A STUDY OF THE BARRIER EXISTING IN THE SUBLIMATION OF ARSENIC AND RED PHOSPHORUS

Kane, James Stewart.

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A STUDY OF THE BARRIER EXISTING IN
THE SUBLIMATION OF ARSENIC AND RED PHOSPHORUS

James Stewart Kane

April 1955

(Thesis)
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A STUDY OF THE BARRIER EXISTING IN
THE SUBLIMATION OF ARSENIC AND RED PHOSPHORUS

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April 1955

ABSTRACT

Part One

The elements red phosphorus and arsenic are found to sublime anomalously in that the rate-controlling step in the sublimation process has a heat of activation greater than the equilibrium heat.

The main experimental work described in this thesis is the measurement of this heat of activation of the rate-controlling step. The partial removal of this barrier by means of a liquid-metal catalyst was attempted and successfully effected. A general discussion concerning the properties responsible for such hindered sublimation is included, with generalizations extended to other materials. Thermodynamic data for the two elements are reviewed.

Part Two

A mass spectrometer investigation was carried out on the vapor subliming from arsenic and red phosphorus solids. Measurements were taken on vapor from free sublimation and on that effusing from small-orificed Knudsen cells.

The tetramer was found to be the principal neutral species subliming, although ions of one, two, three, and four atoms per molecule were observed. The monomer and dimer ions were found to be produced by both dissociative ionization and thermal dissociation of the tetramer.
on the electron-emitting filament. The trimer ion is apparently produced exclusively by electron dissociation.

The $P_8^+$ mass peak which had been reported in the literature was found to be not noticeably different from background. An upper limit of intensity compared to that of $P_4^+$ 100 times less than the literature value is established.

$As_6^+$ and $As_8^+$ ion intensities are compared to that of $As_4^+$. $As_8^+$ is remarkable for its high appearance potential of 25 volts.
Part One

MEASUREMENT OF THE BARRIER EXISTING

IN THE SUBLIMATION OF ARSENIC AND RED PHOSPHORUS
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INTRODUCTION

For virtually all substances which have been studied, the rate of sublimation per unit area of the gaseous species from the solid has been observed to be exactly the same as the rate per unit area at which the solid is struck by its saturated, equilibrium vapor, this rate being calculated from the equilibrium pressure and the kinetic theory of gases. It appears then at least at equilibrium that for materials of this type every gaseous particle striking the surface of the solid must condense.

A much less commonly encountered situation occurs when the rate of departure from the surface is only a fraction of that which would be calculated from the equilibrium pressure. Since at equilibrium there must be the same number of molecules subliming as condensing, it also follows that of the gaseous molecules striking the surface, only a fraction must condense. In such cases a "hindrance" or barrier to both sublimation and condensation must exist, reducing the rate at which these processes take place by some factor less than one.

In a great deal of the literature, the fraction of colliding molecules which condense to the solid is referred to as the "sticking" or "accommodation" coefficient. In this thesis the term condensation coefficient, designated by $\alpha_c$, will be used throughout, and is defined as that fraction of the molecules of a vapor striking a surface composed of the condensed vapor which actually condense to the solid phase.
Similarly the vaporization coefficient, \( \alpha_v \), is the ratio of the rate of departure per unit area to the rate per unit area at which a solid is struck by molecules of its saturated, equilibrium vapor.

It thus appears that for materials with vaporization coefficients less than one, the rate of sublimation is controlled not by the equilibrium free energy, but by a free energy term corresponding to the transition to an activated complex state of higher free energy. Thus in the process of going from the solid lattice to the gaseous species, there must be some step which requires a greater amount of energy than the overall energy difference between initial and final state. If this is true, the variation of the rate of sublimation with temperature should indicate a heat of activation greater than the equilibrium heat.

If such a barrier is responsible for the observed behavior, it can be shown that the vaporization and condensation coefficients will not be constants, but will vary exponentially with the temperature. This can be seen by the following considerations: The equilibrium vapor pressure exerted by a solid is given by the expression

\[ p = \exp \left(\frac{-\Delta F^0}{RT}\right) = \exp \left(\frac{\Delta S^0}{R}\right) \exp \left(\frac{-\Delta H^0}{RT}\right). \]

By means of the kinetic theory of gases this pressure can be related to the number of collisions the gas makes on the surfaces confining it. The rate at which molecules strike the surface of the solid is thus equal to

\[ \frac{A k}{\sqrt{T}} \exp \left(\frac{\Delta S^0}{R}\right) \exp \left(\frac{-\Delta H^0}{RT}\right), \]

where \( A \) is the geometrical area of the solid and \( k \) the constant relating pressure to the rate of impact. If, however, the rate of sublimation is controlled by a free energy greater than the equilibrium free energy, the rate of departure will be

\[ \frac{A k}{\sqrt{T}} \exp \left(\frac{-\Delta F^*}{RT}\right) = \frac{A k}{\sqrt{T}} \exp \left(\frac{\Delta S^*}{R}\right) \exp \left(\frac{-\Delta H^*}{RT}\right), \]

where the terms denoted by the asterisk refer to the difference between the initial state and the activated complex. Since at equilibrium the rate of the departure must equal the rate of
condensation, the fraction condensed is equal to the expression: fraction
\[ \alpha_c = \exp \left( \frac{\Delta S^* - \Delta S^0}{R} \right) \exp \left\{ -\frac{(\Delta H^* - \Delta H^0)}{RT} \right\}. \]

If now the assumption is made that the entropy changes of the hindered and unhindered process are very nearly equal, the vaporization coefficient is seen to reduce to a single exponential involving the difference between the heat of activation and the equilibrium heat.

The relationship between these different expressions is discussed more fully and a schematic diagram given of the quantities on Page 34.

It is realized that this simple model is not adequate to represent the exact behavior of a system of this type. Certainly the assumption of equal entropies for the two processes is not true; however, it is not unreasonable to predict that any entropy effect will be small compared to that of the difference in heats. Moreover, the above model predicts the vaporization and condensation coefficients to be equal under all conditions. Some recent work by Neumann and Hock on potassium vapor has shown that under non-equilibrium conditions the condensation coefficient remains essentially unity, while the vaporization coefficient varies considerably, both with temperature and with the quantity of vapor returning. This variation is small, however, the values of the vaporization coefficient measured varying from 1.7 - 0.9.

The object of the work reported in this thesis was therefore to demonstrate that low vaporization and condensation coefficients are the result of a step in the sublimation and vaporization process which requires a heat of activation greater than the equilibrium heat. Since the model postulated is not expected to represent the exact behavior, the primary purpose of the work was not the precise measurement of the quantities involved, but rather the observation of the general behavior of such substances, with the object of determining what fundamental properties are responsible for such behavior.
As implied earlier, the number of substances which exhibit this low rate of sublimation is quite small. The two crystal modifications of \( \text{As}_2\text{O}_3 \) have been quite thoroughly investigated by Stranski and Wolff, and one of them exhibits the property to a remarkable extent. In addition \( \text{Mg}_3\text{N}_2 \) the ammonium halides, \( \text{Na}_2\text{CO}_3 \) and graphite have been reported to demonstrate this behavior.

It was therefore necessary to find some substance having a low vaporization coefficient in order to make a thorough study of the phenomena. Attention was called to red phosphorus by the paper of Melville and Gray, who reported an extreme discrepancy for this element between the rate of sublimation and the rate to be expected on the basis of its equilibrium pressure. The work reported in this thesis shows arsenic also to have a low vaporization coefficient, being considerably greater, however, than that of red phosphorus.

These materials were very suitable for a study of this type in that the temperatures required to make the necessary rate measurements are easily attainable, requiring a comparatively simple experimental arrangement. Although thermodynamic and structural information concerning these elements is far from complete, a considerable amount of information is in the literature. These data are reviewed in Appendix I.
EXPERIMENTAL

DISCUSSION OF METHODS USED

Measurement of Heats of Activation

The method used to determine the heat of activation was that originated by Langmuir for determining vapor pressures of refractory materials, and consists of measuring $Z$, the rate of sublimation per unit area into a vacuum. The experimental quantities measured are thus the weight loss, temperature, time interval and area, and in addition a knowledge of the molecular weight of the subliming species is required. A plot of $R \ln (Z \sqrt{T})$ against $1/T$ gives a curve whose slope is the desired heat of activation. For such a determination of the slope rather than the pressure, it is not necessary that the area of the subliming surface be known, but it must be the same for each measurement. The problem of determining this area becomes very complex for materials having low vaporization coefficients, as is discussed in a subsequent section. If the equilibrium heat of sublimation is known, the height of the barrier can also be obtained from a measurement of this heat of activation by use of the simple equation previously derived.

Measurement of Barrier Height

Another type of measurement which yields values of the barrier height in cases where the equilibrium pressure is known is the Knudsen effusion method. In this method the material is enclosed in a container provided with a knife-edged orifice; this is then brought to a known temperature, and the quantity of effusate per unit time measured. If the molecular weight of the effusing species is known, the pressure within the cell can be calculated, and this pressure related to the equilibrium pressure by the expression $p_m = p_{eq}/(1 + a/b\alpha)$, where $p_m$ is the measured pressure within the cell, $p_{eq}$ the true equilibrium pressure, $a$ the area of the orifice, $b$ the area of the subliming material, and $\alpha$ the vaporization or condensation coefficient (presumed equal). This expression is derived from a steady-state argument, and is not exact in all cases, as has been discussed by Whitman and more recently Motzfeldt. For the purpose of these measurements, however, it is adequate.
In this investigation a number of measurements was made at different orifice sizes, the cross-sectional area of the container being held constant. By combining the measured pressure with the known equilibrium value, the height of the barrier was calculated. As the results were observed, it became apparent that an additional factor must be considered; that is the area of the subliming material. This problem will arise only in instances where a kinetic barrier exists, and therefore has received little attention from a theoretical viewpoint. A discussion of the nature of the effect is included at this point in the thesis in order to explain the experimental method which it was necessary to use for determining the activation energies of these elements.

AREA DISCUSSION

When the condensation coefficient of a gaseous molecule subliming from a porous or finely granulated solid is less than one, a further complication in the use of the Knudsen or the Langmuir method arises: the determination of the actual area of the solid which is contributing vapor to the gaseous phase. It is clear one must know the area from which the sublimation is taking place in order to deduce the pressure from any measurement of a total rate of sublimation. In the use of the Langmuir method, the rate per unit area must be known; in the Knudsen method, the problem is to evaluate the a/b term, the ratio of orifice to subliming area. Even in the determination of activation energy, where the actual area need not be known, the area must be the same at each temperature.

If a quantity of loosely packed, granular solid is placed in a container of unit cross section, and the rate at which molecules effuse into a vacuum across a plane boundary immediately above the level of the solid is measured at constant temperature, the observed rate will depend on three factors: the rate per unit area with which the molecules leave the solid particles, the total amount of area from which sublimation can take place, and the probability that a molecule, having sublimed, will find its way across the boundary.

In the more common case where the condensation coefficient is unity, although the total area of solid may be large, the last two factors combine to give an effective area equal to the cross section of the cell. Since
every molecule which strikes the solid condenses, the only molecules which can successfully escape are those which vaporize from sites which can "see" out; thus the total area which can contribute is equal to the geometrical cross section of the container. In the case where the condensation coefficient is unity, the condition of the surface, porosity, or extent of subdivision of the solid will thus not affect the rate at which molecules diffuse across a boundary of unit area above the solid, it being assumed that the fineness of the particles is not such as to increase the rate of vaporization per unit area appreciably over that of the gross crystals.

If the same situation is again considered, only now with the condensation coefficient of the material $\ll 1$, the problem of area becomes more complex. Since now any molecule which sublimes into an interstitial channel or a pore will make many collisions with the solid before condensing, there is a probability that the molecule will find its way to the surface and thus contribute to the total vapor leaving the system. The probability of a molecule which sublimes deep within the bulk of the material reaching the surface is therefore inversely proportional to the number of collisions it makes with the walls of the channel through which it must pass on its way to the surface, and also inversely proportional to the condensation coefficient. It is seen that it is possible for the entire area of the solid to contribute to the quantity of material leaving the cell, although of course the contribution from particles of the solid lying deep within the bulk may be very small, due to the small probability of a molecule which sublimes there finding its way to the surface without being condensed.

