



The viscosity and vapor pressure of orthotitanates and related orthoesters
by Norman J Birkholz

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:

Viscosities and densities at various temperatures from 0°C to 60°C are reported for ethyl, n-propyl, and n-butyl orthotitanates; for ethyl, n-butyl, and n-heptyl orthosilicates; and for ethyl, n-propyl, n-butyl, and n-amyl orthocarbonates. The preparative method for n-amyl orthocarbonate from NaOEt and chloropicrin is given.

By the method of Tyuzyo, Evis vs. V plots of the orthotitanates, when compared with similar plots of non-aggregated orthosilicates and orthocarbonates, showed the following degrees of aggregation for the pure liquid orthotitanates: Et, 3; n-Pr, 3; n-Bu, 2.

Melting points of ethyl orthotitanate and the orthocarbonates, all of which supercool, were found by intersection of viscosity - temperature curves ($\log \eta$ vs. $1000/T$). The melting point of ethyl orthotitanate was 33.7°C, while those of the orthocarbonates were: Et, 10.850°C; n-Pr, 24.66°C; n-Bu, 33.8°C; n-Am, 40.8°C.

Vapor pressures of ethyl and n-propyl orthotitanates were measured by effusion, gas transpiration, and "self-manometer" methods. The vapor pressure of n-butyl orthotitanate by the "self-manometer" is also given.

By extending the use of the Trouton constant to low boiling point pressures, the energies of dissociation of ethyl and n-propyl orthotitanates were found to be 59.7 kcal per mole of trimer at 372°K and 64.5 kcal per mole of trimer at 400°K, respectively. The corresponding Ti...O coordinate bond energies were 10.0 and 10.8 kcal per mole of bonds, respectively, based on six equivalent bonds per trimer.

By interpretation of vapor pressure data, ethyl and n-propyl orthotitanates were found to be essentially monomeric in the vapor phase.

The following special apparatus were constructed: "self-manometer", vacuum dilatometer, effusion cell, gas transpiration cell, and vacuum viscometer (capillary type). Equations for use of the vacuum viscometer are derived.

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NORMAN J. BIRKHOIZ

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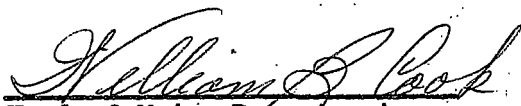
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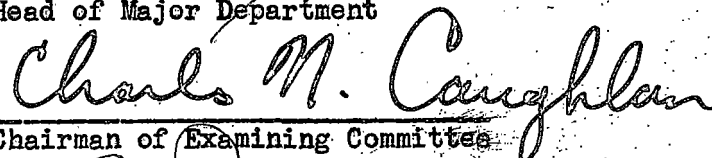
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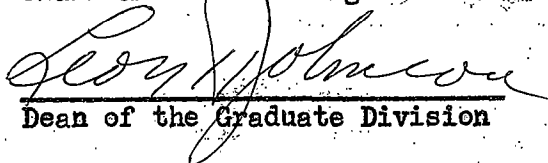
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Montana State College

Approved:


Head of Major Department


Chairman of Examining Committee


Dean of the Graduate Division

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ABSTRACT

Viscosities and densities at various temperatures from 0°C to 60°C are reported for ethyl, n-propyl, and n-butyl orthotitanates; for ethyl, n-butyl, and n-heptyl orthosilicates; and for ethyl, n-propyl, n-butyl, and n-amyl orthocarbonates. The preparative method for n-amyl orthocarbonate from NaOEt and chloropicrin is given.

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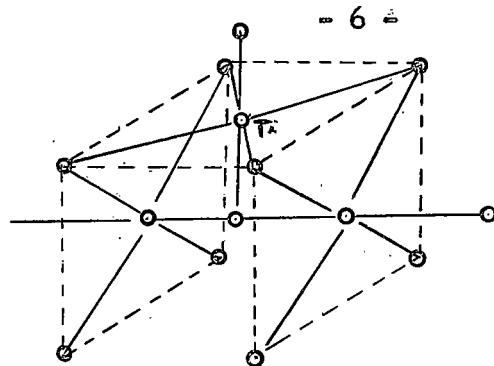
I. INTRODUCTION

The primary objective of this research was the determination of the degree of aggregation of alkyl orthotitanates in the liquid phase. A secondary objective was the calculation of coordinate bond energies in the polymeric materials.

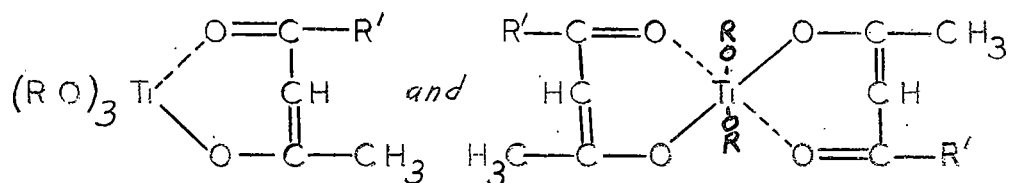
The method of approach for determining the degree of aggregation was by using viscosity data and Tyuzyo's method of calculation (39). Bond energies were calculated from vapor pressure data. Before discussing these methods, however, I will briefly review what is already known about alkyl orthotitanates.

All of the alkyl orthotitanates, with two exceptions, are apparently viscous liquids at room temperature. The exceptions are methyl orthotitanate, which is a high melting solid, and ethyl orthotitanate, which forms a stable solid melting at 34°C . The solid ethyl orthotitanate may be obtained with difficulty either by very slow crystallization at room temperature (several months standing) or by slow warming of the glass formed at -80°C . All of these esters hydrolyze easily and decompose or disproportionate at temperatures below their normal boiling points.

Gaughlan, et al. (10) found that these esters reach an apparent maximum degree of aggregation of 3 in dilute benzene solution. Accordingly, they postulated two structures, one of which is shown on the next page. In both structures titanium was permitted to coordinate to oxygen so that each titanium was surrounded by six oxygen atoms.



Yamamoto and Kambara (43) have made this structure somewhat more plausible by isolating both 5- and 6-coordinate esters such as the following:



(R = Et, n-Pr, or n-Bu; R' = Me or OEt.)

A thorough search of the literature showed that although viscosity is related to liquid structure, no one has yet succeeded in obtaining a satisfactory relationship for complex molecules. The methods which use rheochor (analogous to parachor) are useless. This becomes obvious if one tries to compute the molecular weight of an acid, e. g. acetic acid, from either parachor or rheochor. In either case, empirical "structure" constants must be included to account for the "carboxylic acid group". The molecular weight calculated on this basis will always be that of the monomer. Several methods of relating viscosity to structure by group additivities were examined and found to be of no help for the same reason.

It appears that the relationship of Eyring (17) is still perhaps the most useful. The simplified form of the equation is as follows:

$$\eta = \frac{Nh}{V} \exp \Delta F^*/RT$$

η = viscosity
 N = Avogadro's number
 h = Planck's constant
 V = molar volume
 R = gas constant
 T = absolute temperature
 ΔF^* = free energy of activation for viscous flow.

Calculations from this equation give reasonable viscosities, but the reverse process of calculating molecular weights yields values correct only in order of magnitude. Mackenzie's recent modification (26) of this equation seemed promising until calculations showed that it led to molecular weights smaller than unity for orthotitanates.

Bondi (6) presents very good evidence that molecules of equal molecular weight and similar shape have equal viscosities. He was able to compare viscosities of carboxylic acids and alkanes or esters in this way. For instance, the molecular weight of dimeric valeric acid is 204 and that of tetradecane is 198. The viscosity at 20°C is .022 poise for both compounds.

Hugel (22) presents data on the viscosity of SnR_4 and PbR_4 compounds, from which it appears that the ratio of viscosities is roughly equal to the ratio of molar volumes.

Tyuzyo (39), whose method is utilized in this thesis, found that a plot of E_{vis} , activation energy of viscous flow, vs. molar volume yields a smooth curve for n-paraffins. By finding the point at which the horizontal line from the E_{vis} of some other compound intercepts the curve, a new volume is obtained which is the volume of the unit of flow in the liquid. This volume divided by the observed molar volume of the liquid gives the

degree of aggregation of the liquid. A large number of carboxylic acids gave degrees of aggregation of 2.0 to 2.4, which seems to validate the method. Data for HCN and HF also yielded values in agreement with those from other methods.

The use of Tyuzyo's n-paraffin curve for molecules of different shape does not seem to be justifiable. Whereas dimeric carboxylic acids would have the same general shape as n-paraffins, orthoesters would not. Also, long-chain molecules may flow by using only a fraction of their volume in the process of activation. This would have the effect of giving a value for E_{vis} which would not reflect the unit volume of flow for any molecules except those of similar shape.

Therefore, a new curve was needed as a standard to replace the n-paraffin curve, and it seemed reasonable that compounds of the type $C(OR)_4$ and $Si(OR)_4$ would be satisfactory substitutes. Both of these should be monomeric liquids.

Some uncertainty arises in the determination of E_{vis} . According to the equation

$$\ln \eta = E_{vis}/RT + \text{constant},$$

E_{vis}/R represents $d(\ln \eta)/d(1/T)$, the slope of a curve. Jobling and Lawrence (24) have found this slope at constant pressure to be far different from that at constant volume. Only at high pressures do the two slopes converge. The convention adopted in this thesis will be to represent E_{vis} by $R d(\ln \eta)/d(1/T)$ at constant pressure. Since I will be dealing with empirical functions on a comparative basis only, the only real objection to this may be that this E_{vis} may not be a true measure of activation energy

of viscous flow. Since no author has yet succeeded in defining this term unequivocally, I am no worse off for such an arbitrary definition.

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The bond energy of the $\text{Ti} - \text{O} \cdots \text{Ti}$ coordinate bonds of orthotitanates may be calculated from vapor pressure data. Vapor pressure variation with temperature gives rise to an enthalpy change which involves enthalpies of both dissociation and vaporization. The enthalpy of vaporization can be evaluated from Trouton's rule. This allows calculation of enthalpy of dissociation.

The determination of vapor pressure - temperature functions for the orthotitanates may also be used to evaluate the vapor density. Effusion and gas transpiration methods of vapor pressure determination could be used for vapor pressure and molecular weight determination if both sets of experimental values were of equal precision. This condition was not satisfied in this work, but comparison with a third method of vapor pressure measurement has permitted qualitative evaluation of the vapor phase molecular weight.

II. VISCOSITY

A. Experimental materials

Halides

Chloropicrin, TiCl_4 , and SiCl_4 were reagent grade materials.

Alcohols

Ethanol, n-propanol, n-butanol, n-pentanol, and n-heptanol were carefully refractionated. Fractionation in each case was regulated to insure anhydrous, non-isomeric alcohols.

Ethyl orthotitanate

Ethyl orthotitanate was prepared by reaction of stoichiometric quantities of TiCl_4 and NaOEt in ethanol (about 30 g. Na per liter). The TiCl_4 was added slowly (2-3 hours) to the alkoxide solution maintained at 10°C . Stirring was maintained for 2-3 hours longer while the slurry was being refluxed. After overnight standing, the mixture was centrifuged and the solvent distilled off under vacuum. The ester was purified by fractionation through a 10" Vigreux column. It was not analyzed for titanium, but analysis for chlorine - nitric acid digestion followed by AgNO_3 - was only faintly positive. Densities: $d^{20.00}$ 1.10915 and 1.10928; $d^{60.00}$ 1.07062 and 1.07084. Interpolated densities: d^{25} 1.1044; d^{35} 1.0948. Literature densities: d^{25} 1.1044 (13); d^{35} 1.107 (34). (All densities in g/cc.)

n-Propyl orthotitanate

The method was identical to that described for the ethyl ester. Analysis for chlorine was only faintly positive. Analysis for Ti by nitric acid digestion followed by ignition to TiO_2 gave 16.73 and 16.71% Ti, whereas the theoretical value is 16.83%. Densities: $d^{20.04}$ 1.03924 and

1.03953; $d^{60.00}$ 1.00619; $d^{60.01}$ 1.00645. Interpolated densities:
 d^{25} 1.0353; d^{35} 1.0270. Literature values: d^{25} 1.0329 (13); d^{35} 0.9970
(34).

n-Butyl orthotitanate

The butyl orthotitanate used in this work was obtained as a gift from the DuPont Co. and was purified as necessary by vacuum distillation. Densities: $d^{20.04}$ 0.99836; $d^{20.02}$ 0.99794; $d^{60.01}$ 0.96577; $d^{59.99}$ 0.96577. Interpolated densities: d^{25} 0.9941; d^{35} 0.9860. Literature values: d^{25} 0.9932 (13); d^{35} 0.9927 (34).

Ethyl orthosilicate

The commercially available material was re-fractionated under atmospheric pressure and a middle cut of constant boiling point was taken. The refractive index, $n_D^{20.0}$ 1.3820, agreed with literature values.

n-Butyl orthosilicate

SiCl_4 was added dropwise, with stirring, to a five-fold excess of n-butanol. After overnight standing, the dissolved HCl was removed by vacuum reflux and the solvent was distilled off. The product was then vacuum fractionated through a 10" Vigreux column. Physical constants: $n_D^{20.0}$ 1.4135; $d^{25.00}$ 0.8923; $d^{2.23}$ 0.9127. Interpolated value: d^{20} 0.8966. Literature values: n_D^{20} 1.4128; d^{20} 0.899 (31).

n-Heptyl orthosilicate

To 104 g. cold n-heptanol (representing 20% excess) was added 30.7 g SiCl_4 with stirring. The temperature was gradually raised to room temperature after complete addition. After overnight standing, the mixture was refluxed at 7 mm to remove all HCl. The mixture was distilled through a

10" Vigreux column at 7 mm. After removal of the alcohol the pressure was lowered to 1 mm and the orthosilicate distilled at roughly 200°C.

Nearly 25 g. of n-heptanol was recovered in the distillation, which may be interpreted as nearly quantitative reaction. Chlorine was shown to be absent in the compound by the usual method. Physical constants:

$n_D^{20.0}$ 1.4349; $d^{44.84}$ 0.8620; $d^{19.51}$ 0.8805. Literature value: d^{25} 0.8958 (14).

Ethyl orthocarbonate

The preparative method of Tieckelmann and Post (38) was followed, in which the ester is prepared from NaOEt and Cl_3CNO_2 . The product was vacuum fractionated before use. It had a fragrant odor without olefin character.

Physical constants: $n_D^{20.0}$ 1.3926; $d^{5.85}$ 0.9299; $d^{39.85}$ 0.8942. Literature constants: n_D^{20} 1.3858, d^{20} 1.020 (38); n_D^{20} 1.3864, d^{20} 1.0232 (40).

The infra-red spectrum of the pure liquid showed no peaks characteristic of ethylenic or alkyl carbonate structures. The refractive indices of other authors may be low because of the presence of either ethyl carbonate or degradation products of the ethyl orthocarbonate. Atmospheric fractionation may remove the ethyl carbonate, but serves to break up the orthocarbonate. Support for this view comes from the observation that all of the orthocarbonates have a strong olefin odor when heated at their normal boiling points, and from the low refractive index of ethyl carbonate (n_D^{25} 1.3829 (7)). Also, the boiling points of alkyl carbonates and their orthocarbonate analogs are so close together that simple distillation will not separate them.

n-Propyl orthocarbonate

The method of preparation was similar to that of Tieckelmann and Post (38), but the method of working up the reaction mixture was altered. The method used here was to wash the crude reaction mixture (from about 2 liters n-PrOH, 70 g Na, and 100 g chloropicrin) with one liter of water, then with two 500 ml portions of water. The aqueous fractions were extracted with 200 ml ether, and the combined ether and alcohol portions were vacuum distilled at 10 mm. When about 400-500 ml remained undistilled, a 10" Vigreux column was attached to the distilling flask and the distillation continued until the remaining propanol was removed. The liquid remaining was filtered and fractionated through the Vigreux column at 1 mm. The product did not have any olefinic odor. No alkyl carbonate or ethylenic peaks were found in its infra-red spectrum. Physical constants: $n_D^{20.0}$ 1.4097; b.p. 101°C/13 mm; $d^{22.87}$ 0.8944; $d^{68.94}$ 0.8513. Literature constants: n_D^{20} 1.4100; d^{20} 0.897 (38).

n-Butyl orthocarbonate

The preparative method was similar to that of n-propyl orthocarbonate. Yield was 65% of theory - considerably better than literature values. It was odorless and showed no alkyl carbonate or ethylenic peaks in the infra-red spectrum. Physical constants: $n_D^{20.0}$ 1.4216; $d^{47.48}$ 0.8649; $d^{23.57}$ 0.8849. Literature values: n_D^{20} 1.4216; d^{20} 0.8879 (38).

n-Amyl orthocarbonate

This compound has not previously been prepared. In fact, Arbutzov and Vinogradova (2) stated that they could not prepare alkyl orthocarbonates higher than butyl by the chloropicrin method.

The method was essentially the same as outlined for n-propyl ortho-carbonate. The material was vacuum fractionated in an unpacked column containing a Monel spiral at about 0.1 mm condenser pressure. Even at this low pressure, the still pot temperature was so high as to appreciably decompose the ester into an olefin and other unknown degradation products. The distillate had a very strong skunk odor and decolorized bromine in CCl_4 . The ester was further purified by fractionation through a 10" Vigreux column at 0.1 mm. The middle cut from this fractionation was nearly odorless, did not exhibit alkyl carbonate or ethylenic peaks in its infra-red spectrum, and had the following physical constants: $n_D^{20.0}$ 1.4302; $d^{90.12}$ 0.8260; $d^{28.8}$ 0.8768. The refractive index predicted for the compound (from a study of indices of lower orthocarbonates) was 1.431, and that predicted for n-amyl carbonate was 1.421. Carbon-hydrogen analysis found C: 70.3%; H: 12.5%. Theory predicts C: 70.0%; H: 12.30%.

Benzyl benzoate

Commercial benzyl benzoate may contain benzaldehyde, benzyl alcohol, and benzoic acid. These were removed by washing with sodium bisulfite, NaOH, and water in the order named. Mild heating with application of 10 mm vacuum removed the water, and vacuum fractionation through a 10" Vigreux column purified the compound for use as a viscosimetric standard. It should be noted that vacuum fractionation through a packed column raises the distillation temperature high enough to cause degradation.

Sucrose solutions

For use as viscosimetric standards, 40% and 60% sucrose solutions were prepared from analytical grade sucrose and distilled water.

B. Density determinations

Density determinations were made in dilatometers of 10-15 ml capacity. These dilatometers were calibrated with pure mercury at two temperatures, the capillaries having been calibrated with mercury prior to construction. The coefficient of expansion of the glass was calculated from the mercury calibrations. All measurements were corrected for glass expansion and for buoyancy.

The densities of orthosilicates and orthocarbonates were measured in dilatometers open to the atmosphere, whereas those of the orthotitanates were measured in the vacuum dilatometer shown in Fig. 1. A possible source of error occurs here, in that the dilatometers were calibrated at atmospheric pressure, whereas the orthotitanate densities were determined in vacuum. Ordinary thermometers may read as much as 0.15° low in an evacuated chamber, which illustrates the effect. Thermometer bulbs are made of thin glass, however, whereas these dilatometers were of considerably thicker material, so the error is probably very small.

