GERMANIUM. XXXIX. THE POLYMORPHISM OF GERMANIUM DIOXIDE[1]

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Introduction

Preceding Observations on Germanium Dioxide.—Germanium dioxide, as it is ordinarily prepared by the hydrolysis of the germanium tetrahalides or the alkali germanates, forms an exceedingly fine-grained precipitate, the individual particles of which do not reveal any definite structure under the microscope at the highest attainable resolving power. However, when examined by powder x-ray diffraction methods, the solid gives a well-defined pattern and therefore is microcrystalline. If the dioxide is formed under conditions more favorable for crystal growth, grains of appreciable size may be obtained. According to Goldschmidt,[2] germanium dioxide obtained by crystallization from its aqueous solution yields trigonal crystals that closely resemble the trigonal-trapezohedral low-quartz. Zachariasen[3] has investigated the crystal structure of this form of germanium dioxide by powder x-ray diffraction methods and confirms Goldschmidt's observations. The fundamental lattice is simple hexagonal.

Crystalline germanium dioxide may also be secured by the devitrification of the glass obtained when the fused dioxide solidifies. Müller[4] has shown that crystals prepared in this way give the same x-ray diffraction patterns as the crystals produced by hydrolysis of the tetrachloride or by crystallization from aqueous solution and, therefore, are the same crystalline modification. This form of germanium dioxide is somewhat soluble in water, and hence has been termed "soluble" germanium dioxide.

Müller and Blank[5] announced the discovery of a second crystalline modification, designated by them as "insoluble" germanium dioxide. They prepared the new form by igniting at about 380° the residue left upon evaporation of an aqueous solution of the oxide. Conversion to the insoluble form was never complete and the yield secured depended upon the conditions of evaporation of the solution and upon the time and temperature of ignition of the residue. Higher or lower temperatures of ignition decreased the yield, and it increased with time of ignition at a decreasing rate, approaching a maximum of about 15%. This

[2] Goldschmidt, *Naturwissenschaften*, 14, 295 (1926).

[3] Zachariasen, *Z. Krist.*, 67, 226 (1928).

[4] Müller, *Proc. Am. Phil. Soc.*, 65, 183 (1926).

[5] Müller and Blank, THIS JOURNAL, 46, 2358 (1924).

insoluble form of germanium dioxide is, according to Müller, extraordinarily inert toward substances which readily act on the oxide in its usual condition. Besides being virtually insoluble in water, it does not react with hydrochloric or hydrofluoric acid. It yields a powder x-ray diffraction pattern completely different from that of the "insoluble" modification. No attempt was made by Müller to interpret the diffraction patterns in terms of crystal structure.

It has been established, therefore, by preceding investigations that germanium dioxide can crystallize in at least two different modifications. One of these is moderately soluble in water and is chemically reactive, while the other is practically insoluble in water and is chemically inert. As regards the stability relations, it follows from the data on solubility that the insoluble form is stable at ordinary temperatures, but there is no conclusive evidence as to whether soluble germanium dioxide is monotropic or enantiotropic with respect to the insoluble form. No convenient method for preparing the insoluble modification has been worked out, and its properties have been determined only incompletely.

Object of this Investigation.—In the present investigation a systematic study of germanium dioxide as a one-component system has been undertaken, involving a determination of the phases occurring, their equilibrium relations and their more important properties.

Experimental

I. Materials

The germanium dioxide was prepared by the hydrolysis of redistilled germanium tetrachloride. It was ignited to remove water and traces of chloride and spectroscopic examination[6] showed that the total sum of metallic impurities present was less than 0.01%.

Fused Germanium Dioxide.—Fused germanium dioxide was made by the method described by Dennis and Laubengayer.[7]

Soluble Crystalline Germanium Dioxide.—The soluble crystalline modification was prepared by heating fused germanium dioxide at 1080° for four hours to ensure complete devitrification. The product appeared entirely crystalline and homogeneous under the microscope.

Insoluble Crystalline Germanium Dioxide.—This form was prepared according to Müller's method[5] which was, however, found to be tedious and to yield poorly formed crystals that were so small as to render difficult their identification under the microscope. Preliminary experiments showed that rapid inversion of the soluble dioxide to the insoluble modification could be secured by a hydrothermal method that produced well-formed crystals. Large samples were prepared by this procedure, which will be described later.

These three forms of germanium dioxide were examined and their properties were determined in order to gain familiarity with their distinguishing features, so that they could be identified when they appeared in the course of the investigation.

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[6] The authors wish to acknowledge the kind assistance of Professor J. Papish, who made frequent spectroscopic examinations of the samples.

[7] Dennis and Laubengayer, *J. Phys. Chem.*, **30**, 1510 (1926).

II. Determination of Stability Relationships

Procedure.—The facts already known regarding the behavior of germanium dioxide, and the close analogy between this oxide and silica, made it evident that the changes in the system are of the sluggish type. Therefore the common dynamic methods for the determination of mono-variant equilibrium could not be employed. In the static method the system is maintained at a suitable constant temperature long enough to assure the attainment of equilibrium, and then is rapidly quenched to a temperature where the rate of progress toward equilibrium is very slow. The phase distribution corresponding to equilibrium at the higher tempera-ture is thereby preserved and can be examined at leisure. Upon trial, this static or quenching method was found to be satisfactory for the study of germanium dioxide.