It is apparent that in such a situation the "area" actually contributing will be a complex function of particle size and porosity, closeness of packing, depth of material, and condensation coefficient. Since the openings leading to the interstitial spaces will contribute at a much greater rate than the same area of non-porous solid surface, the quantity of vapor effusing from a unit area of porous surface will be equivalent to that subliming from a larger area of non-porous solid surface. The exact rate of emanation of material from such an opening in comparison to that of a solid surface of the same area is of very complex nature,
and cannot be described quantitatively. However it is certain that the emanation from the opening under Langmuir conditions is somewhere between 1 and $1/a_v$ times that of a similar area of solid surface, depending on how good a Knudsen cell the interstitial cavity contributing to the opening is.

The above discussion has been made with the assumption that effusion was taking place into a vacuum, that is that no molecules returned across the boundary above the solid. If a Knudsen cell type of arrangement is considered, it will be seen that this "effective area" cannot be constant, but will vary with the number of molecules returning, thus with the pressure within the cell, which in turn varies with the orifice area.

This apparent decrease in the area of solid contributing vapor as more molecules return to the surface is due to the different effect a returning molecule has on the contribution from an opening as compared to the contribution from a similar area of non-porous surface. This difference can be seen in the following way: A returning molecule which strikes the plane surface has the probability $\alpha_c$ of being condensed, hence $1 - \alpha_c$ is the probability that it will be reflected. The probability of a returning molecule being "condensed" by the opening is again a complex function of hole size, shape, etc., but must be greater than $\alpha_c$, hence the number reflected by a unit area of opening will be less than the number reflected by the same area of non-porous surface. The orifice is unable to distinguish between molecules being reflected and those undergoing their initial sublimation, and so any reflected molecules will appear to be emanated by the surface or opening, and the increase in apparent rate of emanation as the number of returning molecules is increased will be greater for an area of non-porous solid than for an opening. As the pressure approaches the equilibrium value, there will be no difference in the rate of emanation from opening and surface, as viewed from the position of the infinitely small orifice. As a result, a quantity of material enclosed in a container, which, when no molecules were returning behaved as though it had an area larger than its geometrical cross section, will now appear to have been reduced in area to that of the cross section of the cell.
This whole problem of different contributions from opening and surface is completely analogous to that of the emission of light from surfaces of low emissivity. Thus in the above discussion the solid surface is comparable to a plane surface of low emissivity, in which exist cavities emitting with an emissivity somewhere between that of the plane surface and one. If no light is returning, the cavities will appear brighter than the non-porous portion of the surface. However, if the surface and cavity are enclosed in a container which is a perfect reflector, both cavity and surface will appear of equal brightness.

MATERIALS

The elements studied were reagent-grade commercial chemicals. No attempt was made to insure exceptional purity, since in general the samples were heated to a temperature at which an appreciable fraction of the weight was sublimed, and the first heating in each case was not included in the results. The phosphorus was used as it came from the container; the arsenic was pulverized and the fines which passed through a 25-mesh sieve were used.

APPARATUS

Since sufficiently large pressures of both arsenic and red phosphorus can be obtained at relatively low temperatures, the experimental arrangement was relatively simple. The features necessary are a high vacuum, a constant temperature, the accurate measurement of this temperature, and facilities for removing samples before and after heating to determine weight loss.

For obtaining the vacua, a 12" length of commercial 6"-diameter pyrex pipe was used as a bell jar, being fitted by means of "O" rings to a brass base plate through which power leads, thermocouples, and cooling water were introduced by means of Kovar-glass seals. The base plate was gasketed directly to the high-vacuum flange of a VMF 260 DPI oil diffusion pump, which was in turn backed by a mechanical pump. A vacuum of <10^{-5} mm Hg was quickly and easily obtainable. The upper end of the pipe was closed off by a second brass plate, which was also fitted to the glass pipe with "O" rings. The high-voltage lead to the
Philips pressure gauge was led through this plate with a Kovar seal, the magnet of the gauge being attached to the plate with brackets.

For attaining the temperatures, nichrome-wound resistance furnaces were used. These consisted of alundum-core tubes, upon which the wire was hand wound, the turns being spaced more closely at the ends to compensate for the greater radiation losses. The wire was covered with alundum cement, and core and windings enclosed in a thick-walled mullite tube. The outside of this tube was tightly wrapped with several turns of dimpled molybdenum sheet which served as radiation shielding. Low, variable-voltage energy was supplied to the windings by running the output of a 5-ampere, 0-120-volt variac to the primary of a step-down transformer, and thence to the windings.

For controlling the temperature over a long period of time, in general the method was simply to fix the power input, the line voltage being stabilized by means of a constant-voltage transformer. In some cases the input was regulated by a Brown Electronik recorder-controller. It was found that the constant-input method, as well as being simpler, held the temperature constant to within one degree, or even less if the temperature of the room remained constant.

By far the greatest experimental difficulty encountered was the determination of the temperature of the sample. Since it was necessary to remove the crucible for weighing before and after each heating, it was not possible to attach the thermocouple directly to the sample container. Under these conditions it is very difficult to insure that the temperature indicated by the thermocouple is the same as that of the crucible, since at these temperatures radiation is a very inefficient means of heat transfer, and effects such as the small conduction of heat from the junction by the thermocouple wires can lead to large errors in temperature measurements. Many methods were tried, the ability of each to measure the correct temperature at steady state being checked by filling the crucible with tin and reading its temperature with a second thermocouple. The arrangement finally adopted was to enclose crucible and lid in a snug-fitting molybdenum jacket, to which the flattened thermocouple junction was held firmly by means of a set screw.
and a platinum washer. To minimize conduction along the thermocouple leads 10-mil leads were used, and these were led into the heated zone in such a manner as to have several centimeters of their length exposed to the heated walls of the furnace. Comparing the readings of this thermocouple to that of the one immersed in the tin contained in the crucible gave results which checked to within a half of a degree. The details of this arrangement are shown in Fig. 1.

Even though by utilizing this method the temperature of the container is known accurately, the temperature of the surface of the sample inside the container is still quite uncertain. Particularly at larger orifices, the material within the crucible is "looking at" a much cooler region of the apparatus, and the thermal conductivity of the coarsely granulated solid must be very low. For lack of better information it will be assumed that the sample temperature is that of the crucible, although this certainly must be in error by some unknown amount. Motzfeldt has reported his efforts to reduce this error in Knudsen measurements by better design of the furnace and the incorporation of a small heater which is used to keep the top of the cell at the same temperature as the rest. For measurements of high accuracy it would undoubtedly be wise to utilize an apparatus of this type; however, in this work a high absolute accuracy is not necessary, and this was not done.

The crucibles used were in all cases molybdenum, and no attack or reaction was noted by either phosphorus or arsenic at these temperatures. Lids were also of molybdenum, and were machined and then hand-lapped to a snug fit. The orifices were made as nearly knife-edged as possible, insofar as the orifice channel length was kept to a small fraction of the radius, so that the Clausing factor was close to unity. The larger orifices were bored with a wire drill, and then thinned to the desired thickness in a lathe. The smallest orifices were made from one-mil platinum foil by piercing a hole with a sharp needle and then carefully grinding away the bent-out edges with fine emery. The hole was checked for roundness and the diameter measured with a binocular microscope, using a calibrated scale. The large orifices were measured with an inside gauge and also checked with the microscope. The thick-
Figure 1

APPARATUS FOR
EFFUSION RATE MEASUREMENT

MU-9379
ness of each orifice was measured with a micrometer, in order to calculate the Clausing factor of the orifice.

In all cases, before starting a run the crucible and sample were placed under vacuum and the temperature raised to a sufficiently high value and maintained until the sample weight was reduced by about one fourth. If this was not done, volatile oxides and other impurities rendered the weight loss from the initial heating excessive. At the time these runs were made, the area effect was not recognized, so unfortunately no attempt was made to standardize the quantity or the physical state of the sample. This resulted in extreme experimental variation in the results, especially in the case of phosphorus.

Runs were five hours' duration, the molybdenum crucible, sample, and lid being removed and weighed before and after heating. The long times were necessitated by the uncertainty in time, since the crucible both heated and cooled slowly enough so that the uncertainty in time was several minutes. With five-hour runs this error is estimated to be no greater than two per cent, however. The weight losses in all cases were known to two per cent or better. In retrospect, it is seen that this attempt to minimize the experimental error was futile, the error due to the area effect being orders of magnitude greater than that due to any other measurement.

After the importance of this area effect for these materials was realized, it became necessary to assemble an apparatus in which the weight loss of a given initial amount of sample could be observed continuously. For this purpose the apparatus described previously was modified to include a quartz helix, whose length could be continually measured without disturbing the sample otherwise.

All controls, the vacuum system, and the thermocouple were as previously described. A considerable modification was necessary in both bell jar and furnace, however.

A commercially manufactured quartz helix was used, which gave a linear extension per unit weight up to a total load of fifty milligrams, and which had a total length of 28 inches fully extended. To accommodate this, a 36" length of 6"-diameter pyrex pipe replaced the 12" length used
previously. A different brass top plate was used, which in addition to a pressure gauge also included a vacuum-tight glass windlass attached by means of a Kovar-glass seal. The helix was suspended from a hook on the end of a nylon thread which hung from the drum of the windlass; by means of this windlass the helix could be raised or lowered while the system was under vacuum, the drum being turned through a lubricated ground glass joint.

The length of the helix was measured from outside the system by means of a cathetometer capable of reading to 0.1 mm. Over the area viewed, the pyrex pipe had no seals or flaws, and the error from aberrations in the glass is considered to be negligible.

The sample of the material to be studied was enclosed in a container made of 1/2-mil aluminum foil. These containers were circular in cross section, and about 3 mm diameter by 3 mm high. The exact cross-sectional area from which the vapor sublimed was not measured, since for the determination of slopes the only requirement is that this area be constant. Although both phosphorus and arsenic should react with aluminum, the reaction is apparently slow at the temperatures used, for no evidence of reaction was noted. The weight of these containers was ~4 milligrams. They were connected to the hangdown end of the helix by a small quartz loop. Details of the apparatus are given in Fig. 2.

As before, the most difficult experimental problem is the determination of the temperature. Since this time the sample to be measured is freely suspended, it is impossible to measure the temperature of an object in thermal contact with the sample container, as was done previously. It was therefore necessary to measure the temperature of some object which was exposed to the same thermal environment as the sample. In order to achieve this a considerable revision was made in the furnace used. As before, these were of nichrome wire, hand wound on alundum cores, eight inches long and of one inch internal diameter. This time, however, the furnace was provided with a thick-walled copper liner, to insure an even wall temperature throughout. A 1/4-inch-diameter hole bored in the top of this liner was the opening into which the sample was lowered, and also through which the subliming vapor made its escape.
1. GLASS WINDLASS
2. PHILIPS GAUGE
3. QUARTZ HELIX MICROBALANCE
4. COPPER FURNACE LINER
5. SAMPLE CONTAINER
6. COPPER BLOCK, THERMOCOUPLER ATTACHED WITH SET SCREW

ACTIVATION ENERGY APPARATUS

MU-9380

Figure 2
The area of this opening is at least a factor of ten greater than the orifice area of the sample container, but it is felt that the pressure of phosphorus or arsenic within the core cavity will be considerably less than would be calculated from the ratio of the orifices, since it is observed that hot copper acts as a very efficient getter for the collection of molecular beams of both elements.