The method of filling the vacuum dilatometers is illustrated in Fig. 1. By means of suitably placed stopcocks, the distilled alkoxide is forced into the dilatometer until sufficient liquid rises in the center capillary. This capillary is then sealed off under vacuum. Excess liquid is boiled out of the side capillary and it is also sealed off under vacuum. Some decomposition occurs during the sealing-off process, but not enough to affect the results.

The sealed dilatometer is placed in a thermostat accurately held to 0.01° and the relative height of liquid in the capillaries is measured by a

cathetometer. Following such a determination, the dilatometer may be broken open at the vacuum seals and re-used several times until the capillaries have become too short.

The measured densities are reported in the section describing materials. In most cases there is good agreement with literature values where such are available. I disagree with the densities of Speer (34), but assume his values were primarily for characterization, not for use as accurate physical constants.

G. Viscometry

Description of apparatus

A new method and apparatus were developed for measurement of viscosity in vacuum. This was necessitated by the ease with which the titanium orthoesters hydrolyze. The apparatus is illustrated in Fig. 2. Several viscometers were used, differing in length and bore of capillary, relative height of capillary endings, and bulb volume. These differences were introduced deliberately to provide convenient flow times. Those viscometers having long capillaries had to have many bends in the capillary tubing to keep the viscometers compact.

Since the time of flow is dependent on changes in positioning of the viscometer which affect the pressure head inside, all viscometers were rigidly supported by a system of clamps on a ringstand bolted to the floor of the thermostat. The thermostat was controlled to 0.01° by a sensitive thermoregulator.

Each viscometer was calibrated with reference liquids before final assembly. The construction of the viscometer during calibration is shown

in Fig. 2a. The details of calibration will be presented following a mathematical discussion of viscometry. After calibration, the tubing is bent at (h) in order to bring the free ends together and the loop is sealed. The joint is carefully softened while the viscometer is in its vertical position so as to anneal the joint and remove strains which might affect the calibration geometry. The extra glass shown in the finished viscometer is then sealed on at (f). The narrow tubing at (d) is thickened 8 mm stock. The large tubing is 15 - 20 mm, tubing from (b) to (c) is 8 mm, and the capillary bore is variable (ca. 1 mm or less). Tubing at points (a) and (b) is capillary. Overall height and weight of a typical viscometer were 15 inches and 150 grams.

Mathematical discussion of viscometry

Since this is a new instrument, mathematical treatment of the method had to be developed also. This treatment was designed to permit a given liquid to be vacuum distilled into the apparatus and to permit measurement of its viscosity over a temperature range without re-opening the viscometer.

Poiseuille's equation for flow of liquid through a capillary may be written

$$\eta = \pi Pr^4 \theta / 8VL$$

η = viscosity

P = driving pressure

r = capillary radius

θ = time required for volume, V , to flow

L = capillary length.

For a certain viscometer, this reduces to $\theta = k/P$, where k is a constant. But $P = dgh$, where d = density, g = gravitational acceleration, and h = height of the liquid column giving rise to the pressure, P . Therefore,

$\Theta \equiv k/dgh \equiv c/h$, where c is a new constant. If we now let $h \equiv h_0 + \Delta h$, where h_0 is the height of liquid at some reference time Θ_0 and Δh is the height above this reference, $\Theta \equiv c/(h_0 + \Delta h)$. Since the viscometer has a uniform cylindrical cross section in the region where we will measure Δh , we may write $\Delta h \equiv \Delta V/\pi R^2$, where R is the cylindrical radius. Since density is defined as $d \equiv W/V$, we may say that $\Delta V \equiv \Delta W/d$, where V is the volume, and W is the weight of that volume of liquid. Therefore,

$\Theta \equiv c/(h_0 + \Delta W/\pi dR^2)$. Letting $\Delta W \equiv W - W_0$, where W_0 and ΔW correspond to h_0 and Δh , respectively,

$$\Theta \equiv c/(h_0 + (W - W_0)/dR^2\pi).$$

Since all but Θ and W are constants, this may be simplified into the following expression where a and b are constants:

$$\Theta \equiv a/(b + W).$$

The constants in this expression are then characteristic of a certain liquid in a certain viscometer at a fixed temperature. W is the weight of liquid contained in the viscometer and Θ is the time required for a given volume of liquid to flow through the viscometer between fixed points.

For determination of the constants in this equation, various weights of a calibration liquid may be placed in the viscometer and the times of flow at constant temperature recorded. By plotting $1/\Theta$ vs. W , a straight line is obtained. The equation of this line may then be found by the method of least squares.

Since it is desirable to calibrate the viscometer at only one temperature but use it at other temperatures without re-calibration, it is necessary to show that no correction need be made for the effect of temp-

perature expansion of the glass used in construction. To do this, we may write the following, where α = coefficient of linear expansion of glass and subscripts refer to two different temperatures:

$$r_1^4 = r_2^4(1 - \alpha \Delta t)^4$$

$$L_1 = L_2(1 - \alpha \Delta t)$$

$$V_1 = V_2(1 - \alpha \Delta t)^3.$$

Then we may use the Poiseuille equation to write the following:

$$\frac{\eta_2}{\eta_1} = \frac{P_2 \theta_2 r_2^4 V_1 L_1}{P_1 \theta_1 r_1^4 V_2 L_2}$$

Upon substituting into this equation the equations for temperature expansion and simplifying, we obtain

$$\frac{\eta_2}{\eta_1} = \frac{P_2 \theta_2}{P_1 \theta_1},$$

which is independent of any coefficient of thermal expansion terms!

Actually, the viscometer will be very slightly temperature dependent, since expansion of the glass due to change of temperature will permit the liquid levels within to rise or fall. This will affect the driving pressure, but the effect is certainly too minute to be of concern here.

Calibration of viscometers

The liquids selected for calibration were water, benzyl benzoate, 40% sucrose solution, and 60% sucrose solution. Bingham and Jackson (3) give the following constants for sucrose solutions: 60%; d^{40} 1.27615, d^{25} 1.28399, η^{40} 21.28 cp, η^{25} 43.86 cp. 40%; d^{25} 1.17439, η^{25} 5.187 cp. Bingham and Sarver (4) give the following for benzyl benzoate: d^{40} 1.0780,

η^{40} 5.243 cp. The data for water were taken from the International Critical Tables (45): d^{35} 0.99406, d^{30} 0.99567, $d^{27.5}$ 0.99640, η^{35} 0.7225 cp, η^{30} 0.8007 cp, $\eta^{27.5}$ 0.8452 cp.

To calibrate a viscometer, various weights of the calibration liquid were placed therein and the flow times recorded. The viscometer was allowed to stand 30 min. in the thermostat before taking a reading. Flow times ranged from 6 min. to 60 min. depending on the liquid and the temperature.

Time was measured by a stopwatch to the nearest 0.1 second. A check over 12 hours against the time signal of radio station WWV showed no error in the watch.

A total of five different viscometers were used. The calibration equations for each are presented in Table I.

Operation of viscometers

Before filling, the viscometer and distilling apparatus were cleaned thoroughly with hot acid, rinsed with dust-free distilled water, and oven dried. The viscometer was then evacuated while hot to remove water vapor. After several such evacuations, the viscometer was weighed to the nearest milligram and assembled with the distillation apparatus. This consisted of a Claisen flask fitted with thermometer and condenser by ground glass joints sealed with silicone grease. The condenser in turn was jointed to a movable fraction-cutting device which held a flask for forerun and tailings of the distillation, and the viscometer itself. All joints were of the drip-tip variety so that stopcock grease could not touch the liquid. Some of the less viscous liquids crept into the joints, in which cases it was necessary to use Teflon sleeves instead of grease.

The orthoesters were distilled into the viscometers at approximately 1 mm. Ethyl orthocarbonate and orthosilicate were distilled in at 10 mm because of their lower boiling points, and the pressure was lowered to 1 mm before sealing off. After a good middle cut of the distillate had passed into the viscometer, it was sealed off under vacuum (point (d) in Fig. 2). The joint formerly attached to the viscometer was then cleaned and weighed together with the filled viscometer to determine the weight of liquid which had passed in.

Before each run, the viscometer had to be flamed dry from (e) to (c) in the diagram (going counterclockwise). It was then laid on its side in the thermostat for 30 min., then righted and placed in its flow position. The small surge bulb, e-a, gave sufficient time to clamp the instrument in place and prepare to start the stopwatch. Following each run, the procedure was repeated at the next temperature. After all runs had been made with a particular liquid, the viscometer was scratched and broken open with a heated glass rod at (d) and (m), flushed several times with dry alcohol to remove traces of the orthoester, and cleaned and re-sealed for re-use.

The data obtained from the orthoesters are presented in Tables III to XII.

Calculation of viscosities

If the viscosity of the orthoester is near that of the liquid used for calibration, the viscosity may be found from the following expression, where subscripts 1 and 2 refer to orthoester and calibration liquid, respectively:

$$\frac{\eta_1}{\eta_2} = \frac{d_1 \theta_1}{d_2 \theta_2}.$$

The first step in calculation is to find the volume of the orthoester contained in the viscometer at the temperature of the determination. This can be calculated from the weight and density of the orthoester. From the volume of the orthoester, it is now possible to find the time required for flow of an equal volume of the calibration liquid at its own calibration temperature. When this time has been found, solution for the orthoester viscosity is a matter of plugging data into the equation. The following steps may make this more lucid:

1. $W_1/d_1 = V_1$
2. $V_1 = V_2$
3. $W_2 = d_2V_2 = d_2V_1 = W_1d_2/d_1$
4. $\theta_2 = a/(b + W_2) = a/(b + W_1d_2/d_1)$
5. $\eta_1 = \eta_2d_1\theta_1/d_2\theta_2$

If greater accuracy is desired, the two-constant equation may be used:

$$\eta_i = Ad_i\theta_i + Bd_i/\theta_i.$$

This equation requires two calibration liquids to evaluate the constants A and B, whereupon the orthoester viscosity may be obtained by plugging in.

This two-constant equation should in general yield more accurate viscosities, but had the disadvantage of being more laborious, since each point-set of data requires the solution of simultaneous equations. It was found that the application of this equation to the experimental data in preference to the simpler equation gave viscosities differing from the latter in the third significant figure. This is about the limit of reproducibility, however, so that viscosities calculated from the simpler equation should not be discredited.

Viscosities calculated from the data will be found, together with the original flow times, in Tables III through XII.

Temperature dependence of orthoester viscosities

Temperature dependent viscosity equations were calculated for all the orthoesters by the method of least squares. The general equation,

$$\log_{10} \eta = a/T - b + cT,$$

was used. This is an empirical equation justifiable mainly by the ease - comparatively speaking - with which it can be "least squared". The least squares calculations of even this convenient case had to be carried to 20 digits in order to obtain solutions. This in turn meant calculation of four 3x3 determinants, each containing 20 digit operations - a most laborious task. The simpler two-constant equation ($c = 0$) was therefore used where possible, since 10 digit figures were sufficient there.

Table XIII gives the results of these calculations and the temperature ranges over which they were calculated. It should be noted that ethyl orthotitanate and all four of the orthocarbonates are representable by two separate curves, each in a different temperature range. The point at which these two curves intersect is discussed in the next section.

Fig. 6 is a graph of $\log_{10} \eta$ vs. $1/T$ for all the orthoesters studied.

Melting points of orthocarbonates and of ethyl orthotitanate

Supercooled liquids in general show a viscosity-temperature discontinuity at the melting point, although this phenomenon has been noted by only a very small number of authors. Since this effect may be unknown to many readers, a graph of $\log_{10} \eta$ vs. $1/T$ for benzyl benzoate (Fig. 7) has been plotted from the data of Bingham and Sarver as an illustration.

It will be noted that the curve is not straight in the non-supercooled region. This curvature seems to be general for all liquids, although less noticable in some. The melting point shown on the figure as the intersection of viscosity-temperature lines is identical with that experimentally determined by melting.

To calculate the melting point of a liquid from its temperature dependence of viscosity, it is only necessary to realize that at the melting point the viscosity of both the supercooled and normal liquid is the same. Using the subscripts s and n to indicate supercooled and normal regions of the same liquid, and T_m to indicate the temperature of melting, we have $\log_{10} \eta_n = a_n/T_m - b_n + c_n T_m = \log_{10} \eta_s = a_s/T_m - b_s + c_s T_m$. Then $T_m^2(c_n - c_s) + T_m(b_s - b_n) + (a_n - a_s) = 0$.

This last equation is a quadratic in T_m and may be solved by common methods. Two solutions are possible, but if $c = 0$ only one solution is found.

The melting point of ethyl orthotitanate, obtained in this manner by calculation from the viscosity equations, is found to be 33.7°C , which is in excellent agreement with the value of 34°C reported by Caughlan, et al. (10).

The literature melting point of methyl orthocarbonate, -5.5°C , indicated during the course of this research that the melting points of the higher homologs should be in the range of temperatures available with the experimental equipment. In order to find these melting points, the experimental points were carefully examined to find the break, and experimental points were then taken on both sides of the discontinuity. These discontinuities were easily found by graphing for amyl and butyl ortho-

carbonates, but those of ethyl and propyl orthocarbonates had to be found by least squares calculations. To do this, the region on the graph expected to contain the break was located roughly by visual inspection. Least squares equations were then developed for points on both sides of, but not including, the range of points near the expected melting point. Simultaneous solution of these yielded a value for T_m which was now used as a better approximation. All points on both sides of this new T_m were now included in the least squares calculations, and a second value for T_m calculated. These refined calculations were then found to shift the melting point, and the final shifting of points included in the least squares calculations served to produce a T_m which no longer shifted. In case the final value of T_m was such that too few points were included in either the normal or supercooled region, additional data were taken and the calculations repeated.

Table XIX lists these melting points, and Fig. 8 shows the relationship between m.p. and molecular weight for the orthocarbonate family.

An attempt was made to freeze each of the orthocarbonates in order to obtain verification of these melting points, but all attempts failed.

It should be mentioned that the solution of the three-constant equations yields two values for T_m in the case of ethyl and n-propyl orthocarbonates, whereas the two-constant equations used for other esters yield only one. The extraneous solutions were eliminated by approximating the temperature-viscosity equation in the supercooled region by a two-constant form rather than the three-constant form. This caused one of the melting points to shift somewhat more than the other, and the one which did not

shift appreciably was assumed to be the true melting point. The possibility exists, however, that the discarded values are true and refer to a transition point.

The false melting points were: Ethyl orthocarbonate 20.0°C, n-propyl orthocarbonate 33.9°C. The difference between them, 13.9°, may be compared with the difference between the melting points from Table XIX, 13.8°. The comparison is indeed striking!

Activation energies and molar volumes of orthoesters

As was mentioned in the introduction, calculation of activation energies of viscous flow will be according to the simple, although arbitrary, relationship,

$$E_{vis} = R d(\ln \eta) / d(1/T).$$

Since this is variable with temperature for liquids which are not expressible as linear functions of $1/T$, it is necessary to choose a temperature. The temperature selected for this thesis, 20°C, is completely arbitrary. Some of the data taken from literature sources will not be at 20°C and will merit later explanation.

Molar liquid volume, V , is the experimental volume of one mole of liquid as calculated from molecular weights and densities, assuming the liquid species to be monomeric. Table II lists these values calculated from the experimental data. The values for activation energy have been calculated from the equation for the non-supercooled region, even though the liquid may be supercooled at 20°C. This is mainly done to refer all liquids to the same temperature. The particular choice of 20°C was mainly so that comparison might be more easily made with literature data.

This data is presented in graphical form in Fig. 9.

Activation energies and molar volumes - literature data

In order to make more plausible the general method which will be used here to calculate degree of aggregation, it seemed wise to search the literature for viscosity - temperature equations of homologous series. The data presented in the International Critical Tables are not well suited to the task. Much of it is old and inaccurate, and many values did not agree with those given by recent authors. Several articles were discovered which had the desired information. From one, by Friend and Hargreaves (20), has been taken the information on aldehydes and nitriles. Values for E_{vis} were calculated from their paper, while the densities necessary for calculation of molar volume were estimated from various sources. An exceptional article by Bingham and Stookey (5) presents equations for temperature dependence of viscosity of n-alkanes, n-alkyl bromides, and n-alkanethiols. Densities necessary for the calculation of molar volumes were taken from literature sources too numerous to mention. A third article, by Whitmore (42), gives viscosities of $SiRMe_3$ and $SiREt_3$ compounds at $0^\circ C$, $20^\circ C$, and $60^\circ C$, as well as molar volumes at $20^\circ C$. The three points for each compound did not lie on a straight line when graphed as $\log_{10} \eta$ vs. $1/T$. Activation energies were therefore computed by finding the slopes on both sides of 20° and subtracting $1/3$ the difference from the value calculated using the two lower temperatures. Another set of data taken from literature sources is that of Takatani (37). He lists viscosities and densities for several alkyl orthosilicates and energies of activation for these and related alkoxysiloxanes. His data for n-butyl orthosilicate do not agree well with

my values. For instance, my d^{20} 0.8890 compares with his d^{20} 0.8993; my η^{20} 2.095 compares with his η^{20} 2.055. The purity of his compounds is questionable, since his method of reacting ethyl orthosilicate with an alcohol might not be expected to produce an ester free of ethoxy groups. It is noted that the difference in density and viscosity between his data and mine could be predicted if this were the case. He has calculated his temperature dependent viscosity equations as the two-constant form, whereas my data showed too strong a curvature to permit this. I have not recalculated his data, but suspect that it would exhibit the same curvature as mine. It should be noted that the energies of activation for viscous flow from Takatani's data are averages for 35°C and are temperature independent.

A final literature source of data is that of Hurd (23), who presents work on some methyl siloxanes.

The collected information from these literature sources is presented in Tables XIV to XVIII and in Figs. 9 and 10.

D. Interpretation of viscosities and discussion

Melting points of the orthocarbonates

The smooth curve (Fig. 8) obtained by plotting discontinuities vs. molecular weight should dispel any doubts as to their validity as melting points. The literature melting point of -5.5°C for methyl orthocarbonate ties down the curve adequately.

As was mentioned earlier, solution of simultaneous equations led to two possible melting points for ethyl and n-propyl orthocarbonates. It cannot be definitely stated that the ambiguous solutions mean anything, but the fact that the difference between the melting points listed in

Table XIX for these compounds is 13.8° , whereas the difference between the extraneous points is 13.9° would indicate that they are real discontinuities which may represent transition points.

It may be pointed out that the melting points of ethyl and n-butyl orthocarbonates seem to lie on a curve parallel to that drawn. A similar situation exists in the case of carboxylic acids, where the even and odd number of carbon atoms give rise to two separate melting point curves.

Viscosities of the orthotitanates

The viscosities of n-butyl orthotitanate are lower than those of n-propyl orthotitanate but higher than those of ethyl orthotitanate. In addition, the following E_{vis} values are found: Ethyl; 6780 cal, n-Propyl; 8560 cal, n-Butyl; 6635 cal. These values are not in the order anticipated. My interpretation is as follows:

Apparently the n-butyl orthotitanate is the anomalous case, and the ethyl and n-propyl esters are the "normal" trend here. If a straight line is drawn through the ethyl and n-propyl points (Fig. 9), nothing unusual is found. If a straight line is drawn through the n-propyl and n-butyl, or the ethyl and n-butyl points, the slope is negative. None of the other curves on Figs. 9 or 10 show a negative slope; therefore, these cases are unlikely. It seems likely, then, that n-butyl orthotitanate has a lower degree of aggregation than ethyl or n-propyl orthotitanates. n-Propyl orthotitanate probably has the same or a lower degree of aggregation than ethyl orthotitanate.