Persistence of the Modifications in the Pure State.—In order to ob-tain some information about the readiness with which the various forms of germanium dioxide tend to invert, samples of the soluble crystalline dioxide and of the insoluble dioxide were heated for forty-eight hour periods at 485, 620, 695, 810, 970 and 1050° ($\pm$20°). The samples were quenched by dipping the crucibles in ice water and were examined for signs of inversion. In every instance both forms of the oxide per-sisted unmodified. The inversions are very sluggish and do not proceed with appreciable velocity in the pure state up to at least 1050°. In similar experiments with the fused oxide it was found that complete crystallization occurred at 660°, incipient crystallization at 620°, and no crystallization at 550°. The crystals were invariably the soluble modification.

Inversions by the Hydrothermal Quenching Method.—To secure the inversion of a modification of a substance that, although unstable, persists indefinitely in the pure, dry state, it is necessary to use a catalytically acting solvent or flux, in the presence of which a more rapid approach to equilibrium occurs. In investigations on silica and the silicates the hydrothermal method, employing as the inversion catalyzer water or an aqueous solution confined in a vapor-tight bomb, has been shown to be effective.[8] This method was therefore tried with germanium dioxide.

The bomb and furnace were similar to those developed at the Geo-physical Laboratory at Washington.[9] The bomb, however, was modified according to the simpler design described by Friedrichs.[10] It was made of stainless steel and could be used at temperatures up to 550° without showing appreciable attack. At higher temperatures the threads had a tendency to weld together, even when lubricated with finely powdered graphite, so that the bomb could not be opened.

[8] Fenner, *J. Wash. Acad. Sci.*, **2**, 471 (1912).

[9] Morey and Fenner, This Journal, **36**, 215 (1914).

[10] Friedrichs, *Sprechsaal*, **61**, 282 (1928).

Preliminary tests of this new method showed that the soluble crystalline form of germanium dioxide was rapidly converted to the insoluble modification when heated in the bomb in the presence of water at 350°. Large samples of insoluble dioxide were then prepared. From 8 to 10 g. of soluble germanium dioxide and 8 g. of water were placed in a platinum crucible which was covered with platinum foil and was set in the bomb. The sealed bomb was heated for four or five days at about 350° and then was cooled rapidly to room temperature. The product was found to be discolored by iron oxide, which was removed by digesting the germanium dioxide on a steam-bath with successive portions of 6 N hydrochloric acid. The residue was washed free from acid with hot water, was dried for fifteen hours at 500° and was weighed. Table I gives the data for three preparations.

TABLE I

PREPARATION OF INSOLUBLE GERMANIUM DIOXIDE BY THE HYDROTHERMAL METHOD

Preparation	Soluble oxide, g.	Time heated, hours	Temp., °C. ($\pm 20°$)	Product g.	Yield, %
1	8.023	95	350	7.818	97.5
2	10.481	117	355	10.338	98.6
3	10.407	115	360	9.908	95.2
Total	28.911			28.064	97.1

Spectroscopic examination showed that the product was very pure germanium dioxide. To test for the completeness of inversion to the insoluble form, weighed portions of the material were digested in covered platinum crucibles on the steam-bath with concentrated hydrofluoric acid for one hour. No appreciable weight of the sample dissolved. Microscopic examination also demonstrated that the product was a homogeneous preparation of insoluble crystalline germanium dioxide. The inversion was undoubtedly complete, the 97% yield being due to the loss of slight amounts of the insoluble dioxide in suspension when the product was washed by decantation.

The hydrothermal method of preparing insoluble germanium dioxide possesses several advantages over the method of Müller. By its use a large amount of soluble oxide can be transformed directly and quantitatively into the insoluble modification. Moreover, the product is composed of crystals of resolvable size which can be identified readily under the microscope. Further experience indicated that forty-eight hours' heating is sufficient for effecting complete inversion.

To determine the phase stable at a given temperature by the hydrothermal method, 0.1-g. samples of soluble germanium dioxide, insoluble germanium dioxide and fused germanium dioxide were each placed, with 1.5 cc. of water, in small platinum thimbles which were stacked one above the other in the bomb. The sealed bomb was held at the desired tempera-

ture for forty-eight hours. It was then quenched in ice water and the resulting products, after being dried at 120°, were examined with the microscope to ascertain the nature and relative amounts of the phases present. Identification of the various forms was based primarily on their refractive indices, namely, 1.608 for the fused dioxide, 1.70 for the soluble dioxide and 1.99+ for the insoluble dioxide. The identifications were also checked by testing the solubility of the specimen with hydrofluoric acid. The range between 140 and 550° was investigated and the results are given in Table II.

TABLE II

INVERSIONS BY HYDROTHERMAL METHOD

Inversion catalyzer, water   Time, 48 hours

Temp., °C. ($\pm 10°$)	Soluble	Form of GeO_2 used Insoluble Forms present in product	Fused
140	S	I	S, F
180	I	I	S
220	I	I	S, I
260	I	I	I
320	I	I	I
345	I	I	I
450	I	I	I
550	I	I	I

NOTATION: S, soluble crystalline GeO_2; I, insoluble crystalline GeO_2; F, fused GeO_2.   The more abundant form is listed first.

