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Polymorphism of Bismuth Trioxide[1]

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Bismuth trioxide has been considered to be dimorphous since the preparation of orthorhombic needles by Jacquelain[2a] and Nordenskiöld[2b] and of cubic tetrahedra by Muir and Hutchinson.[3] Guertler,[4] whose work is commonly cited as authoritative in this connection, has also considered pure bismuth oxide to be dimorphous with a transition temperature at 704° on the basis of a cooling curve, even though he was unable to isolate the alleged high temperature form. However, later thermal data by Belladen[5] fail to confirm the earlier work, and Sillén[6] has pointed out that the preparation of Muir and Hutchinson was contaminated with considerable amounts of silica.

Therefore, it is believed that the first valid demonstration of the dimorphous character of bismuth oxide is to be credited to Sillén[6] based on his preparation of a new, pure modification, the β-variety. Such a claim, however, was not made by Sillén, who accepted the conclusions of Guertler and confined himself largely to the preparation[6] and X-ray study[6,7] of the several phases.

From these studies, he has concluded that bismuth oxide exists in four different forms, only two of which are pure, the others being contaminated with foreign substances derived from the vessels employed in the preparation of these phases. Structures for all of these phases have been proposed.[6,7] The various forms with a method of preparation of each, described by Sillén,[6] follow:

I. *Pure Phases*
    A. Monoclinic phase, α-Bi_2O_3, common variety, prepared by quenching or slow cooling of a melt.
    B. Pseudo-cubic or tetragonal phase, β-Bi_2O_3, prepared by sublimation of bismuth oxide, formed by passing oxygen rapidly over metallic bismuth maintained at 800° in a graphite furnace with subsequent rapid cooling of the vapors produced.

II. *Impure Phases*
    A. Body-centered cubic phase, prepared by fusion of bismuth oxide for five minutes at 900° in a porcelain crucible.
    B. Simple cubic phase, prepared by fusion of bismuth oxide for twenty minutes or longer at 900° in a porcelain crucible.

The α-phase corresponds to the "orthorhombic form" reported by earlier workers[2a,2b,4] and the body-centered cubic (impure) phase corresponds to the "tetrahedral crystals" previously mentioned.[3]

It was assumed by Sillén, without supporting experimental proof, that the monoclinic form represents the phase stable at ordinary temperatures and that the tetragonal variety is a high temperature form.

The purpose of the present investigation was the preparation of the several polymorphic forms of pure bismuth oxide, the determination of their relative thermodynamic stabilities and of the transition temperatures between them, the establishment of the true nature of the impure phases that have been reported, and the clarification of the earlier conflicting data on the subject.

Preparation and Properties of the Pure Polymorphic Forms.—α-Bi_2O_3 (monoclinic) was prepared by purification of C. P. bismuth oxide by heating it at about 750° in platinum for several hours to eliminate carbonate and other possible anions, followed by water leaching to remove soluble constituents. The oxide was analyzed by first separating the bismuth as sulfide, precipitating by means of $(NH_4)_2CO_3$ and finally igniting to Bi_2O_3 which was weighed as such. The pale yellow product was found to be $99.99 \pm 0.06\%$ Bi_2O_3 and to consist of highly birefringent, needle-like crystals on microscopic examination. Measurements of a powder photograph led to interplanar-spacing values which were in agreement with those calculated from Sillén's data[6] for the monoclinic phase. The density of α-Bi_2O_3 calculated from his data should be 9.39; the density, as measured with a helium volumeter recently developed by us (to be described elsewhere), was found to be 9.32 ± 0.02 g./cc. This measured value is in better accord with the calculated value than previous measurements, which have been summarized elsewhere.[6]

β-Bi_2O_3 (tetragonal) was first prepared by the method of Sillén,[6] oxidizing metallic bismuth in a graphite furnace, maintained at a high temperature, in a rapid stream of oxygen and condensing the oxide vapor on a cool surface. This method did not lend itself to large-scale preparations inasmuch as a large percentage of the oxide remained in the

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(1) Based in part upon a portion of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Massachusetts Institute of Technology, 1941.

(2) (a) V. A. Jacquelain, *J. prakt. Chem.*, **14**, 3 (1838); (b) A. E. Nordenskiöld, *Pogg. Ann.*, **114**, 622 (1861).

(3) M. M. P. Muir and A. Hutchinson, *J. Chem. Soc.*, **55**, 143 (1889).

(4) W. Guertler, *Z. anorg. allgem. Chem.*, **37**, 222 (1903).

