PROGRESS IN
INORGANIC CHEMISTRY

EDITED BY
F. ALBERT COTTON
DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF
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MASSACHUSETTS

VOLUME 4

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PROGRESS IN
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Volume 4
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The Polymorphic Modifications of Arsenic Trioxide

BY K. A. BECKER, K. PLEETH, and I. N. STRANSKI,
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem,
and Max-Volmer-Institut der Technischen Universität, Berlin-Charlottenburg

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I. Introduction

The basis for related investigations on the modifications of arsenic trioxide and its behavior is provided by the following three rules:

1. The more symmetrical modification should be the more stable at higher temperatures.

2. Crystals can not be superheated above a transition point, especially above the melting point.

3. In accordance with the Ostwald Law of Stages, that modification which is stable at higher temperatures will usually have the greater nucleation frequency.
Considering Rule 1: It seems to be quite reasonable on reflection, that as the amplitude of vibration of the lattice components (in a crystal) increases, the asymmetry of the force field about them should gradually decrease. This makes it possible for the crystal units to adopt, at higher temperatures, a different arrangement, which must be more symmetrical.

Considering Rule 2: Tammann (1) is responsible for the experiment which shows that crystals cannot be superheated above the melting point. He devised it to illustrate the theory that at the melting point the whole of the crystal surface throughout the melt is moist. If this hypothesis holds, then the crystal must be in equilibrium with its vapor at the melting point, and it must also be surrounded with a relatively thick, semi-molten layer which is at a somewhat lower temperature. The crystal is not, therefore, in direct contact with the melt. As it is heated, the crystal surface passes first through a pre-molten state at a temperature lower than the melting point, finally melting to form part of the molten phase.

Later investigations gave disappointing results; even using simple crystals with atomic lattices the surfaces of the equilibrium form were only incompletely moistened by the crystals. This result was confirmed on theoretical grounds by Stranski (2). Even though the equilibrium surfaces concerned occupy the thickest planes, the forces between them and the liquid are not as strong as the corresponding forces within the liquid itself.

Nevertheless, Tammann’s theory (1), suitably modified by Stranski (2), can be assumed to hold. It turns out that the whole surface area of the crystal need not be completely moist. If only small areas of the crystal surface are moist (the equilibrium layers), then the more distant lattice neighbors and other adsorbed foreign atoms are also involved in layer regions with lattice disorders. The process of melting must begin with these isolated elements, and this has been confirmed in an experiment with single crystals of Gallium, carried out with especial care by Volmer and Schmidt (3).

Considering Rule 3: The Ostwald Law of Stages was derived by Stranski and Totomanow (4) from Volmer’s expression (8) for the nucleation frequency. One need only consider the exponential terms in the expression for the nucleation energy:

\[
\left( b \sigma^2 M^2 \right) / \left\{ \rho^2 k R^2 T^3 \left[ \ln \left( p_r / p_m \right) \right]^2 \right\}
\]
Considering the question of modifications which contain the same molecule, the only factors which change from one modification to another are $b$ (a trivial geometrical variable), $\sigma$ (the mean free specific surface energy), $\rho$ (the density of the condensed phase), and $\ln(p_r/p_s)$ (the relative supersaturation). If we limit our discussion to a narrow range of temperature about the transition point the influence of the $\ln(p_r/p_s)$ can be ignored. This leaves the fraction $\sigma^s/\rho^2$ for consideration. The variation of $\sigma$ with temperature is at least linear, and it therefore follows that the modification with the lower density (which, according to the law, is the more stable one at higher temperature) must have lower nucleation energy and thus greater nucleation frequency.

One should not overlook the fact that in the above argument it is implicitly assumed that the difference between the modifications concerned is merely one of rearranging the basic molecular units.

If these rules are applied to the naturally occurring forms of arsenic trioxide, arsenolite, and claudetite, the following exceptions are found:

1. Although arsenolite crystallizes in the cubic form and therefore has greater symmetry than claudetite, which is monoclinic, it is the latter which is more stable at higher temperatures.

2. Arsenolite can be superheated over the whole of the range in which claudetite is the more stable modification, and even beyond the melting points of the two forms.

