



The preparation of diethoxydichlorotitanium and a study of two methods for measuring vapor pressures of titanium tetraethylate-benzene solutions
by Donald Schwartz

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
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Abstract:

Diethoxydichlorotitanium has been prepared by a method different from that used by Jennings, Wardlaw and Way (4). Their method. could not be duplicated with satisfactory results. Diethoxydichlorotitanium was found to be very unstable, decomposing at elevated temperatures and hydrolyzing, very rapidly in air. It was not readily, soluble in many substances. The compound was very soluble in dry alcohol, warm nitrobenzene, and hot ethyl-ortho silicate. When recrystallized from ethyl-ortho-silicate, washed with absolute ether and dried in a vacuum desiccator, it gave analyses for chlor-, ine and titanium which agreed, within experimental error, with theoretical values for diethoxydichlorotitanium. The preparation could not be repeated often enough to substantiate it as a good laboratory method for preparing the compound, but it has served as the best method available. Due to its great instability, and limited solubility only a few of the properties of the compound were determined.

An attempt was made to measure the vapor pressure of solutions of titanium tetratethyl'ate in benzene. Consistent results were not obtained, although two different methods were utilized. Further work to overcome the experimental difficulties encountered is required.

THE PREPARATION OF DIETHOXYDICHLOROTITANIUM AND A
STUDY OF TWO METHODS FOR MEASURING VAPOR PRESSURES
OF TITANIUM TETRAETHYLATE-BENZENE SOLUTIONS

by

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A THESIS

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TABLE OF CONTENTS

	Page
ABSTRACT	3
PART I - THE PREPARATION OF DIETHOXYDICHLOROTITANIUM	
INTRODUCTION	4
EXPERIMENTAL	5
Equipment	5
Preliminary Materials	5
Procedure	6
Analyses	6
Properties	9
DISCUSSION OF EXPERIMENTAL RESULTS	13
LITERATURE CITED AND CONSULTED	14
PART II - A STUDY OF TWO METHODS FOR MEASURING VAPOR PRESSURES OF TITANIUM TETRAETHYLATE-BENZENE SOLUTIONS	
INTRODUCTION	15
PREPARATION OF TITANIUM TETRAETHYLATE	16
EXPERIMENTAL	17
Equipment	17
Preliminary Materials	17
Procedure	20
DISCUSSION OF EXPERIMENTAL RESULTS	23
LITERATURE CITED AND CONSULTED	26
ACKNOWLEDGMENTS	27

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ABSTRACT

Diethoxydichlorotitanium has been prepared by a method different from that used by Jennings, Wardlaw and Way (4). Their method could not be duplicated with satisfactory results. Diethoxydichlorotitanium was found to be very unstable, decomposing at elevated temperatures and hydrolyzing very rapidly in air. It was not readily soluble in many substances. The compound was very soluble in dry alcohol, warm nitrobenzene, and hot ethyl-ortho silicate. When recrystallized from ethyl-ortho-silicate, washed with absolute ether and dried in a vacuum desiccator, it gave analyses for chlorine and titanium which agreed, within experimental error, with theoretical values for diethoxydichlorotitanium. The preparation could not be repeated often enough to substantiate it as a good laboratory method for preparing the compound, but it has served as the best method available. Due to its great instability and limited solubility only a few of the properties of the compound were determined.

An attempt was made to measure the vapor pressure of solutions of titanium tetratethylate in benzene. Consistent results were not obtained, although two different methods were utilized. Further work to overcome the experimental difficulties encountered is required.

PART I - THE PREPARATION OF DIETHOXYDICHLORO-TITANIUM

INTRODUCTION

Inorganic titanates possess extremely high dielectric constants and have because of this property found use as dielectric materials in electrical condensers. An investigation to see whether or not organic titanates are suitable for the same purpose has been started at Montana State College. Crowe (2) has measured the dielectric constants of titaniumtetraethylate, monochlorotriethoxytitanium, and trichloromonophenoxytitanium. He found the dielectric constants to be of the order of 3, which is rather low compared to values for inorganic titanates.

It was one of the aims of this investigation to find a suitable preparation of diethoxydichlorotitanium so that its dielectric constants could be measured and the substance thereby evaluated for possible use as a dielectric material.

