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THE IMPORTANCE OF COMPLEX GASEOUS MOLECULES IN
HIGH TEMPERATURE SYSTEMS

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ABSTRACT

The influence of polymerized gaseous molecules upon equilibrium pressure measurements and upon measurements of rate of vaporization is discussed. Vaporization data for red phosphorus and arsenic are presented and the existence of catalytic effects upon rates of vaporization is demonstrated.

INTRODUCTION

Recent mass spectrometer measurements¹⁻³ have demonstrated that complex polymeric gaseous molecules are rather common in high temperature vapors. In a saturated vapor in equilibrium with a condensed phase, it can be demonstrated that the vapor becomes more complex as the temperature is raised, and the various possible minor species in a vapor have their greatest importance at the boiling point. This may be illustrated by the well-known example of saturated sodium vapor, which consists of 99.9% atomic sodium and 0.1% Na_2 at 400°K, but which contains about 12 mole % Na_2 at 1100°K.⁴ Brewer⁵ has shown that a simple relationship exists between the heats of vaporization of monomeric and dimeric species and the heat of dissociation of the dimer. When the heat of dissociation of

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the dimer, ΔH_2 is equal to the heat of vaporization of the monomer, ΔH_1 , both the monomer and the dimer have equal heats of vaporization, and their proportion remains unchanged as the temperature is changed. It can be shown that the entropies of vaporization will not differ greatly. Thus monomer and dimer species will be of the same order of concentration when ΔH_2 is equal to ΔH_1 . If the heat of dissociation of the dimer is less than ΔH_1 , which is the usual case, the vapor will consist largely of the monomer at low temperatures, but as the temperature is increased, a larger and larger proportion of the saturated vapor will consist of dimeric species with a maximum of dimer at the boiling point. The same is true of higher polymers. In the rarer situation where the heat of dissociation of the dimer is greater than the heat of vaporization of the monomer, the dimer will be the main species at low temperatures, while the percentage of monomer and higher polymers in the saturated vapor will increase as the temperature is increased. Brewer⁵ has illustrated this behavior by examining the stability of dimers of the halides of the elements. A similar behavior is to be expected for the elemental vapors and other saturated vapor systems. Thus if one wishes to study the various minor polymeric gaseous species of a substance, it is usually easier to detect them at higher temperatures where these polymers comprise a higher proportion of the vapor.

When one is studying slightly volatile substances, the Langmuir method, which consists of the measurement of the rate of vaporization in a low pressure system, is commonly used for the determination of the vapor pressure. The rate of vaporization can normally be measured with a high accuracy and with much less difficulty due to the reaction of the

vapor with containers and with much less chance of contamination by gaseous impurities than one encounters with other vapor pressure methods. However, the determination of the equilibrium pressure by this method requires the equating of the rate of vaporization to the rate of condensation. The rate of condensation can be calculated accurately from kinetic theory if the assumption is made that every molecule striking the surface condenses without rebounding. When this condition is met, it corresponds to a unit sticking or condensation coefficient and a unit vaporization coefficient. In the literature, both of these coefficients are commonly called accommodation coefficients. The vaporization coefficients of many materials have been checked, and virtually all materials that have been investigated have been found to have unit vaporization coefficients.⁶ That is, the rates of vaporization are found within experimental error, to be those expected from the equilibrium pressures and the kinetic theory of gases. From experience to date, one can predict that all molecular lattices that consist of the main gaseous molecular species held together by van der Waals forces or weak forces of any type will have unit vaporization coefficient for the main gaseous species. However, as indicated by Guthrie, Scott and Waddington⁷ for rhombic sulfur, minor species that are not present in the molecular lattice and which are not readily formed from the main gaseous species may not be present in the gas vaporizing from a surface under reduced pressures, and thus the rate of vaporization will be slightly lower than that expected from the total equilibrium pressure, since the rate will correspond only to the partial pressure of the main species. All elements that vaporize predominately to atomic species have

been found to have unit vaporization coefficients whenever checked.⁶ All ionic salts such as the alkali halides that vaporize predominately to a monomeric gaseous molecule are believed to have vaporization coefficients close to unity, although some measurements yield values as low as 0.5.⁸ There have been some accurate measurements indicating slightly low values, but there are no indications that vaporization coefficients below the range 0.8-1.0 are to be expected for any ionic substance where the ions required for a gaseous molecule are in contact. Hydrogen-bonded substances have been found to have unit accommodation coefficients whenever checked.⁹⁻¹¹

