



Structural studies of titanium alkoxides
by Robert Dale Witters

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

Dipole moments of four alkyl titanates were determined in n-heptane solution by the method Halverstadt and Kumler. It was found that the values obtained for the ethyl, n-propyl, and n-butyl orthoesters were for the trimers, but those found for tert-butyl titanate were for the monomers. Variations of the dipole moments of these compounds with temperature change indicate the potential energy barrier to rotation of the alkoxy groups is of magnitude kT .

The crystal and molecular structures of monomethyltriethyl titanate was determined by x-ray diffraction techniques. Crystal data obtained are: $a = 12.14 \text{ \AA}$ $\alpha = 76^\circ 56'$ density (meas.) = 1.244 g/cc $b = 12.13$ $\beta = 77^\circ 2'$ density (calc.) = 1.236 g/cc $c = 16.93$ $\gamma = 74^\circ 15'$ $Z = 8$ Space Group $P1$ In the solid state the molecules are linked together to form tetramer units. In the tetramers the four titanium atoms form a planar diamond shape, sharing oxygen atoms so that each titanium atom has a coordination number of six.

A preliminary investigation of an hydrolysis product of tetraethyl titanate was carried out. The unit cell of this crystal contains approximately 60 titanium atoms. Due to the complexity of this crystal and also to the fact that the molecular formula of the compound is uncertain, the structure determination was not completed. Crystal data obtained for this compound are: $a = 27.92 \text{ \AA}$ density = 1.305 g/cc $b = 22.40$ space group $P21/a$ $c = 23.30$ $\beta = 117^\circ 15'$

STRUCTURAL STUDIES OF TITANIUM ALKOXIDES

by

ROBERT DALE WITTERS

A thesis submitted to the Graduate Faculty in partial
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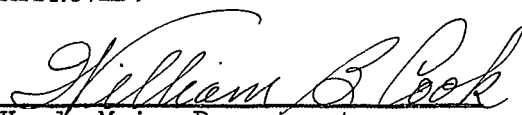
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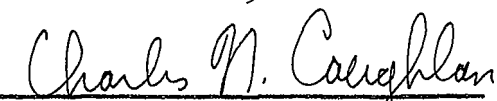
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APPROVED:


Head, Major Department


Chairman, Examining Committee


Dean, Graduate Division

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TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	vii
INTRODUCTION	x
PART I. DIELECTRIC STUDIES OF TETRAETHYL TITANATES	5
Theory and Discussion of Methods	5
Preparation of Compounds	9
Dielectric Constant Apparatus	9
Density Apparatus	9
Temperature Control and Measurement	10
Data and Results	12
PART II. PRELIMINARY INVESTIGATION OF THE HYDROLYSIS PRODUCT OF TETRAETHYL TITANATE	47
Preparation of Crystals	47
Analysis of Crystals	49
Density Determination of the Hydrolysis Product	50
Collection of X-Ray Data	50
Space Group	52
Cell Dimensions	53
Choosing the Axes	54
Indexing Weissenberg Photographs of Monoclinic Crystals	59
Attempt to Determine Structure	63

TABLE OF CONTENTS (cont.)

	Page
PART III. THE CRYSTAL STRUCTURE OF MONOMETHYLTRIETHYL TITANATE	72
Preparation of Crystals	72
Density Determination of $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$	72
Experimental: X-Ray Apparatus and Intensity Measurements	72
Space Group	23
Cell Dimensions and Choice of Axes	75
Indexing Weissenberg Photographs of Triclinic Crystals	81
Determination of the Structure	87
Review of Structure	118
DISCUSSION	119
SUMMARY	122
APPENDIX	123
A. Derivation of Formula. Calculation of Axial Length from a Rotation Picture	124
B. Derivation of a Method for the Determination of Interaxial Angles from Weissenberg Photographs Derivation for a Monoclinic Crystal Derivation for a Triclinic Crystal	128
C. Table of Structure Factors for $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$	141
LITERATURE CITED	175

LIST OF TABLES

PART I. Variation of Dielectric Constant and Specific Volume with Concentration for n-Heptane Solutions of Tetraalkyl Titanates		Page
TABLE I	Tetraethyl Titanate, 50°C	14
TABLE II	Tetraethyl Titanate, 25°C	15
TABLE III	Tetraethyl Titanate, 0°C	16
TABLE IV	Tetrapropyl Titanate, 50°C	17
TABLE V	Tetrapropyl Titanate, 25°C	18
TABLE VI	Tetrapropyl Titanate, 0°C	19
TABLE VII	Tetra-n-butyl Titanate, 50°C	20
TABLE VIII	Tetra-n-butyl Titanate, 25°C	21
TABLE IX	Tetra-n-butyl Titanate, 0°C	22
TABLE X	Tetra-tert-butyl Titanate, 25°C	23
TABLE XI	Results of Dielectric Studies	45
TABLE XII	Densities and Refractive Indices for Pure Liquids	46
PART II.		
TABLE XIII	Determination of c from Rotation Film	55
TABLE XIV	Determination of $a \cdot \sin \beta$ and b from Weissenberg Film	56
TABLE XV	Summary of Crystal Data for Hydrolysis Product	57
PART III.		
TABLE XVI	Determination of Cell Edge b from Rotation Film	76
TABLE XVII	Determination of Interplanar Spacings from Weissenberg Film	77

LIST OF TABLES
(continued)

		Page
TABLE XVII	Summary of Crystal Data $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$	77
TABLE XVIII	Summary of Crystal Data $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$	83
TABLE XIX	Patterson Peaks Used and Predicted	91
TABLE XX	Bond Distances	100
TABLE XXI	Atom Parameters	106
TABLE XXII	O - Ti - O Bond Angles	115
APPENDIX C	Table of Structure Factors for $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$	141

LIST OF FIGURES

INTRODUCTION

Page

- Figure 1. Proposed Structures for Trimeric Tetraethyl Titanate

4

PART I

Figure 2.	Pycnometer Variation of Dielectric Constant and Specific Volume with Concentration for Tetraalkyl Titanates		11
Figure 3.	$\text{Ti}(\text{OC}_2\text{H}_5)_4$	Specific Volume	0°C
			24
Figure 4.	$\text{Ti}(\text{OC}_2\text{H}_5)_4$	Dielectric Constant	0°C
			25
Figure 5.	$\text{Ti}(\text{OC}_2\text{H}_5)_4$	Specific Volume	25°C
			26
Figure 6.	$\text{Ti}(\text{OC}_2\text{H}_5)_4$	Dielectric Constant	25°C
			27
Figure 7.	$\text{Ti}(\text{OC}_2\text{H}_5)_4$	Specific Volume	50°C
			28
Figure 8.	$\text{Ti}(\text{OC}_2\text{H}_5)_4$	Dielectric Constant	50°C
			29
Figure 9.	$\text{Ti}(\text{OC}_3\text{H}_7^{\text{n}})_4$	Specific Volume	50°C
			30
Figure 10.	$\text{Ti}(\text{OC}_3\text{H}_7^{\text{n}})_4$	Dielectric Constant	50°C
			31
Figure 11.	$\text{Ti}(\text{OC}_3\text{H}_7^{\text{n}})_4$	Specific Volume	25°C
			32
Figure 12.	$\text{Ti}(\text{OC}_3\text{H}_7^{\text{n}})_4$	Dielectric Constant	25°C
			33
Figure 13.	$\text{Ti}(\text{OC}_3\text{H}_7^{\text{n}})_4$	Specific Volume	0°C
			34
Figure 14.	$\text{Ti}(\text{OC}_3\text{H}_7^{\text{n}})_4$	Dielectric Constant	0°C
			35
Figure 15.	$\text{Ti}(\text{OC}_4\text{H}_9^{\text{n}})_4$	Specific Volume	50°C
			36
Figure 16.	$\text{Ti}(\text{OC}_4\text{H}_9^{\text{n}})_4$	Dielectric Constant	50°C
			37
Figure 17.	$\text{Ti}(\text{OC}_4\text{H}_9^{\text{n}})_4$	Specific Volume	25°C
			38
Figure 18.	$\text{Ti}(\text{OC}_4\text{H}_9^{\text{n}})_4$	Dielectric Constant	25°C
			39
Figure 19.	$\text{Ti}(\text{OC}_4\text{H}_9^{\text{n}})_4$	Specific Volume	0°C
			40
Figure 20.	$\text{Ti}(\text{OC}_4\text{H}_9^{\text{n}})_4$	Dielectric Constant	0°C
			41

LIST OF FIGURES
(continued)

Figure 21.	$\text{Ti}(\text{OC}_4\text{H}_9^t)_4$	Specific Volume	25°C	Page 42
Figure 22.	$\text{Ti}(\text{OC}_4\text{H}_9^t)_4$	Dielectric Constant	25°C	43
Figure 23.	Temperature Variation of Dipole Moment			44

PART II

Figure 24.	Crystal Growing Apparatus			48
Figure 25.	Apparatus for Growing Crystals for Analysis			51
Figure 26.	Choosing Axes on a*c* Net			58
Figure 27.	Relationship Between the Precession and Weissenberg Films			60
Figure 28.	Arrangement in Reciprocal Space for Upper Level Weissenberg Films			62
Figure 29.	Appearance of b* Axial Lines (Festoons) on 4th Level Weissenberg Films			64
Figure 30.	Indication of Subcells from Weighted a*b* Net			70

PART III

Figure 31.	Chart for Intensity Correction			74
Figure 32.	Arrangement of Axes on Weissenberg and Precession Films			80
Figure 33.	Arrangement of Reciprocal Axes for Upper Level Weissenberg Films			82
Figure 34.	Reciprocal Axes Arrangement			85
Figure 35.	Comparison of 3d and 4th Level Weissenberg Films			88
Figure 36.	Structure of $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer			111
Figure 37.	$\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer			112
Figure 38.	Bond Distances. $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer Unit #1			113
Figure 39.	Bond Distances. $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer Unit #2			114

LIST OF FIGURES
(Continued)

Page

APPENDIX

Figure 40.	Sphere of Reflection and X-Ray Camera	125
Figure 41.	Reciprocal Lattice Setting for an Equi-Inclination Weissenberg Picture when Crystal is Mounted on c Axis, for a Monoclinic Crystal	129
Figure 42.	Reciprocal Lattice Setting for an Equi-Inclination Weissenberg Picture when Crystal is Mounted on c Axis, for a Triclinic Crystal	132
Figure 43.	Relationship Between Reciprocal Lattice Axes and c Axis, for a Triclinic Crystal	133
Figure 44a.	First and Second Settings for b^* Axis	136
Figure 44b.	First and Second Settings for a^* Axis	137

ABSTRACT

Dipole moments of four alkyl titanates were determined in n-heptane solution by the method Halverstadt and Kumler. It was found that the values obtained for the ethyl, n-propyl, and n-butyl orthoesters were for the trimers, but those found for tert-butyl titanate were for the monomers. Variations of the dipole moments of these compounds with temperature change indicate the potential energy barrier to rotation of the alkoxy groups is of magnitude kT.

The crystal and molecular structures of monomethyltriethyl titanate was determined by x-ray diffraction techniques. Crystal data obtained are:

$a = 12.14 \text{ \AA}$	$\alpha = 76^\circ 56'$	density (meas.) = 1.244 g/cc
$b = 12.13$	$\beta = 77^\circ 2'$	density (calc.) = 1.236 g/cc
$c = 16.93$	$\gamma = 74^\circ 15'$	$Z = 8$

Space Group P1

In the solid state the molecules are linked together to form tetramer units. In the tetramers the four titanium atoms form a planar diamond shape, sharing oxygen atoms so that each titanium atom has a coordination number of six.

A preliminary investigation of an hydrolysis product of tetraethyl titanate was carried out. The unit cell of this crystal contains approximately 60 titanium atoms. Due to the complexity of this crystal and also to the fact that the molecular formula of the compound is uncertain, the structure determination was not completed. Crystal data obtained for this compound are:

$a = 27.92 \text{ \AA}$	density = 1.305 g/cc
$b = 22.40$	space group $P2_1/a$
$c = 23.30$	
$\beta = 117^\circ 15'$	

INTRODUCTION

The chemistry of organic compounds of titanium has been of interest for a number of years. In many ways the organic titanates exhibit unusual properties, some of which have lead to industrial uses in the paint and the electrical industries. To a large extent, however, understanding of their chemistry has been limited because the structures were not known. Only in very recent years have attempts been made to determine their structures by any of the various methods now used. The research reported in this dissertation is an attempt to provide some of the first accurate structural information about these compounds. Before describing the methods and results a brief review of the knowledge available at present will be given.

Gilman and Jones⁽²⁴⁾ have summarized early attempts to prepare organic titanium compounds. In 1875 Demarcay⁽²¹⁾ reported the first preparation of an alkyl titanate, but later investigators⁽³¹⁾ were unable to duplicate his work and showed that his compounds were probably a mixture of oxy-ethyl titanates. Probably the first preparation of a pure alkyl titanate was carried out in 1923 by Bischoff and Adkins⁽¹⁾. They reported obtaining the tetraethyl, tetraisopropyl, and tetramethyl titanates.

Since the early 1940's chemists have become concerned with the structures of these compounds and the mechanisms of their reactions, particularly with water. All of the alkyl titanates react with water, the rate of reaction generally increasing with decreasing molecular weight of the compound.

Much of the work carried on in this laboratory and described in this dissertation began with the investigation of tetraethyl titanate, as this

is probably the most unusual of this group. For several years it was reported in the literature to be a liquid at room temperature; however in 1950 Caughlan and Crowe⁽¹⁵⁾ showed that its normal state is solid. The pure compound is obtained as a liquid by distillation. If the liquid is allowed to stand for a considerable length of time, usually several months, small crystals form on the sides of the container, and eventually the entire liquid solidifies.

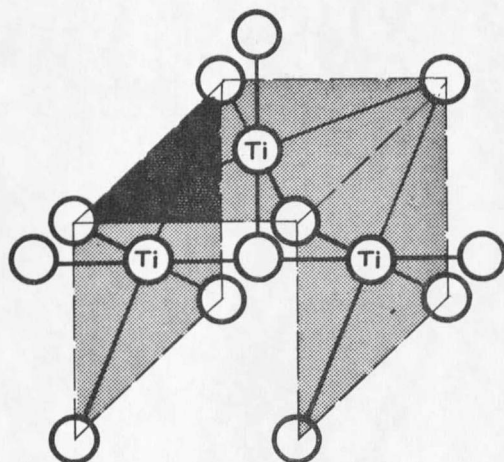
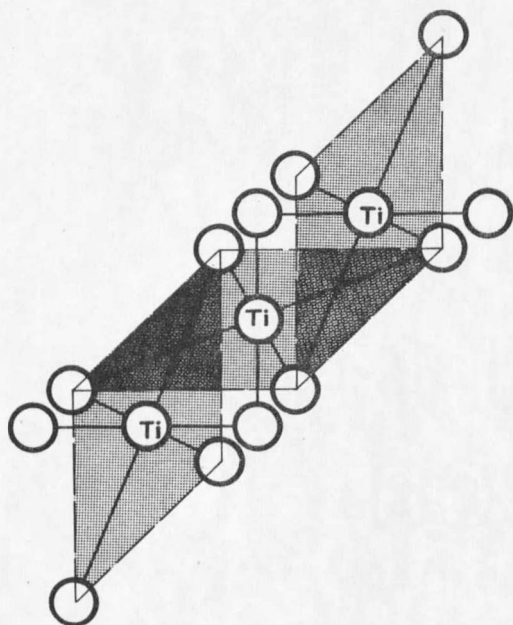
In this laboratory research on organic titanates started with a study of the dielectric properties of these compounds and the molecular weights in solution. Results of the molecular weight investigations showed that all of the orthoesters studied had an association number of three⁽¹³⁾. This association is not surprising when one considers the fact that the coordination number of titanium is six, whereas its primary valence number in the monomeric titanate is only four. To satisfy the coordination number of six, oxygens from surrounding titanate molecules must be used. The structures proposed for the trimer are shown in Figure 1; the linear structure in Figure 1a is the one that most generally has been accepted.

As already mentioned most of the alkyl titanates react readily with water. For small amounts of water the major products of the reaction are polymers, the size of the polymer depending on the amount of water added. D. C. Bradley and his associates have made a very thorough investigation of the hydrolysis of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ and, based on the trimer structure proposed by Caughlan, have proposed a set of reactions for the hydrolysis and structures for the hydrolysis products (2), (3), (4).

In order to confirm the trimeric structure of the alkyl titanates it was decided to determine the structure of the tetraethyl titanate by single crystal x-ray diffraction techniques. Crystals were obtained from an ethanol solution, and cell dimensions were determined from x-ray data. It was apparent in the early stages of this investigation that the crystals were not of the tetraethylate but of one of the hydrolysis products. Since good crystals of the hydrolysis product were now on hand, it was decided to continue the x-ray structure determination of this compound.

Crystals of monomethyltriethyl titanate were obtained by the method described by Varma and Mehrotra⁽³⁴⁾. Since this compound is also trimeric in solution, determination of this structure would serve to verify that proposed for the trimers. Accordingly, a major portion of this research is on the structure of $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$.

In addition to the x-ray examination of the two crystals mentioned, the dielectric properties of tetraethyl titanate, tetra-n-propyl titanate, tetra-tert-butyl titanate, and tetra-n-butyl titanate have been measured in n-heptane at 0°, 25°, and 50°C.



Proposed Structures for Trimeric Titanium Tetraethylate

(Carbons not Shown)

Figure 1

PART I

Dielectric Studies of Alkyl Titanates

The dipole moment of a compound is determined by its molecular structure. Aside from translational or rotational motion of the molecule as a whole, its atoms are not in fixed locations; they are in constant vibration about an average point, and atoms or groups of atoms may rotate about some bond in the molecule. Greater vibrations of the atoms at increased temperatures generally have little effect on the dipole moment since the average positions of the atoms are not changed. The degree to which an atom or group of atoms rotate about an axis may be affected by temperature, however, thus changing the dipole moment of the molecule. Comparison of measured and theoretically calculated dipole moments for alkyl titanates has indicated restriction of rotation of the alkoxy groups.

This dielectric study of the titanates was therefore undertaken to learn how the dipole moments are affected by temperature. From this, insight into the degree of restriction of rotation of the groups and to the energy barrier to rotation may be obtained.

Theory and Discussion of Methods

A detailed review of the theory of dielectric constants, polarization, and dipole moment may be found in the references (14), (20), and (29). However a brief discussion of the general theory will be given here.

Molecules, although neutral, possess small centers of negative and positive charges. In polar molecules there is a finite distance of separation between the centers of the negative and positive charges, and the

polarity of a molecule becomes less as these centers approach each other. When placed in an electric field a polar molecule will tend to orient itself, the charges lining up in the direction of the field. The force required to orient the molecule depends on the magnitude of the charges and on the distance between them. The dipole moment is a measure of these two quantities; it is the product of either charge e by the distance between them: $\mu = er$. It serves as a useful quantitative measure of the extent to which a molecule is polar. Thus dipole, or dielectric, studies provide some information concerning the shape of a molecule.

The dielectric constant of a substance is related to its degree of polarization in an electric field. Polarization is determined in this research by determining the extent to which the substance in the dissolved state in a solution of a nonpolar solvent contributes to the dielectric constant of the solution. By extrapolating the measurements of dielectric constant to infinite dilution, a value is obtained which corresponds to a situation in which the molecules are so far apart that they do not induce charges in each other.

The molar polarization of a substance can be calculated from the dielectric constant ϵ using a formula developed by Clausius and Mosotti on the basis of theories of electric charges induced by electric field:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d}$$

where P is the molar polarization, M the molecular weight, and d the density.

For a binary solution the equation can be written as

$$P_{12} = c_1 P_1 + c_2 P_2 = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \frac{c_1 M_1}{d_{12}} + \frac{c_2 M_2}{d_{12}}$$

where P is the molar polarization, ϵ the dielectric constant, d the density, c the concentration, and M molecular weight. The subscripts 1, 2, and 12 refer to solvent, solute, and solution, resp.

Assuming the dielectric constant and the specific volume of a binary solution to be linear functions of concentration, Halverstadt and Kumler⁽²⁵⁾ arrived at the following equation:

$$P_{\infty} = \frac{\epsilon_1}{\epsilon_1} \frac{-1}{+2} (M_2 v_1 + M_1 B) + \frac{3Av_1 M_1}{(\epsilon_1 + 2)^2},$$

where the meanings of the symbols are as follows:

P_{∞} is the molar polarization of solute at infinite dilution

ϵ_1 is the dielectric constant of solution at infinite dilution (intercept)

v_1 is the specific volume of solution at infinite dilution (intercept)

M_1 and M_2 are the molecular weights of solvent and solute, resp.

A is the slope of the dielectric constant-concentration curve

B is the slope of the specific volume-concentration curve.

The method of Halverstadt and Kumler takes into account the fact that the dielectric constant of the solvent may be considerably different from the measured dielectric constant of the pure solvent. This may be due partially to the absorption of water. This solvent polarization error is essentially eliminated by obtaining the dielectric constant of the pure solvent from extrapolation to infinite dilution. These authors point out that solvents with a low dielectric constant must be used.

The molar polarization determined by this method is the total polarization and is the sum of the orientation polarization, the atomic polarization, and the electronic polarization. The dipole moment of a

molecule can be calculated from the orientation polarization. Thus the atomic and electronic polarizations must be determined and subtracted from P_{∞} . Hence, $P_{\mu} = P_{\infty} - P_e - P_a$ where P_{μ} , P_{∞} , P_e , and P_a are the orientation, total, electronic, and atomic polarizations, resp.

The electronic polarization and molar refraction of a compound theoretically are the same for a high frequency oscillating electric field. According to Maxwell's relation, $\epsilon = n^2$ for a non-polar substance, where n is the refractive index. Thus n^2 is really a measure of the dielectric constant with the effects of the permanent dipoles and atomic effects removed. The reason for this is that the frequencies of optical light are so great that the dipoles of the molecules are unable to orient themselves fast enough, and only the effects due to electronic polarization are manifest. Thus by determining the refractive index of a substance, and its density, the electronic polarization may be determined. The molar refraction R is given by the relation $R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$.

The atomic polarization is not so easily determined. This contribution to the total polarization is usually quite small and is frequently omitted from calculations; sometimes it is assumed to be about 5% of the electronic polarization. In this work on titanium alkoxides the effect due to the atomic polarization has been neglected. Thus in this case the orientation polarization is calculated by subtracting the molar refraction from P_{∞} : $P_{\mu} = P_{\infty} - R - P_a$ where it is assumed that $P_a \approx 0$.

The dipole moment of a compound can be calculated from the orientation polarization by the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{P_{\mu} T} \text{ e.s.u.} = \sqrt{P_{\mu} T} \text{ Debye.}$$

A. Preparation of Compounds

The tetraethyl and tetra-n-propyl titanates were prepared by the sodium alkoxide method.⁽¹⁾⁽³¹⁾ Tetra-tert-butyl titanate was prepared by the pyridine-ammonia method,⁽⁵⁾⁽¹⁹⁾ while the n-butyl ester was obtained from E. I. duPont de Nemours and Co., Inc.

B. Dielectric Constant Apparatus

The electric circuit, the precision condenser, and the dielectric cell have been described before.⁽¹⁴⁾⁽¹⁵⁾ The dielectric cell was modified slightly by placing a thermostated reservoir on top of the cell, increasing the effective volume of the unit from 10 ml to about 25 ml. An opening in the top of the reservoir permitted inserting a metal thermister directly into the dielectric cell for accurate temperature measurement. A second opening permitted addition of solute to the solution in the cell. Both openings in the reservoir were sealed with ground glass stoppers so no evaporation of solvent nor absorption of water could take place except during the brief periods when solute was being added.

C. Density Apparatus

Densities of the solutions at 25° and at 50°C were obtained by the Westphal balance method. An analytic balance was modified for this purpose. A plummet of 15.65 ml capacity was made by sealing several grams of mercury into a glass tube. The solutions were placed in a thermostated container (80 ml) for the readings. Additional solute was easily added to this, the mixture being stirred by moving the bob up and down. A cork stopper sealed the solution from contact with air except for a small hole for the wire leading from the balance to the plummet.

A National Bureau of Standards thermometer also was immersed in the solution.

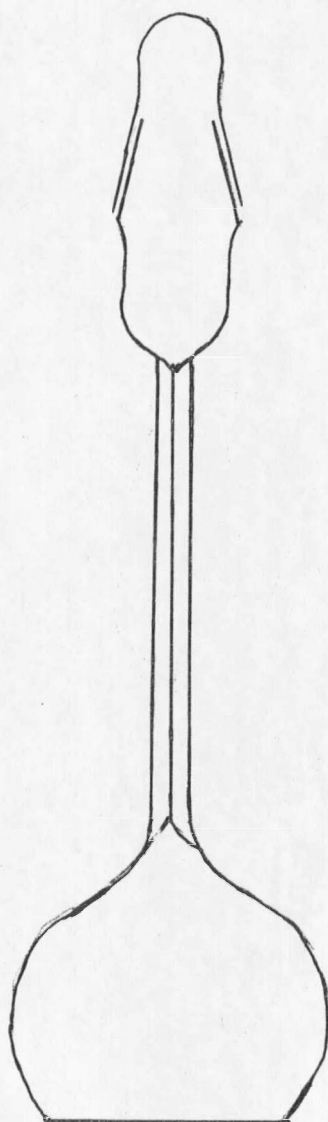
This method of determining densities of the solutions was very satisfactory for measurements at 25° and 50°C. However at zero degrees this apparatus gave very poor results due to rapid absorption of moisture from the air, hydrolyzing the solute. Placing the apparatus in a dry box did not help matters.

For low temperature density measurements two pycnometers (Figure 2) were made, one with a volume of 33.02 ml, the other with a volume of 30.73 ml at 0°C. The bulb of the pycnometer was attached by a capillary to a reservoir which was sealed off from the air by a ground glass stopper. The unit was immersed in a bath at the desired temperature. After thermal equilibrium was established, the volume of the solution was adjusted by removing excess liquid by a very fine capillary connected to an aspirator.

D. Temperature Control and Measurement

For density measurements temperature was maintained for the 25° and 50° runs by circulating water through the jacket of the cell, the water coming from a thermostat. Temperature of the solution in the cell was measured by a calibrated N.B.S. thermometer. Temperature at 0°C was obtained by immersing the pycnometers directly into a water-ice mixture in a Dewar flask.

Temperature of the solutions in the dielectric cell was obtained by passing a liquid (water at 25° and 50°, isopropyl alcohol at 0°) through the jacket of the cell. A constant temperature bath was used at



Pycnometer

Figure 2

the two higher temperatures, a refrigeration unit at the lower temperature. Temperature in the cell itself was determined by measuring the resistance of a metal thermister inserted in the inner cavity of the cylindrical capacitance unit. The thermister was calibrated against the N.B.S. thermometer.

E. Data and Results

The calibration of the pycnometer at 0° and of the dielectric cell at 0°, 25°, and 50° was made using n-heptane as a standard. The dielectric constants of heptane which were used at these temperatures are those reported by Dornste and Smyth;⁽²²⁾ densities are those given by Smyth and Stoops.⁽³⁰⁾ The capacitance of the dielectric cell was determined at the start of each run.

The n-heptane used in these determinations was obtained from Phillips Petroleum Co. and was dried by distillation from sodium.

Dielectric constants and densities were determined as described. Results of these measurements are tabulated in Tables I through X and depicted in Figures 3 through 22. Molar polarizations at infinite dilution were calculated by the method of Halverstadt and Kumler as described on page 6. The slopes and intercepts of the dielectric constant-mole fraction and specific volume-mole fraction curves were obtained by the method of least squares.

For the calculations involved, a program was written for the I.B.M. 650 computer. This program computed the intercepts and slopes of the dielectric constant and specific volume versus mole fraction curves by the method of least squares, and also calculated the total

polarization and the dipole moment. Results of these calculations are shown in Table XI. Values for the refractive indices and densities of the pure liquids are given in Table XII.

In the compounds investigated there is the possibility of rotation of the hydrocarbon chains about the titanium-oxygen bonds. If there is restriction of rotation, the dipole moment should be a function of temperature. As the temperature is increased, more thermal energy is available to overcome the potential energy barrier to rotation. Thus the dipole moment should vary with temperature and approach the theoretical value calculated assuming complete freedom of rotation. Using the Eyring equation⁽²³⁾ Crowe and Caughlan⁽¹⁵⁾ calculated the dipole moment of titanium tetraethoxide assuming complete freedom of rotation of the ethoxy groups and obtained a value of 2.11D.

Figure 23 shows graphically the variation of dipole moment of the ethyl, n-propyl, and n-butyl esters with temperature. The dipole moment of each is seen to increase with temperature toward the computed value of 2.11D for the ethyl titanate, indicating that the molecules do not exhibit complete freedom of rotation. This result suggests that the potential energy barrier is of the same order of magnitude as the thermal energy, i.e., kT .

Tetraethyl Titanate

Table I

<u>Temperature</u>	<u>Dielectric Constant Values</u>		<u>Specific Volume Values</u>	
	<u>mole fraction</u>	<u>dielectric constant</u>	<u>mole fraction</u>	<u>specific volume</u>
50°	0.006412	1.8944	0.001114	1.5189
	.008535	1.8985	.002442	1.5171
	.007135	1.8957	.003686	1.5155
	.003340	1.8888	.004894	1.5138
	.004849	1.8916	.006085	1.5124
	.004826	1.8916	.007409	1.5106
	.009506	1.9005	.000000	1.5205
	.003598	1.8900		
	.004679	1.8908		
	.001959	1.8851		
	.000000	1.8810		

Tetraethyl Titanate

Table II

<u>Temperature</u>	<u>Dielectric Constant Values</u>		<u>Specific Volume Values</u>	
	<u>mole fraction</u>	<u>dielectric constant</u>	<u>mole fraction</u>	<u>specific volume</u>
25°	0.004844	1.9289	0.000942	1.4702
	.005553	1.9305	.002110	1.4687
	.003875	1.9265	.003031	1.4676
	.007396	1.9338	.004004	1.4663
	.003633	1.9273	.004975	1.4652
	.003911	1.9273	.006596	1.4632
	.005824	1.9310	.000000	1.4713
	.007705	1.9346		
	.004567	1.9277		
	.002015	1.9220		
	.009035	1.9363		
	.000000	1.9180		

Tetraethyl Titanate

Table III

<u>Temperature</u>	<u>Dielectric Constant Values</u>		<u>Specific Volume Values</u>	
	<u>mole fraction</u>	<u>dielectric constant</u>	<u>mole fraction</u>	<u>specific volume</u>
0°C	0.006281	1.9671	0.026517	1.3961
	.004279	1.9622	.018505	1.4055
	.002840	1.9597	.012689	1.4125
	.008256	1.9715	.009174	1.4168
	.004876	1.9638	.000000	1.4278
	.004626	1.9638		
	.002860	1.9597		
	.006476	1.9675		
	.006499	1.9678		
	.005259	1.9650		
	.000000	1.9540		

Tetrapropyl Titanate

Table IV

<u>Temperature</u>	<u>Dielectric Constant Values</u>		<u>Specific Volume Values</u>	
	<u>mole fraction</u>	<u>dielectric constant</u>	<u>mole fraction</u>	<u>specific volume</u>
50°	0.004170	1.8892	0.002214	1.5169
	.005630	1.8932	.003541	1.5149
	.003092	1.8883	.005200	1.5122
	.010429	1.9037	.006959	1.5098
	.007441	1.8977	.008907	1.5070
	.007228	1.8969	.000000	1.5205
	.004293	1.8908		
	.006476	1.8957		
	.010867	1.9042		
	.003823	1.8892		
	.000000	1.8810		

Tetrapropyl Titanate

Table V

<u>Temperature</u>	<u>Dielectric Constant Values</u>		<u>Specific Volume Values</u>	
	<u>mole fraction</u>	<u>dielectric constant</u>	<u>mole fraction</u>	<u>specific volume</u>
25°C	0.005723	1.9313	0.000456	1.4705
	.003013	1.9261	.001276	1.4694
	.005762	1.9310	.002206	1.4680
	.003622	1.9265	.003385	1.4661
	.006229	1.9322	.004358	1.4649
	.003499	1.9265	.005409	1.4634
	.003755	1.9269	.000000	1.4713
	.002375	1.9240		
	.009647	1.9391		
	.005315	1.9301		
	.007352	1.9344		
	.000000	1.9180		

Tetrapropyl Titanate

Table VI

<u>Temperature</u>	<u>Dielectric Constant Values</u>		<u>Specific Volume Values</u>	
	<u>mole fraction</u>	<u>dielectric constant</u>	<u>mole fraction</u>	<u>specific volume</u>
0°C	0.006119	1.9679	0.013070	1.4102
	.005425	1.9679	.008754	1.4161
	.001837	1.9589	.006053	1.4197
	.008402	1.9736	.003995	1.4225
	.002579	1.9609	.002863	1.4240
	.005575	1.9670	.000000	1.4278
	.003418	1.9626		
	.006580	1.9695		
	.002777	1.9611		
	.005930	1.9675		
	.010924	1.9784		
	.000000	1.9540		

Tetra-n-butyl Titanate

Table VII

<u>Temperature</u>	<u>Dielectric Constant Values</u>		<u>Specific Volume Values</u>	
	<u>mole fraction</u>	<u>dielectric constant</u>	<u>mole fraction</u>	<u>specific volume</u>
50°C	0.002636	1.8879	0.001418	1.5182
	.003384	1.8891	.002721	1.5160
	.009277	1.9013	.004060	1.5137
	.002555	1.8875	.005265	1.5116
	.005285	1.8924	.006587	1.5092
	.004861	1.8920	.007932	1.5070
	.009510	1.9034	.000000	1.5205
	.004728	1.8916		
	.005445	1.8932		
	.003993	1.8900		
	.005833	1.8944		
	.008346	1.9005		
	.000917	1.8846		
	.007346	1.8976		
	.002251	1.8871		
	.001108	1.8847		
	.000000	1.8810		

Tetra-n-butyl Titanate

Table VIII

<u>Temperature</u>	<u>Dielectric Constant Values</u>		<u>Specific Volume Values</u>	
	<u>mole fraction</u>	<u>dielectric constant</u>	<u>mole fraction</u>	<u>specific volume</u>
25°C	0.003964	1.9285	0.000944	1.4697
	.002845	1.9249	.001911	1.4681
	.006618	1.9338	.002642	1.4672
	.001949	1.9236	.003414	1.4660
	.005114	1.9301	.004168	1.4646
	.001959	1.9232	.005067	1.4634
	.003675	1.9273	.000000	1.4713
	.004093	1.9281		
	.005286	1.9301		
	.000000	1.9180		
	.006321	1.9326		

Tetra-n-butyl Titanate

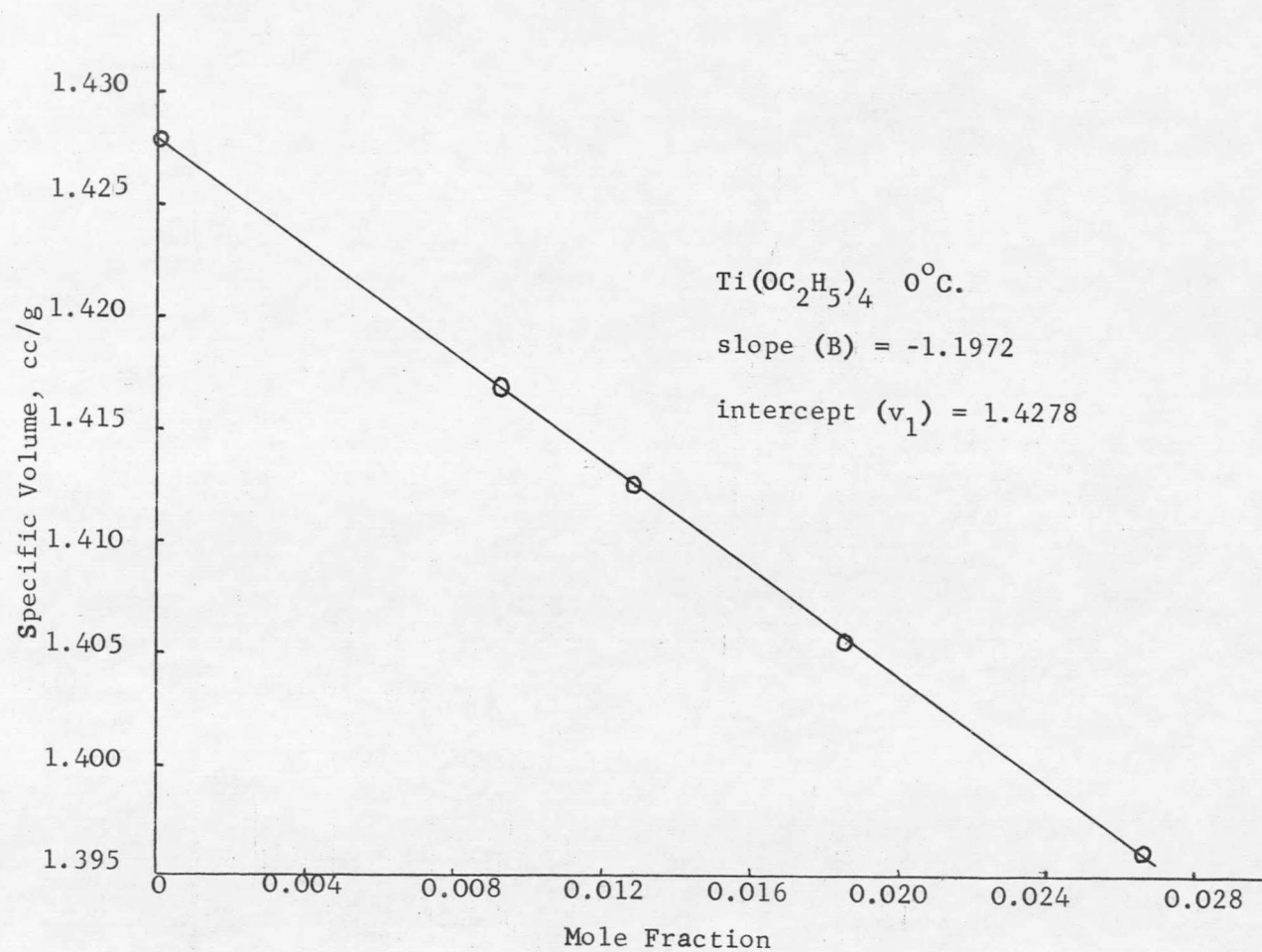
Table IX

<u>Temperature</u>	<u>Dielectric Constant Values</u>		<u>Specific Volume Values</u>	
	<u>mole fraction</u>	<u>dielectric constant</u>	<u>mole fraction</u>	<u>specific volume</u>
0°C	0.004616	1.9658	0.001711	1.4252
	.005135	1.9666	.001278	1.4259
	.003003	1.9610	.003013	1.4233
	.006410	1.9695	.003415	1.4226
	.002782	1.9617	.003742	1.4223
	.002626	1.9609	.001268	1.4259
	.007667	1.9727	.000000	1.4278
	.006703	1.9695		
	.002549	1.9613		
	.008611	1.9748		
	.002860	1.9617		
	.000000	1.9540		

Tetra-tert-butyl Titanate

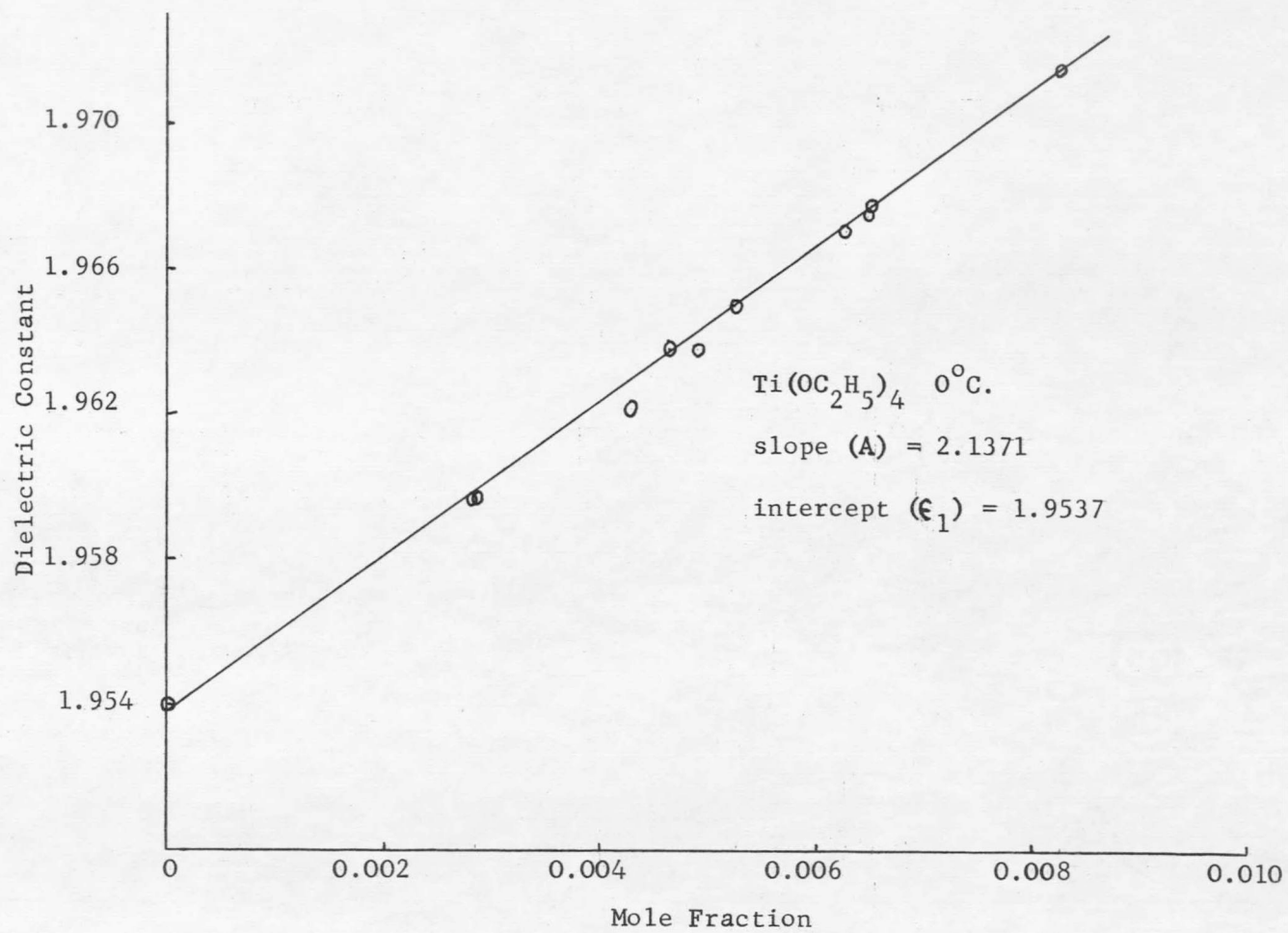
Table X

<u>Temperature</u>	<u>Dielectric Constant Values</u>		<u>Specific Volume Values</u>	
	<u>mole fraction</u>	<u>dielectric constant</u>	<u>mole fraction</u>	<u>specific volume</u>
25°C	0.000000	1.9180	0.000779	1.4705
	.001290	1.9215	.001536	1.4696
	.002295	1.9239	.002326	1.4688
	.003385	1.9272	.003150	1.4678
	.004486	1.9304	.004101	1.4667
	.005017	1.9318	.005216	1.4654
	.005970	1.9345	.000000	1.4713
	.006727	1.9365		
	.007204	1.9383		
	.008103	1.9410		



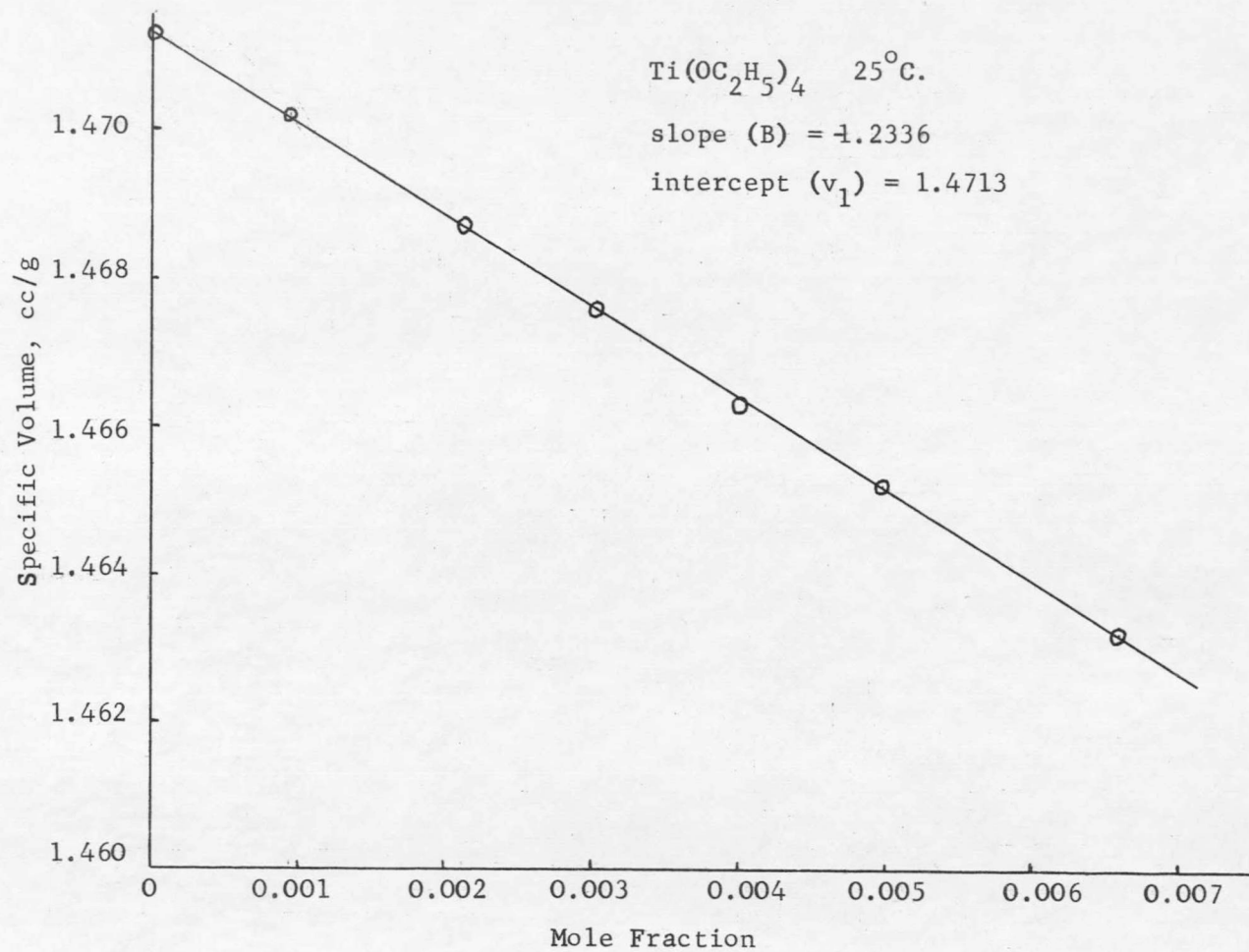
Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_2\text{H}_5)_4$, 0°C .

