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The Polymorphism of Arsenious Oxide[1]

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Known Phases and their Structural Relations

The dimorphism of arsenious oxide was established by Wöhler's[2] discovery of monoclinic crystals of this substance, the octahedral variety having been known since early times.[3] Although the structural relations of the two crystalline modifications are as yet incompletely known, it may be assumed that these structures are very dissimilar by analogy with the forms of antimony trioxide.[4a,b] The structure of the octahedral phase has been found[4a] to be a molecular one, discrete clusters of As_4O_6 being arranged in the diamond-type packing. Work on the crystal structure of the monoclinic phase is in progress.[5]

Besides the two crystalline phases, a third form of arsenious oxide has long been known,[3] namely, the glassy variety or supercooled liquid phase, which devitrifies rather easily even at ordinary temperature to form the octahedral modification. From the ease of devitrification a close relation between the liquid structure and that of the octahedral form may be inferred.

In addition to the above phases, Smits and Beljaars[6] have announced the discovery of three new modifications of arsenic trioxide. These new polymorphic forms were not isolated, the evidence for their existence being based solely on vapor pressure measurements.

Stability Relations

Prior to the work of Welch and Duschak,[7] the prevailing version of the phase diagram of the system As_4O_6 was completely erroneous, being based essentially on the fact that the octahedral form of the oxide was of more common occurrence than the monoclinic form, and upon a loose interpretation of an experiment by Debray.[8]

By direct observation of the transition octahedral $As_4O_6 \rightarrow$ monoclinic As_4O_6, Welch and Duschak[7] demonstrated qualitatively that the latter form was the stable one at all temperatures from 100° up to its melting point, 315°. Due to the low rate of reaction at lower temperatures, no transformation of either form into the other was observed by these investigators below 100°. They conclude: "In fact, there is nothing to show that the transformation from octahedral to monoclinic is not monotropic, that is, irreversible." In spite of the thermodynamic stability of monoclinic As_4O_6 over the above-mentioned wide temperature range, Welch and Duschak demonstrated that (1) the transformation octahedral → monoclinic is extremely slow at all temperatures; (2) it is remarkably accelerated by water vapor or solvents; (3) condensation of the dry vapor below 250° produces the octahedral phase while condensation above 250° generally produces the glassy phase in preference to the monoclinic form.

The system As_4O_6 was further clarified by Rushton and Daniels[9] by means of a study of the vapor pressures of the octahedral and liquid oxide. They corroborated Welch and Duschak's value of the melting point of the monoclinic form, and set 275° as the melting point of the octahedral form under its own vapor pressure.

Until the work of Smits and Beljaars,[6] the only remaining problems concerning the phase diagram of the system As_4O_6 seemed to be: (1) determination of the monotropic or enantiotropic nature of the octahedral → monoclinic transition, and (2) measurement of the transition temperature ($t < 100°$) if the latter type of transition was found to be correct. By extrapolation of the vapor pressure–temperature curves of both forms of the oxide, however, these investigators found an enantiotropic transition occurring at 233.5°. Having prepared their monoclinic sample by transformation from the octahedral form at 218°, Smits and Beljaars assumed a slight departure of

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

(2) F. Wöhler, *Pogg. Ann.*, **26**, 177 (1832).

(3) J. W. Mellor, "Treatise on Inorganic and Theoretical Chemistry," Longmans Green and Co., New York, N. Y., Vol. IX, 1929, pp. 90 ff.

(4)(a) R. M. Bozorth, THIS JOURNAL, **45**, 1621 (1923); (b) M. J. Buerger and S. B. Hendricks, *Z. Krist.*, **A98**, 1 (1937).

(5) Private communication from Professor M. J. Buerger, Dept. of Geology, Massachusetts Institute of Technology.

(6) Smits and Beljaars, *Proc. Kon. Akad. Wetensch. Amst.*, **34**, 1141 and 1318 (1931).

(7) H. V. Welch and L. H. Duschak, Bur. Mines Tech. Paper 81, 1917, Washington, D. C.

(8) H. Debray, *Bull. Soc. Chim.*, [2] **2**, 9 (1864).

(9) E. R. Rushton and F. Daniels, THIS JOURNAL, **48**, 384 (1926).

their log p–$(1/T)$ curves from linearity, and set the triple-point octahedral–monoclinic–vapor provisionally at 200° and 0.26 mm.