The only clearly demonstrated examples of low vaporization coefficients occur when the main molecular gaseous specie does not occur as such in the condensed phase. The investigation of Stranski and Wolff¹² on the rate of vaporization of two crystalline modifications of As_2O_3 , arsenolite and claudetite, serves to illustrate this point. The crystal structure of arsenolite is known to be a molecular lattice of As_4O_6 molecules, while the structure of claudetite is unknown, other than that it is monoclinic, and does not consist of a molecular lattice. In both cases, the saturated equilibrium vapor consists primarily of As_4O_6 molecules. The rate of vaporization of arsenolite is observed to be 10^6 times greater than that of claudetite. There are other examples such as the ammonium halides which vaporize to ammonia and hydrogen halide,¹³ neither of which is present in the condensed phase. Elemental phosphorus is another clear example. White phosphorus, which is a molecular lattice of P_4 molecules, the main gaseous species, has a unit vaporization coefficient, while red phosphorus which is not

believed to contain P_4 molecular units has a vaporization coefficient of about 10^{-6} . Similarly, arsenic, whose lattice is known not to contain As_4 units, has a low vaporization coefficient.¹³

EXPERIMENTAL

In an effort to elucidate the mechanism of vaporization when one has a barrier against vaporization as indicated by a low vaporization coefficient, a study has been made of the vaporization of arsenic under a variety of conditions, and a similar study is under way for red and black phosphorus. Melville and Gray¹⁴ attributed the anomalously low rate of vaporization of red phosphorus to the existence of P_2 units in the solid lattice, and they hypothesized that P_2 was vaporizing with unit vaporization coefficient from the solid, but, because of the small partial pressure of P_2 compared to P_4 , a very low rate of vaporization was obtained. To check this hypothesis for red phosphorus, we have repeated their Langmuir measurements and have obtained results agreeing within an order of magnitude. We have evaluated the data in the literature on the equilibrium between P_4 and P_2 in the gaseous phase and agree with Yost and Russell¹⁵ that the measurements of Preuner and Brockmoller¹⁶ must be in error, and that the measurements of Stock, Gibson and Stamm¹⁷ appear to be reliable. Thus from the known equilibrium pressure of P_4 over red phosphorus as determined by static methods¹⁸ and the equilibrium between P_4 and P_2 , we have been able to calculate the equilibrium partial pressure of P_2 in equilibrium with solid red phosphorus. We find that the rate of vaporization of red phosphorus is smaller than what would be expected from the equilibrium pressure of P_2 . This would indicate that even P_2 has a vaporization

coefficient less than unity. Thus the limiting rate of vaporization in a Langmuir experiment is not necessarily fixed by the P_2 vapor pressure as proposed by Melville and Gray. For arsenic where equilibrium data are not available to determine the pressure of As_2 in equilibrium with the solid, we have examined the vapor from a Langmuir type experiment in a mass spectrometer, and have found the vapor to be predominately As_4 .

To check the correlation between vaporization coefficients and sticking or condensation coefficients, molecular beams of phosphorus and arsenic vapor were impinged upon various targets that had been cooled to a sufficiently low temperature so that any phosphorus or arsenic that would condense upon the target would be incapable of revaporizing. It was found that virtually all of the vapor rebounded without condensation from most target materials. Copper cooled to a low temperature appeared to be the most efficient target.

As the equilibrium pressure of As_4 over arsenic did not appear to be completely established by means of static measurements,^{16,19,20} the vapor pressure of arsenic was evaluated by the Knudsen method using orifice area to vaporizing area ratios ranging from 1.0 to 1.6×10^{-4} . It was found that the orifice to vaporizing area had to be less than 10^{-3} before a vapor pressure near to the equilibrium value and independent of orifice size was reached. Comparison of Langmuir results with the equilibrium pressures indicated vaporization coefficients of about 5×10^{-4} . Some measurements were also made with red phosphorus and with the smallest orifice to vaporizing area tried, 1.33×10^{-4} , the vapor pressure in the Knudsen cell was still only 10^{-3} times the equilibrium value.