For determining the temperature, the thermocouple junction was again attached firmly by means of a set screw to a copper block which was very close to the hanging sample, and thus exposed to the same environment. While it is again not possible to know with certainty that the measured temperature is actually the same as that of the crucible, the purpose of the measurements made with this equipment was the measurement of activation energies by means of a slope. An error in the absolute temperature is therefore of no consequence unless the magnitude of the error changes appreciably with temperature, a possibility which is not likely over the small ranges of temperature measured.
RESULTS

For both elements the experimental work consisted of three different measurements: determination of the heat of activation for the sublimation process, measurements of the vaporization coefficients by obtaining the pressure within a cell as a function of the orifice area; crucible cross section ratio, and the measurement of the effect of adding a liquid-metal catalyst. The data in each case are interpreted by considering the vapor leaving the solid to consist entirely of \( \text{P}_4 \) and \( \text{As}_4 \) molecules, an assumption verified by the mass spectrometer portion of this investigation, which showed the tetramer to be the principal species.

**Activation Heats**

The presence of the area problem makes special precautions necessary if the measurement of the activation heat is to give any sort of accurate results. Since vaporization from within the bulk phase is important, it is not enough that the cross-sectional area of the container be the same for each temperature; in addition, it is also necessary that the total amount of sample, size of sample particles, and the dimensions of the interstitial channels be duplicated at each temperature.

To see how large an effect is observed from this change of area as sublimation proceeds, finely powdered samples of the two elements were placed in a vertical cylinder, and sublimation allowed to proceed at constant temperature until only \( \sim 1/6 \) of the original sample remained. This quantity remaining was still sufficient material to fill the container from wall to wall, so the geometrical area exposed was constant during the sublimation. The weight loss was plotted against time, from which curve the rate of sublimation can be determined at any instant during the course of sublimation by taking the slope. A typical curve for each element is given in Figure 3.
DECREASE IN RATE OF SUBLIMATION AS SAMPLE WEIGHT DECREASED

Figure 3
Both elements showed smooth curves of weight loss versus time, but both also showed a decreasing rate of sublimation as sublimation proceeded. This is what would be expected if the area contributing is not just the cross sectional area of the container, but some function of the total amount of material present. The effect can be seen to be quite small in the case of arsenic, but pronounced for phosphorus. When the rate of sublimation is taken at the initial weight, and again at a point at which one-half the mass of the material has sublimed, it is found that for arsenic the rate has decreased by a factor of 0.81, while that of phosphorus has decreased to 0.48 of the initial value. The appearance of the phosphorus residue illustrates that extensive sublimation is taking place from the bulk of the material, in that the residue was fluffy, light in color, and the surface level did not appear to sink within the container while \( \sim 5/6 \) of the original sample was subliming. A spectroscopic analysis of this residue showed no significant amount of impurities to be present.

The procedure used to measure the rate of sublimation for activation-energy determinations was to place a fixed initial amount of material in the container (the same container was used at each temperature) and then to measure the length of the quartz helix as a function of time. The data were plotted in this form, as in Figure 3, and at definite spring lengths the tangents were drawn. In this way the rate of sublimation was obtained at a point corresponding to exactly the same fraction of the original material at each temperature, and presumably the area contributing will thus be the same.

The results of these measurements gave activation energies of 43 kcals for arsenic and 52 kcals for phosphorus, at mean temperatures of
550°C and 650°C respectively. No limits of error are given; the value listed is the slope of a line drawn through the experimental points "by eye". It should be kept in mind that although the precision of the experimental measurements was excellent, this does not mean that the measured values are susceptible to precise measurement, since the rate of sublimation appears to be so strongly dependent on the physical state and previous history of the sample. Such factors as imperfections in the crystals and the size of the crystals would be expected to affect the sublimation rate strongly. These experimental values are thus useful only as a means of establishing the magnitude of the barrier existing in the sublimation process, and a more exact determination is without meaning unless the state of the solid material is more completely defined.

$\Delta H^*$ - $\Delta H^0$ Values from Vaporization Coefficient Measurements

A series of measurements were made on the rate of effusion of the two elements through orifices of different sizes, using containers of one cm$^2$ cross-section area. These measurements were made before the importance of the area effect was realized, and no precautions were taken to fix the quantity of material in the original sample nor to insure identical previous history from sample to sample. As a result, a considerable scatter was obtained in the results, especially for phosphorus.

For arsenic, the results of the experimental measurements of effusion from various orifices are summarized in Table 1. In order to calculate $\alpha$ and thus the value of $\Delta H^*$ - $\Delta H^0$ from the simple effusion equation, it is necessary to know both the equilibrium pressure and the area from which sublimation is taking place. The former was taken from
Table 1

$\Delta H^* - \Delta H^0$ Values Obtained from Vaporization Coefficients
(Arsenic)

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Orifice Area</th>
<th>Cell Cross Section</th>
<th>$T^0_K$</th>
<th>$P_m/P_{eq}$</th>
<th>$\Delta H^* - \Delta H^0$</th>
<th>Area *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>545</td>
<td>1.25 $\times 10^{-3}$</td>
<td>7320 cal</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>549</td>
<td>1.34 $\times 10^{-3}$</td>
<td>7300</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>551</td>
<td>1.31 $\times 10^{-3}$</td>
<td>7300</td>
<td>28.5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>566</td>
<td>2.28 $\times 10^{-3}$</td>
<td>6900</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>567</td>
<td>2.54 $\times 10^{-3}$</td>
<td>6800</td>
<td>41.1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>575</td>
<td>2.72 $\times 10^{-3}$</td>
<td>6800</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>579</td>
<td>2.92 $\times 10^{-3}$</td>
<td>6770</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.194</td>
<td>575</td>
<td>9.34 $\times 10^{-3}$</td>
<td>7250</td>
<td>25.6</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>6.78 $\times 10^{-2}$</td>
<td>550</td>
<td>1.24 $\times 10^{-2}$</td>
<td>7780</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>6.78 $\times 10^{-2}$</td>
<td>571</td>
<td>1.70 $\times 10^{-2}$</td>
<td>7750</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2.52 $\times 10^{-2}$</td>
<td>526</td>
<td>1.86 $\times 10^{-2}$</td>
<td>8050</td>
<td>16.5</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>7.86 $\times 10^{-3}$</td>
<td>547</td>
<td>3.98 $\times 10^{-2}$</td>
<td>8770</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>7.86 $\times 10^{-3}$</td>
<td>578</td>
<td>7.26 $\times 10^{-2}$</td>
<td>8550</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>7.86 $\times 10^{-3}$</td>
<td>598</td>
<td>8.95 $\times 10^{-2}$</td>
<td>8550</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>4.53 $\times 10^{-4}$</td>
<td>574</td>
<td>0.195</td>
<td>10,500</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>4.53 $\times 10^{-4}$</td>
<td>600</td>
<td>0.268</td>
<td>10,450</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>4.53 $\times 10^{-4}$</td>
<td>621</td>
<td>0.340</td>
<td>10,450</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>1.35 $\times 10^{-4}$</td>
<td>599</td>
<td>0.49</td>
<td>10,800</td>
<td>~ 1</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>1.35 $\times 10^{-4}$</td>
<td>622</td>
<td>0.41</td>
<td>11,550</td>
<td>~</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.35 $\times 10^{-4}$</td>
<td>647</td>
<td>0.41</td>
<td>12,100</td>
<td>~</td>
<td></td>
</tr>
</tbody>
</table>

* Ratio of area actually contributing to container cross section
the literature (see Appendix 1), but the latter term cannot be readily obtained. For the purpose of a preliminary calculation of $\Delta H^* - \Delta H^0$, the area was assumed to be the cross-sectional area of the container. As discussed previously, the effective area decreases as the pressure in the cell approaches the equilibrium value; the result of assuming a constant area is thus to make the calculated $\alpha_v$'s appear to decrease as the orifice is decreased, and $\Delta H^* - \Delta H^0$ appears to increase correspondingly. This effect is shown in the 5th column of Table 1, where $\Delta H^* - \Delta H^0$ seems to increase from $\sim 7000$ to $12000$ kcal as the ratio of orifice area: container cross section is decreased from unity to $\sim 1 \times 10^{-4}$.

The results of the effusion of phosphorus from orifices of several sizes are given in Table 2. As was done with arsenic, for the purpose of calculating $\Delta H^* - \Delta H^0$ the area was assumed to be that of the cell cross section. The data for both elements will be treated more completely in the discussion.

Addition of Liquid-Metal Catalyst

In a sublimation such as this where the rate observed is slower than the equilibrium free energy would predict, there is the possibility that the addition of a suitable catalyst could bring about a lowering or complete removal of this hindering effect. It was noted that the rate of sublimation was always considerably greater for samples which were being heated for the first time, this increased rate being greater than could be explained by the presence of impurities. It is to be expected that such unannealed crystals would have a large number of imperfections and distortions in the lattice, and it thus appears reasonable that sublimation can take place more easily from such points than from the rigid, perfect crystal surface. This implies that the
Table 2

$\Delta H^* - \Delta H^0$ Values Obtained from Vaporization Coefficients

(Phosphorus)

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Orifice Area</th>
<th>Cell Cross Section</th>
<th>$T_K$</th>
<th>$P_m/P_{eq}$</th>
<th>$\Delta H^* - \Delta H^0$</th>
<th>Area *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>643</td>
<td>$3.2 \times 10^{-7}$</td>
<td>19.3 kcal</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>649</td>
<td>4.1 $\times 10^{-7}$</td>
<td>18.8</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>664</td>
<td>2.1 $\times 10^{-6}$</td>
<td>17.4</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>664</td>
<td>1.1 $\times 10^{-6}$</td>
<td>18.3</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>692</td>
<td>7.4 $\times 10^{-6}$</td>
<td>16.3</td>
<td>246</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.78 $\times 10^{-2}$</td>
<td>647</td>
<td>9.8 $\times 10^{-6}$</td>
<td>18.4</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.52 $\times 10^{-2}$</td>
<td>645</td>
<td>1.36 $\times 10^{-5}$</td>
<td>19.2</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>7.24 $\times 10^{-3}$</td>
<td>664</td>
<td>1.68 $\times 10^{-4}$</td>
<td>18.2</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4.53 $\times 10^{-4}$</td>
<td>673</td>
<td>8.8 $\times 10^{-4}$</td>
<td>19.8</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>

* Ratio of area actually contributing to container cross section
atoms at these sites in some way require less energy to rearrange to the As₄ or P₄ molecule, which then sublimes.

Any means whereby the lattice could be "loosened up" would thus tend to lessen the energy required for a molecule to sublime. A possible way of accomplishing this would be the addition of a non-volatile liquid which would not react chemically with phosphorus or arsenic to form intermediate phases, but which would dissolve some of these elements. In the liquid, the unknown species could then be expected to rearrange much more easily to the As₄ and P₄ aggregates.

The only substances which meet the requirements of non-volatility, low melting point and which do not form intermediate phases with phosphorus or arsenic are thallium and lead. Of these, thallium was chosen because of its lower eutectic temperature with both arsenic and phosphorus. Use of thallium thus made possible the measurement of sublimation rates at lower temperatures.

The procedure in all cases was to add sufficient metal so that a liquid phase was present at the temperature used. In the first few experiments the proper amounts of the two elements were added to the container, and the usual heating and re-weighing carried out. Experiments done in this way showed a greatly increased rate of sublimation when first heated, but this rate soon dropped to a value about the same as that when no thallium was present. Examination of the residue showed that very poor contact was obtained between the liquid and solid phases. As a result, the material sublimed rapidly at first, but as the points of contact were used up the catalytic effect was removed, and the sublimation rate decreased to that of the uncatalyzed material. The
procedure was therefore modified to insure an intimate mixture of the phases. To accomplish this, the correct weight of thallium was added to arsenic or red phosphorus and sealed into evacuated quartz bulbs, which were then heated to 1000°K in the case of arsenic and 850°K for red phosphorus. The materials were kept at this temperature for several minutes, then chilled, resulting in a fine intermixture of the two phases. The samples thus prepared behaved consistently in that their rate of sublimation remained quite constant until so much of the subliming element had sublimed that the solid phase no longer existed.

To establish that the effusate was composed entirely of arsenic or phosphorus, samples of the subliming beam were collected on a liquid-nitrogen-cooled copper target. The material so collected was compared spectroscopically to standard alloys containing 1 percent thallium and 99 percent of the other element. For both arsenic and phosphorus the amount of thallium in the effusing beam was many times less than in the standard alloy.