3. It is known that the arsenolite lattice is made up from molecular $\text{As}_4\text{O}_6$ units containing normal valency links. Arsenolite is formed from the vapor phase, which contains $\text{As}_4\text{O}_6$ molecules almost exclusively up to $800^\circ\text{C}$, and, usually, when crystallization takes place from solutions. When the greater density of claudetite is considered, this behavior of arsenolite is seen to be a clear deviation from the third rule. It also shows, however, that the exceptional formation of nuclei of arsenolite is not confined to the neighborhood of the transition points.

The fact that the growth of a claudetite crystal from the gas phase necessitates a cleavage of an $\text{As}_4\text{O}_6$ molecule was taken as a basis for conjecture by Stranski, Korb, and Becker (5,6). The effect of the activated condensation was detected in following up this idea. Stranski and Wolff (7) first modified Volmer's expression (8) for the normal nucleation frequency from $I = B \exp (-A_s/kT)$ to $I = B$
The extra factor $e^{-\Delta/RT}$ represents the activation energy for splitting an As$_4$O$_6$ molecule.

II. The Structures of Arsenic Trioxide

The structure of arsenolite was first investigated in 1923 by Bozorth (9). He took an x-ray photograph of a single octahedral crystal with an x-ray photographic density of $\rho = 3.89$ g-cm$^{-2}$, and was able to assign to it a face-centered cubic lattice with a space group $O_h^7$-Fd3m. The unit cell has a lattice constant of $a = 11.07$ Å, and contains eight As$_4$O$_6$ molecules. The arsenic atoms occupy a set of 32 points having the position coordinate $x = -0.103$, and the oxygen atoms a set of 48 points with the coordinate $y = 0.175$. The most recent results are available in a paper by Almin and Westgren (10), who have made a new determination of the exact positions of the arsenic and oxygen atoms. The arsenolite lattice belongs to the D 61-type, which is related to the A 4-type of the diamond lattice. The arsenolite lattice is obtained by putting the center of gravity of the As$_4$O$_6$ molecule into the position of a carbon atom in the diamond lattice. The As$_4$O$_6$ molecules themselves consist of an octahedron of oxygen atoms containing a tetrahedron of arsenic atoms; the arsenic atoms occupy four of the octahedral faces. The distance within the molecule between arsenic atoms is 3.23 Å, oxygen atoms 2.73 Å, and the shortest arsenic-oxygen distance is 1.80 Å. The distances between the atoms of different molecules are greater than these, so that these units are defined unambiguously, and arsenolite therefore exists as a molecular lattice.

The first results of the determination of the structure of the monoclinic modification of arsenic trioxide, claudetite, were announced almost thirty years later. The data on the measurement of the unit cell and the space group were mentioned in a private, otherwise unpublished communication from Buerger to Palache for the survey in Dana's *System of Mineralogy*. The complete elucidation of the structure was published simultaneously by Frueh (11), and by Becker, Plieth, and Stranski (12). These results were in agreement. The crystals used in the latters' investigations were obtained by transition from arsenolite, and are almost completely identical with those oc-

ARSENIC TRIOXIDE

curring in nature. Contact pairing is usually observed in the (100) direction, but is also described as penetrating pairing. The crystal is characterized by its excellent cleavage along the (010) plane and its great flexibility. The monoclinic lattice found in a single crystal has the following measurements: \( a_1 = 5.25 \text{ Å} \); \( a_2 = 12.90 \text{ Å} \); \( a_3 = 4.53 \text{ Å} \); \( \alpha_2 = 93.9^\circ \).

The x-ray photographic density was \( \rho_r = 4.23 \text{ g cm}^{-2} \). The unit cell contains four \( \text{As}_2\text{O}_3 \) units, and claudetite crystallizes in the monoclinic space group \( C_{2h}^5 - P2_1/n \). The coordinates of all the atoms have been determined by the use of Patterson and Fourier Synthesis, and geometrical relationships, as follows:

\[
\begin{align*}
  x_{\text{As}} &= 0.335 & y_{\text{As}} &= 0.351 & z_{\text{As}} &= 0.026 \\
  x_{\text{As}} &= 0.250 & y_{\text{As}} &= 0.101 & z_{\text{As}} &= 0.020 \\
  x_{\text{O}} &= 0.432 & y_{\text{O}} &= 0.219 & z_{\text{O}} &= 0.949 \\
  x_{\text{O}} &= 0.452 & y_{\text{O}} &= 0.344 & z_{\text{O}} &= 0.411 \\
  x_{\text{O}} &= 0.631 & y_{\text{O}} &= 0.408 & z_{\text{O}} &= 0.925
\end{align*}
\]

