[Contribution from the Department of Chemistry, Cornell University]

GERMANIUM. IX. GERMANIUM TETRA-ETHYL. PREPARATION AND PURIFICATION OF ZINC DIETHYL. ANALYSIS BY COMBUSTION OF A LIQUID CONTAINING CARBON AND HYDROGEN[1]

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Introduction

Clemens Winkler first prepared germanium tetra-ethyl in 1887 by the action of germanium tetrachloride on zinc ethyl.[2] He briefly described its properties and gave the results of determinations of carbon and hydrogen in the substance, which although they varied from the calculated amounts by 0.8% and 0.7%, respectively, sufficed to show that the product consisted chiefly of $Ge(C_2H_5)_4$.

Winkler further states that a determination of the vapor density of the substance by Meyer and Mensching gave a value of 8.50, whereas the calculated density is 6.51.

In view of the unsatisfactory character of these data, it seemed desirable to prepare germanium tetra-ethyl of as high purity as possible and to make further study of its physical and chemical properties.

Experimental Part

Preparation of Germanium Tetra-ethyl.—Winkler employed the reaction, $2\,Zn(C_2H_5)_2 + GeCl_4 = Ge(C_2H_5)_4 + 2\,ZnCl_2$. At that time the Grignard reaction was not known. This latter method would of course be much the simpler and easier of the two. It has been used with success in the preparation of tin tetra-ethyl[3] but it failed to yield the similar alkyl of silicon.[4]

Germanium lies between silicon and tin in Group IV of the Periodic Table. In some respects it closely resembles silicon; in others, tin. Its compounds with hydrogen are directly analogous to the hydrides of silicon and are prepared with comparative ease. Tin, on the other hand, shows much less tendency to form hydrides.[5] Consequently, it seemed probable that germanium tetra-ethyl would more readily result from the interaction of zinc ethyl and germanium tetrachloride than from that between magnesium ethyl chloride and the germanium halide. Nevertheless,

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Winkler, *J. prakt. Chem.*, **144** (N. F. 36), 177 (1887).

[3] Pfeiffer and Schurmann, *Ber.*, **37,** 319 (1904).

[4] Martin and Kipping, *J. Chem. Soc.*, **95,** 302 (1909).

[5] Paneth, *Ber.*, **52,** 2020 (1919).

the Grignard reaction was first tried because of the greater ease of manipulation and because it seemed desirable to ascertain whether, in respect to the formation of the alkyl, germanium more closely resembles silicon or tin.

Our results with the Grignard reagent, in this case $MgCH_3I$ and germanium tetrachloride were quite similar to those obtained by Martin and Kipping with silicon tetrachloride and MgC_2H_5Br. The product contained very little $Ge(CH_3)_4$, but consisted chiefly of a mixture of substances of high boiling points, in which the halogens had partially or completely replaced the methyl groups.

The study of the synthesis with the aid of zinc diethyl, which is described below led, however, to successful results.

Preparation and Purification of Zinc Diethyl.—The reaction employed by Lachman,[6] heating ethyl iodide in contact with a zinc-copper couple to 100°, was used. Lachman found that action between the couple and the ethyl iodide took place only at the surface of the powder and he therefore spread comparatively small amounts of the couple in thin layers over the bottom of a number of Erlenmeyer flasks.

Lachman further describes the pouring of zinc ethyl from one container into another under a large, inverted funnel through the stem of which a rapid current of carbon dioxide is passing. This was found to be an unsatisfactory procedure because, with the most careful manipulation, some zinc diethyl came in contact with the oxygen of the air and a coating of zinc oxide formed on the inner surfaces of the containers. For this reason it seemed desirable to be able to prepare, purify and transfer the zinc ethyl in a closed chain filled with carbon dioxide and to this end the apparatus shown in Fig. 1 was devised.

The zinc-copper couple was prepared by heating a mixture of 25 g. of zinc dust and 200 g. of powdered copper oxide in a current of hydrogen at a temperature of about 550–600° until reduction was complete. The temperature should not be allowed to rise high enough to melt the powder, because this would greatly reduce the surface of the couple.