From these data it is evident that throughout the range studied the insoluble modification of germanium dioxide is stable since it remains unchanged while the soluble and fused dioxide tend to invert to it. At 180° and above, this hydrothermally catalyzed inversion of the soluble crystalline form is completed in forty-eight hours or less. The crystals of insoluble oxide formed, while always very small, are larger the higher the temperature of the inversion. In accordance with Ostwald's rule, the metastable soluble crystalline modification appears as an intermediate product in the process of conversion of the fused oxide to the insoluble oxide at 180 and 220°. No new crystalline form was observed in any of the preparations.

Inversions by the Fusion-Quenching Method.—Since the bomb could not be employed above 550°, it was necessary to use another experimental method to explore the temperature range up to the melting point of germanium dioxide, which was known to be somewhat above 1100°. The addition of a suitable fused salt has been found to accelerate certain sluggish inversions sufficiently to make the equilibrium relations readily ascertainable by a quenching method. Fenner[11] employed sodium tungstate for this purpose in working out the stability diagram for silica,

[11] Fenner, Am. J. Sci., 36, 331 (1913).

and van Nieuwenburg and de Nooijer[12] determined the efficiency of a large number of substances for catalyzing the inversion of quartz to tridymite at 1000°.

To ascertain the best catalyst to use for studying the inversions of germanium dioxide in the range of 550 to 1100°, a series of preliminary experiments with sodium tungstate, sodium molybdate, potassium bisulfate, anhydrous magnesium chloride, boric acid and the alkali chlorides were tried. The eutectic melt mixture of potassium chloride and lithium chloride, containing 44.6% by weight of lithium chloride, and melting at 358°, was found to be the most satisfactory. Using this flux a systematic examination of the stability relations of the various forms of the oxide between 550 and 1100° was made according to the following procedure.

Mixtures of each modification of germanium dioxide and the catalyzing flux were prepared in platinum crucibles by evaporating to dryness a suspension of the oxide in 2–3 cc. of water containing the requisite amount of chlorides. The covered crucibles were held at the desired temperature in a muffle furnace which could be maintained constant within ±10° for periods varying from one-half to thirty-six hours, according to the temperature employed. In some instances it was necessary to carry out several experiments at a single temperature before a satisfactory combination of conditions with respect to relative amounts of oxide, flux and time of heating was obtained. Of the conditions tried, those reported in Table III were the most effective. After the ignition the samples were quenched in ice water and were washed free from chlorides with hot water. The phases present were ascertained by examination under the microscope and by determination of their solubility in hydrofluoric acid.

TABLE III

INVERSIONS BY FUSION METHOD

Flux: 55.4% KCl, 44.6% LiCl

Experiment	GeO₂, g.	Flux, g.	Time, hours	Temp., °C. (±10°)	Soluble	Insoluble	Fused
					Forms present in product		
1	0.05	0.10	36	500	S, I	I	S, F, I
2	.05	.05	18	600	S, I	I	S, I
3	.05	.02	6	700	S, I	I	S, I
4	.05	.005	1	800	S, I	I	I
5	.05	.0005	0.5	905	I	I	I
6	.05	.0005	0.5	980	I, S	I	I
7	.05	.0005	0.5	1020	S, I	I	S, I
8	.05	.0005	0.5	1060	S	I, S	S

These data show that the two crystalline modifications of germanium dioxide are enantiotropic with the reversible inversion point lying between

[12] Van Nieuwenburg and de Nooijer, *Rec. trav. chim.*, **47**, 627 (1928).

1020 and 1060°. At 1020°, and below, the insoluble form persists un-
altered, while the soluble crystals and the glass are both more or less
completely transformed to it. At 1060°, on the contrary, the insoluble
oxide, as well as the fused oxide, invert into the soluble crystalline modifi-
cation while the latter undergoes no change. The fused oxide, at tempera-
tures at which the insoluble modification is stable, does not as a rule pass
directly into the insoluble form, but yields the metastable soluble crystals
as an intermediate phase in accordance with Ostwald's law of successive
reactions.

In order to fix the temperature of the inversion point more closely,
an improved technique was employed. Mixtures of the various modifi-
cations with the potassium chloride–lithium chloride flux were heated in
small platinum thimbles suspended in the center of a platinum-wound
resistance furnace of the type in use at the Geophysical Laboratory.[13]
The thimbles were supported so that the tip of the platinum–platinum-
rhodium thermocouple used for measuring the temperature was just above
the charge. Throughout the series of experiments the relative amount
of catalyst and the time of heating were kept as low as was compatible
with decisive results. Fluctuation of the temperature during an experi-
ment never exceeded ±3°. The charges were quenched, washed and
dried and the phases present were identified.

TABLE IV
QUENCHING EXPERIMENTS TO LOCATE INVERSION POINT
Flux: 55.4% KCl, 44.6% LiCl

Experi-ment	GeO$_2$, g.	Flux, g.	Time, hours	Temp., °C. (±5°)	Form of oxide used Soluble Forms present in product	Insoluble
1	0.05	0.0005	0.5	1018	S, I	I
2	.05	.001	2.0	1025	S, I	I
3	.10	.002	2.0	1028	98.4% S^a 1.6% I	100 % I^a
4	.10	.002	2.0	1033	S, Trace I	98 % I^a 2 % S
5	.10	.002	2.0	1038	100 %S^a	82.5% I^a 17.5% S
6	.05	.0005	2.0	1040	S	I, S
7	.05	.0005	0.5	1051	S	I, S
8	.10	.001	1.0	1075	S	
9	.10	.001	1.0	1094	S	
10	.10	.001	1.0	1110	Glass	

^{a} By weighing residue insoluble in hydrofluoric acid.