Unlike the case of arsenolite, molecules as such do not exist in the monoclinic lattice. On the other hand, there are two continuous spiral layers, in the form of the letter S. They account for the excellent cleavage observed in the (010) direction. Within the layers the arsenic and oxygen atoms are bound together with their normal valences. The interatomic distances arsenic-arsenic, oxygen-oxygen, and arsenic-oxygen are the same as in arsenolite. The schematic projection in the [001] direction is shown in Figure 1. It shows the interatomic distances and the valence angles.

During the seeding investigations in the extraction of claudetite, Becker, Plieth, and Stranski (12) isolated yet another modification. So far, this modification, which has not been described previously, has been given the name claudetite II, on account of its great similarity to the known monoclinic form. It separated as monoclinic crystals in the first investigations of Becker, Plieth, and Stranski (13), and has the lattice constants: \( a_1 = 7.99 \text{ Å} \); \( a_2 = 4.57 \text{ Å} \); \( a_3 = 9.11 \text{ Å} \); \( \alpha_2 = 78.3^\circ \). There are four \( \text{As}_2\text{O}_3 \) units in the unit cell, which, from observations of the extinction, has been assigned to the space group \( C_{2h}^5 - Pn \). The x-ray photographic density is rather less than that of claudetite I; \( \rho_r = 4.02 \text{ g cm}^{-2} \). Using Patterson and Fourier projections it can be shown that the bonding between arsenic and oxygen atoms in this form is equivalent, in contrast to the unpaired
crystals of claudetite I. Here again, normal valence bonds are combined into continuous double layers. More information is available from the exhaustive analyses of Becker (14). Figure 2 shows the schematic projection in the [010] direction of the claudetite II. This

Fig. 1.
is the result of a series of Fourier syntheses. The valence angles and interatomic distances are also given.

Arsenic trioxide belongs to that class of substances which can form a glass. A glass will be obtained normally when the molten substance is quenched, but in this respect arsenic trioxide is anomalous. A partially stable glass may be prepared from the crystalline form by heating them up to 400°C for half an hour in an evacuated, sealed test tube. The resulting very viscous melt has an appreciable vapor pressure. If the system is cooled gradually the arsenic trioxide glass is formed.

Related to the problem of the structures of the crystalline forms of arsenic trioxide is the x-ray investigation of the solid obtained by the process of activated condensation; another related question is that
of the semi-orderly structure found in arsenic trioxide glass. It can be inferred from the x-ray photographs and the corresponding microphotographs of the many particles of condensate which were examined that the main product of activated condensation has a vitreous nature. In spite of the limited stability which was revealed by these investigations diffraction photographs were obtained which show good agreement with those of arsenic trioxide glass (Kürbs, Plieth, and Stranski (15)). It may therefore be concluded that the semi-orderly structures in the glass and in the activated condensate are similar. However, an absolute determination of the structure has only been accomplished in the case of the more stable arsenic trioxide glass.

The elucidation of the number of neighbors in the glass was attempted in two ways. The principal method was that of Bötticher, Plieth, Reuber-Kürbs, and Stranski (16), who tried to compare the coherent diffraction intensity curves obtained from monochromatic x-ray diffraction photographs with calculated intensity curves. The agreement between the experimental and theoretical curves in some cases was excellent, as shown in Figure 3. The dotted curve is the experimental one, for the cases of (a) arsenolite and (b) claudetite. The theoretical curve was obtained by considering the disorder of the atoms in the two crystalline modifications, about a randomly chosen atom, up to a distance of 5 Å. It was assumed that, up to a distance of 8 Å, half of the atoms have ordered positions and the other half...
Fig. 4. Key: —, arsenolite; and ---, arsenic trioxide glass.

Fig. 5. Key: ——, claudetite; and ---, arsenic trioxide glass.

are distributed about the ordered positions statistically. On disregarding the curve at values lower than $s = 2$, where the uncertain limitations between the ordered and statistical distributions are important, it should be possible to establish the agreement between the experimental curve and that for the order of the neighbors in claudetite.
Plieth, Reuber, and Stranski (17) were later able to demonstrate, by the use of Fourier analysis, that the above hypothesis is justified. Both Figures 4 and 5 show the agreement between the radial electron density distribution in arsenic trioxide glass and the distribution curves calculated for a Gaussian distribution in arsenolite and claudetite.

