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SIMULTANEOUS KNUDSEN- AND TORSION-EFFUSION
MEASUREMENTS OF THE VAPOR PRESSURES OF
TETRAPHENYL SILANE AND HEXAPHENYL DISILANE

by

Luz Marina Calle

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment
of the
Degree of Master of Arts

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Luz Marina Calle

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TO MY FATHER

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CHAPTER I

INTRODUCTION

Systematic studies of vapor pressures of related organometallic compounds, have been the task of several investigators in recent years in order to elucidate relationships between their thermal and structural properties. These studies are valuable in providing data to allow calculations of the strengths of metal-to-carbon and metal-to-metal bonds in these compounds.

A common expression for the strength of a chemical bond is the bond energy¹. The bond energies can be evaluated from the standard enthalpies of formation of the compound and the atomic elements in the hypothetical ideal gas state, $\Delta H_f^\circ(g)$. The standard enthalpy of formation of a compound can be calculated from its standard enthalpy of combustion, ΔH_c° , provided that the standard enthalpies of formation of the combustion products are known. If the stable state of a compound at room temperature is the condensed phase, then the standard enthalpy of formation derived from calorimetric measurements is that of the condensed phase.

The standard enthalpy of formation of a compound in the gaseous state, can be calculated from a vaporization or sublimation process according to:

$$\Delta H_v^\circ \text{ (or } \Delta H_{\text{sub}}^\circ) = \Delta H_f^\circ(g) - \Delta H_f^\circ(s) \quad (\text{I-1})$$

The enthalpy change that accompanies the dissociation of a gaseous compound into its gaseous atoms and (or) free radicals, ΔH_d° , can be

calculated from the enthalpies of formation of the gaseous compound and its gaseous fragments according to:

$$\Delta H_d^\circ = \Sigma \Delta H_f^\circ (\text{g, atoms or free radicals}) - \Delta H_f^\circ (\text{g, compound}) \quad (\text{I-2})$$

For a molecule of the type AB_n containing only A-B bonds, it is reasonable to define the average bond energy, $\langle D \rangle(\text{A-B})$ by the expression:

$$\langle D \rangle(\text{A-B}) = \frac{1}{n} \Delta H_d^\circ (\text{AB}_n, \text{g}) \quad (\text{I-3})$$

The purpose of this work was to measure the sublimation pressures of tetraphenyl silane, SiPh_4 , and hexaphenyl disilane, Si_2Ph_6 , in the temperature ranges 408 to 466 K and 511 to 551 K respectively. Values for $\Delta H_{\text{sub}}^\circ$ and $\Delta S_{\text{sub}}^\circ$ were calculated from the linear Clausius-Clapeyron relation:

$$\log_{10} P(\text{atm}) = - \frac{\Delta H_{\text{sub}}^\circ}{2.303RT} + \frac{\Delta S_{\text{sub}}^\circ}{2.303R} \quad (\text{I-4})$$

The enthalpies of sublimation, $\Delta H_{\text{sub}}^\circ$, were utilized to evaluate the average bond energies $\langle D \rangle(\text{Si-Ph})$ in SiPh_4 and Si_2Ph_6 and the bond dissociation energy $D(\text{Ph}_3\text{Si-SiPh}_3)$.

Sublimation pressures were determined from simultaneous measurements of the mass rate-effusion by the Knudsen-effusion technique and of the angular displacement resulting from the torsional-recoil by the torsion-effusion technique.

CHAPTER II

THEORY

The Knudsen-Effusion Method

The Knudsen-effusion method for measuring small vapor pressures in the range 10^{-2} to 10^{-6} Torr is based on the kinetic theory of dilute gases². It follows from this theory that gaseous molecules in equilibrium with their condensed phase, in a closed isothermal container, strike a surface of area A_o at a mass rate, $\frac{\Delta W}{t}$, related to the gas density, ρ , and the mean velocity of the gas molecules, \bar{c} , by the following equation:

$$\frac{\Delta W}{t A_o} = \frac{1}{4} \rho \bar{c} \quad (\text{II-1})$$

In the Knudsen-effusion cell the surface area A_o is the area of the orifice. The mean velocity, \bar{c} , derived from the kinetic theory of gases is given by:

$$\bar{c} = \left(\frac{8RT}{\pi M} \right)^{1/2} \quad (\text{II-2})$$

where M is the molecular weight of the gaseous species. The density, using the ideal gas law is:

$$\rho = \frac{PM}{RT} \quad (\text{II-3})$$

Substitution for \bar{c} and ρ in equation (II-1) leads to the molecular effusion equation³ relating the vapor pressure, as a function of temperature, to the rate of mass effusion in a Knudsen-effusion experiment:

$$P_K = \frac{\Delta W}{A_o t} \left(\frac{2\pi RT}{M} \right)^{1/2} \quad (\text{II-4})$$

where P_K is the vapor pressure of gas molecules in equilibrium with the condensed phase.