Because of the complete conflict between the conclusions of Smits and Beljaars and those of the earlier investigators, it was thought worth while to reinvestigate the system. For this purpose studies of both the solubility–temperature and vapor pressure–temperature relations were carried out.

Preparation of Materials

Octahedral Form.—U. S. P. arsenious oxide was recrystallized from hydrochloric acid solution by the procedure of Anderson and Story[10] to effect purification and to insure complete conversion to the isometric phase.

Monoclinic Form.—Samples of the octahedral form were heated in sealed tubes for forty-eight hours at 250° in the presence of saturated water vapor.

Microscopic and X-ray examination established the homogeneity and crystallographic identity of these phases. Chemical and spectrographic analyses of the products showed the major impurity to be Sb (0.002–0.005%).

Solubility Determinations

The solubilities of the two modifications of arsenious oxide in approximately 1 M HCl (actually 37.66 g. of HCl/100 g. of H_2O) were determined at 2, 15, 25 and 35°. 1 M HCl was chosen as the solvent rather than pure water since the attainment of equilibrium is greatly accelerated by hydrogen ion, yet the molecular species in such a solution is the same as that in a water solution of the oxide, namely, $HAsO_2$, or $HAsO_2 \cdot xH_2O$.[10,11,12,13,14] In dealing with the monoclinic oxide the approach to equilibrium from the supersaturated side is unreliable, and may even be impossible, due to the great facility with which the octahedral form precipitates out on cooling a saturated aqueous solution. For this reason, in the present work equilibrium was approached from the undersaturated side only.

Samples were withdrawn from the thermostat after a minimum rotation time of forty-eight hours in all except the 2° runs, where the minimum was extended to seventy-two hours. Samples taken after a further twenty-four-hour interval in all cases checked the original analyses. The arsenic content of the solutions was determined iodometrically.

The experimental results, summarized in Table I, include measurements of Mallinckrodt reagent arsenious oxide, which had been found to be identical chemically and crystallographically with the authors' octahedral preparation. Each value found in the table is the average of six to ten determinations.

TABLE I

SOLUBILITY OF OCTAHEDRAL AND MONOCLINIC ARSENIC TRIOXIDE IN HCl SOLUTION

(37.66 g. HCl/100 g. H_2O)

Temp., °C., ±0.05	Octahedral form G. As_4O_6/100 g. solvent Found	Calcd.	Monoclinic Form G. As_4O_6/100 g. solvent Found	Calcd.
35.00	2.199 ± 0.007	2.199	2.064 ± 0.004	2.066
25.00	1.738 ± .006	1.737	1.653 ± .006	1.651
15.00	1.351 ± .009	1.352	1.295 ± .007	1.300
2.00	0.948 ± .003	0.948	0.931 ± .005	0.927

Discussion of Results

From the solubility data the qualitative conclusion can be drawn immediately that the monoclinic phase of arsenic trioxide is the thermodynamically stable phase down to temperatures as low as 2°. Whether or not the cubic form is monotropic is a question which requires a quantitative treatment of the data.

At the transition temperature between two enantiotropic forms their free energies are equal, hence their vapor pressures and solubilities in any solvent are equal. This temperature is found from the extrapolated solubility curves of the two forms. For this extrapolation the experimental results are best put in the form

$$\log_{10} S_{\text{octahedral}} = -939.5/T + 3.3928 \qquad (1a)$$

$$\log_{10} S_{\text{monoclinic}} = -894.6/T + 3.2200 \qquad (1b)$$

where S is the solubility in g. of oxide per 100 g. of solvent, and T is the absolute temperature. The agreement between the experimental values and those calculated from equations (1a) and (1b) is illustrated in Table I and in Fig. 1. The intersection of the two curves is found either graphically or analytically at $1/T = 0.003845$, whence $T = 260°$ Abs., or -13°C. Representing the reaction of solution of arsenious oxide in dilute acid by the equation

$$As_4O_6 \text{ (solid)} + 2H_2O \text{ (in 1 } M \text{ HCl)} \longrightarrow 4HAsO_2 \text{ (satd. soln. in 1 } M \text{ HCl)} \qquad (2)$$

we may write the equilibrium constant for the reaction as

$$K_T = [HAsO_2]^4 \qquad (3)$$

assuming the activity of the H_2O constant. Substituting this expression in the van't Hoff equation and transforming

$$\log_{10} S = -\Delta H/4(2.303)RT + \text{constant} \qquad (4)$$

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(10) F. Anderson and L. Story, THIS JOURNAL, **45**, 1102 (1923).