It is evident from these data that at 1028° and below, the insoluble
germanium dioxide is stable, at 1038° and above the soluble modification
is stable, while at 1033° the two forms exist in equilibrium. Allowing for

[13] Shepherd, Rankin and Wright, *Am. J. Sci.*, **28**, 308 (1909).

uncertainties introduced by errors in calibration and temperature measurement, and for the difficulty of deciding the exact point of discontinuity of stability, the inversion point, Insoluble crystalline $GeO_2 \rightleftarrows$ Soluble crystalline GeO_2, may be concluded to be $1033 \pm 10°$.

Experiment 10 at $1110°$ yielded a clear glass due to the lowering of the melting point of germanium dioxide by the presence of the flux. Experience with the chloride mixture as a catalyzing flux justifies the belief that it is exceedingly conducive to the transformation of germanium dioxide to the most stable phase. Since in experiments 5 to 9 the soluble crystalline modification persisted unchanged, it may be concluded that this form is stable between $1033°$ and the stable melting point.

Determination of the Melting Points.—Germanium dioxide has a strong tendency to supercool and superheat and therefore the quenching[14] method for the determination of melting points was used. The procedure consisted, essentially, in holding samples at various different constant temperatures in the vicinity of the melting point, quenching them and observing the phases present. The platinum-wound resistance furnace used for the determination of the inversion point was again employed and was maintained at temperatures constant to $\pm 1°$. The data obtained for the two forms of the dioxide are given in Tables V and VI.

TABLE V

DATA FOR MELTING POINT OF SOLUBLE CRYSTALLINE GeO_2

Experiment	Time of heating, hours	Temp., °C. ($\pm 3°$)	Phases in product
1	2	1107.5	S
2	2	1110.0	S, some glass
3	2	1112.5	S, partly glass
4	2	1115.0	Glass, trace of S
5	2	1117.5	Glass
6	6	1111.0	About half glass, half crystals, the latter much larger than before heating

TABLE VI

DATA FOR MELTING POINT OF INSOLUBLE CRYSTALLINE GeO_2

Experiment	Time of heating, hours	Temp., °C. ($\pm 3°$)	Phases in product
1	0.5	1077.5	I, glass, S
2	.5	1080.0	Glass, S, I
3	.5	1082.5	Glass, S, I
4	.5	1085.0	Glass, S, trace of I
5	.5	1087.5	Glass, S
6	.5	1090.0	Glass, S

If the melting point of soluble crystalline germanium dioxide be taken as the lowest temperature at which the crystalline phase vanishes, and allowance be made for all possible sources of error in the measurements,

14 Morey, *J. Wash. Acad. Sci.*, **13**, 326 (1923)

it follows from the data in Table V that the melting point may be reported as 1116 ± 4°. This agrees well with the value 1115 ± 3° reported by Schwartz, Schenk and Giese,[15] who also used the quenching method.

At the melting point of insoluble germanium dioxide both it and the liquid phase are metastable and there is the possibility of melting to metastable glass, of inverting directly to the stable soluble dioxide, or of changing through the glass phase to the stable soluble dioxide. It is possible to determine the metastable melting point of insoluble germanium dioxide because the second and third of these transformations proceed more slowly than the first. In the experiments recorded in Table VI the time of heating was so regulated as to be long enough to realize approximately the metastable equilibrium between liquid and insoluble germanium dioxide, but not long enough to admit of much displacement toward the stable soluble crystalline germanium dioxide. The melting point of insoluble crystalline germanium dioxide may, therefore, be taken as the temperature at which the last traces of insoluble crystals disappeared, or 1086 ± 5°.
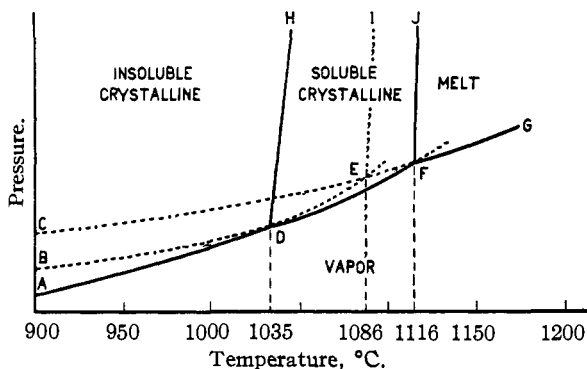

Fig. 1.—Phase diagram of germanium dioxide.

Phase Diagram of Germanium Dioxide.—On the basis of the experimental study it is possible to construct a pressure–temperature diagram of phase equilibria in the one–component system, germanium dioxide. Fig. 1 represents the more important portion of such a diagram. The pressure coördinates have only qualitative significance. Curves ADE, BDF and CEFG are the vapor pressure curves of the insoluble, soluble and fused modifications, respectively. They are constructed on the principle that the form having the lowest vapor pressure is the stable form at a given temperature. The curves intersect at D, the inversion point; F, the melting point of the soluble crystalline modification; and E, the metastable melting point of the insoluble modification. The

[15] Schwartz, Schenk and Giese, *Ber.*, **64**, 364 (1931).

lines DH, EI and FJ represent the probable mode of variation of the inversion point and melting points with pressure. From the relative densities of the three forms, it follows that each of these lines has a positive slope; and unless, as is very unlikely, the heat of inversion is considerably greater than the heat of fusion, line DH makes the greatest angle with the axis of pressures.

