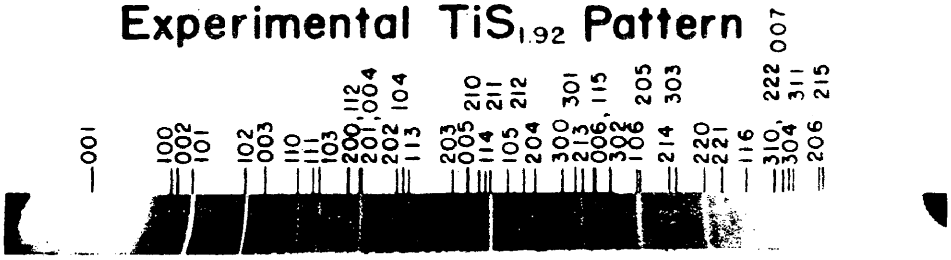
Compound	Present Study Data: X-ray Pattern d_{hkl} (A°)	Present Study Data: Relative Intensity	Reciprocal Lattice Construction d_{hkl} (A°)	Published Data: d_{hkl} (A°)	Published Data: Relative Intensity	Source
Ti$_3$S$_4$ (contd.)	2.06	vw		2.06	m	
	2.34	m		2.34	sst	
	2.63	m		2.64	st	
	--			2.87	ss	
	2.97	vw		2.98	sss	
	5.68	m		5.71	ss	
TiS$_{1.00}$	1.142	m		1.147	40	Bartram
	1.160	w		1.165	20	
	1.180	vw		1.186	10	
	1.298	m		1.305	30	
	1.386	w		1.393	30	
	1.430	vw		1.430	10	
	1.48	vw		1.48	20	
	1.58	s		1.61	90	
	1.65	m		1.65	40	
	1.69	m		1.71	30	
	1.99	vw		--	--	
	2.11	vst		2.13	100	
	2.60	s		2.61	70	
	2.83	m		2.86	60	
	--			3.19	60	

APPENDIX XIII. Reciprocal Lattice Construction for the Composition $TiS_{1.92}$

A. Powder Pattern from Unit Cell Data for $TiS_{1.92}$



B. Comparison of Derived Powder Pattern with Experimental $TiS_{1.92}$ Pattern



APPENDIX XIV. Sources of X-ray Powder Pattern Lines in the Two Phase Region Between $TiS_{1.94\pm0.01}$ and $TiS_{2.58\pm0.01}$.

Composition	d_{hkl} (A°)	Sources of Lines (2 indicates 'TiS$_2$', 3 indicates 'TiS$_3$')
$TiS_{2.57}$	1.091	2
	1.119	3
	1.160	2 and 3
	1.216	3
	1.237	3
	1.306	2
	1.356	2 and 3
	1.393	3
	1.421	2
	1.448	3
	1.55	3
	1.59	2
	1.62	2
	1.69	2 and 3
	1.74	3
	1.82	3
	1.89	2 and 3
	1.98	3
	2.04	2
	2.20	3
	2.27	3
	2.44	3
	2.61	2
	2.67	3
	2.88	3
	3.24	3
	5.68	2
	8.76	3
$TiS_{2.27}$	1.093	2
	1.165	2 and 3
	1.264	2
	1.309	2
	1.364	2 and 3
	1.399	3
	1.427	2
	1.450	3
	1.59	2
	1.63	2
	1.70	2 and 3
	1.77	3

APPENDIX IV
(Contd.)

Composition	d_{hkl} (A°)	Sources of Lines (2 indicates 'TiS$_2$', 3 indicates 'TiS$_3$')
TiS$_{2.27}$ (Contd.)	1.83	3
	2.03	2
	2.28	3
	2.46	3
	2.62	2
	2.68	3
	2.93	2
	3.23	3
	5.72	2
	8.78	3
TiS$_{1.96}$	1.091	2
	1.162	2 and 3
	1.264	2
	1.306	2
	1.425	2
	1.59	2
	1.63	2
	1.70	2 and 3
	1.89	2 and 3
	2.05	2
	2.28	3
	2.47	3
	2.61	2
	2.69	3
	2.94	2
	3.23	3
	5.68	2
	8.76	3

APPENDIX XV. Sources of X-ray Pattern Lines in the Two Phase Regions Between TiS$_{1.74 \pm 0.02}$ and TiS$_{1.52 \pm 0.02}$, TiS$_{1.46 \pm 0.02}$ and TiS$_{1.38 \pm 0.02}$, TiS$_{1.17 \pm 0.02}$ and TiS$_{1.07 \pm 0.02}$, and TiS$_{0.68 \pm 0.02}$ and Ti.