Figure 3



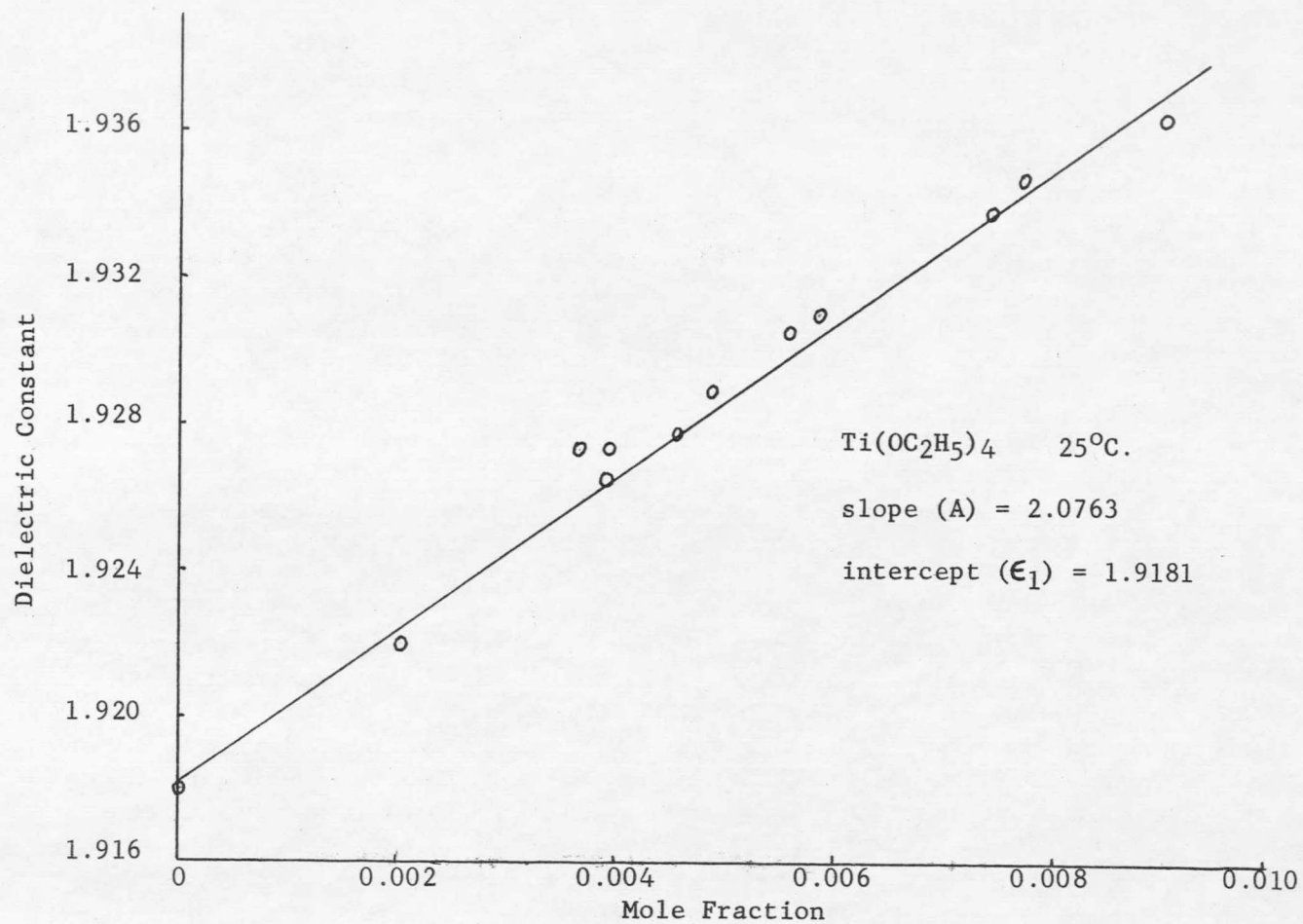
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_2\text{H}_5)_4$, 0°C .

Figure 4



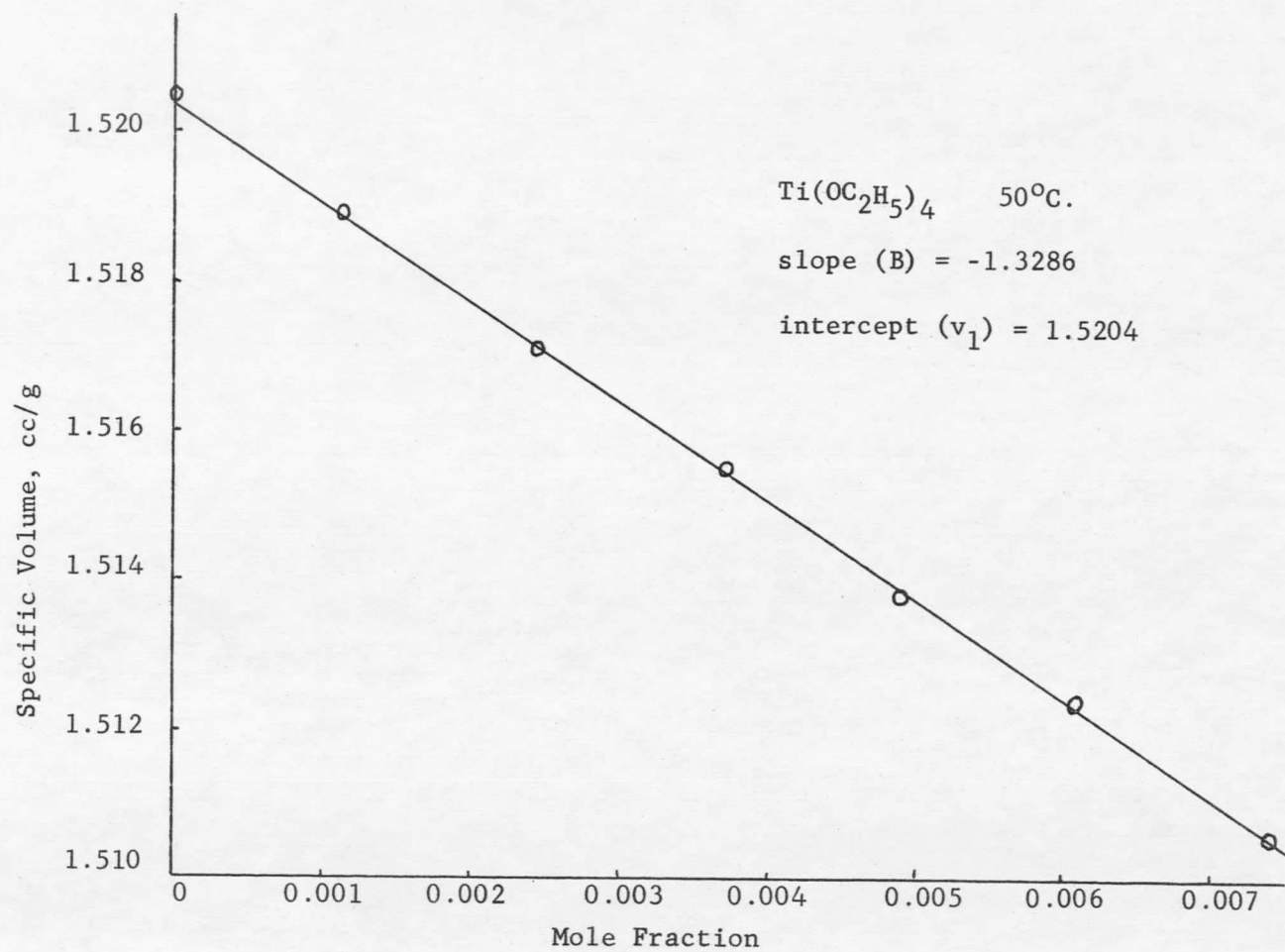
Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_2\text{H}_5)_4$, 25°C.

Figure 5



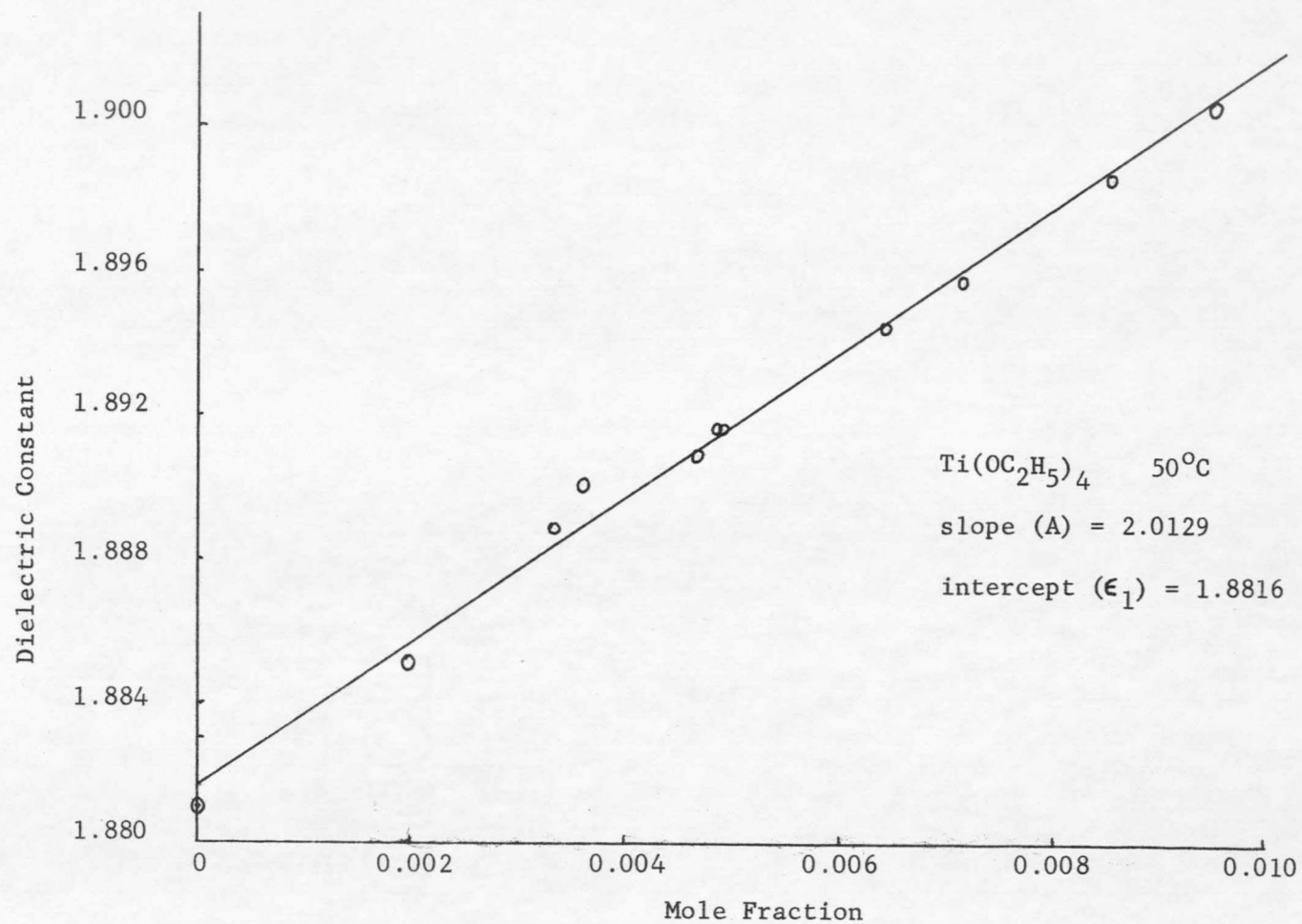
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_2\text{H}_5)_4$, 25°C

Figure 6



Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_2\text{H}_5)_4$, 50°C.

Figure 7



Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_2\text{H}_5)_4$, 50°C .

Figure 8

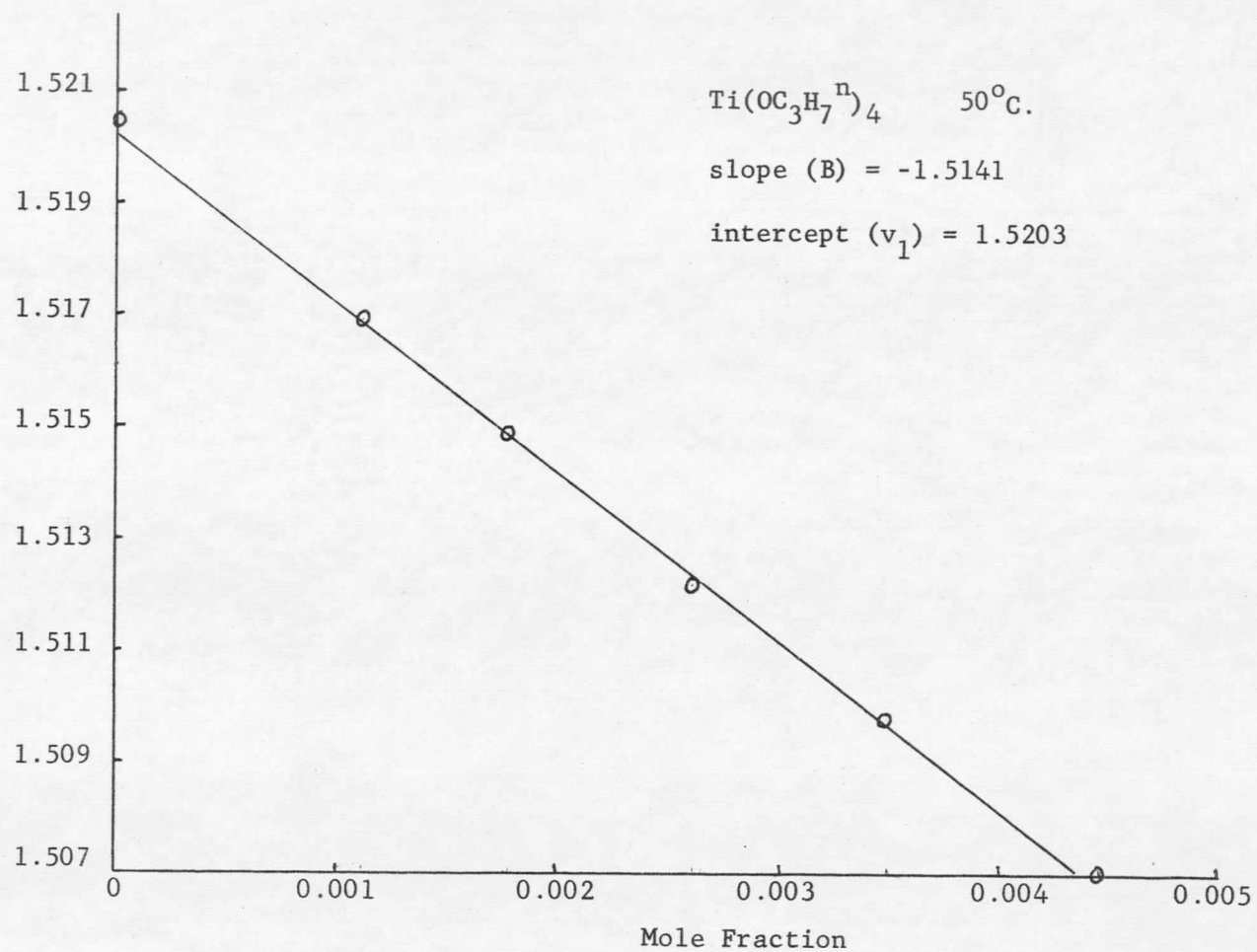
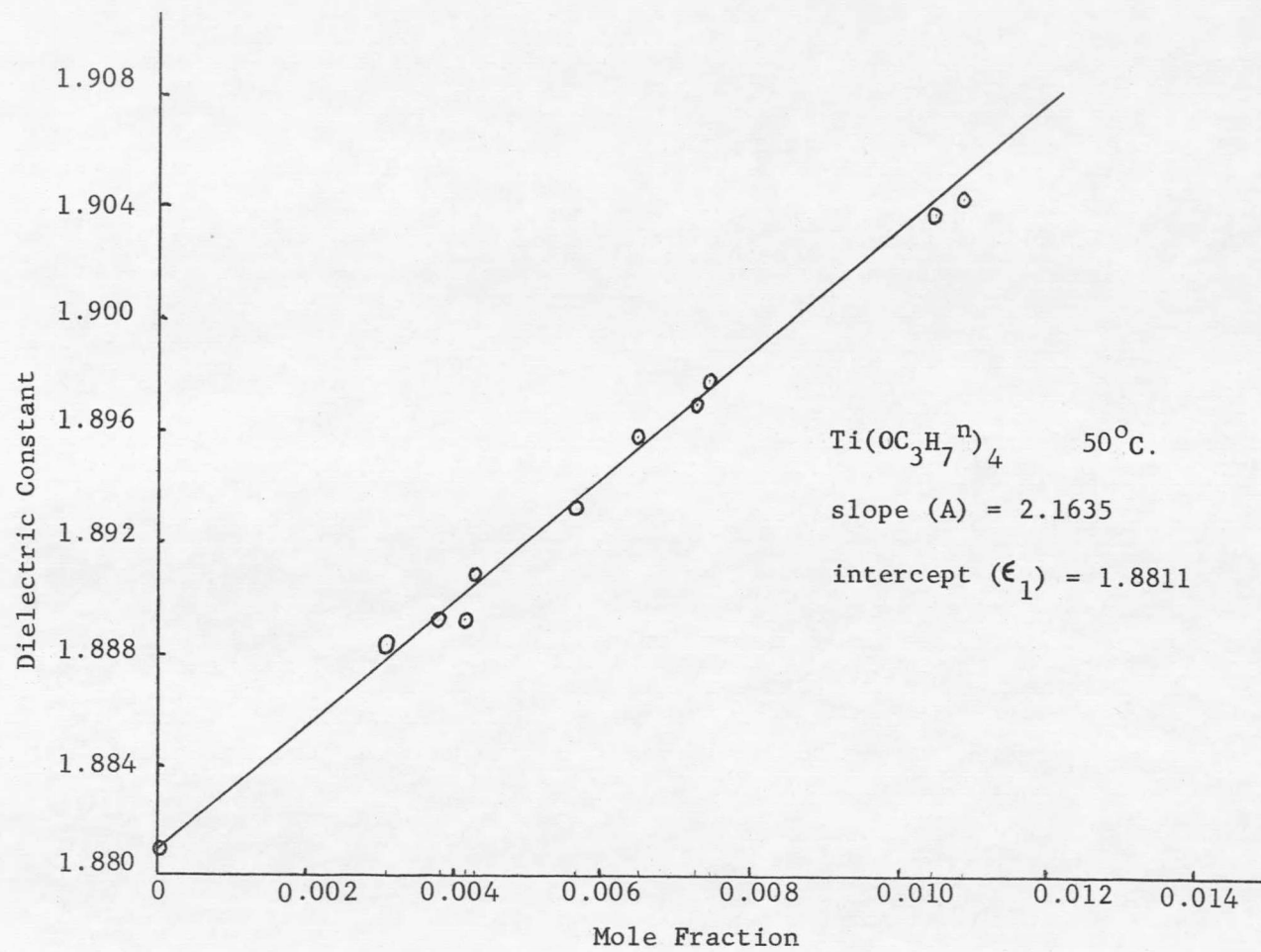
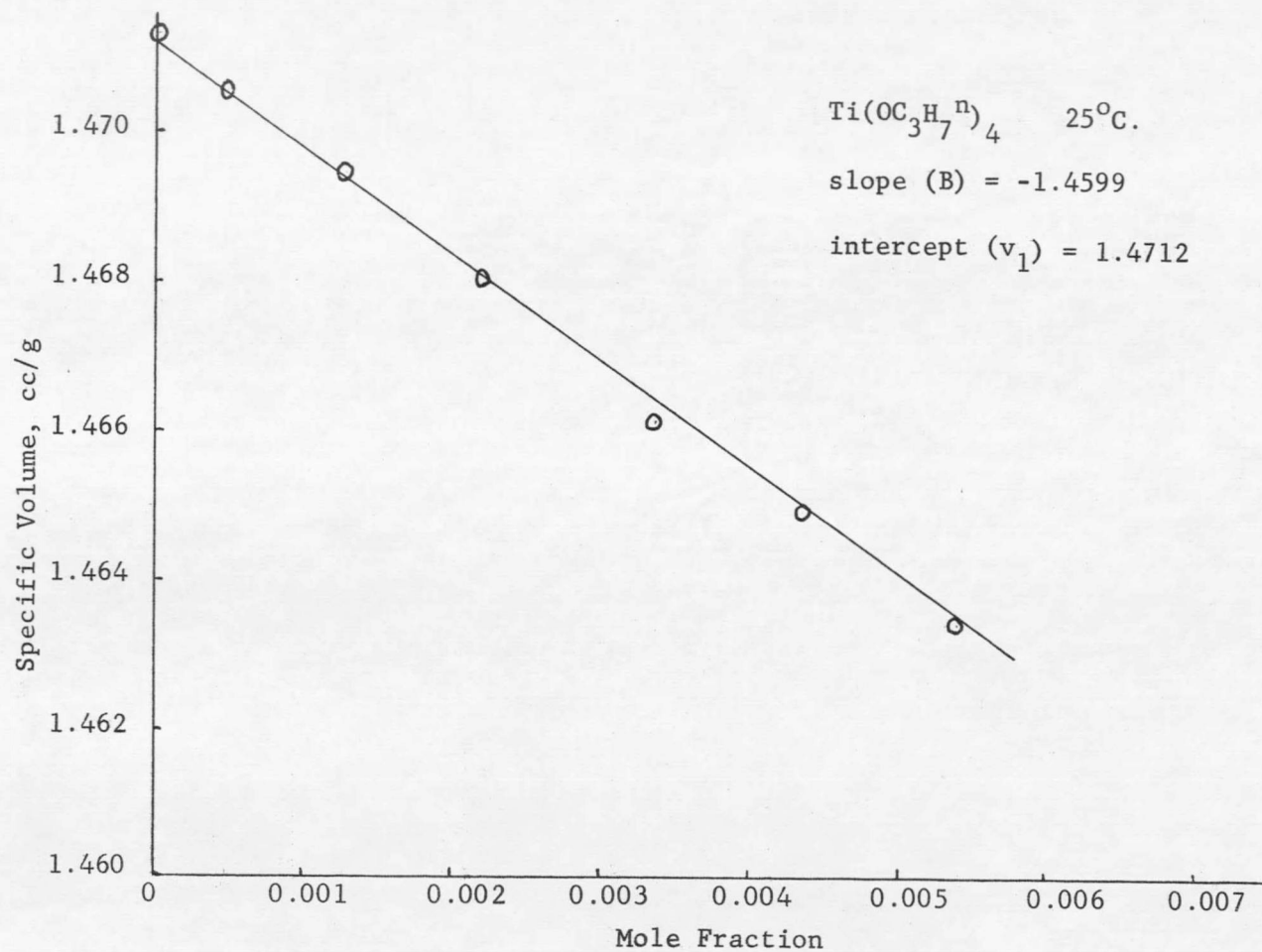


Figure 9



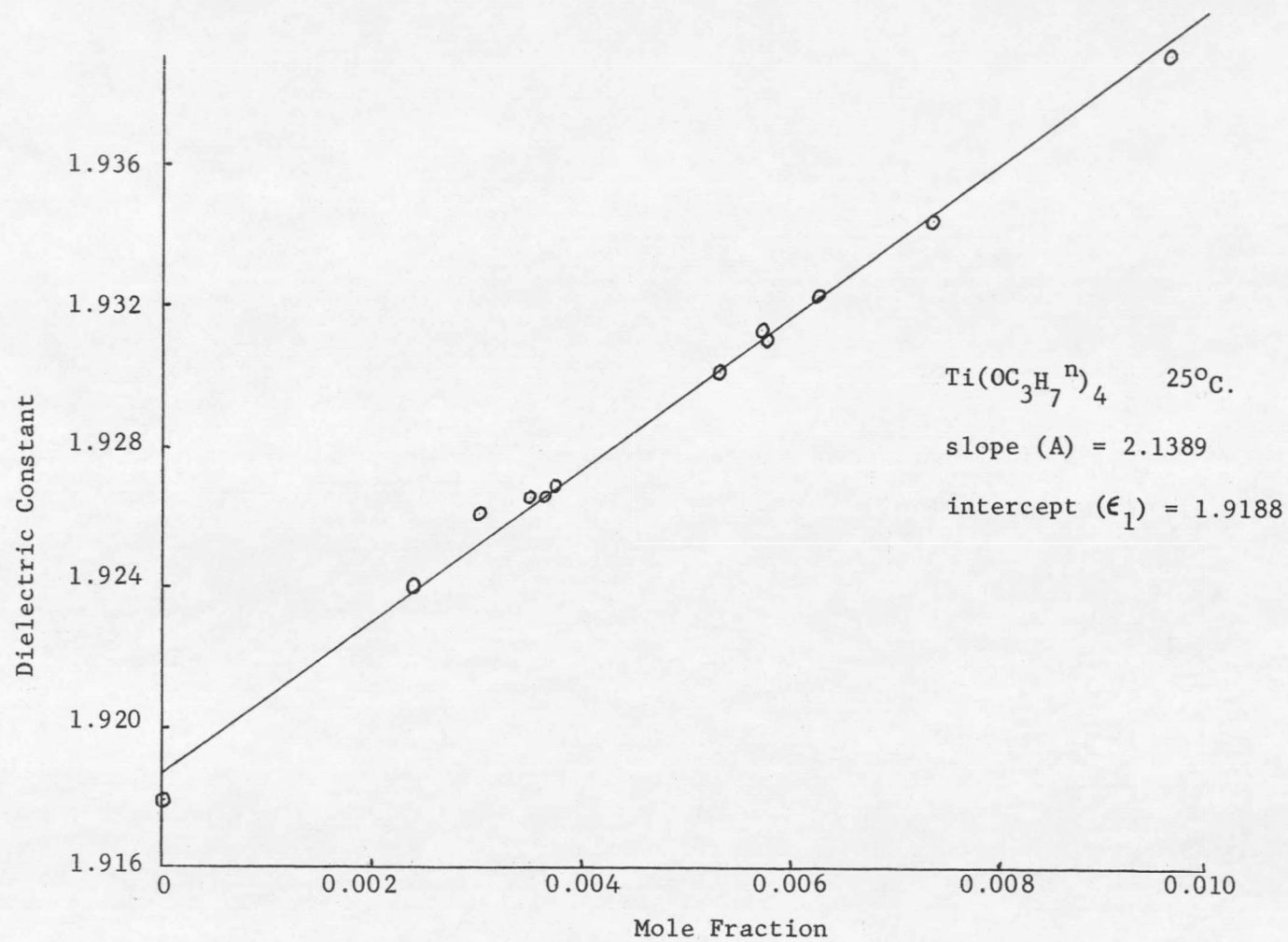
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_3\text{H}_7^n)_4$, 50°C .

Figure 10



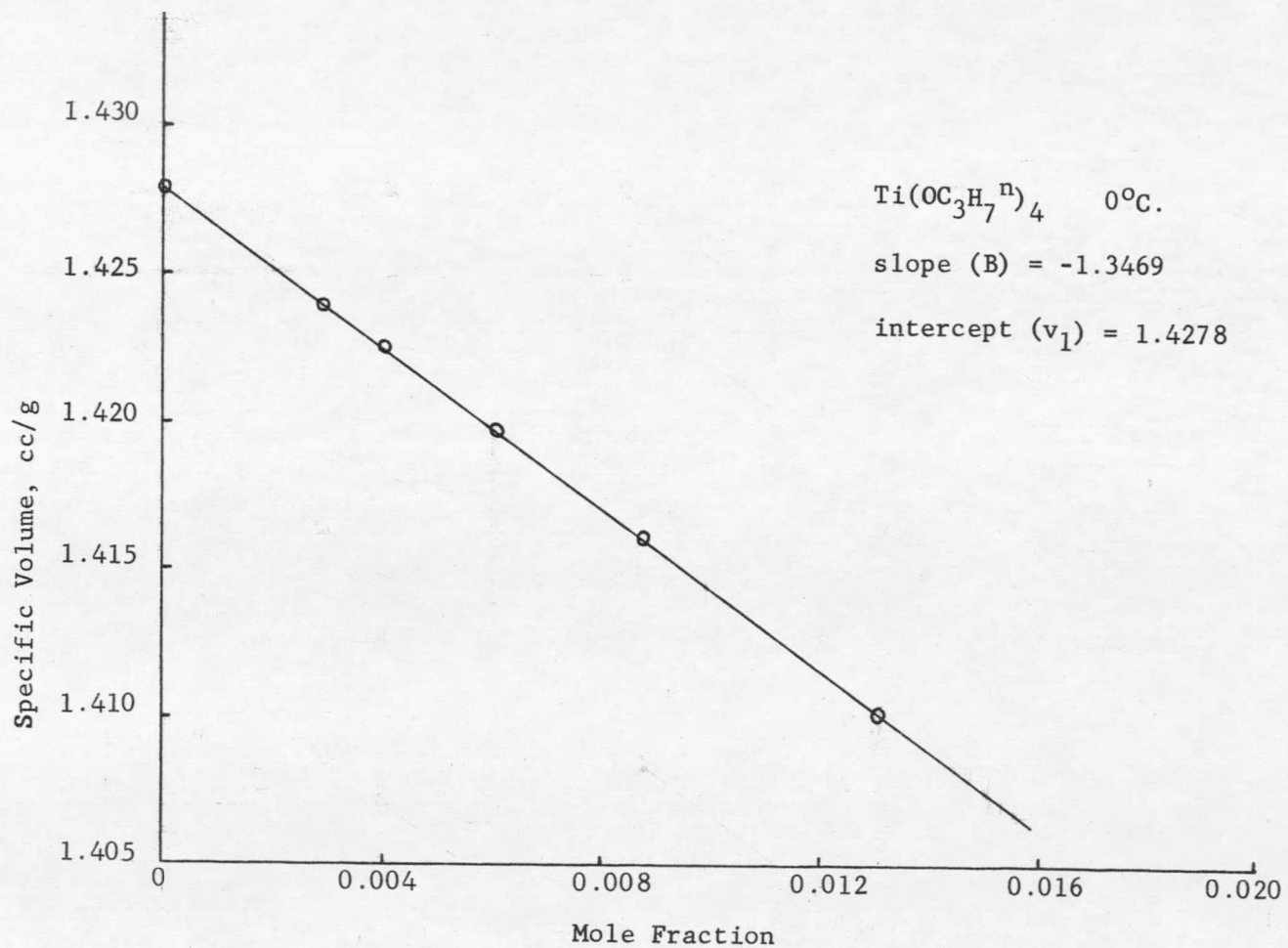
Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_3\text{H}_7^n)_4$, 25°C.

Figure 11



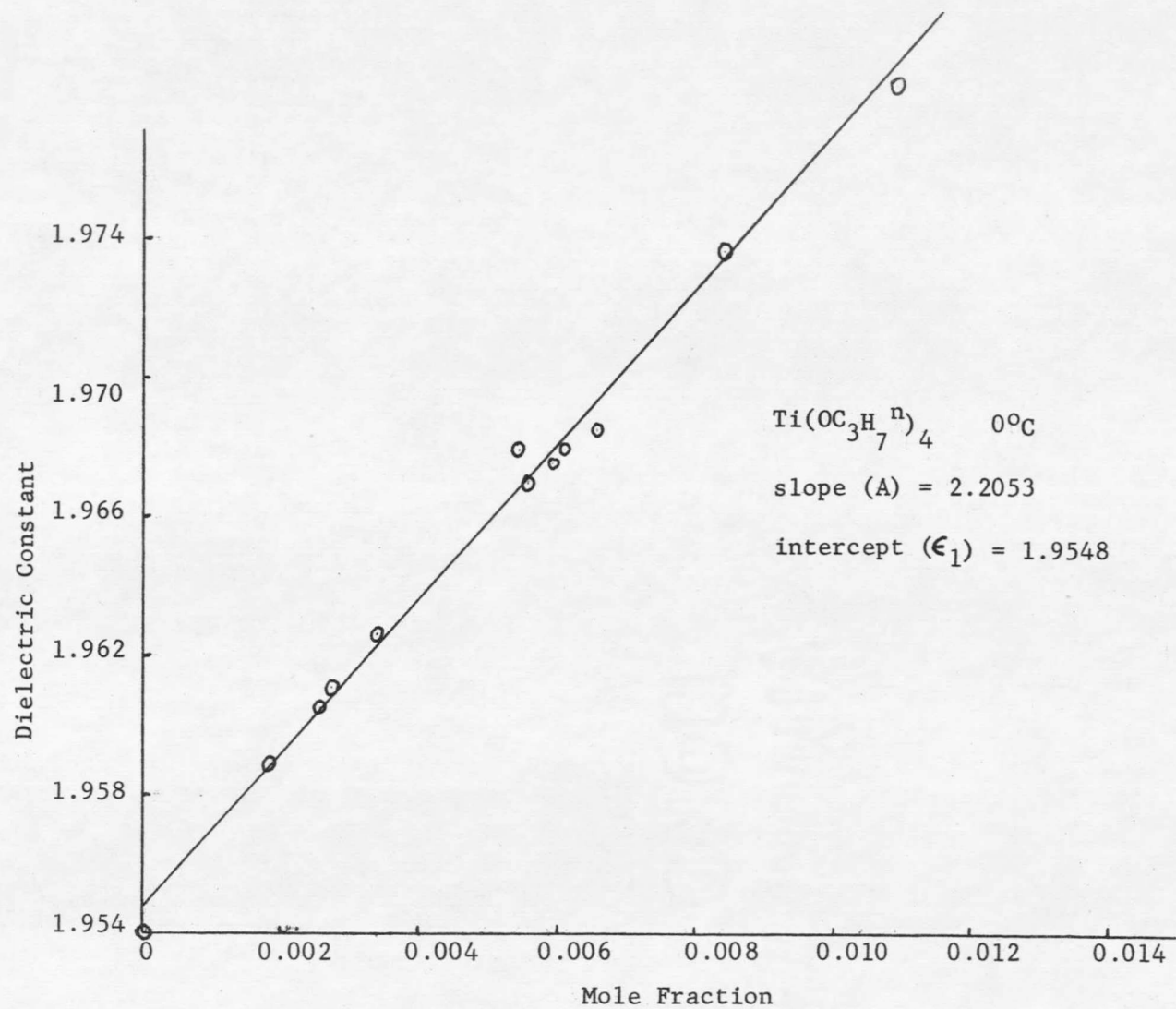
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_3\text{H}_7^n)_4$, 25°C .