(11) Wood, *J. Chem. Soc.*, **93**, 413 (1908).

(12) K. Drucker, *Z. physik. Chem.*, **36**, 173 (1901).

(13) Roth and Schwarz, *Ber.*, **59B**, 338 (1926).

(14) J. Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882, Bd. I, p. 200.

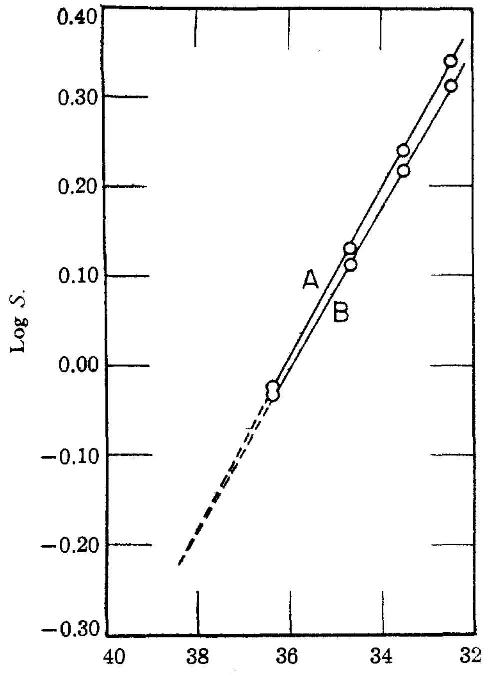

Fig. 1.—A. octahedral form: B. monoclinic form.

assuming ΔH of solution to be constant and replacing the activity of the solute by its concentration as a first approximation. This last equation is identical in form with the empirical equations (1a) and (1b), which makes possible the calculation of the heats of solution of the two forms of arsenious oxide in 1 M HCl.

For octahedral As_4O_6:

ΔH of solution = 17,200 ± 50 cal./mole.

For monoclinic As_4O_6:

ΔH of solution = 16,380 ± 50 cal./mole.

The heat of transition for the reaction octahedral → monoclinic As_4O_6 is then found by difference to be 820 ± 100 cal./mole.

Below the freezing point of the solution of arsenious oxide in 1 M HCl equations (1a) and (1b) obviously lose physical significance. If it seems objectionable to extrapolate these equations into a region where the solvent cannot exist, it need only be pointed out that practically the same values of ΔH are obtained if the calculations are made from the standpoint of free energy, which is independent of the characteristics of the solvent.

As a check on the solubility data and as corroboration of the simplifying assumptions made in the calculations based thereupon, an indirect calorimetric determination was made of the heat of transformation of octahedral to monoclinic arsenious oxide. The calorimeter of Conn, Kistiakowsky and Roberts[15] was employed, the technique of its use with solid reagents being described in a separate publication.[16] Three to four grams of the oxides, sealed into special Pyrex ampoules, were placed in the calorimeter with 1030 g. of approximately 4 N NaOH solution. The reactions were complete in fifty-six minutes after the breaking of the ampoules. The mean temperature of the determinations was 30.5°. The calorimeter was used as a single calorimeter, the usual corrections for heat leak, heat of stirring, and heat of breaking of the sample container being made. The estimated accuracy was 0.5%. The heats evolved by the solution of the two forms of the oxide under the stated conditions were found to be: monoclinic form, 70.53 (±0.35) cal./g.; octahedral form, 67.86 (±0.34) cal./g. The heat absorbed by transition of octahedral to monoclinic As_4O_6 is thus found to be 2.67 (±0.69) cal./g., or 1057 (±230) cal./mole, in good agreement with the value of 820 cal./mole computed from the solubility data.

The conclusion seems justified that the monoclinic and octahedral phases are enantiotropically related with a transition temperature in the nieghborhood of −13°. As with antimony trioxide, the isometric form is stable at low temperatures, the anisometric form stable at higher temperatures.

Experimental Part

Vapor Pressure Determinations

The vapor pressures of both octahedral and monoclinic arsenious oxide were measured using the gas current saturation method.