The results of these runs are given in Table 3. For reasons which will be treated in the discussion it was decided to present the data in the form of the vaporization coefficients rather than in terms of energy differences as was done for the uncatalyzed sublimations. The vaporization coefficients were therefore calculated at a mean temperature of 550°K for arsenic and 575°K for phosphorus. These values are given in column 5 of Table 3. For the purpose of vaporization coefficient calculations the area term in the Knudsen equation was assumed to be the cross sectional area of the container.

It should be explained that for both elements, but especially phosphorus, the measurements were limited to relatively small orifices.
### Table 3
Comparison of Vaporization Coefficients With and Without Thallium Added

<table>
<thead>
<tr>
<th>Orifice Area</th>
<th>Arsenic</th>
<th>Phosphorus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thallium Added</td>
<td>No Thallium</td>
</tr>
<tr>
<td></td>
<td>$T^0_K$ of</td>
<td>$\frac{p_m}{P_{eq}}$</td>
</tr>
<tr>
<td></td>
<td>measurement</td>
<td>(uncorrected</td>
</tr>
<tr>
<td>Cross Section</td>
<td>$p_m$</td>
<td>for activity)</td>
</tr>
<tr>
<td>2.52 x 10^{-2}</td>
<td>531</td>
<td>0.46</td>
</tr>
<tr>
<td>532</td>
<td>0.35</td>
<td>1.6 x 10^{-2}</td>
</tr>
<tr>
<td>539</td>
<td>0.37</td>
<td>1.6 x 10^{-2}</td>
</tr>
<tr>
<td>7.86 x 10^{-3}</td>
<td>533</td>
<td>0.52</td>
</tr>
<tr>
<td>539</td>
<td>0.44</td>
<td>7.3 x 10^{-3}</td>
</tr>
<tr>
<td>549</td>
<td>0.35</td>
<td>4.3 x 10^{-3}</td>
</tr>
<tr>
<td>553</td>
<td>0.37</td>
<td>4.5 x 10^{-3}</td>
</tr>
<tr>
<td>559</td>
<td>0.37</td>
<td>6.1 x 10^{-3}</td>
</tr>
<tr>
<td>753</td>
<td>0.42</td>
<td>4.6 x 10^{-3}</td>
</tr>
<tr>
<td>7.26 x 10^{-3}</td>
<td>600</td>
<td>0.45</td>
</tr>
<tr>
<td>1.68 x 10^{-3}</td>
<td>563</td>
<td>0.63</td>
</tr>
<tr>
<td>582</td>
<td>0.64</td>
<td>2.1 x 10^{-3}</td>
</tr>
<tr>
<td>600</td>
<td>0.63</td>
<td>1.7 x 10^{-3}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Orifice Area</th>
<th>Thallium Added</th>
<th>No Thallium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T^0_K$ of</td>
<td>$\frac{p_m}{P_{eq}}$</td>
</tr>
<tr>
<td></td>
<td>measurement</td>
<td>$p_m$</td>
</tr>
<tr>
<td>Cross Section</td>
<td>$P_{eq}$</td>
<td>$\alpha_{575^0K}$</td>
</tr>
<tr>
<td>1.68 x 10^{-3}</td>
<td>575</td>
<td>0.088</td>
</tr>
<tr>
<td>7.24 x 10^{-3}</td>
<td>673</td>
<td>8.8 x 10^{-4}</td>
</tr>
<tr>
<td>1.35 x 10^{-4}</td>
<td>575</td>
<td>0.24</td>
</tr>
</tbody>
</table>
It is obviously necessary that the temperature be sufficiently high so that some liquid is present, and at this temperature the catalyst so increased the sublimation rate that the use of a large orifice resulted in excessive weight loss. For this reason only two runs were made with phosphorus, both at the lowest possible temperature and with relatively small orifices.
DISCUSSION

Before beginning the treatment of the experimental data it would perhaps be helpful to review the relationships existing between the various quantities which will be discussed. These quantities are related by the following three basic equations:

1. \[ \frac{\Delta F^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} = \ln p_{eq} \]

2. \[ \frac{\Delta F^*}{RT} = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} = \ln p^* = \ln \alpha p_{eq} \]

3. \[ \frac{(\Delta F^* - \Delta F^0)}{RT} = \frac{\Delta S^*}{R} - \frac{\Delta S^0}{RT} - \frac{(\Delta H^* - \Delta H^0)}{RT} = \ln \alpha_v \]

The assumption will also be made that \( \Delta S^* \approx \Delta S^0 \).

The three values represented by these equations may be related schematically by the use of a free-energy diagram of the following type, in which the sublimation of solid red phosphorus to gaseous \( P_4 \) molecule is used as an example:

![Free Energy Diagram](attachment:image.jpg)

Equation (1) is seen to contain only terms involving state functions, thus on the diagram it represents the difference between initial and final states. No measurements of these values were made in this thesis; the values used are those of the literature.
The terms denoted by the asterisk appearing in Equations (2) and (3) are those to which the major part of the experimental work of this thesis was devoted. These values are the difference between the initial state and the peak of the free-energy curve in the diagram, thus \( \Delta H^* \) is the heat of activation, \( \Delta S^* \) the entropy of activation, and \( p^* \) is the Langmuir pressure, which corresponds to the rate at which \( P_4 \) molecules are passing over this point of highest free energy. Equation (3) is the difference between (2) and (1), taken in order to solve explicitly for \( \alpha_v \). Here the assumption will be made that the entropy of activation is the same as the equilibrium entropy of sublimation; the agreement of the experimental data will serve as a check on this assumption.

The most important factor to be kept in mind in the treatment of the data is the effect which the indefinite area has on the various calculations. A number of experimental observations make it apparent that for these two elements the area contributing vapor is not just the cross-sectional area of the container in which they are confined. For example, both elements, when sublimed in vacuo under conditions where the exposed cross-sectional area was held constant, showed rates of sublimation which decreased as the quantity of sample remaining in the container decreased. (Fig. 3) Further proof of sublimation taking place within the bulk of the sample was particularly noticeable for phosphorus, in which the level of the solid material did not appear to sink during a period of heating in which \( \sim 5/6 \) of the material was sublimed. The material remaining was much less dense than the original, and appeared to be of uniform density from top to bottom. In addition, the apparent area contributing vapor in the Knudsen runs becomes smaller as the orifice area decreases, which, as discussed earlier, would
be expected for a material displaying this type of sublimation. This change in area is obvious from the data of Tables 1 and 2, in which the Knudsen measurements were interpreted with the incorrect assumption that the area contributing was constant and equal to the container cross section. The result is that $\Delta H^* - \Delta H^0$ (and hence $\alpha_v$) appears to vary with orifice size, when in reality it is the area contributing which is changing.

It is then seen to be essential that in treating the data the effect of the area must be carefully considered if the results are to be meaningful. In the case of the more complete and accurate data on arsenic, moreover, there are two independent methods by which the vaporization coefficient can be calculated without the necessity of evaluating the area actually contributing. These methods and the results obtained will therefore be discussed first.

In Eq. (3) it is seen that a value of $\alpha_v$ can be obtained if the difference between the heat of activation and the equilibrium heat is known. Since $\Delta H^0$ is available, if a determination of $\Delta H^*$ is possible without the evaluation of the area contributing vapor, the vaporization coefficient can be calculated. By means of the kinetic theory the term $p^*$ may be equated to the expression $\frac{z \sqrt{MT}}{44.3A}$, where $z$ is the rate of departure in moles per second, $M$ the molecular weight of the gaseous species, $T$ the absolute temperature, and $A$ the true area from which the vapor is subliming. If the area $A$ is the same at the instant the rate $z$ is measured for each temperature, a plot of $R \ln (z \sqrt{T})$ against $1/T$ will give a curve whose slope is the desired activation heat. To insure the constancy of $A$ at every measurement, the following experimental procedure was adopted: Precisely the same mass of material was initially
placed in the container at each temperature. The sublimation was then allowed to proceed and measurements were made of the helix length, L, at frequent time intervals. A smooth curve was drawn through these experimental points, and at helix lengths corresponding to several definite fractions of the original sample weight the tangents were drawn. The slope at each point is thus dL/dt, and is proportional to z. For each of the several fractions, the plot of R ln (dL/dt√T) was made against 1/T, the slope being the desired heat of activation. With this method the area, porosity, channel size, and previous history of the sample are all presumably the same at each temperature. In support of this assumption, it was observed that the plots corresponding to different fractions of the original sample remaining gave heats of activation which agreed to within a fraction of a kilocalorie.

**Arsenic**

The heat of activation determined in this way for arsenic was 43 kcols. When the equilibrium heat of sublimation at the same temperature is subtracted, the resulting value for ΔH* - ΔH⁰ is 10.0 kcols.

In the Knudsen cell measurements on arsenic, at the smallest orifices used the pressure within the cell is noted to be approaching the equilibrium value. Since under these conditions the area contributing approaches the cross-sectional area of the container, the values of ΔH* - ΔH⁰ calculated by assuming the subliming area to be equal to the container cross section will approach the true value at zero orifice. The value of ΔH* - ΔH⁰ obtained by a rough extrapolation of the data is 12.5 kcols, in fair agreement with the result of the heat-of-activation measurements. Unfortunately the calculation of the vaporization coefficient at values of p_m/p_eq approaching unity is very sensitive to errors in both p_m and
peq. Since for arsenic the value of p_eq is not accurately known, the results of the activation-heat measurements were weighted more heavily than those of the Knudsen measurements, and a value for \( \Delta H^* - \Delta H^0 \) of 11.0 kcals was chosen, with a probable limit of error of \( \pm 1 \) kcal.

The value of \( \alpha_v \) thus established should be the true vaporization coefficient that would be calculated if it were possible to measure the rate of sublimation from a perfect, non-porous surface. This value may now be used to calculate the magnitude of the area effect which was present in the various measurements of the rate of sublimation. For the Langmuir type measurements the measured \( p^* \) is really the true \( p^* \) multiplied by the area factor, therefore the area factor is equal to \( p^*/(p_{eq}\alpha_v) \), where \( p^* \) in this case is the measured Langmuir pressure. The Knudsen cell area values are obtained by solving the \( \frac{p_m}{p_{eq}} = \frac{1}{1 + \frac{\alpha}{b\alpha}} \) equation for \( b \), using the calculated vaporization coefficient. The results of these calculations are given in Table 1, Column 6.

The results of this area calculation show that for an arsenic sample of the physical characteristics and dimensions used, the total area contributing under Langmuir conditions is \( \sim 30 - 40 \) times the cross sectional area of the container, with the limit of error quoted making this uncertain by about a factor of two. The values of \( \Delta H^* - \Delta H^0 \) calculated originally in Table 1, Column 5 are thus entirely fictitious, being calculated on the basis of a grossly incorrect area. It should also be pointed out that the apparent temperature coefficient of this fictitious value of \( \Delta H^* - \Delta H^0 \) as observed in the largest-orifice measurements is for the most part caused by this same area error, rather than by a temperature-dependent error in the measurements.
Phosphorus

The experimental data for phosphorus are in all cases considerably poorer than those for arsenic, since at the time the experiments were made the magnitude of the area effect was not realized, and no attempt was made to standardize the sample quantity or its previous history. In addition, the results show phosphorus to have an extremely low vaporization coefficient, so that it was impossible to go to orifices sufficiently small to approach the equilibrium pressure. In no case was a pressure reached which was within 1/1000 that of the equilibrium pressure; to achieve a pressure within an order of magnitude of the equilibrium value would, for the crucible dimensions used, require an orifice area of $10^{-6}$ cm$^2$. In the method used, the metal foil cover is press-fitted to the crucible top, and even with a most careful lapping of the two surfaces followed by a press fitting with a force of several tons, the possibility of a leak larger than such an orifice is considerable.