In the simplest thermodynamical application of the Knudsen-effusion method⁴⁻⁶, the vapor of a single species, in equilibrium with its condensed phase, is allowed to effuse from an isothermal container into an evacuated space through a small thin edged orifice. However, in order to apply the molecular-effusion equation to the measurements of small equilibrium vapor pressures, the following conditions must be satisfied:

1. Equilibrium between the condensed and vapor phases in the cell must be established, by congruent vaporization and by a much greater rate of evaporation than the rate of effusion.
2. The system must be maintained at a constant uniform temperature.
3. Pressure outside the enclosure of the cell, into which the vapor is effusing, must be negligible compared to the pressure inside the cell.
4. There must be a laminar flow of molecules through the orifice i.e. there must be no collisions between the vapor molecules within the orifice.
5. The cell must be inert or at least be recognized as a part of the equilibrium system.
6. The number of molecules that collide with the orifice walls and return to the cell must be negligible.

The first and second conditions can be met experimentally by allowing the system to equilibrate at a constant temperature for sufficient time. The third condition can be met by using a vacuum system of

relatively low pressure outside the cell. A pressure of 10^{-6} Torr should be satisfactory. The fourth condition implies that the method is limited to a maximum vapor pressure, to be measured with reasonable accuracy. A high vapor pressure corresponds to a high frequency of collisions. The fifth condition restricts the choice of the cell material. The sixth condition implies an ideal orifice which means one that is both perfectly round and infinitely thin. In practice, an orifice has finite thickness within which collisions between a significant number of molecules and the walls occur, thus causing the rebound of these molecules back into the cell. Clausing^{7,8} developed a correction factor to account for this phenomenon.

The underlying principles for the derivation of the Clausing factor and the more recent and accurate analyses of DeMarcus⁹ were discussed by Carlson¹⁰. In the mathematical formulation, the complexity of the evaporation process is recognized by accounting for the gas-solid boundary interactions and gas phase interactions, both, within the cell and the orifice. The effect of these interactions is explained in terms of geometric factors that are functions of the dimensions of the cell and of the orifice.

The dependence of the effusion rate on the geometry of the cell, is qualitatively explained by failure of all molecules leaving the surface of the condensed phase to reach the orifice, either by specular or by random reflections. The dependence on the geometry of the orifice, is also explained, in terms of restricted molecular flow as a result of reflections from an assumed cylindrical orifice back into the cell. Thus the Clausing factor, W_o , is viewed as a transmission coefficient

of the orifice; it represents the probability that a molecule having entered the orifice inlet will escape through the orifice outlet.

The Clausing factor is a function of the ratio of the length of the orifice to its radius, $\frac{l}{r}$. Incorporation of the Clausing factor into the molecular-effusion equation leads to the modified equation:

$$P_K = \frac{\Delta W}{t A W_o} \left(\frac{2\pi RT}{M} \right)^{1/2} \quad (\text{II-5})$$

Accurate values for W_o are available⁹ as a function of $\frac{l}{r}$.

The Torsion-Effusion Method

The torsion-effusion method for measuring small pressures is based on the principle of the torsion pendulum and on the definition of the pressure as the rate of momentum transferred by the gas molecules to a unit surface area. The method was first developed by Volmer¹¹ as a variation of the Knudsen-effusion method in determinations of molecular weights from simultaneous measurements of the rate of mass effusion and the torsional recoil. Later, Neumann and Volker¹² used torsion measurements only for the determination of vapor pressures.