The apparatus used for the determinations was a modification of that employed by Welch and Duschak.[7] with the following exceptions. The air was dried by passage through calcium chloride towers prior to its entrance into the saturator. Similar drying towers were likewise placed between the saturator and the aspirator. to prevent back diffusion of water vapor from the latter. Mercury manometers were inserted at proper points to allow correction for pressure drops due to resistance to air flow through the saturator and calcium chloride tubes. At the rates of flow used (maximum of 200 ml. air per hour). the pressure drops observed were of the order of a few millimeters of mercury. The essential features of the saturator are shown in Fig. 2. The tube C. fitting closely in B. served as a collector of the As_4O_6 carried over by the gas stream. the oxide condensing on the walls in octahedral crystals. Tube C. joined to B and to the aspirating device by short lengths of rubber tubing. could be removed without dis-

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[15] J. Conn, G. Kistiakowsky and R. Roberts, THIS JOURNAL, 62, 1895 (1940).

[16] Conn, Kistiakowsky, Roberts and Smith, *ibid.*, 64, 1747 (1942).

turbing the rest of the apparatus. The condensate was dissolved out with sodium hydroxide solution and the arsenic determined iodometrically. The saturator was kept at the desired temperatures by immersion in the vapor bath D. different temperatures being obtained by the use of various organic liquids. Temperatures were measured with a chromel–alumel thermocouple T and a potentiometer, and are known to ±1°.

When it became necessary to cool down the saturator in the runs made with the monoclinic phase, contamination of the main charge with an octahedral condensate was prevented by drawing a moderately fast stream of air through the apparatus while it cooled. The oxide vapor carried over by the air then condensed as usual in tube C and was removed.

In the calculations the molecular species in the vapor was assumed to be As_4O_6, on the basis of the molecular weight determinations of Biltz.[17] A summary of the results is given in Table II.

TABLE II

VAPOR PRESSURE OF ARSENIC TRIOXIDE

Monclinic			Octahedral		
t(°C.)	Runs	Av. vapor pres., mm.	t(°C.)	Runs	Av. vapor pres., mm.
...	..	....	171	3	0.118 ± 0.007
199	4	0.143 ± 0.026	199	2	0.54 ± .01
231	4	1.31 ± .05	231	5	3.44 ± .11
257	4	6.88 ± .27	257	3	13.60 ± .15
275	4	17.00 ± .56	275	5	26.7 ± .6
297	5	37.6 ± 2.1	...	..	.....

Discussion of Results

From the low value of the heat of transition of octahedral to monoclinic As_4O_6 reported earlier in this paper, it may be inferred that the log p *vs.* $1/T$ curves of both modifications will have very nearly the same slope. Even neglecting the variation of the heat of sublimation with temperature, it is not to be expected under these conditions that the present vapor pressure data—requiring as they would an extrapolation of some two hundred degrees—should yield confirmation of the transition temperature found from the solubility measurements previously described. Indeed the uncertainty in the literature as to the heat of sublimation of the octahedral form alone is greater than the heat of transition found in the present work. Thus Welch and Duschak[7] give as ΔH of sublimation 28,000 cal./As_4O_6 in the neighborhood of 120° and 26,500 cal. near 260°; Rushton and Daniels[9] give 30,550 cal. over the range of 250–300°[18]; and Smits and Beljaars[6] give 29,830 cal. over the same range. The average value of this thermal quantity calculated from the present data is 27,100 cal. In the lower temperature ranges, the pressures calculated from the static measurements of Rushton and Daniels and of Smits and Beljaars differ by several hundred per cent. from those found directly by Welch and Duschak, using the gas saturation method, the latter giving higher values.

The present vapor pressure data are adequate, however, to demonstrate that there is no octahedral–monoclinic transition temperature in the temperature region above 200° as claimed by Smits and Beljaars.[6] This result is independent of the assumptions involved in the gas-saturation method. The results of the above workers are apparently due to the lack of precautions to prevent the formation of octahedral arsenic trioxide during measurements on the monoclinic phase. Their preliminary 300° heat treatment of the monoclinic phase *in situ* prior to the sealing off of the vapor pressure apparatus, probably followed by cooling of the vessel, is a procedure which would cause introduction of the octahedral contaminant, *this form crystallizing from the vapor, even on slow cooling, in the presence of seed crystals of the monoclinic phase.* The check results reported on approaching the monoclinic–vapor equilibrium from both sides are thus further indications of the presence of the octahedral modification. In the present measurements, contamination of the monoclinic phase by an octahedral condensate was carefully avoided by the technique already described.