This product was pulverized in an agate mortar and was then mixed with an equal weight of dry sand which had previously been treated with boiling hydrochloric acid. The presence of sand facilitated the penetration of the powder by the ethyl iodide and thus made it possible to carry out the reaction on a fairly large scale in a single flask.

One kg. of this mixture was placed in the 3-liter, Pyrex flask H, Fig. 1 and 500 g. of ethyl iodide was introduced into the separatory funnel G. The apparatus was permanently connected at A with an apparatus supplying pure carbon dioxide which was made by dropping dil. sulfuric acid upon primary sodium carbonate that had been moistened with boiled water. The sulfuric acid was placed in a separatory funnel about

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[6] Lachman, *Am. Chem. J.*, **24,** 36 (1900).

1 meter above the evolution flask and was kept under an atmosphere of carbon dioxide to prevent absorption of oxygen from the air. The carbon dioxide was dried by calcium chloride in the towers B, B, by sulfuric acid in the Friedrichs gas-washing bottle C, and finally by phosphorus pentoxide in the tube D.[7]

With the stopcocks 1 and 8 closed, the apparatus was next exhausted of air through W by an oil pump and the various cork stoppers were then coated with Colvar cement which quickly dried and thoroughly sealed the apparatus. The chain was filled with dry carbon dioxide by opening Stopcock 1. This was now closed and the apparatus was again exhausted, the filling and pumping being repeated several times to remove air and moisture from the apparatus and the couple.

The apparatus was then filled with carbon dioxide under slightly diminished pressure, Stopcock 2 was opened and the ethyl iodide was run in upon the couple in H. Stopcock 3 was then closed and 9 was opened to V which contained sulfuric acid. Stopcock 1 was opened and H was thus kept under a pressure of carbon dioxide. Any excess of pressure was relieved by the escape of gas to the room through E and V. A water-bath was brought up around H which was heated until ethyl iodide ceased to flow back from F. This completed the first stage of the reaction, $Zn + C_2H_5I = ZnC_2H_5I$.

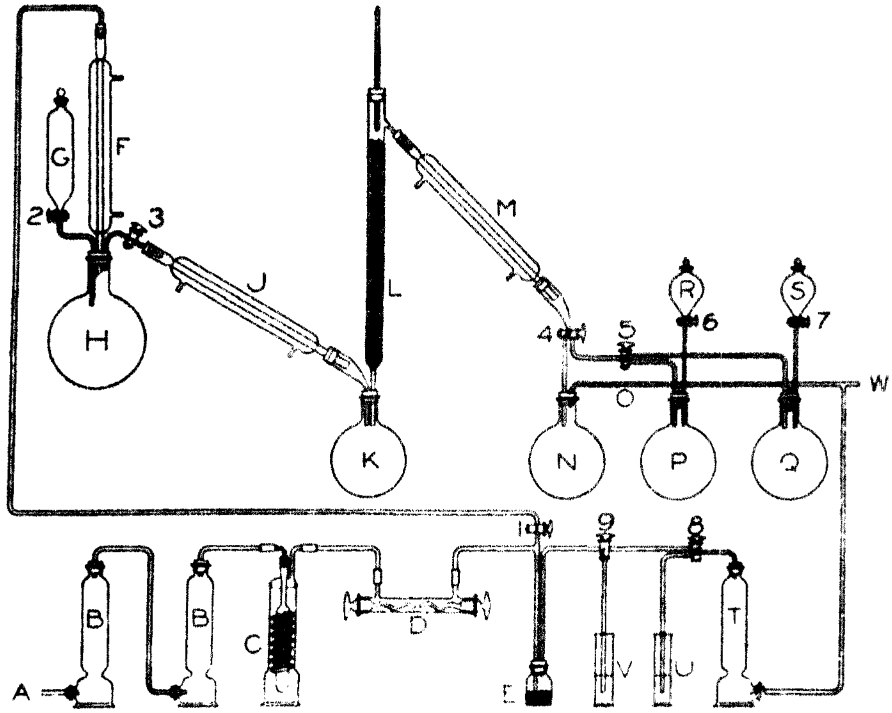

Fig. 1.