In the simplest application of the torsion-effusion method the torsional recoil is measured under conditions of molecular flow analogous to those of the Knudsen-effusion technique. In practice¹³ the sample is placed in a cylindrical (or rectangular) cell, suspended horizontally from a suspension system of a fine filament. The geometric center of the cell coincides with the axis of the suspension system. The gas molecules effuse from two orifices that are perpendicular to the plane that contains the cell horizontal axis and the axis of the suspension

system. These orifices are 180° out of phase with respect to each other, and equally spaced from the suspension axis.

Under isothermal and equilibrium conditions, the constant rate of effusion of the vapor molecules, generates a recoil force which rotates the cell through an angle. In this respect, the experimental arrangement resembles a torsion pendulum and the pressure of the effusing vapor may be related to the angular displacement according to the principle of the torsion pendulum.

The recoil force on the cell, generated by the effusing molecules, is equivalent to the external force applied to the disc of a torsion pendulum. The effusion of molecules through an orifice constitutes a transfer of momentum across the plane of the orifice. The transfer of momentum indicates the presence of force and an equal and opposite reaction force (recoil force).

The vapor pressure, P_T , is directly related to the recoil force, F , of the effusing vapor and to the cross sectional area of the orifices, A_o , by the following expression²:

$$P_T = \frac{2F}{A_o} \quad (\text{II-6})$$

The recoil force exerts a torque, T_r , dependent on the moment arm of the cell, d ,

$$T_r = Fd \quad (\text{II-7})$$

The moment arm of the cell is the distance from the axis through the center of the orifice to the axis of rotation. The resulting torque on a cell is the sum of the torques due to effusion from the two orifices:

$$T_r = F_1 d_1 + F_2 d_2 \quad (\text{II-8})$$

The recoil torque (its equivalent in the mechanical torsion pendulum is the external torque) rotates the cell by an angle, θ , proportional to the torque, T_r . As the cell rotates, the filament tends to twist and its elastic reaction exerts a torque (torsional-recoil torque), T_w , which exactly counterbalances the recoil torque:

$$T_r = -T_w = \tau\theta \quad (\text{II-9})$$

The proportionality constant, τ , is the torsion constant of the filament measured in torque units per angular displacement (newton meter radian⁻¹).

Substitution from equations (II-8) and (II-9) into equation (II-6) and introduction of a correction factor, f_i , for each orifice yields a direct relation between the vapor pressure and the angular displacement:

$$P_T = \frac{2\tau\theta}{(A_1 d_1 f_1 + A_2 d_2 f_2)} \quad (\text{II-10})$$

The correction factor, f_i , referred to as a "pressure factor" or the "recoil force factor" is similar to the "Clausing factor" in the Knudsen-effusion equation. It combines Clausing correction for the diminution of flow in a non-ideal orifice and partial collimation of velocities of the effusing molecules by such orifice. It represents the ratio of the recoil force resulting from effusion through an orifice of finite thickness to that expected for an ideal orifice. Searcy and Freeman¹⁴ and more recently Schulz and Searcy¹⁵ have reported values for the pressure factor in terms of the $\frac{1}{r}$ ratios.

Correlation between Knudsen- and Torsion-Effusion Methods

Calculations of vapor pressures from measurements of the rate of mass effusion in a Knudsen experiment according to equation (II-5) require identification of the vapor species at the corresponding temperatures, so that their molecular weight is accurately evaluated. Such identification of the vapor species is, in practice, a more difficult problem than the measurement of material transport. It requires either elaborate instrumentation such as a mass spectrometer or analytical techniques. On the other hand, the torsional-recoil method provides direct measurements of the vapor pressure, P_T , through equation (II-10) where knowledge of the molecular weight is not necessary. At a given temperature, simultaneous measurements of P_K and P_T with the same cell enable determination of the vapor pressure as well as the molecular weight of the effusate.

Combination of equation (II-5) and (II-10) yields a calculated molecular weight M^* :

$$M^* = 2\pi RT \left(\frac{\Delta W}{t P_T W A_o} \right)^2 \quad (\text{II-11})$$

Deviation of the calculated molecular weight, M^* , from the molecular weight of the condensed phase would indicate polymerization and (or) dissociation of the original sample, during the evaporation process. M^* is related to the molecular weights of the individual constituents of the effusate by the following expression¹³:

$$M^* = \left[\sum_{i=1}^s m_i M_i^{-1/2} \right]^{-2} \quad (\text{II-12})$$

where m_i is the mass fraction of the vapor species i , in the effusate, and M_i is the molecular weight of that species. Thus M^* is a weighted

average molecular weight of the vapor in equilibrium with the condensed phase in the cell.