Many organic derivatives of $TiCl_4$ have been prepared. As far back as 1875 the preparation of tetraethoxytitanium was reported by Demarcay (3). He claimed it to be a white solid. Tetraethoxytitanium, as known today, exists as a colorless liquid which boils at $145^\circ C$ at 8.5 mm. Bischoff and Adkins (1) prepared several titanates including pure tetraethoxytitanium and triethoxymonochlorotitanium. They claimed to have obtained diethoxydichlorotitanium but gave no details for its preparation. Jennings (4) gives a detailed method for the preparation of diethoxydichlorotitanium but Crowe (2) and Katz (5) were unable to prepare successfully the compound according to his directions.

EXPERIMENTAL

Equipment

Figure 1 shows the apparatus used in the first step in the preparation of diethoxydichlorotitanium. The reaction was carried out in a three necked 250 cc flask fitted with glass joints. A reflux condenser, e, with a drying tube at the top was fitted at glass joint, d. A mercury-seal glass rod stirrer, f, was fitted at e. A dropping funnel, m, with a drying tube, a, at the top was fitted at g. The three necked flask was kept in a large ice bath during the course of the reaction.

Figure 2 shows the apparatus used in the distillation of the compound. An extension was blown at p from a 150 cc Claisson flask, m, and a glass joint attached. The Claisson flask was fitted with new, tight rubber stoppers, b' and b, containing a capillary tube, c, and a thermometer, a, respectively. A round bottom flask, n, with a ground glass joint, e, was altered with three extensions. The extension at g was for evacuation. The glass joints at f and f' were fitted with two receivers, k and j. Precautions were taken to keep the extension from the Claisson flask to the round bottom flask short to prevent the compound from solidifying during distillation. The angle between the two receivers was kept large enough to permit free rotation and the reception of two distillate fractions. The ground glass joints were greased thoroughly to prevent leakage which would result in the hydrolysis of $TiCl_4$ and subsequent freezing of the glass joints.

Preliminary Materials

Phosphoric acid anhydride (P_2O_5) was used as a desiccant in the drying

tubes. The tubes were changed frequently as the phosphoric acid anhydride soon became syrupy from the absorption of water and tended to close the system. Anhydrous calcium chloride could have been used in place of the P_2O_5 . The ethyl alcohol used was anhydrous and distilled from calcium oxide prior to use.

Procedure

25 grams of absolute ethyl alcohol were placed in a three necked flask fitted with reflux condenser, stirrer and dropping funnel. The reflux condenser and dropping funnels were fitted with drying tubes. The three necked flask was placed in an ice bath. 25 grams of $TiCl_4$ were added dropwise to the ethyl alcohol with constant stirring. After the addition of the $TiCl_4$, the resulting yellow mixture was refluxed for forty hours over a water bath. This mixture was not allowed to cool, as in Jennings' method, but vacuum distilled immediately. The first fraction to come over was collected in one of the receivers (see figure 2) and contained some unreacted ethyl alcohol and hydrochloric acid. The higher boiling fraction which came over at $134^\circ C$ and 16 mm pressure was diethoxydichlorotitanium. On cooling it solidified to a white solid. A second method of obtaining the compound from the reaction mixture was attempted. Instead of vacuum distilling the mixture obtained after the 40 hour reflux, the mixture was cooled for about 40 hours in a vacuum desiccator and then recrystallized from ethyl-ortho-silicate. Analyses of the product obtained by this method for chlorine and titanium are given in Table III.

Analyses

An analysis of the second fraction was made for chlorine and titanium.

