Title

A COMPARISON OF THE INTERNAL ENERGY OF P4 MOLECULES PRODUCED BY FREE SURFACE SUBLIMATION AND BY EFFUSION

Authors

Mar, Raymond W.
Searcy, Alan W.

Publication Date

1969-04-01

Submitted to Journal of Chemical Physics

UCRL-18804
Preprint

A COMPARISON OF THE INTERNAL ENERGY OF P_4 MOLECULES PRODUCED BY FREE SURFACE SUBLIMATION AND BY EFFUSION

Raymond W. Mar and Alan W. Searcy

April 1969

AEC Contract No. W-7405-eng-48

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-18804

DISCLAIMER

A COMPARISON OF THE INTERNAL ENERGY OF P_4 MOLECULES PRODUCED BY FREE SURFACE SUBLIMATION AND BY EFFUSION

Raymond W. Mar† and Alan W. Searcy

Inorganic Materials Research Division, Lawrence Radiation Laboratory
Department of Materials Science and Engineering, College of Engineering
University of California, Berkeley, California

As far as we are aware, the only reported attempt to detect internal energy of excitation in evaporating molecules is that of Brown, Brewer, and Klemperer,[1] who sought evidence for excess vibrational energy in iodine molecules produced in free surface sublimation. But the apparent enthalpy of activation for iodine sublimation is less than the enthalpy of the equilibrium reaction.[2] A recent theoretical analysis of evaporation kinetics[3] indicates that in this circumstance no excess excitation energy is to be expected in the escaping molecules. The analysis suggests, however, that internal excitation is possible for molecules that escape in a process for which the apparent enthalpy of activation exceeds the enthalpy of the evaporation reaction and for which the apparent entropy of activation is nearly equal to the entropy of evaporation. By these criteria, the P_4 and As_4 produced in free surface sublimation of red phosphorous[4,5] and arsenic[4-6] are identified as molecules which may possess more internal energy than the molecules of the equilibrium vapor. Kane expected that P_4 or As_4 molecules from free surface sublimation might possess excess internal energy,[7] but Kane and Reynolds[5] did not evaluate the implications of their appearance potential data to this question.

For sublimation of P_4 from red phosphorous the apparent enthalpy of activation exceeds the enthalpy of the equilibrium reaction by about 1.4 eV.[5] Molecules with this much excess internal energy should show different appearance potentials and fragmentation patterns as functions

of electron voltages in a mass spectrometer from those of unexcited P_4 molecules. Kane and Reynolds found no significant difference between phosphorous ion intensities at various electron voltages for sublimation of a red phosphorous powder surface and for sublimation from Knudsen cells with small orifices. But Kane noted[7] that the surface level of the free surface sublimation sample did not appear to sink while about 5/6 of the sample sublimed. Most of the molecules in the beam from Kane and Reynolds open crucible sublimation experiments must have originated inside pores and therefore must have experienced multiple collisions before leaving the sample. Successful detection of excess internal energy requires the minimization of the chances for collision deactivation of excited molecules and requires comparison to molecules for which equilibrium internal energies are established. It seemed worthwhile to repeat intensity versus electron voltage studies for red phosphorous under conditions that would reduce chances of collisional deactivation. Since single crystals of red phosphorous are not available, we attempted to obtain improve free surface sublimation conditions by supporting a polycrystalline lump of red phosphorous against the lower surface of the conical orifice of the lid of a graphite effusion cell. The geometry was such that most P_4 molecules would reach the ionization chamber without undergoing collisions with any exterior surface.

The same cell and orifice were used for Knudsen effusion runs with phosphorus powder in the cell. Three molybdenum inserts with eccentrically drilled holes were placed between the powder and the cell orifice to insure that each vapor molecule would make a number of collisions with the cell walls and the inserts before effusing through the orifice.

Four different runs were made at 620°K in an Atlas mass spectrometer with each type of experimental arrangement. The beam path was about

10 cm long so that internal excitations with lifetimes in excess of about 10^{-4} seconds could be detected. The variation of P_3^+, P_2^+, and P^+ intensities relative to P_4^+ intensities are shown in Fig. 1 These relative intensities show no significant difference between free surface and effusion experiments when electron energies were varied from below the threshold of measureable intensities to 70 eV.

Unfortunately, this negative result neither proves that P_4 molecules are not internally excited at the instant of leaving a red phosphorus surface nor sets an upper limit to a lifetime before deactivation by spontaneous emission. The polycrystalline lump used in "free surface sublimation" showed no visible evidence of surface recession as a result of heating. It seems probable that most of the molecules of the beam from this sample were, like those in the study of Kane and Reynolds, produced in pores of the sample where they could be deactivated by multiple collisions.

A study of single crystals of arsenic, which have been shown to sublime without developing pores,[6] might provide a more definitive test, although the smaller difference between activation enthalpy and equilibrium enthalpy of reaction would make detection of excess energy with a mass spectrometer difficult.