It was therefore impossible to make Knudsen measurements with a sufficiently small orifice to eliminate the area effect, and so calculate a limiting value for $\Delta H^\# - \Delta H^0$. For phosphorus the results of the heat-of-activation measurements alone must be relied on, which, in view of the agreement between $\Delta H^\# - \Delta H^0$ values obtained by the two methods in the study of arsenic, should be satisfactory. The measurement was made in exactly the same manner as that for arsenic, the resulting heat of activation being 52 kcals. When the equilibrium heat of sublimation of red phosphorus at the temperature of the measurements is subtracted from this, a value of 24.0 kcals is obtained for $\Delta H^\# - \Delta H^0$.

As in the treatment of the arsenic data, it is now possible to utilize this value for calculating the magnitude of the area actually
contributing vapor in the sublimation of phosphorus. The results of this calculation are given in Table 2, Column 6.

Again, as in the case of arsenic, the ΔH* - ΔH0 values calculated on the basis of the geometrical area are grossly in error. The agreement of the results on phosphorus is unfortunately so poor that it is not possible to establish a value for the area factor under Langmuir conditions, other than that it appears to be about 100 times that of the geometrical, with again a possible error of at least a factor of two. In consideration of the much lower vaporization coefficient for phosphorus than for arsenic, coupled with the much more marked change for phosphorus in the rate of sublimation as a function of the percent sample sublimed, it would seem that an area factor of 100-1000 is not unreasonable.

Addition of Catalyst

The measurements made with the liquid-metal catalyst present show that for both elements the rate of sublimation is increased considerably over that in which there was no catalyst present. The comparison of the results is unfortunately not a simple matter, since there is now present both a solid-liquid boundary and a liquid-gas boundary. The measurements made show only the total rate of transfer out of the system, and we cannot therefore distinguish between a barrier occurring at the solid-liquid interphase and the one at the liquid-gas boundary. The results will therefore be presented not in the form of a misleading heat term, but as effective vaporization coefficients, calculated with the assumption that the area contributing vapor is the cross-sectional area of the cell. Such a coefficient would be correct in the case where the rate-limiting step occurs at the gas-liquid boundary, since the area of this is the same as the cell cross section.
The results of the sublimations carried out in the presence of liquid metal were thus calculated on this basis to give the \( \alpha \)'s listed in Column 4, Table 3. The values given are for a median temperature of 550\(^\circ\)K for arsenic and 575\(^\circ\)K for phosphorus. To illustrate the effect brought about by the catalyst, the previous measurements made with similar orifices on uncatalyzed material are presented in Column 7, Table 3, with calculations made at the same temperatures and with the same incorrect area assumption. The ratio of the \( \alpha \)'s determined in the presence of the liquid to those of the uncatalyzed sublimations will thus be the increase in rate of sublimation which would be observed upon the addition of the catalyst. Thus for arsenic at 535\(^\circ\)K and an orifice ratio of 2.52 \( \times \) 10\(^{-2}\) the addition of catalyst has increased the evolution by a factor of 1.6 \( \times \) 10\(^{-2}\)/6.8 \( \times \) 10\(^{-4}\) = \( \approx\) 24.

There are two further sources of error which make the calculation of these vaporization coefficients in the presence of the liquid very uncertain for arsenic as the orifice becomes small. The first is that the true equilibrium pressure is uncertain by some unknown amount which will influence the calculated \( \alpha \)'s more and more severely as \( p/p_{eq} \) approaches unity. The second and perhaps more serious source of error is the unknown solubility of thallium in arsenic solid, with the result that the activity of the arsenic in the liquid phase will be lowered below that of pure arsenic solid. For this reason it is difficult to choose which value to use for \( p_{eq} \). It is seen in Column 3, Table 3, that at the smallest orifice used for arsenic the value of \( p/p_{eq} \) has become constant, which strongly suggests that under these conditions the equilibrium pressure has been reached within the cell. This would indicate that the activity of the arsenic has been lowered
to ~ 0.6 that of the pure material. By using this factor to correct the $p/p_{eq}$ values at larger orifices, the vaporization coefficients in Column 5, Table 3 were obtained.

In both the catalyzed and the uncatalyzed sublimations, there is seen to be a definite trend in the values of $\alpha_v$ with orifice size. In the case of the uncatalyzed sublimation this trend is known to be caused by the assumption of an incorrect area which, instead of being constant, is changing with orifice area. Since the same trend is apparent in the $\alpha$'s in which the liquid metal is present, it must be concluded that here too there is some process which results in the change of effective area. This would imply that the solid-to-liquid mass transfer is still in part accomplished by sublimation into interstitial cavities or pores, which then contribute their contents by gas phase transport through openings leading to the liquid. Since the concentration of arsenic in the liquid is fixed at any one temperature, the reduction in orifice area will result in an increased return to the liquid, which will correspondingly increase the return to the arsenic solid. The situation is then completely analogous to the previous problem of a Knudsen cell containing a porous solid in which returning molecules have a different effect on the net contribution of openings compared to that of the non-porous surface, and the area would appear to decrease as the pressure in the cell nears the equilibrium value.

The addition of the catalyst so increased the rate of sublimation of phosphorus that it was not possible to make the measurements at any but the smallest orifice sizes, and at the lowest temperature at which a liquid phase is present. The measurement using the smallest orifice indicates that the equilibrium pressure is being approached, giving a value for $\alpha_v (575^\circ K)$ which is still only $3 \times 10^{-5}$ even in the presence of the liquid catalyst. Although this still indicates a large barrier, the catalyst has increased the evolution of vapor by a factor of $\sim 10^3$. 
In the uncatalyzed sublimations, the magnitude of the area effect for both elements is of considerable interest, being of course a direct result of the extremely small condensation coefficients peculiar to these materials. In order to measure the true values of the vaporization coefficients by any direct method, it would be necessary to perform the measurements upon samples in which this effect had in some manner been eliminated, such as a single crystal or fused material. The effect is seen to be much more pronounced for phosphorus than for arsenic. In the measurement of the rate of sublimation of phosphorus from a fixed starting amount of sample, the instantaneous rate of sublimation seemed to depend almost exactly upon the amount of material remaining in the container, although the geometrical area of exposed material was kept the same at all times. This behavior implies that under the conditions of the experiment, virtually all molecules which sublime within the bulk of the material make their escape, and thus the total area of the sample is the factor controlling the rate of departure from the container.

In connection with this point, it is interesting to note that Melville and Gray, who measured the rate of sublimation from very thin films of red phosphorus deposited upon glass plates, obtained rates of sublimation in all cases less than 1/10, and in some measurements less than 1/100 those of the Langmuir type experiments of this thesis. Unfortunately the quantity of phosphorus which they deposited on the plates originally was not given, although from the text one infers it could not have been more than a few milligrams. On the basis of total area present, it is quite reasonable that they should have gotten a much lower rate of sublimation than the measurements of this
thesis, in which samples of up to 600 milligrams were used. But even with such a technique as used by Melville and Gray it is probable that the total area of the deposited films which contributes vapor is somewhat greater than the geometric area of the deposit, and thus a vaporization coefficient calculated from their results would still be larger than the true value.

One means of ascertaining whether or not the rate of sublimation is controlled by the total area of phosphorus present would be to measure the rate of sublimation of a sample, with a simultaneous determination of the area. This could be done by making a number of runs in which the weight-versus-time curves were plotted, and at a definite time different for each run, removing the sample for an area determination by gas adsorption techniques. The rate of sublimation could be determined by drawing the tangent at a point corresponding to the time the heating was stopped. A measurement of this type was not possible on the microbalance utilized in this work since a mass of material larger than the capacity of the micro-balance would be required to perform area determinations on particles the size of the red phosphorus crystals.

Relation of Structure of Solid to Vaporization Coefficients

From the results obtained in this work as well as the work of other investigators, it is possible to speculate upon those properties of substances which are responsible for low vaporization coefficients, and how those properties differ from those of materials which sublime without hindrance.

As mentioned initially, only a small number of substances are known to have markedly low vaporization coefficients. The two crystalline modifications of As₂O₃ have been thoroughly studied by Stranski and Wolff.
and one of them is observed to have a very low rate of sublimation compared to that expected from the equilibrium pressure, while the other sublimes normally. These substances are interesting in that their behavior is similar to that of phosphorus, whose white modification is unhindered in subliming, the red being exceedingly so. For both \( \text{As}_2\text{O}_3 \) and phosphorus, the modification exhibiting the normal behavior has a crystal structure which consists of the gaseous species (\( \text{As}_4\text{O}_6 \) and \( \text{P}_4 \), respectively) in the form of a molecular lattice, held together by only van der Waals' forces. The modifications exhibiting hindered sublimation, on the other hand, have infinite layer structures in which the gaseous molecule does not appear as an entity, although the gaseous molecules in the saturated vapor are the same for both hindered and unhindered modification.

This criterion of the existence of the gaseous molecule in the solid lattice can be extended to the other substances having low vaporization coefficients. Thus the ammonium halides \( ^4 \) sublime to ammonia and hydrogen halide, neither of which is present as a unit in the condensed phase. Magnesium nitride \( ^3 \) sublimes to magnesium atoms and \( \text{N}_2 \) gas, but the nitrogen atoms are widely separated in the rigid lattice. In the sublimation of graphite, the experiments of Goldfinger and Doehard \( ^6 \) have demonstrated the existence of some species in the subliming vapor whose pressure increased as very small orifice sizes were used. Subsequent mass spectrometer investigations \( ^{10} \) appear to indicate that the \( \text{C}_5 \) molecule has an extremely low vaporization coefficient such that although it makes up a negligible portion of the subliming vapor, it may be quite important under equilibrium conditions. The \( \text{C}_5 \) molecule of course does not exist in the graphite lattice.
Elemental arsenic, too, in its common solid modification has a puckered graphite-like lattice in which $\text{As}_4$ molecule does not exist.

No case of vaporization coefficients differing greatly from one has therefore been observed for materials whose gaseous molecular species is present as a structural unit in the crystal, or, in the case of ionic crystals, where the ionic components of the gaseous molecule are in contact in the lattice. Examples of this type are the sublimation of crystals to the gaseous atoms, sublimation where the lattice consists of the gaseous molecule held together by van der Waals' forces, and the sublimation of ionic crystals, such as the alkali halides. In all these examples the rate-controlling step is the breaking of the lattice bonds, and this energy is also the net heat of the sublimation process.

Conversely, any substance which does not have the gaseous molecule appearing as a structural unit in the crystal lattice could therefore be expected to demonstrate a low vaporization coefficient. In materials whose crystal bonds are extremely rigid the vaporization coefficient would undoubtedly be very small, while for lattices more capable of being deformed, a vaporization coefficient closer to unity would be expected. It is quite possible, then, that if the gaseous molecule does not exist in the crystal lattice, the sublimation process is no longer simply the breaking of the crystal bonds, but may also require a considerable rearrangement or distortion of the atomic positions before the gaseous configuration can be formed. It is thus quite reasonable that some step such as the initial rupture of the crystal bonds or the bending that these bonds must undergo will require an amount of energy larger than the overall net heat of the process.

The elements studied, red phosphorus and arsenic, are unusual in that the net number of bonds remains unchanged going from solid to gas,
in both phases the atom being bonded to three others. However, the tetrahedral gaseous molecule has bonds which are somewhat weaker due to the strain which the bonds, mostly $p$ in character, must undergo in order to form the tetrahedron. In the case of phosphorus, the gaseous bonds are $5$ kcal weaker than those of the lattice, for arsenic $\sim 5.6$. The overall heat in going from solid to gas is thus very low compared to the heat required to break a bond in the solid. In the case of red phosphorus, where the strength of the solid bond is known, the energy required to break an average $P-P$ bond is $53$ kcals while the overall heat of sublimation to $P_4$ is only $31$ kcals. Although the exact structure of red phosphorus is not known, it is certain that at least one such bond must be broken before the solid structure can rearrange to form a $P_4$ molecule. If exchange of energy is for some reason not easily accomplished, the rate-determining step could be due to the high energy required for this initial rupture. It is interesting to note that Pauling and Simonetta have proposed a structure for red phosphorus which would involve breaking a "normal", unstrained $P-P$ bond for each four atoms vaporized. Their calculated value for the energy of this bond is $51.3$ kcals, in agreement with the heat of activation measured in this thesis.