Figure 12



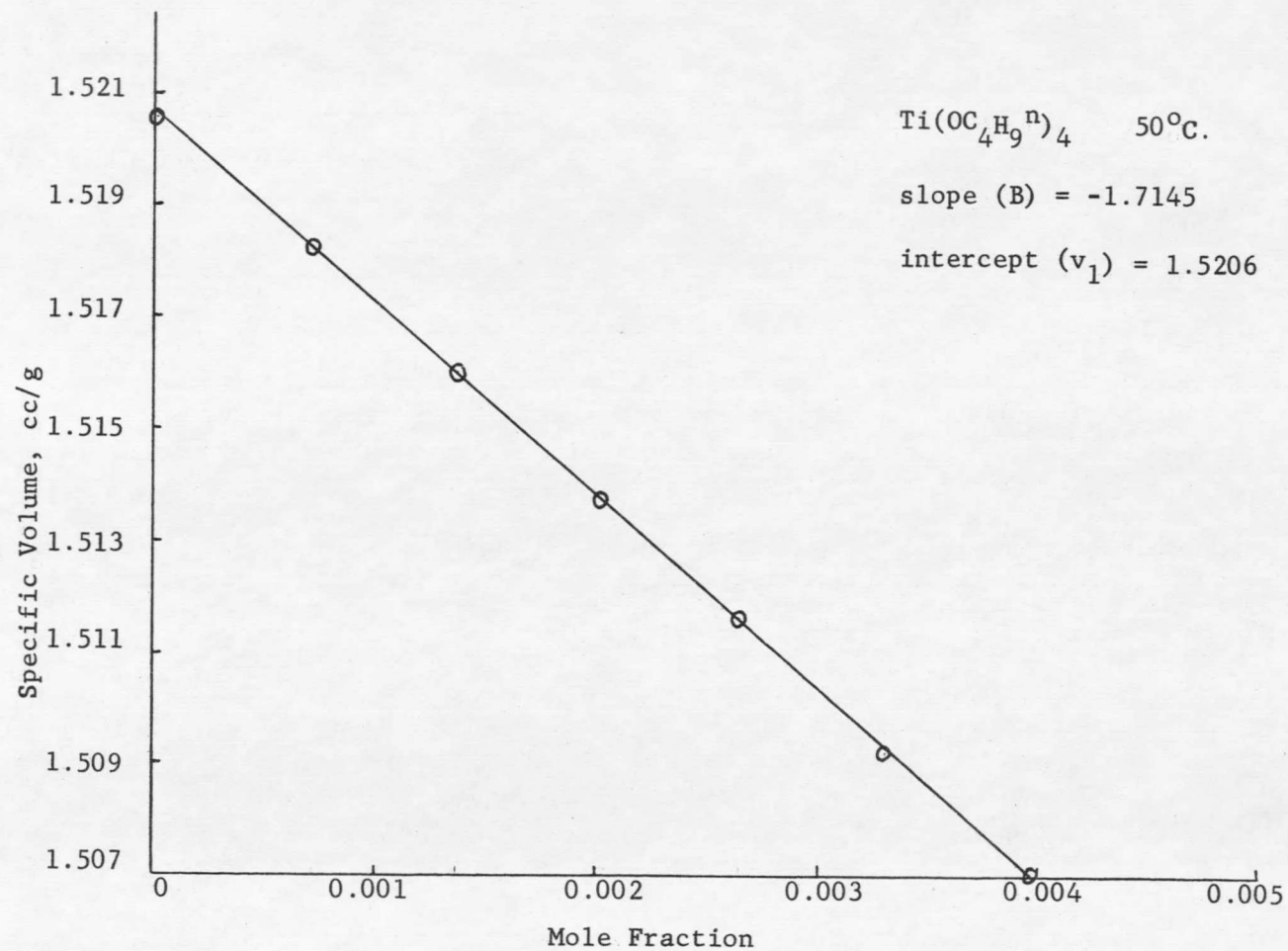
Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_3\text{H}_7^n)_4$, 0°C.

Figure 13



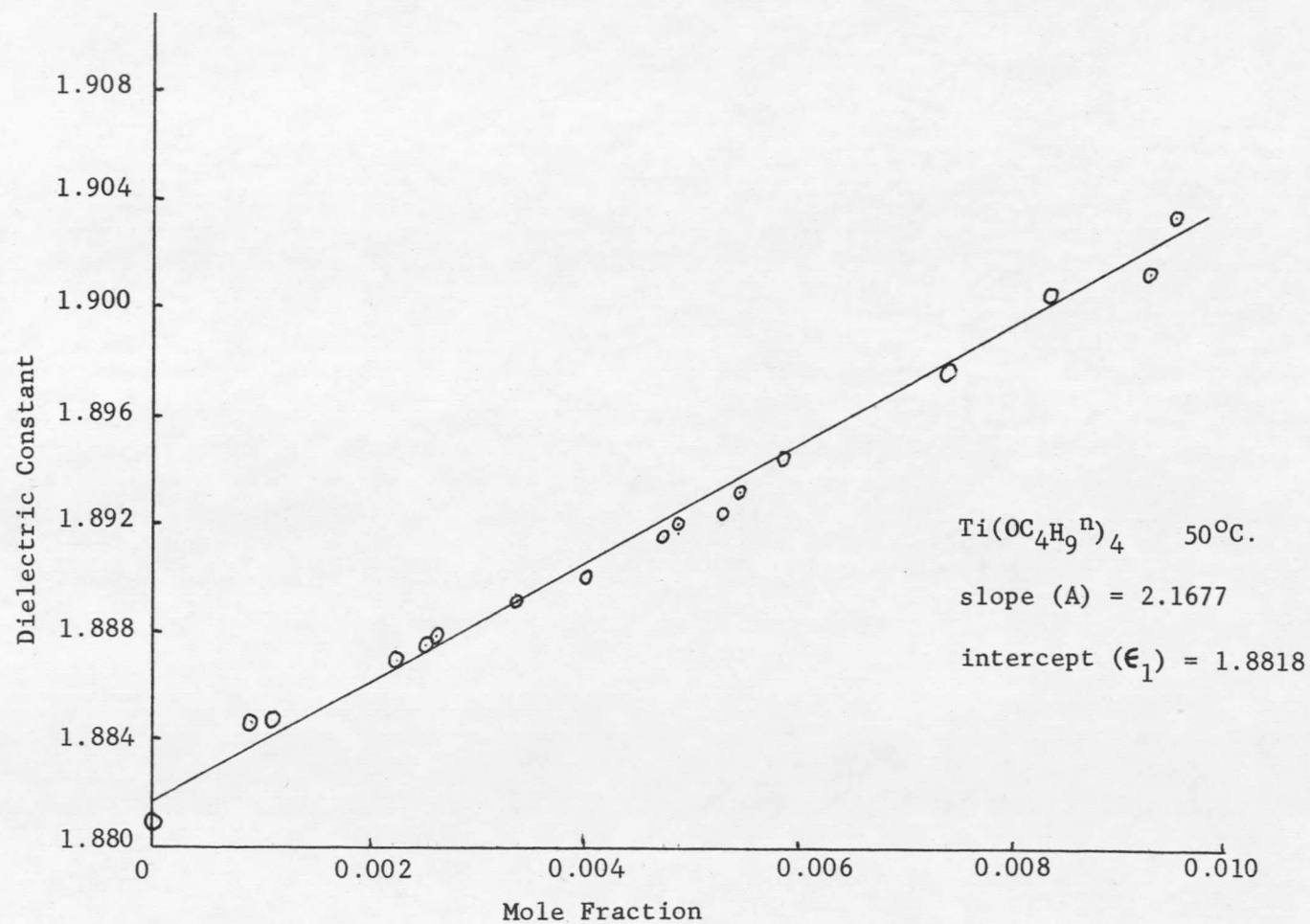
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_3\text{H}_7^n)_4$, 0°C .

Figure 14



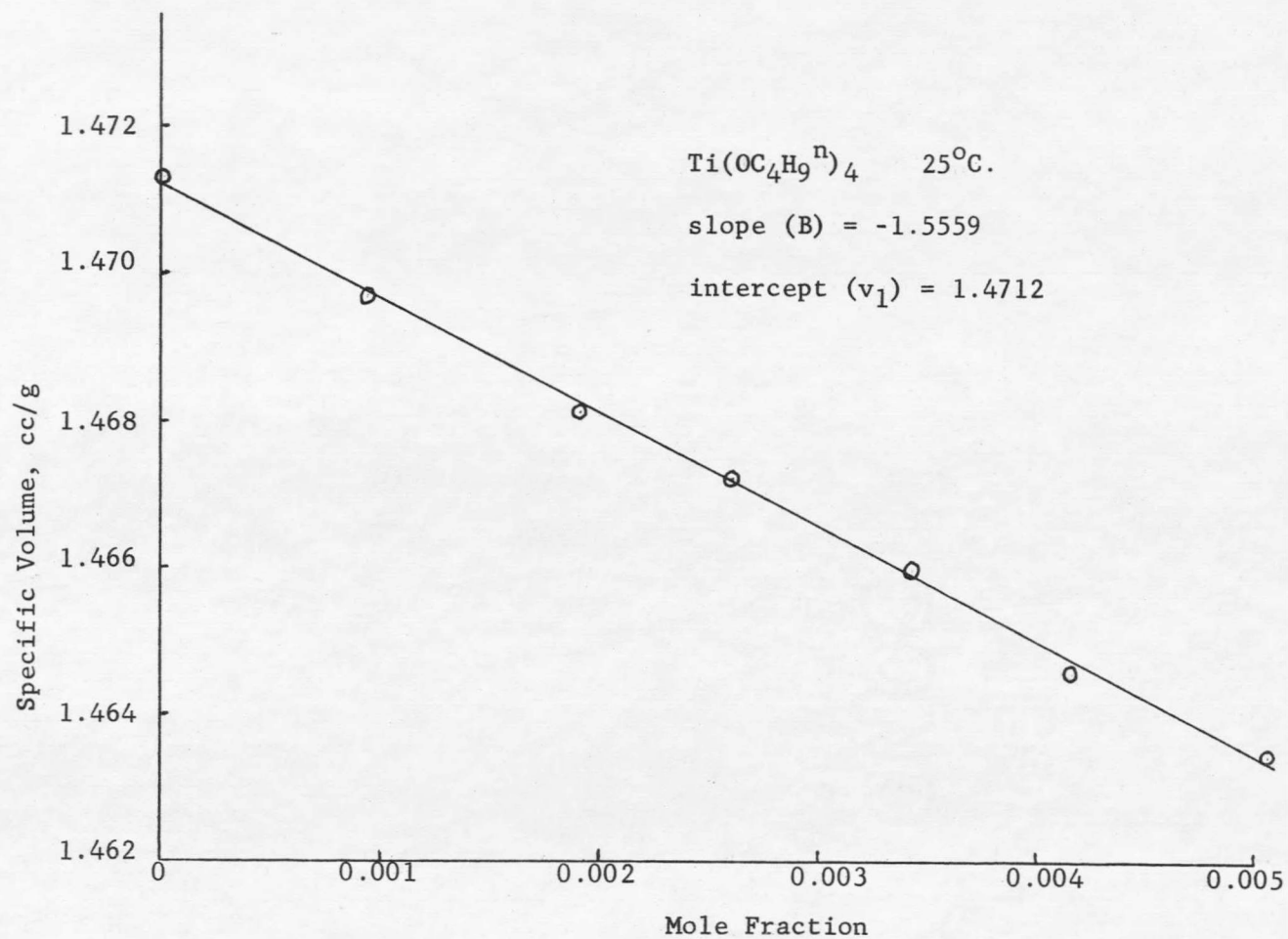
Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_4\text{H}_9^n)_4$, 50°C

Figure 15



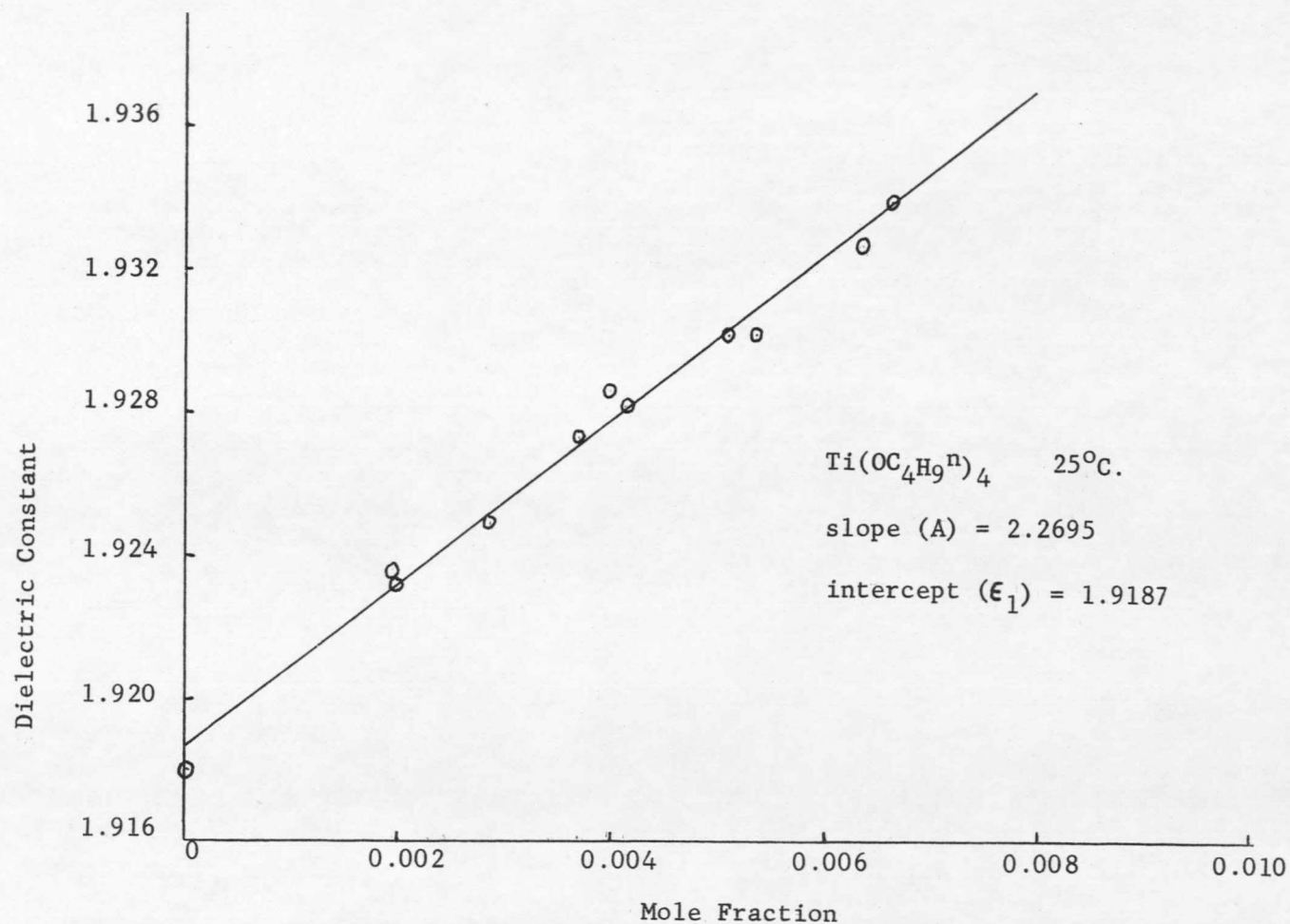
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_4\text{H}_9^n)_4$, 50°C .

Figure 16



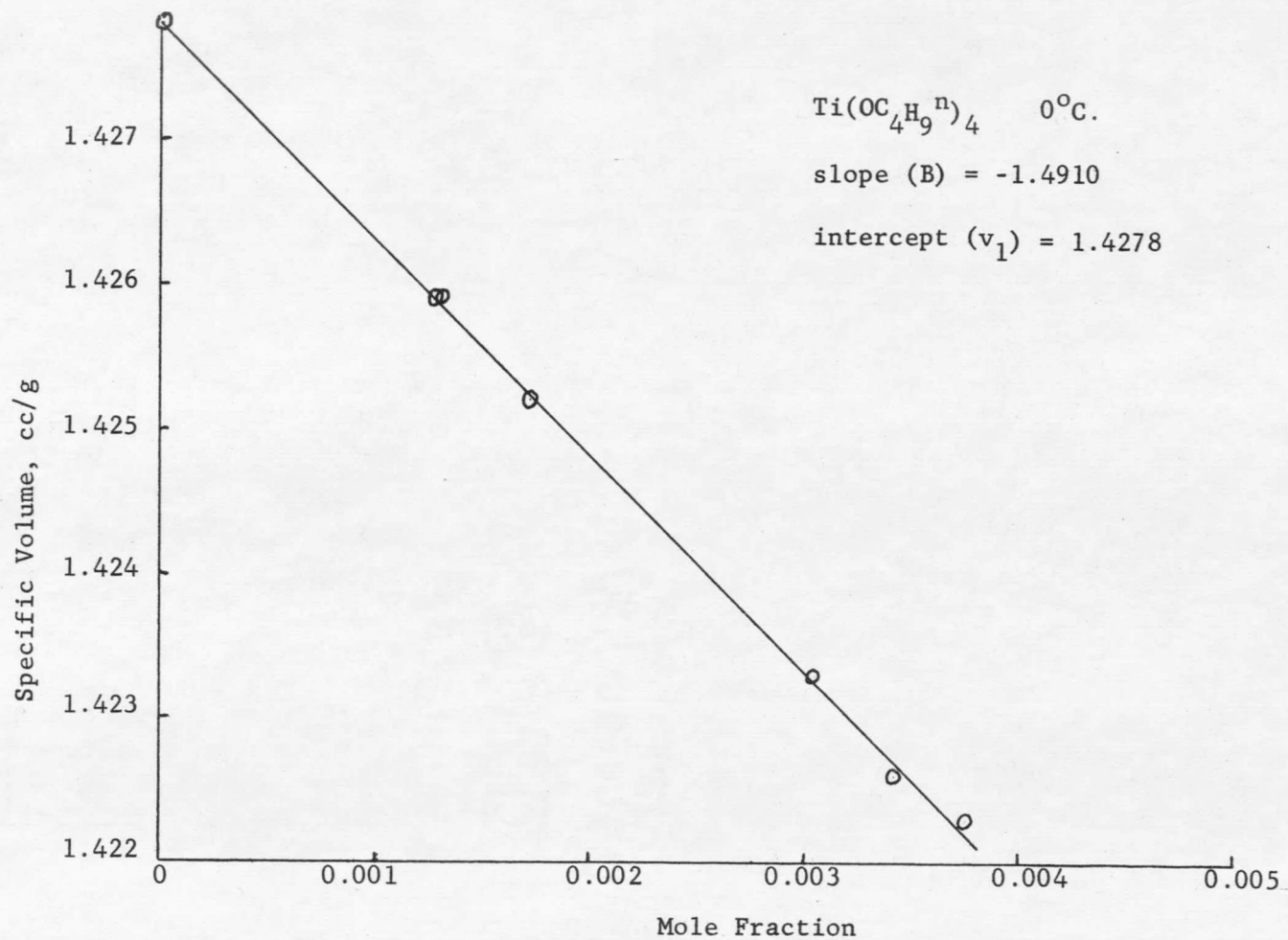
Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_4\text{H}_9^n)_4$, 25°C.

Figure 17



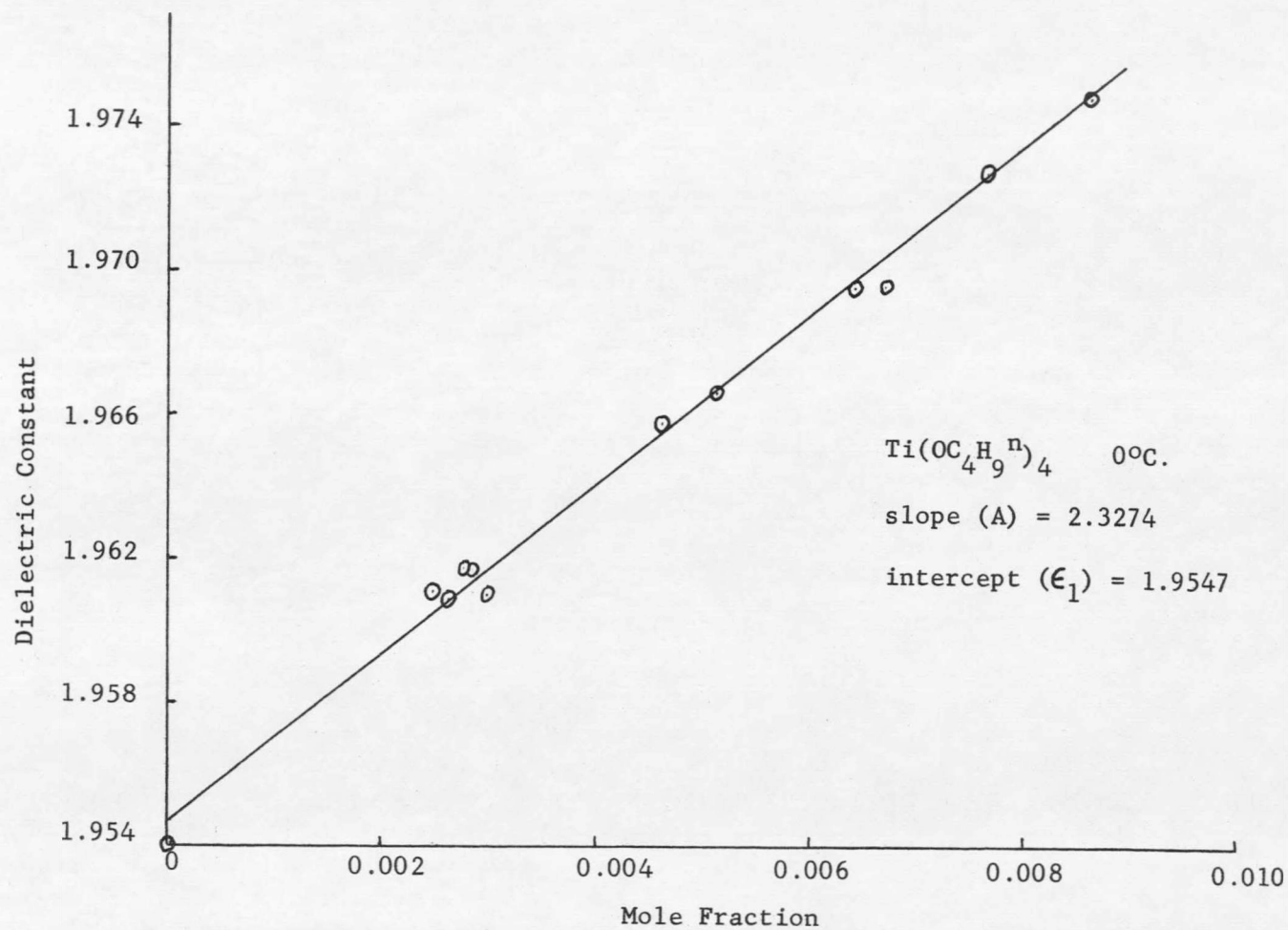
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_4\text{H}_9^{\text{n}})_4$, 25°C

Figure 18



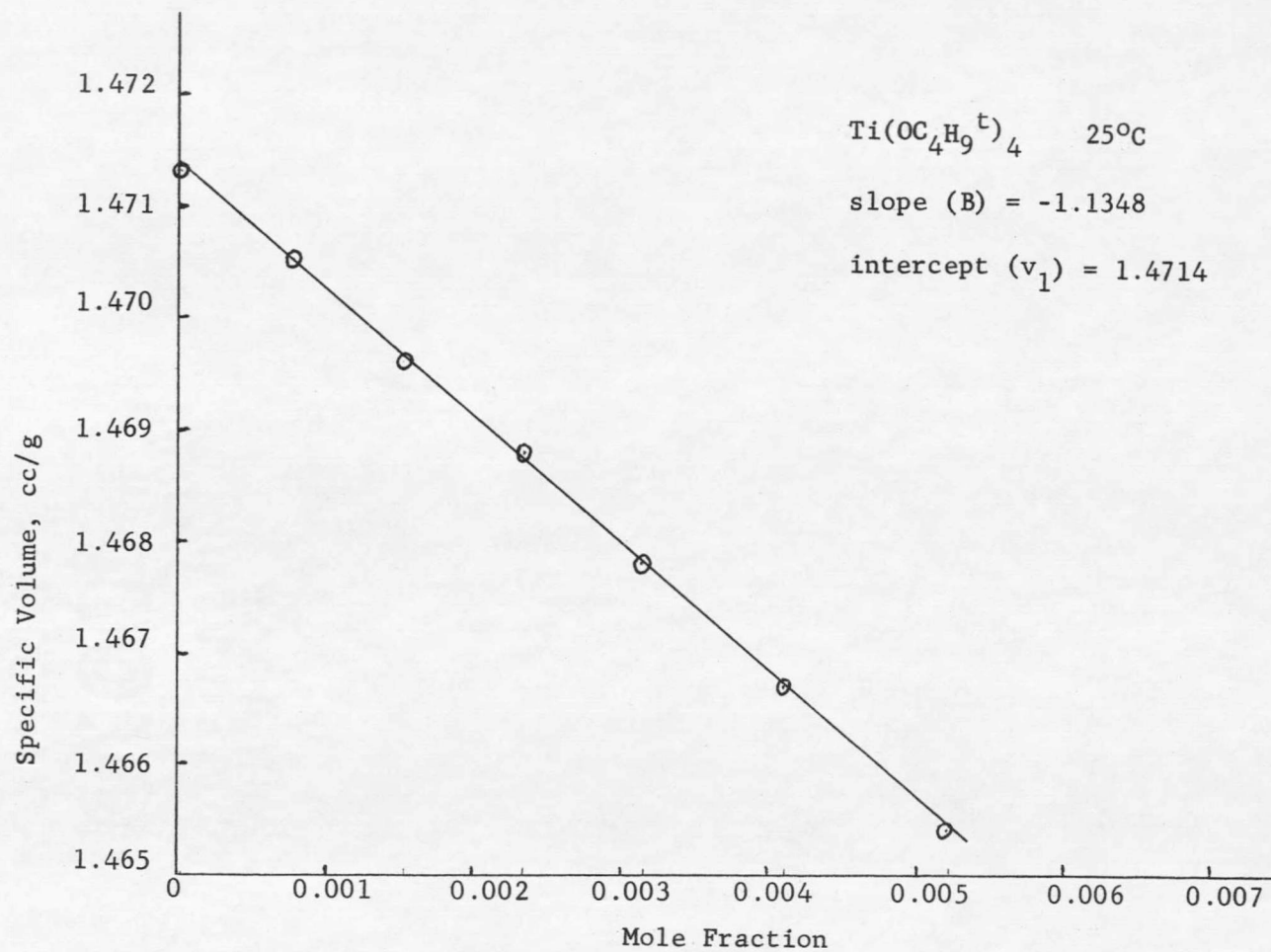
Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_4\text{H}_9^{\text{n}})_4$, $0^\circ\text{C}.$

Figure 19



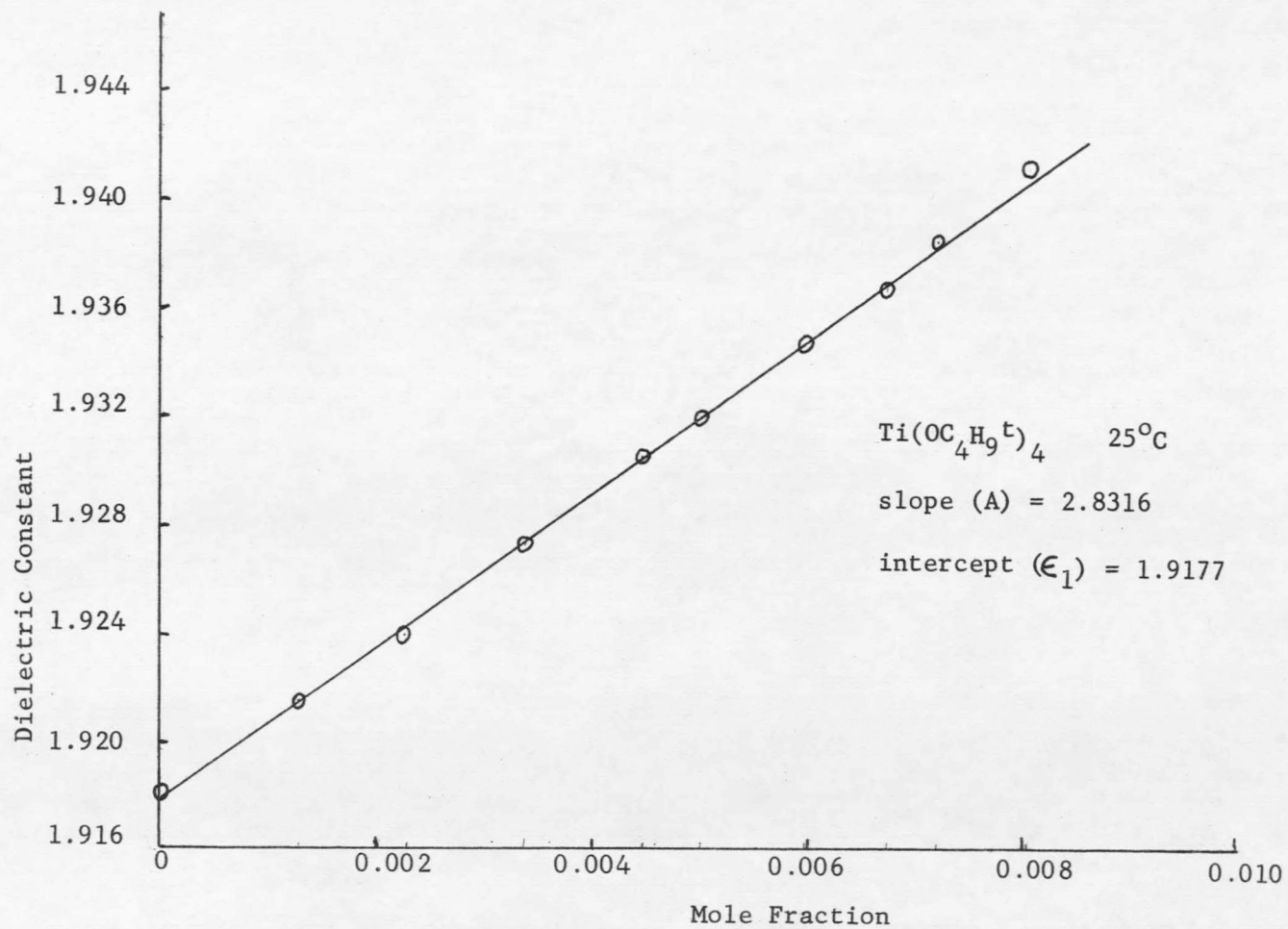
Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_4\text{H}_9^n)_4$, 0°C .

Figure 20



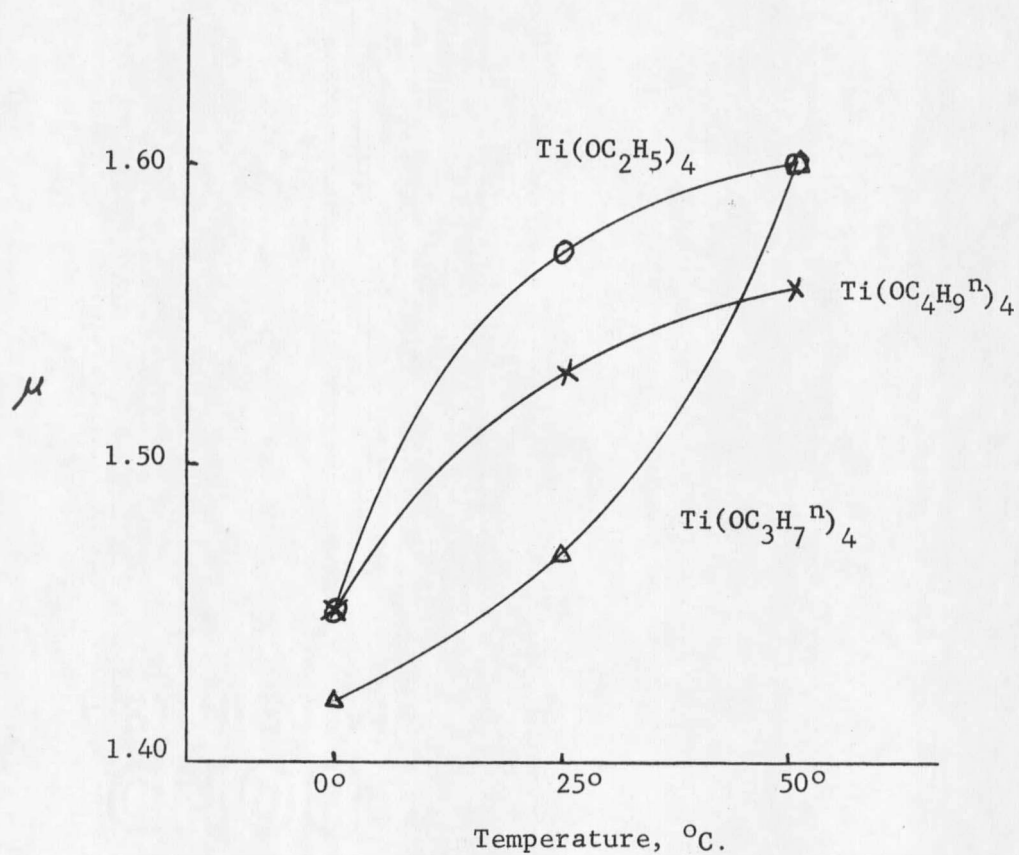
Specific Volume vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_4\text{H}_9^t)_4$, 25°C

Figure 21



Dielectric Constant vs. Mole Fraction Curve for $\text{Ti}(\text{OC}_4\text{H}_9^t)_4$, 25°C.

Figure 22



Temperature Variation of Dipole Moment

Figure 23

Table XI

Results of Dielectric Studies

<u>Compound</u>	<u>Temperature</u>	<u>A</u>	<u>B</u>	<u>ϵ_1</u>	<u>V_1</u>	<u>P</u>	<u>μ</u>
Ti(OC ₂ H ₅) ₄	50°C	2.0129	-1.3286	1.8816	1.5204	109.60	1.60
	25°C	2.0763	-1.2336	1.9181	1.4713	109.51	1.54
	0°C	2.1371	-1.1972	1.9537	1.4278	108.32	1.45
Ti(OC ₃ H ₇) ₄	50°C	2.1635	-1.5141	1.8811	1.5203	129.30	1.60
	25°C	2.1389	-1.4599	1.9188	1.4712	125.34	1.47
	0°C	2.2053	-1.3469	1.9548	1.4278	125.92	1.42
Ti(OC ₄ H ₉ ⁿ) ₄	50°C	2.1677	-1.7145	1.8818	1.5206	144.29	1.56
	25°C	2.2695	-1.5559	1.9187	1.4712	146.20	1.53
	0°C	2.3274	-1.4910	1.9547	1.4278	145.11	1.45
Ti(OC ₄ H ₉ ^t) ₄	25°C	2.8316	-1.1348	1.9177	1.4714	172.27	1.86

Table XII

Densities and Refractive Indices
for Pure Liquids⁽³¹⁾

<u>Compound</u>	<u>$\frac{n^t}{d}$</u>	<u>$\frac{d^t}{4}$</u>
$\text{Ti}(\text{OC}_2\text{H}_5)_4$	1.5051/35°	1.107/35°
$\text{Ti}(\text{OC}_3\text{H}_7)_4$	1.4803/35°	0.9970/35°
$\text{Ti}(\text{OC}_4\text{H}_9)_4\text{-n}$	1.4863/35°	0.9927/35°
$\text{Ti}(\text{OC}_4\text{H}_9)_4\text{-tert}$	1.4436/20°	0.8893/20°

PART II

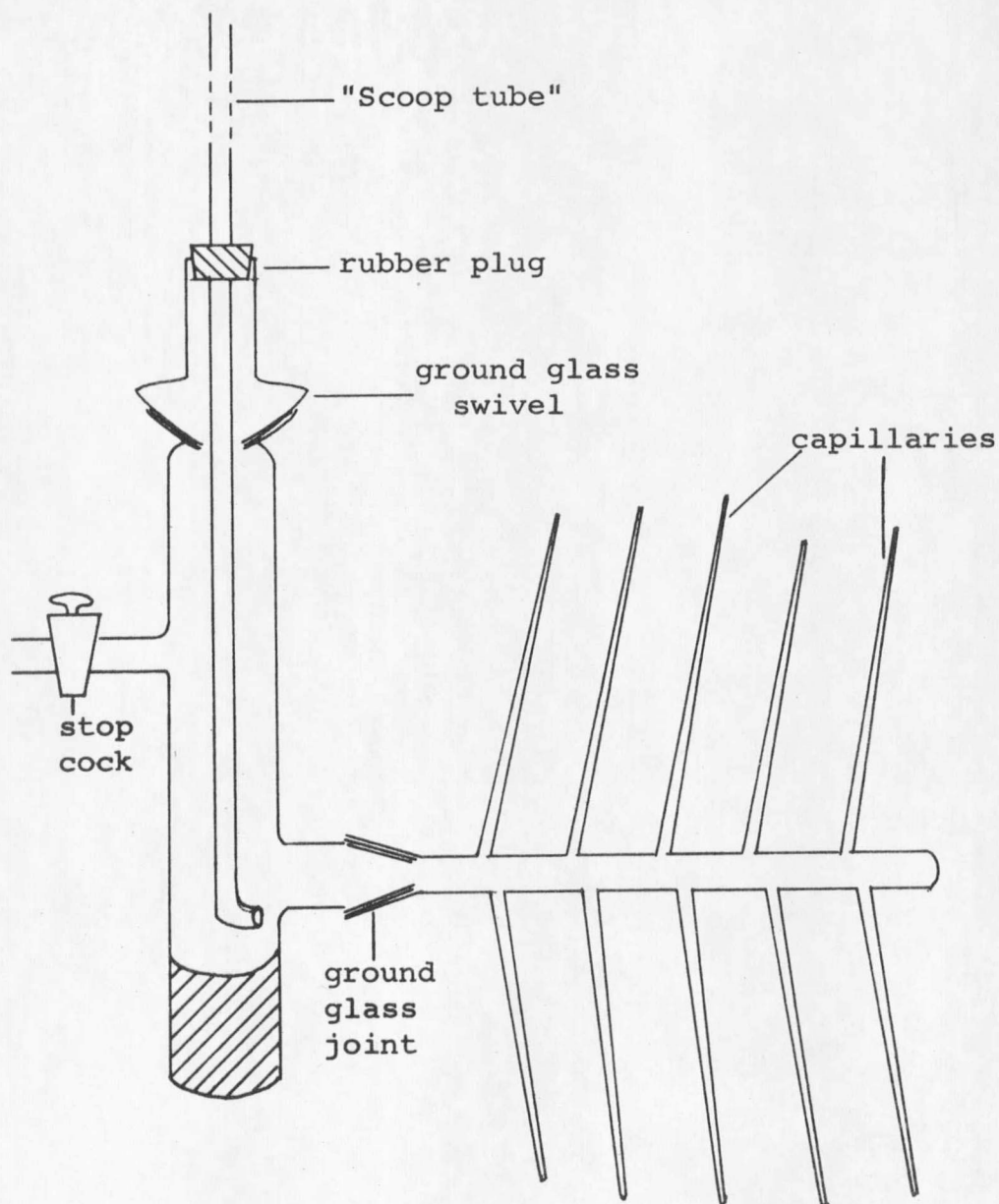
PRELIMINARY INVESTIGATION OF THE HYDROLYSIS PRODUCT OF TETRAETHYL TITANATE

This crystal structure investigation began with the intent of determining the structure of tetraethyl titanate. Analysis of the crystals obtained by evaporation of alcohol solution indicated that they were not $\text{Ti}(\text{OC}_2\text{H}_5)_4$ but were one of the hydrolysis products of the alkyl titanate. In this section, the crystal structure investigation, although incomplete, is described.

Preparation of Crystals

The best method found for obtaining crystals was to grow them by slow evaporation of alcohol solution in the apparatus shown in Figure 24. The apparatus was constructed from a large test tube. The rubber plug at the top was obtained from a hypodermic kit.

Alcohol, distilled after refluxing over calcium hydride, was used to prepare a solution of $\text{Ti}(\text{OC}_2\text{H}_5)_4$. The concentration of the solution was about 1 part ethyl titanate to 10 parts alcohol by volume. This solution was placed in the apparatus and dry air was passed slowly through the system to evaporate the alcohol. In about two weeks crystals of convenient size formed on the side of the tube. These were then knocked to the bottom and scooped up by the spoon which extended up through the rubber plug. The scoop was then raised to the side arm, as much supernatant liquid as possible was drained off, and dry alcohol was run through the scoop tube to wash the crystals into the side tube with the capillaries. This side tube was then disconnected from the crystal-



Crystal Growing Apparatus

Figure 24

growing apparatus and immediately attached to an aspirator to remove the alcohol. The dried crystals were shaken into the capillaries and sealed off under vacuum.

Chemical analysis showed that the crystals were not the ethyl titanate but a hydrolysis product. Apparently enough moisture got into the system to cause crystallization of the hydrolysis product instead of the ethyl titanate, even though the air which was passed through the apparatus during formation and growth of the crystals was dried with a long column of sodium hydroxide pellets and two bubble chambers containing concentrated H_2SO_4 .

Analysis of Crystals

Crystals for chemical analysis were grown in the apparatus shown in Figure 25. The alcohol solution of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ was placed in the tube and dry air was passed slowly through the system via the stopcocks to remove alcohol. When a sufficient number of crystals were obtained, the solution was poured off; the crystals were rinsed twice with dry alcohol. The remaining alcohol was removed by applying a vacuum to the system. Dry air was then admitted and the apparatus weighed. Crystals were then transferred into a previously ignited and weighed crucible, the apparatus being reweighed to determine the weight of the sample. The crystals were converted to TiO_2 by acid hydrolysis following the method of Speer ⁽³¹⁾. The results of the analysis are shown below.