ACKNOWLEDGEMENTS

Comments on this study by Leo Brewer were very helpful. This work was supported by the United States Atomic Energy Commission.

REFERENCES

+ Present address: University of Leeds, Leeds, England.

1. R. L. Brown, R. G. Brewer, and W. Klemperer, J. Chem. Phys. 36, 1827 (1962).

2. J. H. Stern and N. W. Gregory, J. Phys. Chem. 61, 1226 (1957).

3. A. W. Searcy, The Kinetics of Evaporation and Condensation Reactions, (Abstracted from UCRL-18631, December 1968) to appear as Chapter 5 of the proceedings of the First International Conference on Materials Science, Sponsored by the National Academy of Lincei, Italy, A. W. Searcy, D. V. Ragone, and U. Colombo, eds., (Interscience, New York).

4. L. Brewer and J. S. Kane, J. Phys. Chem. 59 105 (1955).

5. J. S. Kane and J. H. Reynolds, J. Chem. Phys. 25, 342 (1956).

6. G. M. Rosenblatt and P. K. Lee, J. Chem. Phys. 49, 2995 (1968).

7. J. S. Kane, Ph.D. Dissertation, University of California, Berkeley (1955).

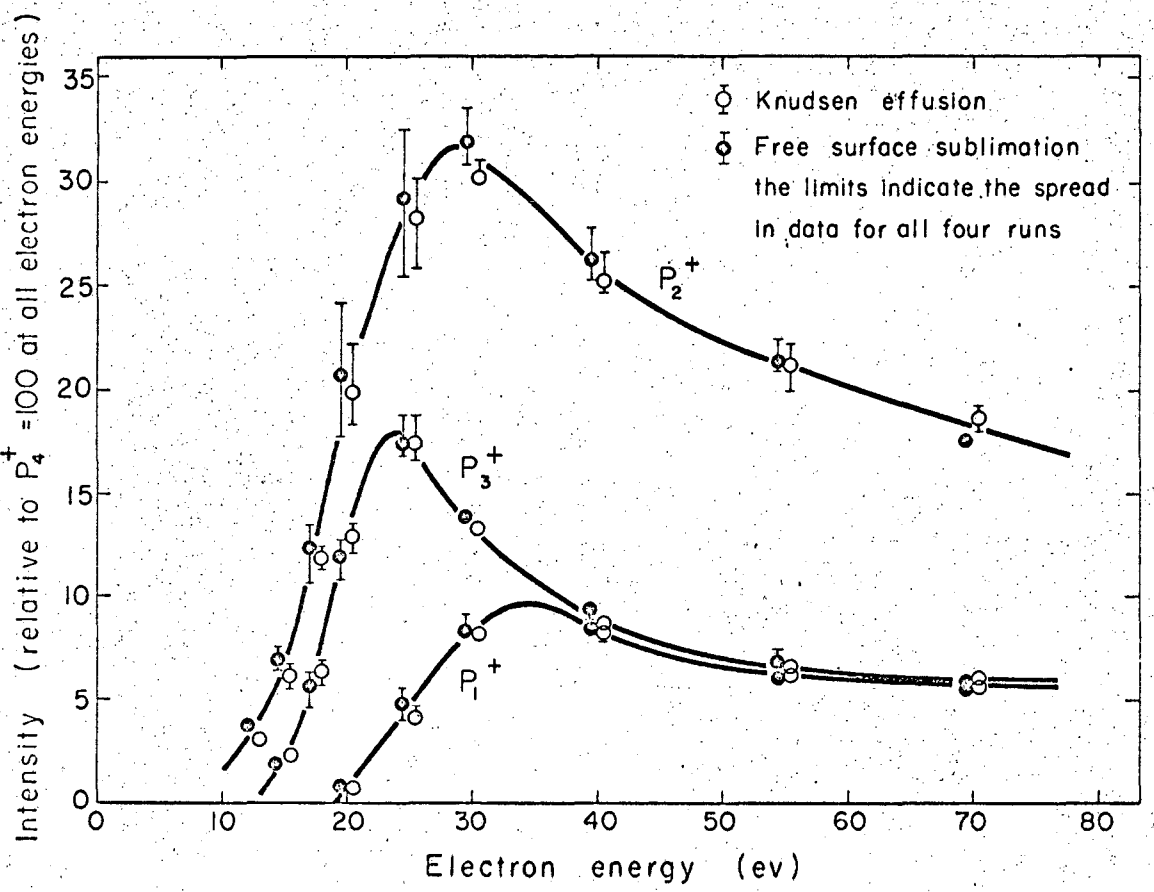

Figure 1

XBL693 - 2218

Relative intensities versus electron energies for phosphorus ions in free surface sublimation and effusion. All intensities are normalize relative to P^+_4 = 100 at each electron voltage.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720