Composition	d_{hkl} (A°)	Sources of Lines (2 indicates 'TiS$_2$', 1.50 indicates 'Ti$_2$S$_3$') (1.33 indicates 'Ti$_3$S$_4$', 1 indicates 'TiS') (0 indicates 'Ti')
TiS$_{1.72}$	1.093	1.50 and 2
	1.164	2
	1.269	1.50 and 2
	1.310	1.50 and 2
	1.372	1.50
	1.423	1.50 and 2
	1.59	1.50 and 2
	1.62	1.50 and 2
	1.67	1.50
	1.70	1.50 and 2
	1.80	1.50
	1.89	1.50 and 2
	1.98	1.50
	2.04	1.50 and 2
	2.25	1.50
	2.31	1.50
	2.42	1.50
	2.60	1.50 and 2
	2.85	1.50
	2.97	1.50 and 2
	5.68	1.50 and 2
TiS$_{1.54}$	1.094	1.50 and 2
	1.164	2
	1.272	1.50 and 2
	1.308	1.50 and 2
	1.375	1.50
	1.425	1.50 and 2
	1.60	1.50 and 2
	1.64	1.50 and 2
	1.66	1.50
	1.72	1.50 and 2
	1.82	1.50
	1.90	1.50 and 2

APPENDIX XV.
(Contd.)

Composition	d_{hkl} (A°)	Sources of Lines (2 indicates 'TiS_2', 1.50 indicates 'Ti_2S_3') (1.33 indicates 'Ti_3S_4', 1 indicates 'TiS') (0 indicates 'Ti')
$TiS_{1.54}$ (Contd.)	1.98	1.50
	2.05	1.50 and 2
	2.25	1.50
	2.35	1.50
	2.45	1.50
	2.64	1.50 and 2
	2.85	1.50
	2.96	1.50 and 2
	5.68	1.50 and 2
$TiS_{1.44}$	1.098	1.33 and 1.50
	1.175	1.33
	1.250	1.33
	1.275	1.33 and 1.50
	1.315	1.33 and 1.50
	1.374	1.50
	1.385	1.33
	1.428	1.33 and 1.50
	1.439	1.33
	1.60	1.33 and 1.50
	1.65	1.33 and 1.50
	1.67	1.50
	1.72	1.33 and 1.50
	1.81	1.33 and 1.50
	1.89	1.33 and 1.50
	1.98	1.50
	2.06	1.33 and 1.50
	2.23	1.50
	2.35	1.33 and 1.50
	2.42	1.50
	2.62	1.33 and 1.50
	2.85	1.50
	2.98	1.33 and 1.50
	5.68	1.33 and 1.50
$TiS_{1.40}$	1.100	1.33 and 1.50
	1.171	1.33
	1.250	1.33

APPENDIX XV
(Contd.)

Composition	d_{hkl} (A°)	Sources of Lines (2 indicates 'TiS_2', 1.50 indicates 'Ti_2S_3') (1.33 indicates 'Ti_3S_4', 1 indicates 'TiS') (0 indicates 'Ti')
$TiS_{1.40}$ (Contd.)	1.269	1.33 and 1.50
	1.310	1.33 and 1.50
	1.385	1.33
	1.426	1.33 and 1.50
	1.439	1.33
	1.60	1.33 and 1.50
	1.63	1.33 and 1.50
	1.67	1.50
	1.72	1.33 and 1.50
	1.81	1.33 and 1.50
	1.90	1.33 and 1.50
	2.06	1.33 and 1.50
	2.35	1.33 and 1.50
	2.42	1.50
	2.63	1.33 and 1.50
	2.85	1.50
	2.97	1.33 and 1.50
	5.68	1.33 and 1.50
$TiS_{1.09}$	1.094	1.33 and 1
	1.145	1
	1.173	1.33
	1.253	1.33
	1.270	1.33
	1.300	1.33 and 1
	1.389	1.33 and 1
	1.425	1.33 and 1
	1.440	1.33
	1.59	1.33 and 1
	1.64	1.33 and 1
	1.71	1.33 and 1
	1.80	1.33
	1.90	1.33
	1.99	1
	2.05	1.33
	2.11	1
	2.33	1.33
	2.61	1.33 and 1
	2.84	1
	5.68	1.33

APPENDIX XV
(Contd.)

Composition	d_{hkl} (A°)	Sources of Lines (2 indicates 'TiS_2'; 1.50 indicates 'Ti_2S_3') (1.33 indicates 'Ti_3S_4'; 1 indicates 'TiS') (0 indicates 'Ti')
$TiS_{0.58}$	1.095	1
	1.140	1
	1.229	0
	1.245	0
	1.276	0
	1.295	1
	1.333	0
	1.389	1
	1.427	1
	1.47	0
	1.60	1
	1.63	1
	1.70	1 and 0
	1.99	1
	2.11	1
	2.23	0
	2.34	0
	2.55	0
	2.58	1
	2.84	1

BIBLIOGRAPHY

Abendroth, R. P., and Schlechten, A. W., 1959, A thermodynamic study of the titanium-sulfur system in the region $TiS_{1.93}$ to $TiS_{0.80}$:AIME Trans., v. 215, p. 145-151.

Abendroth, R. P. 1957, A thermodynamic study of the titanium sulfides: Ph.D. Thesis, Missouri School of Mines and Metallurgy, Rolla, Mo., 105 p.