From the results obtained to date, it appears clear that it will be extremely difficult to obtain any reliable vapor pressure results for red phosphorus by the conventional Knudsen method. The orifice size required for any reasonable cell must be so small that cracks and fissures and porosity of the cell material will become comparable to the orifice area. To eliminate this difficulty, an attempt to find a catalyst for the vaporization reaction was made. It had been observed that fresh samples of phosphorus and arsenic gave abnormally high rates of vaporization which decreased as vaporization proceeded. This might be attributed to impurities such as oxides, etc., but the effect seemed larger than might be attributed to impurities. Our hypothesis was that fresh material contained many distorted or defective crystals in which the atoms were not so rigidly fixed. Thus they could reorganize to form P_4 or As_4 molecules whereas in a perfect lattice, it would be extremely difficult to distort the rigid lattice to produce a P_4 or an As_4 molecule. Thus we believed that the abnormal vaporization rate was due to the distorted crystals that were soon removed. The effect of the nature of the material was also apparent in the reproducibility of Langmuir type measurements or Knudsen measurements with large orifice. The results appeared to vary from sample to sample for no obvious reason, whereas measurements with the same materials made by Knudsen method with small enough orifices to produce the equilibrium pressure of As_4 were much more reproducible. It thus appeared that we might be able to catalyze the rate of vaporization by loosening up the lattice. A simple procedure to accomplish this would be to add some non-volatile liquid which would not react chemically with phosphorus or arsenic to form any intermediate

phases, but which would dissolve some of these elements. In the mobile liquid, it should be possible for the atoms to rearrange to form the P_4 and As_4 aggregates necessary for attainment of equilibrium pressures. Thallium and lead appeared to be liquids that would meet the requirements. Thallium was added to phosphorus and arsenic in Knudsen cells with relatively large orifices, and heated above the melting point of thallium. The pressures observed were 30 times greater than those observed without addition of the liquid catalyst, all other experimental conditions being the same. Upon further heating the same sample, the pressure steadily decreased, although the quantity of arsenic present was still sufficient to maintain a solid arsenic phase. Examination of the system upon cooling indicated that the phosphorus or arsenic in contact with the liquid had dissolved, leaving very few points of contact between the solid and liquid. Thus the transfer of material between the solid and liquid became slower and slower. To minimize this, mixtures of thallium and arsenic were heated in sealed quartz tubes to 1000°K and then chilled, resulting in a fine intermixture of arsenic and thallium. When these mixtures were again heated in Knudsen cells with large orifices, the pressures were again about 30 times higher than observed without the catalyst present, and in fact were very close to the extrapolation of the equilibrium vapor pressure curve determined at higher temperatures by static methods. Further, continued heating of the samples gave consistent results, showing that slowness in transfer between the liquid and solid has been greatly reduced. The main experimental results demonstrating the effects are given in Figure I. The small dependence upon orifice size even in the presence of thallium liquid shows that the transfer from solid to liquid still limits the rate of

evaporation to some extent, however. Because of the large arsenic pressure when liquid thallium was present, large Knudsen orifices or a Langmuir type measurement would have given too rapid a loss of material for accurate measurements. Extrapolation of the thallium results to unit orifice to surface area ratio shows that addition of thallium has increased the rate of vaporization of arsenic almost 100 fold. Thus by means of the thallium catalyst it is possible to accelerate the rate of vaporization sufficiently to allow the determination of pressures closely approaching the equilibrium values using a Knudsen cell of comparatively large orifice. To insure that the effusate in these runs was arsenic only, spectroscopic analyses were utilized; the quantity of thallium found being much less than in a standard alloy mixture containing 1% thallium, 99% arsenic. Similar experiments are now in progress with red and black phosphorus.