The melting point of ethyl orthotitanate, 33.7°C , gives rise to a consideration of supercooling. It is entirely possible that the melting

point of n-propyl orthotitanate is lower than the temperature range studied here, although a melting point higher than 33.7°C was expected. Since no melting point was found for the propyl ester, the possibility of supercooling must be considered. If supercooling occurs, energy of activation will be abnormally high. The experimental energy of activation will then set a maximum on the degree of aggregation to be calculated.

n-Butyl orthotitanate may also be supercooled, since no melting point was discovered, but it is likely that it is not supercooled in the range studied. If it is supercooled, the degree of aggregation will be a maximum value when determined from its energy of activation.

In summary, both n-butyl and n-propyl orthotitanates may be supercooled. If they are supercooled, degrees of aggregation determined from energy of activation of viscous flow will be slightly higher than the actual case. If they are not supercooled, n-butyl orthotitanate must have a lower degree of aggregation than the other esters, whereas n-propyl orthotitanate may have the same or a lower degree of aggregation than ethyl orthotitanate.

General discussion of E_{vis} vs. V curves

Fig. 10 shows the general relationship obtained by plotting E_{vis} against molar volume, V, for homologous series.

In the case of end-substituted n-alkanes, it is noticed that increasing size of the characteristic group shifts the curves to the left of the graph. n-Alkanethiols and n-alkyl bromides are of interest in that they lie on nearly the same curve. The covalent volume of the -Br and -SH groups is nearly the same.

Cyclosiloxanes are found to have higher activation energies than linear siloxanes of the same molar volume. This is reasonable, since the linear compounds may flow by using only a fraction of their total volume to drive a wedge into an available hole, whereas cyclic structures would find this mode of travel more difficult. An extremely interesting occurrence in the siloxane family, pointed out by Hurd (23), is that decamethyl tetrasiloxane and methyl, tri-(trimethylsiloxy)silane, which have nearly identical molar volumes, 364 cc and 365 cc, respectively, have nearly identical activation energies - 2670 and 2702 cal, respectively. This, together with the information concerning equal volumes of -Br and -SH groups, tends to establish the tenet that energy of activation is a function of molar volume.

My orthocarbonate curve (Fig. 9) seems to have a point out of line. There is no valid reason for rejecting any of these points on the grounds of experimental error. A large amount of data was taken for each, and two different samples of each orthocarbonate were used in the viscosity determinations. It is possible, however, to consider the ethyl orthocarbonate point as anomalous. Fig. 6 shows that this is so. The viscosity of the orthocarbonates at a given temperature increases as molecular weight increases, except that ethyl orthocarbonate is anomalous here also. Considering only the n-propyl, n-butyl, and n-amyl orthocarbonate points, I have drawn an extrapolated orthocarbonate curve as shown on Fig. 9. The extrapolated portion of the curve has been drawn nearly straight to agree with the trends set by other homologous series.

My orthosilicate curve does not agree with that plotted from the

data of Takatani (37). His compounds are of questionable purity, since they were prepared by transesterification. Considering my data only, it is again necessary to consider the first point, ethyl orthosilicate, as anomalous. My three points lie on a straight line, but this is probably fortuitous. Fig. 6 shows that the viscosity of ethyl orthosilicate at any temperature is unexpectedly higher than viscosities of either n-butyl or n-heptyl orthosilicates. The extrapolated orthosilicate curve I have drawn is slightly curved in the same direction as that plotted from Takatani's data.

It is interesting to note that the orthosilicate curve is below the orthocarbonate curve in Fig. 9, although the atomic volume of an orthosilicate is larger than that of an orthocarbonate. It is probable that the slightly larger covalent radius of silicon permits greater freedom of motion of the R-groups. This would result in an orthosilicate flowing with smaller activation energy, which is what is observed.

Analogously, monomeric orthotitanates should require even less activation energy for flow than orthosilicates of comparable size. If the orthotitanates are dimers or trimers, activation energy would be greater per unit of volume, thus reversing this trend. The average values for degrees of aggregation as calculated by use of both the orthocarbonate and orthosilicate curves then seem reasonable.

Degree of aggregation of orthotitanates

By moving along the dotted line from the ethyl orthotitanate point (Fig. 9) until it strikes the orthocarbonate curve, then dropping down to the V axis, I find that a volume of 550 ccs represents the volume of

the unit of flow of ethyl orthotitanate. Similarly, a volume of 700 ccs is found from the extrapolated orthosilicate curve. Then $550/206 = 2.5$ is the degree of aggregation from the orthocarbonate curve, and $700/206 = 3.4$ is the degree of aggregation from the orthosilicate curve. The average of these two values is 3.0. The value of 206 represents the molar volume of ethyl orthotitanate obtained by dividing its monomeric molecular weight by its density at 20°C.

The corresponding calculations for n-propyl orthotitanate are $680/274 = 2.5$ from the orthocarbonate curve, $790/274 = 2.9$ from the orthosilicate curve, and 2.7 from the average.

A similar operation for n-butyl orthotitanate gives $540/341 = 1.6$ from the orthocarbonate curve, $690/341 = 2.0$ from the orthosilicate curve, and 1.8 from the average.

If the n-propyl and n-butyl esters are supercooled, degrees of aggregation would be lowered as much as 0.5.

From this rough treatment, it is concluded that ethyl orthotitanate is trimeric in the liquid state, n-propyl orthotitanate is also trimeric, and n-butyl orthotitanate is dimeric.

III. VAPOR PRESSURE

A. Introduction

Since the orthotitanates are not monomeric in the liquid state, it was thought worthwhile to obtain vapor densities to determine the molecularity of the vapor. If the bonding in these compounds is by Ti.....O coordination, these bonds were expected to be strong enough to permit a dimeric or trimeric molecule to vaporize intact.

No simple methods are available for determination of vapor densities of materials with low vapor pressures from .001 micron to 1 mm, and recourse was made to indirect methods. The method of gas transpiration for measurement of vapor pressure gives the vapor pressure in terms of molecular weight. The Knudsen effusion method gives a similar expression of vapor pressure as a function of molecular weight. An absolute method, called the "self-manometer" was also devised here, wherein absolute vapor pressures could be obtained in the desired pressure range. By these three methods it was hoped to determine the molecular weight of the vapor.

B. Materials

Benzophenone was recrystallized from MeOH-water and vacuum fractionated for use as a vapor pressure standard.

Rhombic sulfur was prepared by melting flowers of sulfur in vacuo. The flask was immediately plunged into boiling water (95°C) and kept at that temperature for 10 hours. The sulfur was then dissolved in analytical grade CS₂ and filtered. The clear filtrate was set in a Dewar containing Dry Ice, whereupon large, block-shaped crystals formed. The mother liquor

was decanted off and the crystals allowed to air dry. They were then crushed and evacuated at 90°C in a high vacuum chamber (.0000001 mm) for 24 hours before use as a vapor pressure standard.

Mercury was vacuum distilled in grease-free glassware for this purpose.

Mercuric chloride was resublimed in vacuo for use as a vapor pressure standard.

Orthotitanates were prepared as described in the viscosity section.

C. The self-manometer

The measurement of vapor pressures in the range 0.01 - 5 mm was made possible by this apparatus. The apparatus is pictured in Fig. III. In operation, a sample of the orthotitanate being measured was vacuum distilled into the large bulb. The apparatus was connected to the evacuating pumps and placed in the thermostat at a high temperature to be degassed. Following degassing, the orthotitanate was permitted to flow into the U-tube by tilting the apparatus. After a few minutes allowance for temperature equilibrium to take place, the manometer, in its upright position in the thermostat, was observed by a cathetometer which measured the difference in height between the two liquid levels. Much trouble occurred in attempting to read these levels to .05 mm, but with practice the readings became somewhat reproducible. The temperature was gradually changed and a large number of points taken for each liquid, both with temperature rising and falling.

The theory here is that the difference in liquid levels will be a measure of the vapor pressure, since one arm is under this pressure, while the other is at such a low pressure that it is essentially zero pressure.

By use of the densities determined for the orthotitanates, pressures could be calculated. Some uncertainty exists, since the evacuated arm is really under a pressure gradient of unknown magnitude. As the pump capacity increases, the effect of this gradient becomes smaller, but still not calculable.

In order to assess the method, a liquid for which the vapor pressure-temperature curve was known was used as a check. The only liquid fitting the requirements was benzophenone. Its vapor pressures from 1 to 760 mm are given by Stull (35) and from .005 to .02 mm by Neumann and Volker (30). The two sets of values seem to be in agreement, as may be seen from Fig. 11.

It is seen that the experimental pressures by the self-manometer method are somewhat lower than expected. This should be the case if a pressure gradient on the evacuated side exists. Unfortunately, the particular liquid chosen as a standard here is difficult to control in the self-manometer. Although the orthotitanates could be studied up to 5 mm without trouble, benzophenone vaporized too rapidly to permit reproducible measurements, even below 1 mm. If vaporization was too rapid, the returning condensate caused pressure surges so that readings could not be made rapidly enough.

The vapor pressures given by Stull (35) can be questioned. His method consisted of plotting literature values by other authors on a board by means of tacks, then drawing a string across the most reasonable ones. The majority of his original references were in obscure journals not readily available, hence I did not check them. Most experimenters, when recording

boiling points below 50 mm, and especially below 15 mm, report the manometer reading for condenser pressure, not the pressure at the thermometer. For this reason, such boiling points are actually taken at a pressure somewhat higher than recorded. Therefore, it is likely that the self-manometer points shown are not as far off as the literature points would indicate, but still indicate that the method is of doubtful validity.

The self-manometer vapor pressures recorded for the orthotitanates were far too numerous to list here, but the general curve is indicated in Figs. 12, 13, and 14. The n-butyl orthotitanate curve (Fig. 14) could not be checked by either the effusion or gas transpiration methods because of the high temperatures required.

D. Vapor pressures by gas transpiration

The apparatus is illustrated in Fig. 4. The nitrogen used as the sweeping gas was purified by passage through three alkaline pyrogallol scrubbers, lead acetate solution, two conc. sulfuric acid bubblers, and finally through a U-tube immersed in liquid air. This treatment should have removed most of the oxygen and all of the water. There was no trace of hydrogen sulfide.

The operation is as follows: Pure nitrogen is bubbled through successive columns of the orthotitanate and thereby saturated with the orthotitanate vapor at thermostat temperature. The saturated gas then bubbles through a dilute nitric acid solution, also immersed in the thermostat. The nitric acid hydrolyzes the orthotitanate, and the nitrogen, now free of orthotitanate vapor but containing nitric acid vapor, is bubbled through 2 conc. sulfuric acid bottles and back through a U-tube

immersed in liquid air for moisture and HNO_3 removal. Passage of the dry nitrogen through a water bubbler in a separate thermostat is the final step.

In practice, the acid absorber was strongly flamed and then weighed as the first step. The male joint was coated with silicone grease and fitted to its mate, to which it was then tightly wired. After passage of dry nitrogen through the apparatus at room temperature for several hours, about 3 cc of the orthotitanate was pipetted in through the top joint of the orthotitanate absorber. Following several hours of nitrogen passage through this system to remove volatile materials, about 5 ccs dilute nitric acid was poured into the acid absorber. The condenser, lightly greased, was fitted into the top of this absorber and flow of water through it was begun. Rubber tubing was then added to connect this absorber to the subsequent drying train. The apparatus was then lowered into the hot thermostat. After a wait of about a minute to permit the temperature of the apparatus to rise, the water absorber, in its thermostat, was connected and its stopcocks opened. The nitrogen flow, which had been very slow up to this time, was then increased until steady bubbling was observed in the orthotitanate cell.

After a period of flow long enough to obtain at least 0.01 g TiO_2 (6 to 24 hours), the apparatus was raised out of the thermostat, let cool for about a minute, and the stopcocks of the water absorber closed. The nitrogen flow was decreased and the acid and water absorbers removed from the system. The water absorber was wiped free of visible water and let stand in air until dry on the outside. It was then weighed to determine

the amount of water it had lost.

Special precautions had to be taken with the acid absorber because of the silicone grease on its joints and because of the mineral oil coating it had acquired. Mineral oil had to be used as the thermostat liquid because of the high temperatures necessary. It was carefully wiped free of grease, then connected to an aspirator so as to suck air through the acid, which at this time usually was a thin slurry of the partially hydrolyzed orthotitanate. By use of a flame, the liquid was rapidly removed. The entire absorber was then flamed (still sucking air through it) to the point at which the hot glass colored the flame. All organic materials were thus removed. After cooling for two hours, in a balance, its weight was recorded. This gave the weight of titanium dioxide obtained from hydrolysis.

Calculation of the results was by use of the following equation, which has been derived by use of the ideal gas law:

$$kP_{Ti} = \frac{18.02(W_{Ti})(P_{bar} + 63)(P_{water})}{79.9(W_{water})(P_{bar} - P_{water})}$$

k == degree of aggregation of the orthotitanate vapor
 P_{Ti} == partial pressure of orthotitanate k-mer in the vapor
 18.02 == molecular weight of water
 79.9 == molecular weight of TiO_2
 W_{Ti} == weight of titanium dioxide found in the acid absorber
 W_{water} == weight of water lost by the water absorber
 P_{bar} == barometric pressure
 P_{water} == vapor pressure of water in the water absorber
 63 == pressure drop, in mm Hg, between the atmosphere and the point at which nitrogen enters the acid absorber.

The results of gas transpirations are found in Tables XX and XXI for ethyl orthotitanate and n-propyl orthotitanate. No data for n-butyl ortho-

titanate were taken because of temperature difficulties.

The data from ethyl orthotitanate have been treated by the method of least squares to obtain the following equation:

$$\ln kP_{Ti} \text{ (mm)} = 33.2652 - 13049.6/T.$$

The data from n-propyl orthotitanate are not treatable by this method, and further treatment will be made in the discussion of effusion pressures.

The gas transpiration data of both these esters are graphed on Figs. 12 and 13.

E. Effusion vapor pressures

Introduction

Knudsen's method of measuring vapor pressures by effusion of vapor through a very small orifice into a highly evacuated chamber has been much in use by recent workers, and many variations of the experimental apparatus are to be found in the literature. Some of interest are those of Rodebush and DeVries (32) and Andrews (1).

The method of calculation depends somewhat on the apparatus. References consulted here include Rodebush and DeVries (32), Egerton (16), Farber and Darnell (18, 19), Clausing (11), Motzfeldt (28), and Whitman (41). The basic equation used in this thesis is

$$q = cAPM^{0.5}(2\pi RT)^{-0.5}.$$

q = rate of weight loss of the effusion cell, weight per unit time
 c = a constant depending on cell geometry and accommodation coefficient
 A = orifice area
 P = vapor pressure of the sample
 M = molecular weight average of the effusing vapor
 T = absolute temperature
 R = gas constant.

This equation assumes that the pressure in the evacuated chamber due to

presence of the effusing species is so small as to be negligible.

The effusion apparatus

Several attempts were made to devise a suitable apparatus. The first of these utilized a stainless steel box as the effusion cell. This box was machined so as to provide a tight fitting screw lid. Unfortunately, this was so tight that upon strong heating to burn out volatile materials the tight fit became a shrink fit.

A second attempt was made to fabricate cells from soft glass. These consisted of two parts. The bottom piece was a male joint, sealed shut and flattened on the bottom. The top piece was the mating joint, onto the top of which was sealed a sheet of thin platinum. Before sealing the platinum on, a very small hole had been drilled in its center. The area of this hole was measured by use of a microscope and calibrated stage. These cells were then partially filled with orthotitanates and placed in the evacuation chamber. Results were not reproducible.

The final apparatus devised is shown in Fig. 5. In constructing the effusion cell, a round bottom tube of 15 mm Pyrex was ground flat on the rounded bottom until a small hole was formed. This hole was ground circular with a 45° tapered edge by use of a tapered steel rod. Tapering was such that the upper surface of the orifice, with the cell in the position illustrated, is flat. This tube was then sealed by a ring seal to the larger tubing (40 mm) shown. The larger tube was then sealed at its other end to the wide-bore stopcock (15 mm bore). This stopcock was lubricated with silicone grease. A check on the grease showed that it did not lose enough volatile materials to be an important source of error. The total weight of

the finished cell was 250 g.

The cell was filled as follows: By means of a ground glass joint connected to the filling arm (b), the cell was connected to a fraction cutter on a vacuum distillation apparatus, and a middle cut of 3 to 5 cc of orthotitanate was distilled into the bottom of the cell (c). The apparatus was provided with drip-tips on important ground joints so that the liquid passing into the cell did not come into contact with grease. The filling arm was then sealed off under vacuum at (d). The cell was then connected to the high vacuum system and very thoroughly degassed at about 70°C. It was then disconnected from the high-vacuum chamber (stop-cock closed), wiped carefully with an acetone-soaked rag, and weighed to 0.0001 g. The cell did not gain weight upon standing for a day or more, which means that there was no leakage.

The high vacuum system was provided with a two-stage mercury diffusion pump backed by a mechanical fore-pump. A McLeod gauge sealed to the all-glass system showed the pressure inside to be between 0.005 and 0.001 microns after several hours of running. This gauge was found troublesome and was removed before any of the runs reported here were made. There should be no question as to the order of vacuum attained. If there had been leakage, this would have been observed as gross irreproducibility of determinations.

The high vacuum system was attached to the diffusion pump by a ground joint sealed with silicone grease. All tubing in the system was at least 20 mm stock. The cold trap (e) was immersed in acetone - Dry Ice, and effectively prevented mercury and moisture from reaching the evacuated cell.

Dry air was admitted to the system at the end of each run. It was bled in between the fore-pump and the diffusion pump, and was dried by passage through CaCl_2 , NaOH pellets, and conc. sulfuric acid, in that order. After removal of the sample cell, a sealed-off joint was attached in its stead and the system re-evacuated to prevent adsorption of moisture.

During a run, the effusion cell and part of the built-in Dewar flask above it (f) were immersed in a water thermostat, controlled to 0.01°C . The stopcock of the effusion cell was wrapped with a balloon to prevent stopcock grease from being lost. After several hours evacuation, the stopcock was opened and a stopwatch started. The effusing vapor was condensed on the built-in Dewar, which was filled with acetone - Dry Ice.

Some difficulties were experienced which should be mentioned. The silicone grease is preferable to Apiezon N, since the latter is not fluid enough to permit easy turning of the stopcock. At temperatures above 60°C , silicone grease flows. This did not appreciably affect results, but was objectionable. In order to open and close the stopcock of the effusion cell, which was immersed in the thermostat, heavy rubber gloves were worn to delay scalding.

Calibration of the effusion cell

It may be observed that the orifice area in the effusion cell was not determined. Instead, calibration of the cell with a reference material was used for its determination. Since there is also an apparatus constant in the Knudsen equation, this is also eliminated, and the factor (cA) becomes a new entity which will be called A^0 here. The working equation now becomes as follows:

$$P = 760W(1.61968/T)^{0.5}/3600A^{\frac{1}{2}}\Theta(M)^{0.5}$$

P = vapor pressure of the liquid, mm Hg.
W = weight lost by effusion cell, grams.
 Θ = time required for this weight loss, hours.
T = absolute temperature.
M = average molecular weight of effusing vapor.

As calibrating materials, four substances were tried. These were liquid mercury, solid mercuric chloride, rhombic sulfur, and liquid benzophenone. Bradley and Cleasby (8) used the latter and found about 1% disagreement with values calculated from the cell geometry. The values of $A^{\frac{1}{2}}$ as determined by each of these materials will be found in Tables XXII through XXV.