	% TiO_2
Analysis of sample	43.2
Theoretical for $\text{Ti}(\text{OC}_2\text{H}_5)_4$	35.0

Theoretical for $\text{Ti}_6\text{O}_4(\text{OC}_2\text{H}_5)_{16}$	44.7
Analysis of hydrolysis product by Bradley ⁽³⁾	43.5

It was apparent from these results that the crystals formed were not $\text{Ti}(\text{OC}_2\text{H}_5)_4$. The formula $\text{Ti}_6\text{O}_4(\text{OC}_2\text{H}_5)_{16}$ is the first hydrolysis product proposed by Bradley⁽³⁾, formed by combining two trimer units after splitting off four $-\text{OC}_2\text{H}_5$ groups. The analysis suggests that the crystals formed are this compound. Accordingly, since crystals of this were available, a crystal structure analysis of this compound was started.

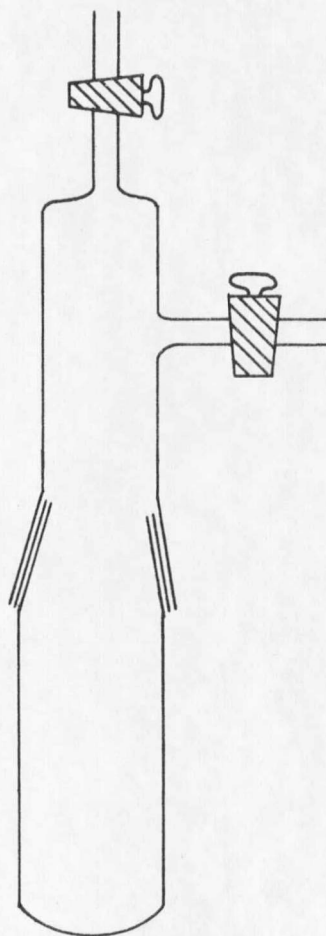
Density Determination of the Hydrolysis Product

The flotation method was used to determine the density of the crystals. Benzene, dried over sodium, and carbon tetrachloride, dried over calcium chloride, were mixed to give a solution in which the crystals remained suspended. The density of this solution was determined by a Westphal balance which was adjusted with distilled water at 26°C.

A measurement gave for the crystal a density of 1.305 g/cc. Two additional measurements confirmed this value.

Collection of X-Ray Data

One of the crystals sealed in a pyrex capillary was selected for the x-ray analysis. This crystal was used throughout the collection of data for cell dimensions and intensities. The x-ray data were collected using a Norelco X-ray power supply Type 12045, and a copper tube, type 32112. Cu K_α radiation was obtained by using a Ni filter.



Apparatus for Growing Crystals for Analysis

Figure 25

Rotation and Weissenberg pictures were obtained with Supper Weissenberg camera. Integrated intensity data were obtained by placing three films in a Weissenberg camera which had been modified for integration. Precession photographs were used to determine the interaxial angle.

The film used was Kodak Medical X-ray Film--No Screen. The pictures were developed 10 minutes in Kodak X-ray Developer, immersed in a stop bath, and fixed 15 minutes in Kodak Rapid Fix with Hardener. The films were then washed for one hour, rinsed with distilled water, and dried. The development and fixation of the films were carried out at a constant temperature of 25°C.

Intensities were read visually by comparing the photograph with a standard intensity scale. This scale was made by exposing a triple film through a small hole at 5 second intervals, up to 120 seconds, the film being displaced a few millimeters after each exposure. All levels of the Weissenberg photographs were given the same exposure, 100 hours, and the same development. Thus it was assumed that the intensities from level to level were on the same scale. One thousand two hundred fifty eight unequivalent reflections were observed on levels zero through six.

Space Group

The angle between the reciprocal lattice axes on the zero level Weissenberg film was measured as 90°. On upper level pictures the b^* axial line was no longer straight, thus indicating that the crystal

belongs to the monoclinic system. Conditions for reflection were $h = 2n$ for $h0\ell$ and $k = 2n$ for $0k0$; thus the symmetry must be that of space group $P2_1/a$. The condition $(0k0, k = 2n)$ implies a two-fold screw axis along the axis b ; the condition $(h0\ell, h = 2n)$ implies a glide plane along axis a .

The term "b* axial line" refers to a line parallel to the b^* axis and passing through a reciprocal lattice point. This connotation will be used throughout this thesis.

Cell Dimensions

The camera diameter was calibrated with a sodium chloride crystal which was ground to a very slender rod. From a zero level Weissenberg picture measurements were made on 4 reciprocal lattice points, and an effective camera diameter calculated for each measurement. The following results were obtained for the diameter: 56.85, 56.67, 56.81, and 56.75 mm. The value used for my calculations is the arithmetic average, 56.77 mm.

From the distances measured between layer lines on a rotation or oscillation picture the cell edge can be calculated directly. Since the crystal was mounted on the c axis,

$$c = \frac{n\lambda (r^2 + y_n^2)^{1/2}}{y_n}$$

where n is the level to which the measurement is made, y_n is the distance to the n -level line from the zero level line, and r is the effective camera radius. The derivation of this expression is given in Appendix A. From this the average value of c is 23.30 Å. These measurements

are shown in Table XIII.

Since the monoclinic crystal was mounted on the c axis, b and $a \cdot \sin \beta$ could be calculated from measurements on a zero level Weissenberg film. For a camera of 57.3 mm. diameter, the distance in millimeters from the center line on the film to the particular reflection is the angle θ in degrees. However, since the effective camera diameter is less than 57.3 mm, $\theta = 57.3/56.77$ deg. Table XIV shows the measurements from the center line to the reflections on the a^* and b^* axial lines and shows the values of $a \cdot \sin \beta$ and b calculated therefrom. The average values from these measurements are

$$a \cdot \sin \beta = 24.82 \text{ \AA}^{\circ} \quad \text{and} \quad b = 22.40 \text{ \AA}^{\circ}.$$

The angle β was measured from a zero level precession picture and is $117^{\circ}15'$. (The angle also was calculated from measurements on an upper level Weissenberg film by a formula derived in Appendix B.) With this value of β , $a = 27.92 \text{ \AA}^{\circ}$.

Using these cell dimensions, the density of the crystal, and a molecular formula of $\text{Ti}_6\text{O}_4(\text{OEt})_6$, the number of molecules per unit cell was calculated to be 9.50.

A summary of the crystal data is given in Table XV.

Choosing the Axes

The reciprocal lattice axes on precession photographs were chosen in the following manner. Since the crystal is mounted on the c axis and is precessing about b , the vertical line on a precession photograph is a^* . c^* could be chosen in two ways as indicated in Figure 26.

Table XIII

Determination of c from Rotation Film

effective camera diameter = 56.77 mm

calculation from formula $c = \frac{n \lambda (r^2 + y_n^2)^{\frac{1}{2}}}{y_n}$

<u>Layer Line (n)</u>	<u>y_n</u>	<u>c</u>
3	5.75	23.28 Å
4	7.81	23.27
5	9.95	23.29
6	12.25	23.34
7	14.85	23.28
8	17.70	23.31
9	21.05	23.30

average: $c = 23.30 \text{ Å}$

Table XIV

Determination of $a \cdot \sin \beta$ and b from Weissenberg Film

effective camera diameter = 56.77 mm

$$\theta = \frac{57.3}{56.77} X = 1.0093X$$

X = distance in mm from center line to spot

calculation from Bragg's law: $d = n\lambda / 2\sin \theta$ $\lambda = 1.542 \text{ \AA}$ Calculation of $a \cdot \sin \beta$

<u>Reflection Used</u>	<u>X</u>	<u>θ</u>	<u>$a \cdot \sin \beta$</u>
(400)	7.066	$7^\circ 7.8'$	$24.851 \text{ \AA}$
(16,0,0)	29.56	$29^\circ 50'$	$24.795 \text{ \AA}$
average: $a \cdot \sin \beta = 24.82 \text{ \AA}$			

Calculation of b

<u>Reflection Used</u>	<u>X</u>	<u>θ</u>	<u>b</u>
(040)	7.825	$7^\circ 52'$	$22.42 \text{ \AA}$
(060)	11.80	$11^\circ 54'$	$22.38 \text{ \AA}$
(0,12,0)	24.13	$24^\circ 20'$	$22.40 \text{ \AA}$
average: $b = 22.40 \text{ \AA}$			

Table XV

Summary of Crystal Data for
Hydrolysis Product

$$a = 27.92 \overset{\circ}{\text{A}}$$

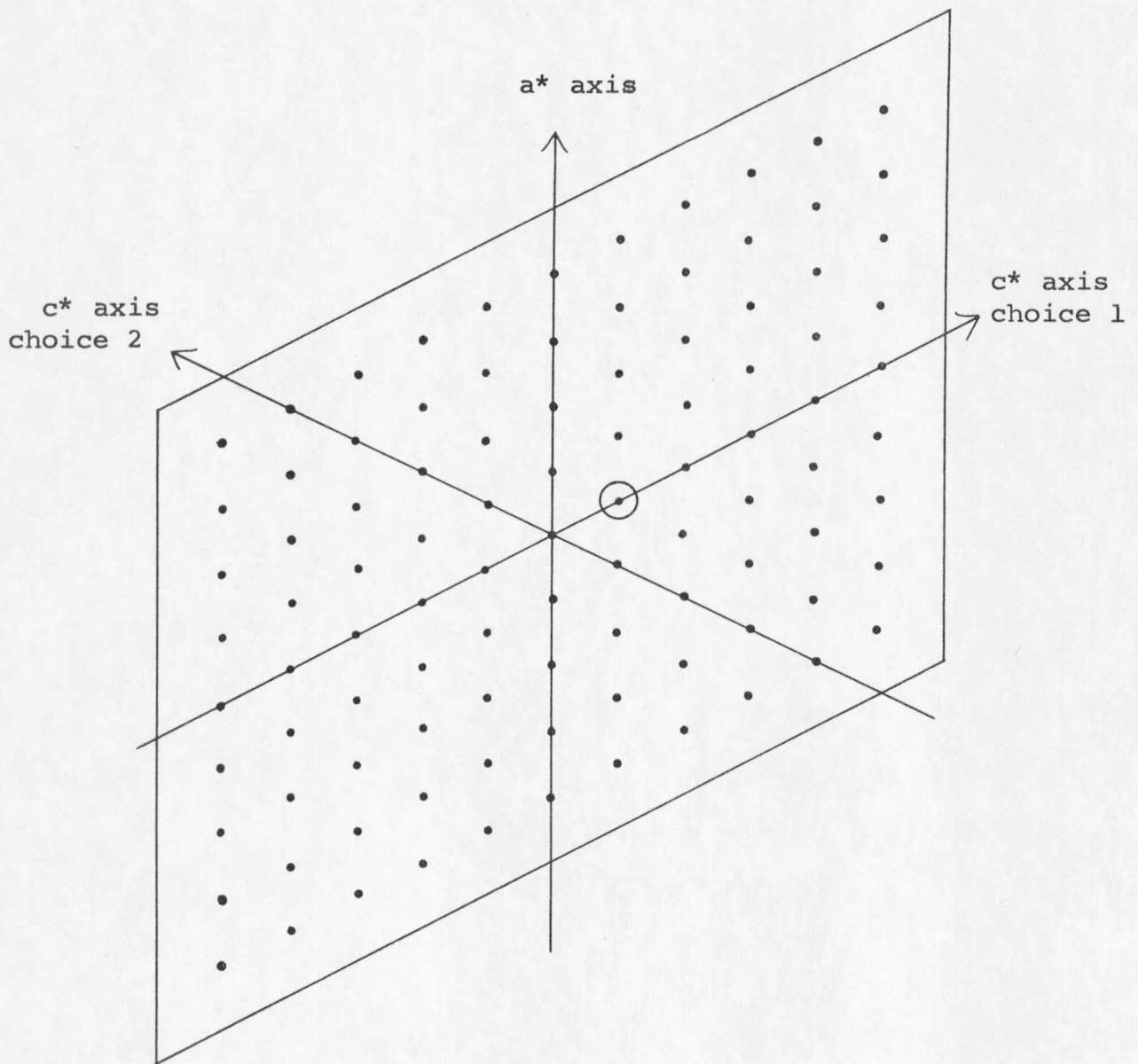
$$b = 22.40 \overset{\circ}{\text{A}}$$

$$c = 23.30 \overset{\circ}{\text{A}}$$

$$\beta = 117^{\circ}15'$$

$$\text{Molecules per unit cell} = 9.50$$

$$\text{Density} = 1.305 \text{ g/cc}$$



Choosing Axes on a c Net

Figure 26

Consider the index of the circled reciprocal lattice point. With choice #1 for the c^* axis the spot would be indexed as $Ok\bar{l}$; with choice #2 the index would be $lk\bar{l}$.

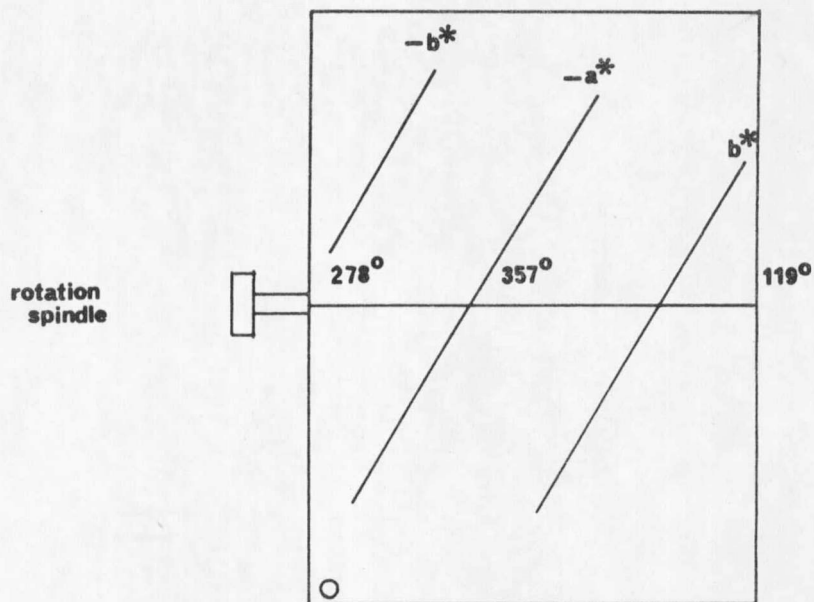
In choosing the c^* axis for this crystal one choice would make the value of β about 112° , the other 117° . Generally one would probably choose the axis so as to give β a value as near to 90° as possible. However, the larger angle was chosen to keep the indexing consistent with that required for space group $P2_1/a$. If the smaller angle had been chosen, the reflection condition ($h0l$, $h = 2n$) would have been violated for values of l odd. Figure 27 shows the choice of axes and the correspondence between axes on the zero level Weissenberg film and the precession pictures. Azimuth values are indicated on the Weissenberg drawing. Also this choice of axes gave positive " l " values for higher level Weissenberg pictures.

Indexing Weissenberg Photographs of Monoclinic Crystals

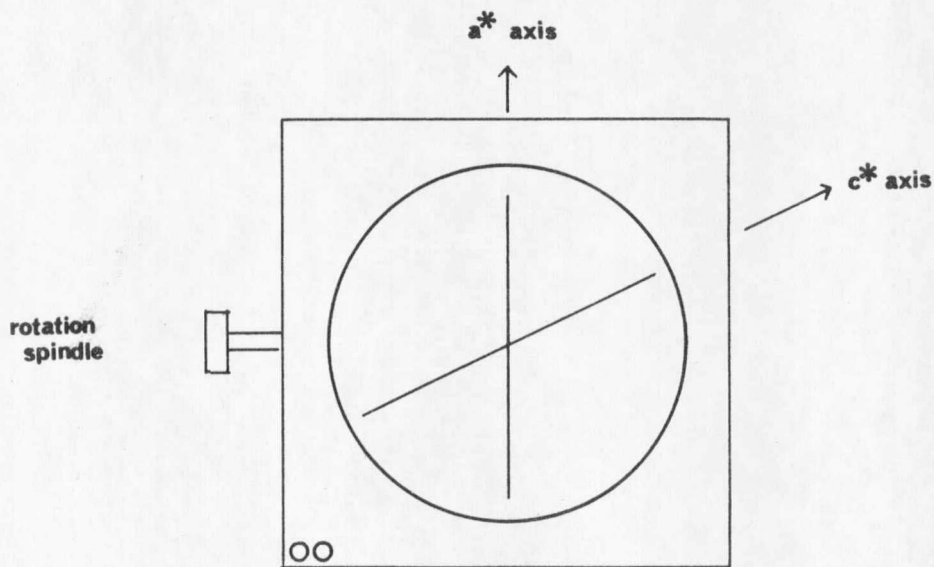
Once the reciprocal lattice axes have been chosen, the indices of the reflections are fixed. Indexing a zero level Weissenberg film using a template can be done without problems. However, for monoclinic crystals not mounted on the b axis indexing upper level photographs is slightly more complicated since the line $Ok\bar{l}$ for any particular level ($l = n$) is no longer a straight line.

For lower level films the b^* axial line which passes through the point ($00l$) is usually the first festoon above (or below) the center line of the film. If the angle β is large, however, the first festoon on the bottom half of the film on a lower level photograph may become the first

60



zero-level Weissberg



b^* out of plane

azimuth $\approx 175^\circ 20'$

zero-level precession

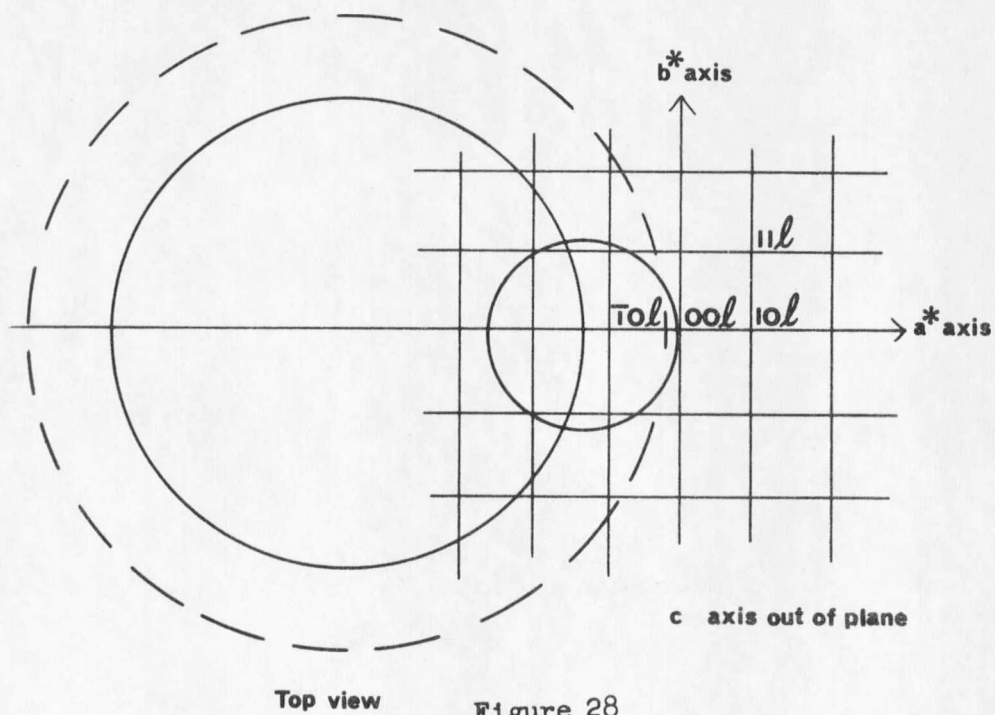
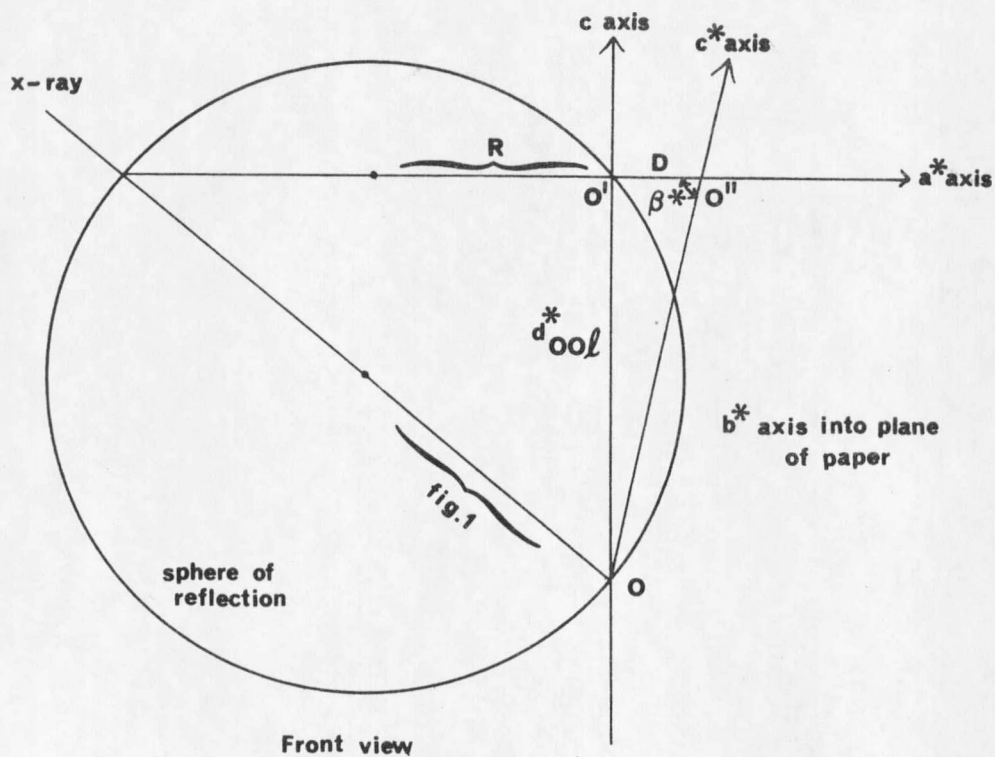
Relationship between the Precession and Weissberg Films

Figure 27

festoon on the upper half of some higher level film. Then the first b^* axial line on the upper half of the film will pass through the point $(\bar{1}0\ell)$, (or through (10ℓ) , depending on how the axes were chosen). Another "crossing over" of a b^* axial line may happen again on some higher level film. The following method allows one to calculate the k index of the first b^* axial line on any level Weissenberg photograph. Once this is known for any level, indexing is done as usual.

Refer to Figure 28 which depicts the arrangement of the reciprocal lattice axes with respect to the sphere of reflection for an equi-inclination Weissenberg picture. The top drawing is a front view, the bottom drawing a top view. Rotation is about the c axis. The point O is the reciprocal lattice point (000) ; the point O' is the point at which the rotation axis cuts the sphere of reflection (at the ℓ level); and the point O'' is the reciprocal lattice point (00ℓ) . R is the radius of the circle of reflection for the ℓ level; D is the radius of the circle formed by the point O'' as it rotates about the rotation axis; and $d_{00\ell}^*$ is the distance from the point O to the ℓ level. The distance along the a^* axis between reciprocal lattice points is called a^* .

D increases as ℓ increases. As long as D remains smaller than a^* , no particular problem arises; the first b^* festoon above the center line will be the b^* axial line passing through the point O'' (or 00ℓ). However, when D exceeds a^* , the first festoon is the b^* axial line passing through the point $(\bar{1}0\ell)$; then the axial line passing through the point (00ℓ) is the second festoon above the center line. On some higher level film D may exceed $2a^*$; then the first b^* festoon passes through the point



($\bar{2}0\bar{2}$). Of course when this happens, the first b^* festoon on the opposite half of the film passes through the point ($\bar{3}0\bar{2}$).

From the figure it is seen that $D = d_{002}^* \cot \beta^*$. There also exists the relation $d_{002}^* = \frac{1}{c}$ and $a^* = \frac{1}{d_{h00}} = \frac{1}{a \cdot \sin \beta}$. Thus D and a^* are easily determined and one can readily calculate when a festoon changes to the other half of the film.

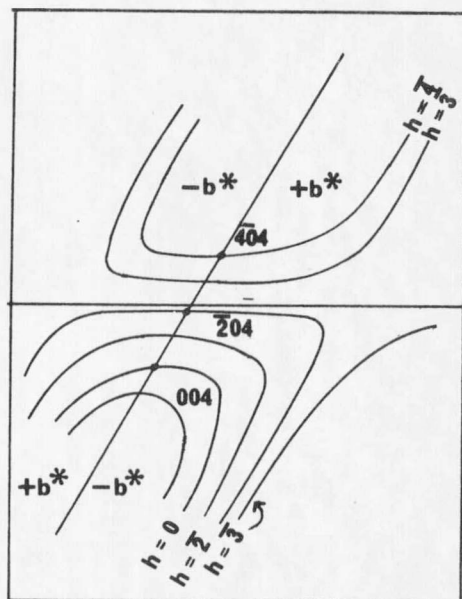
D was calculated for each level and was compared with $a^* = \frac{1}{a \cdot \sin \beta} = \frac{1}{24.82} = 0.04029$. The results are shown in the following table.

level (l)	d_{002}^*	D	$\frac{D}{a^*}$
1	.04292	.02212	0.5490
2	.08584	.04424	1.098
3	.12876	.06636	1.647
4	.17168	.08848	2.196
5	.21460	.11060	2.745
6	.25752	.13272	3.294

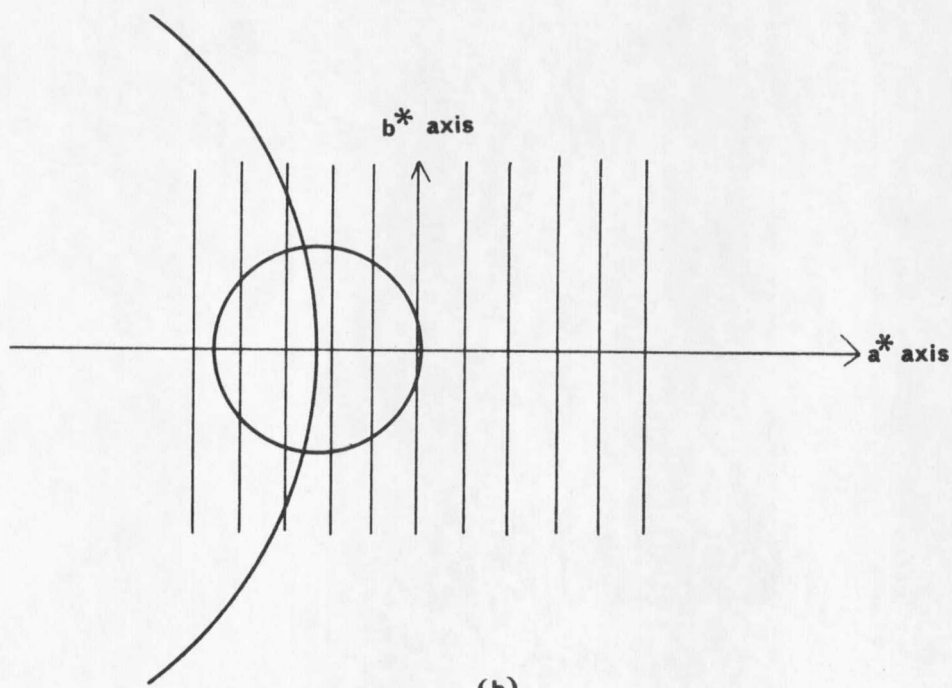
Thus it is seen that on the 2nd, 4th, and 6th levels the first b^* festoons pass through the points (012), (024), and (036), resp. The general appearance of the 4th level Weissenberg picture is as pictured in Figure 29a. Figure 29b shows the reciprocal lattice arrangement with respect to the circle of reflection.

Attempt to Determine Structure

The raw intensities were reduced to structure factors by correcting for Lorentz-polarization and extracting the square roots with the University of Washington Data Reduction Program 5303. The computer used for this and subsequent calculations on this crystal was the IBM 650.



(a)



(b)

Appearance of b^* Axial Lines (Festoons) on 4th Level Weissenberg Films

Figure 29

Wilson ⁽³⁵⁾ has shown that $\overline{|F_o|}^2 / \sum_j f_j^2 = K e^{-(2B \sin^2 \theta) / \lambda^2}$, where B is the overall temperature factor of the atoms and K is the constant which scales $|F|^2$ to $|F_o|^2$. Thus by plotting $\ln (\overline{|F_o|}^2 / \sum_j f_j^2)$ against $\sin^2 \theta / \lambda^2$, the intercept obtained is $\ln K$, and the slope is $-(2B)$. The graph is made by dividing the reciprocal lattice into a number of $\sin^2 \theta$ zones. The average value of the observed structure factors is obtained for each zone, and the plot is made. For this to be valid there must be a large number of reflections (reciprocal lattice points) in each zone so that an appropriate averaging takes place. The absolute scale factor and overall temperature factor were obtained in this manner giving values of $K = 0.023$ and $B = 6.95$. To scale the F_o 's to the F_c 's, the F_o 's must be divided by $\sqrt{K}$.

A three dimensional Patterson map was calculated. Each section has a center of symmetry since in developing the Patterson map with the Fourier series all sine terms drop out.

This can be seen from the following. $|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})|$ for this space group. Thus the squares of these terms are equal. The general form of the Patterson function is

$$P_{xyz} = \frac{1}{V} \sum_{-h}^h \sum_{-k}^k \sum_{-l}^l |F(hkl)|^2 \cos 2\pi (hx + ky + lz).$$

Since the crystal is mounted on the b axis, this expression, by applying Friedels' law, can be written as

$$\begin{aligned} P_{xyz} &= \frac{2}{V} \sum_{-h}^h \sum_{\substack{k \\ 0}}^k \sum_{\substack{l \\ -l}}^l |F(hkl)|^2 \cos 2\pi (hx + ky + lz) \\ &= \frac{2}{V} \sum_{-h}^h \sum_{\substack{k \\ 0}}^k \sum_{\substack{l \\ -l}}^l |F(hkl)|^2 \cos 2\pi ky \cos 2\pi (hx + lz) \\ &\quad - \sum_{-h}^h \sum_{\substack{k \\ 0}}^k \sum_{\substack{l \\ -l}}^l |F(hkl)|^2 \sin 2\pi ky \sin 2\pi (hx + lz). \end{aligned}$$

Since the expression is summed from $-h$ and $-\ell$ to $+h$ and $+\ell$, the sine term will drop out, for $\sin 2\pi(hx + \ell z) = -\sin 2\pi(-hx - \ell z)$. Thus the function for each Patterson section contains only cosine terms and will be centrosymmetric on each section.

This can also be seen from the equivalent positions of this space group, i.e. x, y, z ; $\bar{x}, \bar{y}, \bar{z}$; $x + 1/2, 1/2 - y, z$; and $1/2 - x, y + 1/2, \bar{z}$. The vectors to the points from the origin of the unit cell are

$$\vec{r}_1 = \vec{i}x + \vec{j}y + \vec{k}z$$

$$\vec{r}_2 = -\vec{i}x - \vec{j}y - \vec{k}z$$

$$\vec{r}_3 = \vec{i}(x + 1/2) + \vec{j}(1/2 - y) + \vec{k}z$$

$$\vec{r}_4 = \vec{i}(1/2 - x) + \vec{j}(1/2 + y) - \vec{k}z.$$

The coordinates of the peaks on a Patterson map represent the vector distances, in crystal space, between atoms. On a three-dimensional map there are eight origins, one at each corner of the parallelepiped forming the unit cell in vector space. Thus a peak in a Patterson map is the vector distance from each of the origins. If a peak is obtained by the vector distance between two atoms in crystal space from a given origin in vector space, the same peak would be formed due to the same atoms with respect to a different origin.

The peaks arising on the vector map for the crystal are due to differences of the above vectors. There thus will appear points as determined by the following vectors:

$$1) \quad \vec{r}_1 - \vec{r}_2 = 2x\vec{i} + 2y\vec{j} + 2z\vec{k}$$

$$2) \quad \vec{r}_1 - \vec{r}_3 = -1/2\vec{i} + (2y - 1/2)\vec{j}$$

$$3) \vec{r}_1 - \vec{r}_4 = (2x - 1/2)\vec{i} - 1/2\vec{j} + 2z\vec{k}$$

$$4) \vec{r}_2 - \vec{r}_3 = -(2x + 1/2)\vec{i} - 1/2\vec{j} - 2z\vec{k}$$

$$5) \vec{r}_2 - \vec{r}_4 = -1/2\vec{i} - (2y + 1/2)\vec{j}$$

$$\text{or } \vec{r}_4 - \vec{r}_2 = 1/2\vec{i} + (2y + 1/2)\vec{j}$$

$$6) \vec{r}_3 - \vec{r}_4 = 2x\vec{i} - 2y\vec{j} + 2z\vec{k}$$

$$\text{or } \vec{r}_4 - \vec{r}_3 = -2x\vec{i} + 2y\vec{j} - 2z\vec{k}.$$

These vectors are with respect to the origin at $x = 0$, $y = 0$, and $z = 0$. However, for an adjacent cell in vector space this same origin will have coordinates $x = 0$, $y = 1$, and $z = 0$. Then with reference to the new origin vector (2) will be

$$2) \vec{0} + \vec{j} + \vec{0} - 1/2\vec{i} + (2y - 1/2)\vec{j} = -1/2\vec{i} + (2y + 1/2)\vec{j}.$$

In a similar manner with reference to the origin at $x = 1$, $y = 0$, and $z = 0$, vector (3) becomes

$$3) \vec{i} + \vec{0} + \vec{0} + (2x - 1/2)\vec{i} - 1/2\vec{j} + 2z\vec{k} = (2x + 1/2)\vec{i} - 1/2\vec{j} + 2z\vec{k}.$$

Since there is no unique origin, all of these vectors arise from each origin.

For a section on y to be centrosymmetric the x and z coordinates of two of these vectors must be of equal magnitude but opposite in sign. The three pairs that satisfy this condition are (1) and (6), (2) and (5), and (3) and (4). Therefore each section on y will be centrosymmetric.

Calculation of the number of molecules per unit cell gave a value of 9.50, assuming the molecular formula to be $\text{Ti}_6\text{O}_4(\text{OC}_2\text{H}_5)_{16}$. The height of the origin peak on the Patterson map is proportional to the sum of the squares of the atomic numbers of all atoms in the unit cell. Assuming ten molecules per unit cell, this makes the height of the origin

peak 54160. The program was scaled to give an origin peak of 640. Thus all the other peaks on the map will be $640/54160$ of actual absolute magnitude. The heights of some single vectors on the map are calculated below:

<u>type vector</u>	<u>$z_i z_j$</u>	<u>peak height</u>
Ti - Ti	$22 \times 22 = 484$	$\frac{484}{54160} \times 642 = 5.7$
Ti - O	$22 \times 8 = 176$	2.1
O - O	$8 \times 8 = 64$	0.8

Even a single titanium-titanium vector peak would probably be lost in the background. In addition to the origin peak there were eleven peaks with a height over 100 on the map, and many were over 25. Thus any peak observed on the map is due to the superposition of several peaks.

Little progress was made beyond this point. I was unable at that time to interpret the Patterson map although one large peak of magnitude 310 is probably due to superposition of several titanium-titanium vectors. The length of the vector is approximately $3.2 \overset{O}{\text{A}}$, which is about the correct distance between two titanium atoms sharing one or more oxygens. One other peak, of height 250, appears to hold considerable information. This peak is found at coordinates (.5, 0, 0) indicating many of the atoms are separated by one-half a cell edge along the a axis from other atoms.

One other observation that may shed light on the crystal structure is the occurrence of a larger cell in reciprocal space, this large cell being formed by regions of reciprocal lattice points of large magnitude. (The magnitude of a reciprocal lattice point is the magnitude of the

structure factor bearing that particular index.) If there is a small group of atoms of fixed arrangement which repeats itself in a regular manner within the unit cell, this group of atoms is called a subcell, or substructure. The subcell causes the large cell in reciprocal space. Taking the reciprocal of the large reciprocal cell gives back the subcell. Vand and Bell⁽³³⁾ used this method as an aid in solving the structure of trilaurin. Buerger⁽⁸⁾ gives considerable discussion to the subject.

A zero level precession picture indicated the possibility of a substructure. A plot was made of the $hk0$ net, the reciprocal lattice points being given the weight of the structure factor of the corresponding index (figure 30). Two possible large reciprocal cells were found on this net. The side of one cell corresponds to an interatomic distance of $3.20 \text{ \AA}$, likely a titanium-titanium distance, while a side of the other cell indicates an interatomic distance of $1.55 \text{ \AA}$ which may be a carbon-carbon distance or possibly a titanium-oxygen distance.

A review of the progress and findings at this point brought about the decision to suspend work on this crystal. It appears to be very complicated, especially when one considers the very large number of atoms per unit cell. Furthermore there was no previous knowledge of organic titanates to give a clue to the possible arrangement of atoms.

In addition, the value obtained for the number of molecules per unit cell, 9.50, indicated an uncertainty in the assumed molecular formula. The cell dimensions are quite accurate so the calculated number of molecules should be much closer to a whole number. Even if

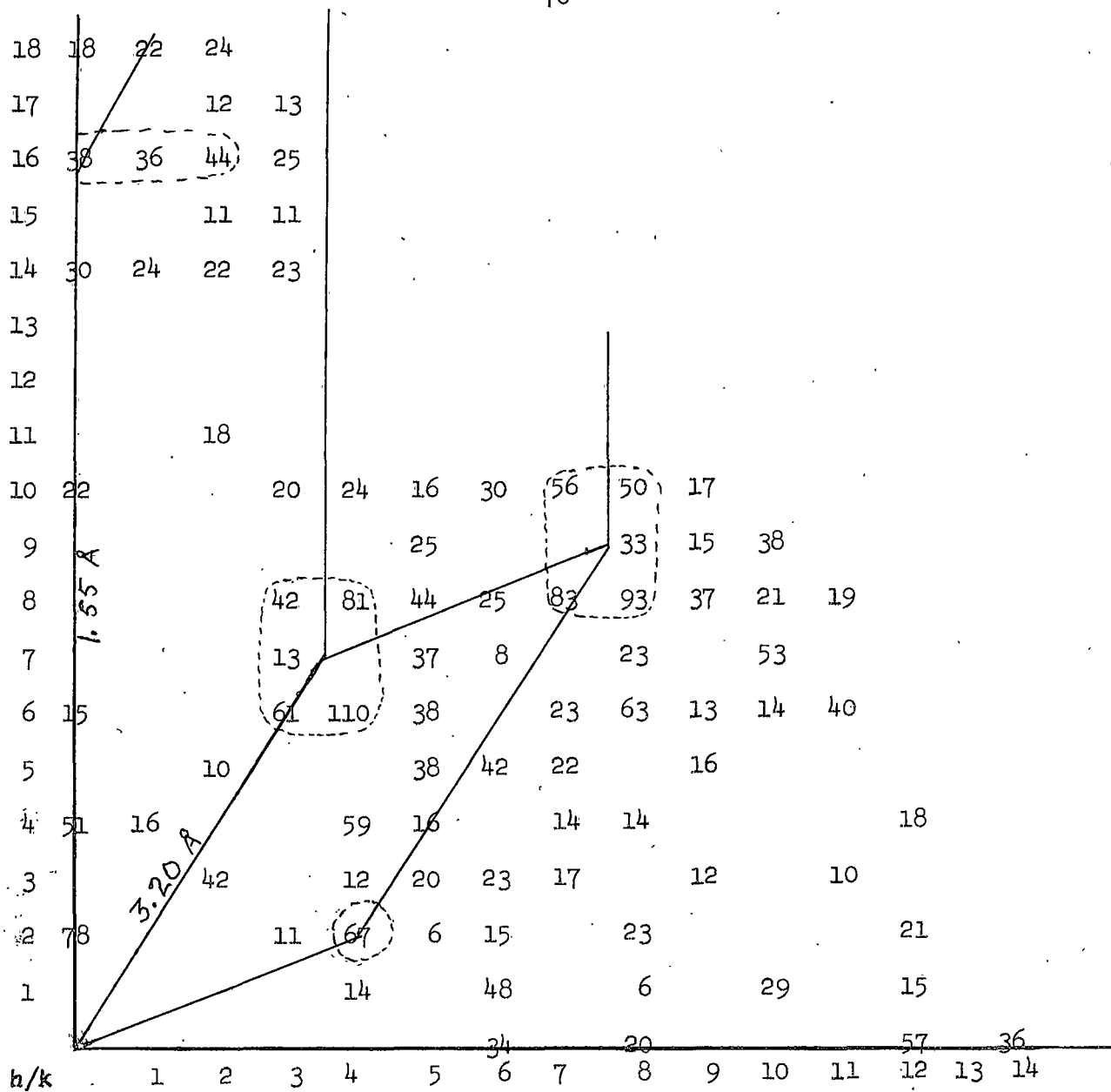
Indication of Subcells from Weighted a^*b^* Net

Figure 30

the calculated volume were slightly in error the number of molecules would be either 9 or 10. Nine molecules per unit cell would be impossible for this space group and ten would be rather unusual.

Thus before continuing with the solution of this structure it was decided to investigate a simpler compound in hope that this might give a clue to the structure of the more complex hydrolysis product and to its molecular formula.

PART III

THE CRYSTAL STRUCTURE OF MONOMETHYLTRIETHYL TITANATE

Preparation of Crystals

$\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ was prepared by the method of Varma and Mehrotra.⁽³⁴⁾ $\text{Ti}(\text{OC}_2\text{H}_5)_4$ and methanol were mixed in stoichiometric proportions in dry benzene. The compound is very soluble in hot benzene but much less soluble in cold benzene. The crystals were dissolved by warming the mixture. The hot solution was poured into the apparatus shown in Figure 24. Crystals from the cool solution were obtained in capillaries by the procedure described for the hydrolysis product in Part II.