(5) L. Belladen, *Gazz. chim. ital.*, **52**, **II**, 160 (1922).

(6) L. G. Sillén, *Arkiv. Kemi, Mineral. Geol.*, **12A**, No. 18, 1 (1937).

(7) Sillén, *Naturwiss.*, **18**, 206 (1940); *Z. Krist.*, **103**, 274 (1941).

furnace as a melt and as the procedure rapidly destroyed the graphite furnace, even when lumps of graphite were mixed with the bismuth to serve as "fuel." Moreover, the oxide so prepared was usually contaminated with from 0.5 to 1.0% of graphite. The technique of preparing this form was altered to obviate these difficulties. A high temperature was achieved by striking an arc between a graphite electrode and a pool of molten bismuth metal contained in a graphite crucible within a large jar to which oxygen was continuously admitted. The bismuth oxide condensed in solid form upon the walls of the jar and also as a smoke which slowly settled out on the bottom. The bismuth metal employed for this purpose proved on analysis to be 99.95 ± 0.05% Bi, and the graphite electrode was of the spectroscopic variety. The β-Bi_2O_3 so formed was contaminated by finely-divided bismuth if oxygen was not supplied sufficiently rapidly. Fortunately, such finely-divided bismuth is rapidly oxidized at temperatures between 750 and 800° to β-Bi_2O_3, which can be preserved by quenching in water or by contact with a cool metal surface. By this means the product from the arc preparation could be purified readily. Analysis of the bright yellow to deep orange material so formed gave 99.8 ± 0.2% Bi_2O_3.[8] From an X-ray powder photograph, it was determined that this phase is tetragonal, a_0 = 10.93 Å., c_0 = 5.63 Å., in good agreement with the values given by Sillén.[6] From the X-ray data the calculated density of β-Bi_2O_3 was 9.18; the measured value was 9.04 ± 0.04 g./cc.

A new form of Bi_2O_3, which may be denoted γ-Bi_2O_3 has been obtained in the following way. A small platinum crucible of about 10 mm. diameter, whose bottom was covered to a depth of about 3 mm. with a sample of β-Bi_2O_3 was placed within a second porcelain crucible maintained at a temperature of from 750–800°. After a few minutes, to permit establishment of thermal equilibrium, the cover was hastily applied to the porcelain crucible which was removed from the furnace and allowed to cool in the air. The use of the outer porcelain crucible merely provided the proper rate of cooling for the sample, more rapid cooling preserving the original tetragonal form, less rapid cooling causing a transition to the α-form. The same results were achieved irrespective of the time of heating at 750–800°. The bright yellow product obtained by means of this procedure was found on analysis to be 99.8 ± 0.2% Bi_2O_3. A powder photograph showed no evidence for the existence of α- or β-Bi_2O_3 in the product, and from measurements on the film it was determined that γ-Bi_2O_3 has a body-centered cubic lattice with a_0 = 10.25 Å. A more accurate value of the lattice constant, obtained by the use of a symmetrical focusing camera, was a_0 = 10.245 ± 0.001 Å. From this datum and the assumption that there are thirteen Bi_2O_3 per unit cell, the calculated X-ray density is 9.30. The measured density was 9.22 ± 0.04 g./cc. It was concluded from the similarity of the spacing and intensities of the lines on the powder photographs that γ-Bi_2O_3 has essentially the same structure as the impure body-centered cubic phase.[6] The X-ray data on γ-Bi_2O_3 are tabulated below.

TABLE I

POWDER PHOTOGRAPH OF γ-Bi_2O_3. (Cu Kα RADIATION)

hkl	*d*	*I*	*hkl*	*d*	*I*
220	3.51	W	930 851 754	1.070	W
310	3.17	S	932 763	1.055	W
222	2.90	W	941 853 770	1.034	S−
321	2.71	S	950 943	0.995	W+
400	2.53	VW	1031 952 765	0.975	M
411 330	2.39	W	1033 961	0.941	W
420	2.27	W−	1110 954 873	0.927	M−
332	2.16	W+	1121 1051 963	0.913	W
422	2.06	W+	1130 970	0.898	W+
510 431	1.991	W+	1044 882	0.891	W+
521	1.839	W	1132 1053 972 776	0.885	M
530 433	1.750	S	1141 875	0.871	W
600 442	1.670	M	965	0.860	M−
611 532	1.650	S	1211 1150 1143 981 974	0.848	S
631	1.504	S	1152 1071 1055	0.838	M−
710 550 543	1.441	M			
721 552 633	1.390	W			
730	1.345	W			
732 651	1.296	W			
811 741 554	1.258	W−			
653	1.218	S−			
822 660	1.203	S−			
831 750 743	1.187	S−			
910 833	1.128	W−			
842	1.117	W−			
921 761 655	1.100	W			