Considerable disagreement exists in the value for $A^{\frac{1}{2}}$ as calculated from the different materials. The Hg values vary in a regular manner with temperature. The values from $HgCl_2$ calibration are in excellent internal agreement, but lower than those by other methods. The values probably differ because the various materials may not have the same accommodation coefficients. That value obtained by benzophenone calibration is taken to be the most reasonable, mainly because Bradley and Cleasby used it successfully. The sulfur and mercuric chloride were solids, and might have accommodation coefficients much different from 1.00. The mercury has given several other experimenters trouble, and its accommodation coefficient depends on its purity. The value of $A^{\frac{1}{2}} = 0.0235$ sq. cm. is therefore used in subsequent calculations.

Vapor pressure of orthotitanates by effusion

The vapor pressures of ethyl and n-propyl orthotitanates were measured by this method. The data are presented in Tables XXVI and XXVII, and are

graphed on Figs. 12 and 13. The pressures calculated are on the basis of monomeric vapor, but the reason for this will not be presented until a general discussion of the graphs.

F. Comparison of vapor pressure methods and discussion of results

The self-manometer has already been discussed. It is used here only as a guide.

Considering the vapor pressure of *n*-propyl orthotitanate first, we see (Fig. 13) that all three methods of measurement converge rather nicely. There is no agreement with literature points, however (taken from data presented by Cullinane, et al. (13)). As noted when reporting the transpiration data, the two lowest transpiration points are probably bad. There was a visible channel in one greased joint at the end of these runs, which indicated some nitrogen had been lost, which would throw the errors toward the high-pressure side. A definite curvature of the entire graph is noticeable, but this is a normal phenomenon, since heat of vaporization changes with temperature. The curvature is of the shape expected from such curves. It is to be noted that if the vapor were dimeric or trimeric, the transpiration values would be moved downward on the graph by an increment of $\log 2$ or of $\log 3$, whereas the effusion curve would be lowered by half this amount. This would result in the two curves no longer meeting nicely, and the transpiration curve would be below the self-manometer curve. But this is unlikely, since the self-manometer values can only be lower than transpiration values. Therefore, it is established that *n*-propyl orthotitanate is monomeric in the vapor phase, or at least is considerably less than dimeric. There is no indication as to whether

aggregation in the vapor increases at lower temperatures.

Turning now to the vapor pressure curves for ethyl orthotitanate (Fig. 12), it is found that the transpiration values agree nicely with literature values of Cullinane, et al. (13), Crowe (12), and Kraitzer, et al. (25). The self-manometer values are about where expected, but the effusion values resemble those of skatole more than they do ethyl orthotitanate. The transpiration method measures only the titanium content of the vapor. The slope of this curve will therefore be a measure only of enthalpy changes in vaporization and depolymerization processes. The effusion pressures, on the other hand, are a measure of the sum total vapor pressure due to all species, and may reflect decomposition processes other than depolymerization.

If the ethyl orthotitanate decomposes with evolution of low molecular weight materials, this enthalpy change should increase the slope of the curve, which is observed. It seems likely, therefore, that decomposition occurs.

If this explanation of the lack of the ethyl orthotitanate effusion curve to agree with other curves is acceptable, we may make a decision as to degree of aggregation of the vapor. The agreement between transpiration measurements and literature data is strong enough to indicate that the curve is at the right altitude on the graph. If the vapor were dimeric, the transpiration curve would have to be lowered by an amount equal to $\log 2$, which would place it below the self-manometer curve, which is unlikely. Therefore, it is concluded that the vapor is essentially monomeric.

G. Heats of vaporization and dissociation energies

For the process $X_m(\text{liquid}) \rightleftharpoons mX(\text{vapor})$, it is necessary that the free energies be equal at equilibrium. Thus,

$$F_l = mF_v$$

$$\text{and } dF_l = m dF_v.$$

Since $dF = VdP - SdT$,

$$(VdP - SdT)_l = m(VdP - SdT)_v.$$

The subscripts may be removed from P and T at equilibrium, and

$$dP/dT = (mS_v - S_l)/(mV_v - V_l).$$

Using the perfect gas law and neglecting the liquid volume in comparison with volume of the vapor, this expression becomes

$$d(\ln P)/d(1/T) = -\Delta H/mR,$$

where $(mS_v - S_l) = \Delta S = \Delta H/T$.

This means that the slope obtained from a plot of $\ln P$ vs. $1/T$ yields a value of $\Delta H_{\text{experimental}}$ based on $1/m$ moles of X_m , or the equivalent of one mole of X . In other words, the slope determined experimentally as $Rd(\ln P)/d(1/T)$ refers to one mole of the vapor species.

To calculate the dissociation energy contained in the above enthalpy term, two processes may be considered:

$$\begin{array}{lcl} \text{Process I:} & 1. & 1/m X_m(\text{liquid}) \rightleftharpoons 1/m X_m(\text{vapor}) \quad \Delta H_{\text{vap}} \text{ (for } 1/m X_m) \\ & 2. & 1/m X_m(\text{vapor}) \rightleftharpoons X(\text{vapor}) \quad \Delta H_{\text{diss}} \text{ (vapor phase)} \\ & \hline & 3. & 1/m X_m(\text{liquid}) \rightleftharpoons X(\text{vapor}) \quad \Delta H_{\text{experimental}} \\ & \text{and } \Delta H_{\text{exp}} & = \Delta H_{\text{diss}} \text{ (vapor phase)} + \Delta H_{\text{vap}} \text{ (for } 1/m X_m). \end{array}$$

Since $\Delta H = \Delta E + \Delta(PV) = \Delta E + RT\Delta n$ for a perfect gas,

$$\Delta E_{\text{diss}} = \Delta H_{\text{exp}} - RT\Delta n = \Delta H_{\text{vap}} \text{ (for } 1/m X_m).$$

$$\begin{array}{lll}
 \text{Process II:} & 1. & 1/m X_m(\text{liquid}) = X(\text{liquid}) \quad \Delta H_{\text{diss}}(\text{liquid phase}) \\
 & 2. & X(\text{liquid}) = X(\text{vapor}) \quad \Delta H_{\text{vap}}(\text{for } X) \\
 & \hline
 & 3. & 1/m X_m(\text{liquid}) = X(\text{vapor}) \quad \Delta H_{\text{exp}}
 \end{array}$$

Since dissociation occurs in the liquid phase here, the $\Delta(PV)$ term is negligible and $\Delta E_{\text{diss}} = \Delta H_{\text{diss}}$. Then the overall equation becomes

$$\Delta E_{\text{diss}} = \Delta H_{\text{exp}} - \Delta H_{\text{vap}}(\text{for } X).$$

It is now apparent that ΔE_{diss} can be calculated if ΔH_{vap} is known. This can be calculated by use of the Trouton Rule, which states that in "corresponding states", all liquids have the same entropy of vaporization. The ordinary Trouton constant of 21.0 is thus seen to be the entropy change associated with the class of liquids which boil at 760 mm and are not associated in either liquid or vapor phases. There seems to be no reason why this should be restricted to one arbitrary pressure, and I have calculated from literature data (15) the vapor pressure and Trouton constants for 11 representative organic compounds (all are ring structures, but many have long side chains) at pressures of 1, 10, 30, 100, and 760 mm. The compounds, together with the Trouton constants (T_c), are tabulated in Table 28 and the Trouton constants are graphed as a function of $\log P$ in Fig. 15. A three-constant least squares equation,

$$\log_{10} P(\text{mm}) = 4.436 - .05313 T_c - .0013888 T_c^2,$$

has been developed for the purposes of extrapolation and interpolation.

It is now possible to calculate the Trouton constant by direct use of experimental data rather than the extremely risky procedure of extrapolation to 760 mm of the vapor pressure curves. The equation relating T_c and ΔH_{vap}

is $\Delta H_{\text{vap}} = T_b T_b / 1000$, where ΔH_{vap} is in kcal per mole.

An extremely important point must now be considered. It may be noted that ΔH_{vap} refers to $1/m X_m$ in Process I, but refers to X in Process II. Although ΔE_{diss} as calculated by either process should be nearly the same, it is obvious that the correct value of T_b must be used.

The basic problem is then that of deducing the species to which the experimental T_b refers. As shown by the viscosity data, ethyl and n-propyl orthotitanates appear to be trimeric in the liquid state, whereas n-butyl orthotitanate is dimeric. This implies that the major species present in the liquid phase is not monomeric. If dissociation occurs in the gaseous phase, then obviously the boiling point refers to X_m rather than X and Process I applies. If dissociation occurs in the liquid phase, two major possibilities may be distinguished. In both, the monomeric and m-meric units form a solution in which the monomer is a dilute solute. In the case that the monomer is very much more volatile than the m-mer, the experimental T_b would refer to the boiling point of a solution intermediate between the boiling points of pure monomeric and pure m-meric liquid. If the monomer is not appreciably more volatile, but has a boiling point quite near that of the m-mer, the experimental T_b would refer to a solution which boils closer to the boiling point of the m-mer. In both cases it would seem that the experimental T_b could not be accurately correlated with any particular species.

As a guide to the proper choice of referent species for T_b , it is of interest to note that Caughlan, et al. (10) found ethyl orthotitanate to be trimeric in dilute benzene solution. This would indicate that in the

presence of other ethyl orthotitanate molecules the equilibrium is such that very few, if any, occur as monomers. This in turn means that Process I is the more probable.

Speer (34) lists the following boiling points for the orthotitanates: Et: 104°/1 mm; n-Pr: 170°/3 mm; n-Bu: 134-6°/0.5-1 mm; iso-Bu: 141°/1 mm; sec-Bu: 90-92°/0.5-1 mm; tert-Bu: 62-63°/1 mm. Within the butyl series, it is observed that T_b decreases steadily as degree of branching increases. Two major effects are responsible for this. The first is that increased branching decreases the boiling point by increased shielding of the carbon and titanium atoms from intermolecular forces. The second is that increased branching shields the central titanium atom from coordination with oxygen of other orthotitanate molecules. Tertiary butyl orthotitanate thus should have a lower degree of aggregation than n-butyl orthotitanate and should also have the lowest boiling point. Both of these effects tend toward the same direction, which makes it very difficult to separate them in even a qualitative manner. It may be noted that iso-butyl and n-butyl boiling points are close together, whereas sec-butyl is considerably lower. It would be expected that the iso-butyl and sec-butyl boiling points would be very close together if the only effect were that of branching. The difference of 40 - 50° between them indicates that degree of aggregation is responsible for most of the difference, since the sec-butyl ester should have the smaller degree of aggregation.

Further, the boiling point of the tert-butyl ester is appreciably lower than that of the ethyl ester. This also indicates that the ethyl ester is boiling as an m-meric liquid. A brief search of handbook comparisons

between ethyl and tertiary butyl compounds, such as halides and substituted benzenes, reveals that the ethyl compounds are always of considerably lower boiling point.

Qualitatively, then, it is considered established that the experimental T_b refers to the boiling point of the m-mer rather than the monomer. Whether the dissociation process occurs in the liquid or in the vapor is then unimportant, since calculation by Process I will yield a true value for ΔE_{diss} which will be nearly identical with the value that would be calculated by Process II. The only reason for not calculating ΔE_{diss} by use of Process II is the inability to assign a value to T_b for the ΔH_{vap} term in it.

Upon slight rearrangement, the overall equation for Process I becomes:

$$\Delta E_{diss} = \Delta H_{exp} - RT(1 - 1/m)/1000 - T_c T_b (1/m)/1000.$$

For ethyl orthotitanate, $\Delta H_{exp} = 25.9$ kcal at roughly 372°K and $\log_{10} 10^4 P(\text{mm}) = 3.2$. This value is obtained from the least squares equation of the gas transpiration data and represents the average slope over the range studied. From Fig. 15, the Trouton constant at this pressure is found to be 45.5. Using the value of $m = 3$ and plugging in,

$$\begin{aligned} \Delta E_{diss} &= 25.9 - (1 - 1/3)(1.9865)(372)/1000 - (1/3)(372)(45.5)/1000 \\ &= 25.9 - 0.5 - 5.5 \end{aligned}$$

$= 19.9$ kcal per 1/3 mole of trimer, or 59.7 kcal per mole of trimer. If there are six equivalent Ti....O coordinate bonds per trimer which must be broken to form three monomeric units, each must contribute $59.7/6 = 10.0$ kcal per mole of bonds. Since the actual structure is as yet unknown, it must be assumed for calculation purposes that all six

bonds are equivalent, which is probably not true.

n-Propyl orthotitanate has the value $\Delta H_{\text{exp}} = 27.4$ kcal at roughly 400°K as determined from the slope of the straight line drawn through the transpiration data of Fig. 13. The Trouton constant at the pressure this represents is found from Fig. 15 to be 40.5. Assuming trimer ($m = 3$),

$$\Delta E_{\text{diss}} = 27.4 - (1 - 1/3)(1.9865)(400)/1000 - (1/3)(400)(40.5)/1000$$

$$= 27.4 - 0.5 = 26.9 \text{ kcal}$$

$$= 26.9 \text{ kcal per } 1/3 \text{ mole of trimer, or } 80.7 \text{ kcal per mole of}$$

trimer. If six equivalent Ti...O coordinate bonds are assumed to be broken when the trimer dissociates to three monomeric units, each must contribute $80.7/6 = 13.45$ kcal per mole of bonds.

n-Butyl orthotitanate has the value $\Delta H_{\text{exp}} = 37.9$ at 425°K from the self-manometer curve. Trouton's constant at the corresponding pressure is 42.8. Viscosity data show this compound to be dimeric in the liquid state, so that $m = 2$. Substituting,

$$\Delta E_{\text{diss}} = 37.9 - (1 - 1/2)(1.9865)(425)/1000 - (1/2)(425)(42.8)/1000$$

$$= 37.9 - 0.4 = 37.5$$

$$= 37.5 \text{ kcal per } 1/2 \text{ mole of dimer, or } 75.0 \text{ kcal/mole of dimer.}$$

If both titanium atoms of the dimer are pentacoordinate, two bonds will be broken in dissociation, and each will contribute 37.5 kcal per mole. This seems unreasonable, and should not be strongly regarded. The self-manometer data for this compound disagreed radically with literature data, and this calculation is included here only for the sake of completeness.

H. Structure of orthotitanates

From the energies of dissociation calculated for ethyl and n-propyl orthotitanates, it is now possible to discuss probable structures of these compounds. The energies, 10.0 and 10.8 kcal per mole of coordinated Ti.....O bonds, respectively, are not greatly different from the bond energy due to hydrogen bonding in carboxylic acids. Various authors report values for dissociation of formic, acetic, and propionic acid dimers of about 7.5 kcal per mole of hydrogen bonds broken.

If the trimeric structures contain less than six coordinate bonds, the dissociation energy per bond rises alarmingly to values which are so high that dissociation would not easily occur. The structures postulated by Caughlan, et al. (10) seem reasonable in this light.

IV. SUMMARY

Tyuzyo's method (39) of relating energy of activation of viscous flow to molar volume has indicated ethyl and n-propyl orthotitanates to be trimeric in the pure liquid state, and n-butyl orthotitanate to be dimeric. This should not be regarded as meaning that only one molecular species is present in the liquid, however, since the method is far from quantitative.

These aggregation values have been obtained by determining E_{vis} vs. molar volume curves for orthosilicates and orthocarbonates. The E_{vis} values were obtained as slopes calculated from least squares temperature dependent viscosity equations, and the molar volumes were calculated from liquid densities and monomeric molecular weights. Intersection of the horizontal line from the E_{vis} values of the orthotitanates with these curves resulted in two values for molar volume of viscous flow. These values were averaged and divided by the calculated molar volumes for the monomer to give the degree of aggregation.

It was necessary to assume that n-propyl orthotitanate and n-butyl orthotitanate might be supercooled in the temperature region studied. Ethyl orthotitanate was shown to be supercooled below 33.7°C.

The effect of supercooling upon temperature dependence of viscosity has been utilized in this thesis to determine the ethyl orthotitanate melting point as well as the melting points of ethyl, n-propyl, n-butyl, and n-amyl orthocarbonates. These melting points were obtained by simultaneous solution of viscosity - temperature equations for the supercooled and normal liquid regions, respectively. At the melting point, an abrupt

change in slope and curvature occurs.

Vapor pressures of ethyl and n-propyl orthotitanate have been determined by each of three different methods: Effusion, gas transpiration, and "self-manometer". Comparison of these methods did not result in quantitative vapor molecular weights, but did show qualitatively that these two esters are essentially monomeric in the vapor phase. Vapor pressures of n-butyl orthotitanate were measured only by the "self-manometer" and are not reliable.

From the experimental slopes of vapor pressure - temperature curves for ethyl and n-propyl orthotitanates, together with an extension of the Trouton Rule to pressures other than 1 atm., dissociation energies have been calculated. Assuming six equivalent bonds to be broken per mole of trimer, bond energies of 10.0 and 10.8 kcal per mole of bonds (Ti...O coordination) were calculated for the ethyl and n-propyl esters, respectively. These may be compared with hydrogen bond energies of about 7.5 kcal per mole of bonds in associated carboxylic acids.

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Table I - Viscometer calibration equations

$$\theta = a/(b + W)$$

Viscometer #	Temp.	Liquid	a	b
1	40.00°C	60% sucrose	70447.93	15.583
1	40.00	Benzyl benzoate	17074.34	12.737
2	25.00	60% sucrose	276065.0	50.935
2	25.00	40% sucrose	31608.08	45.155
3	30.00	Water	10850.59	5.568
4	40.00	Benzyl benzoate	69628.21	3.855
4	27.50	Water	11229.78	3.729
5	27.50	Water	19218.45	0.432

Table II - Molar volume and activation energies of orthoesters at 20°C.

Compound	E_{vis}	V
Ethyl orthotitanate	6780 cal	206 cc
n-Propyl "	8560	274
n-Butyl "	6635	341
Ethyl orthosilicate	1990	224
n-Butyl "	3230	357
n-Heptyl "	4835	556
Ethyl orthocarbonate	3140	210
n-Propyl "	4510	277
n-Butyl "	4705	343
n-Amyl "	5130	408

Table III - Viscosity (calc.) and data for Ti(OEt)₄.

1. Viscometer #1, sample weight 37.851 g. Calculated viscosities are from the two-constant equation.

Temp. °C.	Flow times in seconds	Calculated viscosities in centipoises
60.00	834.2, 835.4	12.84, 12.86
57.50	887.4	13.67
55.00	956.7, 956.6	14.74, 14.74
50.00	1114.5, 1121.4	17.19, 17.29
47.50	1213.8	18.73
45.00	1314.0, 1319.3	20.28, 20.36
40.00	1569.7, 1573.7	24.25, 24.31
37.50	1724.4	26.66
35.00	1902.3, 1902.1	29.42, 29.42
30.00	2360.7, 2361.5	36.55, 36.56
27.50	2646.0	40.98
25.00	2984.5, 2985.3	46.25, 46.27
22.50	3390.9	52.58
20.00	3874.0, 3887.2	60.10, 60.31

2. Viscometer #2, sample weight 28.303 g. Calculated viscosities are from the two-constant equation.

Temp. °C.	Flow times in seconds	Calculated viscosities in centipoises
60.00	1120.6	12.62
57.50	1201.0	13.54
55.00	1290.2	14.56
50.00	1543.6	17.46
47.50	1625.8	18.42
45.00	1768.3	20.05
40.00	2107.3	23.96
37.50	2312.8	26.33
35.00	2544.8	29.01
30.00	3155.4	36.06
27.50	3536.3	40.46
25.00	3987.4	45.68
22.50	4528.5	51.94
20.00	5175.6	59.45

Table IV - Viscosity (calc.) and data for Ti(O n-Pr)₄.