Density Determination of $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$

The density of the crystals was determined by measuring the density of a solution of carbon tetrachloride in benzene in which the crystal remained suspended. The density of the crystals was determined to be 1.244g/cc.

Experimental: X-Ray Apparatus and Intensity Measurement

The X-Ray power supply and the method of development of the films were as described in Part II.

Intensities were measured visually as previously described from multiple-film, non-integrated pictures using the Supper camera. Intensities measured on the second and third films were put on the same scale as those measured on the first film by multiplying by the factors 3.56 and 12.3, resp. These film factors were determined by comparing intensities of the same reflections on the three films. All the films used for

intensity measurements were given the same exposure and the same development. Thus it was assumed that the intensities from level to level were on the same scale: 751 unique reflections were observed on levels zero through six.

The intensities were corrected for spot size by using a method similar to that of Phillips⁽²⁸⁾. The formulas and curves given by Phillips are approximations and do not hold for reflections of small reflection angles. The formulas given by Phillips were used for large angles while an empirical correction was used for reflections of small angles. The curves used for the intensity corrections are shown in Figure 31. Intensities measured on the top half of the films were multiplied by the factor obtained from the necessary curve; intensities on the bottom half were multiplied by the value obtained by subtracting this factor from 2.0. The values of k were measured using the chart of Figure 144 in reference 9.

In later stages of refinement the levels were scaled together by running a structure factor calculation for each level, obtaining a scale constant for each level, and rescaling each level from these individual scale factors.

Space Group

From the zero level Weissenberg film the angle between the reciprocal lattice axes was measured to be different from 90° . In addition, both axes trailed off and became festoons on upper level pictures. Thus the crystal belongs to the triclinic system. There are only two space groups

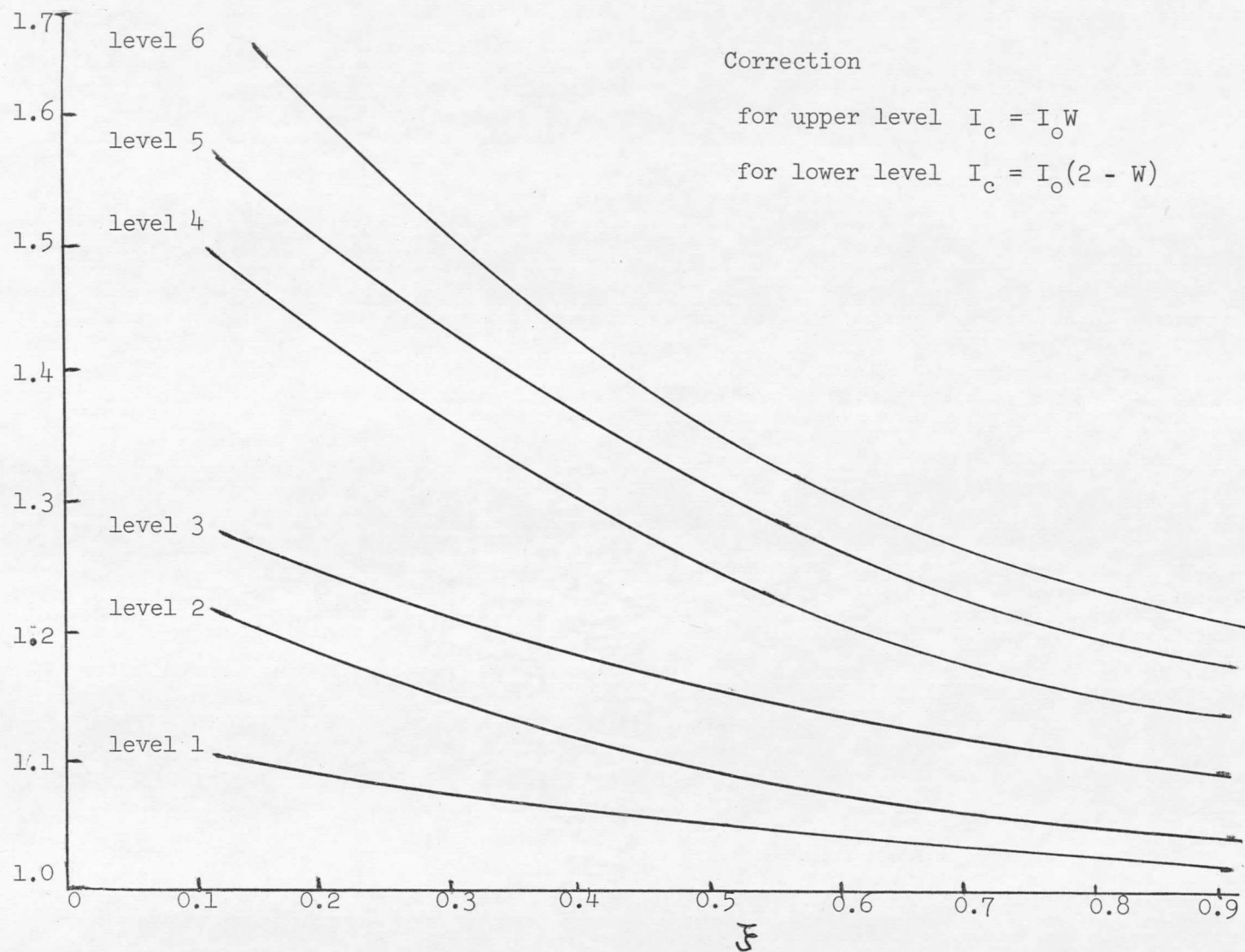


Chart for Intensity Correction

Figure 31

in the triclinic system, one centric ($\bar{1}$) and one noncentric (P1). In the early stages of the structure determination it was assumed that the crystal was centric. This greatly facilitated calculations. However in the final stages of refinement it was put in space group P1. Refinement proceeded faster and further than in the centric space group. Thus it was concluded that the space group is P1.

None of the statistical methods was applied to distinguish between the two space groups since half of the titanium and oxygen atoms were very nearly related to the other half by a center of symmetry. This pseudo-centric character of these heavier atoms would probably completely dominate the statistics giving ambiguous results.

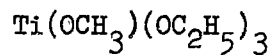
Cell Dimensions and Choice of Axes

After obtaining the cell dimensions it turned out that the crystal was mounted on the b axis. Thus from measurements on an oscillation film the value for b is determined directly using the formula $b = \frac{n\lambda (x^2 - y_n^2)^{\frac{1}{2}}}{y_n}$ (see Appendix A). The value of b thus obtained is 12.13 Å. Table XVI shows the measurements and results.

From a zero level Weissenberg picture one reciprocal lattice angle and two interplanar spacings can be determined. The two cell edges, a and c, cannot be determined until the remaining angles have been found. The results of measurements made on the zero level Weissenberg film are $d_{100} = 11.51 \text{ Å}$, $d_{001} = 16.24 \text{ Å}$, and $\beta^* = 80.0^\circ$. The measurements and results from this film are given in Table XVII. Bragg's law was used to calculate the interplanar spacing.

Table XVI

Determination of Cell Edge b from Rotation Film



effective camera diameter used = 56.62mm

 calculation from formula $b = \frac{n\lambda(r^2 + y_n^2)^{\frac{1}{2}}}{y_n}$

<u>Layer Line (n)</u>	<u>y_n</u>	<u>b</u>
2	7.45 mm	12.12 $\overset{\circ}{\text{A}}$
3	11.65	12.15
4	16.75	12.11
5	23.30	12.13

average: $b = 12.13 \overset{\circ}{\text{A}}$

Table XVII

Determination of Interplanar Spacings from Weissenberg Film

effective camera diameter used: 56.62 mm

$$\theta = \frac{57.3}{56.62} X = 1.0120X$$

X = distance in mm from center line to spot

calculation from Bragg's law

$$\lambda = 1.542 \text{ \AA}$$

Calculation of d_{100}

<u>Reflection Used</u>	<u>X</u>	<u>θ</u>	<u>d_{100}</u>
020	7.60mm	7°41.4'	11.52 $\overset{\circ}{\text{A}}$
030	11.425	11°33.7'	11.54
040	15.40	15°35'	11.48

$$\text{average: } d_{100} = 11.51 \overset{\circ}{\text{A}}$$

Calculation of d_{001}

<u>Reflection Used</u>	<u>X</u>	<u>θ</u>	<u>d_{001}</u>
002	5.40mm	5°27.8'	16.20 $\overset{\circ}{\text{A}}$
004	10.80	10°55.7'	16.26
006	16.30	16°29.6'	16.28

$$\text{average: } d_{001} = 16.24 \overset{\circ}{\text{A}}$$

For sake of completeness the general arrangement of the precession and Weissenberg photographs are given along with the axial directions in Figure 32.

The convention in choosing axes and angles for a triclinic cell is to select them in such a manner as to have the angles all obtuse or all acute. With this convention as a restriction, there are two types of triclinic cells: (1) those with all interaxial angles obtuse and (2) those with all interaxial angles acute, if one is to maintain a right-handed coordinate system (7). There are also two types in a left-handed coordinate system.

If one is to choose a right-handed coordinate system with either all angles acute or all obtuse, one is limited to labeling the reciprocal axes and angles as shown in Figures 32 and 33 to be consistent with the settings for the Weissenberg and precession pictures.

The crystal is rotating about the b axis, the positive direction being away from the rotation dial. Thus upper level Weissenberg pictures will have positive values for the k index.

The reciprocal angles were measured from the precession pictures giving $\alpha^* = 100^\circ 12'$ and $\gamma^* = 103^\circ 26'$. All the cell dimensions can be calculated using the following relations (10):

$$\cos \alpha = \frac{\cos \beta * \cos \gamma * - \cos \alpha *}{\sin \beta * \sin \gamma *}$$

$$\cos \beta = \frac{\cos \alpha * \cos \gamma * - \cos \beta *}{\sin \alpha * \sin \gamma *}$$

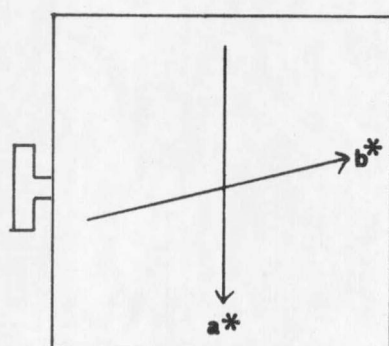
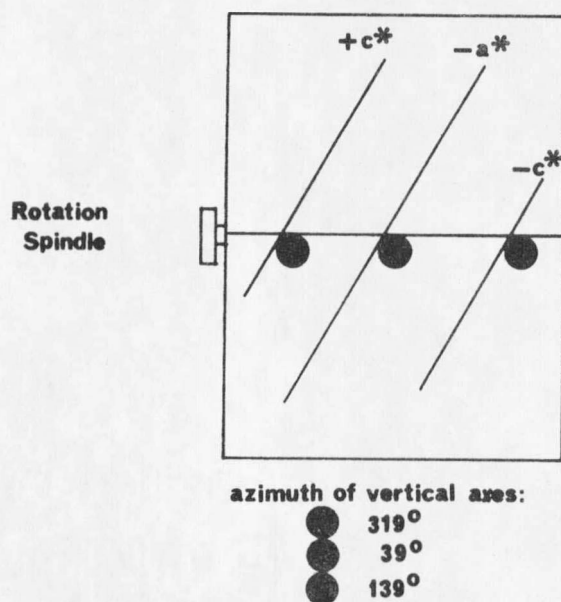
$$\cos \gamma = \frac{\cos \alpha * \cos \beta * - \cos \gamma *}{\sin \alpha * \sin \beta *}$$

α^* and γ^* are required to calculate the rest of the cell dimensions. These angles are most easily measured from precession pictures. A derivation is given, however, of a method by which these two reciprocal lattice angles can be determined from measurements on upper-level Weissenberg films. This method is derived in Appendix B.

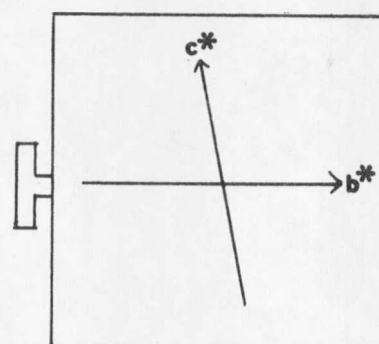
Care must be taken to mount the crystal on the goniometer head in a specific position in order to obtain precession pictures of the desired reciprocal lattice nets. Since none of the interaxial angles is 90° , when the crystal is transferred from the Weissenberg to the precession camera and the azimuth set so that one of the reciprocal lattice axes is vertical, the desired reciprocal lattice plane is not parallel to the film. In other words, the horizontal axis will not record on the film. The crystal must thus be rotated about the vertical reciprocal lattice axis to bring the plane into the desired position. Unless the crystal is mounted in a special manner, this rotation involves both axis of the goniometer head and the process becomes very complicated.

After a zero level Weissenberg picture was taken to determine the setting of the crystal on the goniometer head, the crystal mounting was readjusted so that the reciprocal lattice axes appearing on the Weissenberg film were approximately parallel to the axes of the goniometer head. Then to take a precession picture only one arc needed to be moved. By mounting the crystal in such a manner it was quite simple to obtain precession pictures of both the a^*b^* and the b^*c^* nets.

In choosing the axes of a triclinic crystal great care must be taken in correlating the precession pictures with the Weissenberg films.



Precession, a^*b^* Net
azimuth $38^\circ 50'$
 c^* axis out of plane



Precession, b^*c^* Net
azimuth 321°
 a^* axis out of plane

Arrangement of axes on Weissenberg and Precession Films

Figure 32

$$a = \frac{\lambda}{a^* \sin \beta \sin \gamma^*}$$

$$a^* = \frac{\lambda}{d_{100}}$$

$$c = \frac{\lambda}{c^* \sin \alpha \sin \beta^*}$$

$$c^* = \frac{\lambda}{d_{001}}$$

$$b^* = \frac{\lambda}{b \sin \alpha^* \sin \gamma}$$

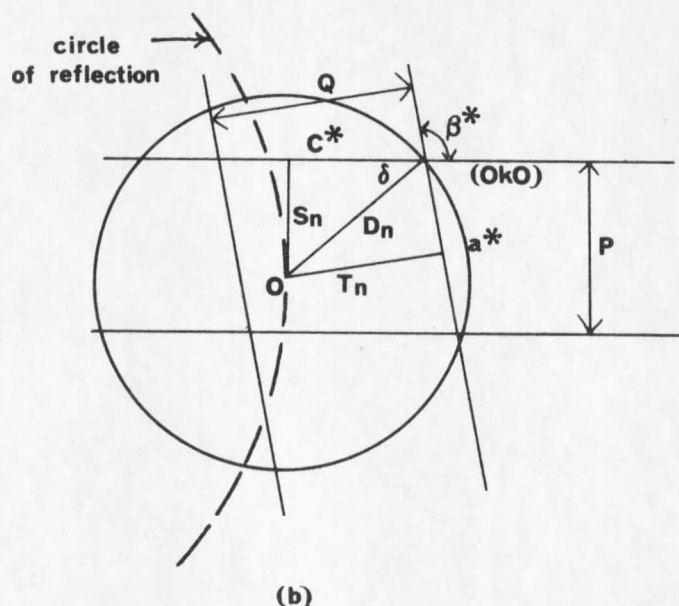
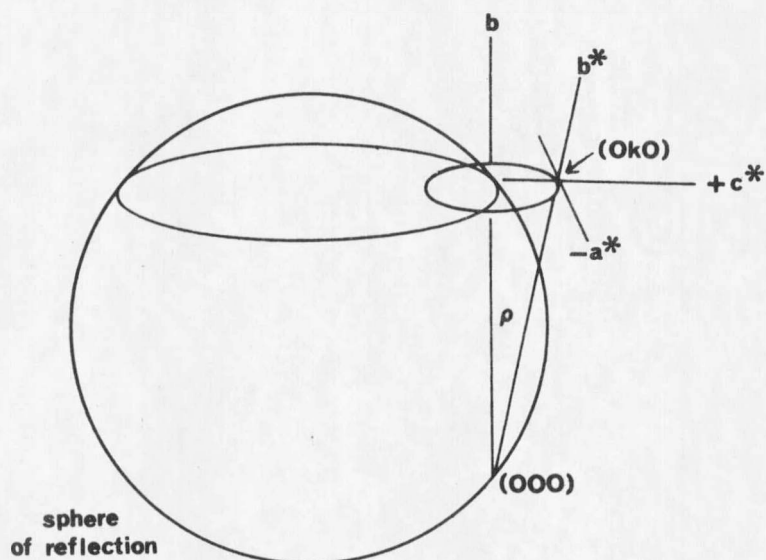
From the values thus obtained the number of molecules per unit cell was calculated to be 8.05. A summary of the cell dimensions of this compound is given in Table XVIII. The calculated density is 1.236g/cc. Since such excellent agreement was obtained between the measured and calculated densities, no analysis was made of the compound.

Indexing Weissenberg Photographs of Triclinic Crystals

It was shown in Part II that the indexing of Weissenberg pictures for monoclinic crystals mounted on the a or c axis required more caution than for crystals of higher symmetry since the b^* axial line is no longer straight on upper-level pictures. Moreover, occasionally a festoon on the lower half of the film shows up on the upper half of the film at a higher level.

For indexing a triclinic crystal the situation is still more complicated. Both axial lines on the zero level Weissenberg films become curved on upper levels. The method used to determine the positions of the festoons on upper-level Weissenberg films will now be given.

Figure 33a shows a stereographic projection of the arrangement of the sphere of reflection and the reciprocal lattice axes for a triclinic cell set for an upper-level equi-inclination Weissenberg picture. Figure



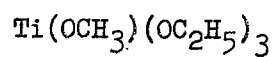
(a) Stereographic projection of arrangement of reciprocal axes.

(b) Circle of rotation and reciprocal axes.

Figure 33

Table XVIII

Summary of Crystal Data



$$a = 12.14 \text{ \AA}$$

$$a^* = 0.1340$$

$$b = 12.13$$

$$b^* = 0.1342$$

$$c = 16.93$$

$$c^* = 0.09495$$

$$\alpha = 76^\circ 56'$$

$$\alpha^* = 100^\circ 12'$$

$$\beta = 77^\circ 2'$$

$$\beta^* = 100^\circ 0'$$

$$\gamma = 74^\circ 15'$$

$$\gamma^* = 103^\circ 26'$$

$$\text{density (measured)} = 1.244 \text{ g/cc}$$

$$\text{density (calculated)} = 1.236 \text{ g/cc}$$

$$\text{molecules per unit cell} = 8$$

$$\text{space group } P1$$

33b shows the top view of the circle of reflection and the reciprocal lattice axes a^* and c^* . The crystal is rotating about the b axis.

As is seen from the figure neither reciprocal axis passes through O' , the point of rotation. Thus on upper-level pictures both of these axes will appear as curves. For both axes some festoon may pass from the lower to the upper half of the picture for some n -level picture. To determine when this occurs it is necessary to calculate the values of S_n and T_n and compare these with the values of the reciprocal lattice interplanar spacings, P and Q , resp. S_n and T_n are the respective distances from the point of rotation to the c^* and a^* axes; D_n is the radius of the circle formed by the point $(0k0)$ as the crystal rotates, and δ is the angle between D_n and c^* .

The magnitude of D_n depends on the distance from the point (000) to the point $(0k0)$ and on the size of the angle φ , the angle between the b axis and the b^* axis (Figure 34).

From Figure 34, the following relations are obtained:

$$D_n = kb^* \sin \varphi, \quad (1)$$

$$E = D_n \cos \delta = kb^* \sin \varphi \cos \delta,$$

but also, $E = kb^* \cos (180^\circ - \alpha^*)$.

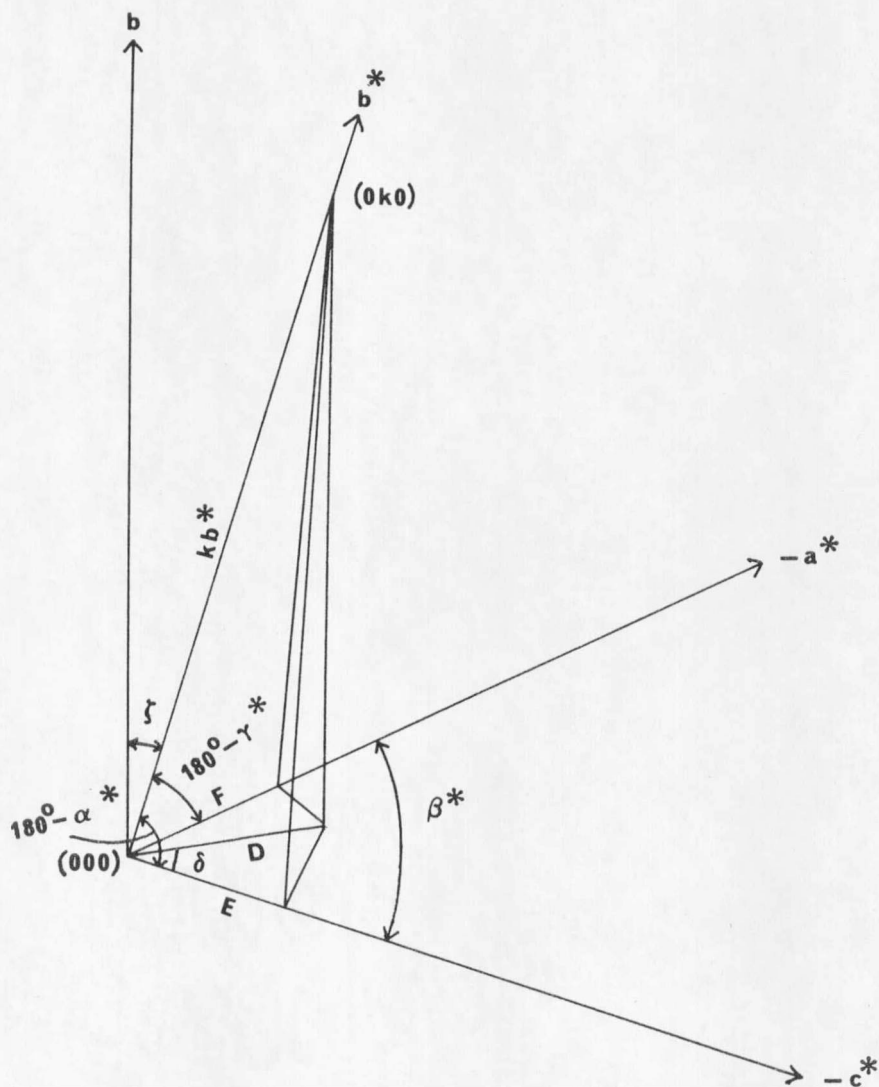
Therefore $\cos(180^\circ - \alpha^*) = \sin \varphi \cos \delta. \quad (2)$

Similarly for F , one finds

$$F = D_n \cos (\beta^* - \delta) = kb^* \sin \varphi \cos (\beta^* - \delta),$$

and $F = kb^* \cos (180^\circ - \gamma^*)$.

Therefore $\sin \varphi \cos (\beta^* - \delta) = \cos (180^\circ - \gamma^*). \quad (3)$



Reciprocal Axes Arrangement

Figure 34

Dividing equation (3) by equation (2), one obtains

$$\frac{\cos(\beta^* - \delta)}{\cos \delta} = \frac{\cos(180^\circ - \gamma^*)}{\cos(180^\circ - \alpha^*)}.$$

With a little manipulation this equation becomes

$$\tan \delta = \frac{\cos(180^\circ - \gamma^*)}{\cos(180^\circ - \alpha^*)} - \cos \beta^* / \sin \beta^*. \quad (4)$$

Rearranging equation (2) gives

$$\sin = \frac{\cos(180^\circ - \alpha^*)}{\cos \delta} \quad (5)$$

From equations (4) and (5) the values of δ and ρ are found, and then D_n is found from (1).

Now from Figure 33b it is seen that $T_n = D_n \sin(\beta^* - \delta)$ and $S_n = D_n \sin \delta$. Thus the values of T_n and S_n are determined. From the same figure the values of P and Q are seen to be $Q = c^* \sin \beta^*$ and $P = a^* \sin(180^\circ - \beta^*)$.

To determine when a particular festoon will have changed from one half of the film to the other it is only necessary to compare P and Q with S_n and T_n .

Using the reciprocal cell dimensions for $\text{Ti}(\text{OCH}_2)(\text{OC}_2\text{H}_5)_3$ it is found that $\delta = 56^\circ 27.5'$ and $\rho = 18^\circ 41.5'$. Also, $Q = 0.0934$ and $P = 0.132$. These values are to be compared with those of S_n and T_n given in the following tabulation.

	(c*)	(a*)
	$Q = 0.0934$	$P = 0.132$
$D_1 = 0.0430$	$T_1 = 0.0296$	$S_1 = 0.0358$
$D_2 = .086$	$T_2 = .0592$	$S_2 = .0716$
$D_3 = .129$	$T_3 = .0888$	$S_3 = .1075$

$D_4 = .172$	$T_4 = .1185$	$S_4 = .1433$
$D_5 = .215$	$T_5 = .1481$	$S_5 = .1791$
$D_6 = .258$	$T_6 = .1778$	$S_6 = .215$
$D_7 = .301$	$T_7 = .2074$	$S_7 = .251$

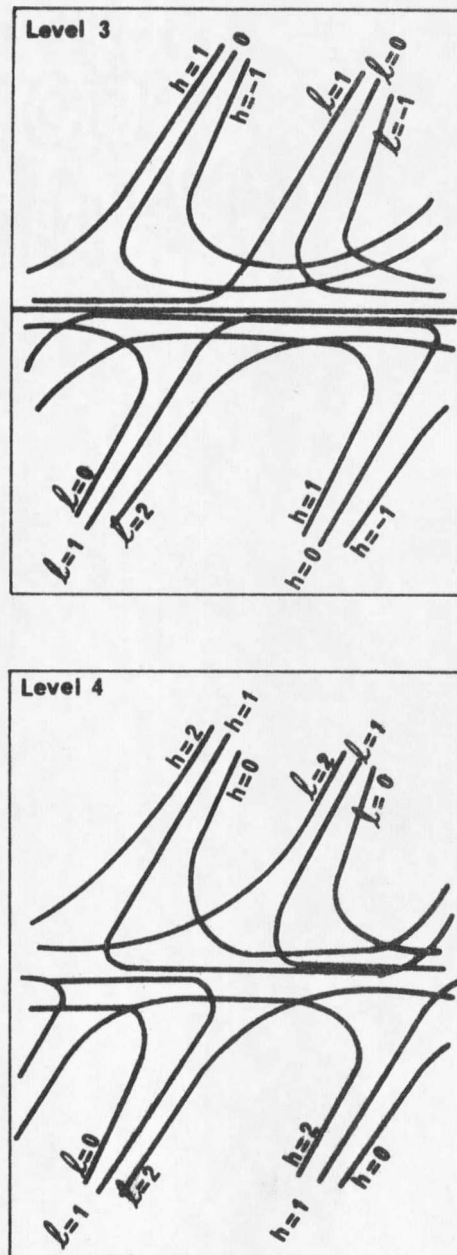
From this table it is seen that a* festoons will change from the lower half of the film to the upper half on levels 4 and 7, and c* festoons also on levels 4 and 7. This indeed was observed. Figure 35 shows how the festoons on the 3rd level differ from those on the 4th.

Determination of the Structure

An IBM 1620 Digital Computer was used for most of the calculations in structure determination.

Reduction of the raw intensity data was corrected for Lorentz and polarization effects using a program of Chi Tang Li. At the same time a Wilson plot ⁽³⁵⁾ was obtained giving an approximate over-all temperature factor of 4.73 and an approximate absolute scale factor of 0.112 for putting the structure factor on an absolute basis. Dividing the structure factors obtained from the data reduction program by this scale factor puts them on an approximate absolute scale.

Three dimensional Patterson and sharpened Patterson maps were calculated. Before trying to interpret the maps, peak heights due to single interatomic vectors were calculated. The origin peak is proportional to $\sum_j z_j^2 = 8080$. The Patterson function was scaled so that the height of the origin peak was 999. The peak height due to the vector between atoms i and j is then $\frac{999}{8080} z_i z_j$, where z_i and z_j are the atomic numbers of the



Comparison of 3d and 4th Level Weissenberg Films

Figure 35

atoms. This gives the following peak heights for the type peaks indicated.

<u>Type Peak</u>	<u>Peak Height</u>
Ti - Ti	60
Ti - O	22
Ti - C	16
O - O	8

Any peak due to an oxygen-oxygen vector or any peak due to the interaction of smaller atoms would be lost in the background. Even a Ti - O peak would not be seen if it were in the neighborhood of a large peak formed from super-position of individual peaks. Twenty peaks had a height of over 100, and many more were greater than 75. Thus there is much overlapping of peaks on the maps, and it is doubtful that a peak representing a single vector could be found.

Ibers ⁽²⁷⁾ reported the approximate structure for titanium tetrathylate determined by X-ray methods. He reported a tetramer with the titanium atoms lying in a plane and forming a diamond-shaped pattern. The first thing I looked for on the Patterson map was a diamond. These peaks were found in the ab plane almost immediately as they were quite large.

Also exactly half way down the c axis on the Patterson map was a peak one-half as high as the origin peak. This immediately suggested the other tetramer unit to be one-half a unit cell length along the c axis, parallel to the first tetramer unit, with corresponding titanium atoms in the two units having the same x and y coordinates, or nearly so. The vectors on the Patterson map indicated a center of symmetry in the tetramer

unit with respect to the titanium atoms, and also a center of symmetry between the two units of titaniums.

Eight titanium atoms were given coordinates such that each tetramer unit had a center of symmetry and so that there was a center between the units. From these coordinates positions of other possible peaks on the Patterson map were calculated. This gave rise to six additional peaks which were found on the map, giving support to this arrangement of atoms. The heights of the peaks were approximately proportional to the number of superposing Ti - Ti peaks. However there was some lack of agreement with the predicted heights probably due to superposed Ti - O or O - O vector peaks. These predicted peaks and their observed heights are listed in Table XIX.

The eight titanium atoms were given the coordinates as tabulated below and a structure factor calculation was made to determine the discrepancy index at this point.

<u>Number of titaniums</u>	<u>x</u>	<u>y</u>	<u>z</u>
1	0.700	0.300	0.250
2	.300	.700	.250
3	.5875	.5875	.250
4	.4125	.4125	.250
5	.700	.300	.750
6	.300	.700	.750
7	.5875	.5875	.750
8	.4125	.4125	.750

Table XIX

Patterson Peaks Used for Locating Titaniums

<u>Peak Height</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>Multiplicity of Peak</u>
498	.000	.000	.000	4
442	.105	.720	.005	4
197	.180	.175	.985	2
390	.287	.890	.995	4

Additional Patterson Peaks Predicted from Titanium Locations

<u>Peak Height</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>Multiplicity of Peak</u>
223	.105	.720	.505	4
65	.180	.180	.490	2
220	.283	.897	.495	4
390	.287	.890	.995	4
147	.390	.605	.995	2
130	.390	.610	.495	2

An overall temperature factor of 4.73 was used. The discrepancy index was 58.52%. The discrepancy index (reliability factor or R factor) as used throughout is a measure of the agreement between observed and calculated structure factors and is defined as $R = \sum |k|F_o| - |F_c|| / \sum |F_o|$. In this expression F_o and F_c are the observed and calculated structure factors, resp., and k is the scale constant to scale the F_o 's and F_c 's to the same scale.

It was observed that when any of the titanium atoms were removed, the R factor decreased. This caused some confusion, but then it was realized that this was due to the effect on reflections for which l is odd. The structure factor is calculated from the expression

$$F_{hkl} = \sum_{n=1}^N f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

$$= \sum_{n=1}^N f_n [\cos 2\pi(hx_n + ky_n + lz_n) + i \sin 2\pi(hx_n + ky_n + lz_n)],$$

where the sum is over the N atoms. Since the titanium atoms were assigned coordinates such that there was a center of symmetry between the two tetramer units, for each x, y, z there was a $-x, -y, -z$. This made the sine terms drop out of the expression. Also, for every value of x, y, z there was an equivalent position $x, y, z + 1/2$. This caused the cosine terms to cancel out whenever l was odd. This caused $\sum |k|F_o| - |F_c||$ to be unusually large, since $F_c = 0$ whenever l is odd. Accordingly, if the titanium atoms were near the correct positions, only the oxygens, carbons, and hydrogens would contribute to the structure factors when l is odd. Since the titanium atoms are the strongest x-ray scatterers in the crystal, the F_o 's would be rather weak for all odd values of l . On checking the F_o 's this was indeed the case.

Next an electron density map was run using only the reflections for which F_c and F_o were both large. This map showed peaks at the postulated titanium positions, and also showed 24 other large peaks on the map covering half the unit cell. If one entire tetramer unit be considered, this put 48 peaks around the four titanium atoms, all of which gave bond distances to the titaniums too short to be titanium-carbon distances. The peaks thus were due to oxygens. Since only reflections were used for which F_c and F_o were both large, this involved only those for which l values were even. Essentially this had the effect of treating the four titanium atoms in one tetramer unit as being equivalent to those in the other unit, so on each tetramer unit appeared its own oxygens plus all the oxygens from the other unit.

Considerable time was spent in trying to obtain structures which were chemically likely, one of the restrictions imposed being the fact that the coordination number of titanium is 6. After such consideration, only one structure could be found, and this was essentially the same as that reported by Ibers for the titanium tetraethylate.

Assuming the structure to be centric, a new structure factor calculation was made, the unequivalent atoms being four titaniums and twelve oxygens. The discrepancy index with these atoms was 42%. After placing the oxygens on the tetramer units there no longer could be a center of symmetry between the tetramers, if it is assumed that there is a center of symmetry for the tetramer unit itself. If there were centers in the tetramers and also one between them, one unit would be generated from the other by simple translation, and this would have the effect of reducing the length of the c axis by half. Thus a center of symmetry could not

exist between the two molecules.

As mentioned, it was assumed that each tetramer had a center of symmetry, at least with respect to the titanium and oxygen atoms. This assumption came from the appearance of the electron density map and from the tetraethylate structure reported by Ibers. With the planes of the titanium atoms situated at $z = 0.250$ and 0.750 , it was difficult to code the structure factor programs with a center of symmetry within each tetramer unit. Thus the z coordinates of all atoms were changed so the titanium planes were in the ab plane at $z = 0.000$ and 0.500 .

By including the twelve oxygens for the second electron density map the ambiguity found on the first map was removed. The remaining oxygens were located from this map. A structure factor calculation was determined with all the titanium and oxygen atoms included, giving a discrepancy index of 36%. Slight refinement of these gave an R-factor of 33%. The carbon positions could not be determined from the electron density maps since the carbon peaks were hidden in the larger oxygen peaks. This lack of resolution is probably caused by insufficient data.

A difference map was calculated using the most intense reflections. From this four carbons were located. Several minimum function maps (8) were calculated using various numbers of vectors, from one to five. When only titanium-titanium vectors were used the same ambiguity was present as on the first electron density maps; oxygens and carbons belonging to one tetramer unit appeared on both units on the map, but not all the oxygens appeared on these maps. When oxygen-titanium vectors were

used, the ambiguity was removed.

From the minimum function maps nine additional possible carbon positions were located. At this point in the structure determination the atom positions were refined by several cycles of least squares. The program used was the one written by van der Helm ⁽³²⁾ for the IBM 1620 with tape input, modified by G. Svetich for card input. An approximation is obtained to the solution of the normal equations by using a block-diagonal matrix. A full matrix solution is not possible on the 1620 computer. A discussion of the use and theory of the least squares refinement method can be found in references (6), (16), (17), (18) and (26).

Least squares cycles were begun with fourteen carbons plus all of the oxygens and titaniums. Since I was unfamiliar with the use of least squares I did not use all of the observed reflections at first. The reflections used were those included in the $(h0l)$, $(hk0)$, $(0kl)$ zones plus selected reflections with large structure factors for (hkl) indices. This was done to decrease the time per least squares cycle. About 300 reflections were used.

Refinement by least squares began with the discrepancy index at 32.2%, for these selected reflections. During the first six cycles of refinement four additional carbons, located from minimum function maps, were added. At the end of six cycles the discrepancy index dropped to 21.7%. For the next cycle all observed reflections were used. The R-factor jumped to 32%. This indicated the necessity of using all data when refining by the least squares method, in order to be overdetermined by as much as possible. The unknown parameters included the three

coordinates of an atom and its isotropic temperature factor, i.e. four parameters per atom. In this series of refinements the number of atoms being refined was 38, or 152 parameters. Thus for 300 reflections it was only over-determined by a factor of four for least squares refinement, and many investigators require at least a factor of six.

Carbons which appeared to be in bad positions were removed, and least squares refinement began again using all oxygens and titaniums plus six carbons. All observed reflections were used. Refinement began at $R = 36.5\%$. Six cycles reduced this value to 26.28% . During this period five reflections were removed as they appeared to be suffering from extinction.

At this point each level of the reflection deck was rescaled by obtaining a scale factor for each level from a structure factor calculation. Reflections of each level were multiplied by the individual scale factor.

A difference map was then calculated and fourteen carbon positions were selected. The next seven cycles of refinement decreased the discrepancy index from 28% to 23% . Refinement apparently stopped at this point.

Consideration of the possible structure of the crystal suggested that even if the titaniums and oxygens in the tetramer unit were related by a center of symmetry, there was no reason to believe the structure was centric with respect to the carbons. In the first place there are four methyl groups per tetramer, and there is no reason to suspect that these methyl groups are related by a center of symmetry. In the second place

there is a possibility of partial rotation of the methyl and ethyl carbons about the axis of the titanium-oxygen bond which might cause the carbons to be non-centric with respect to each other. Therefore it was decided to continue refinement by putting the crystal into the non-centric space group P1. If the crystal is actually centric, the atoms should refine to centric positions.

Least squares refinement for space group P1 was carried out on 60 atoms -- 8 titaniums, 32 oxygens, and 20 carbons. This more than doubled the time per cycle. At the start of this refinement $R = 28.58\%$; at the end of six cycles the R-factor had dropped to 20.43% . Then a difference map was run using all data, observed and unobserved, and twenty-six more carbons were located. The parameters of the other atoms were adjusted somewhat, and refinement continued starting with R at 24.80% . Five cycles reduced R to 15.41% . Bond distances and angles were calculated by a program written by the author. Many bond distances looked chemically unreasonable.

It was decided to take the data to the University of Washington for a full matrix least squares cycle on the IBM 709 computer. The program used was that of Busing and Levy.⁽¹²⁾ Three passes were made for one cycle, 30 atoms being refined on each of the first two passes and 26 on the third pass. The reflection deck had been scaled again level-to-level before going to Seattle.

At the beginning of the run the R factor was 15.1% . It dropped to 14.7% on the first pass, 14.3% on the second pass, and was predicted to be 13.6% after the third pass. On the first cycle the temperature factor of

one atom went non-positive definite and another dropped to less than unity. These two temperature factors were reset to 5.0 for the second pass. After this one cycle of the full matrix least squares, the temperature factors of some carbons were quite large -- one as high as 18.9. The weighting scheme used with the 1620 program was that of Hughes,⁽²⁶⁾ which was built into the program. The program was not functioning when an external weighting scheme was applied. The weighting scheme used on the IBM 709 was one used by Jensen of the University of Washington. This gives unit weight for reflections for which $F_o < 4F_{min}$, and a weight of $\frac{4F_{min}}{F_o}$ for reflections for which $F_o > 4F_{min}$.

At this point bond distances were calculated. Many still looked improbable. Undoubtedly this is due to a lack of data. With 86 atoms being refined with isotropic temperature factors, the number of parameters to be adjusted is 344. The number of observed reflections used was 746, giving an overdetermination of 2.17. Evidently this is not enough even for a full matrix.

Intensities were rechecked for those reflections which had poor agreement between the observed and calculated structure factors. Two intensities had been recorded incorrectly. These were corrected, and minor adjustments were made on thirteen additional reflections. Three more reflections were coded extinct, while one which had been coded extinct was removed from extinction.

Due to the lack of data the atomic coordinates obtained from least squares refinement were likely rather poor. Probably more correct coordinates could be obtained from an electron density map. Using the coordinates

and temperature factors obtained from the full matrix least squares refinement, and using the above-mentioned corrections, structure factors were calculated, giving an R-factor of 16.35%. For these calculations seven carbons which seemed to be in very unlikely positions were removed. Also all temperature factors which were greater than 10 were set to 9.999, the maximum allowable for our structure factor programs.

This F_c deck was used to calculate an electron density map. From this, atomic positions were recorded for all peaks which were resolved and which had a peak height over 100. Titanium peak heights were approximately 900. Coordinates were thus obtained for all the titanium and oxygen atoms, plus eighteen carbon atoms. All remaining carbon peaks were unresolved or had a peak height less than 100.

Bond distances were calculated using parameters from the full matrix least squares refinement and also using the parameters obtained from the electron density map. These are compared with each other in Table XX. Table XXI gives the atomic coordinates obtained from the two methods. Figures 36 and 37 show the general arrangement of the titanium and oxygen atoms in a tetramer unit. Two numbers are by each atom referring to the atoms in the different tetramer units. Figures 38 and 39 show the structure with bond distances included.

Table XXII gives O - Ti - O bond angles using parameters obtained from the least squares refinement.