Stability Relationships from Thermal Studies.—In order to throw light upon the relative stability of the various forms of bismuth oxide and to determine possible transition temperatures, samples were placed in platinum crucibles, heated to different temperatures (known to within ±1%)

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(8) In passing, it is interesting to note that whereas very finely divided bismuth obtained from the arc experiment oxidized to β-Bi_2O_3 at about 750°, coarser bismuth powder (obtained by grinding the C. P. metal and passing it through a 100-mesh sieve) when subjected to identical conditions oxidized to α-Bi_2O_3. Recently, the importance of particle size in influencing the form of PbO obtained from decomposing $PbCO_3$ or hydrated PbO has been pointed out by M. Petersen (THIS JOURNAL, **63**, 2617 (1941)).

for varying lengths of time, and then cooled rapidly, either by shaking the powder upon a cool metal surface or by quenching in water, and the product examined by means of X-ray photographs. The following table summarizes the results so obtained.

TABLE II

TRANSITIONS EFFECTED BY HEATING

Temp., °C.	Time	Resulting phase
	1. α-Bi_2O_3	
380	1 month	α
650	1 week	α
760	5 min.	α
800	16 hrs.	α
800	6 days	α + some orange particles
800	23 days	α + less than 10% β[a]
825	1 hr.	Solidified liquid (α)
	2. β-Bi_2O_3	
300	1 month	β
345	1 month	$\beta + \alpha$
380	1 month	α
500	1 month	α
585	1 day	α
650	5 min.	α
705	1.5 min.	α
710	10 min.	β
720	10 min.	β
740	5 min.	β
755	5 min.	β
765	5 min.	β
770	5 min.	β
790	5 min.	β
800	2 min.–18 hrs.	β
810	10 min.	β
825	1 hr.	solidified liquid (α)
	3. γ-Bi_2O_3	
390	1 month	γ
500	1 month	γ
600	6 days	α
650	5–10 min.	α
675	7 min.	α
705	5 min.	α
740	10 min.	β
760	5 min.	β
800	5–10 min.	β
825	1 hr.	solidified liquid (α)

[a] Microscopic examination kindly conducted by Dr. Clifford Frondel, Department of Mineralogy and Petrography, Harvard University.

The data indicate that both β-Bi_2O_3 and γ-Bi_2O_3 are unstable with respect to the α-form at temperatures up to 710°, the rate of conversion being very low at temperatures below about 350° in the former case and below about 550° in the latter instance. Between 710° and the melting point of the β-form (which is the same as the melting point of α-Bi_2O_3 within the large experimental error) β-Bi_2O_3 is apparently the stable phase, γ-Bi_2O_3 and α-Bi_2O_3 both reverting to the β-form, the former rapidly and the latter most sluggishly.

Stability Relationships from Conversions in Solvents and Solubility Data.—To determine the relative stability of the α, β, and γ forms at 25 and 100°, use was made of the accelerating action of a solvent in converting unstable phases to the stable modification. The solvent selected for this purpose was 2 N sodium hydroxide, inasmuch as the work of Knox[9] and Moser[10] has shown that this base dissolves appreciable quantities of Bi_2O_3 and $Bi(OH)_3$ at 25 and 100°, and as moderate concentrations of common acids and salts were found to convert Bi_2O_3 to basic salts, whereas Bi_2O_3 was found to dissolve in NaOH without change of the solid phase to another chemical species.

Samples of α-, β- and γ-Bi_2O_3 were allowed to stand in contact with 2 N sodium hydroxide in closed platinum crucibles maintained at 100° for fifteen to eighteen hours. Under this treatment the α-Bi_2O_3 remained unchanged, β-Bi_2O_3 was completely changed to the α-form, and the γ-variety was largely converted to the α-form. Hence, both the β and γ forms are unstable with respect to α-Bi_2O_3 at 100°.