1. Viscometer #1, sample weight 33.053 g. Calculated viscosities are from the two-constant equation.

Temp. °C.	Flow time in seconds	Calculated viscosities in centipoises
60.00	2582.9	35.35
55.00	3140.1	43.03
50.00	3841.6	52.70
45.00	4718.1	64.79
40.00	5824.2, 5818.5	80.03
35.00	7249.5	99.77
30.00	9163.3	126.25
25.00	11688.7	161.23
20.00	15023.0	207.45

2. Viscometer #2, sample weight 30.539 g. Calculated viscosities are from the two-constant equation.

Temp. °C.	Flow times in seconds	Calculated viscosities in centipoises
60.00	3146.0	35.22
55.00	3809.5	42.74
50.00	4648.0	52.27
45.00	5701.0	64.25
40.00	7030.4	79.42
35.00	8716.7	98.69
30.00	10969.4	124.48
25.00	14025.7	159.53
20.00	18197.9	207.46

Table V - Viscosity (calc.) and data for $\text{Ti}(\text{O n-Bu})_4$.

1. Viscometer #1, sample weight 29.492 g. Calculated viscosities are from the two-constant equation.

<u>Temp.</u> <u>°C.</u>	<u>Flow times</u> <u>in seconds</u>	<u>Calculated viscosities</u> <u>in centipoises</u>
60.00	1812.4	22.60
55.00	2102.3	26.24
50.00	2450.8	30.62
45.00	2877.2	35.99
40.00	3379.5	42.31
35.00	4005.8	50.22
30.00	4797.1	60.22
25.00	5792.6	72.80
20.00	7071.8	88.98

2. Viscometer #2, sample weight 28.637 g. Calculated viscosities are from the two-constant equation.

<u>Temp.</u> <u>°C.</u>	<u>Flow times</u> <u>in seconds</u>	<u>Calculated viscosities</u> <u>in centipoises</u>
60.00	2118.7	22.54
55.00	2458.6	26.22
50.00	2875.1	30.73
45.00	3356.5	35.96
40.00	3947.5	42.39
35.00	4672.5	50.29
30.00	5583.5	60.23
25.00	6749.9	72.99
20.00	8223.1	89.13

Table VI - Viscosity (calc.) and data for Si(OEt)₄.

Densities necessary for calculation were from Sugden and Wilkins (36).
The viscometer used was #3 and the sample weight was 19.772 g.

Temp. °C.	Flow time in seconds				Calculated viscosities (using average time) - centipoises
	Run 1	Run 2	Run 3	Avg.	
60.05	260.8	251.6	257.9	256.8	.4675
55.00	270.1	270.7	264.4	268.4	.4894
50.00	280.3	280.5	283.4	281.4	.5139
44.98	295.9	291.7	291.4	293.0	.5359
40.00	312.4	308.7	305.7	308.9	.5658
35.02	325.7	325.9	323.4	325.0	.5962
29.98	341.9	344.8	343.1	343.3	.6308

Table VII - Viscosity (calc.) and data for Si(O n-Bu)₄.

Temp. °C.	Flow times in seconds	Calculated viscosities in centipoises
4.95	2767.4	2.857
10.20	2467.7	2.547
15.47	2215.6	2.287
19.59	2044.8	2.110
25.68	1828.7	1.887

Table VIII - Viscosity (calc.) and data for Si(O n-Heptyl)₄.

Temp. °C.	Flow times in seconds	Calculated viscosities in centipoises
24.84	5856.7	6.053
29.84	5138.5	5.310
34.84	4556.5	4.708
39.84	4061.9	4.197
44.84	3646.8	3.768

Table IX - Viscosity (calc.) and data for C(OEt)₄.

Viscometer #5, sample weight 24.447 g.

<u>Temp.</u> <u>°C.</u>	<u>Flow time</u> <u>in seconds</u>	<u>Calculated viscosities</u> <u>in centipoises</u>
21.78	838.8	.9164
21.76	840.4	.9182
26.27	775.1	.8468
26.28	775.8	.8475
33.40	689.6	.7533
37.60	645.4	.7049
41.41	610.9	.6672
47.25	563.6	.6155
3.58	1213.4	1.3262
6.85	1126.0	1.2306
13.40	982.7	1.0738
17.02	915.5	1.0003
30.00	729.1	.7965
23.53	812.0	.8871
18.57	888.4	.9707
15.22	947.0	1.0348
10.74	1037.1	1.1333
8.50	1087.7	1.1887
4.48	1188.3	1.2987
5.10	1172.4	1.2813
9.53	1062.5	1.1611
8.47	1087.8	1.1888
7.69	1105.2	1.2078

Table X - Viscosity (calc.) and data for C(0 n-Pr)₄.

1. Viscometer #4, sample weight 23.508 g. Viscosities are calculated from the two-constant equation.

<u>Temp.</u> <u>°C.</u>	<u>Flow times</u> <u>in seconds</u>	<u>Calculated viscosities</u> <u>in centipoises</u>
22.60	1131.4	2.276
26.50	1025.4	2.062
30.26	935.7	1.881
34.91	843.3	1.695
39.03	770.6	1.548
42.90	713.6	1.433
46.17	669.3	1.344
28.16	984.7	1.980
32.29	893.3	1.796
41.26	739.2	1.485
44.52	690.9	1.387
47.42	653.8	1.314
36.95	806.8	1.621
24.54	1076.7	2.166
19.35	1232.8	2.481
57.50	547.4	1.098
57.50	547.4	1.098
54.56	575.7	1.155

Table X - continued:

2. Viscometer #4, sample weight 21.370 g. Viscosities are calculated from the two-constant equation.

<u>Temp.</u> <u>°C.</u>	<u>Flow times</u> <u>in seconds</u>	<u>Calculated viscosities</u> <u>in centipoises</u>
25.31	1147.0	2.122
30.51	1013.2	1.874
35.62	903.7	1.670
41.93	808.2	1.493
44.48	754.0	1.393
48.57	699.0	1.291
29.00	1049.2	1.941
21.69	1259.8	2.332
30.41	1017.0	1.881
33.55	946.2	1.749
40.90	808.7	1.494
49.86	679.6	1.255
54.87	622.5	1.149
30.76	1007.0	1.862
28.68	1056.4	1.954
32.29	973.2	1.800
31.21	996.8	1.843
29.72	1032.8	1.910
16.25	1463.3	2.710
14.47	1538.0	2.849
19.16	1348.1	2.496
24.34	1178.4	2.181
26.17	1124.0	2.080

Table XI - Viscosity (calc.) and data for C(O n-Bu)₄.

Viscometer #4, sample weight 21.195 g.

Temp. °C.	Flow times in seconds	Calculated viscosities in centipoises
23.57	2170.0	3.980
24.53	2106.1	3.863
25.51	2049.2	3.758
26.50	1987.7	3.645
27.83	1913.0	3.508
28.73	1866.4	3.422
29.51	1824.7	3.345
30.01	1797.6	3.295
30.35	1782.4	3.267
31.53	1725.9	3.163
31.89	1709.3	3.133
32.11	1697.7	3.111
34.92	1578.6	2.892
37.52	1475.8	2.703
40.00	1387.4	2.541
42.51	1309.0	2.396
45.01	1234.4	2.259
47.48	1169.2	2.139

Table XII - Viscosity (calc.) and data for C(O n-Am)₄.

Viscometer #4, sample weight 22.110 g.

Temp. °C.	Flow times in seconds	Calculated viscosities in centipoises
30.72	2813.5	5.376
31.09	2783.1	5.317
32.70	2649.4	5.061
33.38	2596.6	4.959
36.14	2395.8	4.574
39.80	2164.1	4.130
41.70	2045.8	3.921
43.80	1944.8	3.710
45.81	1849.5	3.527
47.75	1759.3	3.354
50.17	1662.5	3.169
51.96	1579.9	3.011
53.96	1507.9	2.873
57.85	1411.7	2.689
58.98	1346.8	2.564

Table XIII - Least squares viscosity equations for orthoesters.

$$\log_{10} \eta \text{ (cp.)} = a/T - b + cT$$

compound	Visc. #	a	b	c	Temperature range
Ti(OEt) ₄	1&2 comb.	1928.75	4.80429	-	20.00 - 30.00°C.
"	"	1481.425	3.34656	-	35.00 - 60.00
Ti(On-Pr) ₄	1	1871.707	4.07109	-	20.00 - 60.00
"	2	1870.492	4.07060	-	20.00 - 60.00
"	1&2 comb.	1871.098	4.07085	-	20.00 - 60.00
Ti(On-Bu) ₄	1	1448.445	2.99606	-	20.00 - 60.00
"	2	1451.611	3.00584	-	20.00 - 60.00
"	1&2 comb.	1450.028	3.00095	-	20.00 - 60.00
Si(OEt) ₄	3	435.1519	1.63658	-	29.98 - 60.05
Si(On-Bu) ₄	5	1192.6125	5.40821	.0056660255	4.95 - 25.68
Si(On-Hp) ₄	5	1863.7413	8.26848	.0093830810	24.84 - 44.84
C(OEt) ₄	5	1646.29	8.97270	.0113697	3.58 - 9.73
"	5	1127.8843	5.37876	.0051424261	10.74 - 47.25
C(On-Pr) ₄	4	2010.1185	9.87388	.011612941	14.47 - 22.60
"	4	1724.835778	8.01941	.00860184868	24.54 - 57.50
C(On-Bu) ₄ *	4	1130.92	3.21190	-	23.57 - 32.11
"	4	1028.95	2.87972	-	34.92 - 47.48
C(On-Am) ₄ *	4	1200.82	3.22154	-	30.72 - 36.14
"	4	1121.64	2.96936	-	41.70 - 58.98

* These two liquids showed from their least square equations that a better fit might have been obtained by the 3 constant equation.

Table XIV - E_{vis} and V for aldehydes and nitriles at 20°C.

Calculated from the work of Friend and Hargreaves (20).

Compound	E_{vis}	V	Compound	E_{vis}	V
Methyl cyanide	1860 cal	52 cc	Acetaldehyde	1560 cal	57 cc
Ethyl "	1940	70	Propionaldehyde	1990	72
n-Propyl "	2230	87	Butyraldehyde	1990	90
n-Butyl "	2360	104	iso-Valeraldehyde	2220	108
n-Amyl "	2550	120	Chloral	2530	98
			Paraldehyde	3050	133

Table XV - E_{vis} and V for n-alkanes, n-alkyl bromides, and n-alkanethiols at 20°C.

Calculated from the work of Bingham and Stookey (5).

Compound	E_{vis}	V	Compound	E_{vis}	V
n-Pentane	1560 cal	115 cc	n-Butyl bromide	1855 cal	106 cc
n-Hexane	1750	131	n-Amyl "	2115	124
n-Heptane	1930	147	n-Hexyl "	2360	141
n-Octane	2135	163	n-Heptyl "	2665	158
n-Nonane	2435	179	n-Octyl "	3025	173
n-Decane	2735	195	n-Nonyl "	3345	190

Compound	E_{vis}	V
n-Propanethiol	1730 cal	89 cc
n-Butanethiol	1900	105
n-Pentanethiol	2085	122
n-Hexanethiol	2320	140
n-Heptanethiol	2560	154
n-Octanethiol	2735	172
n-Nonanethiol	3220	190

Table XVI - E_{vis} and V for tetra-alkylsilanes at 20°C.

Calculated from the work of Whitmore (42).

Compound	E_{vis}	V
Trimethyl Hexyl silane	2630 cal	213 cc
Trimethyl Heptyl silane	2960	230
Trimethyl Octyl silane	3230	246
Trimethyl Decyl silane	3800	278
Trimethyl Dodecyl silane	4390	311
Triethyl pentyl silane	2970	238
Triethyl hexyl silane	3250	254
Triethyl heptyl silane	3560	271
Triethyl octyl silane	3810	286
Triethyl decyl silane	4320	319

Table XVII - E_{vis} and V for alkoxy silicon compounds at 35°C.

From the values given by Takatani (37).

Compound	E_{vis}	V
Methyl orthosilicate	2270 cal	151 cc
Ethyl orthosilicate	2320	224
iso-Propyl orthosilicate	2840	298
n-Butyl orthosilicate	2900	364
iso-Amyl orthosilicate	3590	434
n-Octyl orthosilicate	5110	629
Hexaethoxydisiloxane	2580	341
Octaethoxytrisilane	2800	444 (estimated)
Octaethoxycyclotetrasiloxane	3680	491

Table XVIII - E_{vis} and V for polymethylsiloxanes at 20°C.

From the compilation of Hurd (23).

Compound	E_{vis}	V
Hexamethyl disiloxane	2166 cal	212 cc
Octamethyl trisiloxane	2446	288
Decamethyl tetrasiloxane	2670	364
Dodecamethyl pentasiloxane	2782	439
Tetradecamethyl hexasiloxane	2892	515
Octamethyl cyclotetrasiloxane	3417	310
Decamethyl cyclopentasiloxane	3714	386
Dodecamethyl cyclohexasiloxane	4099	460
Tetradecamethyl cycloheptasiloxane	4369	533
Methyl, tri-(trimethylsiloxy)silane	2702	365

Table XIX - Melting points of alkyl orthocarbonates

<u>Compound</u>	<u>Melting point</u>
Methyl orthocarbonate	- 5.5°C (literature value)
Ethyl "	10.85
n-Propyl "	24.66
n-Butyl "	33.8
n-Amyl "	40.8

Table XX - Gas transpiration vapor pressure of ethyl orthotitanate

Temp. °C	water Temp. °C	water vapor pressure	P _{bar}	W _{Ti}	W _{water}	kP _{Ti}	1000/T
85.9	22.0	19.83 mm	637 mm	.0200 g	2.1237 g	.0477 mm	2.785
89.6	20.6	18.20	633	.0187	1.3010	.0668	2.756
95.1	20.5	18.10	629	.0244	1.0342	.109	2.715
100.1	20.35	17.92	631	.0193	0.4751	.186	2.679
107.9	21.5	19.23	637	.0413	0.5464	.372	2.624
113.3	23.9	22.24	637	.0652	0.5967	.624	2.587

Table XXI - Gas transpiration vapor pressure of n-propyl orthotitanate

Temp. °C	water Temp. °C	water vapor pressure	P _{bar}	W _{Ti}	W _{water}	kP _{Ti}	1000/T
115.9	19.75	17.26 mm	640 mm	.0428 g	0.5672 g	.331 mm	2.570
121.3	18.9	16.37	633	.0830	0.6283	.550	2.535
109.4	19.45	16.95	630	.0468	1.1211	.180	2.614
101.9	20.5	18.09	633	.0409	1.4236	.133*	2.666
94.9	21.7	19.47	635	.0314	1.9137	.0816*	2.7165

* These last two values are believed high because of loss of nitrogen loss from the system by leakage through a greased joint.

Table XXII - Calibration of effusion cell with mercury

Literature values for the vapor pressure of mercury have been taken from the Handbook of Chemistry and Physics (44).

Temp.	W	θ	P_{Hg}	A^1
34.88°C.	.1919 g	17.15 hrs	.004098 mm	.01609 sq. cm.
34.88	.2349	21.183	.004098	.01597
40.00	.1417	8.450	.006079	
40.00	.1530	9.200	.006079	.01629 (average of three values)
40.00	.1473	8.917	.006079	
45.00	.2340	9.684	.008827	.01642
50.00	.1140	3.258	.01267	.0167
55.00	.1524	2.998	.01797	.01745
60.00	.7528	10.40	.02524	.01760

Table XXIII - Calibration of effusion cell with HgCl_2 .

Vapor pressures are calculated from the equation given by Ruf and Treadwell (33). Their data were taken by nitrogen entrainment.

Temp.	W	θ	P_{HgCl_2}	A^1
50.00°C.	.0611 g	12.82 hrs	.001615 mm	.01530 sq. cm.
60.00	.1303	11.000	.00409	.01529

Table XXIV - Calibration of effusion cell with liquid benzophenone

All runs were at 54.60°C. The vapor pressure at this temperature, .01799 mm, was taken from the data of Neumann and Volker (30).

Run #	θ	W	$q = W/\theta$	
1	2.250 hrs	.1461 g	.0650 g/hr	
2	2.300	.1550	.0674	
3	2.250	.1553	.0691	The average, $q = .0670$, is used to calculate the average value, $A^1 = 0.0235$ sq. cm.
4	2.250	.1522	.0677	
5	2.250	.1481	.0659	

Table XXV - Calibration of effusion cell with rhombic sulfur

All runs were at 88.90°C. Neumann (29) lists the vapor pressure at this temperature as 0.02089 mm.

Run #	θ	W	A^1
1	3.0000 hrs	.0207 g	.0187 sq. cm.
2	11.583	.0817	.0191
3	15.500	.1164	.0204
4	6.5896	.0478	.0197
5	3.1000	.0212	.0186
6	3.1000	.0235	.0205
7	4.0000	.0276	.0187
8	3.0000	.0220	.0199
9	4.1000	.0287	.0190

The average value for A^1 is 0.0194 sq. cm.

Table XXVI - Vapor pressures of ethyl orthotitanate by effusion

These determinations were all on the same sample, and were made in the order presented. Pressures refer to monomer.

Temp.	W	θ	1000/T	$\log_{10} 10^4 P$ (mm)
75.02°C	.1484 g	3.000 hrs	2.872	2.093
80.00	.1959	2.000	2.8316	2.393
85.00	.2124	1.100	2.7920	2.690
89.98	.3410	1.010	2.7544	2.936
64.98	.0349	2.8506	2.9574	1.480
90.00	.5116	1.510	2.754	2.938

Table XXVII - Vapor pressures of n-propyl orthotitanate by effusion

Of the three samples used, sample #2 is probably most pure. It was redistilled three times before use. The runs were made in the order of listing. Pressure is on the basis of monomeric vapor.