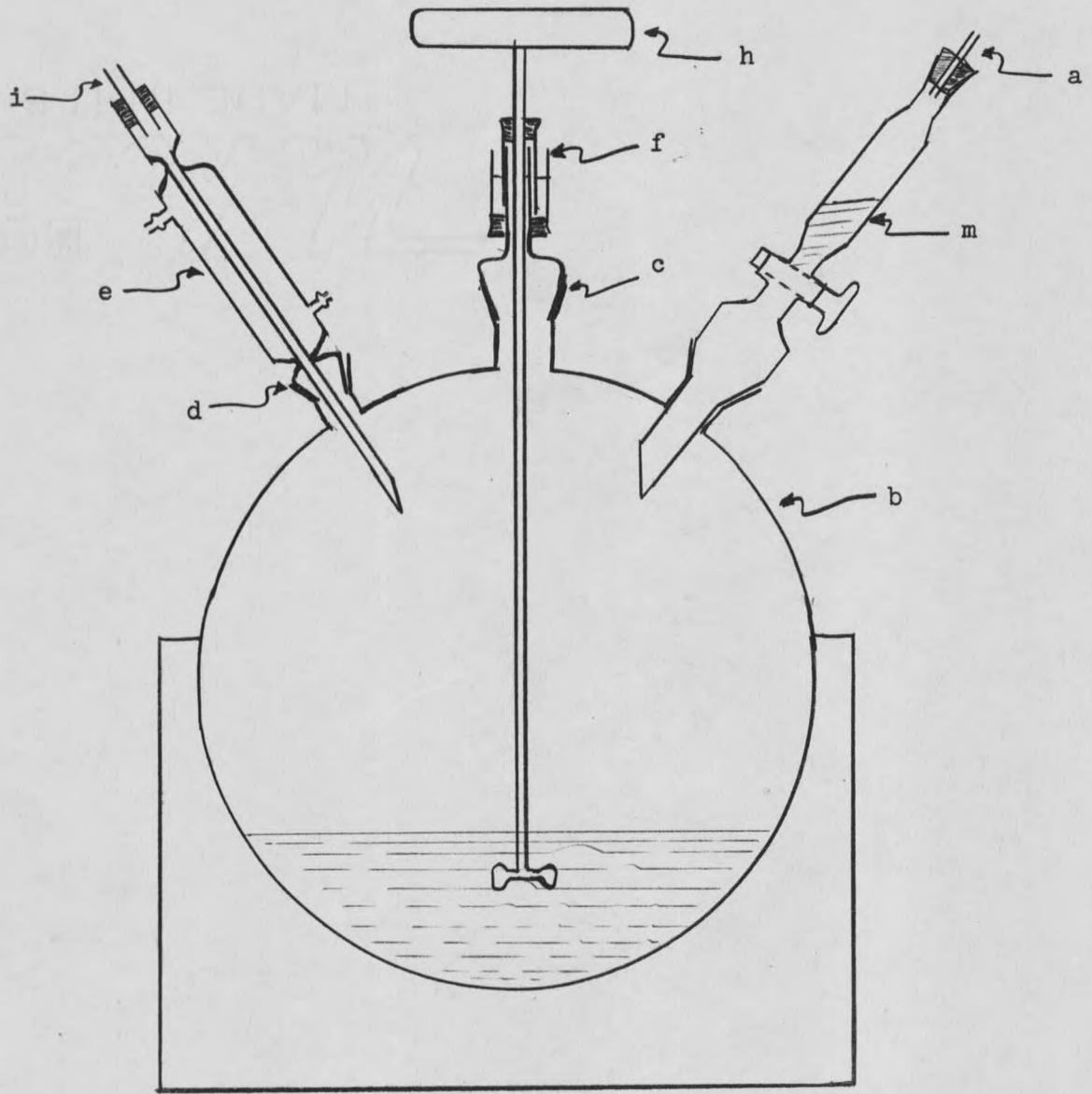


Figure 1

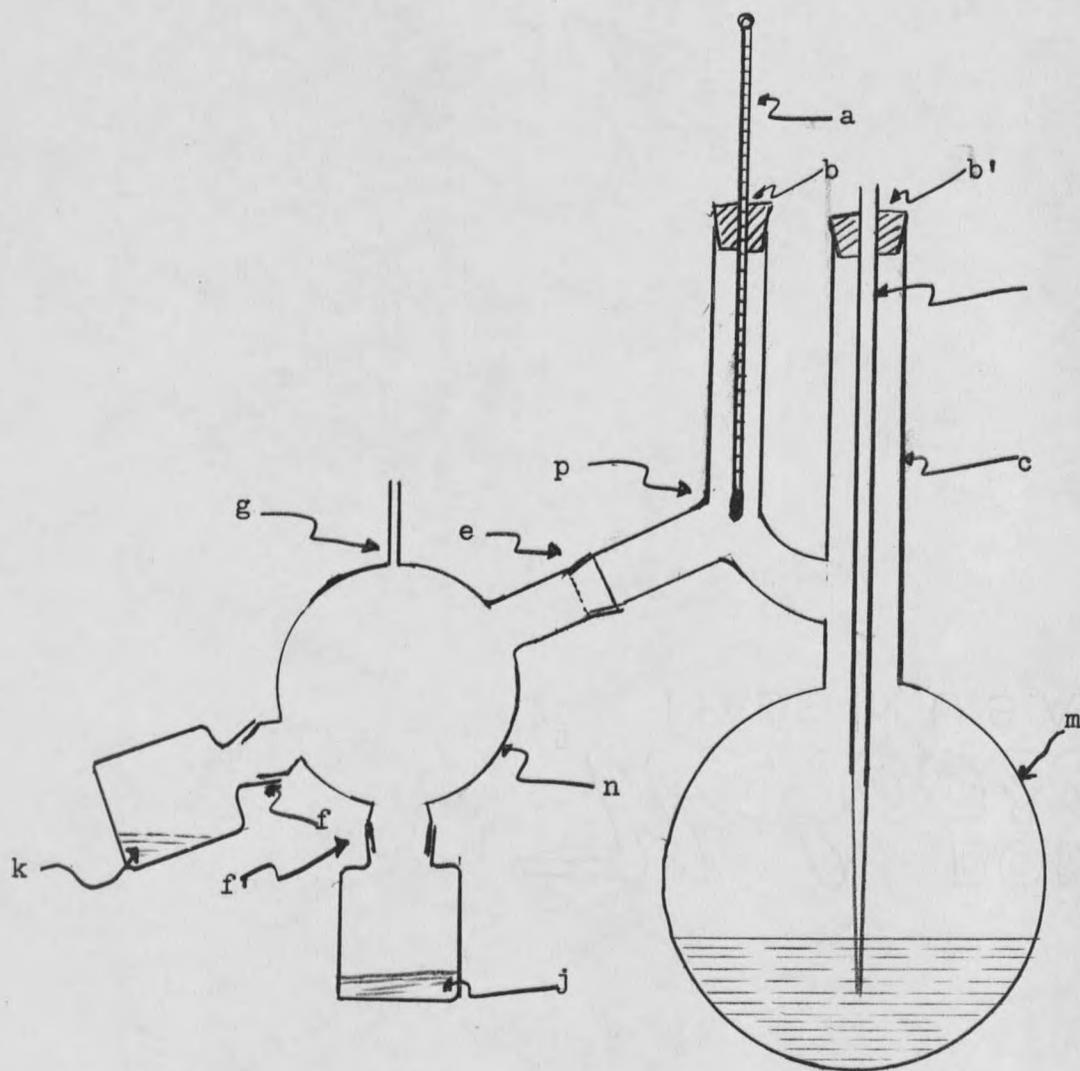


Figure 2

In the titanium analysis a 0.2 gram sample of the fraction was ignited in a weighed crucible to TiO_2 . From the weight of TiO_2 the weight of titanium was calculated. A sodium alcohol method was used in the analyses of chlorine. About 0.2 gram of sample was placed in a small round bottom flask equipped with a reflux condenser. For every gram of sample used, 157 cc of absolute ethyl alcohol and 19.5 grams of sodium were added. This mixture was refluxed until all the sodium dissolved, care being taken to have a drying tube containing fresh phosphoric acid anhydride (P_4O_{10}) or anhydrous calcium chloride at the end of the condenser. About 40 cc of distilled water was then added and the alcohol distilled off. The remaining residue was filtered, made acid with 6 N HNO_3 (5 ml), and allowed to digest for about 12 hours. $AgCl$ was precipitated by the addition of $AgNO_3$, filtered, and then dissolved with NH_4OH . The NH_4OH precipitated the occluded titanium as the hydroxide, which was removed by filtration. The filtrate was made acid and the precipitated $AgCl$ filtered onto a weighed gooch crucible. The precipitate was dried and weighed as $AgCl$.

The results of these analyses are listed in Tables I and II. They compare favorably with the theoretical titanium and chlorine contents. The possibility of having an equimolecular mixture of monochlorotriethoxytitanium and trichloromonethoxytitanium was not considered likely since the monochloro derivative is a liquid and the trichloro derivative has not been reported in the literature. Furthermore, the material obtained had a relatively narrow melting point range.

Properties

Diethoxydichlorotitanium is a white solid. It melts in the range

101° - 103°C and boils at 134°C and 16 mm pressure. The solubility of the compound in various solvents is listed in Table IV. When recrystallized from ethanol it contains alcohol of crystallization, which is difficult to remove. Diethoxydichlorotitanium hydrolyzes in air rapidly. Contrary to the findings of Jennings, Wardlaw and Way (4) it was observed that the compound hydrolyzed in water to give a cloudy solution, presumably due to the formation of TiO_2 .