Improbability of a Third Crystalline Modification.—From the fact that the soluble crystalline form undergoes no inversion when heated with a flux at temperatures between 1033 and 1090°, and that it persists unchanged at temperatures just below its melting point, we have inferred that no third enantiotropic crystalline modification of germanium dioxide exists. This does not exclude the possibility of a monotropic modification, but, if such a form occurs, it has not appeared in appreciable amount in any of our preparations.

Müller and Blank[5] have postulated the existence of three crystalline modifications of germanium dioxide to explain the fact that only a limited fraction of their "evaporated" oxide can be converted to the insoluble form, no matter how long the material is heated, and the fact that this maximum yield varies with different preparations according to the conditions of evaporation. They suggest that the residue from the evaporation of the aqueous solution is not homogeneous, but contains two soluble modifications, one of which undergoes rapid transformation to the insoluble form while the other inverts very slowly if at all.

The presence of two crystalline modifications, however, was not borne out by the x-ray patterns Müller obtained nor by the patterns secured for similar material in the course of the present investigation, although, according to Müller's theory, from 15 to 20% of the third form should be present.

Another explanation for Müller's results, which does not require the existence of a second soluble crystalline modification, may be suggested. The "evaporated" oxide used in the experiments of Müller and Blank always contained moisture. In view of our own hydrothermal experiments, it appears that this moisture should catalyze the inversion. The inversion will be incomplete because the process stops as soon as the moisture has been expelled. The hypothesis that the presence of moisture is necessary to bring about the inversion may also account for the peculiar form of Müller and Blank's yield–temperature curve, which shows an apparent maximum rate of transformation at 380°. At low temperatures, the rate of inversion is itself small, regardless of the amount of water present. At high temperatures, the excess moisture is expelled before the inversion has progressed very far. At 380° the rates of inversion and of evaporation of the water are so related that the amount of inversion in a given time is a maximum.

It is still necessary to explain why different preparations of the "evaporated" oxide, under identical conditions, show different yields of the insoluble modification, and also why the "hydrolyzed" oxide, which ordinarily contains more water than the "evaporated" variety, is not converted at all upon ignition. It is possible that the "evaporated" oxide, although consisting mainly of the soluble modification, contains also nuclei of the insoluble crystals, formed during the protracted evaporation, which serve as centers of crystallization under conditions favoring a transformation. If these nuclei are sufficiently small, they may be numerous and still escape detection by x-ray analysis, microscopic examination, or solubility tests. The amount of conversion of two different samples, similarly treated, will depend on the comparative number of "insoluble" nuclei initially present in each sample, as well as on the amount of water present. The "hydrolyzed" oxide, having been precipitated from solution by a rapid chemical reaction, may conceivably contain no "insoluble" nuclei whatever.

It is very doubtful whether a third monotropic crystalline modification of germanium dioxide exists. There is no direct evidence of its existence, and the indirect evidence offered by Müller and Blank can, as we have shown, be otherwise interpreted. Recently Schwartz and Huf[16] have reported that solubility measurements for the various forms of germanium dioxide do not warrant the assumption of the existence of a third crystalline modification.

III. Properties of the Crystalline Forms

The existing data concerning the properties of the crystalline modifications of germanium dioxide were so incomplete and, in some cases, so contradictory, that it appeared desirable to determine systematically the more important physical and chemical properties.

Crystal Structure.—Zachariasen's[3] analysis of the crystal structure of the soluble crystalline modification has already been cited in the introduction to this article. A table of sine-squares which we calculated from measurements of x-ray powder diffraction photographs of this form agreed closely with his values.

The crystal structure of the insoluble modification of germanium dioxide was determined[17] entirely from x-ray powder diffraction photographs, taken with a General Electric x-Ray Diffraction Apparatus of the type described by Davey.[18]

[16] Schwartz and Huf, Z. anorg. allgem. Chem., 203, 188 (1932).

[17] The authors are indebted to Prof. C. C. Murdock, of the Department of Physics, for his kind assistance in obtaining the x-ray patterns and in the solution of the crystal structure.

[18] Davey, J. Optical Soc. Am., 5, 479 (1921).

It was found that the fundamental lattice is simple tetragonal, with $c/a = 0.649 \pm 0.002$, and that the dimensions of the unit cell are

$$a_0 = 4.395 \pm 0.010 \text{ Å.}, \quad c_0 = 2.852 \pm 0.015 \text{ Å.}$$

The observed interplanar distances corresponding to the first twenty-five lines on the film agreed well with the distances calculated from these parameters.

To correspond to the observed density, 6.239 g./cc., there must be two molecules of GeO_2 in the unit cell. The calculated density is then 6.26 $\pm$ 0.06 g./cc.

These data support the hypothesis, already suggested by Zachariasen,[19] that the insoluble modification of GeO_2 has the "rutile" type of structure. In this structure the unit cell is a tetragonal prism, and contains two molecules. The centers of the two metal ions are at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while those of the four oxygen ions are at $(u, u, 0)$, $(\frac{1}{2} - u, \frac{1}{2} + u, \frac{1}{2})$, $(\frac{1}{2} + u, \frac{1}{2} - u, \frac{1}{2})$ and $(1 - u, 1 - u, 0)$. For rutile, $u = 0.30 \pm 0.01$. The space group is D_{4h}^{14}.