The zinc-ethyl iodide was next converted to zinc ethyl, $2ZnC_2H_5I = Zn(C_2H_5)_2 + ZnI_2$, by heating the mixture to a higher temperature. In carrying this out, Stopcock 3 was opened, 8 was opened to V which contained sulfuric acid, 9 was closed and a slow current of carbon dioxide was steadily admitted through 1.

An oil-bath was then brought up around H and was heated to 190°. Since the boiling point of zinc diethyl is 118°, it distilled into K as fast as it was formed. When it was desired to store the crude zinc diethyl in K for any length of time before proceeding with its purification, Stopcock 3 was closed and by suitable adjustment of 9 and 8 the appa-

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[7] This tube, recently devised by one of us (L. M. D.), will be described elsewhere.

ratus from 3 to 1 was filled with carbon dioxide at the full generator pressure. Stopcock 8 was then closed.

The zinc diethyl was purified by fractional distillation through the column L, the first impure portion which contained some ethyl iodide being collected in the flask N by turning Stopcock 4 to the position shown in Fig. 1. When the thermometer in the top of L showed that a fraction of constant boiling point was passing, 4 was turned and the distillate was run into Flask P or Q, as desired, by suitable adjustment of 5. A slow current of carbon dioxide was passed through the apparatus during distillation. The fraction that was collected in equal volumes in P and Q showed a boiling point of 117°, uncorrected and was clear and colorless. No fog or deposit of zinc oxide appeared anywhere in the chain.

Conversion of Germanium Tetrachloride into Germanium Tetra-ethyl.—Preliminary experiments developed the same difficulty in controlling the reaction that Winkler describes. He resorted to lowering the temperature to avoid sudden and violent interaction. We soon found, however, that the reaction between zinc diethyl and germanium tetrachloride, $2Zn(C_2H_5)_2 + GeCl_4 = 2ZnCl_2 + Ge(C_2H_5)_4$, is catalyzed by one or both of the products and, with the purpose of ascertaining which catalyst gave the best results, the zinc diethyl was divided between the flasks P and Q and there was added to the germanium tetrachloride which was run in through R and S, zinc chloride in the one case and germanium tetra-ethyl in the other.

About 5% less than the calculated amount of germanium tetrachloride was placed in each funnel and a small crystal of zinc chloride was added to one and a few drops of germanium tetra-ethyl to the other. The funnels were then gently shaken until these substances dissolved in the germanium tetrachloride, whereupon the solutions in R and S were slowly admitted to the flasks P and Q. It was found that the zinc chloride apparently did not affect the speed of the reaction, but that when germanium tetra-ethyl was used the reaction, although starting slowly, soon proceeded with such rapidity as to make its control difficult. When, however, in another trial germanium tetrachloride containing both zinc chloride and germanium tetra-ethyl was run into the zinc diethyl in successive, small portions, the reaction started at once and quietly and steadily continued until complete.

The material in the flask then consisted of a pasty mixture of germanium tetra-ethyl, zinc chloride and unchanged zinc diethyl. This was transferred to a distilling flask and small pieces of ice were dropped into it until the zinc diethyl had been decomposed. A 10% solution of sodium hydroxide was then added, a loose plug of glass wool was placed in the neck of the flask and the mass was subjected to distillation in a current of steam. Germanium tetra-ethyl and water collected in the receiver in two liquid layers. After a second distillation in steam, the tetra-ethyl was separated from the water, dried over calcium chloride and was once more distilled.

Analysis of Germanium Tetra-ethyl

Determination of Carbon and Hydrogen by Combustion.—The sample used for the analysis was that described below under "Boiling point," which had been four times distilled in steam and twice fractionally distilled and which showed a boiling point of 163.5°. In the determination of carbon and hydrogen by combustion with copper oxide in a current of air, we used an arrangement of apparatus quite similar to that described by Reid,[8] but the accuracy of the results which we obtained may justify a brief description of the minor modifications that were made in Reid's procedure.