Sample #1

Temp.	W	θ	1000/T	$\log_{10} 10^4 P$ (mm)
40.00	.0074 g	57.93 hrs	3.1933	-0.4795
50.00	.0145	22.55	3.0944	0.1429
55.00	.0292	24.133	3.0478	0.4207
60.00	.0545	20.933	3.0020	0.7568

Sample #2

70.02	.0366	4.0167	2.9139	1.3074
80.0	.0909	2.0333	2.831	2.0043
80.00	.1403	3.4324	2.8316	1.9654
75.07	.1000	5.208	2.8717	1.6348
85.00	.0898	1.2314	2.7920	2.2198
90.00	.1391	1.0296	2.7536	2.4906
90.00	.1213	1.000	2.7536	2.4438
87.50	.0910	1.000	2.7727	2.3175
82.55	.0509	3.1319	2.8125	2.0084

Sample #3

82.51	.0562	1.0000	2.8116	2.1051
81.24	.0479	1.0000	2.8217	2.0350
77.50	.0378	1.3333	2.8518	1.8049
78.75	.0342	1.5000	2.8417	1.7111
78.75	.0440	1.4000	2.8417	1.8504
78.75	.0735	2.1000	2.8417	1.8972
76.25	.0552	2.1000	2.8620	1.7713
64.99	.0251	4.3000	2.9573	1.1107
60.01	.0242	8.200	3.0015	0.8112
60.01	.0302	8.5000	3.0015	0.8919
60.02	.0247	9.0000	3.0014	0.7798

Table XXVIII - Trouton constants at various pressures

Compound	Trouton constants				
	1 mm	10 mm	30 mm	100 mm	760 mm
Benzene	39.5	34.0	30.8	27.3	20.0
Toluene	40.6	33.6	30.4	27.1	19.7
Ethylbenzene	40.8	33.7	30.8	27.4	19.7
o-Xylene	39.9	33.8	30.8	27.4	19.8
Propylbenzene	40.5	34.2	31.1	27.6	19.7
Tetrahydronaphthalene	40.5	34.3	31.2	27.6	19.2
Cyclopentane	39.7	32.8	29.7	26.4	19.8
1-Cyclopentyl heptane	42.6	35.8	32.5	28.7	19.1
Cyclohexane	40.1	33.2	30.2	26.6	19.6
1-Cyclohexyl hexane	40.8	34.4	31.4	27.9	18.8
Spiropentane	40.9	33.2	31.1	26.8	20.1
Averages:	40.5	34.0	30.8	27.3	19.6

Least squares equation: $\log_{10} P \text{ (mm)} = 4.436 - .05313 T_c - .0013888 T_c^2$

(T_c = "Trouton constant")

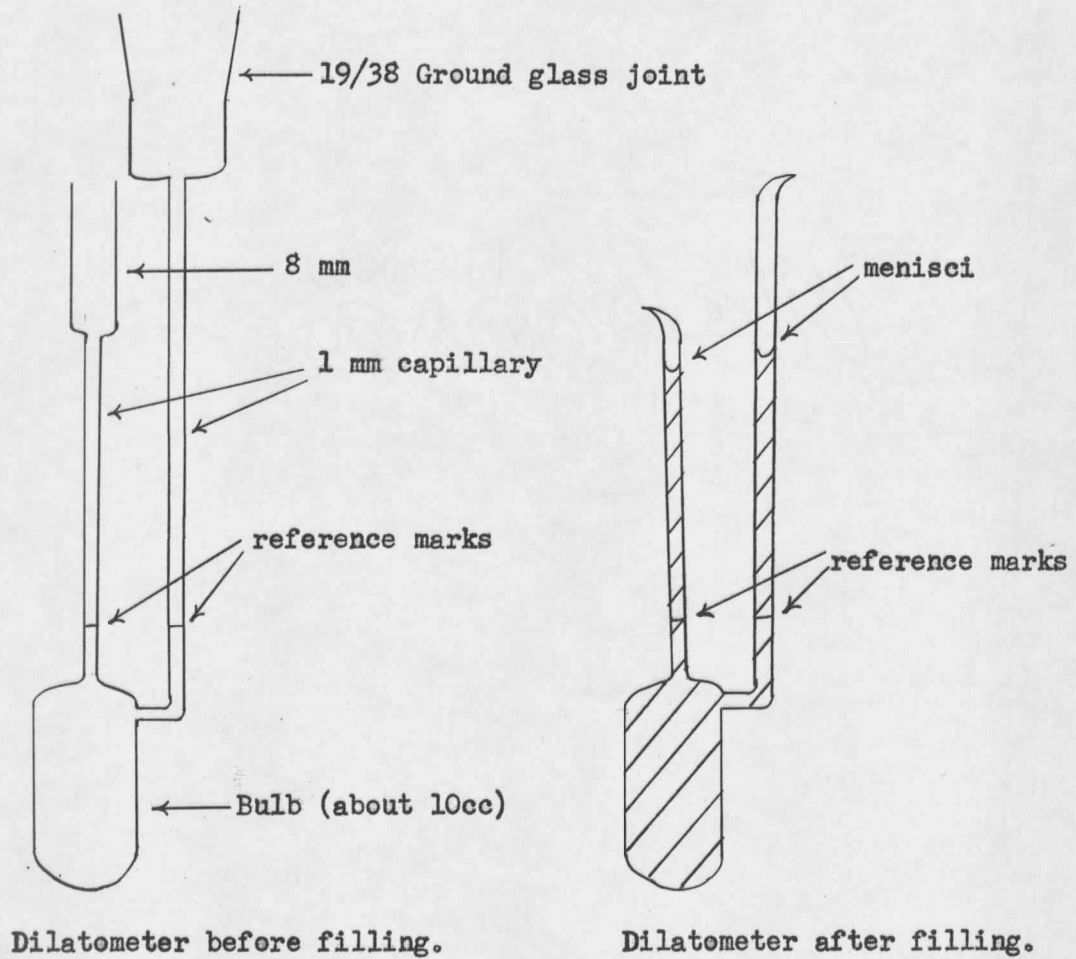


Figure 1 - Dilatometer.

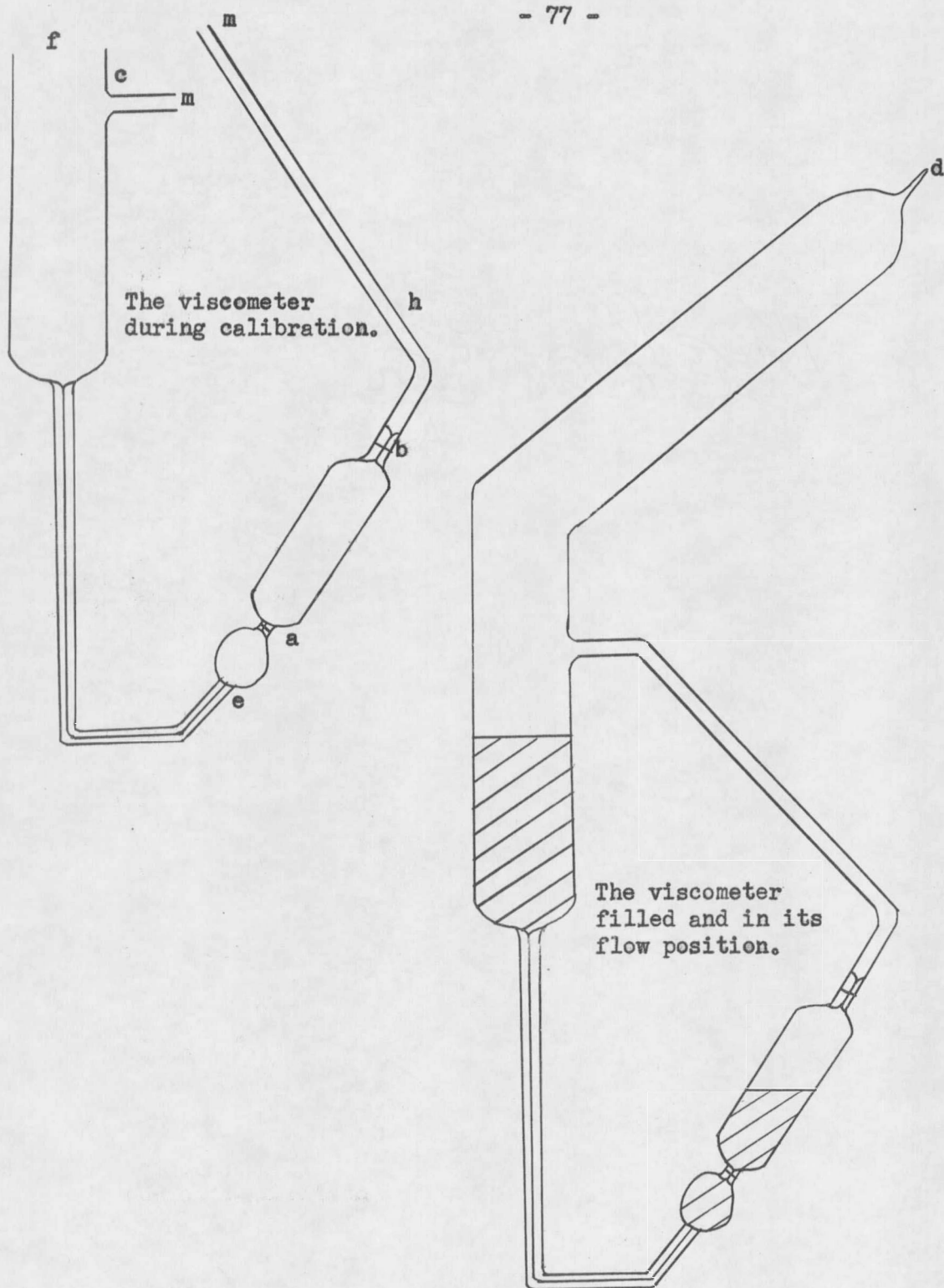


Figure 2 - Vacuum viscometer.

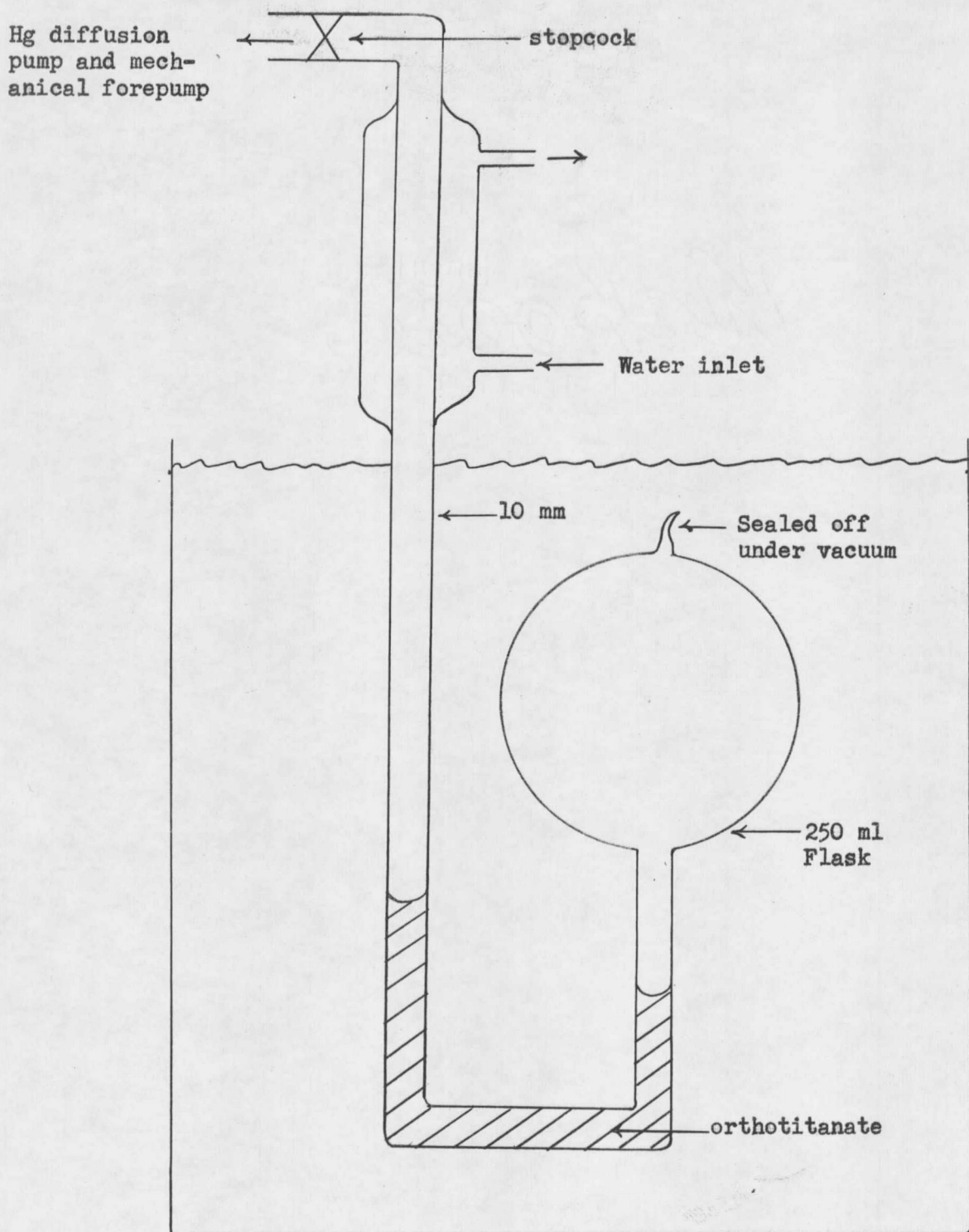
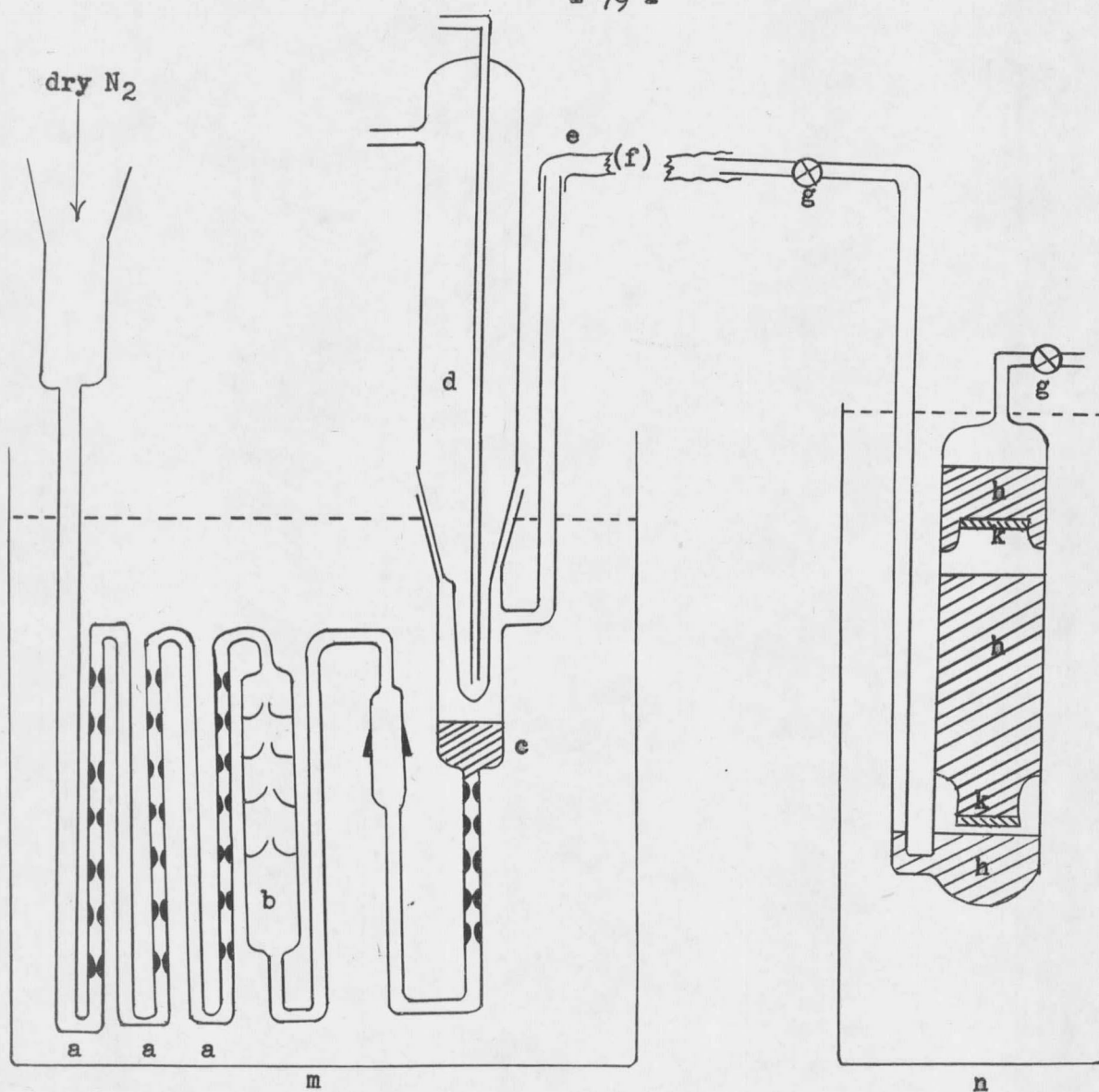
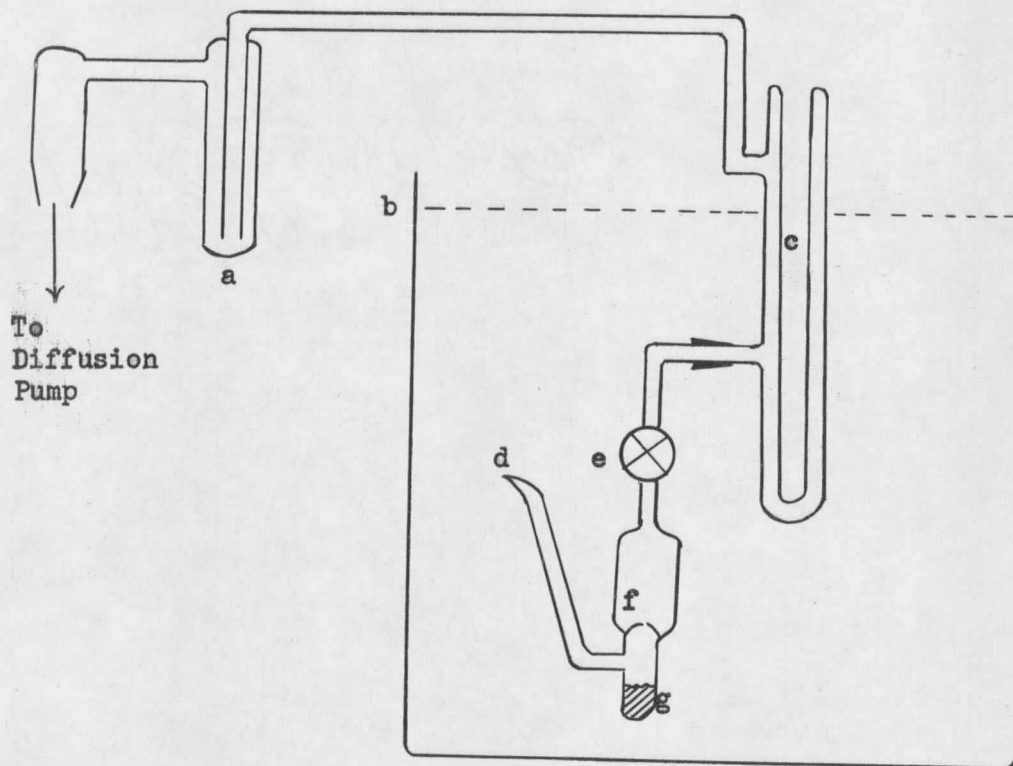


Figure 3 - "Self-manometer".