The manner in which arsenic trioxide glass is formed from the melt, and in which crystalline arsenolite melts, as well as the very high viscosity of the melt itself, all indicate that the bonding of the atoms in the melt resembles that in claudetite. Direct investigations of the structure of the melt have not yet been successful.

The end of the above descriptions gives an indication of the treatment of the molecular structure in the vapor phase. The first investigations were made by Maxwell, Hendricks, and Deming (18), and more accurate ones were subsequently made by Hampson and Stosick (19). These show, from a comparison of electron diffraction pictures and intensity curves calculated from models, that the molecules in arsenic trioxide vapor have the same structure and meas-
It appears that this type of molecule is stable up to about 800°C, above which, as indicated by Biltz (20), dissociation into $\text{As}_2\text{O}_3$ entities takes place.

The above observations on the structure make it obvious that the $\text{As}_4\text{O}_6$ molecules found in the arsenolite lattice, and the normal valency bonding of the arsenic and oxygen atoms in the claudetite lattice are sufficient to account in almost all details for the known forms of arsenic trioxide. A thorough analysis of the two crystalline structures shows that they contain an elementary unit from which the structures of any phase can be reconstructed. This unit consists of a three-sided pyramid, with an arsenic atom at its apex, and oxygen atoms at the other three corners. The formation of the individual structures can only be explained by bonding these units together by the corner oxygen atoms. Each oxygen atom will thus belong to two such units in general, which may therefore be written formally as $\text{AsO}_3/2$ coordination polyhedra. The bonding of the units together can result in either large occlusions, or, by continuous bonding with more polyhedra, continuous double layers, or continuous disordered triple phases. The formation of larger occlusions originates in the molecular lattice of arsenolite and in molecules in the vapor phase. In both cases four polyhedra have united to give the unit $\text{As}_2\text{O}_6$. The bonding to form continuous double layers is found in the claude-
tite modification and, in an open form, in arsenic trioxide glass, in the activated condensate, and most probably in the melt. Both Figures 6 and 7 should give an impression of the structures formed from these coordination polyhedra. The former shows the view in the [111] direction of the arsenolite lattice. Four tetrahedral molecules and their reverse arrangement in the lattice are characteristic. Figure 7 shows the structure of a layer of claudetite. The continuous bonding of the polyhedra is evident. One can also see the formation of non-isolated six-membered rings. These rings, usually with six sides, but possibly with five or seven, too, form in arsenic trioxide glass, in the activated condensate, and in the melt.

III. Stability Ranges of the Individual Modifications

An important factor in questions concerning the arsenic trioxide system is a knowledge of the ranges of stability of the various modifications and the transition points. The data quoted above the dashed lines in Table I, which follows, make it clear that the transition data can not be evaluated unambiguously. The reason for the existence of these discrepancies lies in the fact that many workers have not questioned the accuracy of their results, which have been obtained from observations on the formation of arsenolite from its elements, by condensation from the gas phase, or by crystallization from solution. These authors, however, did observe heavy seeding

![Graph](image-url)

Fig. 8. (1) Claudetite; (2) arsenolite; · and x, Kirschning et al. (21); and O, Anderson (22).
during the transition from one phase to another. In addition, the variation of the equivalent weights in different phases was not considered, so that mistaken interpretations may be suspected on these grounds.

A number of workers have tried to determine the transition point by several independent methods. The most popular one was the thermodynamic method; this was based on the measurement of the molar heat, with a determination of the absolute entropy. The required absolute enthalpies of reactions were measured electrochemically. The molar heats measured by Kirschning, Plieth, and Stranski (21), from 20°K upwards for both the crystalline forms, are given in Figure 8, which also contains the molar heats of arsenolite obtained by Anderson (22). The direct determination of the bonding enthalpies was not possible, and was first measured by reference to the enthalpy of the reduction of arsenic trioxide with hydrogen. This reaction:

\[ \text{As}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{As} + 3\text{H}_2\text{O} \]

has the advantage that very pure samples of the various modifications are available. It is also clear that this reaction can be observed by electrochemical means, using an arsenic/arsenic trioxide electrode.
<table>
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<td>Schumb</td>
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<td>240 ± 30°K</td>
<td>calorimetric, EMF</td>
<td>Kirschning, Plieth, and Stranski</td>
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<td></td>
<td>303°K</td>
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Free enthalpy of formation