Speculations can be made as to whether decomposition or polymerization occurs in the sublimation process by considering the ratio $\frac{P_T}{P_K}$, where P_K is calculated from equation (II-5) with an assumed value for the molecular weight, M . This ratio can be expressed as:

$$\frac{P_T}{P_K} = \left(\frac{M}{M^*} \right)^{1/2} \quad (\text{II-13})$$

The assumed molecular weight, M , is that of the condensed phase. Three cases are expected:

Case 1: If $\frac{P_T}{P_K}$ is equal to unity, then M^* is equal to M and the evaporation or sublimation is a simple phase transition.

Case 2: If $\frac{P_T}{P_K}$ is less than unity, then M^* is greater than M and polymerization may have taken place.

Case 3: If $\frac{P_T}{P_K}$ is greater than unity, then M^* is less than M and decomposition of some sort may have taken place.

In practice Case 1 is not realizable in an apparatus of simultaneous Knudsen- and Torsion-effusion measurements even for substances that are known to sublime as monomers. It is speculated that the deviation of $\frac{P_T}{P_K}$ from unity might be attributed to systematic difference between the two methods, see p 30.

Relative concentrations of various species in the effusate may be calculated from the known ratio $\frac{P_T}{P_K}$ and other chemical evidence concerning a given system. A discussion of such application was presented by Freeman¹³ and by Taylor¹⁶.

Deviation from Equilibrium in an Effusion Cell

The molecular-effusion equation (equation II-4) is exact for an equilibrium system. An equilibrium system, from the view point of vaporization studies, is a totally closed isothermal system of an inert enclosure, a vaporizing material and vapor in which gas phase collisions are absent. At equilibrium the following assumptions are considered:

1. There are no radial inhomogeneities.
2. There are no pressure discontinuities in the enclosure.
3. The rate of evaporation and the rate of condensation on the sample surface are equal.

In a Knudsen cell, the presence of an orifice destroys some of these assumptions. However, a cell with a small orifice, approximates an equilibrium system since the orifice inlet acts as a source of saturated vapor. Even for an ideal orifice a steady state is established at a pressure lower than the equilibrium pressure. As a result the rate of effusion is given by the gross rate of evaporation minus the gross rate of condensation. If effusion is through a real orifice of finite length, additional under-saturation results from depletion by channeling effects. Collisions with the orifice wall result in a lower rate of effusion than that expected from the idealized equation, (equation II-4).

A detailed analysis for effusion from a real Knudsen cell, as used in laboratory experiments, has been given by Whitman^{17,18} and by Motzfeldt¹⁹. The relation between the measured pressure, P_m , and the equilibrium pressure, P_e , is given by:

$$P_m \left[1 + f \left(\frac{1}{\alpha_c} + \frac{1}{W_c} - 2 \right) \right] = P_e \quad (\text{II-14})$$

where α_c is the condensation coefficient (the fraction of total number of gas molecules, which condense on the sample surface upon collision); W_c is the Clausing factor for the cell i.e. the probability that a molecule leaving the sample surface, at the bottom of the cell, will reach the orifice inlet, at the top; f is defined by:

$$f = \frac{W_o A_o}{A_s} \quad (\text{II-15})$$

W_o and A_o are as in the previous notation, and A_s is the surface area of the sample.

Speiser and Spretnak²⁰ derived a still simpler equation for relating P_m to P_e . Their independently derived equation is a simplification of equation (II-14). They assumed $\frac{1}{W_c} = 2$, which is fairly typical for Knudsen cells. Thus equation (II-14) is reduced to:

$$P_m \left[1 + \frac{f}{\alpha_c} \right] = P_e \quad (\text{II-16})$$

Paule and Margrave²¹ criticized the work of the authors of equation (II-14) and (II-16) since they did not distinguish between the Langmuir coefficient α_L , and the condensation coefficient, α_c . They argued that the Langmuir coefficient, α_L , defined as the ratio of the rate of evaporation from a surface into a vacuum to the equilibrium rate does not equal α_c except at the equilibrium vapor pressure or when α_L equals unity. They further criticized equation (II-16) where Speiser and Spretnak assumed the absence of a pressure gradient within the cell, which is not true because of mass effusion through the orifice. In a treatment similar to that of Whitman and Motzfeldt they accounted for these effects and rederived equation (II-14) in the form:

$$P_m \left[1 + f \left(\frac{1}{\alpha_c} + \frac{1}{W_c} - 2 \right) \right] = \frac{\alpha_L}{\alpha_c} P_e \quad (\text{II-14a})^{13}$$

and equation (II-16) as:

$$P_m \left(1 + \frac{f}{\alpha_c} \right) = \frac{\alpha_L}{\alpha_c} P_e \quad (\text{II-16a})$$