TABLE I

ANALYSIS OF TITANIUM IN PRODUCT OBTAINED AFTER
DISTILLATION AT 134°C AT 16 mm

	1	2	3
Weight of Crucible	16.8258 gms.	16.3889 gms	16.6516 gms.
Weight of Sample	.2547	.2611	.1099
Weight of Crucible and TiO_2	16.9251	16.4906	16.6945
Weight of TiO_2	.0993	.1017	.0429
Weight of Ti	.0584	.0598	.0252
% of Ti	22.9	22.9	22.9
Theoretical % of Ti	22.92		

TABLE II

ANALYSIS OF CHLORINE IN PRODUCT OBTAINED AFTER
DISTILLATION AT 134°C and 16 mm

	1	2	3
Weight of Sample	.1758 gms.	.0936 gms.	.2020 gms.
Weight of Gooch	17.9959	25.4049	18.1141
Weight of Gooch and AgCl	18.2327	25.5327	18.3908
Weight of AgCl	.2368	.1278	.2767
Weight of Cl	.0585	.0316	.0684
% of Cl	33.3	33.7	33.8
Theoretical % of Cl	33.94		

TABLE III

ANALYSIS OF DICHLORODIETHOXYTITANIUM OBTAINED BY
DIRECT RECRYSTALLIZATION FROM ETHYL-ORTHO-SILICATE
FOR TITANIUM AND CHLORINE

	1	2	3
% Ti	22.9 %	22.9	22.9
Theoretical % Ti	22.92 %		
% Cl	33.1 %	32.9 %	32.8 %
Theoretical % Cl	33.94 %		

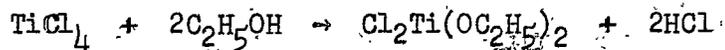
TABLE IV

SOLUBILITY OF DIETHOXYDICHLOROTITANIUM IN VARIOUS SOLVENTS

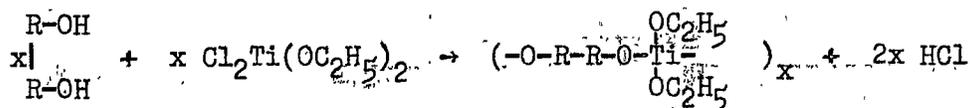
	Cold Solvent	Hot Solvent.
Heptane	Insoluble	Insoluble
Benzene	Insoluble	Insoluble
Ethyl Alcohol	Insoluble	Soluble
Carbon Tetrachloride	Insoluble	Insoluble
Cyclohexane	Insoluble	Insoluble
Nitrobenzene	Insoluble	Soluble
Acetone	Slightly Soluble	Slightly Soluble
Ethyl-ortho-silicate	Insoluble	Soluble

DISCUSSION OF EXPERIMENTAL RESULTS

With satisfactory equipment and necessary precautions, one can prepare diethoxydichlorotitanium in the laboratory by the method herein described. The overall reaction is expressed by the following equation:



At present the compound has no important use. However, it is believed that this compound may find use as a dielectric material if its dielectric constant is high enough. There is the further possibility that this compound can be polymerized with glycols in the following manner:



The polymers so obtained might find uses similar to those of the analogous silicon organic compounds.

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PART II - A STUDY OF TWO METHODS FOR MEASURING VAPOR PRESSURES OF TITANIUM
TETRAETHYLATE-BENZENE SOLUTIONS

INTRODUCTION

It has been found from freezing point determinations that organic titanium compounds associate in solution. Smith (4) determined the molecular weight of titanium tetraethylate in hexane by the freezing point method and calculated from his results that approximately three simple molecules associate to form a complex. Nothing else appears in the literature regarding the association of organic titanium compounds.

A primary aim of this part of the investigation was to check the association of titanium tetraethylate in benzene by a method other than that used by Smith. It was decided to use vapor pressure depression method. Two procedures were tried, one of which was new.

PREPARATION OF TITANIUM TETRAETHYLATE

Titanium tetraethylate, $\text{Ti}(\text{OC}_2\text{H}_5)_4$, was prepared by the method of Bischoff and Adkins (1). The chemical equation for the reaction is:



750 ml of absolute ethyl alcohol were placed in a three necked flask, which was equipped with a mechanical stirrer, dropping funnel and a reflux condenser. 50 grams of sodium were added in large pieces while the reaction mixture was being cooled in an ice bath. As soon as the reaction ceased, heat was gently applied until all the sodium dissolved.

After the reaction mixture had cooled, 58.5 ml of TiCl_4 were added dropwise through the dropping funnel over a period of three hours with continuous stirring. Again, the flask was cooled in ice. The reaction between TiCl_4 and $\text{C}_2\text{H}_5\text{ONa}$ is exothermic.

The solid material, containing NaCl and other solids formed in the reaction, were removed by centrifuging the mixture. The excess alcohol was then distilled from the solution containing the $\text{Ti}(\text{OC}_2\text{H}_5)_4$.

The clear, viscous, yellow liquid remaining after the removal of the alcohol was vacuum distilled and stored for further use. Immediately before use the $\text{Ti}(\text{OC}_2\text{H}_5)_4$ was again vacuum distilled at 158°C and 20 mm pressure. An analysis for titanium by hydrolyzing and igniting to TiO_2 gave a titanium content of 21.08, 21.07 and 21.04 per cent. The theoretical value is 21.05 per cent.