Molecules of sufficient energy to surmount this energy barrier will escape from the solid with excess energy compared to the equilibrium state of the molecule at the given temperature. Because of this excess energy the molecules may all be in an excited electronic state or in a group of highly excited vibrational or rotational states. Under equilibrium conditions a high concentration of these excited states would be attained only at very high temperatures where the gas would have a high entropy due to the large population of many other high-temperature states. The vapor surmounting the barrier, however, does not have any greater number
of states populated than does the equilibrium gas at the temperature of the experiments, although the states of the excited gas which are populated are different from those occupied in the equilibrium gas. Thus the entropy of the excited gas will not differ much from that of the equilibrium vapor. In other words specific excitation of a few high-energy levels at the expense of low energy levels does not produce an appreciable entropy increase. If this excess energy were to appear entirely in the form of translational energy, the entropy considerations are not quite so clear, but similar arguments must apply.

Apart from the interest which such behavior arouses in the mechanics of sublimation of these materials, it is well to note that such hindered sublimation can prove to be a considerable hazard to workers interested in obtaining equilibrium thermodynamic data. Since the effect of such behavior is to reduce the rate of sublimation and condensation, any means whereby the rate of removal of material from the system is measured to evaluate an equilibrium pressure must be utilized with great care if it is to yield thermodynamically meaningful results. Since methods of this type (Langmuir, Knudsen, transpiration) are widely used, particularly with the more refractory substances, results are not usually reliable when $\alpha \ll 1$, unless great care has been taken to insure that the rate of removal of material from the system is much slower than the total rate at which sublimation is taking place into the system. Even with the so-called "static" methods, where a definite quantity of material must be sublimed to fill the system, the presence of an extremely small $\alpha_v$ will require that a considerable time be allowed to elapse before the pressure approaches the equilibrium value to the desired accuracy.

It is thus mandatory that the possibility of a low vaporization coefficient be eliminated if the results of measurements involving rates
are to be used for obtaining thermodynamic data. This can be done for the Knudsen measurements by a variation in orifice area, in transpiration experiments by varying the flow rate, and in the Langmuir method by changing the total area while the geometrical area remains constant.\(^{16}\)

According to the model postulated in the introduction, the condensation and vaporization coefficients should be equal at all times, as they must be at equilibrium. Therefore a measurement of the condensation coefficient should indicate the value of the vaporization coefficient. As a preliminary investigation to the study of phosphorus and arsenic, measurements were made on the reflection of beams of different vapors from water-cooled platinum targets. In the case of arsenic, antimony, and bismuth there was definite evidence of diffuse reflection. This reflection was so extreme in the case of arsenic that little material remained on the primary target. On the other hand a number of other metals known to have unit vaporization coefficients failed to be reflected. It thus appears that a quick and simple check of the vaporization coefficient could be made in this way, since no knowledge of equilibrium values need be known.

The situation occurring in systems having low vaporization coefficients is further complicated when more than one gaseous species exists in equilibrium with a condensed phase. Since in general \(\alpha_v\) will be different for the different species a measurement of the rate of vaporization from a free surface into a vacuum will not indicate the relative abundances of the different species at equilibrium. In fact, a species having a large partial pressure at equilibrium may leave the surface at a rate many times slower than other species which are minor constituents of the saturated vapor.
The second part of this thesis was therefore devoted to the mass spectrometric investigation of red phosphorus and arsenic vapors, in which the equilibrium composition of the saturated vapor is known, but the identity of the subliming species is in doubt.
Part Two

MASS SPECTROMETRIC INVESTIGATION OF THE VAPOR

SUBLIMING FROM ARSENIC AND RED PHOSPHORUS
INTRODUCTION

Although vapor density measurements have shown the saturated, equilibrium vapor of red phosphorus\textsuperscript{17,18} and arsenic\textsuperscript{17} to be virtually all the tetramer molecule, the composition of the vapor subliming from the solid in the primary sublimation process is not known. Since these elements are observed to have such a hindered rate of sublimation, it is possible that a molecule such as the dimer or the monomer, which makes up a negligible part of the saturated vapor, could be the principal subliming species.

Melville and Gray\textsuperscript{7}, who first called attention to the extremely low rate of sublimation of red phosphorus compared to the rate one would calculate from the equilibrium pressure, hypothesized that P\textsubscript{2} is the main species leaving the solid. Since P\textsubscript{4} - P\textsubscript{2} equilibrium lies very far to the P\textsubscript{4} side, this implies an extremely low vaporization and condensation coefficient for P\textsubscript{4}. The measurements made in the first part of this thesis agree with those of Melville and Gray to within roughly an order of magnitude, but if one combines the heat of dissociation of P\textsubscript{4} to 2P\textsubscript{2}\textsuperscript{18} with the heat of sublimation of solid red phosphorus to P\textsubscript{4}\textsuperscript{19} it is found that the observed rate of sublimation is still less than the rate P\textsubscript{2} molecules would leave the surface if they sublimed without encountering a barrier. Thus even if Melville and Gray are correct, it is necessary to postulate a low vaporization coefficient for P\textsubscript{2} as well as P\textsubscript{4} in order to explain the observed low rate of sublimation.

No definitive experimental work has been done for the establishment of the vaporizing species of these elements. Recently Kerwin\textsuperscript{20} has observed subliming red phosphorus vapor mass spectrometrically, and
using high-energy electrons (70 v) gave $F_4^+; F_2^+; F^+; F_3^+$ ion intensity ratios of 100:50:16:6. Such large electron energies are most likely giving rise to the lower ions by dissociation, but at least his observations indicate the tetramer molecule to be the principal one, if one assumes reasonable ionization cross sections for the different neutral molecules.

For arsenic, too, the composition of the subliming vapor is in doubt. Metzger, using a momentum-effusion method, gives the average number of atoms per subliming molecule as 2.6. Honig, in a mass spectrometer study of germanium metal in which he observed arsenic as an impurity, gave ion intensities in the order $As_4^+; As_2^+; As^+; As_3^+$. His electron energies were 45 volts, however, which--as in the study of phosphorus--raises some doubt as to the origin of the lower ion species. Also Michel has observed the sublimation of As solid mass spectrometrically, using voltages as low as 20 volts, and reports the same species and in the same order of intensities as Honig.

The object of this investigation was therefore to attempt to determine mass spectrometrically the relative concentrations of the various neutral molecules subliming from the solid elements, insofar as is possible through measurement of the corresponding ion intensities. In addition it was hoped to measure the change in composition of the vapor as the size of the effusion orifice was reduced, in order to determine roughly the vaporization coefficients of the different species. Unfortunately, it was found that with the experimental arrangement used thermal decomposition of the tetramer on the hot filament of the mass spectrometer gave dimer and monomer ion intensities which completely obscured any contribution from neutral
molecules in the subliming vapor. Nevertheless, a considerable amount of valuable information was obtained.
APPARATUS

The element under investigation was sublimed into the ion source located at the lower end of a 9-inch-radius, 60°-deflection, single-direction focusing mass spectrometer. The essential details of the ionizing region are shown in Figure 4. To lead the source, the detachable oven was removed from the spectrometer and a new molybdenum liner, into which a few milligrams of sample had been weighed, was inserted. For the runs with reduced orifice, a punctured foil prepared in the manner described in Part I was pressed into the mouth of the liner. In the last runs with phosphorus, an auxiliary ribbon filament was installed in the position shown in the figure. The use of this filament will be discussed in a later section of this paper. The spectrometer tube was closed after loading by sealing the Pyrex glass at a point 30 or 40 cm below the ion source.

The filament was powered by alternating current stabilized by a constant-voltage transformer. This degree of stabilization was entirely adequate if a brief time was allowed for the system to reach equilibrium after each change in the heating power of the sample oven. The emission current was kept below 100 microamperes at all times; under these conditions the current from the filament was strictly temperature-limited, as evidenced by a negligible change of this quantity with electron voltage. The electron beam was aligned by a magnetic field of about 100 oersteds from an auxiliary permanent magnet. The total ion-accelerating voltage was always 4000 volts.

The use of 60-cycle alternating current for heating the filament will inevitably introduce a 120-cycle component in the emission current. It is thus mandatory that the filament-shield impedance be kept as low as possible if it is desired to obtain reasonably monoenergetic electrons.
Figure 4
Since it was hoped to obtain accurate appearance potential data, the relatively high-impedance electronically regulated emission supply ordinarily used was discarded in favor of a temporary supply in which the voltage was entirely obtained from batteries. The essential features of this supply were ten 1-1/2-volt dry cells and a 45-volt battery, so connected with a rotary switch that any desired number of dry cells could be used separately or added to the 22-1/2-volt or the 45-volt tap of the 45-volt battery. As a source of variable voltage, two heavy-duty 4-volt wet batteries were connected in series across a low (7-ohm) potentiometer, which could give any voltage up to 8 volts. By suitable combinations of batteries, it was thus possible to obtain any voltage up to 66-1/2 volts, yet the impedance across the entire voltage supply is only a few ohms. A sensitive microammeter (2500 ohms impedance) was used to monitor the emission current, but was always instantaneously shorted out when recording data.

The procedure adopted in the taking of data was first to adjust the mass spectrometer on one of the ion species and then to record the ion current for various electron voltage settings. No data were taken at a given oven temperature until the ion currents had stabilized to the extent that fluctuations over a five-minute period did not exceed ten percent. Since the small fluctuations remaining were usually steady drifts, readings of a "standard peak" (usually the P₄⁺ or As₄⁺ ion at 22.5 electron volts) were interspersed among the other data. By connecting these standard peaks on the recorder charts with "drift lines" it was a simple matter to correlate each ion-current reading with the probable value of the standard peak at that instant. All data were normalized in this manner.
The ion detector used in these studies was a 9-stage, Allen type electron multiplier terminated by a $10^6$ or $10^7$-ohm resistor; the voltage across this resistor was measured with a vibrating-reed electrometer driving a recording strip-chart potentiometer. That the multiplier could have been eliminated by employing a higher resistor is evident. This device was retained as a matter of convenience in reading the wide range of ion currents encountered as the electron voltage was advanced from threshold value to saturation value. The overall sensitivity could be conveniently adjusted to the requirements of the situation by setting the inter-dynode potentials for the multiplier structure at one of a series of standard values, for which the relative multiplier gain was frequently checked.
RESULTS

The first measurements made were appearance potential curves for the various ion species present in the vapor of subliming arsenic and red phosphorus. The procedure was to adjust the mass spectrometer to the mass under observation, and then to vary the electron voltages by increments of 0.2 volts at the low voltages, then in larger increments up to the full voltage of the supply (66.5 v). As a source of the vapor, the elements were sublimed into the ion source from an open-topped crucible, so the vapor corresponded closely to that of free, Langmuir type sublimation. Arsenic and phosphorus behaved so similarly that the two elements will be discussed together.

For both elements, ions corresponding to the tetramer, trimer, dimer, and monomer were detected. Plots of the appearance potential curves of these ions are given in Figures 5, 6, 7, and 8. The tetramer and dimer gave typical appearance curves in that both exhibited a very short (< 1 v) region in which ion intensity rose slowly with increasing voltage; the curves then rose very steeply from this point. Onset voltages were 9.5 and 8 for P$_4^+$ and As$_4^+$ respectively, and 11 and 10.5 for P$_2^+$ and As$_2^+$. The curve for P$_3^+$ was noticeably different in that the steeply rising portion was preceded by a portion of ~ 3 volts energy range in which the intensity increased slowly with increasing voltage before rising in the conventional rapid manner. The trimer ion was the least intense at all voltages above 25 volts.