Although it appears possible to saturate the liquid metal with arsenic or phosphorus by obtaining a large surface contact between the solid and liquid, the resulting vapor pressures for arsenic appear to be about 40% lower than the extrapolation of the equilibrium curve obtained from static methods.^{16,19,20} With regard to these static measurements, consideration of the data in the literature does not enable the equilibrium pressure to be fixed precisely. A considerable variation is found between different investigators in the values given for the equilibrium vapor pressures, and since the molecular constants are not known for the As_4 molecule, one is not able to subject the data to a third law check. Therefore, for this work, a heat capacity for the gas was estimated, a constant ΔC_p was assumed over the temperature

range of the experiments, and the "best" line was drawn through the experimental points. The equilibrium pressures calculated in this manner are therefore uncertain to a relatively large degree. The Σ plot of the data is shown in Figure II. $\Sigma = -R \ln P + \Delta G_p / RT$. The ΔG_p used over this range was -8.6.

In addition to the fact that the equilibrium pressure is uncertain, the difference between the pressures of the arsenic-thallium experiments and the equilibrium values may be attributed to another factor. Thallium undoubtedly forms a solid solution with arsenic to some extent and the saturated solution of arsenic in liquid thallium may not be quite at unit activity with respect to pure arsenic solid. In the phosphorus thallium system there is a solid solubility of thallium in phosphorus of 25 atomic %.²¹ The results using liquid lead will give us a check on reduction of activity due to solid solubility.

It is of interest to compare the equilibrium heat of vaporization of 33 ± 1 kcals at 550°K with the heat of 41 kcals obtained from the temperature coefficient of a number of Langmuir type measurements which were made. The barrier of 8 kcals indicated by these data should correspond to a vaporization coefficient of $\exp^{-8000/2 \times 550}$ or a factor of about 6×10^{-4} . The observed accommodation coefficients were of this order of magnitude, although a distinct trend to smaller accommodation coefficients was observed with the smaller orifices.

DISCUSSION

It is believed that some generalization can be made about systems with low vaporization coefficients. From the available data, low

vaporization coefficients can be expected whenever the main vaporizing gaseous species are not present as such in the condensed phase and the atoms or molecules in the condensed phase are held so rigidly that they cannot readily reorganize to form the main gaseous species. It appears very unlikely that materials vaporizing predominately to atomic gaseous species will have low vaporization coefficients. Further, it is reasonable to expect that materials vaporizing to predominately diatomic gaseous species will have low vaporization coefficients in cases where the two component atoms are so separated in the condensed phase that they cannot readily contact each other. Thus Margrave²² reports a low vaporization coefficient for the vaporization of magnesium nitride that vaporizes under equilibrium conditions to Mg atoms and N₂ molecules because of the separation of nitrogen atoms in the rigid magnesium nitride lattice. In general we would expect low vaporization coefficients when the main gaseous species is a polyatomic molecule that does not exist as such in the condensed phase and because of the rigidity of the lattice cannot readily form within the lattice. The examples of red phosphorus, arsenic, arsenic oxide, ammonium halides etc., fall in this class. For a similar reason, materials that vaporize predominately to atomic species with a vaporization coefficient close to unity may produce a different vapor when vaporizing in a Langmuir type experiment compared to the equilibrium vapor. This is due to low vaporization coefficients for the various complex polymeric species that do not affect the observed rate of vaporization materially because of their small percentage contribution, particularly at low temperatures. However, at higher temperatures where they become more important the effect of the polymeric

species may become noticeable. Also mass spectrometer studies that can detect these minor polymeric species may yield different results with vapors produced in a Langmuir type experiment in contrast to a vapor obtained from a Knudsen cell with a small orifice. Although liquids generally would be expected to yield vaporization coefficients close to unity because of a better chance of rearrangement to produce the desired molecular species, two interesting examples giving evidence to the contrary may be noted. In the study by Motzfeldt²³ of the vaporization of liquid sodium carbonate to produce sodium atoms, oxygen molecules, and carbon dioxide molecules, he found a low vaporization coefficient which he attributed to the difficulty of bending a triangular carbonate ion in the liquid to form a linear carbon dioxide molecule. Also, Stranski¹² in his study of the arsenic oxides, observes that although the vaporization coefficient from the molecular lattice modification (arsenolite) is unity, measurements made on the supercooled liquid show the vaporization coefficient to be considerably less. In this case the attraction between adjacent As_4O_6 molecules is apparently stronger in the liquid than in the solid.