Likewise, samples of α- and β-Bi_2O_3 were covered with 2 N sodium hydroxide and rotated in a thermostat at 25.0° for a period of two weeks. At the end of this time the solid phases were examined and both were found to consist of the α-form. It was found possible to repeat this experiment using a solution of only 0.1 N barium hydroxide in place of the sodium hydroxide. Hence, β-Bi_2O_3 is unstable with respect to α-Bi_2O_3 at 25°. However, γ-Bi_2O_3, on subjection to identical treatment, remained unchanged. It therefore became necessary to obtain solubility data at 25° on α- and γ-Bi_2O_3 in order to determine their relative stability at this temperature. The calculation of the difference in free energy content of both phases entails also a knowledge of the molecular species present in solution. This can be accomplished by measurements of the solubility of Bi_2O_3 in sodium hydroxide as a function of the sodium hydroxide concentration. The data of Knox cover a wide range of sodium hydroxide concentrations in large steps; hence it was deemed

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(9) J. Knox, *J. Chem. Soc.*, **95**, 1760 (1909).

(10) L. Moser, *Z. anorg. allgem. Chem.*, **61**, 386 (1909).

advisable to obtain further data near the concentration at which the solubility of both forms was to be compared.

Samples of the Bi_2O_3 phases were covered with sodium hydroxide solution in Pyrex glass bottles[11] and were rotated in a thermostat at 25.0 ± 0.1° for two weeks. At the end of this time the saturated solutions were decanted through fine, sintered glass filters, and measured volumes of the filtrates were analyzed for OH^- concentration by titration against standard hydrochloric acid and for bismuth content by colorimetric means after developing a color with potassium iodide in dilute nitric acid solution. That equilibrium had been attained within this time was assured by covering the solid phases with the unused portion of the filtrates and rotating at 25.0° for an additional nine days and again analyzing, and also by approaching equilibrium from the supersaturation side in the case of one sample. The data so obtained are shown in Table III.

TABLE III

SOLUBILITY OF Bi_2O_3 AS FUNCTION OF NaOH CONCENTRATION

Solid phase	Normality of NaOH	Solubility expressed as g. Bi_2O_3/l. soln.	No. of detns.	$\left[K = \frac{(BiO_2^-)}{(OH^-)} 10^6\right]$
α-Bi_2O_3	0.50	0.0063 ± 0.0003	2	5.4
α-Bi_2O_3	0.99	.012 ± .001	2	5.2
α-Bi_2O_3	1.41	.016 ± .001	4	4.9
α-Bi_2O_3	1.97	.023 ± .001	5	5.0
α-Bi_2O_3	2.46	.0290 ± .0005	2	5.1
γ-Bi_2O_3	1.42	.0190 ± .0005	2	...

The solubility data on the α-phase can be considered to be in agreement with those of Knox[9] at least at the lower concentrations of sodium hydroxide, within the sum of the experimental errors of both sets of results. These data can best be explained by assuming that the reaction $Bi_2O_3 + 2NaOH = 2NaBiO_2 + H_2O$ occurs, whence from the law of mass action $(BiO_2)^-/(OH)^- = K$. The constancy of K can be seen by reference to the last column of Table III.

γ-Bi_2O_3 appears to be slightly more soluble than α-Bi_2O_3 at 25° and is therefore to be regarded as an unstable form at this temperature. The value of the free energy change for the transition $\gamma\text{-}Bi_2O_3 \rightarrow \alpha\text{-}Bi_2O_3$ at 25° is given by $2RT \ln \left(\frac{0.019}{0.016}\right) = 200 \pm 80$ cal./mole Bi_2O_3.

Transition Temperatures from Cooling Curve Experiments.—An attempt was made to repeat the cooling curve work of Guertler.[4] Since the kind of crucible employed in his work was not stated, and since bismuth oxide is known to be very corrosive in the liquid state, samples of the oxide were fused in a number of different kinds of crucibles for from fifteen minutes to several hours and the fusion products analyzed for the presence of contaminating crucible materials. The crucible materials included graphite, Ag, MgO, Ni, ZrO_2, SiO_2, porcelain. The experiments demonstrated that many common crucible materials react to a sufficient extent with molten bismuth oxide so that a cooling curve investigation conducted in them represents the cooling of a two-component system. Thus it becomes possible in such cases for a liquid phase to exist well below the melting point of pure bismuth oxide. In fact, samples of bismuth oxide placed in nickel, magnesia, and silver vessels maintained at 50–100° below the melting point of Bi_2O_3 for a long enough period of time to ensure contamination all gave rise to liquid phases. The solidification of the liquid would give rise to pronounced heat effects which might erroneously be interpreted as indicative of solid state transitions.