Powder diffraction patterns of insoluble GeO_2 and rutile were photographed beside each other on the same film. The patterns were very similar; for every line in one pattern there was a corresponding line in the other, having, usually, about the same relative intensity. The odd order reflections from the 100, 001 and 201 planes were absent from both patterns.

The theoretical intensities of the lines in the pattern of GeO_2, for an assumed rutile type of structure, were calculated and compared with the experimental values. In the calculations, the general formula for powder patterns,[20]

$$I_{hkl} \propto F^2 s \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \tag{1}$$

and the atomic scattering powers of O^{2-}, Ti^{4+} and Ge given by James and Brindley,[21] were employed. The intensities were obtained, not by comparing the lines of the pattern of GeO_2 with each other, but by comparing each GeO_2 line with its counterpart in the pattern of rutile, the intensity of which was calculated from the known crystal structure by formula (1). The observed intensities, and those calculated using values of u from 0.26 to 0.34, are listed in Table VII. All values are expressed as percentages of the intensity of the 002 reflection. The lines beyond those listed were, with few exceptions, too faint to allow of accurate estimates of intensity.

The general agreement between calculation and experiment is best

[19] Ref. 3, p. 233.

[20] Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 2d edition, 1931, p. 165.

[21] James and Brindley, Z. Krist., 78, 470 (1931).

for $u = 0.30$, and appears close enough to confirm the assumption of the rutile type of structure for insoluble GeO_2. Values of u below 0.28, or above 0.32, appear to be excluded: otherwise the 120 line would be invisible or else decidedly more intense than the 400 line.

TABLE VII

COMPARISON OF THE THEORETICAL AND OBSERVED INTENSITIES OF THE LINES IN THE POWDER PATTERN OF INSOLUBLE GeO_2

Obs. spacing, Å.	Indices	Obs. intensity	Calculated intensity				
			$u = 0.26$	0.28	0.30	0.32	0.34
3.10	110	1500	1162	1197	1267	1371	1504
2.390	101	920	1043	929	825	730	647
2.194	200	320	144	158	185	228	287
2.104	111	130	126	118	104	85	65
1.965	120	30	2	13	30	47	56
1.618	121	910	700	759	799	812	788
1.556	220	220	268	252	224	194	168
1.424	002	100	100	100	100	100	100
1.389	130	160	203	191	172	152	139
1.299	301 112	660[a]	348	392	433	464	479
1.195	202	40	59	62	69	80	93
1.117	231	100	172	140	125	128	147
1.096	400	50	76	68	55	41	31

[a] Probably too high. The intensity of this compound line is really not comparable with that of the corresponding line in the pattern of rutile, because the component lines in the case of rutile do not fully coincide, on account of its lower axial ratio.

While the sequence of intensities of the lines in the patterns of GeO_2 and of rutile was, for the most part, the same, there were certain exceptions. Of these, the most striking was in the case of the lines 200, 111 and 120. For GeO_2, $I_{200} > I_{111} > I_{120}$; for TiO_2, $I_{111} > I_{120} > I_{200}$. This difference in order is accounted for by the difference in the scattering powers of the titanium and germanium ions, and does not necessitate any difference in the ionic arrangement. This is shown in Table VIII, in which the values of F^2s (formula (1)), for a rutile structure with $u = 0.30$ are given.

TABLE VIII

Reflection	F^2s	
	GeO_2	TiO_2
200	3615	522
111	2216	2413
120	740	810

It is concluded that the arrangement of ions in the unit cell of insoluble GeO_2 is of the rutile type, and that the value of the parameter u is 0.30 $\pm$ 0.02.

Drawings of this structure are given by Wyckoff.[22] Each germanium ion is surrounded by six oxygen ions, whose centers lie at the corners of a somewhat distorted octahedron. The shortest Ge—O distance is 1.86 Å.;

[22] Ref. 20, p. 231.

and the effective radius of the Ge^{4+} ion, on the basis of 1.32 Å. for the radius of the oxygen,[23] is 0.54 Å.

Optical and Crystallographic Properties.—Specially selected, well-defined crystals of both modifications were kindly examined for us under the microscope by Professor C. W. Mason, who reports on them as follows:

"**Soluble GeO$_2$.**—Well-formed approximately cubical crystals, which are rhombohedra of the hexagonal system. They show strong double refraction and symmetrical extinction, and yield uniaxial positive interference figures. $\omega = 1.695 \pm 0.005$; $\epsilon = 1.735 \pm 0.005$.

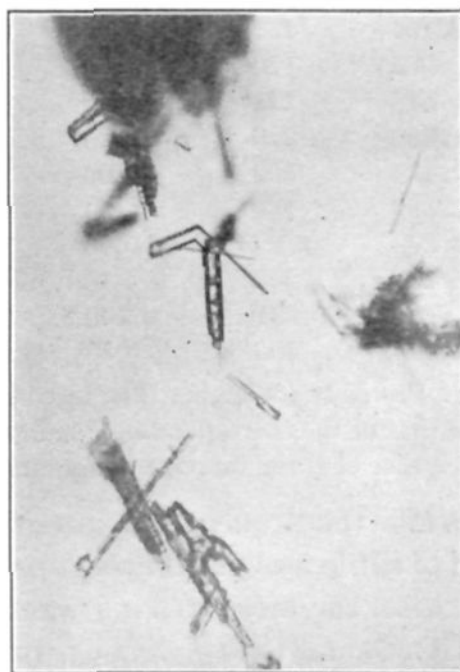Fig. 2.—Soluble crystalline germanium dioxide.