The sample was introduced into the small, constricted, weighed glass tube E, Fig. 2, through a miniature funnel which was then withdrawn without allowing its tip to touch the inner wall of the tube. The sample was then solidified by dipping E into liquid air, whereupon it was sealed off at the constriction. The arrangement of the combustion chain may be readily understood from the figure. Air is *drawn* through A, B, C and D and F, G and H by applying gentle suction by a water pump at O. The tip of the sample tube is broken and it is dropped into D as shown. If the substance has a low boiling point, the procedure described by Reid would of course be preferable. To insure slow but steady passage of the germanium tetra-ethyl into the combustion tube, the U-tube D was immersed in a bath of molten Crisco which was heated by an electric plate to a temperature about 20° below the boiling point of the compound. Although the end of the exit tube from D was brought close to the hot copper oxide in J, it was observed that some of the vapor of the substance diffused back and condensed on the cork in the end of J. To prevent this, the second current of washed air was drawn through F, G and H, the exit tube ending just within the stopper. The volatilization of the germanium tetra-ethyl proceeded quite slowly, but once the temperature of E and the strength of suction at O had been adjusted, the apparatus could be left to itself for several hours. We usually made the apparatus ready for a combustion during the daytime, and allowed it to run through the night without attention. The combustion was complete by the following morning.

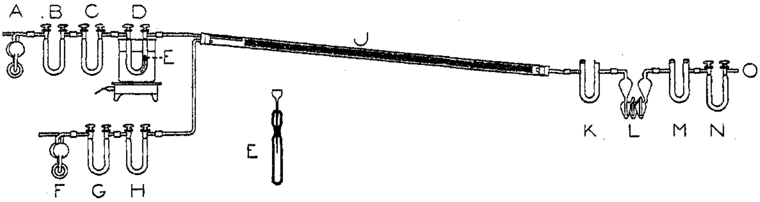

Fig 2.

The germanium in the compound was determined by first dissolving a sample in ice-cold, fuming nitric acid. A little *dil.* sulfuric acid and some solid ammonium persulfate were then added and the mixture was gently heated until reaction ceased and the mass, which at first turned dark, had become white. It was evaporated to dryness in a platinum dish and the residue was ignited to drive off all volatile matter. The germanium oxide was then dissolved in a 10% solution of sodium hydroxide, the solution was filtered and sulfuric acid sufficient to make the filtrate 6 *N* was added. The germanium was then precipitated by hydrogen sulfide as GeS_2, the precipitate was washed with 3 *N* sulfuric acid that had been saturated with hydrogen sulfide, was dissolved on the filter with ammonium hydroxide, the excess of that reagent was removed by evaporation, nitric acid was added and the solution was evaporated to dryness. The residue

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[8] Reid, This Journal, **34**, 1037 (1912).

was again heated with a little concd. nitric acid and finally ignited over a Méker burner to constant weight.

In the calculation of these results, the value 72.6 was used as the atomic weight of germanium.[9]

Anal. Subs., 0.4606, 0.6163. Calcd. for $C_8H_{20}Ge$: C, 0.2342, 0.3135 = 50.86%, H, 0.0492, 0.0658 = 10.68%. Found: C, 0.2334, 0.3139; av., 50.80%; H, 0.0488, 0.0657; av., 10.625%.

Subs., 0.3835, 0.6120. Calcd.: Ge, 0.1475, 0.2354 = 38.46%. Found: 0.1477, 0.2355; av., 38.495%.

Properties of Germanium Tetra-ethyl

Boiling Point.—The germanium tetra-ethyl prepared as above described was fractionally distilled from a Pyrex flask through a short Hempel tube packed with washed glass wool. A middle fraction of constant boiling point 163.8°, corrected, was then twice distilled in steam and again fractionally distilled. The boiling point of the middle fraction from this run was 163.5°. Spectroscopic examination of this product by Dr. Papish of this Department showed that it was entirely free from metals other than germanium and that the only impurity disclosed by the arc-spectrum photograph was a trace of boron which presumably came from the Pyrex flask.