Bartram, S. F., 1958, The crystallography of some titanium sulfides: Ph.D. Thesis, Rutgers University, New Brunswick, N. J., 131 p.

Biltz, Wilhelm; Ehrlich, Paul; and Meisel, Karl, 1937, Uber die sulfide des titans: Zeitschr. Anorg. Allg. Chem., v. 234, no. 2, p. 97-116.

Braune, H., Peter, S., and Neveling, W., 1951, Die dissoziation des schwefeldampes: Zeitschr. Naturf., v. A6, p. 32.

Freeman, R. D., 1962, Thermodynamic properties of binary sulfides: Oklahoma State University Research Foundation Report 60, p. 24.

Grimmeis, H. G., Rabenau, A., Hahn, A., Ness, P., 1961, Uber electrische und optische eigenshaften einiger chalkogenide von elementen der IV. nebengruppe: Zeitschr. Elecktrochem., v. 65, p. 776.

Haag, Gunnar, and Schonberg, Nils, 1954, X-ray studies of sulfides of titanium, zirconium, niobium, and tantalum: Arkiv for Kemi, v. 7, p. 40.

Hahn, Harry, 1958, Recent results of researches on metal sulfide structure: Chem. Soc. Sym., London, Spec. Pub. no. 12, p. 275.

Hahn, Harry, and Harder, Bernhard, 1956, Zur kristallstructur der titansulfide: Zeitschr. Anorg. Allg. Chem., v. 288, no. 5-6, p. 241-256.

Bibliography (Continued)

Hahn, Harry, and Ness, P., 1957, Zur frage der existenz von subchakogenidephasen des titans: Naturvissenschaften, v. 44, p. 581.

Haraldsen, Haakon: Kjekshus, Arne; Rost, Erling; Steffensen, Arne; 1963, On the properties of TiS_3, ZrS_3, and Hf S_3: Acta Chem. Scand., v. 17, no. 5, p. 1285-1292.

Jeanin, Y., and Benard, J., 1958, Structure et stabilite du trisulfur de titane: Comptes Rendus, v. 246, p. 614-617.

____________________, 1959, Etude de la phase non stoichiometrique TiS_2: etendue du domaine et nature des defauts: Comptes Rendus v.248, p. 2875-2877.

Klemm, W., and Kilian, H., 1941, Das moleculargewicht von gasformegem schwefel: Zeitschr. Physik. Chem., B 49, p. 279-283.

Kubaschewski, O., and Evans, E. L., 1958, Metallurgical Thermochemistry: New York, The Macmillan Co., p. 139-174, 342.

Larson, A. H., and Schlechten, A. W., 1964, A thermodynamic study of the zirconium-sulfur system in the region $ZrS_{1.49}$ to $ZrS_{2.00}$: AIME Trans., v. 230, p. 862-866.

McTaggart, F. K., and Wadsley, A.D., 1958, The sulfides, selenides, and tellurides of titanium, zirconium, hafnium, and thorium: Austral. Jour. Chem., v. 11, p. 445.

Oftedal, Ivar, 1928, Rontgengraphische Untersuchungen von SnS_2, TiS_2, $TiSe_2$, Ti Te_2: Zeitschr. Physik. Chem. v. 134, p. 301-310.

Preuner, G., and Schupp, W., 1910, Dissociationsisothermen des schwefels zwischen 300° and 850°C: Zeitschr. Physik. Chem., v. 68, p. 129.

Rosenqvist, T., 1954, A thermodynamic study of the iron, cobalt, and nickel sulphides: Jour. Iron and Steel Inst., v. 176, p. 37.

Schaefer, S. C., Larson, A. H., and Schlechten, A. W., 1964, Sulfur pressure variation of molybdenum disulfide at 1100°C: AIME Trans., v. 230, p. 594-595.

Vermaut, N. A., 1964, A thermodynamic study of the zirconium-sulfur, titanium-sulfur, hafnium-sulfur systems in the disulfide-trisulfide region: Ph.D. Thesis, University of Missouri at Rolla, Rolla, Mo., p. 151-153.

West, W. A., and Menzies, W.A.C., 1929, The vapor pressures of sulfur between 100° and 550° with related thermal data: Jour. Phys. Chem., v. 39, p. 1880-1892.

VITA

The author was born on May 3, 1941 in Bethany, Missouri. He received his primary and secondary school education in Princeton, Illinois.

He entered the Colorado School of Mines, Golden, Colorado in September 1959, transferred to the Missouri School of Mines, Rolla, Missouri in January 1962, and received his Bachelor of Science degree in Metallurgical Engineering from the latter institution in January 1964. He has been enrolled in the Graduate School of the Colorado School of Mines from February 1964 to the present.

While enrolled in the Graduate School of the Colorado School of Mines, the author was a research assistant on a project supported by the National Science Foundation from February 1964 to September 1964 and held a National Education Defense Act Fellowship from September 1964 to the present.