Fig. 3.—Insoluble crystalline germanium dioxide.

"**Insoluble GeO$_2$.**—Clusters and rosets of prisms and lath-shaped forms, also very fine needles. Some knee turns. The surfaces of the larger crystals are rough and apparently eroded. End faces of definite form are not evident. Double refraction is strong, with the sign of elongation and parallel extinction exhibited by all side views of the prisms. The crystals belong to the tetragonal system. $\omega = 1.99$, $\epsilon = 2.05$–2.10 (estimated)."

Photomicrographs of the samples examined are reproduced in Figs. 2 and 3. The crystals of the soluble oxide, which are embedded in the fused oxide, were produced by heating the insoluble modification for two hours at 1100°. It would appear that the insoluble oxide melted almost immediately; but the melt was unstable with respect to the soluble modification, which accordingly crystallized out.

[23] Goldschmidt, "Geochemische Verteilungsgesetze," Oslo, Vol. VII, 1926, p. 15.

The specimen of insoluble germanium dioxide shown in Fig. 3 was isolated by extracting with hydrofluoric acid the product of heating the soluble oxide with 1% of its weight of potassium chloride–lithium chloride mixture at 1020°. It contained numerous elbow twins, like the one appearing in the photograph, with an angle of 114 ± 1° between the two members. On the assumption that in these twins the components lie on 010 faces and are joined on the 011 plane, the axial ratio c/a calculated from this angle is 0.65 ± 0.015, thus confirming the x-ray value, 0.649. Contact twins of this type are often observed on rutile and cassiterite.[24]

Density.—The values for the density of soluble crystalline germanium dioxide given by different investigators are very discordant, probably due to the difficulty in securing well-crystallized, homogeneous samples.

The densities of our preparations of soluble and insoluble crystalline germanium dioxide were determined pycnometrically, using toluene as the immersing liquid. The samples were dried to constant weight at 950° immediately before each determination. All weighings were corrected to vacuum. The results of duplicate determinations are given together with the value secured by x-ray methods by Zachariasen for the soluble oxide and that obtained by x-ray methods in the present investigation for insoluble germanium dioxide.

<div align="center">

TABLE IX

Modification	Density at 25° (1)	(2)	Av.	x-Ray density
Soluble crystalline GeO_2	4.233	4.224	4.228	4.28
Insoluble crystalline GeO_2	6.234	6.244	6.239	6.26

</div>

It will be noticed that in both cases the difference between the pycnometric and x-ray densities is slight and is in the expected direction, inasmuch as the value measured directly tends to be lowered by the presence of voids in or between the crystals. The samples used by the authors in the determinations cited above consisted of well-formed crystals of appreciable size. When less perfectly crystallized material was used the results were always lower.

Solubility in Water at 25°.—Solubility determinations were made by agitating the solid with water in a Pyrex glass flask in a thermostat until equilibrium was established and then evaporating a given weight of the saturated solution to dryness and weighing the residue; 4.53 g. of soluble crystalline germanium dioxide was found to dissolve in 1000 g. of water at 25°. This is in good agreement with the value 4.47 g. per 1000 g. of water at 25° reported by Pugh.[25] The insoluble crystalline modification was not appreciably soluble.

[24] Groth, "Elemente der physikalischen und chemischen Krystallographie," 1921, p. 200.

[25] Pugh, *J. Chem. Soc.*, 1537 (1929).

Chemical Properties.—Samples of 0.2 g. of the insoluble crystalline oxide, previously dried at 950°, were digested on the steam-bath with 10 cc. of each of the following reagents: 25 N hydrofluoric acid, 12 N hydrochloric acid, 36 N sulfuric acid and 5 N sodium hydroxide. After one hour the undissolved residue was separated from the liquid by de-cantation and filtration, and was washed, ignited and weighed. There was no appreciable solution in any of the three acids, but in the case of the 5 N sodium hydroxide, the losses in weight of the sample, in two determinations, were 16.8 and 17.8%, respectively. These figures were corroborated by determining the amount of germanium dioxide in the filtrate and washings by the method of Johnson and Dennis.[26] Contrary to the statement of Müller and Blank[27] the insoluble oxide is not wholly unattacked by hot alkaline solutions. The rate of solution, however, is slow compared with that of the soluble crystalline form.

In similar tests, the soluble modification was rapidly attacked by 25 N hydrofluoric acid, 12 N hydrochloric acid and 5 N sodium hydroxide, but scarcely at all by 36 N sulfuric acid.

The insoluble oxide reacted readily when fused with ten times its weight of sodium hydroxide at 550°, or with five times its weight of sodium carbonate at 900° or above. In both cases the melt was completely soluble in water.