EXPERIMENTAL

Equipment

Figure 3 shows the apparatus used in the first procedure followed for the determination of molecular weights by the vapor pressure lowering method. A U-tube was fitted by glass joints, d, to the tubes, e and f, containing respectively pure solvent and the substance whose molecular weight was to be determined dissolved in the solvent. The stopcock at g made possible the distillation of the pure solute into tube f, without contamination or hydrolysis. Mercury seal stopcocks at c helped keep the system evacuated. This first procedure was based on the work of Wright (5).

Figure 4 shows the apparatus used in the second procedure followed for determining molecular weights by the vapor pressure lowering method. The apparatus was made of two pyrex tubes, one of which was graduated.

Preliminary Materials

The solvent used in all the molecular weight determinations was benzene; it was first dried over metallic sodium and then distilled before use. By far the greatest difficulty in these determinations was that of finding a stopcock grease insoluble in benzene. "Nonaq," made by Eimer & Amend, New York City, New York, was found to be insoluble in benzene but soluble in water. The procedure finally adopted was to coat the center of all stopcocks with "Nonaq" and the outer edge with regular stopcock grease. The titanium tetraethylate was prepared by the method of Bischoff and Adkins (1) and vacuum distilled immediately before use.

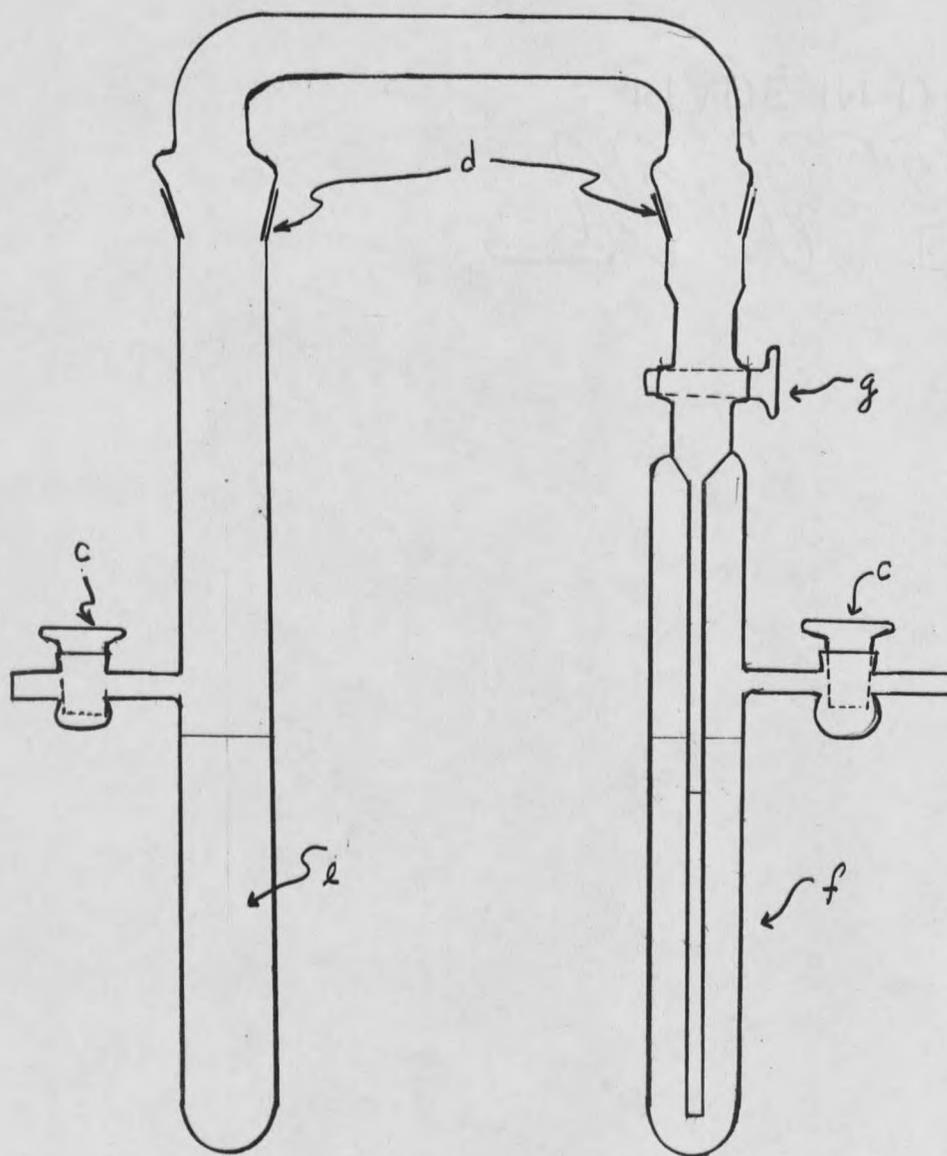


Figure 3

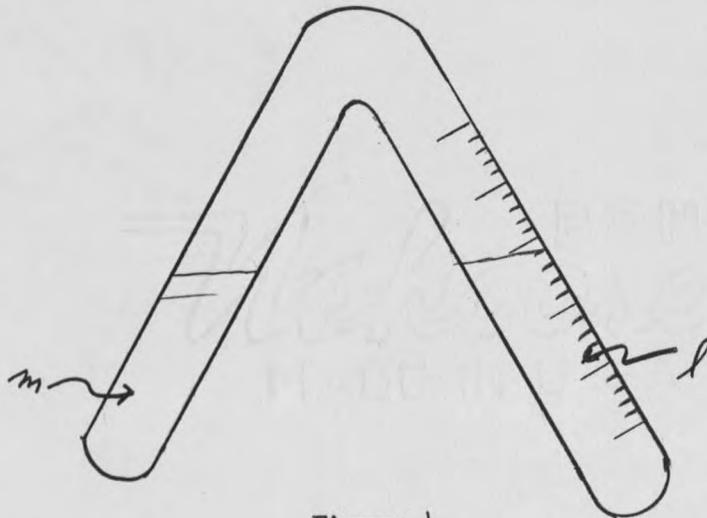
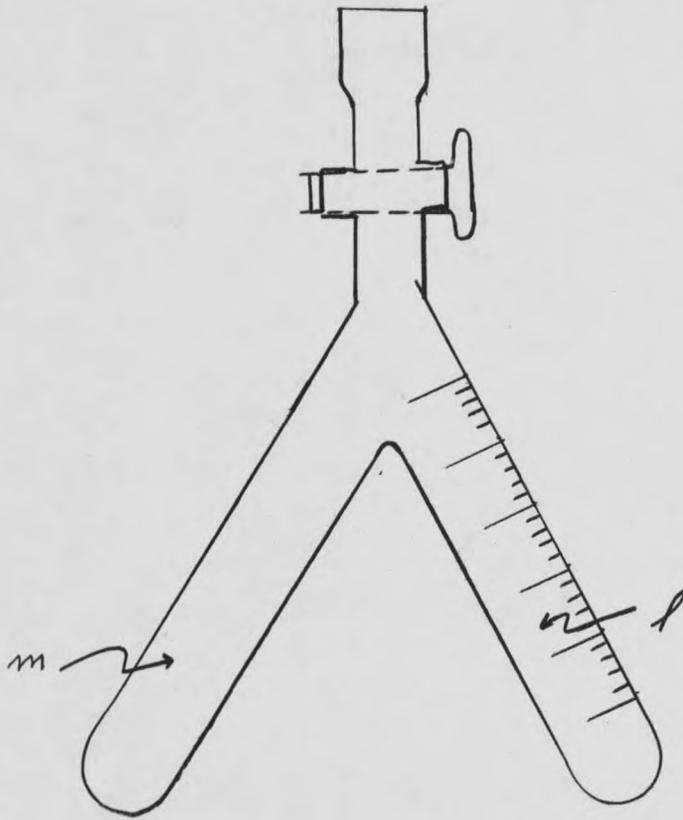


Figure 4

Procedure

The part of the apparatus, f, in Figure 3, which was to contain the solution was weighed empty. Then the substance whose molecular weight was to be determined was distilled into tube f, and weighed again. The solvent was then distilled into tubes e and f and the apparatus assembled as shown. After freezing both solvent and solution in a dry ice-methanol mixture, air and solvent vapor were evacuated through the mercury seal stopcocks. After the apparatus and its contents had been allowed to reach temperature equilibrium in a constant temperature bath, the difference in heights of solution in tube f was measured with a cathetometer. This difference in heights was corrected for capillarity and converted to mm Hg pressure. The weight of the solvent was found by weighing the apparatus at the conclusion of the experiment. The molecular weight of the solute was calculated from the following equation:

$$(1) \quad M = \frac{M^{\circ} P^{\circ} m}{m^{\circ} (P^{\circ} - P)}$$

M is the molecular weight of the solute, M° is the molecular weight of the solvent, m is the weight of the solute in grams, m° is the weight of the solvent in grams, P° is the vapor pressure of the solvent at the temperature of the constant temperature bath, and P is the pressure of the solution at the same temperature.