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Entropy of formation

(arsenolite)

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</thead>
<tbody>
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<td>-64.7 cal/deg</td>
<td>calculated from standard entropy values</td>
<td>Maier</td>
</tr>
<tr>
<td>-64.44 cal/deg</td>
<td>calorimetric</td>
<td>Kirschning, Plieth, and Stranski</td>
</tr>
<tr>
<td>(claudetite)</td>
<td>-61.00 cal/deg</td>
<td>calorimetric</td>
</tr>
</tbody>
</table>

Molar heats

(arsenolite)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>50-400°K</td>
<td>calorimetric</td>
<td>Anderson</td>
</tr>
<tr>
<td>20(10)-400°K</td>
<td>calorimetric</td>
<td>Kirschning, Plieth, and Stranski</td>
</tr>
<tr>
<td>(claudetite)</td>
<td>20(10)-400°K</td>
<td>calorimetric</td>
</tr>
</tbody>
</table>

Absolute entropy (at 298°K)

(arsenolite)

<table>
<thead>
<tr>
<th>Value</th>
<th>Method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>+25.6 cal/deg</td>
<td>from molar heats</td>
<td>Anderson</td>
</tr>
<tr>
<td>+25.89 cal/deg</td>
<td>calorimetric</td>
<td>Kirschning, Plieth, and Stranski</td>
</tr>
<tr>
<td>(claudetite)</td>
<td>+29.33 cal/deg</td>
<td>calorimetric</td>
</tr>
</tbody>
</table>
connected to a hydrogen electrode in a cell. The validity of the data obtained for the transition point by this method must be checked; there should be a true equilibrium between arsenolite and claudetite in the aqueous solutions used. In other words, it must be possible to obtain claudetite, assuming the nucleation difficulties to have been overcome, from the saturated solution of arsenolite used in the electrode compartment when the system is in equilibrium. If this condition is not fulfilled, then the equilibrium will not be a true one, and should not be employed to determine the transition data. Kirschning and Plieth (23), using perchloric acid, achieved this condition. Their results for arsenolite are in good agreement with those of Schuhmann (24). The results of the determination of the temperature dependence indicate that the transition point is in the neighborhood of 240°K, and the calorimetric measurements made independently of these were checked by determining the entropy change for the transition reaction at 298°K. These values are in good agreement; \( \Delta S_{298}^1 = +3.44 \text{ cal/deg (calorimetric)}, \) and \( \Delta S_{298}^2 = +3.11 \text{ cal/deg (electrochemical)} \), indicating that a real equilibrium exists in the aqueous solution. The enthalpy of formation of the two modifications can therefore be determined by reference to the reduction reaction, and, in the case of arsenolite, compared with the thermochemical value. The final values are given in Table I. The variation of the free enthalpies of formation of arsenolite and claudetite with
temperature is given in Figure 9. In Figure 10 the temperature-dependence of the enthalpies and free enthalpies of transition (and therefore for the reaction $\text{As}_2\text{O}_3\text{ arsenolate} \rightarrow \text{As}_2\text{O}_3\text{ claudetite}$) are plotted. It is clear from these results that above about $-30^\circ\text{C}$ claudetite is stable with respect to arsenolite.

At the same time as the thermodynamic investigations, experiments were started on the direct observation of the transition process. First of all, it was necessary to establish that the transition from claudetite to arsenolite never took place at the working temperature of $30^\circ\text{C}$ and above, but only the reverse change. It was shown, however, by Stranski, Plieth, and Zoll (25), that these transitions only take place if a certain amount of water is present in the system. The lowest transition temperature observed also involved irradiation with ultraviolet light. These experiments confirmed that the transition point is certainly below $30^\circ\text{C}$.