To facilitate comparison, the properties of the two crystalline forms and of the glass are tabulated in Table X. The information on the glass is as given by Dennis.[28]

TABLE X

PROPERTIES OF GERMANIUM DIOXIDE

	Insoluble crystalline	Soluble crystalline	Glass
Crystal system	Tetragonal	Hexagonal	Amorphous
Crystal structural type	Rutile	Low-quartz	
Density at 25°, g./cc.	6.239	4.228	3.637
x-Ray density, g./cc.	6.26	4.28	
Indices of refraction	$\omega = 1.99$	$\omega = 1.695$	
	$\epsilon = 2.05$–2.10	$\epsilon = 1.735$	1.607
Inversion point	$1033 \pm 10°$	$1033 \pm 10°$	
Melting point	$1086 \pm 5°$	$116 \pm 4°$	
Solubility at 25°, g./1000 g. H₂O	Insoluble	4.53	5.184 g./l. (at 30°)
Action of HF	None	Reacts, giving H₂GeF₆	Reacts, giving H₂GeF₆
Action of HCl	None	Reacts, giving GeCl₄	Reacts, giving GeCl₄
Action of 5 N NaOH at 100°	Slowly dissolves	Rapidly dissolves	Rapidly dissolves

[26] Johnson and Dennis, THIS JOURNAL, **47**, 790 (1925).

[27] Ref. 5, p. 2359.

[28] Dennis, *Z. anorg. allgem. Chem.*, **174**, 97–141 (1928).

Discussion

Morphotropic Relationships.—A classification of the dioxides of the elements of group IV according to crystal structures is given in Table XI. The soluble or high-temperature modification of germanium dioxide is isomorphous with low-quartz, while the insoluble or low-temperature modification is isomorphous with the dioxides of tin and lead.

TABLE XI

CRYSTAL STRUCTURES OF DIOXIDES OF GROUP IV

Hexagonal low-quartz structure	Tetragonal rutile structure
Low-quartz, SiO_2 (below 575°)	Insoluble GeO_2 (below 1033°)
Soluble GeO_2 (above 1033°)	Cassiterite, SnO_2
	Plattnerite, PbO_2

It is thus evident that the effect on the crystal structure of germanium dioxide of raising the temperature is the same as that of substituting a small cation for the germanium.

The occurrence of two modifications of germanium dioxide is in accordance with Goldschmidt's[29] views on the relation of the crystal structures of compounds of the type AX_2 to the ratio of the ionic radii. The geometrical boundary between structures with coördination numbers 2 and 4, such as the low-quartz type, and those with coördination numbers 3 and 6, such as the rutile type, is at $r_A/r_X = 0.414$. Taking our value of 0.54 Å. for the radius of the germanium ion, and Goldschmidt's value of 1.32 Å. for that of the oxygen ion, $r_{Ge}/r_0 = 0.409$. That is, the ionic radial ratio for germanium dioxide is so close to the theoretical boundary between the two structural types that the compound can assume one structure or the other, depending on external conditions of temperature and pressure.

The value of 0.44 Å. given by Goldschmidt for the radius of the germanium ion is evidently too low. It is to be noted that Pauling's calculated value is 0.53 Å.

Summary

1. The polymorphism of germanium dioxide is confirmed and methods of preparing the soluble and insoluble modifications in a well-crystallized condition are described.

2. Inversion from either crystalline modification to the other is shown to be of the sluggish type. By the use of the quenching method with an accelerating flux, it is shown that the two modifications are enantiotropic, with the inversion point at 1033 ± 10°.

3. Using the quenching method, the stable melting point of the soluble modification, 1116 ± 4°, and the metastable melting point of the insoluble modification, 1086 ± 5°, have been determined.

[29] Goldschmidt, *Trans. Faraday Soc.*, **25**, 253 (1929).

4. The phase relations in the one-component system germanium dioxide are represented diagrammatically and are discussed.

5. From a consideration of the available evidence, it is concluded that a third crystalline modification of germanium dioxide probably does not exist.

6. The crystal structure of the insoluble modification, and the density, solubility, indices of refraction and chemical activity of both modifications have been determined.

7. A discussion of the crystallo-chemical relationships of germanium dioxide to the dioxides of the other elements of the fourth periodic group is submitted.

ITHACA, N. Y.

THE SPARK-IN-FLAME METHOD OF SPECTROGRAPHIC ANALYSIS AND A STUDY OF THE MUTUAL EFFECTS OF ELEMENTS ON ONE ANOTHER'S EMISSION[1]

BY RALPH HULTGREN

Introduction

In recent years the development of methods for the use of the spectrograph as an instrument for the quantitative as well as qualitative chemical determination of elements has proceeded to such an extent that they may now be regarded as suitable for application to many microchemical problems. While spectrographic methods cannot in general compete with ordinary chemical quantitative analysis in point of accuracy, they possess two important advantages which make them of great value in many special cases. These are great sensitivity, which permits of the semi-quantitative estimation of amounts of material too small to be analyzed by other methods, and the great rapidity with which an analysis can be conducted. For details of procedure, accuracy of estimation, etc., the reader is referred to the literature.[2]

The three principal means of exciting emission spectra which have been used in quantitative analysis are the electric arc, the spark and the flame. The arc and spark methods combine the advantages of a high and to some extent controllable excitation with certain drawbacks. While the high

[1] Original manuscript received August 19, 1931.

[2] F. Löwe, "Handbuch der Physik," 21, 663 (1929); H. Lundegårdh, "Die quantitative Spektralanalyse der Elemente," G. Fischer, Jena, 1929; Eugen Schweitzer, Z. anorg. Chem., 164, 127 (1927); Walter Gerlach, ibid., 142, 383 (1925); A. de Gramont, Bull. soc. chim., 33, 1693 (1923).