Investigation of the crystal structure was stopped at this point. It is apparent that more data is needed to locate the remaining carbon atoms. Also additional data will very probably give more reliable bond

Table XX

Bond Distances

<u>From Atom</u>	<u>To Atom</u>	<u>Distance, from Least Squares</u>	<u>Distance, from Electron Density</u>
1	3	3.3987 Å ^O	3.3731 Å ^O
1	4	3.3713	3.3460
1	29	1.7894	1.9514
1	31	2.0011	2.2353
1	33	1.3492	1.9028
1	35	1.5959	1.5613
1	37	2.4413	2.2010
1	39	2.3540	2.1865
2	3	3.2743	3.3186
2	4	3.2862	3.2840
2	30	1.8218	1.7425
2	32	2.0919	2.1902
2	34	1.5561	1.7816
2	36	2.0247	2.0300
2	38	1.9473	1.9607
2	40	2.0302	2.0182
3	4	3.4179	3.3765
3	25	2.1455	1.9916
3	27	1.5300	1.7347
3	31	2.3083	2.2122
3	32	2.2377	2.3082

Table XX
(continued)

<u>From Atom</u>	<u>To Atom</u>	<u>Distance, from Least Squares</u>	<u>Distance, from Electron Density</u>
3	37	2.0387	2.0983
3	40	2.0625	2.0755
4	26	1.7460	1.8609
4	28	1.8589	1.9345
4	31	1.9940 $\overset{\circ}{\text{A}}$	2.0358 $\overset{\circ}{\text{A}}$
4	32	2.1993	2.0949
4	38	2.0502	2.1130
4	39	2.0925	2.0893
5	7	3.4630	3.3347
5	88	3.4216	3.3279
5	9	1.8285	1.9600
5	11	1.9935	2.1984
5	13	1.7459	1.8201
5	15	1.7273	1.7289
5	17	2.2996	2.2830
5	19	2.2167	2.0941
6	7	3.3323	3.3491
6	8	3.3471	3.3880
6	10	1.7399	1.8132
6	12	2.1665	2.2306
6	14	1.8059	1.9073
6	16	2.0046	1.9433

Table XX
(continued)

<u>From Atom</u>	<u>To Atom</u>	<u>Distance, from Least Squares.</u>	<u>Distance, from Electron Density</u>
6	18	1.7074	2.0796
6	20	2.0110	2.1109
7	8	3.5259	3.4168
7	11	2.4307	2.2435
7	12	2.3821	2.2992
7	17	1.8685	1.8742
7	20	2.2167	2.1299
7	21	1.6452	1.9798
7	23	2.3319	1.9353
8	11	2.2361	2.0825
8	12	2.0908	2.2188
8	18	2.1083	2.1034
8	19	2.1804	1.9727
8	22	1.4972	1.7189
8	24	2.1604	1.9211
11	47	1.0860	
11	61	2.1883	
12	48	1.3619	
12	62	1.6339	
15	57	2.1326	1.8587
16	58	1.9434	1.8618
17	63	2.9948	

Table XX
(continued)

<u>From Atom</u>	<u>To Atom</u>	<u>Distance, from Least Squares</u>	<u>Distance, from Electron Density</u>
17	85	1.2391	1.5955
18	64	2.6059	2.0868
18	86	0.9025	
19	43	1.7802	1.5482
19	53	1.9760	
20	44	1.6392	1.5517
20	54	2.3130	
21	55	2.4174	2.0391
21	65	1.3818	
22	56	1.8924	
22	66	1.2432	
23	59	1.6261	1.8521
24	60	1.6132	1.7587
25	67	1.6192	
25	69	1.9516	1.9015
26	68	1.9500	
26	70	2.6057	
29	77	1.7370	
29	79	1.7216	1.6849
30	78	1.9648	
30	80	2.6675	
31	45	1.4410	1.3872
32	46	1.1466	

Table XX
(continued)

<u>From Atom</u>	<u>To Atom</u>	<u>Distance, from Least Squares</u>	<u>Distance, from Electron Density</u>
33	81	1.5469	
33	83	1.0785	
34	84	2.9452	
35	71	1.7645	1.8659
35	73	1.9982	
36	72	1.6898	
36	74	2.3741	
37	49	1.7759	1.6806
37	75	2.5545	2.3729
38	50	1.5789	1.5331
38	76	2.0759	
39	41	1.1604	
39	51	2.0419	2.0293
40	42	1.7779	
40	52	2.4956	2.0898
41	51	1.4625	
42	52	1.6314	
43	53	1.6705	
44	54	1.6433	
47	61	1.1317	
48	62	0.7111	
49	75	2.1824	1.9310

Table XX
(continued)

<u>From Atom</u>	<u>To Atom</u>	<u>Distance, from Least Squares</u>	<u>Distance, from Electron Density</u>
50	76	1.3169	
55	65	1.3905	
56	66	1.5983	
63	85	1.8272	
64	86	1.9362	
67	69	1.0692	
68	70	1.8355	
71	73	1.1696	
72	74	2.3863	
77	79	1.6995	
78	80	1.8310	
81	82	1.7416	
83	84	2.5098	

Table XXI

Atom Parameters

Atom Type and Number	from Least Squares				from Electron Density		
	x	y	z	B	x	y	z
Ti 1	0.3013 (.0021)	0.6951 (.0024)	0.0162 (.0019)	6.830 (.875)	0.3050	0.7000	0.0050
Ti 2	.6946 (.0022)	.3085 (.0024)	-.0029 (.0018)	6.048 (.886)	.6940	.3050	.0000
Ti 3	.4146 (.0019)	.4103 (.0023)	.0012 (.0017)	4.760 (.843)	.4110	.4130	.0030
Ti 4	.5910 (.0022)	.5878 (.0024)	.0002 (.0018)	6.668 (.855)	.5900	.5850	-.0010
Ti 5	.3021 (.0020)	.7055 (.0022)	.4899 (.0016)	4.830 (.829)	.3050	.7030	.4960
Ti 6	.6925 (.0022)	.3055 (.0024)	.5066 (.0018)	7.969 (.894)	.6940	.3050	.5030
Ti 7	.4075 (.0020)	.4069 (.0024)	.5098 (.0018)	6.250 (.874)	.4090	.4170	.5050
Ti 8	.5925 (.0022)	.5937 (.0025)	.4930 (.0019)	6.372 (.881)	.5880	.5950	.4970
O 9	.1949 (.0066)	.6713 (.0071)	.4444 (.0049)	9.870 (2.42)	.2020	.6600	.4400
O 10	.7676 (.0070)	.3193 (.0074)	.5788 (.0052)	9.705 (2.47)	.7780	.3290	.5710
O 11	.4399 (.0063)	.5963 (.0070)	.4385 (.0053)	5.000* (2.32)	.4580	.5840	.4390
O 12	.5598 (.0063)	.4371 (.0070)	.5641 (.0052)	5.977 (2.32)	.5520	.4280	.5700
O 13	.1934 (.0065)	.7641 (.0068)	.5660 (.0048)	7.970 (2.26)	.1900	.7800	.5670
O 14	.7773 (.0069)	.2535 (.0074)	.4145 (.0051)	7.979 (2.32)	.7880	.2200	.4200
O 15	.3608 (.0059)	.8091 (.0068)	.4175 (.0045)	9.420 (2.10)	.3610	.8050	.4200
O 16	.6557 (.0063)	.1545 (.0070)	.5687 (.0048)	6.002 (2.31)	.6620	.1600	.5690
O 17	.3096 (.0063)	.5220 (.0069)	.5669 (.0047)	9.450 (2.25)	.2950	.5200	.5650
O 18	.6947 (.0062)	.4411 (.0075)	.4503 (.0049)	5.579 (2.09)	.7080	.4680	.4350

*On the first pass of the full matrix least squares the temperature

factor of oxygen-11 dropped to 1.260. This was put back to 5.00 for the

remainder of the cycle. Numbers in parentheses are standard deviations.

Table XXI
(continued)

Atom Type and Number	from Least Squares				from Electron Density		
	x	y	z	B	x	y	z
0 19	0.4342 (.0064)	0.6750 (.0072)	0.5690 (.0050)	8.360 (2.89)	0.4390	0.6580	0.5650
0 20	.5679 (.0065)	.2992 (.0074)	.4480 (.0056)	7.284 (2.38)	.5570	.3080	.4440
0 21	.3949 (.0057)	.2830 (.0069)	.5712 (.0045)	7.330 (2.15)	.3900	.2720	.5830
0 22	.6403 (.0064)	.6859 (.0072)	.4307 (.0049)	5.139 (2.13)	.6420	.6970	.4210
0 23	.3171 (.0063)	.4239 (.0068)	.3983 (.0045)	8.580 (2.14)	.3150	.4000	.4320
0 24	.6949 (.0066)	.5953 (.0068)	.5818 (.0049)	8.749 (2.41)	.6820	.6000	.5370
0 25	.2662 (.0063)	.3827 (.0065)	.0930 (.0046)	8.830 (2.28)	.2700	.3830	.0830
0 26	.6984 (.0062)	.6221 (.0066)	-.0827 (.0046)	5.469 (2.08)	.7100	.6280	-.0820
0 27	.4036 (.0059)	.3341 (.0067)	-.0560 (.0045)	6.830 (2.19)	.4120	.3250	-.0650
0 28	.6010 (.0063)	.6606 (.0070)	.0830 (.0048)	7.872 (2.28)	.6000	.6700	.0800
0 29	.1842 (.0056)	.6265 (.0063)	.0656 (.0042)	6.240 (2.04)	.1700	.6400	.0650
0 30	.8178 (.0066)	.3458 (.0070)	-.0784 (.0050)	11.366 (2.44)	.8160	.3350	-.0700
0 31	.4321 (.0060)	.5651 (.0066)	.0517 (.0051)	4.270 (2.26)	.4350	.5500	.0600
0 32	.5849 (.0065)	.4511 (.0066)	-.0636 (.0057)	2.881 (2.35)	.5850	.4580	-.0650
0 33	.2774 (.0064)	.7594 (.0073)	-.0568 (.0054)	8.920 (2.33)	.2180	.8080	-.0720
0 34	.7315 (.0068)	.2033 (.0075)	.0655 (.0052)	8.116 (2.30)	.7600	.1850	.0700
0 35	.3097 (.0065)	.7733 (.0071)	.0778 (.0049)	5.930 (2.29)	.3150	.7730	.0670
0 36	.6738 (.0064)	.1809 (.0070)	-.0534 (.0049)	7.796 (2.42)	.6770	.1850	-.0600
0 37	.3287 (.0060)	.5513 (.0064)	-.0709 (.0046)	4.730 (2.05)	.3290	.5650	-.0690
0 38	.6733 (.0062)	.4307 (.0065)	.0602 (.0047)	5.844 (2.00)	.6680	.4250	.0670
0 39	.4781 (.0056)	.7036 (.0064)	-.0746 (.0050)	2.980 (2.01)	.4750	.7050	-.0720
0 40	.5374 (.0057)	.2739 (.0062)	.0508 (.0045)	4.609 (1.93)	.5350	.2850	.0600

Table XXI
(continued)

Atom Type and Number	from Least Squares				from Electron Density		
	x	y	z	B	x	y	z
C 41	0.4994 (.0097)	0.7591 (.0129)	-.1391 (.0088)	7.940 (3.83)			
C 42	.5203 (.0093)	.2001 (.0113)	.1547 (.0079)	7.475 (3.95)			
C 43	.4592 (.0086)	.7207 (.0104)	.6549 (.0073)	4.730 (3.07)	.4450	.7100	.6390
C 44	.6121 (.0104)	.2758 (.0109)	.3531 (.0082)	5.982 (3.63)	.6000	.3800	.3600
C 45	.4243 (.0101)	.5812 (.0111)	.1347 (.0091)	5.890 (4.01)	.4150	.5400	.1450
C 46	.6232 (.0108)	.4604 (.0109)	-0.1325 (.0091)	2.392 (3.93)			
C 47	.4567 (.0092)	.6334 (.0097)	.3735 (.0081)	5.000*			
C 48	.5448 (.0081)	.4383 (.0090)	.6461 (.0067)	0.645 (2.72)			
C 49	.2717 (.0094)	.6132 (.0103)	-.1632 (.0073)	5.810 (3.59)	.2700	.6070	-.1550
C 50	.6885 (.0094)	.4525 (.0102)	.1452 (.0074)	2.967 (3.13)	.7100	.4400	.1420
C 51	.4972 (.0098)	.8700 (.0125)	-.1177 (.0076)	9.230 (3.75)	.4800	.8750	-.1100
C 52	.5006 (.0098)	.0841 (.0120)	.1317 (.0078)	8.914 (3.65)	.5080	.1270	.1320
C 53	.4714 (.0092)	.8231 (.0110)	.5709 (.0075)	7.880 (3.47)			
C 54	.5419 (.0097)	.1713 (.0109)	.3749 (.0075)	7.739 (3.34)			
C 55	.3070 (.0095)	.1345 (.0102)	.6636 (.0070)	7.510 (3.46)	.3200	.1400	.6550
C 56	.7000 (.0105)	.7902 (.0112)	.3405 (.0078)	12.966 (3.85)			
C 57	.2942 (.0093)	.9779 (.0100)	.3520 (.0067)	7.420 (3.31)	.3000	.9540	.3670
C 58	.7084 (.0099)	-.0047 (.0114)	.6233 (.0077)	6.467 (3.51)	.7120	.0030	.6120
C 59	.2442 (.0087)	.3542 (.0097)	.3655 (.0066)	5.700 (3.02)	.2360	.3600	.3650

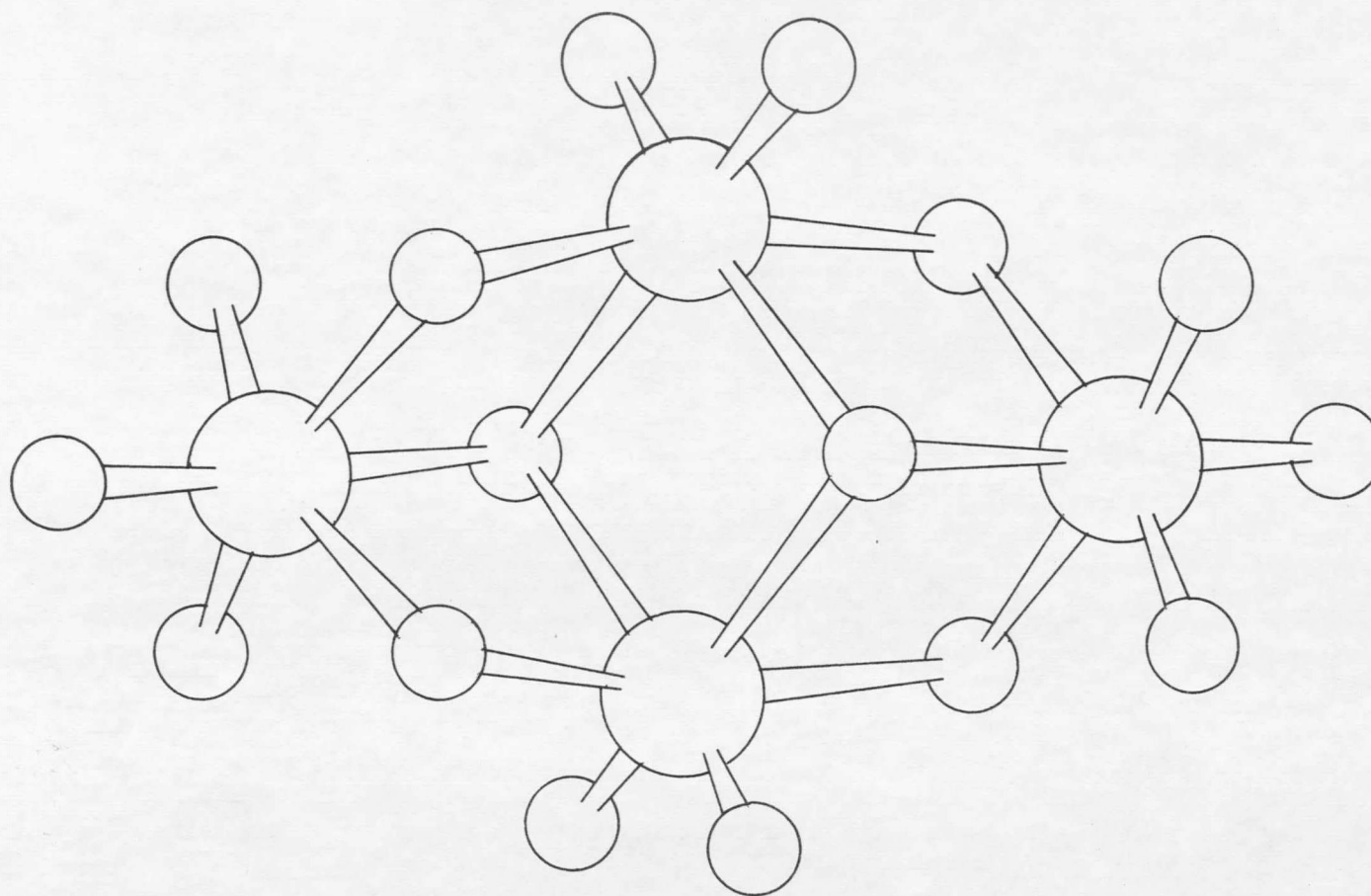
On the first pass of the full matrix L. S. the temperature factor of carbon-47 went negative. This was put back to 5.00 for the remainder of the cycle.

Table XXI
(continued)

Atom Type and Number	from Least Squares				from Electron Density		
	x	y	z	B	x	y	z
C 60	0.8130 (.0106)	0.6251 (.0107)	0.5904 (.0074)	9.270 (3.57)	0.8030	0.6460	0.5830
C 61	.4472 (.0097)	.6930 (.0108)	.3122 (.0070)	9.312 (3.34)			
C 62	.5120 (.0107)	.3951 (.0118)	.6616 (.0081)	12.985 (3.93)			
C 63	.1043 (.0098)	.4154 (.0106)	.6333 (.0071)	3.879 (3.46)			
C 64	.8889 (.0110)	.4967 (.0116)	.3732 (.0079)	4.840 (3.88)	.8670	.5060	.3750
C 65	.3641 (.0118)	.1775 (.0125)	.5866 (.0087)	14.859 (4.68)			
C 66	.6451 (.0123)	.7850 (.0126)	.4360 (.0091)	16.220 (4.29)			
C 67	.1452 (.0126)	.3427 (.0129)	.1073 (.0099)	9.027 (4.64)			
C 68	.8115 (.0120)	.7043 (.0126)	-.0738 (.0095)	7.561 (4.54)			
C 69	.1724 (.0104)	.2737 (.0107)	.1558 (.0083)	3.504 (3.71)	.1630	.2930	.1450
C 70	.8712 (.0113)	.6958 (.0108)	-.1825 (.0083)	7.809 (4.16)			
C 71	.2755 (.0112)	.8483 (.0130)	.1613 (.0090)	9.387 (4.25)	.2700	.8780	.1400
C 72	.7135 (.0112)	.2193 (.0126)	-.1562 (.0079)	12.307 (4.21)			
C 73	.2525 (.0017)	.9300 (.0133)	.1106 (.0093)	9.290 (4.16)			
C 74	.7815 (.0109)	.0152 (.0112)	-.1122 (.0076)	7.877 (3.60)			
C 75	.1422 (.0098)	.5156 (.0103)	-.0958 (.0071)	6.776 (3.46)	.1630	.5150	-.0900
C 76	.7994 (.0111)	.4505 (.0114)	.1175 (.0078)	12.544 (4.07)			
C 77	.1661 (.0116)	.5698 (.0124)	.1703 (.0082)	14.017 (4.27)			
C 78	.8880 (.0127)	.3695 (.0128)	-.1956 (.0088)	17.069 (4.20)			
C 79	.0550 (.0106)	.6691 (.0112)	.1301 (.0079)	7.733 (3.49)	.0470	.6630	.1350
C 80	.0268 (.0112)	.2798 (.0112)	-.1686 (.0078)	13.117 (3.77)			

Table XXI
(continued)

Atom Type and Number	from Least Squares				from Electron Density		
	x	y	z	B	x	y	z
C 81	0.1684 (.0124)	0.8263 (.0134)	0-.0952 (.0085)	15.536 (4.46)			
C 82	.1763 (.0132)	.9701 (.0142)	-.1349 (.0095)	18.869 (4.79)			
C 83	.7702 (.0121)	.2040 (.0121)	.1168 (.0086)	13.566 (4.55)			
C 84	.8933 (.0119)	.0009 (.0125)	.1429 (.0083)	8.003 (4.11)			
C 85	.2238 (.0123)	.4889 (.0123)	.6104 (.0087)	10.062 (4.19)	.1990	.5000	.6450
C 86	.7278 (.0110)	.4873 (.0113)	.4071 (.0084)	6.454 (4.13)			



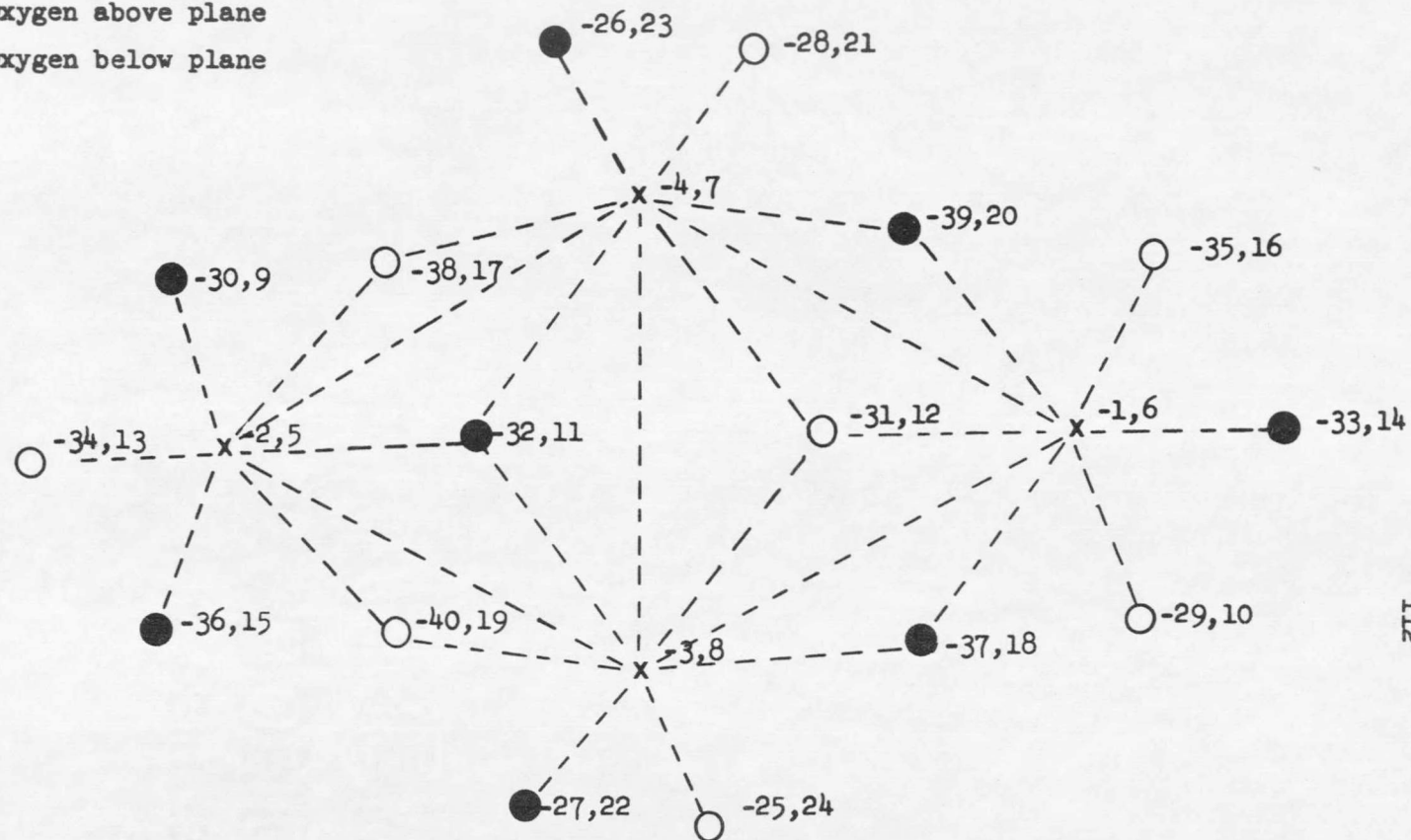
large atoms are titanium atoms

small circles are oxygen atoms

Structure of $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer

Figure 36

- x = Titanium
 ○ = Oxygen above plane
 ● = Oxygen below plane



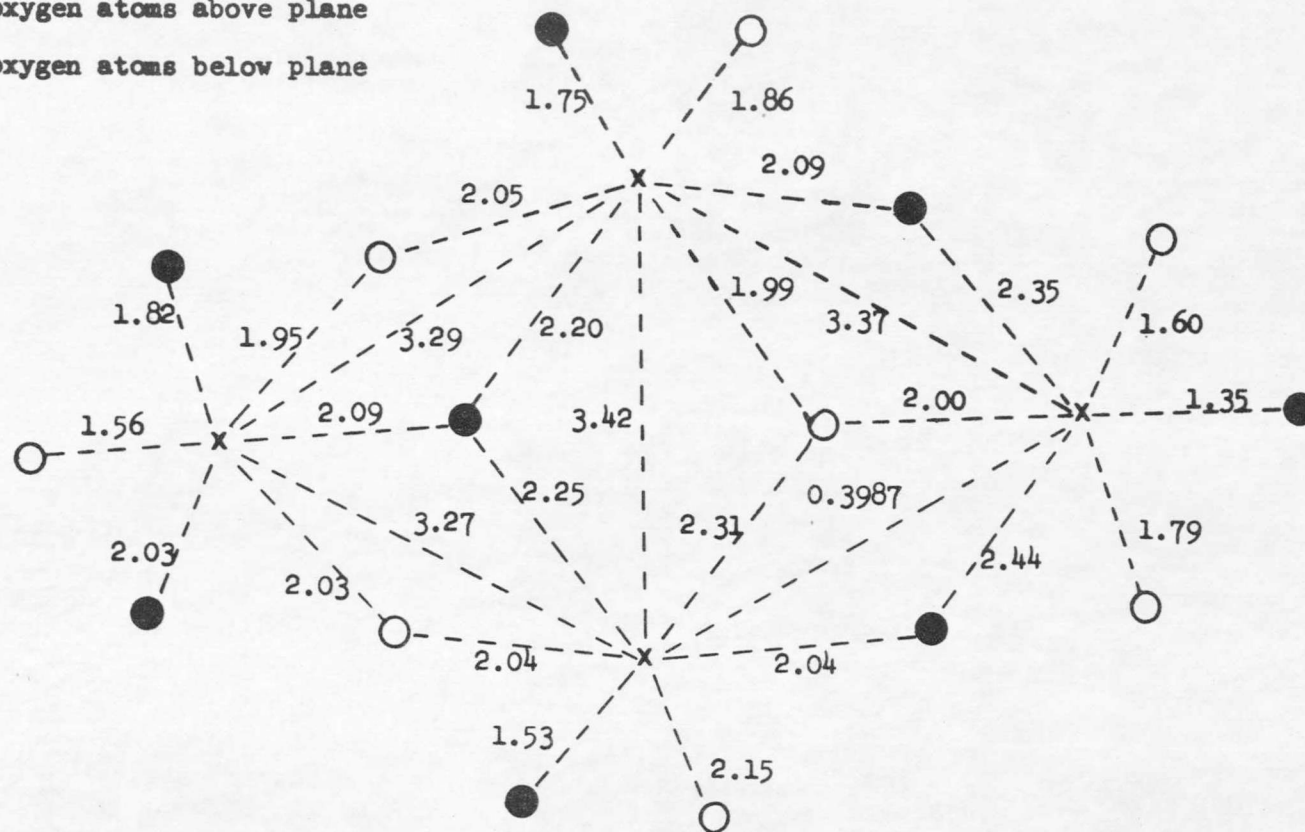
$\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer

Figure 37

x = titanium atoms

○ = oxygen atoms above plane

● = oxygen atoms below plane



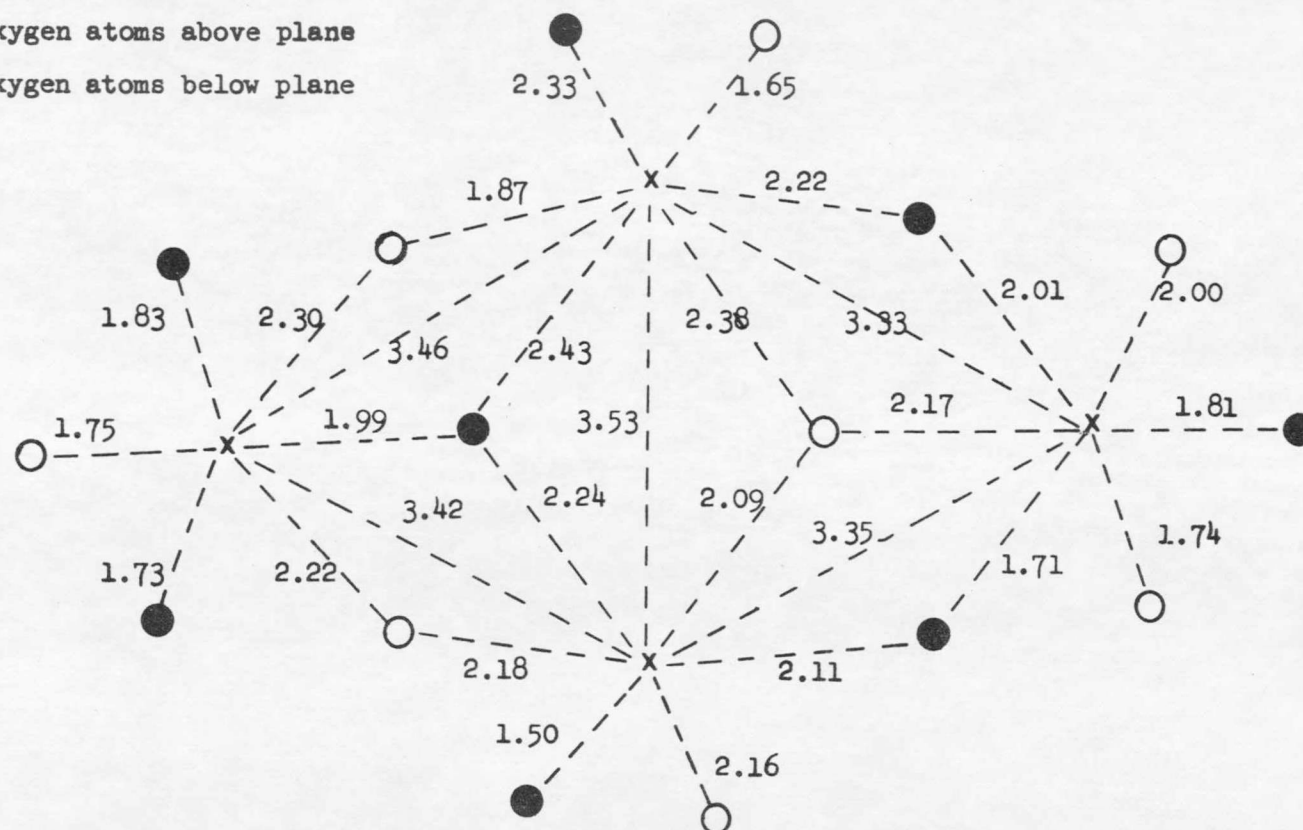
$\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer Unit #1

Bond Distances

using parameters from least squares refinement

Figure 38

- x = titanium atoms
 ○ = oxygen atoms above plane
 ● = oxygen atoms below plane



$\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ Tetramer Unit #2

Bond Distances

using parameters from least squares refinement

Figure 39

Table XXII

O-Ti-O Bond Angles

<u>Atoms</u>	<u>Bond Angle</u>	<u>Atoms</u>	<u>Bond Angle</u>
(O-29)-(Ti-1)-(O-31)	97.95° (3.65°)	(O-32)-(Ti-2)-(O-40)	79.74° (3.24°)
(O-29)-(Ti-1)-(O-33)	108.97° (4.81°)	(O-34)-(Ti-2)-(O-36)	81.58° (4.24°)
(O-29)-(Ti-1)-(O-35)	105.86° (4.24°)	(O-34)-(Ti-2)-(O-38)	97.20° (4.24°)
(O-29)-(Ti-1)-(O-37)	79.13° (3.26°)	(O-34)-(Ti-2)-(O-40)	79.66° (4.08°)
(O-29)-(Ti-1)-(O-39)	152.58° (3.53°)	(O-36)-(Ti-2)-(O-38)	165.03° (3.71°)
(O-31)-(Ti-1)-(O-33)	134.81° (4.18°)	(O-36)-(Ti-2)-(O-40)	72.15° (3.35°)
(O-31)-(Ti-1)-(O-35)	93.61° (4.10°)	(O-38)-(Ti-2)-(O-40)	92.92° (3.35°)
(O-31)-(Ti-1)-(O-37)	74.47° (3.13°)	(O-25)-(Ti-3)-(O-27)	96.98° (3.87°)
(O-31)-(Ti-1)-(O-39)	68.21° (3.15°)	(O-25)-(Ti-3)-(O-31)	93.38° (3.10°)
(O-33)-(Ti-1)-(O-35)	112.07° (5.19°)	(O-25)-(Ti-3)-(O-32)	163.24° (3.29°)
(O-33)-(Ti-1)-(O-37)	75.85° (4.35°)	(O-25)-(Ti-3)-(O-37)	96.68° (3.26°)
(O-33)-(Ti-1)-(O-39)	71.48° (4.36°)	(O-25)-(Ti-3)-(O-40)	98.00° (3.18°)
(O-35)-(Ti-1)-(O-37)	167.74° (3.99°)	(O-27)-(Ti-3)-(O-31)	162.95° (3.97°)
(O-35)-(Ti-1)-(O-39)	98.75° (3.87°)	(O-27)-(Ti-3)-(O-32)	98.42° (3.86°)
(O-37)-(Ti-1)-(O-39)	74.42° (2.81°)	(O-27)-(Ti-3)-(O-37)	88.47° (3.91°)
(O-30)-(Ti-2)-(O-32)	88.86° (3.68°)	(O-27)-(Ti-3)-(O-40)	89.23° (3.84°)
(O-30)-(Ti-2)-(O-34)	112.88° (4.53°)	(O-31)-(Ti-3)-(O-32)	73.30° (3.02°)
(O-30)-(Ti-2)-(O-36)	97.73° (3.82°)	(O-31)-(Ti-3)-(O-37)	76.88° (3.13°)
(O-30)-(Ti-2)-(O-38)	96.46° (3.75°)	(O-31)-(Ti-3)-(O-40)	102.69° (3.12°)
(O-30)-(Ti-2)-(O-40)	163.10° (3.82°)	(O-32)-(Ti-3)-(O-37)	90.25° (3.22°)
(O-32)-(Ti-2)-(O-34)	158.01° (4.35°)	(O-32)-(Ti-3)-(O-40)	75.72° (3.09°)

Table XXII
(continued)

<u>Atoms</u>	<u>Bond Angle</u>	<u>Atoms</u>	<u>Bond Angle</u>
(O-32)-(Ti-2)-(O-36)	99.28° (3.50°)	(O-37)-(Ti-3)-(O-40)	165.29° (3.42°)
(O-32)-(Ti-2)-(O-38)	76.26° (3.35°)	(O-26)-(Ti-4)-(O-28)	105.97° (3.99°)
(O-26)-(Ti-4)-(O-31)	154.11° (3.92°)	(O-15)-(Ti-5)-(O-17)	153.51° (3.78°)
(O-26)-(Ti-4)-(O-32)	85.98° (3.57°)	(O-15)-(Ti-5)-(O-19)	93.47° (3.75°)
(O-26)-(Ti-4)-(O-38)	102.80° (3.68°)	(O-17)-(Ti-5)-(O-19)	73.49° (3.19°)
(O-26)-(Ti-4)-(O-39)	83.49° (3.60°)	(O-10)-(Ti-6)-(O-12)	81.61° (3.90°)
(O-28)-(Ti-4)-(O-31)	93.42° (3.73°)	(O-10)-(Ti-6)-(O-14)	117.57° (4.41°)
(O-28)-(Ti-4)-(O-32)	160.59° (3.74°)	(O-10)-(Ti-6)-(O-16)	94.55° (4.02°)
(O-28)-(Ti-4)-(O-38)	90.33° (3.61°)	(O-10)-(Ti-6)-(O-18)	94.34° (4.43°)
(O-28)-(Ti-4)-(O-39)	108.82° (3.66°)	(O-10)-(Ti-6)-(O-20)	164.14° (4.29°)
(O-31)-(Ti-4)-(O-32)	80.51° (3.32°)	(O-12)-(Ti-6)-(O-14)	149.62° (4.00°)
(O-31)-(Ti-4)-(O-38)	93.86° (3.41°)	(O-12)-(Ti-6)-(O-16)	104.34° (3.54°)
(O-31)-(Ti-4)-(O-39)	73.95° (3.33°)	(O-12)-(Ti-6)-(O-18)	69.16° (3.88°)
(O-32)-(Ti-4)-(O-38)	71.86° (3.17°)	(O-12)-(Ti-6)-(O-20)	85.05° (3.59°)
(O-32)-(Ti-4)-(O-39)	87.43° (3.21°)	(O-14)-(Ti-6)-(O-16)	97.64° (3.95°)
(O-38)-(Ti-4)-(O-39)	157.56° (3.44°)	(O-14)-(Ti-6)-(O-18)	85.23° (4.31°)
(O-9)-(Ti-5)-(O-11)	96.23° (3.80°)	(O-14)-(Ti-6)-(O-20)	78.13° (3.98°)
(O-9)-(Ti-5)-(O-13)	91.23° (4.01°)	(O-16)-(Ti-6)-(O-18)	168.06° (4.22°)
(O-9)-(Ti-5)-(O-15)	106.48° (4.08°)	(O-16)-(Ti-6)-(O-20)	80.44° (3.66°)
(O-9)-(Ti-5)-(O-17)	83.90° (3.54°)	(O-18)-(Ti-6)-(O-20)	88.86° (4.12°)
(O-9)-(Ti-5)-(O-19)	157.33° (3.82°)	(O-11)-(Ti-7)-(O-12)	73.86° (2.98°)
(O-11)-(Ti-5)-(O-13)	159.35° (4.00°)	(O-11)-(Ti-7)-(O-17)	70.57° (3.37°)

Table XXII
(continued)

<u>Atoms</u>	<u>Bond. Angle</u>	<u>Atoms</u>	<u>Bond. Angle</u>
(O-11)-(Ti-5)-(O-15)	82.86° (3.82°)	(O-11)-(Ti-7)-(O-20)	97.53° (3.23°)
(O-11)-(Ti-5)-(O-17)	71.66° (3.03°)	(O-11)-(Ti-7)-(O-21)	169.84° (3.91°)
(O-11)-(Ti-5)-(O-19)	75.33° (3.43°)	(O-11)-(Ti-7)-(O-23)	82.40° (2.98°)
(O-13)-(Ti-5)-(O-15)	113.42° (4.15°)	(O-12)-(Ti-7)-(O-17)	85.93° (3.48°)
(O-13)-(Ti-5)-(O-17)	90.11° (3.61°)	(O-12)-(Ti-7)-(O-20)	75.74° (3.24°)
(O-13)-(Ti-5)-(O-19)	90.50° (3.71°)	(O-12)-(Ti-7)-(O-21)	96.94° (3.80°)
(O-12)-(Ti-7)-(O-23)	150.06° (3.20°)	(O-11)-(Ti-8)-(O-24)	160.70° (3.41°)
(O-17)-(Ti-7)-(O-20)	160.51° (3.82°)	(O-12)-(Ti-8)-(O-18)	64.18° (3.47°)
(O-17)-(Ti-7)-(O-21)	105.00° (4.17°)	(O-12)-(Ti-8)-(O-19)	84.93° (3.46°)
(O-17)-(Ti-7)-(O-23)	103.32° (3.51°)	(O-12)-(Ti-8)-(O-22)	165.65° (4.48°)
(O-20)-(Ti-7)-(O-21)	84.06° (3.91°)	(O-12)-(Ti-8)-(O-24)	87.50° (3.40°)
(O-20)-(Ti-7)-(O-23)	89.84° (3.25°)	(O-18)-(Ti-8)-(O-19)	147.38° (3.65°)
(O-21)-(Ti-7)-(O-23)	107.66° (3.82°)	(O-18)-(Ti-8)-(O-22)	101.54° (4.34°)
(O-11)-(Ti-8)-(O-12)	83.82° (3.35°)	(O-18)-(Ti-8)-(O-24)	97.80° (3.46°)
(O-11)-(Ti-8)-(O-18)	93.88° (3.41°)	(O-19)-(Ti-8)-(O-22)	109.37° (4.30°)
(O-11)-(Ti-8)-(O-19)	71.43° (3.26°)	(O-19)-(Ti-8)-(O-24)	90.68° (3.35°)
(O-11)-(Ti-8)-(O-22)	99.37° (4.19°)	(O-22)-(Ti-8)-(O-24)	93.28° (4.19°)

All numbers in parentheses are standard deviations.

distances. The essential features of the structure, however, have been determined.