The P$_4^+$ and As$_4^+$ curves were the only ones whose appearance immediately suggested that the ions were being formed from different processes at different voltages. Both showed a long portion (10-16.5 v) where the increase in intensity with voltage was small and nearly linear.
Fig. 5. $\text{As}_3^+$, $\text{As}_2^+$, and $\text{As}^+$ curves normalized to maximum intensity $= 100\%$

$\text{As}_4^+$ curve was normalized to intensity at 45 volts $= 100\%$
Fig. 6. $P_3^+$, $P_2^+$, and $P^+$ curves normalized to maximum intensity = 100%

$P_4^+$ curve was normalized to intensity at 45 volts = 100%
Fig. 7. $\text{As}_3^+$, $\text{As}_2^+$ and $\text{As}^+$: Full scale = 1% maximum intensity
$\text{As}_4^+$: Full scale = 0.1% intensity at 45 volts
Fig. 8.  $P_3^+$, $P_2^+$, and $P^+$: Full scale = 1% maximum intensity

$P_4^+$: Full scale = 0.1% intensity at 45 volts
At ≈ 17 volts the curves broke sharply, rising many times more steeply with voltage, and at high voltages became comparable in intensity to the dimer and tetramer ions. It should be mentioned that none of these curves would be expected to extrapolate to the exact ionization potential of the molecules, since there is undoubtedly some contact potential present. The measurements made on Hg gave appearance potentials agreeing with the known ionization potential to within < 0.5 volt, showing this effect to be small.

For both elements at all voltages the tetramer ion is the most intense. It should be noted also, however, that the ratios of intensities of the different species are strongly voltage-dependent. For example, at 45 volts, where the intensity is only weakly voltage-dependent for all species, the abundances of As$_4^+$, As$_3^+$, As$_2^+$, and As$^+$ are in the ratios 1:0.13:0.33:0.29, whereas at 15 volts the same abundances are in the ratios 1:4.4x10$^{-2}$:1.95x10$^{-2}$:4.3x10$^{-4}$. The corresponding ratios for phosphorus are very similar. It is apparent that any conclusions drawn as to the relative abundances of the neutral species are apt to be of questionable value. Further, there is no particular reason to believe that simple, non-dissociative ionization is the only process leading to the formation of these ions. Surely the origin of the lower ion species must be investigated before any conclusions as to abundances of neutral species can be made.

The next part of the investigation was to establish that the ion species formed were derived entirely from one-electron processes, to eliminate reactions in which two consecutive low-energy electron collisions lead to products which would require a single electron of higher energy. If such multiple-electron processes are appreciable
contributors to the ion intensity, the ion intensity observed should have a greater-than-one power dependence on the number of ionizing electrons, when electron voltage and the vapor concentration are held constant. Measurements of ion intensity versus electron current were made at 30, 20, and 15 volts, in each case varying the electron current by about a factor of 10. For the ion species of both elements, the curves of intensity versus current were either linear or bent slightly downward, whereas multi-electron processes would bend the curve upward. The cause of the slight curvature was not explained, but at any rate multi-electron processes do not appear to be important.

As mentioned in the introduction, the main purpose of this portion of the investigation was to determine if the composition of the vapor changes as the conditions of sublimation go from that of free sublimation to the equilibrium situation. For this purpose the appearance-potential curves were again taken, examining this time the vapor emanating from a Knudsen cell having an orifice; cell cross section ratio of \( \sim 10^{-4} \) that of the previous measurements. If both the tetramer and the dimer are subliming from the lattice, the intensity of the species having the largest \( \Delta \mu^f - \Delta \mu^0 \) value (i.e., the smallest vaporization coefficient) should be the most affected by the change in orifice size, and thus the ion intensity ratio will differ at different orifice sizes.

The general appearance of the curves obtained from vapor effusing from a small orifice was very similar to the curves taken on the Langmuir type sublimation. In order to bring out any difference, the \( \text{As}_{4}^+/\text{As}_{2}^+ \) and \( \text{P}_{4}^+/\text{P}_{2}^+ \) ratios were tabulated as a function of voltage for the two orifices. The values at several voltages are given in Table 4.
Table 4: Tetramer - Dimer Ion Intensity Ratios
Under Langmuir and Knudsen Conditions

<table>
<thead>
<tr>
<th>Volts</th>
<th>$P_{4}^{+}/P_{2}^{+}$</th>
<th>$P_{4}^{+}/P_{2}^{+}$</th>
<th>$As_{4}^{+}/As_{2}^{+}$</th>
<th>$As_{4}^{+}/As_{2}^{+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Knudsen $^a$</td>
<td>Langmuir</td>
<td>Knudsen $^b$</td>
<td>Langmuir</td>
</tr>
<tr>
<td>12</td>
<td>118</td>
<td>77</td>
<td>730</td>
<td>1300</td>
</tr>
<tr>
<td>16</td>
<td>17.3</td>
<td>15.2</td>
<td>24.9</td>
<td>19.5</td>
</tr>
<tr>
<td>20</td>
<td>5.22</td>
<td>5.20</td>
<td>6.35</td>
<td>4.52</td>
</tr>
<tr>
<td>25</td>
<td>3.08</td>
<td>3.09</td>
<td>3.24</td>
<td>2.36</td>
</tr>
<tr>
<td>30</td>
<td>2.79</td>
<td>2.56</td>
<td>3.17</td>
<td>2.30</td>
</tr>
</tbody>
</table>

(a) Orifice area : container cross section = $2.3 \times 10^{-4}$

(b) Orifice area : container cross section = $9.5 \times 10^{-4}$
Interestingly, the 4:2 ratios proved to change but little with orifice size, agreeing within a factor of ~2 at the point of farthest separation, and virtually coinciding over most of the voltage range.

One possible explanation of the failure of the ratios to change with decreasing orifice size is that the two molecules have identical vaporization coefficients. This would lead to a ratio of intensities independent of orifice size. A second mechanism which would give a constant tetramer-dimer ion ratio is one whereby the dimer ion is obtained by some process which depends on the concentration of the tetramer. Such a process would explain the experimental observations, since any change in tetramer concentration would change the dimer concentration proportionately.

In order to rule between these two mechanisms, a series of measurements were made on both phosphorus and arsenic, in which the ion intensities accompanying large-orificed sublimation were observed as a function of temperature. If the vaporization coefficients are the same for dimer and tetramer (the first possibility listed above) the $\Delta H^\ddagger - \Delta H^0$ values must be the same for both. For phosphorus the values of $\Delta H^0$ are known for both tetramer and dimer, and differ by 13 kcal. The difference is not known for arsenic, but would presumably not be greatly different than that for phosphorus. Thus if the $\Delta H^\ddagger - \Delta H^0$ values are the same for the two molecules, the measured heats of activation must differ, and by a sufficiently large amount to be easily detectable in a plot of $R \ln (I T)$ against $1/T$ for the two species, where $I$ is the intensity of the ion peak in question.
A careful measurement of $P_4^+$ and $P_2^+$ and a corresponding run on arsenic were therefore carried out, using vapor subliming under Langmuir conditions over a range of temperatures. At each temperature an appearance potential curve was run for each ion; that is, measurements were made over a considerable range of voltages beginning at onset. From these measurements plots were made of $R \ln (I/T)$ versus $1/T$ at voltages of 10.5, 11, and 11.5 volts. These plots are given in Figures 9 and 10. At all voltages the slopes were identical for dimer and tetramer; yielding activation energies of 56 kcal for phosphorus and 41 kcal for arsenic, in good agreement with the values of 52 kcal for phosphorus and 43 kcal for arsenic obtained by weight-loss methods in Part I. In addition, a preliminary measurement on phosphorus only in which intensities of all four ions were measured showed the temperature coefficient to be identical for all.

For both elements the nearly perfect coincidence of the slopes of dimer and tetramer ions clearly rules out the possibility that the $\Delta H^* - \Delta H^o$ values are the same for the two species. It therefore seems that the dimer -- and very likely the trimer and monomer also-- are obtained in some manner from the neutral tetramer. This of course could be by a process of dissociation by high-energy electrons, as appears probable at the higher voltages where the intensities of all species becomes comparable. It is certain, however, that dissociative ionization is not solely responsible for the observed ions, since $P^+$ appears at electron voltages within 0.5 v of its true ionization potential, yet is observed to have the same temperature coefficient as the tetramer ion. Such behavior makes it almost certain that the $P^+$ ion is coming from the neutral monomer rather than from a dissociative process, yet this neutral monomer concentration appears to be somehow
TEMPERATURE COEFFICIENT - ARSENIC

$\Delta H \approx 41$ KCAL

Figure 9
TEMPERATURE COEFFICIENT
PHOSPHORUS

ΔH' = ~ 56 KCal

Figure 10
a function of the tetramer concentration.

A possible explanation of the breakdown of the tetramer molecule is that it is being thermally dissociated at the mass spectrometer filament. From Figure 4 it is seen to be quite reasonable that a considerable concentration of the neutral dimers could be formed in this manner. The geometry of the source is such that the tetramer molecules would have to make at least one rebound from the nichrome walls before they could strike the filament, but observations in Part I of this thesis have shown that both phosphorus and arsenic vapors are very reluctant to condense on surfaces of room temperature, and many reflections could thus take place within the ion source.

Since the presence of the hot filament is necessary for the operation of the instrument, the method of demonstrating what effect, if any, this filament has on the observed ion intensities was to add a second filament, of slightly larger area, placed in the position shown in Figure 4. This filament was powered by a separate power supply, and at all times was kept sufficiently cool so no thermionic emission took place. The temperature of this auxiliary filament was established roughly by means of an optical pyrometer.

A final series of appearance potentials were taken on phosphorus vapor subliming under Langmuir conditions. The measurements were made on all 4 ions, first with the auxiliary filament off, then with this filament at a temperature of \( \sim 1200^\circ C \).

It is not possible to compare the results of the two measurements directly, since the extra filament caused a considerable increase in the temperature of the sample, with a corresponding increase in the intensities of all ions. The procedure was therefore adopted whereby
the readings were normalized by dividing each by its "standard peak," this being chosen as the \( P_4^+ \) ion intensity at 22.5 \( v \). Since the fraction of the \( P_4 \) neutral species being ionized or dissociated is surely very small, such a normalization should reduce all the results to a comparable basis.

The data so obtained are extensive and will not be reproduced in full. Two methods of comparison which best bring out the effect of the auxiliary filament are (1) "difference" curves, in which the normalized intensity with the filament off, \( I_{\text{off}} \), is subtracted from the normalized intensity with the filament on, \( I_{\text{on}} \), and these differences plotted as a function of voltage and (2) fractional increase curves, in which \( I_{\text{on}} - I_{\text{off}} / I_{\text{off}} \) is plotted as a function of voltage. The latter is especially good for pointing out the region in which the effect of the auxiliary filament is not pronounced.

\( P_2^+ \). The auxiliary filament was found to have a completely negligible effect on this ion; the normalized curves taken with filament on and filament off were coincidental over their entire length within the accuracy of measurements. This behavior, coupled with the observation of an identical temperature coefficient for trimer and tetrramer ion, makes it quite certain that the trimer ion is derived completely from the \( P_4 \) molecule by dissociative ionization, there being no evidence for the existence of the neutral trimer.

\( P_4^+ \)

The normalized curves for \( P_4^+ \) must of course coincide at 22.5 electron volts, since this point was used for the normalization. At voltages near onset, however, the fractional-increase plot showed an anomaly which was not interpreted. This is shown in Figure 11-A.
Fig. 11-A-B-C. Fractional-Increase Curves for Phosphorus
The magnitude of this fractional increase is such that it is not thought to be caused by experimental error, although the plot is of course very sensitive to slight errors in measurement at these low values of intensities. A change in contact potential occurring between the two measurements would have the effect of causing the curve to approach positive infinity or -1, which it does not do. Another possible explanation is that a certain number of tetramer molecules leave the filament in some way highly excited, and in this condition they are more easily ionized by low-energy electrons. No conclusions as to the cause of this effect were drawn. The \( P_4^+ \) on-off curves coincided over the rest of the voltage range measured.