It is of interest to apply these generalizations to the rate of vaporization of graphite for which vaporization coefficients less than unity are known to exist. It is of interest to note that black phosphorus and arsenic have structures that are closely related to the graphite structure and that red phosphorus is believed also to have a similar structure.^{24,25} Goldfinger, Waelbroeck and Doehard²⁶ have presented a model for the vaporization of graphite based on the Herzberg-Herzfeld-Teller model which would require a low vaporization coefficient for monatomic carbon, a unit vaporization coefficient for C_2 , and a much larger than unit vaporization coefficient for C_3 . Although their model

is self-consistent and quite conceivable, it would be much more reasonable on the basis of experience with other systems that the atomic products would vaporize with a high vaporization coefficient while more complex molecules might have a low vaporization coefficient. The more recent mass spectrometer results of Inghram and Chupka⁵ and Hoch, Blackburn, Dingley and Johnston²⁷ now clearly demonstrate that monatomic carbon must have a vaporization coefficient between 0.1 and 1 and could not have a vaporization coefficient of 10^{-3} as has been proposed. Their results together with the Langmuir method measurements would be consistent with a vaporization coefficient for C_2 between 0.5 and 1, a coefficient for C around 0.5, and a coefficient for C_3 of about 0.1. Thus none of these species could account for the high vapor pressure observed by Goldfinger, Doehard and Waelbroeck using Knudsen cells with extremely small orifices, and one is forced to attribute their results to a more complex species. Chupka and Inghram have reported observations that indicate that the C_5 molecule has an extremely low vaporization coefficient and becomes very important in a Knudsen cell measurement. Although these measurements require verification before they can be fully accepted, such a species would adequately explain Goldfinger's results as well as the various static determinations of the total vapor pressure of graphite. Examination of the structure of graphite shows that it would be extremely difficult to form a C_5 molecule from the graphite structure and one would expect a low vaporization coefficient for such a molecule. From its required high stability, it must be a ring or other compact structure. It is of interest to note that Brewer, Gilles and Jenkins²⁸ report that graphite powder gives an abnormally high vapor pressure upon first heating that gradually decreases just as observed with phosphorus and arsenic, and the same explanation might apply. Thus imperfect or

strained graphite crystals might allow the necessary distortion to form C_5 molecules and thus would vaporize more rapidly than the more perfect crystals from which it would be very difficult to form C_5 molecules. If the mass spectrometer observations of C_5 can be verified, a ready reconciliation of all the apparently contradictory data on the vapor pressure of graphite can be made. With C_5 the main species under true equilibrium conditions, one would expect high vapor pressures under static conditions or with Knudsen cells with extremely small orifices as used by Goldfinger, Doehard and Waelbroeck. However with the very small vaporization coefficient of probably 10^{-4} or smaller for C_5 , other kinetic methods of determining the vapor pressure would give little indication of C_5 , and the measured vapor pressures would correspond mainly to C and C_3 , as the C_2 pressure is considerably smaller. As both C and C_3 are present in comparable amounts, third law calculations using total vapor pressure measurements obtained by the usual Langmuir and Knudsen methods will give the heat of sublimation of graphite to monatomic carbon within a few kilocalories. It should be possible to check the importance of C_5 by using a catalyst as has been done with phosphorus and arsenic. A suitable liquid that would dissolve graphite without forming an intermediate phase or without reducing the carbon activity would be liquid platinum or another relatively non-volatile platinum group metal. Preliminary experiments with platinum and graphite have indicated that liquid platinum will dissolve appreciable amounts of carbon at $2100^{\circ}C$. If the same effect is obtained as has been observed with phosphorus and arsenic, one should observe high pressures similar to those observed by Goldfinger, Doehard and Waelbroeck, even with Knudsen cells of large orifice.