Review of Structure

The crystal data are shown in Table XVIII. There are eight molecules of $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ per unit cell, the molecules being grouped together into two tetramer units. The titanium atoms of one tetramer are very nearly parallel to the ab plane of the crystal and form a diamond shaped structure, the oxygens lying approximately in two planes above and below the plane of the titaniums. The other tetramer is displaced one-half a cell length along the c axis and is turned over with respect to the first.

Each titanium atom has a coordination number of six, oxygens being shared between titaniums. This gives rise to three different types of oxygen atoms in the tetramer with respect to bonding. Eight oxygen atoms are bonded to only one titanium atom, four oxygens are bonded to two titaniums, and two oxygens are bonded to three titanium atoms. In general, the titanium-oxygen bond distances are greater to those oxygens which are shared with the greater number of titanium atoms. This is essentially the structure reported for titanium tetraethylate by Ibers. (27)

DISCUSSION

The purpose of determining the dipole moments of the various titanium alkoxides at different temperatures was to obtain some idea of the potential energy barrier to restriction of rotation of the alkoxy groups, if rotation was at all hindered. It was shown that with an increase in temperature the dipole moments increased toward the theoretical value calculated assuming complete freedom of rotation, and from this it was concluded that rotation is hindered and that the potential energy barrier is of the same order of magnitude as the thermal energy, i.e., kT .

Although some of these titanates have been shown to be trimers in solution, the calculations for the dipole moments were made assuming the compounds to be monomers. By obtaining the molar polarizations by extrapolating the curves to infinite dilution, it seemed reasonable to expect that values for monomers were being obtained.

As would be expected, for each temperature at which measurements were made, the dipole moments determined for the ethyl, the n-propyl, and the n-butyl titanates are very nearly the same. However, the dipole moment for tert-butyl titanate is considerably higher than for the other three esters at the same temperature (at 25°C , 1.86 D. for the tert-butylate and 1.54 D. for the ethylate). One would expect less freedom of rotation of the alkoxy groups in the tert-butyl compound than in the other titanates, due to greater steric hindrance. However, restriction of rotation would tend to cause the tert-butylate to have a lower dipole moment than the others. A different explanation for this difference in

values must then be found.

In a private communication to C. N. Caughlan, D. C. Bradley stated that he and his co-workers have made very careful molecular weight measurements of tetraethyl titanate cryscopically and have found its association number to remain 3 in very dilute solution. This then might indicate that the dielectric measurements obtained are for trimers, not monomers. A second consideration of the dielectric constants and the specific volumes as a function of concentration (Figures 3 through 22) suggests that for a given temperature the association number of these compounds does not change with concentration. If there were a decrease in molecular complexity as the concentrations were decreased, these curves might be expected to be non-linear, especially at lower concentrations. The fact that these curves are linear gives support to Bradley's findings that the molecular association is not dependent on concentration, at least in dilute solutions.

Bradley also reported that tert-butyl titanate is monomeric in solution.⁽⁵⁾ Thus the differences between the dipole moment of tert-butylate and those of the other alkyl titanates is probably due to the fact that the tert-butylate is monomeric and the other esters studied are trimeric in solution.

In Part I the interpretation of the increase of the dipole moments with temperature was that there was more rotation of the alkoxy groups at the higher temperature, the values approaching the theoretical value calculated assuming complete freedom of rotation. Even if the titanate molecules are trimers as is indicated, it is very likely that at least part of the variation of dipole moment with temperature is due to a change in

the degree of restriction of rotation. This variation may also be due to a decrease in the molecular complexity with an increase in temperature. Molecular weights of alkyl titanates determined ebulliometrically are lower than those measured cryoscopically. Thus part of the increase of dipole moment with temperature may be due to a decrease in association number.

X-ray investigation of $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ was undertaken in an attempt to determine the general structure for the trimeric alkyl titanates. However, the structure which was found shows that the titanates are tetrameric in the solid state. The structure of the trimer in solution is still unknown.

Molecular formulas which have been proposed for the hydrolysis products of tetraethyl titanate have been based in part on the assumption that they are formed from the trimers. The preliminary x-ray investigation of the hydrolysis product obtained indicate that the proposed formula is incorrect, as mentioned in Part II. Possibly this compound is formed from the hydrolysis of tetramer units.

The crystal study of the hydrolysis product was not carried very far due to (1) the calculation of 9.5 molecules per unit cell, (2) the high degree of complexity of the crystal--over 60 titanium atoms per unit cell, and (3) the lack of chemical hints toward structure elucidation. In view of the structures of simpler alkyl titanates, $\text{Ti}(\text{OCH}_3)(\text{OC}_2\text{H}_5)_3$ in this dissertation and $\text{Ti}(\text{OC}_2\text{H}_5)_4$ by Ibers,⁽²⁷⁾ a fresh look at the Patterson map of the hydrolysis product may yield some clues as to its structure.

SUMMARY

Research reported in this dissertaion has provided the following information.

(1) Dipole moments of ethyl, n-propyl, and n-butyl titanates have been measured at 0°, 25°, and 50°C and of tert-butyl titanate at 25°C.

(2) The increase in dipole moment with temperature for the alkyl titanates may be due to two factors: (a) a decrease in the degree of restriction of rotation of the alkoxy groups, and (b) a decrease in molecular complexity.

(3) The essential features of the crystal and molecular structure of monomethyltriethyl titanate has been determined by x-ray diffraction techniques.

(4) A preliminary x-ray investigation of the crystal structure of a hydrolysis product of tetraethyl titanate has indicated that the proposed molecular formulas for the hydrolysis products are in error.

APPENDIX

APPENDIX A

Derivation of Formula. Calculation of Axial Length from a Rotation Picture.

Consider a sphere of reflection chosen to be of such a size that its diameter is equal to the camera diameter. The reciprocal lattice is proportionately as large. Refer to Figure 40.

Circles A and B represent the circles of reflection for the zero level and the n-level reciprocal lattice planes, resp. Let r be the radius of circle A (and of the circle of reflection) and $r-x$ be the radius of circle B. Q is the distance from the center, M , of the sphere to the point N which is any point on the n-layer line recorded on the film. The distance from the zero-layer line on the film to the n-layer line is designated y_n . O is the projection of the point N onto the plane of circle A.

From the figure it is seen that

$$\frac{x}{r-x} = \frac{z-r}{r} \quad \text{and} \quad z = (r^2 + y_n^2)^{\frac{1}{2}}.$$

These two equations are solved simultaneously to give the relation

$$r-x = \frac{r^2}{(r^2 + y_n^2)^{\frac{1}{2}}} \quad (1)$$

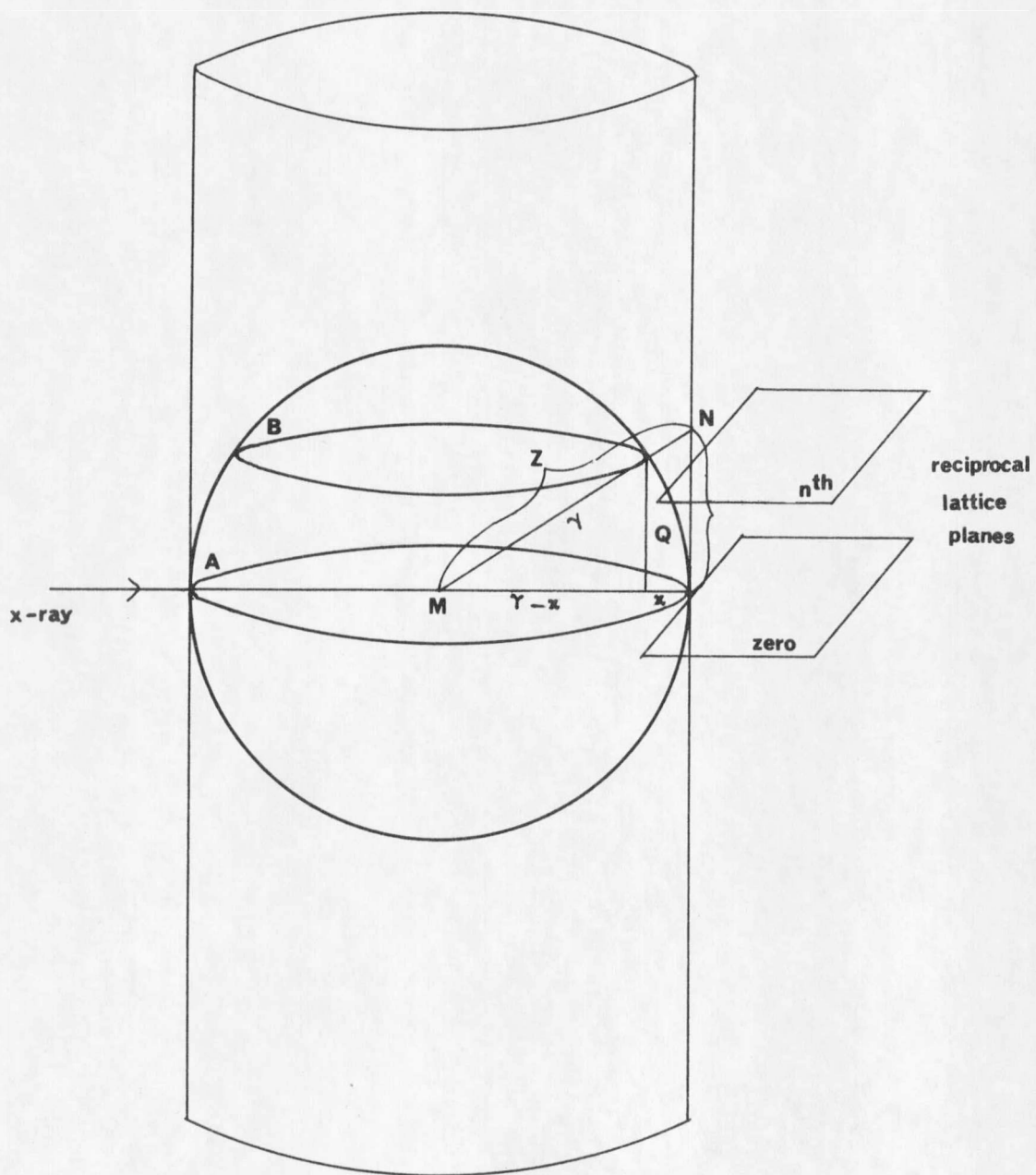
Also it is seen that

$$Q^2 = r^2 - (r-x)^2. \quad (2)$$

Solving (1) and (2) simultaneously, one obtains

$$Q = \frac{ry_n}{(y_n^2 + r^2)^{\frac{1}{2}}}.$$

Q is the distance between the two reciprocal lattice planes with



Sphere of Reflection and X-Ray Camera

Figure 40

the radius of the sphere of reflection equal to that of the camera, which has a radius r . The "normalized" sphere of reflection has a radius of unity, in absolute units. To convert to a "normalized" sphere one must divide by the camera radius. Q/r is then the distance between the zero level and the n -level reciprocal planes in the normalized case. Dividing this distance by n gives the distance between adjacent reciprocal planes:

$\frac{Q}{rn} = d^*$, where d^* is in absolute units. Substituting the expression found for Q , one obtains

$$\begin{aligned} d^* &= \frac{Q}{rn} = \frac{y_n r}{(y_n^2 + r^2)^{\frac{1}{2}}} / rn \\ &= \frac{y_n}{n(r^2 + y_n^2)^{\frac{1}{2}}} \end{aligned}$$

Depending on the axis about which the crystal is rotating, d^* is d^*_{100} , d^*_{010} , or d^*_{001} . The relations between the unit cell edges and the d^* 's are

$$a = \frac{\lambda}{d^*_{100}}, \quad b = \frac{\lambda}{d^*_{010}}, \quad \text{and} \quad c = \frac{\lambda}{d^*_{001}}.$$

Therefore the unit cell edge is found by the equation

$$\text{cell edge} = \frac{\lambda}{d^*} = \frac{n\lambda(r^2 + y_n^2)^{\frac{1}{2}}}{y_n}$$

where λ = the wave length of x-rays,

n = layer line to which measured

y_n = distance on film from zero layer line to n -layer line,

and r = camera radius. This equation holds for all crystal systems.

Now it will be shown that this expression is equivalent to the one given on page 386, X-Ray Crystallography, by Buerger. Buerger's equation is

$$\text{cell edge} = \frac{n\lambda}{\sin \tan^{-1}(y_n/r)}.$$

Assume the two expressions are equal: $\frac{n\lambda}{\sin \tan^{-1}(y_n/r)} = \frac{n\lambda(r^2 + y_n^2)^{\frac{1}{2}}}{y_n}$

Rearranging, one obtains $\sin \tan^{-1}(y_n/r) = \frac{y_n}{(r^2 + y_n^2)^{\frac{1}{2}}}$, so that

$$\tan^{-1}(y_n/r) = \sin^{-1} \frac{y_n}{(r^2 + y_n^2)^{\frac{1}{2}}}.$$

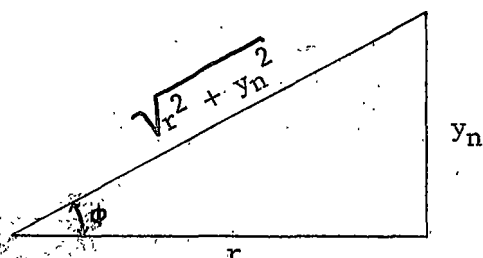
From the figure it is seen that

$$\phi = \sin^{-1} \frac{y_n}{(r^2 + y_n^2)^{\frac{1}{2}}}$$

and also that

$$\phi = \tan^{-1}(y_n/r).$$

Thus $\sin^{-1} \frac{y_n}{(r^2 + y_n^2)^{\frac{1}{2}}} = \tan^{-1}(y_n/r).$



Therefore the two equations are equivalent.

APPENDIX B

Derivation of a method for the Determination of Interaxial Angles from Weissenberg Photographs

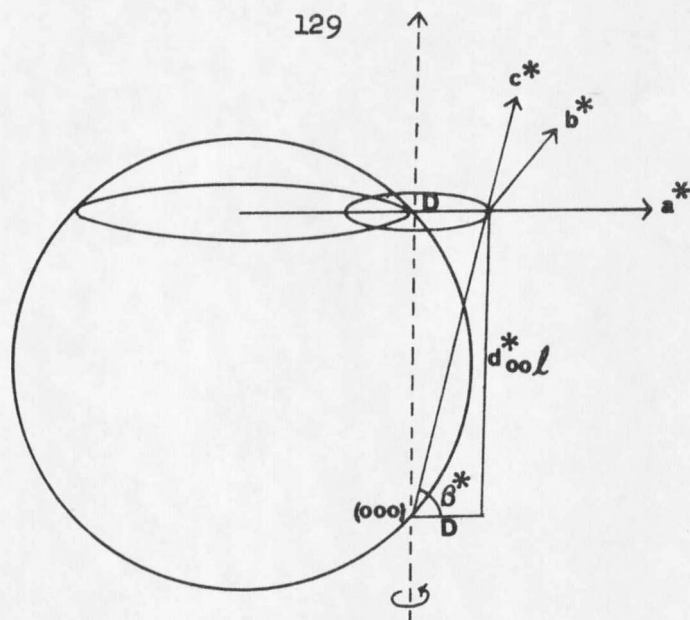
In obtaining values for the unit cell angles of a triclinic crystal the precession method is very convenient. One reciprocal lattice angle is measured from a zero level Weissenberg photograph, while the other two angles are easily measured from photographs from appropriate crystal orientations on the precession camera.

If a precession camera is not available, those two angles can be obtained from upper level Weissenberg films. Buerger⁽¹¹⁾ describes a method of angular lag by which this can be accomplished. Here is presented a derivation of a different method, also a method of angular lag, by which these angles can be evaluated. First, the derivation will be carried out for the monoclinic case; the derivation then will be extended to the more general and much more complicated case of a triclinic crystal.

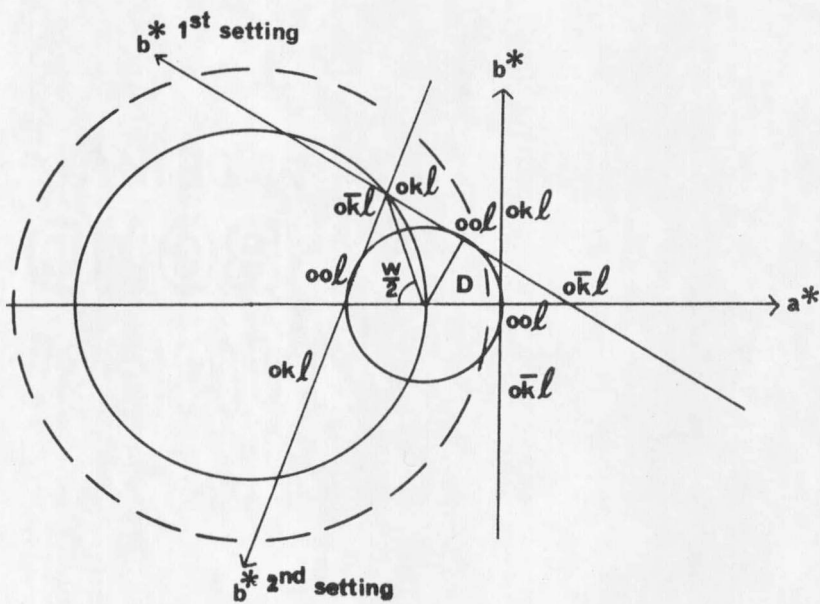
Determination of the angle β for a monoclinic crystal from the equi-inclination Weissenberg photograph by the method of angular lag.

If the crystal is mounted on the b axis, the angle β can be measured directly from a zero level photograph. If, however, the crystal is mounted on the a or c axis, upper level Weissenberg films can be used for this determination.

Consider the sphere of reflection and the orientation of the reciprocal lattice for a h -level picture (Figure 41). Assume rotation about the c axis. The top figure is approximately a front view, the



Front



Top

Reciprocal Lattice Setting for an Equi-inclination Weissenberg
 Picture when Crystal is Mounted on c Axis, for a Monoclinic
 Crystal

Figure 41

bottom a top view. For a discussion of the reciprocal lattice see reference 9.

Rotate the crystal (reciprocal lattice) until the point $Ok\ell$ makes contact with the sphere of reflection (1st setting). We wish to find a relation between β^* and ω , the angle through which the crystal must further be turned until the point $Ok\ell$ makes contact with the sphere of reflection (2nd setting). Since $d_{00\ell}^*$ is the perpendicular distance between the zero level and the ℓ -level reciprocal lattice planes, then

$$d_{00\ell}^* = \frac{\ell\lambda}{c}.$$

From Figure 41 it is seen that $\tan \beta^* = \frac{d_{00\ell}^*}{D} = \frac{\ell\lambda}{cD}$.

$$\text{Therefore } D = \frac{\ell\lambda}{c \tan \beta^*}.$$

$$\text{Hence } \tan \frac{\omega}{2} = \frac{kb^*}{D} = \frac{kb^* c \tan \beta^*}{\ell\lambda}.$$

Rearranging, we obtain the expression

$$\tan \beta^* = \frac{\ell\lambda}{kb^*c} \tan \frac{\omega}{2}.$$

But for a monoclinic crystal $\frac{\lambda}{b^*} = b$.

Therefore the usable expression for β^* is

$$\beta^* = \tan^{-1} \left(\frac{\ell b}{kc} \tan \frac{\omega}{2} \right).$$

The cell constant c is determined from a rotation picture, b^* from a zero level Weissenberg picture, and the angle ω from the upper level Weissenberg picture. For a monoclinic crystal, of course, $\beta = 180^\circ - \beta^*$.

β^* as determined from this formula was compared with that measured directly from a precession picture. The data used for this comparison is

that for the hydrolysis product of $\text{Ti}(\text{OC}_2\text{H}_5)_4$.

$b = 22.4 \text{ \AA}$	$c = 23.3 \text{ \AA}$		
$l = 6$	$k = 4$	$\omega/2 = 53.1^\circ$	$\frac{\beta^*(\text{calc.})}{62^\circ 30'}$
$l = 5$	$k = 6$	$\omega/2 = 67.3^\circ$	$62^\circ 26'$
$l = 4$	$k = 4$	$\omega/2 = 63.5^\circ$	$62^\circ 35'$

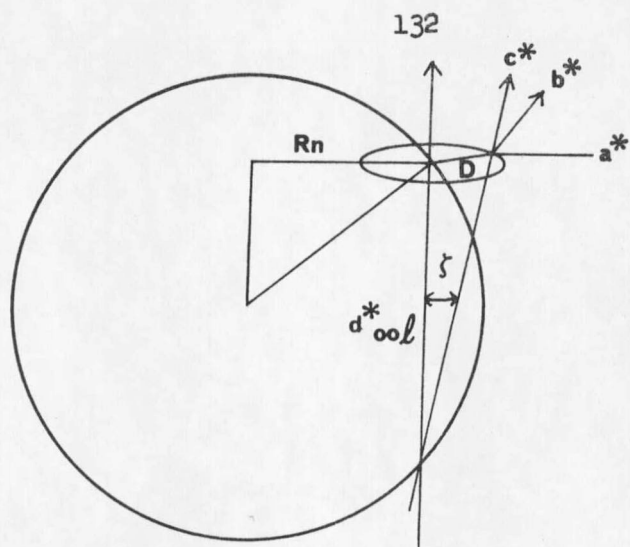
These values of β^* agree very well with $62^\circ 16'$ as measured from a zero level precession picture.

Determination of interaxial angles for a triclinic crystal from an equi-inclination Weissenberg photograph by the method of angular lag.

Now the derivation will be extended to the triclinic case. By measuring the distance between appropriate spots on the same layer line, on both axes, the other two angles can be determined. The equations which are derived, however, are very cumbersome.

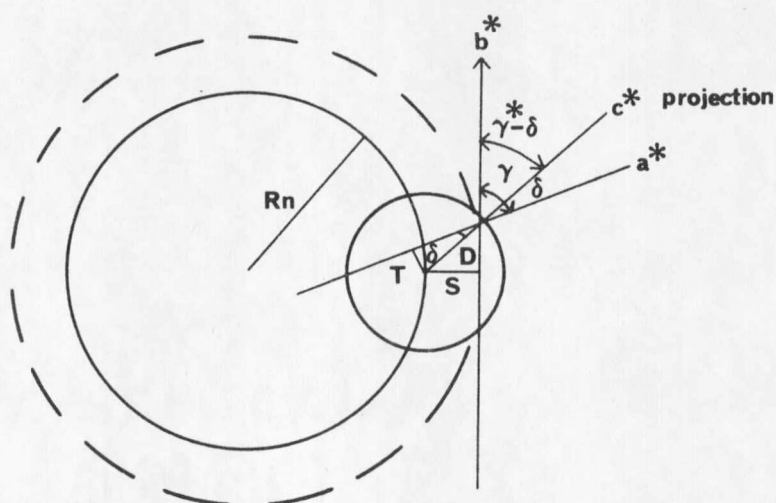
Again consider the reciprocal lattice setting with respect to the sphere of reflection for an upper level equi-inclination Weissenberg photograph (Figure 42). In the triclinic case, in general, neither reciprocal lattice axis passes through the axis of rotation. Thus both axes appear as festoons on these upper level pictures. Figures 42a and b represent, respectively, the front and top views of the reciprocal lattice and sphere of reflection; Figure 43 represents a stereographic view of the reciprocal lattice axes with respect to the axis of rotation. Again assume rotation is about the c axis. Figures 44a and b are enlarged views of Figure 42b, with the sphere of reflection removed. From Figure 42a it is seen that

$$R_n = (1 - (d_{00l}^*/2))^{\frac{1}{2}}$$



Front

(a)



Top

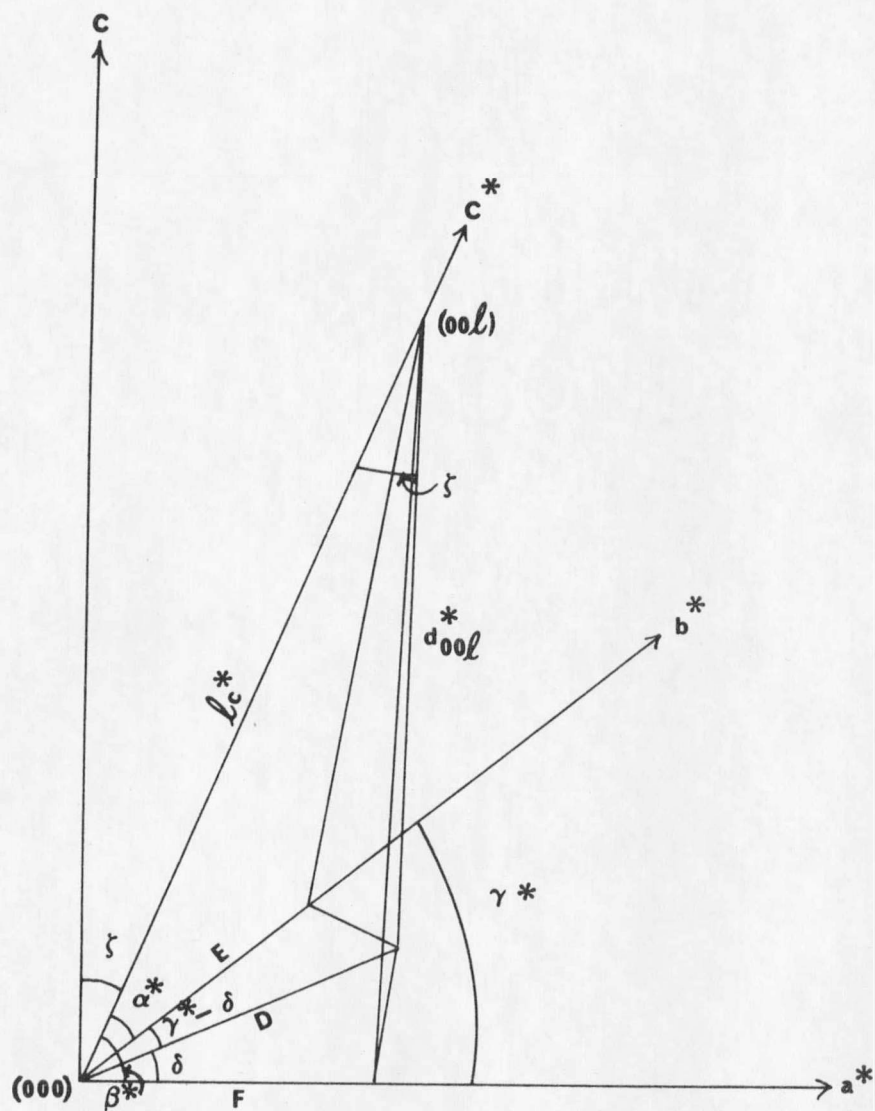
(b)

Reciprocal Lattice Setting for an Equi-inclination Weissenberg

Picture when Crystal is Mounted on c Axis, for a Triclinic

Crystal

Figure 42



Relationship Between Reciprocal Lattice Axes and c Axis,
for a Triclinic Crystal

Figure 43

where R_n is the radius of the circle of reflection for the n -level. Letting D be the radius of the precession circle (the radius of the circle formed by the spot 00ℓ when the crystal is rotated), and letting T and S be the distances from the a^* and b^* axes to the center of this circle, resp., Figure 42 shows the following relations:

$$D = d_{00\ell}^* \tan \varphi$$

and $S = D \sin (\gamma^* - \delta)$

where φ is the angle between the c axis and the c^* axis, and δ is the angle between the a^* axis and the projection of c^* onto the a^*b^* plane (or the angle between a^* and D).

As in the monoclinic case we must determine the angle through which the crystal must be rotated to bring the point $OK\ell$ into reflecting position after the point $Ok\ell$ was in position. In addition we must determine the angle through which the crystal must be rotated to bring the point $hO\ell$ into reflecting position after the point $\bar{h}O\ell$ was in position. Denote the first of these angles by ω_1 , the second by ω_2 .

Now an expression for ω_1 will be derived. The meaning of the symbols used is apparent from a glance at Figure 44a, which shows settings 1 and 2 for the b^* axial lines. In setting 1 the reciprocal lattice point $Ok\ell$ is in reflecting position; in setting 2, point $Ok\ell$ is in position. From Figure 44a the following relations are obtained:

$$v_1^2 = S^2 + [kb^* + D \cos (\gamma^* - \delta)]^2$$

$$m_1^2 = S^2 + [kb^* - D \cos (\gamma^* - \delta)]^2.$$

From the law of cosines

$$\cos(\omega_1 + \psi_1) = \frac{v_1^2 + m_1^2 - 4k^2 b^{*2}}{2v_1 m_1}$$

Therefore

$$\omega_1 = \cos^{-1} \left(\frac{v_1^2 + m_1^2 - 4k^2 b^{*2}}{2v_1 m_1} \right) - \psi_1.$$

The following equations also are obtained from Figure 44a:

$$\cos \phi_1 = \frac{v_1/2}{R_n}$$

$$\phi_1 = \cos^{-1} \frac{v_1}{2R_n}$$

$$\cos(\phi_1 + \psi_1) = \frac{m_1}{2R_n}.$$

Therefore

$$\psi_1 = \cos^{-1} \frac{m_1}{2R_n} - \phi_1 = \cos^{-1} \frac{m_1}{2R_n} - \cos^{-1} \frac{v_1}{2R_n}.$$

So

$$\omega_1 = \cos^{-1} \left(\frac{v_1^2 + m_1^2 - 4kb^{*2}}{2v_1 m_1} \right) - \cos^{-1} \frac{m_1}{2R_n} + \cos^{-1} \frac{v_1}{2R_n}.$$

Substituting the values of v_1 and m_1 , and simplifying as much as possible, one obtains

$$\begin{aligned} \omega_1 = \cos^{-1} & \frac{S^2 - k^2 b^{*2} + D^2 \cos^2(\gamma^* - \delta)}{[S^4 + 2S^2 k^2 b^{*2} + \{k^2 b^{*2} - D^2 \cos^2(\gamma^* - \delta)\}^2 + 2S^2 D^2 \cos^2(\gamma^* - \delta)]^{\frac{1}{2}}} \\ & - \cos^{-1} \frac{[S^2 + \{kb^* - D \cos(\gamma^* - \delta)\}^2]^{\frac{1}{2}}}{2R_n} + \cos^{-1} \frac{[S^2 + \{kb^* + D \cos(\gamma^* - \delta)\}^2]^{\frac{1}{2}}}{2R_n} \end{aligned}$$

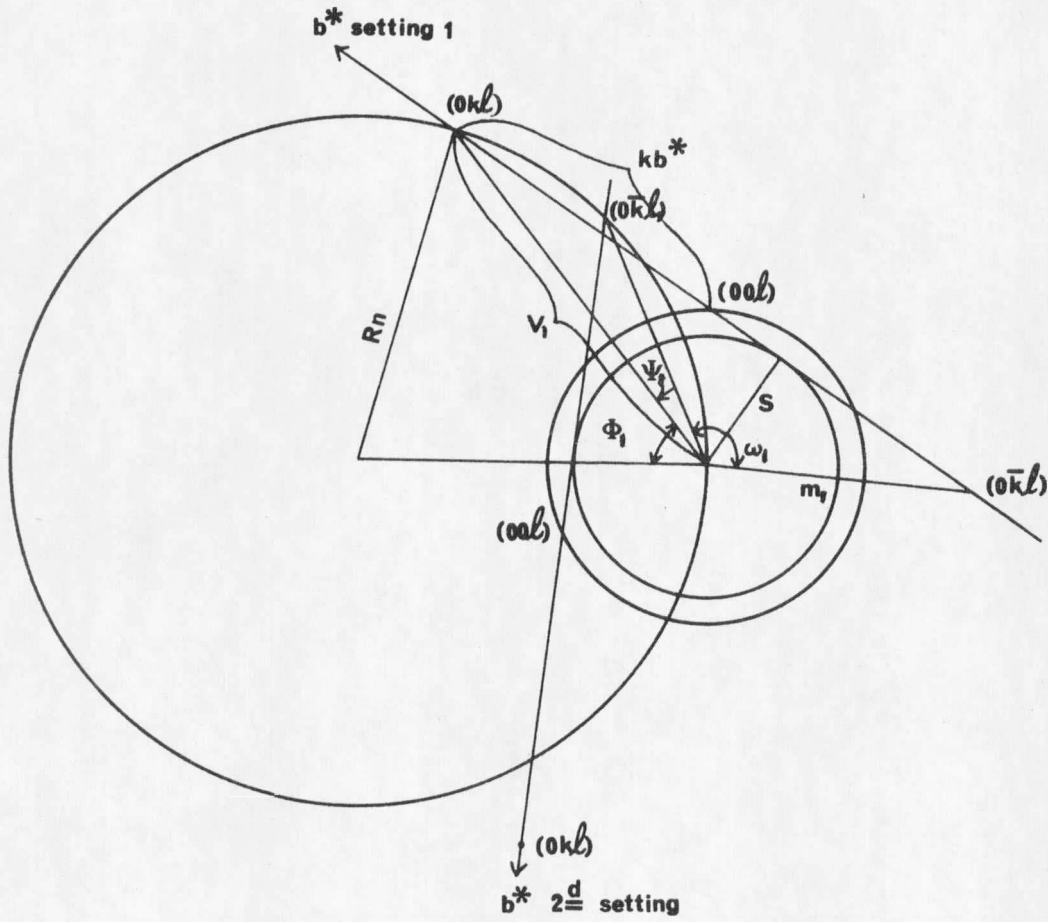
where $S = D \sin(\gamma^* - \delta)$, $R_n = [1 - (d^*/2)^2]^{\frac{1}{2}}$, and $D = d_{ool}^* \tan \rho$.

Now in a similar manner with reference to Figure 44b, an expression will be derived for ω_2 .

$$u_2 = D \cos \delta$$

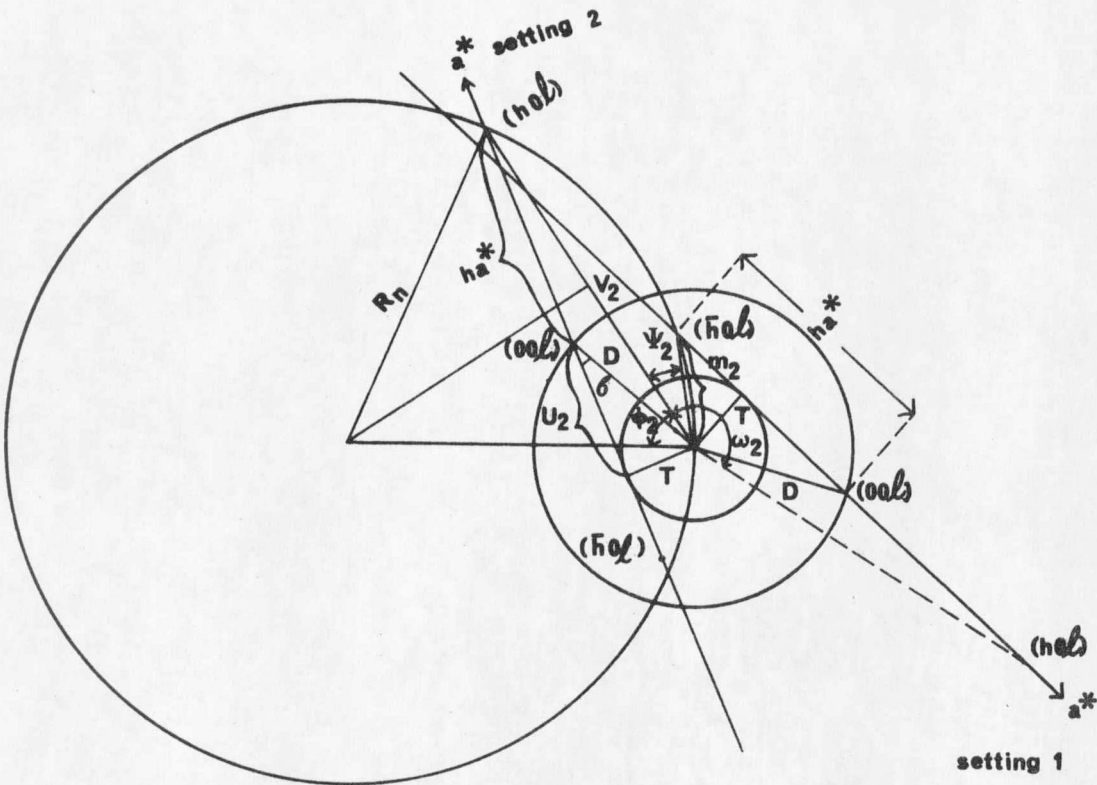
$$v_2^2 = T^2 + (ha^* + D \cos \delta)^2$$

$$m_2^2 = T^2 + (ha^* - D \cos \delta)^2.$$



First and Second Settings for b* Axis

Figure 44a



First and Second Settings for a* Axis

Figure 44b

From the law of cosines,

$$\cos(\omega_2 - \psi_2) = \frac{v_2^2 + m_2^2 - 4h^2 a^{*2}}{2v_2 m_2}.$$

Therefore

$$\omega_2 = \cos^{-1} \frac{v_2^2 + m_2^2 - 4h^2 a^{*2}}{2v_2 m_2} + \psi_2.$$

The following equations are obtained from Figure 44a:

$$\cos \phi_2 = \frac{v_2}{2R_n}$$

$$\phi_2 = \cos^{-1} \frac{v_2}{2R_n}$$

$$\cos(\phi_2 + \psi_2) = \frac{m_2}{2R_n}.$$

Therefore

$$\psi_2 = \cos^{-1} \frac{m_2}{2R_n} - \phi_2 = \cos^{-1} \frac{m_2}{2R_n} - \cos^{-1} \frac{v_2}{2R_n}.$$

So,

$$\omega_2 = \cos^{-1} \left(\frac{v_2^2 + m_2^2 - 4h^2 a^{*2}}{2v_2 m_2} \right) + \cos^{-1} \frac{m_2}{2R_n} - \cos^{-1} \frac{v_2}{2R_n}.$$

Substituting the values for v_2 and m_2 , and simplifying, one obtains

$$\begin{aligned} \omega_2 = & \cos^{-1} \frac{T^2 - h^2 a^{*2} + D^2 \cos^2 \delta}{[T^4 + 2T^2 h^2 a^{*2} + 2T^2 D^2 \cos^2 \delta + (h^2 a^{*2} - D^2 \cos^2 \delta)^2]^{\frac{1}{2}}} \\ & + \cos^{-1} \frac{[T^2 + (ha^* - D \cos \delta)^2]^{\frac{1}{2}}}{2R_n} - \cos^{-1} \frac{[T^2 + (ha^* + D \cos \delta)^2]^{\frac{1}{2}}}{2R_n} \end{aligned}$$

The relations

$$D = d_{ool}^* \tan \varphi \quad \text{and} \quad R_n = [1 - (d_{ool}^*/2)^2]^{\frac{1}{2}}$$

have already been given. From Figure 42b it is seen that also

$$T = D \sin \delta.$$

Since d_{00l}^* is obtained from the rotation picture and γ^* is determined from the zero level Weissenberg photograph, the only unknowns are δ and φ . The two equations for ω_1 and ω_2 are solved simultaneously to find δ and φ .

Once δ and φ are known (and γ^*), α^* and β^* can be found from the following relations. Refer again to Figure 43.

$$\ell c^* = d_{00l}^* / \cos \varphi$$

$$E = D \cos(\gamma^* - \delta)$$

$$\begin{aligned} \cos \alpha^* = E / \ell c^* &= \frac{D \cos(\gamma^* - \delta)}{\ell c^*} = \frac{d_{00l}^* \tan \varphi \cos(\gamma^* - \delta)}{d_{00l}^* / \cos \varphi} \\ &= \cos \varphi \tan \varphi \cos(\gamma^* - \delta). \end{aligned}$$

Thus, $\cos \alpha^* = \sin \varphi \cos(\gamma^* - \delta)$.

$$\text{Also, } F = D \cos \delta.$$

$$\text{Therefore } \cos \beta^* = F / \ell c^* = \frac{D \cos \delta}{\ell c^*} = \frac{d_{00l}^* \tan \varphi \cos \delta}{d_{00l}^* / \cos \varphi} = \tan \varphi \cos \varphi \cos \delta.$$

Thus, $\cos \beta^* = \sin \varphi \cos \delta$.

From the reciprocal lattice angles α^* , β^* , and γ^* the crystal angles can be found using the relations (Ref. 10)

$$\cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*}$$

$$\cos \beta = \frac{\cos \alpha^* \cos \gamma^* - \cos \beta^*}{\sin \alpha^* \sin \gamma^*}$$

$$\text{and } \cos \gamma = \frac{\cos \alpha^* \cos \beta^* - \cos \gamma^*}{\sin \alpha^* \sin \beta^*}.$$

Also the cell edges then can be found.

$$a = \frac{\lambda}{a^* \sin \beta \sin \gamma^*}$$

$$b = \frac{\lambda}{b^* \sin \gamma \sin \alpha^*}$$

The difficulty in using this method for determining cell dimensions is in solving the two simultaneous equations. This humble person is unable to do so.