The difference curves and the fractional increase curve for \( P_2^+ \) are given in Figures 12-1 and 11-B respectively. Both these curves illustrate that the presence of the auxiliary filament has increased the \( P_2^+ \) ion intensity by a large amount, the fractional increase being the greatest in the low-energy regions and dropping off at higher voltages. This behavior suggests that the production of \( P_2 \) ions is caused by different processes at different voltages. Since there are only two processes which can lead to the production of \( P_2^+ \), the difference curve is in this case the true appearance potential of \( P_2^+ \) from the neutral dimer; any production from the tetramer will be unchanged by the presence of the auxiliary filament, and thus will be subtracted out in taking the difference. The onset of this difference curve coincides with the onset of the \( P_2^+ \) curves previously obtained, indicating that at the lower voltages the process leading to the formation of \( P_2 \) ions is the ionization of the neutral dimer.
Fig. 12. Intensity Difference Curves for Phosphorus
Although there clearly must be a second onset potential at which the $P_2^+$ is first obtained from $P_4$, no "breaks" were ever observed in the $P_2^+$ appearance potential curves (See Figures 6, 8). An appearance potential curve without irregularities is thus seen to be no guarantee that a single process is producing the ions at all voltages.

Again for the monomer, the presence of the auxiliary filament is seen to have a marked effect on the ion intensity. The difference curve and the fractional increase curve are shown in Figures 12 and 11-C respectively. The effect of the auxiliary filament is seen from the fractional increase curve to be pronounced at low voltages, increasing to a maximum at ~ 16 volts, and then dropping rapidly at higher voltages. Such a variation in the fractional difference curve is not surprising when it is realized that $P^+$ ion can come from at least 3 processes, two of which one would expect to be influenced by thermal dissociation on the filament. Thus the $P^+$ ion can be obtained directly from neutral monomers which have been formed at the filament, presumably by dissociation of $P_2$. A second process is the dissociative ionization of the neutral dimer, which would also be filament-produced from $P_4$. Both these processes would have the effect of increasing the difference-curve value. The third source of $P^+$, which is the only one not augmented by the auxiliary filament, is the dissociative ionization of the tetramer.

One can thus explain the shape of the $P^+$ fractional increase curve by postulating the low-voltage (11-15) process to be the ionization of neutral atoms, the process at intermediate voltages to include the dissociation of $P_2$ as well, and the process occurring at the high voltages
to be principally the dissociation of the tetramer. It would be expected from the known heats of dissociation that the dissociation to $P_2$ would be the reaction most increased by the auxiliary filament and the fractional increase for $P^+$ is greater in the region corresponding to the production of $P^+$ from $P_2$ molecule.

By combining the known ionization potential of $P^+$ (10.55 v) with the dissociation energy of $P_2$ (5 v) one can predict that $P^+$ originating from $P_2$ will not occur at voltages lower than 15.5 v. It is interesting to notice that the fractional increase curve increases sharply at approximately this point.
In addition to the observations summarized above, a search for molecules containing more than four atoms was made for both elements. This effort was prompted by the paper by Kerwin, who reports the presence of $P_8^+$ ion with an intensity 1/2 percent that of the $P_4^+$ ion.

The mass spectrum was therefore scanned carefully for any species of mass greater than the tetramer in the vapor of both arsenic and red phosphorus subliming under Langmuir conditions. Only the ions $As_6^+$ and $As_8^+$ were detected, and an upper limit for the $P_8^+$ concentration was established which is much less than that reported by Kerwin.

**Phosphorus**

The examination of phosphorus vapor for higher-mass species was done over the mass range 200-300, since $P_8^+$ would have a mass of 248. The instrument was adjusted to give high sensitivity, and the slit so narrowed as to clearly resolve the adjacent mass units over this mass range. The mass scale was positively established by scanning the $Hg^+$ peaks, and then counting each mass peak as the instrument swept up, since with the extreme sensitivity available with the electron multiplier sufficient background is present in this region to give a peak at each mass. Electrons of 45 volts energy were used.

The only peaks which were significantly above background over this mass range were the following, with their tentative identifications:

- $212$ ($As_2P_2^+$), $225$ ($As_3^+$), $252$ ($P_4O_8^+$), $256$ ($As_2P^+$), $268$ ($P_4O_9^+$), $284$ ($P_4O_{10}^+$) and $300$ ($As_4^+$). The peak corresponding to $P_8^+$ (248) was not measurably different in intensity from its neighboring background peaks. Assuming the $248$ peak to be entirely $P_8^+$, the intensity of the $P_4^+$ ion is still a factor of 20,000 greater in intensity, compared to a factor of 200 reported by Kerwin.
Arsenic

The search for the higher species of arsenic was considerably more difficult than for phosphorus, since at these high masses the background peaks do not occur at each mass unit. This of course precludes the method of counting up from a known mass peak to establish the mass of a peak in question, but is on the other hand an advantage when measuring ion peaks of very low intensity.

Since the ions of interest were $\text{As}_6^+$ and $\text{As}_8^+$, the method used was to adjust the instrument to the mass peak corresponding to one-half the higher mass ($\text{As}_{11}^+$ and $\text{As}_{12}^+$ being easily identified), and then without changing the magnetic field to cut the ion-accelerating voltage exactly in half, which doubles the mass under observation in the analyzer. The instrument was adjusted to give high sensitivity, and 45-volt electrons were used throughout the scanning process.

The peak observed at mass 600 was remarkable for its high appearance potential. The ion first appeared at 25 volts, and the intensity then rose with voltage to the highest measured voltage, 45 volts, where the intensity was $\sim 10^{-5}$ that of the $\text{As}_4^+$ ion. The $\text{As}_6^+$ ion intensity was about 1/3 that of the $\text{As}_8^+$. The appearance potential curve for $\text{As}_8^+$ is given in Figure 13.
Figure 13
DISCUSSION

It thus appears that for both elements, the principal species in the subliming vapor is the tetramer. Unfortunately the presence of the neutral dimer and monomer formed at the filament completely obscures any neutral molecules which might be subliming from the solid. The only method of distinguishing between molecules formed on the filament and those in the subliming vapor is the temperature coefficients, which are rather insensitive. At any rate, although it is not possible to measure the importance of the lower neutral species subliming from the solid in the instrument available, one can say that the amount of these lower species must be an order of magnitude less than the tetramer, probably much less than this.

The failure to find any appreciable quantity of \( P_2 \) and \( As_2 \) in the subliming vapor is evidence that the vaporization coefficient for the dimer of both elements is small, perhaps as small as that of the tetramer. It is therefore necessary to postulate that some sort of free-energy barrier similar to that present in the sublimation of the tetramer must exist in the process whereby the dimer molecule is formed from the lattice configuration.
APPENDIX I

Arsenic

The vapor pressure of crystalline arsenic solid has been measured by Horiba,23 Gibson,24 and Preuner and Brockmoller.17 These measurements encompass a range of pressures from fractions of a mm Hg to 34 atmos (triple point), and were all made with static, manometric methods. Preuner and Brockmoller have also measured vapor densities of arsenic vapor, and from these have calculated the dissociation constants. Their results, although not sufficiently accurate to give reliable heats of dissociation from a second-law plot, nevertheless indicate that at temperatures below 800°C the gas consists only of $\text{As}_4$ molecules, within their limits of measurement.

The total vapor-pressure measurements of the three investigators were therefore used to obtain a heat for the reaction $4\text{As}(c) = \text{As}_4(g)$ by means of a $\Sigma$ plot. For this purpose it was necessary to estimate a heat capacity for $\text{As}_4(g)$, since there are insufficient spectroscopic data to calculate this quantity. The gaseous $\Delta C_p$ value taken for the average temperature of the experimental measurements was 20 cal/mol-degree, obtained by an estimation in comparison with the known value of 18.5 cal/mol-degree for $\text{P}_4(g)$, since it would be expected that the phosphorus molecule would have stronger bonding than the arsenic molecule. This value, when combined with the known heat capacity of the solid,25 yields a $\Delta C_p$ value of -8.6 cal/mol-degree, which was assumed constant over the temperature range of the plot. At high pressures the fugacities were calculated from pressures by the method of Brewer and Searcy.26

The agreement between the three sets of data used is not particularly good; however, the slope of the $\Sigma$ plot was evaluated, giving a value of

$$\Delta H^o_298 = 34.7 \pm 1 \text{ kcal.}$$

The intercept gives a value of 42.0 e.u. for
\( \Delta S_{298} \), which, when combined with the known entropy of the solid\(^{25} \) gives a value for \( \text{As}_4(g) \) of \( S_{298} = 75.6 \text{ e.u.} \).

If it were not for the lack of data on the vibrational frequencies in the \( \text{As}_4 \) molecule, one could apply a third-law check to these data, since the entropy of the crystal and the interatomic distances in the gas\(^{27} \) are known. As a partial check, the translational and rotational entropy of \( \text{As}_4 \) were calculated, giving a total \( S_{298}^{\text{trans.+ rot.}} = 67.85 \text{ e.u.} \). This indicates a vibrational entropy of 7.75 e.u., which is not unreasonable in comparison with the presumably much more tightly bonded \( \text{P}_4 \) molecule, which has a vibrational entropy of 4.86 e.u.

**Red Phosphorus**

The heat of sublimation of red phosphorus has been until recently based entirely on the temperature coefficient of vapor-pressure measurements, since the entropy of the red crystalline modification was not known. These heats are not at all concordant, and as a result there was considerable uncertainty in any vapor pressure calculated.

Recently, the author was informed that Professor C. C. Stephenson of the Massachusetts Institute of Technology has been engaged in a thorough investigation of the heat capacities and entropies of the various modifications of phosphorus solid. Professor Stephenson is now readying these results for publication, but has been kind enough to forward a number of the pertinent experimental results\(^{19} \) with the comment that they are preliminary in nature, and may be subject to minor revisions. He has also included a measurement of vapor pressure of the red modification.

In view of the excellent molecular data available for calculating the entropy of the \( \text{P}_4 \) gaseous molecule\(^{19, 28} \), the measurements of Professor Stephenson are to be preferred over those of the other investigators.
The calculations of this thesis were therefore made with the entropy and vapor-pressure measurements of Stephenson.

The author is taking the liberty of reproducing some of the values so kindly sent him by Professor Stephenson. As was mentioned previously, the values are of a preliminary nature; for this reason only those values pertinent to the calculations of this thesis will be presented. The publication of the complete results of Professor Stephenson's investigation is to be expected at an early date.

DATA ON CRYSTALLINE RED PHOSPHORUS

Entropy: $S_{298}^o = 5.54$ e.u.

Sublimation Data: ($\mu_{\text{red}}^o = P_4(g)$) $\Delta H_{298}^o = 30840$ cal/mol

$\Delta F_{298}^o = 17500$ cal/mol

The above values were combined with the high-temperature heat capacities and entropy data taken from Kelley\textsuperscript{25} for calculating the pressure of $P_4$ gas at any temperature.

In addition to the values pertaining to the sublimation process, there are also data on the reaction $P_4(g) = 2P_2(g)$ which appear reliable. The vapor-density measurements of Stock, Gibson, and Stamm\textsuperscript{18} have been subjected to a third-law check by Stevenson and Yost\textsuperscript{22} who used spectroscopic data to calculate entropies for $P_4(g)$ and $P_2(g)$. The measured free-energy values of Stock, Gibson, and Stamm yielded $\Delta H_{298}^o$ values which varied by only 130 calories over a temperature range of 400°K. Such consistency is strong evidence that the experimental measurements are correct, and a dissociation heat of $\Delta H_{298}^o = 54.5$ kcal was therefore used for the reaction $P_4(g) = 2P_2(g)$. This value, when combined with the heat of sublimation quoted above, gives a value of 42.7 kcal for $2P_{\text{red}} = P_2(g)$.
The heat of the reaction $\text{P}_2(g) = 2\text{P}(g)$ has been evaluated by Stevenson and Yost, who obtained the equilibrium constants of the reaction using only spectroscopic data. Their value of 116.4 kcal, when combined with the heat of sublimation above, gives for the reaction $\text{P}(\text{red}) = \text{P}(g)$ a value of $\Delta H^\circ_{298} = 79.5$ kcal.
18. A. Stock, G. Gibson and E. Stamm, Ber. 45, 3527 (1912).
ACKNOWLEDGMENT

The author is pleased to make use of this opportunity to express his sincere appreciation to Professor Leo Brewer, under whose inspiring leadership the investigation reported in this thesis has been carried out. He is indebted too, to Professor John Reynolds of the Department of Physics, whose efforts and abilities made possible the mass spectrometric portion of this investigation.

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