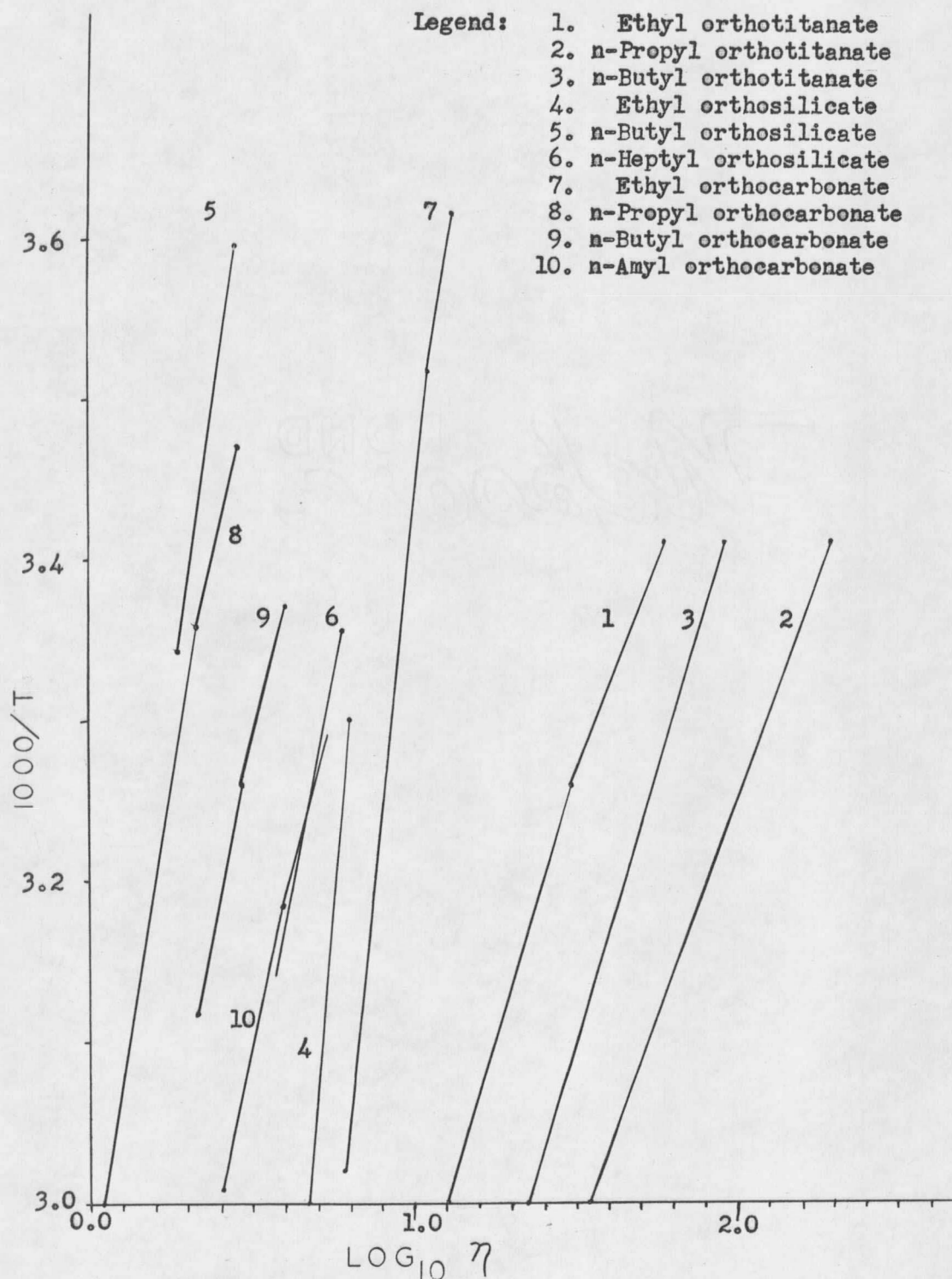
- Legend:
- a ... orthotitanate absorber cells.
 - b ... overflow safety chamber.
 - c ... dilute nitric acid - acid absorber
 - d ... condenser
 - e ... rubber tubing
 - f ... drying system: Conc. sulfuric followed by liquid air.
 - g ... stopcocks.
 - h ... pure water
 - k ... fritted glass disks
 - m ... hot thermostat - mineral oil filled
 - n ... cold thermostat - water filled.

Figure 4 - Gas transpiration apparatus



- Legend:
- a ... Cold finger set in acetone - Dry Ice.
 - b ... Thermostat water level.
 - c ... Interior of built-in Dewar is filled with acetone - Dry Ice.
 - d ... Orthotitanates are distilled in here and sealed-off under vacuum.
 - e ... Wide-bore stopcock.
 - f ... Effusion cell orifice.
 - g ... Orthotitanate sample.

Figure 5. Effusion vapor pressure apparatus



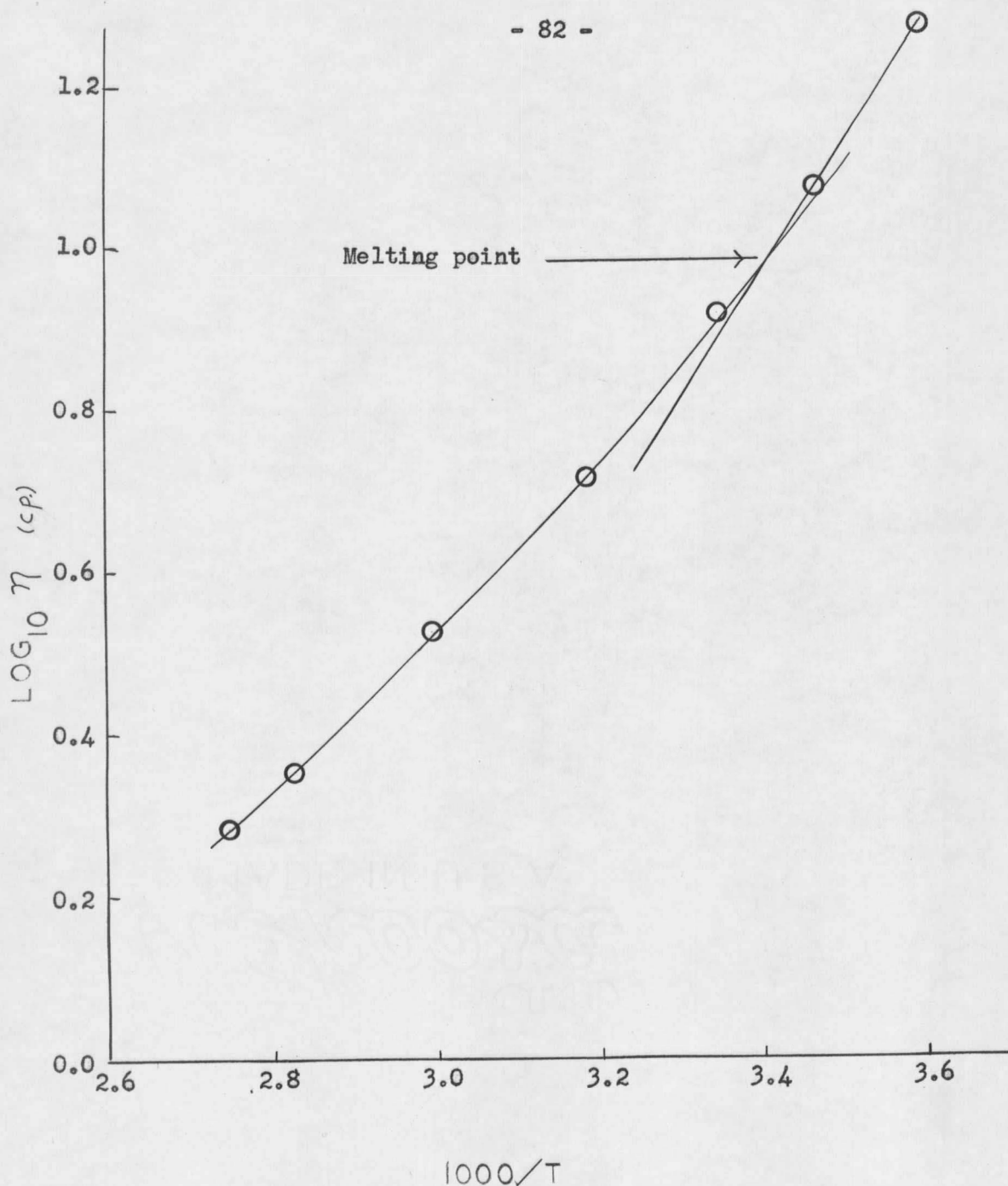


Figure 7 - Viscosity - temperature function of benzyl benzoate (4), showing melting point as a viscosity discontinuity.

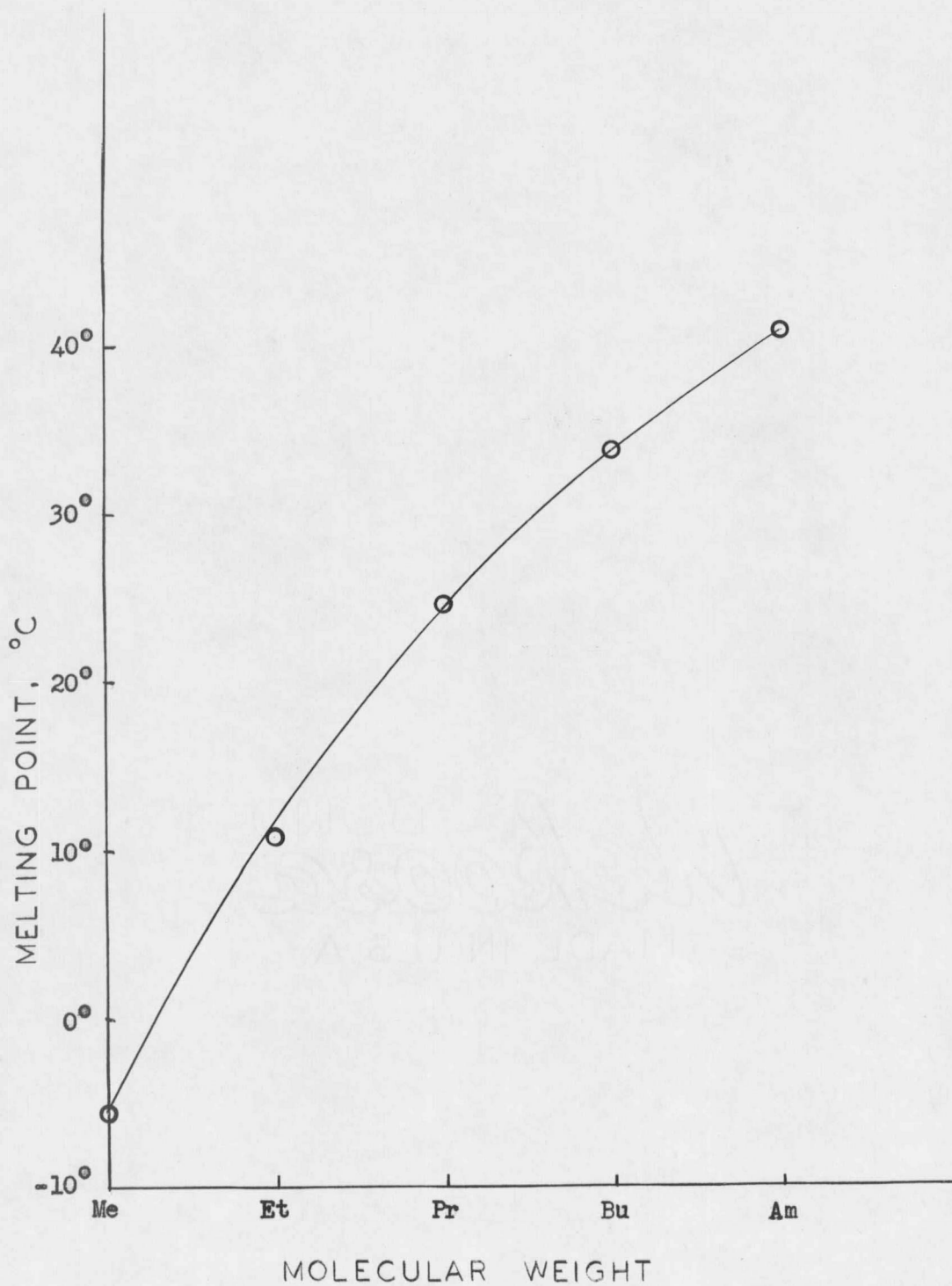


Figure 8 - Melting point vs. molecular weight for n-alkyl orthocarbonates.

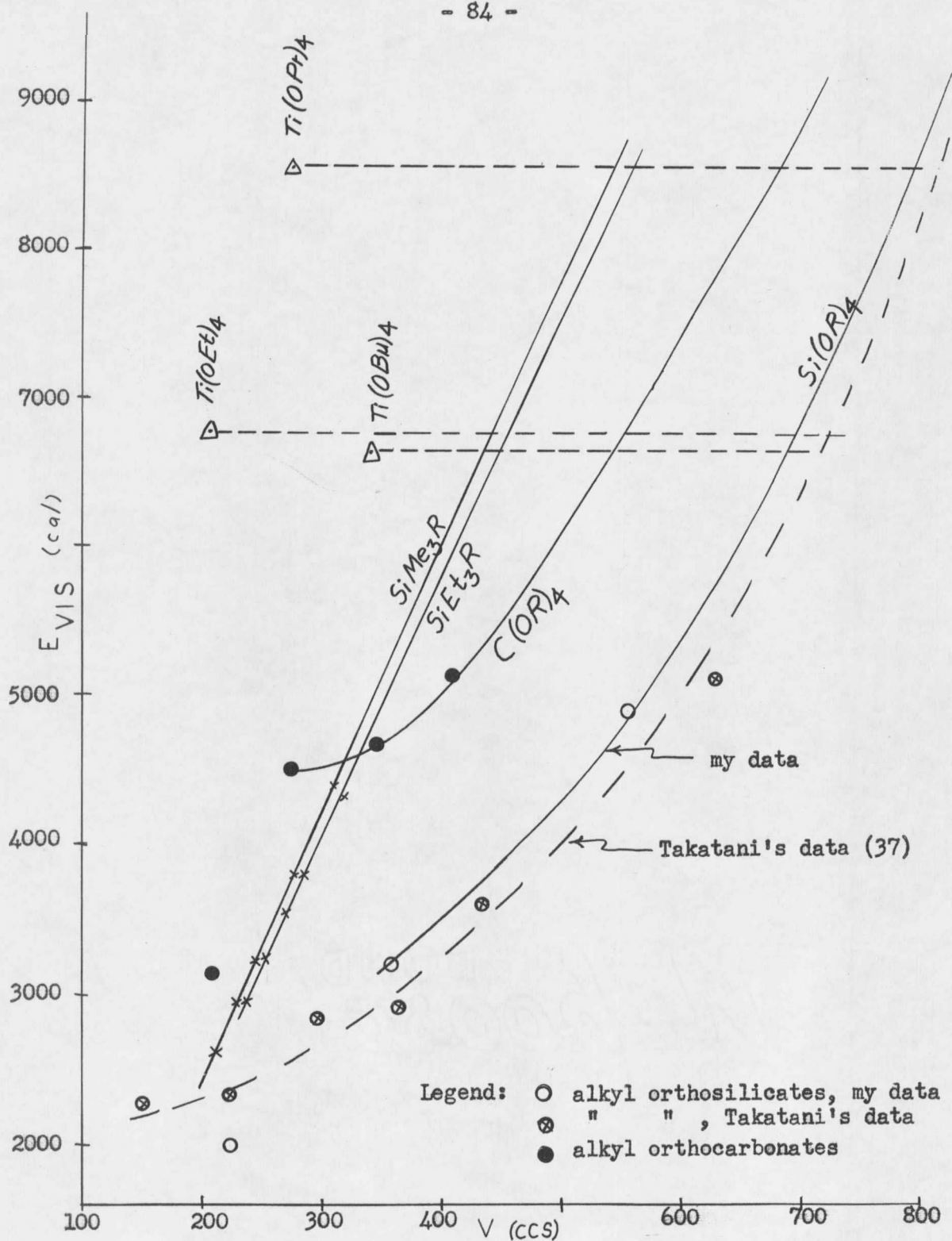


Figure 9 - E_{vis} vs. V - orthoesters

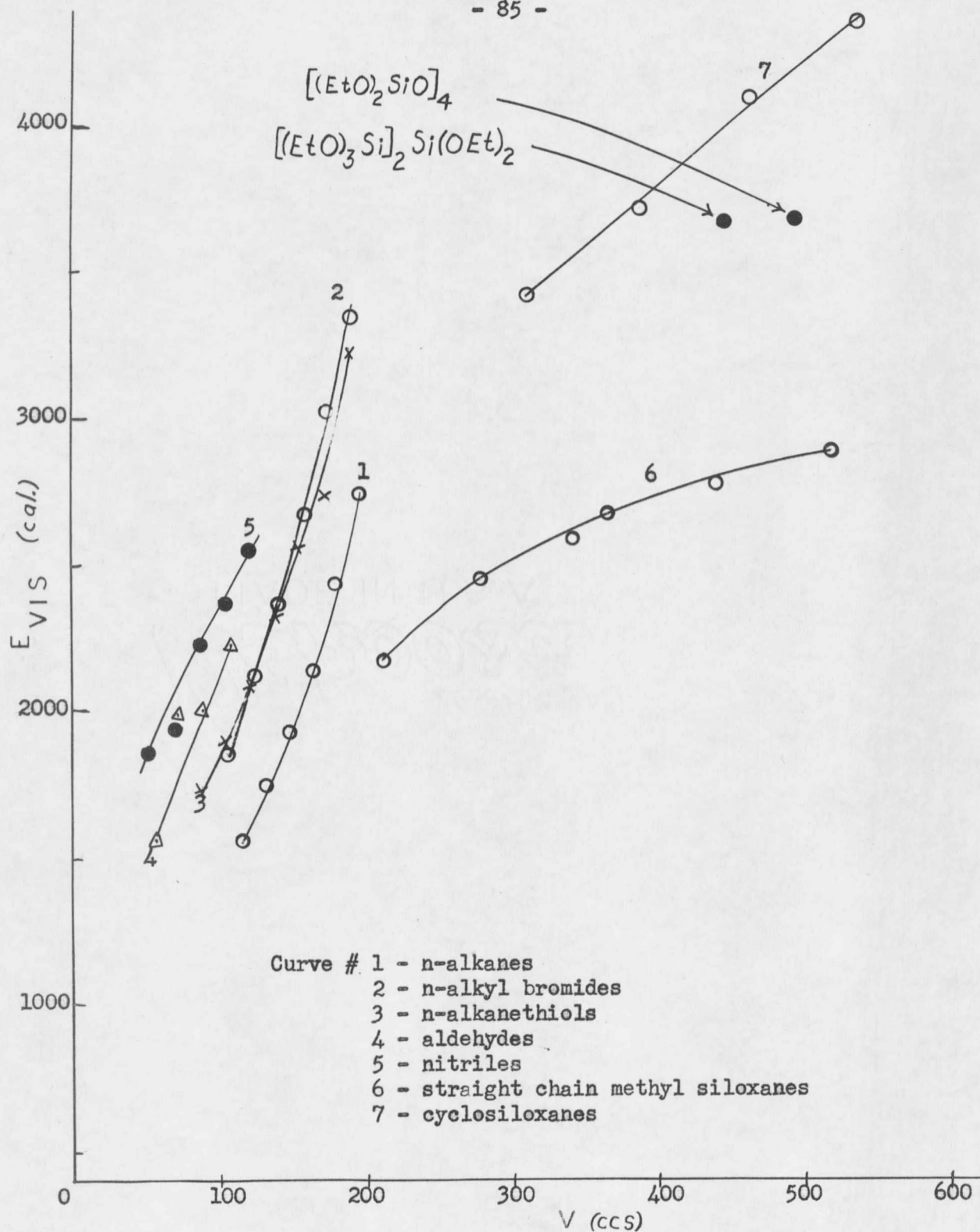


Figure 10 - E_{vis} vs. V - Literature data.