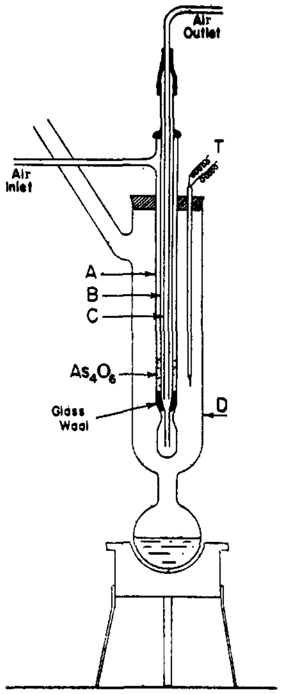

Fig. 2.

The Transition of Octahedral As_4O_6 to Monoclinic As_4O_6.—It has been demonatrated above that over the range from −13° to the melting point of the monoclinic phase, the cubic form is thermodynamically unstable with respect to the former. As is the case most frequently in the polymorphism of inorganic substances, this fact has no bearing at all on the stability of the cubic form in the ordinary sense of the word. In fact, natural arsenolite remains untransformed indefinitely.

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[17] H. Biltz, *Z. physik. Chem.*, **19**, 417 (1896).

[18] The octahedral phase can be superheated.

Striking examples of the sluggishness of the transformation even at high temperatures are cited by Welch and Duschak,[7] who also demonstrated the tremendous accelerating effect of water vapor on this reaction.

In order to gain some insight into the transition phenomenon, in the present work finely ground octahedral As_4O_6 was heated at 180 ± 5° for thirty-six to forty hours in sealed Pyrex capillary tubes in the presence of the saturated vapors of various substances. Runs were made with water, nitrobenzene, toluene, bromobenzene, glacial acetic acid, acetic anhydride, *n*-butyl alcohol, air, carbon tetrachloride, cyclohexane, *n*-heptane, benzene and iodine. Direct contact of the oxide with the liquid was avoided.

Only in the presence of water vapor was any sign of transformation to the monoclinic phase observed. With water vapor the transformation was complete under the stated conditions of temperature and time. No attempt was made to see if this transition was complete in less than thirty-six hours, but it is probable that such was the case.

These experiments demonstrate that the "catalysis" of the cubic → monoclinic transformation is not due to the high pressure exerted by the saturated water vapor on the solid oxide phase, for among the substances tried are some whose vapor pressures at 180° are as great as or even greater than that of water at this temperature.

The experiments likewise showed that there is no obvious single property of the water molecule that is responsible for its catalytic effect. Both molecules with and without dipole moment gave the same negative effect. Both alcoholic and acidic OH groups were ineffective as demonstrated by the experiments with *n*-butyl alcohol and glacial acetic acid.

A helpful, although admittedly qualitative and incomplete picture of the kinetics of the octahedral → monoclinic transition, may be constructed from the following considerations.

Assuming, by analogy with antimony trioxide,[3,4] that the structural unit making up the octahedral phase is fundamentally different from that constituting the monoclinic phase, the phase change under discussion would be hard to effect or sluggish, in common with most transitions requiring the breaking of primary valence bonds.[19,20] The bonds most easily broken in the thermal disintegration of the octahedral form are the weak intermolecular bonds between the As_4O_6 groups, thus giving rise to the gas phase. In the gas phase the preponderant molecular species is again the As_4O_6 unit,[17] which is very stable as evidenced by its existence as such up to temperatures of 800°. At temperatures much lower than 800° dissociation into As_2O_3 or other molecular species is inappreciable. No ready mechanism for the transformation then exists, even via the gas phase. Water vapor apparently acts in some specific way to disrupt the stable As_4O_6 groups, after which aggregation into the stable monoclinic structure becomes possible.

The same considerations, applied to the problem of the generation of unstable forms, are illustrations of the viewpoint of Niggli,[21a] later independently announced and further elaborated by Bloom,[21b] that in deciding which of the two crystalline structures will be generated, the controlling factor is the relation of the structural configuration in the antecedent phase to the structural units in the possible polymorphic forms. If the relation is very close for one crystal structure but not for the other, the probability of the precipitation of the first form is very high, and of the second form proportionally low.