Melting Point.—Preliminary measurements with a calibrated pentane thermometer gave a melting point of —90° ± 0.2°. Two determinations on different samples with a calibrated Chromel-Alumel wire couple[10] gave exactly agreeing results of —90°.

Specific Gravity.—Two determinations by the pycnometer method, using a volume of 10 cc., gave 0.9910 and 0.9912 at 24.5°; av., $d_{24.5}^{24.5}$, 0.9911. Mendeléeff's prediction in 1872 as to the density of the compound, 0.96, was remarkably close to the truth.[11]

Refractive Index.—Determinations with an Abbé refractometer gave the following results.

Temp., °C.	14	15	20	25	30	35	40
n	1.421	1.417	1.400	1.376	1.351	1.330	1.308

Molecular Weight.—This was determined by the depression of the freezing point of benzene.

Mol. wt. Subs., 0.2850, 0.2850: in 14.7668 g. of benzene: Δt, 0.511°, 0.513°. Calcd. for $Ge(C_2H_5)_4$: mol. wt., 188.76. Found: 188.63, 188.24; av., 188.42.

These results are interesting because they show that germanium tetra-ethyl is neither dissociated nor associated in benzene.

Vapor Density.—Victor Meyer determined the vapor density of germanium tetra-ethyl for Winkler and obtained 8.50. The calculated value is 6.51. Winkler was at a loss to explain this discrepancy for he felt

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[9] Baxter and Cooper, *Proc. Am. Acad. Arts Sci.*, **59**, 235 (1924).

[10] See Dennis, Corey and Moore, THIS JOURNAL, **46**, 662 (1924).

[11] *Ann.*, 8th Suppl., **1872**, p. 202.

sure that his preparation was pure. It now seems clear, however, that this was not the case and that his extraction of the germanium alkyl with ether will account for various impurities in the product which do not pass over with the tetra-ethyl when it is distilled in steam.

The determination of the vapor density of the pure substance was made with the Victor Meyer apparatus as modified by Weiser,[13] except that the tube was heated electrically and the displaced air was collected and measured in a Hempel gas buret. The temperature was held at 220° or slightly lower, because in preliminary experiments it was observed that the vapor of germanium tetra-ethyl readily took fire at temperatures somewhat above this. Three determinations of the vapor density gave the values 6.53, 6.54 and 6.64; calcd., 6.51.

Other Physical Properties.—Germanium tetra-ethyl is a colorless, oily, liquid having a pleasant characteristic odor somewhat suggestive of the lighter paraffin hydrocarbons. The onion-like odor mentioned by Winkler must have been due to impurities, for it disappears when the compound is rectified.

Germanium tetra-ethyl burns in the air. The outer part of the flame is dark yellow and the inner part is red shading off to blue at the surface of the burning liquid. The residue in the dish after combustion showed many colors running from black through reddish-brown and brown to white, the tints probably being due to different oxides of germanium which have not yet been investigated.

The substance is very slightly soluble in water, but was found to be soluble without decomposition in 18 organic solvents which were selected to include various structural types.

Chemical Properties

Chlorine acts slowly upon it at room temperature and fairly rapidly at 90°. When the gas was bubbled through the warmed alkyl, the chlorine was absorbed and the solution first became yellow, then colorless and finally passed through a pink shade to orange. After chlorination had proceeded for about six hours, an ethereal compound of low boiling point was found to have collected in the cold water through which the escaping gas had been passed. The residue in the chlorination flask was distilled and was found to pass over between 94° and 250°. The distillate was brownish-yellow in color and of unpleasant odor.

Bromine first dissolved in the alkyl and then reacted upon it with the formation of ethereal gases of pleasant odor and the production of a dark colored precipitate.

Iodine dissolved in the alkyl and formed a brilliant purple solution which decomposed after several days.

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[13] Weiser, *J. Phys. Chem.*, **20**, 532 (1916).

Sulfur dioxide has no action upon germanium tetra-ethyl at room temperature or at 100°.