In the second procedure, the substance whose molecular weight was to be determined was distilled into the calibrated half of the weighed apparatus (figure 4). The apparatus was weighed again. The solvent was then distilled in and the apparatus reweighed. Both solvent and solution

were frozen in a dry ice-methanol mixture and the apparatus sealed off with an oxygen-gas torch under vacuum at a. The arm containing the solvent was submerged in one constant temperature bath and the arm containing the solution in a second constant temperature bath. The latter bath was at the higher temperature. The system was allowed to come to equilibrium and the concentration of the solution corrected to account for distillation of the solvent to or from the solution as determined by the change in volume.

The molecular weight of the solute as determined by the second procedure was calculated from the equation:

$$(2) \quad M = \frac{M^{\circ} P_{T_1}^{\circ} m}{m^{\circ} (P_{T_2}^{\circ} - P_{T_1}^{\circ})}$$

M is the molecular weight of the solute, M° is the molecular weight of the solvent, m is the weight of the solute, m° is the weight of the solvent in the solution, $P_{T_1}^{\circ}$ is the vapor pressure of the solvent at the lower temperature and $P_{T_2}^{\circ}$ is the vapor pressure of the solvent at the higher temperature.

Equation (2) is based on Raoult's law, according to which the partial pressure of any volatile component of a liquid solution is equal to the product of its mole fraction and its vapor pressure in the pure state at the same temperature, i.e.,

$$(3) \quad P = P^{\circ} x$$

P is the partial vapor pressure of the component whose mole fraction is x. In the case at hand we are considering a binary solution consisting of a volatile solvent and a nonvolatile solute. P will be the total vapor

pressure of the solution in this case.

When equilibrium is reached the pressure of the solution at the higher temperature T_2 must equal the pressure of the pure benzene at the lower temperature T_1 , i.e.,

$$(4) \quad P_{T_2} = P_{T_1}^{\circ}$$

But according to the equation (3)

$$(5) \quad P_{T_2} = P_{T_2}^{\circ} x_1$$

x_1 is the mole fraction of the solvent in the solution and equals

$$(6) \quad x_1 = \frac{\frac{m^{\circ}}{M^{\circ}}}{\frac{m^{\circ}}{M^{\circ}} + \frac{m}{M}}$$

The combination of equations (4), (5), and (6) gives

$$P_{T_1}^{\circ} = P_{T_2}^{\circ} \frac{\frac{m^{\circ}}{M^{\circ}}}{\frac{m^{\circ}}{M^{\circ}} + \frac{m}{M}}$$

Rearrangement of this equation gives equation (2).

Equation (1) can be derived in a similar manner from Raoult's law.

DISCUSSION OF EXPERIMENTAL RESULTS

No reproducible or reliable experimental results were obtained with the first procedure. An obstacle not overcome was the construction of an apparatus capable of holding a high vacuum. The apparatus employed required the use of a stopcock grease insoluble both in organic solvents and in water. The inability to meet this requirement caused the experiments to fail continuously.

In the second procedure the use of a stopcock grease was avoided. The procedure showed some promise when used to determine the molecular weight of a known solute, o-nitro toluene. Results are shown in Table V. Results obtained for the molecular weight of titanium tetraethylate, however, were inconclusive and not reproducible as shown in Table VI. More work to determine and remove the causes of such variable results is necessary.

TABLE V

MOLECULAR WEIGHT DETERMINATION OF O-NITROTOLUENE BENZENE SOLUTION

T_1	T_2	P_{T_1}	P_{T_2}	M^o	m	m^o	M
26.5°C	22.1°C	100.80 mm	82.24 mm	78.11	2.0593	5.6666	126
25.0°C	20.2°C	93.95 mm	74.97 mm	78.11	2.0593	5.6402	113

Theoretical calculated molecular weight. - 137

TABLE VI

MOLECULAR WEIGHT DETERMINATION OF TITANIUM TETRAETHYLATE IN A BENZENE SOLUTION

T_1	T_2	P_{T_1}	P_{T_2}	M°	m	m°	M
23.9°C	21.8°C	89.3 mm	80.9 mm	78.11	.4952	2.6873	139
25.9°C	21.8°C	97.9 mm	80.9 mm	78.11	.4952	2.6433	69
24.8°C	20.8°C	93.1 mm	77.1 mm	78.11	.3666	9.5767	14

Theoretical value unknown.

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