Other Solid Phases of Arsenic Trioxide.—Smits and Beljaars[6] have reported what they consider to be three new forms of arsenic trioxide. In all cases their criterion for the existence of a new phase is its vapor pressure–temperature curve, measured by a static method.

The first of these new forms, designated as "γ"-As_4O_6, was obtained by annealing the octahedral phase at a temperature slightly above 258° for an unstated length of time ("a very long time"). The vapor pressure curve of this phase intersects that of the liquid phase near 289°, a temperature intermediate between the melting points of the octahedral and monoclinic forms. The possibility seems to have been overlooked by these authors that prolonged heating of the octahedral form may very slowly give rise to nuclei of the monoclinic phase. A difference in the rate of volatilization of the octahedral variety and the rate of condensation of the vapor into the monoclinic form might suffice to maintain a system in dynamic equilibrium whose measured pressures were taken by Smits and Beljaars as proof of the ex-

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(19) P. Niggli, "Lehrbuch der Mineralogie," Berlin, 1924, Vol. I, p. 530.

(20) M. J. Buerger and M. C. Bloom, *Z. Krist.*, **A96**, 182 (1937).

(21) (a) P. Niggli, *op. cit.*, p. 494; (b) M. C. Bloom, *Am. Mineral.*, **24**, 281 (1939).

istence of a new phase. This possibility is further supported by their statement that in order to measure the vapor pressures of the new form, at other temperatures, the temperature must be raised "*extremely slowly*." According to Tammann and Bätz,[22] such a dynamic equilibrium seems to be the most reasonable explanation of the vapor pressure values obtained with superheated octahedral As_4O_6 by Smits and Beljaars[6] and Rushton and Daniels,[9] the equilibrium in this case being established between the octahedral and liquid phases.

Several attempts were made in the course of the present investigation to prepare the "γ"-phase by heating octahedral As_4O_6 at 262 ± 2° in evacuated sealed tubes. The duration of the longest experiment was fifty hours, after which time microscopic and X-ray examination showed the presence of the octahedral phase only.

Smits and Beljaars further state that the distillate from the fractional sublimation of the monoclinic phase has an abnormally high vapor pressure (greater even than that of the octahedral or liquid phases) while the residue has a lower vapor pressure than the original monoclinic phase. This observation is cited in support of Smits'[6,23] theory of "pseudocomponents," which is in conflict with modern knowledge of the solid state.[20]

X-Ray and microscopic examination of the distillate and residue from the partial sublimation of monoclinic As_4O_6 performed in the present work showed the former to be identical with the ordinary octahedral form and the latter with the original monoclinic phase.

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Summary

1. The monoclinic form of arsenious oxide has been shown by solubility measurements to be thermodynamically stable with respect to the more common octahedral form at temperatures as low as 2°.

2. By calculations based upon the measured temperature dependence of the solubilities, it has been shown that an enantiotropic relation exists between the two forms, the transition temperature being approximately −13°.

3. The heat of solution of both forms of the oxide in 1 *M* hydrochloric acid and the latent heat of the transformation of octahedral As_4O_6 to the monoclinic form have been calculated from the above data.

4. The latent heat of this transformation has likewise been determined calorimetrically by measurement of the heats of solution of both forms in sodium hydroxide solution. The value so obtained has been found to be in good agreement with the calculated value.

5. The vapor pressures of the octahedral and monoclinic oxides have been measured, and the data obtained by previous investigators have been reviewed.

6. The vapors of several substances have been found ineffective for accelerating the transformation of octahedral to monoclinic As_4O_6 at 180°, while the effectiveness of water vapor at this temperature has been confirmed. A qualitative picture of the mechanism of the transition has been presented.

7. The preparation of three new forms of arsenious oxide, whose existence was assumed by previous investigators on the basis of vapor pressure measurements, was attempted without success. It has been shown by X-ray and crystallographic studies that only the well-known octahedral and monoclinic forms of the oxide resulted under the conditions prescribed by these workers.

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[22] G. Tammann and G. Bätz, *Z. anorg. Chem.*, **156**, 94 (1926).

[23] A. Smits, "The Theory of Allotropy," translated by J. S. Thomas, London, 1922.