As a third means of determining the transition point, Stranski, Plieth, and Zoll (26) measured the solubilities of the two oxides in aqueous solution. This method had already been used by Smits and Beljaars (27) and by Schulman and Schumb (28), the former using ethyl benzoate and the latter strong salt solutions. Their results were greatly different, as Table I shows. The experiments were repeated but gave the same results. The equilibrium obtained using ethyl benzoate is not a true one, and the results cannot be used for calculating the transition point. Otherwise, the results should have
been in agreement. The temperature-dependence of the solubility is summarized in Figure 11. Measurements made in 1N HCl give a transition temperature of \(-7^\circ\)C, and a heat of transition of \(+650\) cal, calculated from the heats of solution. From this it can be shown that the process of solution may be represented empirically by the equation:

\[
\text{As}_4\text{O}_6 + 2\text{H}_2\text{O} \rightarrow 4\text{HAsO}_2
\]

This leads to a value of \(+17350\) cal/mole for the differential heat of solution of arsenolite, and \(+16700\) cal/mole for claudetite.

The above have just been obtained by Karutz and Stranski (29) from vapor-pressure measurements over a wide range of temperature. They also lead to values for the transition point, but again the equilibrium is not a true one. The results of the measurements of the vapor pressures for both crystalline modifications, obtained from the melt by Rushton and Daniels (30), are given in Figure 12. These were obtained in three different ways. The melting point of arsenolite
is 278°C, and that of claudetite is 312°C. The heats of sublimation are +24930 cal/mole and +24165 cal/mole, respectively, and the heat of transition is therefore approximately +765 cal/mole. Extrapolation of the vapor pressure curves to their point of intersection gives a transition temperature of approximately +30°C, but this result can naturally only serve as an indication.

IV. Vaporization and Condensation

A. VAPORIZATION

After the description of the structural details and the stability ranges of the phases of arsenic trioxide, it is now necessary to discuss the behavior of the element of vaporization.

The effect of activated condensation gave the first indication of the extremely low rate of vaporization of the phase of arsenic trioxide which is obtained by steeping arsenolite. Disregarding the hypothesis that the surface of the condensate becomes blocked by adsorption, the formation of the activated condensate could only be explained by the fact that it has a very much smaller rate of vaporization than the arsenolite. Accordingly, Stranski (31,32) was able to infer, without using the results of structural investigations, that there is a covalent network in the lattice of the activated condensate, as in claudetite, which is also slow to vaporize. As already shown, this is confirmed by later investigations.

In general, previous experimental work on the rates of evaporation of crystals had been carried out on metals or on substances having molecular lattices. The condensation coefficient $\alpha$ was usually found to be approximately one. This leads to the conclusion that in the expression for the rate of vaporization as a function of temperature, there is an exponential term with the heat of vaporization $\Delta$ in the exponent.

The value of $\Delta$ as the apparent activation energy of vaporization is an exception, although not an infrequent one. In general, the rate of vaporization must be characterized by an (apparent) activation energy which may be either larger or smaller than the heat of vaporization. Because of their differing structures, the modifications of arsenic trioxide provide very useful models for “normal” and “anomalous” vaporization.

The rate of vaporization of arsenolite between 50 and 100°C was
measured by Karutz and Stranksi (29), using a molecular distillation method. Small polished plane-parallel crystal plates, 1.0 to 1.5 mm thick, were used. It can be shown that the structure of the surfaces, once they were formed, was preserved up to about 95°C during vaporization, but above this there was a marked roughening of the surface. The rate of vaporization was calculated from the loss in weight of the crystal plates after correction for the additional losses during heating and cooling.

In the higher temperature ranges, up to 245°C, it seemed more convenient to determine the vaporization by a pressure-time method (33). The substance was vaporized in an evacuated sealed chamber having a known surface area and at a definite temperature. The variation of pressure with time, $p(t)$, was followed up to the saturation pressure, $p_s$. If $F$ (cm$^2$) is the area of the vaporizing surface and $i$ (mole/cm$^2$/sec) is the rate of vaporization, the increase in pressure in a volume $v$ (cm$^3$) in an interval of time $dt$ is:

$$dp = (F/v)kT idt$$

From the Hertz-Knudsen equation

$$i = [\alpha(p_s - p)]/\sqrt{(2\pi mkT)}$$

where $\alpha$ is the condensation coefficient, $k$ the Boltzmann constant, and $m$ the molecular weight of the vaporizing molecules. On substituting