Further experiments are in progress to combine mass spectroscopic examination with Langmuir and Knudsen type experiments to establish the vaporization coefficients of the minor species as well as of the major species of systems like phosphorus and arsenic and to check some of the generalizations made above.

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FIG I

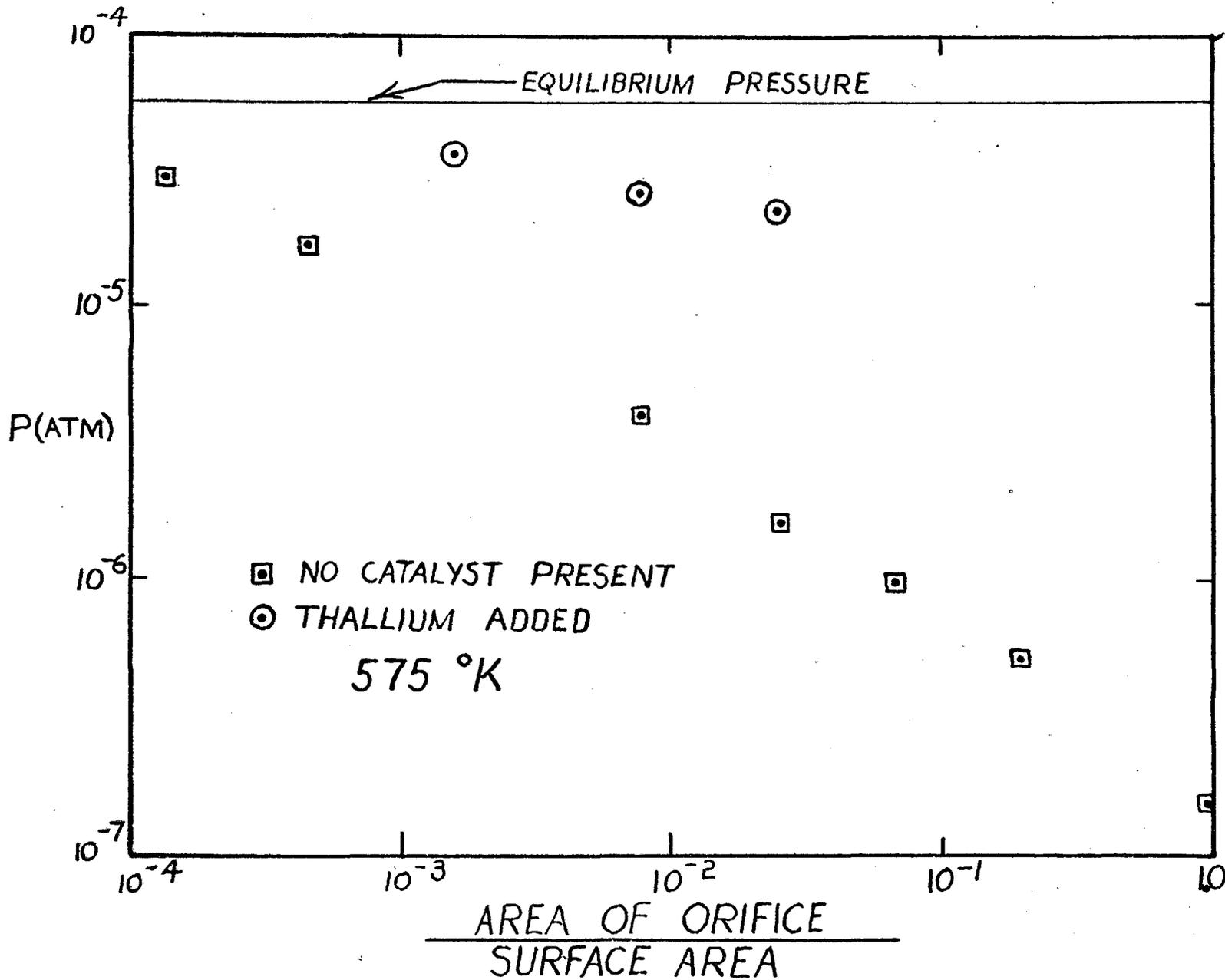


FIG II