Moreover, there is reason to doubt that a transition temperature in the solid state could be detected by means of a cooling curve conducted on the molten oxide. It was confirmed that the product obtained on cooling a melt of bismuth oxide is the monoclinic phase. Any possible effect of the crucible was avoided in this instance by directing a tiny flame on a pile of the oxide powder and fusing a small quantity to form a button, and noting that the monoclinic form resulted. The rate of cooling was varied widely, in one case, by water-quenching the melt, and in another, by cooling the melt slowly, over a period of five to six hours; and in every case the α-form resulted. It has also been shown (see Table II) that the monoclinic form, once produced, cannot thermally be converted to any other form at any temperature up to the melting point within a day.

Furthermore, there can be no question of a very rapid transition of the high temperature form to the monoclinic, a transformation which cannot be suppressed even by quenching (as Guertler suggested), inasmuch as it is possible to cool β-Bi_2O_3 from 800° to room temperature by water-quenching without the occurrence of a change in phase.

Since the monoclinic phase is always produced by cooling molten Bi_2O_3, either rapidly or slowly,

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(11) The same results also were obtained in platinum and nickel vessels.

and since the monoclinic phase cannot be thermally converted to any other phase at any temperature below the melting point within a reasonable period of time, it is hardly to be expected that a transition temperature between the various forms of Bi_2O_3 could be detected by means of the standard cooling curve technique.

Impure "Bismuth Oxides."—Products whose X-ray photographs consisted only of lines of a body-centered cubic phase with a lattice constant, $a_0 = 10.09$ Å., independent of composition within the limits cited below, were prepared in the following ways: (1) fusion of bismuth oxide in a porcelain crucible at 875° for ten minutes; (2) fusion by application of a flame to a pile of bismuth oxide mixed with silica corresponding in composition to from 8 to 35 mole % SiO_2; (3) treatment of a Bi_2O_3–SiO_2 mixture containing 14 mole % SiO_2 with $2N$ sodium hydroxide in platinum at 100° for forty-eight hours.

Products corresponding to the "simple cubic form"[12] described by Sillén[6] were obtained as follows: (1) Fusion of Bi_2O_3 in a silica crucible at 875° for fifteen minutes followed by water quenching. The thermally unstable product contained 18 mole per cent. SiO_2 and longer periods of fusion resulted in the destruction of the crucible. (2) Fusion of Bi_2O_3 in a porcelain crucible at 875° for thirty minutes followed by water quenching. (3) Fusion of Bi_2O_3 in porcelain at 875° for two hours followed by water quenching and subsequent crystallizing of the amorphous product by heating to 700° for thirty minutes. X-Ray photographs of the products showed lines only of a face-centered cubic phase possessing a lattice constant $a_0 = 5.525$ Å. in every case.

It seems unlikely from the methods of preparation described above that a phase of essentially the composition Bi_2O_3 could result in any of these cases. Therefore, the previous consideration of such phases as polymorphic forms of Bi_2O_3, without supporting chemical evidence for the purity of the Bi_2O_3 samples, becomes unjustifiable.

Discussion

Pure bismuth trioxide has been found to crystallize in three forms—the commonly occurring α variety; the β phase, first prepared by Sillén; and a new phase, γ, not previously reported. It has been demonstrated that the α-form represents the stable modification between 25 and 710°, above which temperature the β-phase is stable until its melting point is reached. This verifies the assumptions made by Sillén with respect to the relative stability of the α- and β-phases, assumptions which were based mainly on the fact that β-Bi_2O_3 was prepared by a high temperature process followed by rapid cooling. No region of stability between 25° and the melting point of the β-variety has been found for the γ-phase. Whether this form is truly monotropic, or else the stable variety at some temperature below 25° might be ascertained by the accurate determination of the solubilities of both α- and γ-Bi_2O_3 as a function of temperature.

X-Ray data obtained from powder photographs of α, β, and both impure "bismuth oxide" phases are essentially in agreement with those reported by Sillén.[6] In addition, the γ-form has been found to be body-centered cubic with a lattice constant of 10.245 Å.

It has been concluded that information concerning transitions occurring in the solid state cannot be obtained by applying the standard cooling curve technique to bismuth oxide. This conclusion invalidates the work of Guertler, but is in agreement with the more recent findings of Belladen, who was unable to find a significant break in the cooling curve of Bi_2O_3 below the melting point. Another interpretation of Guertler's data has been offered, namely, that contamination of the molten oxide by its containing vessel (the composition of which was not stated) led to a two-component system. Indeed, the shape of the temperature–time curve obtained by him conforms in general with that to be expected on rapidly cooling the melt of a simple eutectic mixture containing a small percentage of one of the components; whereas the conclusions drawn by him from this curve imply that the heat effect attending a transition of one solid phase to another is many times as great as that occurring on solidification of the liquid, a most unusual state of affairs.