APPENDIX C

Table of Structure Factors

R = 13.6%

h	k	$F_c = A + iB$		E = coded extinct	
		F_o	$ F_c $	A	B
1	0	162.1 E	-225.1	-239.2	-4.0
2	0	96.9	98.4	-102.3	21.8
3	0	50.3	46.6	48.9	7.9
4	0	21.5	21.3	-10.2	-20.2
7	0	46.6	52.0	55.1	5.1
8	0	37.7	39.8	40.3	12.5
3	1	13.3	12.2	12.8	2.3
3	-1	39.2	36.1	36.1	-12.7
0	2	189.4 E	270.0	286.5	7.2
1	2	145.0 E	182.4	-193.1	-16.7
2	2	69.6	61.1	-63.6	13.5
3	2	63.6	65.7	69.9	-1.2
4	2	19.2	24.7	-26.1	2.8
7	2	51.8	52.1	55.4	2.0
8	2	45.9	44.5	-46.9	-6.7
1	-2	110.3	111.4	-118.0	-8.7
2	-2	42.2	50.5	-51.1	16.2
3	-2	82.9	83.6	85.7	23.3
4	-2	39.2	36.0	-31.0	-22.4

Table of Structure Factors
(continued)

h	<i>l</i>	F _o	F _c	A	B
7	-2	25.9	25.1	26.3	-4.4
8	-2	24.4	27.0	-25.3	13.5
2	3	17.8	22.2	6.8	-22.6
3	3	58.5	50.8	50.8	18.1
4	3	17.8	12.5	-6.6	11.6
3	-3	17.0	19.6	-19.1	-8.3
0	4	77.0	39.7	-40.4	12.2
1	4	52.5	54.5	-57.6	6.2
3	4	71.8	67.0	71.1	-2.3
4	4	21.5	25.3	-26.2	-6.4
7	4	32.6	35.8	38.0	2.0
8	4	28.9	32.1	-33.9	3.2
1	-4	54.0	39.2	-41.0	-7.8
3	-4	48.1	58.2	60.8	-10.9
4	-4	114.0	40.9	-41.7	-12.1
3	5	17.0	24.2	25.3	4.9
4	5	17.8	14.8	-14.7	-5.6
0	6	13.3	14.0	14.8	1.4
1	6	33.3	37.1	-39.4	-0.6
3	6	42.1	31.4	23.7	-23.6
7	6	24.4	30.0	31.7	-3.5
1	-6	18.5	18.4	-9.3	17.2

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
3	-6	20.0	27.9	27.6	-10.7
0	-12	35.5	35.6	37.8	0.5
$k = 1$					
0	0	126.5 E	221.1	-234.8	-6.2
1	0	126.5 E	209.4	222.1	12.6
2	0	46.6	32.5	-27.7	-20.6
-2	0	43.7	28.8	28.5	11.1
3	0	51.8	84.0	-88.9	8.4
-3	0	51.1	41.0	40.2	16.9
4	0	85.1	72.9	76.5	11.9
-4	0	20.0	12.4	3.5	-12.7
-5	0	47.4	54.5	-53.6	21.8
6	0	24.4	24.0	-23.8	-8.9
-6	0	73.3	79.8	83.9	-11.8
-7	0	94.7	78.3	83.2	-2.3
-8	0	30.3	36.4	38.4	4.5
-2	1	25.2	28.0	-3.7	29.5
3	1	15.5	24.6	26.1	-1.2
-3	1	32.6	21.9	19.2	-13.1
4	1	14.8	15.1	15.8	2.6
1	-1	16.3	26.4	27.2	-6.9
2	-1	29.6	18.9	-17.2	-10.4

Table of Structure Factors
(continued)

h	k	F_o	$ F_c $	A	B
-2	-1	11.8	18.0	15.2	-11.5
3	-1	153.9	96.1	-100.9	-15.7
-3	-1	15.5	14.0	-12.3	8.3
4	-1	94.0	97.7	103.8	-0.8
5	-1	45.1	30.4	-30.3	-0.6
0	2	132.5	171.8	-182.3	-10.3
1	2	227.9	202.3	214.8	-9.0
2	2	28.9	26.7	28.0	-4.3
3	2	67.3	76.0	-80.2	9.7
-3	2	48.1	47.9	34.8	37.1
4	2	84.4	82.6	87.7	3.8
-4	2	39.2	37.0	-33.5	-20.7
5	2	12.6	16.7	-17.5	-3.0
6	2	38.5	30.8	-30.6	-11.5
-6	2	46.6	44.1	46.0	-9.3
-7	2	50.3	43.3	-46.0	-2.4
0	-2	90.3	101.4	-107.6	-4.7
1	-2	117.7	117.9	125.1	-7.4
2	-2	17.8	21.7	-23.0	2.6
-2	-2	20.7	31.6	32.1	10.0
3	-2	134.7	123.0	-130.6	-4.6
-3	-2	55.5	49.0	48.0	-20.4
4	-2	85.8	79.8	84.7	-5.7

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
-4	-2	27.4	28.5	-28.6	10.0
5	-2	41.4	34.2	-36.3	2.7
-5	-2	41.4	49.3	-48.2	20.7
-6	-2	79.9	77.9	81.5	-14.5
-7	-2	91.0	86.8	-91.8	8.4
-8	-2	45.1	44.1	44.7	-14.0
0	3	8.9	10.0	-9.7	4.4
2	3	37.0	21.9	-22.8	4.3
-2	3	23.7	24.7	-26.2	1.5
3	3	151.7	103.6	110.0	-2.4
-3	3	36.3	41.0	43.5	-1.8
4	3	107.3	94.0	-99.5	-8.3
5	3	34.8	32.2	33.5	6.7
2	-3	22.9	30.1	-31.8	3.1
3	-3	12.6	10.5	-10.5	3.7
-3	-3	32.6	27.1	-28.8	0.4
4	-3	47.3	47.7	50.7	-1.1
5	-3	34.8	33.8	-33.0	-13.9
0	4	59.2	58.9	-62.6	2.5
1	4	90.3	95.4	100.8	-10.8
-1	4	28.1	32.2	20.7	-27.3
2	4	48.1	32.7	-27.6	21.2

Table of Structure Factors
(continued)

h	<i>l</i>	F _o	F _c	A	B
-2	4	17.8	16.5	8.3	15.4
3	4	134.7	110.2	-117.0	-4.5
-3	4	20.7	26.8	27.8	6.2
4	4	94.7	94.6	100.5	1.4
-4	4	51.1	47.3	-47.6	-15.9
5	4	34.0	28.1	-28.5	-8.9
-6	4	45.1	38.3	39.6	9.8
-7	4	25.9	25.8	-27.3	-2.7
0	-4	47.4	33.6	-35.7	-2.4
1	-4	59.9	62.4	64.9	-13.6
-1	-4	21.5	28.1	29.8	-0.4
2	-4	28.1	25.3	-4.1	26.6
3	-4	54.0	42.8	-45.0	6.3
-3	-4	42.9	50.8	53.7	-5.1
4	-4	68.8	77.0	81.7	-4.0
-4	-4	43.7	53.0	-56.3	-2.5
5	-4	38.5	42.2	-44.8	1.8
-5	-4	16.3	14.9	12.1	-10.2
-6	-4	44.4	43.1	45.8	0.8
-7	-4	53.3	52.1	-55.0	6.2
-8	-4	20.0	24.8	26.3	-1.6
0	5	14.1	19.2	15.7	13.0

Table of Structure Factors
(continued)

h	k	F_o	$ F_c $	A	B
-1	5	14.1	25.7	-25.5	-9.7
2	5	14.8	18.2	17.5	8.1
-2	5	14.1	19.5	-16.9	-12.0
4	5	51.1	51.5	-54.7	-1.4
5	5	37.7	42.0	44.0	7.3
-1	-5	14.1	22.2	23.6	-0.0
-2	-5	24.4	31.2	33.0	-3.1
-3	-5	18.5	18.6	-17.1	-9.9
4	-5	17.0	17.1	12.8	13.0
0	6	43.7	32.3	-25.3	23.3
1	6	56.2	49.3	52.3	3.7
-1	6	21.5	21.1	16.9	-14.7
2	6	44.4	50.6	-53.4	6.4
3	6	57.0	59.9	-63.5	-2.7
-3	6	14.1	13.1	12.0	-7.1
4	6	82.1	71.5	76.0	3.0
-4	6	26.6	24.2	-25.2	-5.0
5	6	39.2	33.2	-33.7	-10.6
-6	6	32.6	37.3	37.4	13.0
0	-6	17.8	16.8	-9.9	14.9
1	-6	23.7	26.1	24.8	-12.3
-1	-6	14.8	15.0	13.1	-9.1

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
2	-6	20.7	25.6	-25.6	7.5
3	-6	17.0	24.0	-25.4	2.3
4	-6	57.7	67.5	71.6	4.4
-4	-6	48.1	46.5	-46.9	-15.5
5	-6	23.7	25.8	-27.1	-4.1
-6	-6	33.3	39.1	37.2	18.5
-7	-6	26.6	22.3	-23.2	-4.8
3	7	15.5	16.5	-17.5	0.2
1	8	12.6	20.3	20.8	5.7
2	8	17.8	17.6	-10.2	-15.7
3	8	14.1	20.3	-21.5	0.7
4	8	57.7	53.6	56.6	-7.1
5	8	28.1	34.8	-36.8	3.2
3	-8	114.7	50.5	-53.0	-8.6
4	-8	41.4	49.5	52.4	4.9
-4	-8	25.2	29.6	-30.2	-8.8
-6	-8	27.4	27.5	29.2	1.7
3	9	14.1	19.2	19.9	4.1
3	10	25.9	17.8	-17.3	-7.8
4	10	48.8	43.0	45.7	1.8
5	10	20.7	24.1	-25.5	2.6
0	12	23.7	24.6	-25.7	-5.0

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
1	12	25.2	21.5	21.8	6.8
3	12	23.7	21.3	-22.4	-2.6
4	12	28.1	27.4	28.0	8.2
0	14	24.4	23.5	-24.6	-3.8
1	14	18.5	25.7	26.8	4.9
$k = 2$					
-2	0	34.0	53.9	57.2	1.6
3	0	30.3	25.9	24.8	-12.0
-3	0	84.4	53.3	-56.3	6.0
4	0	67.3	67.0	-71.1	-1.9
5	0	27.4	27.8	29.2	-4.3
-5	0	29.6	31.9	33.5	4.6
-6	0	69.6	54.8	-58.2	2.0
7	0	42.9	40.6	-42.8	-5.1
-7	0	46.6	40.9	43.4	1.7
8	0	28.9	29.8	28.1	-14.7
-2	1	136.9	68.8	-72.6	8.6
-3	1	74.0	47.9	50.9	0.2
4	1	22.9	16.9	-17.9	1.8
-4	1	30.3	35.9	-30.9	22.3
5	1	27.4	23.3	24.7	-2.1

Table of Structure Factors
(continued)

h	k	F_o	$ F_c $	A	B
6	1	17.8	22.6	-18.2	-15.7
1	-1	26.6	26.5	-20.6	-19.2
-1	-1	20.7	22.4	-23.2	-5.4
-2	-1	131.7	96.8	100.7	-20.8
3	-1	40.0	41.8	-38.0	23.1
-3	-1	49.6	45.8	-47.6	-10.0
4	-1	69.6	67.9	-69.9	-18.2
5	-1	96.2	87.5	93.0	0.7
6	-1	31.8	25.0	-21.4	-15.8
1	2	30.3	29.3	28.9	-11.6
-1	2	22.9	25.3	-26.6	-3.9
-2	2	100.6	85.2	90.5	-3.6
3	2	28.9	36.7	38.8	3.9
-3	2	84.4	88.2	-93.7	1.8
4	2	62.2	40.2	-42.7	-1.4
-4	2	25.2	27.8	26.2	13.8
5	2	9.6	13.0	13.5	2.7
-5	2	35.5	32.7	34.1	-6.7
-6	2	48.8	38.7	-40.8	5.2
7	2	22.9	21.4	-18.5	-13.4
-7	2	22.2	19.2	20.3	-1.4
8	2	21.5	27.6	28.8	-5.4

Table of Structure Factors
(continued)

h	<i>l</i>	F _o	F _c	A	B
0	-2	34.8	35.0	-35.6	-10.6
1	-2	16.3	21.8	-21.5	8.6
2	-2	25.2	35.8	31.7	-21.0
-2	-2	91.8	80.8	85.9	-0.5
3	-2	47.4	38.3	40.2	6.4
-3	-2	86.6	67.9	-72.0	-4.0
4	-2	83.6	87.9	-92.9	-9.3
5	-2	67.3	71.4	75.9	1.2
-5	-2	24.4	28.1	29.8	2.3
-6	-2	55.5	51.7	-54.9	0.6
7	-2	45.1	48.8	-51.1	9.2
-7	-2	42.9	41.3	42.0	-12.8
8	-2	22.9	25.8	25.5	-10.1
0	3	17.0	17.7	1.1	-18.7
1	3	33.3	22.6	23.5	4.8
-1	3	16.3	14.4	15.2	1.9
-2	3	85.8	64.8	-67.9	11.0
3	3	27.4	24.7	13.9	-22.3
-3	3	67.3	56.1	59.6	1.2
4	3	74.7	58.5	59.8	17.1
-4	3	37.7	33.0	-35.0	2.2
5	3	70.3	64.8	-68.8	-2.1

Table of Structure Factors
(continued)

<i>h</i>	<i>l</i>	F_o	$ F_c $	A	B
6	3	27.4	28.5	23.1	19.7
1	-3	23.7	17.1	1.1	18.2
-1	-3	20.0	15.8	3.4	-16.5
-2	-3	88.1	61.6	63.8	-14.9
3	-3	11.8	14.0	-9.2	11.7
-3	-3	88.8	67.4	-68.4	21.2
4	-3	39.2	38.1	-40.5	0.0
-4	-3	41.4	37.9	36.7	-16.5
5	-3	59.2	53.9	56.9	-7.0
-6	-3	20.0	19.9	-21.1	1.8
7	-3	18.5	15.4	-5.4	15.4
1	4	47.4	47.9	-49.7	10.8
2	4	42.9	38.7	36.7	-18.5
-2	4	91.8	82.3	84.9	-21.1
3	4	57.7	55.1	58.0	8.2
-3	4	85.8	96.5	-101.6	-14.4
4	4	88.1	76.6	-81.1	-6.7
-4	4	45.1	45.1	46.5	11.4
5	4	53.3	50.5	57.8	9.7
-5	4	34.8	32.3	34.3	-0.2
-6	4	41.4	39.0	-41.0	6.3
7	4	41.4	37.0	-39.2	-3.6

Table of Structure Factors
(continued)

h	k	F_o	$ F_c $	A	B
8	4	20.0	22.6	23.3	5.8
1	-4	23.7	32.2	-33.6	6.8
-1	-4	14.1	16.7	-4.0	17.3
2	-4	27.4	24.0	19.5	-16.5
-2	-4	89.5	76.6	81.3	-3.4
3	-4	31.1	33.8	32.5	15.3
-3	-4	82.1	82.0	-86.5	-10.7
4	-4	71.8	69.1	-73.2	4.7
-4	-4	34.8	35.9	38.1	-1.7
5	-4	65.1	73.7	78.3	-2.9
-5	-4	30.3	22.6	24.0	1.1
-6	-4	31.8	33.9	-35.9	-3.0
7	-4	26.6	31.4	-32.9	5.8
-7	-4	18.5	20.1	21.3	1.8
1	5	11.1	18.6	-0.9	-19.7
-1	5	24.4	18.9	-7.9	18.4
-2	5	36.3	39.9	39.9	-14.3
3	5	24.4	19.6	-17.2	-11.8
-3	5	25.9	26.1	16.5	-22.3
4	5	54.0	50.6	53.8	-2.2
-4	5	18.5	16.9	-17.0	-5.9
5	5	85.1	66.9	-69.1	16.5

Table of Structure Factors
(continued)

h	k	F_o	$ F_c $	A	B
6	5	22.9	26.2	25.2	11.9
-2	-5	39.2	32.4	-32.4	11.6
-3	-5	35.5	28.2	-27.3	12.4
-4	-5	36.3	35.4	37.6	-2.8
-5	-5	16.3	11.6	-3.2	-11.9
-6	-5	16.3	24.6	-19.6	17.3
1	6	47.4	50.8	-52.4	13.1
2	6	39.2	40.3	42.0	-8.0
-2	6	32.6	28.6	29.9	5.0
3	6	35.5	26.8	28.4	2.2
-3	6	65.9	67.6	-70.6	-13.2
4	6	88.1	97.2	-102.6	-12.0
-4	6	30.3	33.8	35.9	-2.8
5	6	77.0	68.0	71.0	13.8
-5	6	21.5	23.9	25.4	0.6
-6	6	41.4	34.7	-36.8	-2.3
7	6	42.9	53.6	-56.9	3.1
8	6	22.2	23.8	21.3	13.6
-2	-6	22.2	30.1	31.7	4.3
3	-6	19.2	23.8	25.2	-0.8
-3	-6	68.8	76.6	-79.9	-15.7
4	-6	54.8	63.5	-66.6	10.9

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
-4	-6	48.1	40.0	40.7	12.4
5	-6	46.6	49.2	51.6	-8.3
-6	-6	28.9	26.8	-28.0	-5.2
4	7	25.2	25.0	26.1	-4.8
5	7	44.4	41.9	-41.1	17.3
-7	7	21.5	10.9	-9.7	-6.4
1	8	12.6	9.3	-2.8	-9.5
2	8	12.6	16.4	6.8	16.1
-2	8	23.7	27.4	24.4	15.9
-3	8	51.8	45.8	-48.7	0.3
4	8	67.3	79.8	-84.3	-8.7
-4	8	20.0	21.1	22.4	1.7
5	8	68.8	66.0	70.0	5.5
7	8	22.2	26.2	-27.6	3.5
8	-8	20.0	24.2	24.3	8.5
-2	-8	25.9	25.5	21.7	16.2
-3	-8	56.2	61.6	-63.9	-14.2
4	-8	39.2	39.3	-41.7	-1.6
-4	-8	38.5	42.7	43.1	14.0
3	9	16.3	21.3	-20.9	8.6
-2	10	26.6	30.0	31.9	-0.1
-3	10	36.3	33.3	-35.4	-0.5

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
4	10	56.2	45.7	-48.4	-3.4
5	10	53.3	53.7	57.1	2.3
-3	-10	30.3	41.7	-43.9	5.7
-2	12	18.5	19.5	20.5	-3.2
4	12	31.8	28.0	-29.7	-0.8
5	12	20.0	29.9	31.7	-1.0
$k = 3$					
-1	0	47.4	49.3	50.8	-12.8
2	0	31.8	47.9	49.1	-13.3
-2	0	81.4	73.6	-77.4	11.2
4	0	12.6	12.6	-0.2	-13.4
-4	0	11.1	11.0	7.7	8.8
5	0	19.2	21.3	-22.6	-0.7
7	0	34.0	34.7	36.7	-2.9
8	0	48.1	38.1	-40.5	2.0
9	0	25.2	15.4	16.2	2.8
-1	1	18.5	26.6	18.5	-21.3
-2	1	50.3	32.0	32.6	9.7
-3	1	55.5	57.2	-59.1	14.1
-4	1	18.5	16.6	4.9	-17.0
5	1	10.4	14.4	-14.5	4.8

Table of Structure Factors
(continued)

h	k	F_o	$ F_c $	A	B
6	1	19.2	25.4	26.9	-1.3
1	-1	95.5	86.9	91.5	12.2
-1	-1	28.1	31.9	-33.3	6.4
2	-1	35.5	27.7	18.4	-23.0
-2	-1	71.0	63.3	-65.7	14.2
-3	-1	51.8	49.5	52.2	-6.4
4	-1	17.0	18.0	-8.6	17.1
5	-1	45.1	34.3	-36.4	2.6
6	-1	37.0	26.5	27.2	7.4
-1	2	42.9	39.7	38.8	16.5
2	2	25.2	12.5	-10.7	-7.9
-2	2	83.6	66.0	-70.0	-4.5
-3	2	36.3	35.2	36.9	5.8
4	2	30.3	30.6	15.7	-28.4
7	2	18.5	21.1	22.3	2.0
8	2	43.7	40.2	-42.0	7.9
0	-2	58.5	61.5	64.1	12.8
1	-2	104.3	102.2	-108.6	-0.5
-1	-2	43.7	44.5	47.3	-0.3
2	-2	40.0	50.5	51.2	-16.0
-2	-2	79.9	82.7	-82.5	-30.3
3	-2	13.3	13.3	10.4	9.5

Table of Structure Factors

h	k	F_o	$ F_c $	A	B
-3	-2	31.8	30.2	30.6	9.7
4	-2	25.9	25.3	15.3	22.2
5	-2	47.4	45.6	-48.4	1.5
6	-2	18.5	21.9	22.8	4.5
7	-2	33.3	30.1	31.4	-6.2
8	-2	46.6	43.6	-46.3	-1.1
0	3	47.4	30.9	4.9	32.5
1	3	126.5	114.0	-121.1	2.7
-1	3	31.8	29.9	30.2	-9.8
2	3	26.6	20.7	-7.4	20.7
-2	3	85.8	71.8	76.3	-1.0
-3	3	90.3	80.5	-85.3	-6.8
4	3	25.9	21.6	19.1	-12.7
-4	3	29.6	23.8	25.3	-0.9
5	3	31.1	27.2	28.8	2.4
6	3	14.8	16.5	-10.6	-14.1
0	-3	16.3	9.6	-9.1	-4.6
-1	-3	33.3	25.4	-27.0	-0.2
2	-3	12.6	9.6	-2.8	-9.8
-2	-3	65.9	66.9	-70.8	5.6
-3	-3	89.5	93.7	97.8	-18.6
-4	-3	23.7	27.2	-8.1	27.7
5	-3	35.5	30.5	-31.2	8.8

Table of Structure Factors
(continued)

h	<i>l</i>	F _o	F _c	A	B
6	-3	25.9	25.9	25.0	-11.4
0	4	65.9	60.5	63.8	8.0
1	4	101.4	108.0	-114.5	7.7
-1	4	44.4	30.4	23.2	22.5
2	4	57.7	43.3	42.8	-16.7
-2	4	74.7	78.9	-81.6	-19.1
-3	4	65.9	59.3	61.5	13.6
4	4	27.4	29.0	30.0	7.0
5	4	40.0	41.0	-42.7	-8.6
-5	4	21.5	21.4	-21.4	7.6
6	4	15.5	18.4	18.7	-5.8
7	4	24.4	26.6	25.3	12.6
8	4	43.7	43.7	-46.4	0.8
0	-4	44.4	38.4	39.4	-10.6
1	-4	40.0	52.4	-55.2	7.1
-1	-4	20.0	13.4	13.2	-5.4
2	-4	28.9	29.8	31.6	-3.0
-2	-4	82.9	71.5	-75.5	-8.2
3	-4	16.3	20.2	-19.6	-8.7
-3	-4	68.1	61.9	65.6	5.1
4	-4	13.3	15.4	16.1	2.7
5	-4	28.1	30.9	-32.6	-4.4

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
7	-4	22.2	16.3	17.4	0.9
8	-4	28.9	30.9	-32.8	1.8
0	5	17.8	15.2	-15.9	2.8
-1	5	20.0	18.8	15.8	12.3
2	5	24.4	15.0	-15.9	0.7
-2	5	37.7	31.2	33.1	-1.3
-3	5	48.1	44.9	-47.6	3.1
4	5	17.0	21.0	5.4	-21.6
-4	5	14.8	12.5	13.2	-1.0
5	5	47.4	36.3	36.7	-11.7
6	5	45.9	30.8	-29.7	13.8
-2	-5	37.7	27.9	-28.5	8.2
-3	-5	50.3	45.7	48.2	-5.8
-4	-5	19.2	23.7	-24.8	-4.4
6	-5	14.8	14.8	5.0	-14.9
0	6	43.7	50.5	52.1	-13.0
1	6	57.7	43.9	-46.6	0.9
-1	6	20.0	24.3	23.5	-10.8
2	6	39.2	43.4	45.9	-4.1
-2	6	74.7	71.4	-75.3	-9.1
3	6	16.3	20.7	-21.7	-3.6
-3	6	65.9	61.1	64.9	3.0

Table of Structure Factors
(continued)

h	<i>l</i>	F _o	F _c	A	B
4	6	28.1	21.8	17.8	14.7
5	6	57.7	51.5	-54.2	-7.6
-5	6	17.8	24.1	-25.6	0.7
6	6	22.2	18.5	19.6	1.3
7	6	37.0	40.5	42.8	5.2
8	6	47.4	37.6	-38.6	-10.4
0	-6	20.7	26.3	23.4	15.3
1	-6	22.9	34.1	-34.8	9.9
-1	-6	16.3	18.3	5.8	-18.5
2	-6	21.5	28.4	29.7	5.7
-2	-6	65.9	68.8	-71.2	16.2
-3	-6	63.6	74.8	79.3	-4.5
5	-6	20.7	16.9	-16.9	-6.1
1	7	17.0	15.1	15.4	-4.5
-2	7	16.3	19.2	18.7	-8.2
4	7	11.1	13.8	-14.7	-1.2
5	7	37.7	27.1	27.1	-9.9
6	7	24.4	26.8	-16.3	23.3
0	8	17.0	9.9	9.3	-4.9
1	8	17.8	26.9	-28.3	3.6
-1	8	21.5	22.3	23.4	-3.5
2	8	13.3	17.0	14.2	11.2

Table of Structure Factors
(continued)

h	<i>l</i>	F _o	F _c	A	B
-2	8	68.8	67.8	-71.9	-3.6
-3	8	54.0	57.3	60.9	-2.5
4	8	26.6	27.7	29.0	5.1
5	8	48.1	44.4	-46.9	-5.5
7	8	22.9	22.2	23.1	-4.6
8	8	35.5	36.6	-38.2	-7.0
-2	-8	50.3	47.3	-50.2	-2.1
-3	-8	52.5	54.3	57.6	-3.9
1	9	14.8	20.0	-20.8	-4.4
-1	9	13.3	12.0	-12.8	-0.4
2	9	14.1	19.8	21.1	0.6
1	10	41.4	42.4	-41.2	-18.1
-1	10	26.6	20.9	20.5	8.4
2	10	19.2	21.7	21.0	9.6
-2	10	53.3	51.8	-55.0	1.7
-3	10	27.4	35.3	37.1	4.9
4	10	16.3	19.1	20.3	1.2
5	10	37.0	42.4	-45.0	-2.7
-2	-10	28.9	35.3	-37.5	-1.8
-3	-10	20.7	26.3	26.8	-7.6
-2	11	18.5	19.3	-20.5	0.2
1	12	43.7	33.3	-27.9	-21.9
-2	12	21.5	26.6	-28.2	0.2

Table of Structure Factors
(continued)

h	ℓ	F_o	$ F_c $	A	B
k = 4					
0	0	26.6	23.0	-14.7	-19.5
1	0	36.3	57.0	59.9	8.9
-1	0	26.6	21.5	4.1	22.5
2	0	64.4	59.5	-63.2	2.5
3	0	17.8	14.5	5.0	-14.6
4	0	36.3	40.7	41.8	11.0
5	0	20.7	18.0	-16.4	-9.9
-6	0	33.3	28.0	29.7	2.1
8	0	24.4	21.1	21.4	6.6
9	0	18.5	19.6	-20.1	-5.1
2	1	18.5	21.6	22.6	-4.0
-2	1	14.8	17.7	-16.7	8.7
1	-1	60.7	74.0	-78.6	-3.3
2	-1	61.4	39.6	37.0	20.2
-2	-1	32.6	31.4	31.1	12.3
3	-1	20.7	23.3	-16.2	-18.7
-3	-1	16.3	17.2	-17.6	-5.0
0	2	20.7	22.7	-12.8	-20.5
-1	2	33.3	21.5	-14.6	-17.6
2	2	50.3	46.8	-48.3	11.7
3	2	31.8	31.2	17.9	-27.9

Table of Structure Factors
(continued)

h	<i>l</i>	F _o	F _c	A	B
4	2	88.1	65.4	51.1	47.1
5	2	30.3	31.5	-28.8	-17.1
-5	2	35.5	29.7	-30.1	9.6
-6	2	36.3	29.5	31.1	-3.6
8	2	43.7	28.7	30.3	-3.9
9	2	20.7	16.9	-15.8	8.6
0	-2	37.0	31.1	-29.7	14.4
1	-2	69.6	74.3	77.9	12.8
-1	-2	42.9	34.9	-32.4	-18.1
2	-2	74.7	68.5	-72.6	-4.4
-2	-2	27.4	23.4	18.2	17.0
3	-2	22.9	19.1	-2.9	-20.1
5	-2	31.8	27.5	-29.1	-1.4
-5	-2	34.8	38.0	-39.8	6.6
-6	-2	30.3	23.5	24.2	6.1
8	-2	17.8	17.8	17.4	7.5
9	-2	19.2	20.1	-20.9	-4.8
0	3	18.5	18.1	11.1	-15.7
1	3	69.6	83.6	88.8	0.4
2	3	61.4	49.4	-46.1	-25.2
-2	3	42.9	45.9	-46.7	-14.2
3	3	25.9	27.7	9.8	27.8

Table of Structure Factors
(continued)

<i>h</i>	<i>l</i>	<i>F</i> ₀	<i>F</i> _c	<i>A</i>	<i>B</i>
-3	3	34.8	35.7	31.5	21.1
1	-3	37.0	43.6	-46.3	0.9
2	-3	39.2	35.2	36.2	-9.3
-2	-3	42.2	49.8	52.5	-6.9
-3	-3	29.6	25.8	-26.3	7.7
0	4	32.6	27.1	-26.7	10.8
1	4	82.9	74.9	78.3	14.1
-1	4	52.5	60.5	-44.8	-46.1
2	4	77.7	76.0	-80.7	-3.2
-2	4	41.4	42.8	38.3	24.6
3	4	26.6	22.8	23.9	-3.8
4	4	18.5	23.8	3.8	25.0
5	4	22.2	16.0	-16.1	-5.5
-5	4	28.1	21.5	-22.2	-5.4
-6	4	22.2	23.1	24.4	2.5
8	4	35.5	23.7	24.8	-4.7
9	4	28.9	17.6	-18.7	1.6
1	-4	63.6	73.5	78.1	1.8
-1	-4	48.8	46.1	-47.3	-13.0
2	-4	73.3	67.4	-71.1	7.8
-2	-4	51.8	47.3	49.6	-8.0
4	-4	40.0	33.7	35.6	3.6

Table of Structure Factors
(continued)

h	<i>l</i>	F_o	$ F_c $	A	B
5	-4	35.5	34.4	-35.5	8.9
-5	-4	28.9	27.9	-29.1	-5.6
-6	-4	28.1	26.2	27.9	-0.2
0	5	22.2	23.1	19.5	15.0
1	5	48.1	44.8	46.9	-8.3
2	5	62.9	51.6	-53.2	13.0
-2	5	34.0	31.3	-31.3	-11.3
3	5	12.6	12.6	-11.6	6.8
-3	5	25.2	26.2	27.0	6.8
1	-5	14.1	11.1	-11.1	-4.0
2	-5	16.3	20.6	21.8	-0.8
0	6	12.6	21.7	-21.7	7.9
1	6	77.7	73.8	78.4	-1.0
-1	6	59.2	50.7	-53.0	9.4
2	6	88.8	82.1	-87.2	-4.2
-2	6	55.5	51.3	54.6	0.9
3	6	31.8	38.6	40.7	5.4
5	6	22.2	21.4	-20.0	10.8
8	6	21.5	19.4	19.8	5.8
9	6	25.9	27.7	-28.9	-5.9
1	-6	57.0	66.4	69.2	-13.7
-1	-6	25.2	24.4	-24.5	8.7

Table of Structure Factors
(continued)

h	<i>l</i>	F _o	F _c	A	B
2	-6	59.2	64.5	-67.5	12.2
-2	-6	36.3	36.7	33.7	-19.6
4	-6	25.9	26.7	26.9	-9.0
1	7	11.8	9.5	4.6	-8.9
2	7	25.2	22.6	-21.4	11.1
1	8	75.5	77.7	81.2	-14.6
-1	8	45.9	46.0	-47.9	9.7
2	8	73.3	74.6	-79.3	-1.6
-2	8	45.1	37.5	39.8	-2.4
3	8	29.6	20.4	21.2	-4.1
4	8	31.8	33.6	34.9	-7.6
5	8	30.3	27.6	-28.9	4.9
1	-8	48.1	56.7	59.3	-10.5
2	-8	48.1	50.9	-54.0	2.0
2	9	15.5	15.4	-14.5	-7.5
3	9	14.1	17.7	18.8	0.5
1	10	68.8	65.4	69.2	6.3
-1	10	26.6	26.8	-26.8	-9.6
2	10	82.1	71.4	-74.7	-13.0
-2	10	26.6	29.9	31.6	-3.7
3	10	20.0	14.3	8.4	12.6
4	10	15.5	20.6	21.9	1.4

Table of Structure Factors
(continued)

h	<i>l</i>	F ₀	F _c	A	B
1	12	39.2	33.9	32.7	15.0
2	12	45.1	37.3	-36.0	-16.6
k = 5					
1	0	10.4	10.8	-0.3	-11.5
-1	0	49.6	46.2	-49.0	-2.9
2	0	22.9	19.6	1.5	20.8
-2	0	33.3	36.2	37.0	10.2
3	0	24.4	20.6	-21.8	0.6
4	0	20.7	24.9	-22.3	-14.3
-4	0	21.5	19.6	-19.1	8.3
5	0	61.4	47.5	49.2	11.2
-5	0	34.0	28.6	28.4	10.9
6	0	54.8	40.8	-43.3	0.5
-6	0	22.9	19.2	-17.9	-9.8
3	1	14.8	15.6	16.6	-1.3
1	-1	28.9	25.0	26.4	3.4
2	-1	67.4	68.8	-71.9	-12.8
3	-1	37.7	30.8	32.3	5.8
-1	2	49.6	40.3	-42.7	3.4
-2	2	30.3	31.9	29.9	15.9
3	2	7.4	13.7	-8.3	-11.9
4	2	35.5	36.6	-25.3	-29.6

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
-4	2	28.9	31.9	-29.2	17.3
5	2	74.7	69.1	71.2	17.9
-5	2	40.0	40.7	43.2	-0.9
6	2	62.9	46.9	-47.6	-14.9
1	-2	25.9	26.4	-26.1	-10.2
2	-2	44.4	52.9	56.2	-0.9
-2	-2	38.5	37.2	39.0	6.2
3	-2	38.5	31.9	-33.8	3.4
4	-2	24.4	26.6	-28.1	-2.6
-4	-2	25.2	24.3	-25.0	6.2
5	-2	55.5	51.3	53.9	7.9
-5	-2	42.2	29.7	31.6	0.7
6	-2	38.5	36.0	-37.1	9.3
1	3	23.7	21.7	-23.0	-0.8
2	3	58.5	56.7	56.2	21.7
3	3	30.3	29.0	-21.0	-22.5
1	-3	19.2	15.5	14.9	6.9
2	-3	48.1	42.5	-43.3	12.9
3	-3	28.9	30.4	32.3	0.6
1	4	25.2	28.5	-30.3	1.2
2	4	44.4	50.6	53.7	-2.7
-2	4	35.5	27.6	24.5	-16.1

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
3	4	40.0	32.1	-29.7	-16.9
4	4	19.2	18.0	-18.9	-2.7
-4	4	30.3	32.4	-30.6	16.0
5	4	79.9	64.5	68.3	5.0
-5	4	42.2	38.8	41.0	-3.6
6	4	61.4	40.6	43.0	2.1
1	-4	31.1	38.9	-41.1	4.9
2	-4	52.5	74.9	79.6	2.2
-2	-4	33.3	33.2	32.5	13.5
3	-4	23.7	27.7	-29.0	5.0
-3	-4	23.7	19.9	-21.2	-1.1
4	-4	31.1	26.1	-27.7	-2.5
-4	-4	25.2	22.5	-23.9	1.0
5	-4	58.5	51.6	54.5	5.5
-5	-4	42.9	40.8	43.0	-5.2
6	-4	34.0	31.2	-32.7	-5.4
1	5	31.1	32.0	-33.2	7.2
2	5	82.9	68.0	69.0	-21.5
3	5	42.2	44.0	-46.6	3.7
1	6	39.2	43.8	-46.6	0.7
2	6	68.0	64.3	68.2	3.2
-2	-6	20.7	24.0	23.3	-10.4

Table of Structure Factors
(continued)

h	k	F_o	$ F_c $	A	B
3	6	57.0	52.5	-55.7	-3.1
4	6	14.8	16.0	-13.6	10.1
5	6	60.7	49.8	52.9	-0.0
-5	6	25.2	32.2	34.0	4.0
6	6	48.8	40.0	-41.7	8.3
1	-6	23.7	30.4	-29.8	12.5
2	-6	45.1	44.5	46.2	-10.1
3	-6	19.2	24.4	-24.4	9.0
4	-6	16.3	17.8	-18.9	-0.5
5	-6	37.0	34.6	36.0	-7.3
-5	-6	26.6	33.3	35.2	-3.3
2	7	45.1	45.3	38.4	-28.9
3	7	37.0	39.6	-39.8	13.5
1	8	34.0	30.9	-32.9	0.9
2	8	73.3	77.8	82.6	-1.4
3	8	49.6	49.9	-52.0	10.2
4	8	29.6	29.4	-29.9	-9.0
5	8	65.1	57.6	60.0	11.9
6	8	48.8	34.9	-35.6	-10.2
2	-8	21.5	30.1	30.6	-9.4
1	10	29.6	29.4	-31.0	4.5
2	10	74.0	62.3	65.9	-6.7

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
3	10	41.4	36.8	-39.0	2.0
5	10	43.7	37.6	39.1	8.1
6	10	25.9	20.8	-16.6	-14.6
1	12	20.0	20.3	-20.5	6.9
2	12	35.5	30.3	32.2	1.4
3	12	22.9	23.6	-23.7	-8.4
5	12	17.8	10.6	11.2	-1.0
$k = 6$					
-1	0	66.6	67.6	69.3	19.2
-2	0	68.1	69.8	-74.2	-0.3
-4	0	25.2	21.0	20.1	9.7
5	0	42.9	39.6	-40.7	-10.6
-5	0	24.4	17.3	-15.8	-9.4
6	0	51.1	52.3	55.5	0.8
7	0	28.9	28.6	-30.3	-1.7
8	0	15.5	8.4	-4.0	8.0
9	0	16.3	19.0	19.8	3.9
3	1	14.8	13.9	-12.4	8.0
5	1	11.1	12.5	-0.1	-13.3
2	-1	13.3	11.6	11.4	4.7
3	-1	22.2	21.7	-22.3	-6.0
0	2	19.2	25.8	-13.8	-23.7

Table of Structure Factors
(continued)

h	k	F_o	$ F_c $	A	B
-1	2	74.7	64.3	66.9	13.6
-2	2	64.4	57.9	-59.7	-15.2
-4	2	27.4	30.7	31.5	8.4
5	2	51.1	42.6	-42.4	-16.0
6	2	82.1	80.5	85.3	6.7
7	2	53.3	45.9	-48.1	-8.3
9	2	20.7	22.4	23.3	-4.5
-1	-2	46.6	53.0	55.6	9.2
-2	-2	44.4	39.1	-40.5	-9.1
3	-2	11.8	13.4	12.5	-6.8
-4	-2	24.4	19.5	20.1	5.1
5	-2	34.8	25.7	-27.2	1.8
6	-2	31.8	33.7	35.8	-0.3
2	3	15.5	21.3	-22.7	-0.5
-2	3	19.2	19.3	13.3	15.7
3	3	14.8	16.2	14.7	9.0
3	-3	18.5	10.3	-10.4	-3.5
0	4	20.0	22.3	-20.8	11.3
-1	4	41.4	42.6	45.0	-5.6
-2	4	43.7	31.8	-32.8	-8.2
3	4	8.9	13.6	6.2	13.0
-4	4	33.3	31.1	32.9	-2.8

Table of Structure Factors
(continued)

h	<i>l</i>	F _o	F _c	A	B
5	4	48.8	36.8	-39.0	-2.3
-5	4	20.0	21.4	-22.6	-2.7
6	4	77.7	80.0	84.8	-5.4
7	4	48.1	46.9	-49.8	1.9
9	4	20.7	19.4	20.6	-1.9
-1	-4	37.7	37.6	40.0	1.7
-2	-4	30.3	28.0	-29.4	-4.1
-4	-4	19.2	19.9	21.0	-2.5
5	-4	26.6	28.8	-30.4	3.0
6	-4	19.2	16.9	16.9	6.3
2	5	22.9	23.8	-17.1	-18.6
3	5	34.0	33.7	33.9	-11.3
0	6	17.0	22.8	-22.4	9.3
-1	6	34.0	40.3	42.2	-7.0
-2	6	28.9	34.4	-36.5	2.2
3	6	22.2	25.2	21.0	-16.5
5	6	42.2	38.2	-40.6	0.5
6	6	50.3	48.1	51.0	-4.6
7	6	32.6	20.9	-19.7	10.3
9	6	16.3	18.7	19.9	-0.3
-1	-6	21.5	30.5	32.4	-2.3
-2	-6	25.2	31.5	-33.4	2.7

Table of Structure Factors
(continued)

h	l	F_o	$ F_c $	A	B
3	7	26.6	20.2	19.4	-9.3
0	8	22.2	19.2	-20.4	-0.2
-1	8	34.8	39.1	41.0	7.1
-2	8	22.2	30.7	-28.2	-16.4
3	8	21.5	24.7	26.1	2.6
5	8	42.9	32.7	-32.1	-13.3
6	8	37.7	31.0	27.5	18.1
-1	10	20.0	21.1	21.5	6.6
3	10	14.1	18.9	19.5	4.9
5	10	32.6	24.2	-24.9	-6.4
6	10	22.9	19.8	14.7	15.1

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