Germanium tetra-ethyl is difficult to oxidize. It is not completely decomposed even at boiling temperatures by alkaline, 3% hydrogen peroxide, alkaline Perhydrol, alkaline Superoxol, or fuming nitric acid. When, however, the compound is dissolved in fuming nitric acid and 3 *N* sulfuric acid and ammonium persulfate are added, the tetra-ethyl is completely oxidized if the mixture is heated to the boiling point for a considerable length of time.

Summary

This article deals with the preparation of zinc ethyl, with the description of an apparatus in which it can be caused to react with germanium tetrachloride without contact with air, and with the purification of germanium tetra-ethyl, its analysis, boiling point, melting point, specific gravity, refractive index, molecular weight, vapor density and some of its chemical properties.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

SOME DOUBLE SELENATES OF THALLOUS SELENATE AND THE SELENATES OF BIVALENT METALS

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An exhaustive study of the double sulfates and double selenates of the type $R_2M(SO_4)_2.6H_2O$ and $R_2M(SeO_4)_2.6H_2O$, where R is potassium, rubidium or cesium and M is magnesium, zinc, iron, cobalt, nickel, copper, manganese or cadmium, has been made by Tutton.[1] Of the series $Tl_2SeO_4.R''SeO_4.6H_2O$, Tutton studied only one—$Tl_2SeO_4.ZnSeO_4.6H_2O$. Five new compounds of this type are described below.

The conditions most favorable to the formation of each double salt were first studied under the microscope and the relative amounts of the two salts, the concentration and the temperature thus indicated were then followed on a larger scale.

Thallous Copper Selenate, $Tl_2SeO_4.CuSeO_4.6H_2O$.—This compound crystallizes best from a solution containing an excess of copper selenate in the proportion of 8 g. of the copper salt to 3 g. of thallous selenate. The light blue crystals were finely ground and then air-dried between filter papers.

ANALYSIS.—Water of crystallization was determined by heating a weighed sample to constant weight at 105°. Copper, thallium and selenium were determined in a single sample by dissolving the substance in water, adding a few drops of acetic acid,

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[1] Tutton, *J. Chem. Soc.*, **69**, 344, 495, 507 (1896).

and then an excess of a solution of potassium iodide, which precipitates thallous iodide and cuprous iodide. The precipitate was collected on a filter and the amount of copper in the salt was ascertained by titration of the free iodine in the filtrate with sodium thiosulfate solution. This solution, which contained most of the selenium, was preserved. The mixture of thallous iodide and cuprous iodide was treated with ammonium hydroxide which dissolved the copper salt. The filtrate and washings were added to the first filtrate and the selenium was precipitated by hydrazine hydrate.[2] The thallous iodide was collected in a Gooch crucible, dried at 120° and weighed. The method was first tested with solutions containing known amounts of thallous selenate and cupric selenate and was found to give results that were sufficiently accurate for the purpose in view.

Anal. Calcd. for $Tl_2SeO_4\ CuSeO_4.6H_2O$: Tl, 47.11; Se, 18.28; Cu, 7.34; H_2O, 12.48. Found: Cu, 47.10, 47.20; Se, 18.26, 18.20; Cu, 7.30, 7.285; H_2O, 12.80, 12.82.

Thallous Cobalt Selenate, $Tl_2SeO_4.CoSeO_4.6H_2O$.—The method of preparation was essentially the same as that for the copper salt.

In the analysis, two slightly different methods were used. With one sample, the thallium was first precipitated with potassium iodide, the cobalt in the filtrate with sodium carbonate and the selenium in the final filtrate with hydrazine hydrate. With the second sample, the cobalt was first precipitated with sodium carbonate, the precipitate was washed with hot water until free from thallium, the thallium then precipitated as the iodide, and the selenium as before with hydrazine hydrate.

Anal. Calcd. for $TlSeO_4.CoSeO_4.6H_2O$; Tl, 47.36; Se, 18.38; CO, 6.84; H_2O, 12.54. Found: Tl, 47.497, 47.305; Se, 18.30, 18.33; CO, 6.93, 6.96; H_2O, 12.66, 12.58.