The impure "body-centered cubic" and "simple cubic" forms previously reported have been indicated to represent phases of composition materially differing from pure Bi_2O_3. In the former case, since the structure is so similar to a pure form of Bi_2O_3, the γ form, it might at first be inferred that the impure phase represents a solid solution

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[12] The designation "simple cubic" arose from a complete structure determination by Sillén of a sample prepared by fusion in porcelain based, however, upon the assumption that the constitution of the phase could be represented by the formula Bi_2O_3.

of SiO_2 (or other oxides) in Bi_2O_3. However, the lattice constant of γ-Bi_2O_3 (10.245 Å.) was found to be larger than that of the impure phase (10.090 Å.) formed by fusing mixtures of Bi_2O_3 and SiO_2. Hence, the latter phase would have to represent a substitutional type of solid solution—if it were a solid solution at all—inasmuch as in an interstitial type of solid solution "solute atoms are crammed in between the solvent atoms and as a result always cause an enlargement of the unit cell regardless of the size of solute atoms."[13] Moreover, the possibility of this phase representing a substitutional solid solution is rendered unlikely by the very unfavorable size factor for the replacement of Bi by Si atoms and by the lack of variation in lattice constant with composition exhibited by the Bi_2O_3–SiO_2 fusion products. The possibility that this phase represents a compound between Bi_2O_3 and SiO_2 (or other oxides) seems more favorable and a likely composition of such a compound, $Me^{III}{}_2Bi_{24}O_{39}$ or $Me^{IV}{}_2Bi_{24}O_{40}$, has been advanced by Sillén,[5] based mainly upon structural considerations. The most direct attack upon the problem would be a determination of the equilibrium temperature-composition diagram for the Bi_2O_3–SiO_2 system, but this awaits the availability of a crucible material which will not be attacked by molten Bi_2O_3 at temperatures above 800°.

The "simple cubic form" is probably an intermediate phase in the multi-component system formed by bismuth oxide and porcelain.

Summary

1. Pure Bi_2O_3 has been found to crystallize in at least three forms.
2. The tetragonal, β, form has been found to represent a high temperature modification with respect to the monoclinic, α, variety, and the transition temperature has been determined as 710°.
3. A new form of Bi_2O_3 (γ-Bi_2O_3) has been discovered and found to be body-centered cubic; a_0 = 10.245 Å. No region of stability between 25° and the melting point has been found for this phase.
4. A new method of preparing β-Bi_2O_3 and a method of preparing γ-Bi_2O_3 have been described.
5. Evidence has been cited to indicate that it is hardly to be expected that the cooling curve technique applied to molten Bi_2O_3 could furnish any indication of a transition occurring in the solid state. A more likely interpretation of Guertler's cooling curve evidence for the existence of two polymorphic forms of Bi_2O_3 with a transition temperature at 704° has been proposed, namely, that contamination of the molten oxide by the containing vessel led to a two-component system.
6. The impure "body-centered cubic" and "simple cubic" phases previously reported have been indicated to be of substantially different composition from that represented by the formula Bi_2O_3.
7. The solubility of Bi_2O_3 in NaOH has been found to be proportional to the NaOH concentration up to 2.46 *N*, from which the molecular species present in the solution has been shown to be $NaBiO_2$.

Cambridge, Massachusetts

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[13] I. M. Kolthoff and D. R. Moltzau, *Chem. Reviews*, **17**, 316 (1935).

[Contribution from the Department of Chemistry of Duke University]

Complex Ions. IV. Monammine-silver Ion

By W. C. Vosburgh and Ruth Stockdale McClure

In the determination of the instability constant of the diammine silver ion Randall and Halford[1] and Derr, Stockdale and Vosburgh[2] assumed that the diammine ion is the only complex ion formed when silver chloride and silver iodate, respectively, are dissolved in ammonia solutions. The constants found in the two investigations agreed well and were consistent with the assumption. Bjerrum[3] has found evidence that a monammine exists.

Bjerrum's method involved a fairly large uncertainty in the determination of the stability constants of the silver-ammonia ions. It was thought desirable, therefore, to check his results for the monammine ion by a different method, and some solubility determinations have been made

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[1] Randall and Halford, This Journal, **52**, 178 (1930).

[2] Derr, Stockdale and Vosburgh, *ibid.*, **63**, 2670 (1941).

[3] Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941, p. 130.