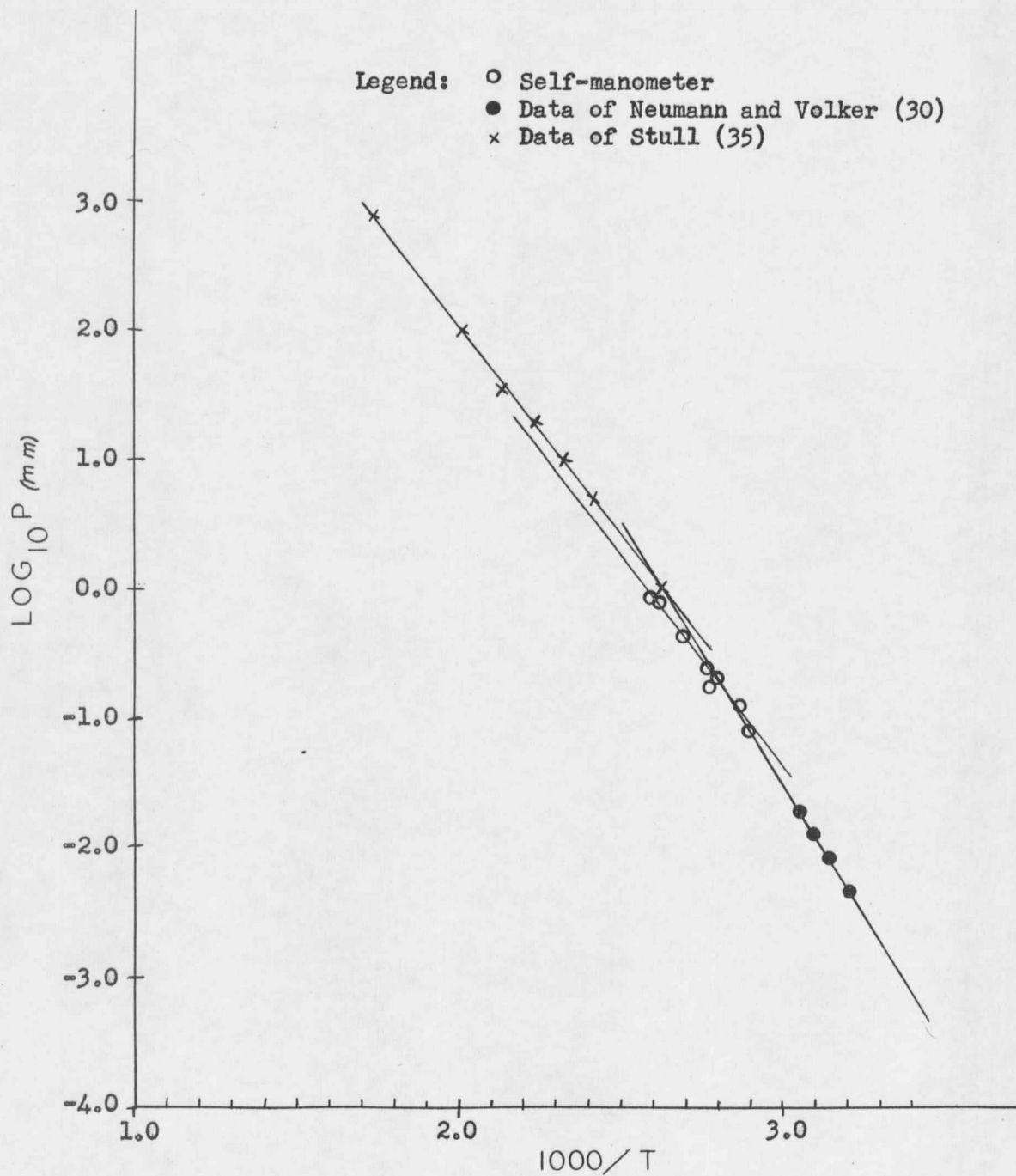


Figure 11 - Vapor pressure of benzophenone by self-manometer

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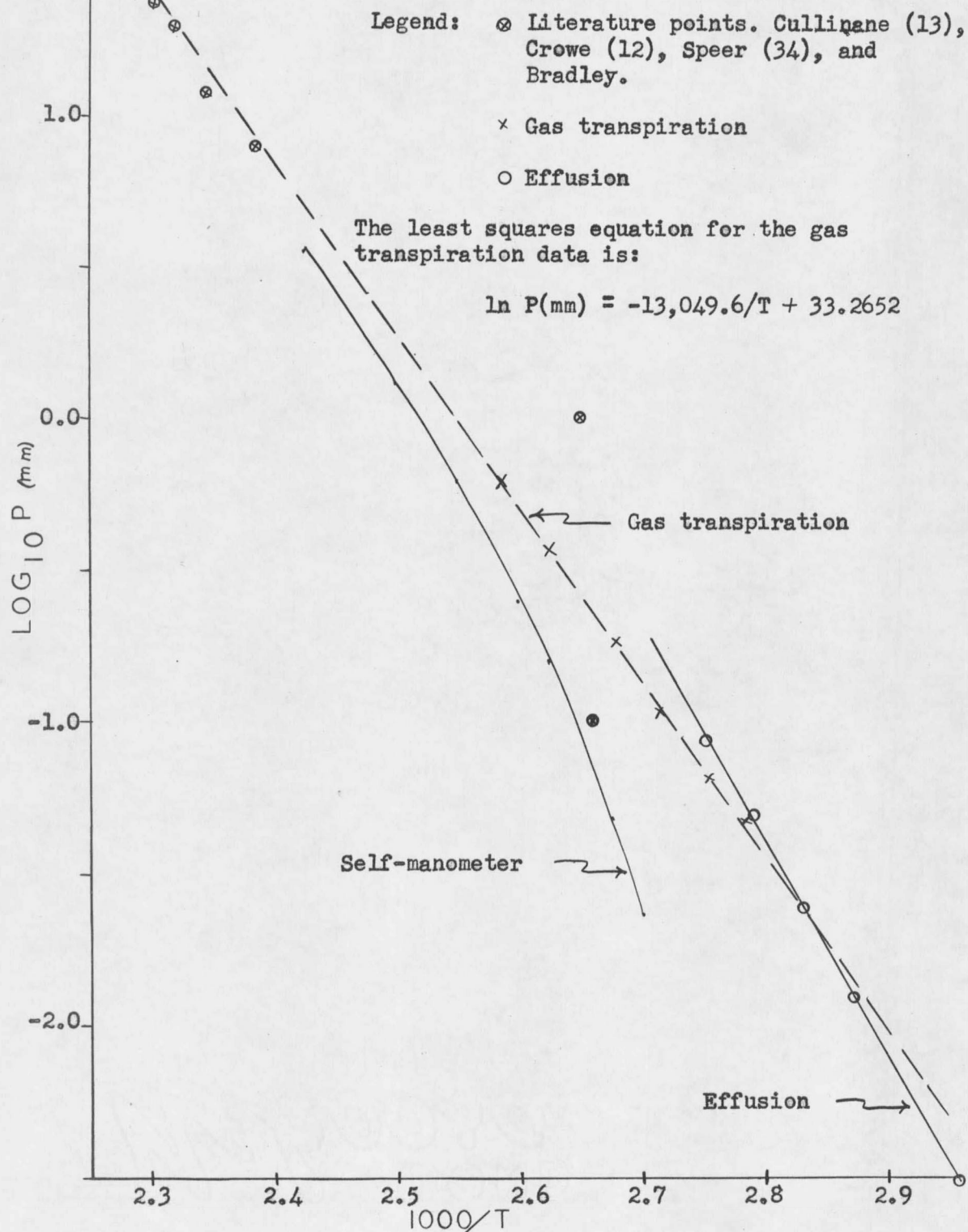


Figure 12 - Vapor pressure of ethyl orthotitanate.

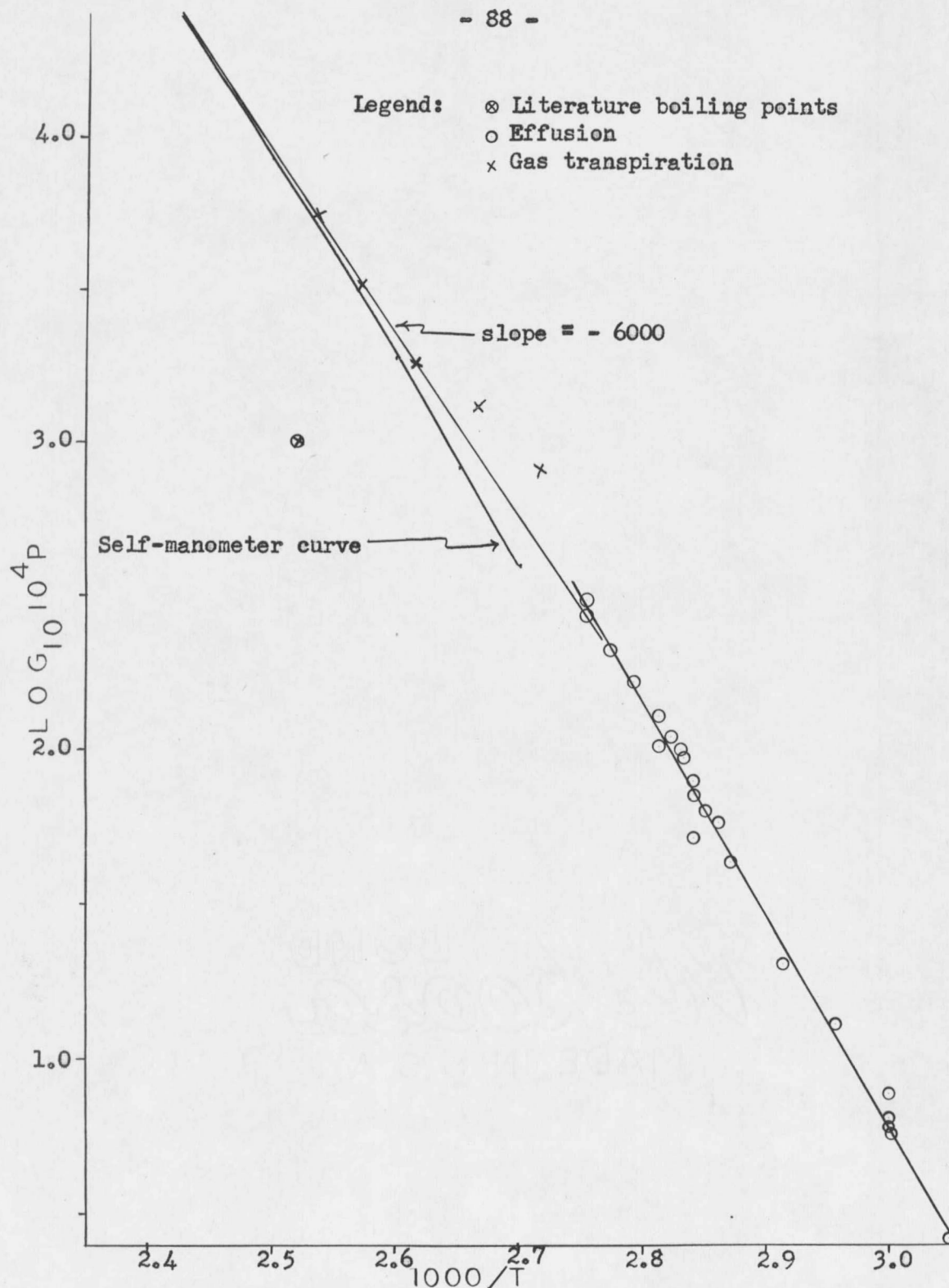


Figure 13 - Vapor pressure of n-propyl orthotitanate

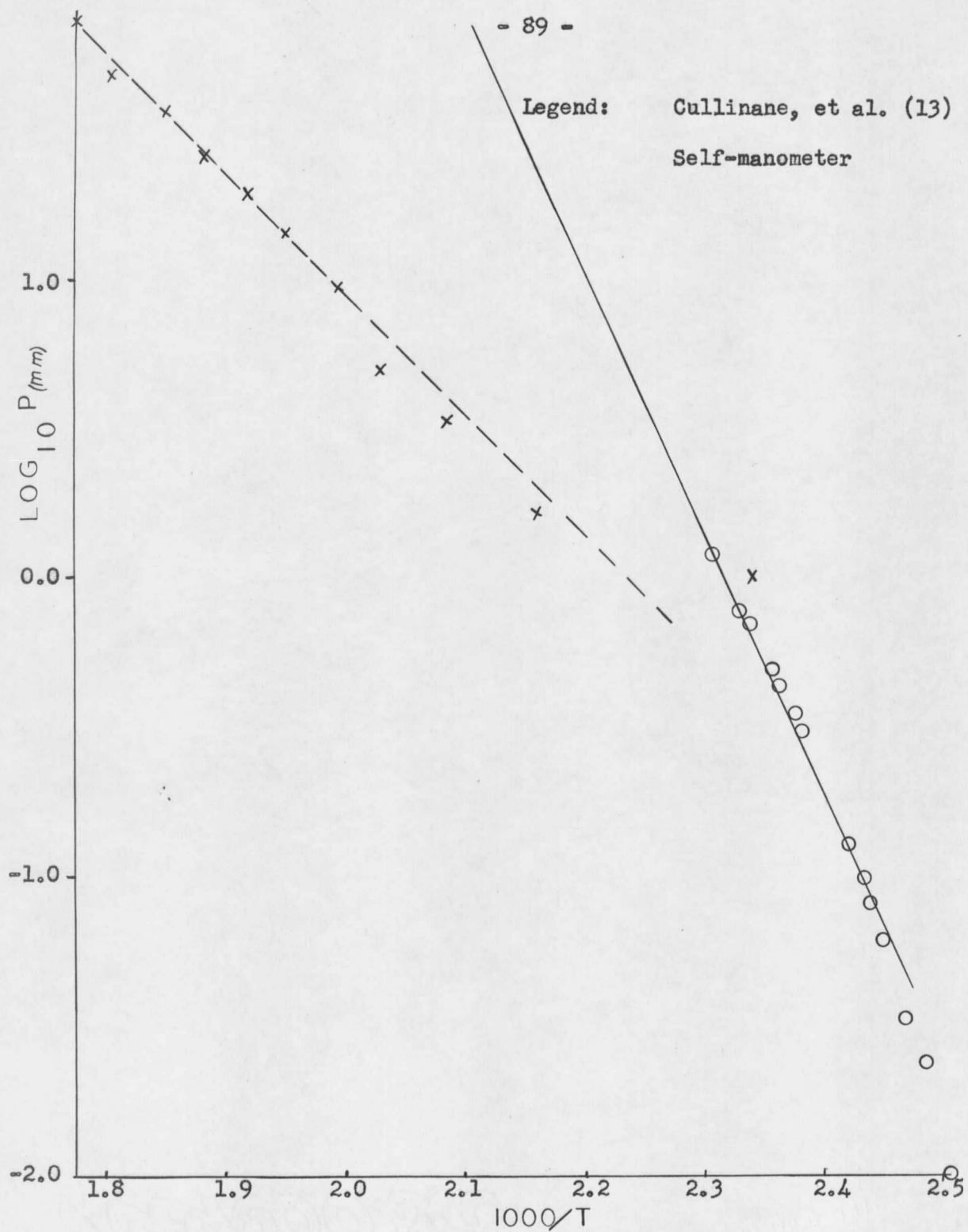


Figure 14 - Vapor pressure of n-butyl orthotitanate by "self-manometer".

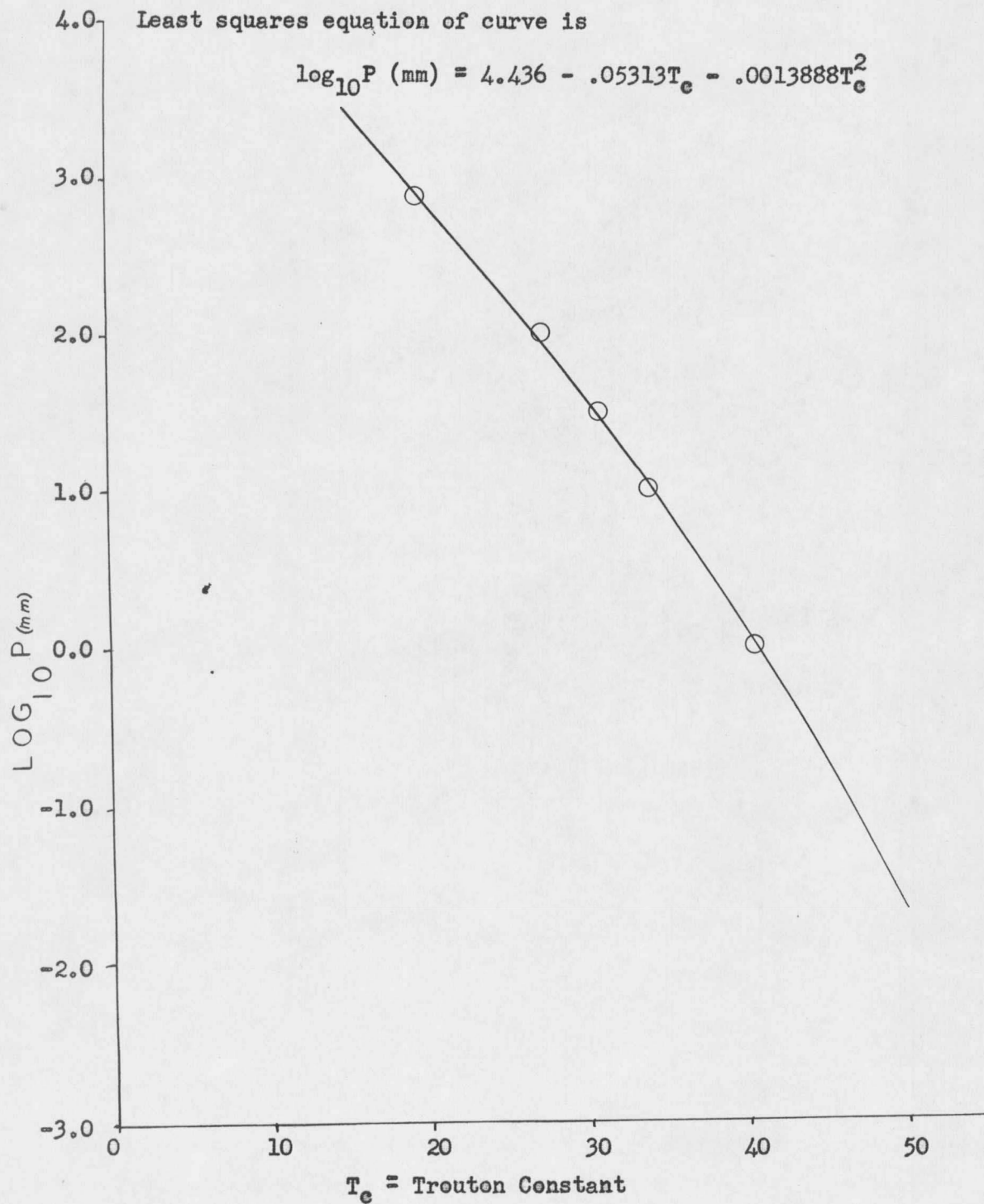


Figure 15 - Variation of Trouton constant with $\log_{10} P$



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NAME AND ADDRESS
R. B. Birkholz

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