Thallous Nickel Selenate, $Tl_2SeO_4.NiSeO_4.6H_2O$.—This compound required a higher temperature, 120°, for its dehydration than either of the preceding salts, The anhydrous compound is yellow.

The analysis was made by the first method described under the cobalt salt.

Anal. Calcd. for $TlSeO_4.NiSeO_4.6H_2O$; Tl, 47.37; Se, 18.39; Ni, 6.81; H_2O, 12.55. Found: Tl, 47.47, 47.30; Se, 18.34, 18.30; Ni 6.72, 6.76; H_2O, 12.51, 12.60.

Thallous Magnesium Selenate, $Tl_2SeO_4.MgSeO_4.6H_2O$.—The salt was heated at 125° to expel water of crystallization.

Magnesium was determined as the pyrophosphate, the thallium and selenium as with the nickel salt.

Anal. Calcd. for $TlSeO_4.MgSeO_4.6H_2O$; Tl, 49.34; Se, 19.15; Mg, 2.94; H_2O, 13.07. Found: Tl, 49.40, 49.21; Se, 19.20, 19.22; Mg, 2.90, 2.86; H_2O, 13.05, 13.07.

Thallous Manganese Selenate, $TlSeO_4.MnSeO_4.6H_2O$.—In the analysis, manganese was precipitated as ammonium manganous phosphate and was weighed as manganese pyrophosphate.

Anal. Calcd. for $TlSeO_4.MnSeO_4.6H_2O$: Tl, 47.58; Se, 18.47; Mn, 6.41; H_2O, 12.60. Found: Tl, 47.51, 47.30; Se, 18.38, 18.58; Mn, 6.54, 6.34; H_2O, 12.80, 12.70.

Crystal Forms and Angles of the Thallous Double Selenates

The crystal system of the salts above described is uniformly monoclinic, and the crystal class is prismatic. The crystals are highly refractive.

Tutton states that the differences in the angles of isomorphous com-

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[2] Dennis and Koller, This Journal, 41, 951 (1919).

pounds should not be over two degrees. Two angles of each of the new salts were measured and the results, together with those of Werther[3] on the double sulfates, and of Tutton on the thallous zinc selenate, follow:

Double Sulfates
$R''SO_4.TlSO_4.6H_2O$

R''	Angles	
	70° +	109° +
Fe	38′	24′
Zn	48′	12′
Ni	54′	6′
Mg	54′	6′

Double Selenates
$R''SeO_4.TlSeO_4.6H_2O$

R''	Angles	
	71° +	108° +
Zn	32′	28′
Mn	17′	48′
Cu	50′	54′
Mg	35′	25′
Co	28′	26′
Ni	34′	26′

The substitution of selenium for sulfur in these double salts causes an increase of about 40′ in the acute angles and a corresponding decrease in the obtuse angles.

Summary

New double selenates of thallous selenate and the selenates of copper, cobalt, nickel, magnesium and manganese are described, together with confirmatory analyses. Composition and crystal measurements show that the compounds are directly analogous to the corresponding double sulfates.

Ithaca, New York

[Contribution from the Havemeyer Chemical Laboratory, New York University]

THE KINETICS OF THE REACTION BETWEEN THE HALOGENS AND SATURATED ALIPHATIC KETONES IN DILUTE AQUEOUS SOLUTION[1]

By F. O. Rice and Charles F. Fryling

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In order to test, effectively, current theories relating to reaction velocity and its variation with temperature, it is necessary to have available accurate measurements for a number of different reactions; for hydrolytic reactions such as sugar inversion or ester hydrolysis the results of hundreds of investigations are now available, but comparatively few complete investigations have been made of non-hydrolytic reactions, partly because these are often so complicated that the mechanism is uncertain or the presence of simultaneous reactions necessitates uncertain corrections.

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[3] Werther, *J. prakt. Chem.*, **92**, 128 (1864).

[1] The work included in this paper is from the thesis presented by Charles F. Fryling in fulfilment of part of the requirement for the degree of Doctor of Philosophy in New York University.