An alternate treatment which within the context of the kinetic theory of gases is an exact expression for an equilibrium system, was presented by Carlson¹⁰. He derived for the extent of saturation the relation:

$$P_m = P_e (1 - \Delta) \quad (\text{II-17})$$

The value of Δ is a complicated function which depends on the cell parameters (depth, L , and radius R) and on the corresponding parameters of the orifice (l and r). The derived value of Δ for a Knudsen cell with $\frac{L}{R} = 2$ and $\frac{r}{R} = 0.1$ is less than 0.04. Ignoring the radial dependence of the pressure gradient in the cell, as Whitman and Motzfeldt did, the expression for Δ is simplified to:

$$\Delta = \frac{\left(\frac{r}{R} \right)^2 (1 - W_c)}{W_c + \left(\frac{r}{R} \right)^2 (1 - W)} \quad (\text{II-18})$$

Substitution for Δ into equation (II-17) leads directly to:

$$P_m = P_e \left[1 + \left(\frac{r}{R} \right)^2 \left(\frac{1}{W_c} - 1 \right) \right]^{-1} \quad (\text{II-19})$$

which is equivalent to equation (II-14) where $\alpha_c = \alpha_L = 1$. Equation (II-19) yields a value for P_m more than 99% of the equilibrium value, P_e , for a cell of $\frac{L}{R} = 2$ and $\frac{r}{R} = 0.1$. Thus the right order for realizable experimental conditions in a cell of these parameters seems to justify the assumption that such Knudsen cell approximates an equilibrium system.

Various researchers have used equation (II-16) rewritten as:

$$P_m = P_e - \frac{W_o A_o}{\alpha_c A_s} P_m \quad (\text{II-16b})$$

by measuring the vapor pressure, P_m , at the same temperature with cells of different orifices (varying A_o). A plot of P_m versus $(W_o A_o P_m)$ may be extrapolated to obtain P_e as intercept and $1/(\alpha_c A_s)$ as slope. It would be possible, therefore, to make inferences concerning the order of magnitude of α_c . Here the sample surface area, A_s , is assumed to be equivalent to that of the cell cross sectional area. Although this assumption is used, its validity is questioned.

CHAPTER III

EXPERIMENTAL

Description of the Apparatus

The apparatus used to measure the rate of mass effusion and torsional recoil simultaneously is essentially a combination of a balance, a torsion effusion assembly, an optical-lever system, a heating chamber, a furnace and temperature control-and measurement- system. The apparatus has been fully described elsewhere²². A general schematic is shown in Figure 1. Only details pertinent to the present work will be mentioned.

The Torsion-Effusion Assembly

The torsion filament

The torsion filament is an annealed high purity tungsten wire, 3.8×10^{-2} mm in diameter and 34.6 cm long.

The effusion cell

The same cell was used throughout the entire set of experiments. The cell was machined from spectroscopic graphite and its dimensions are: 15.9 mm in outside diameter, 38.1 mm long and 3.2 mm wall thickness. Two orifices were drilled on opposite sides of the cell, 1.9 cm apart from each other and 0.8 cm from each end of the cell. The walls around the orifices were milled to 0.23 mm in thickness. The two end openings of the cell were fitted with graphite tapered plugs. Connection to the torsion assembly was by means of a dovetail, matching a keyway in the main body of the cell. A sketch of the cell is shown in Figure 2.

KEY TO FIGURE 1.

Schematic of Knudsen- and Torsion-Effusion Apparatus

1. Vacuum recording balance
2. Balance stand
3. Brass extension tube
4. Brass evacuation line
5. Liquid nitrogen trap
6. Oil-diffusion pump
7. Thermocouple gauge
8. Ionization gauge
9. Pyrex tube
10. Mechanical pump
11. Roughing valve
12. Main-gate valve
13. Fore-line vacuum valve

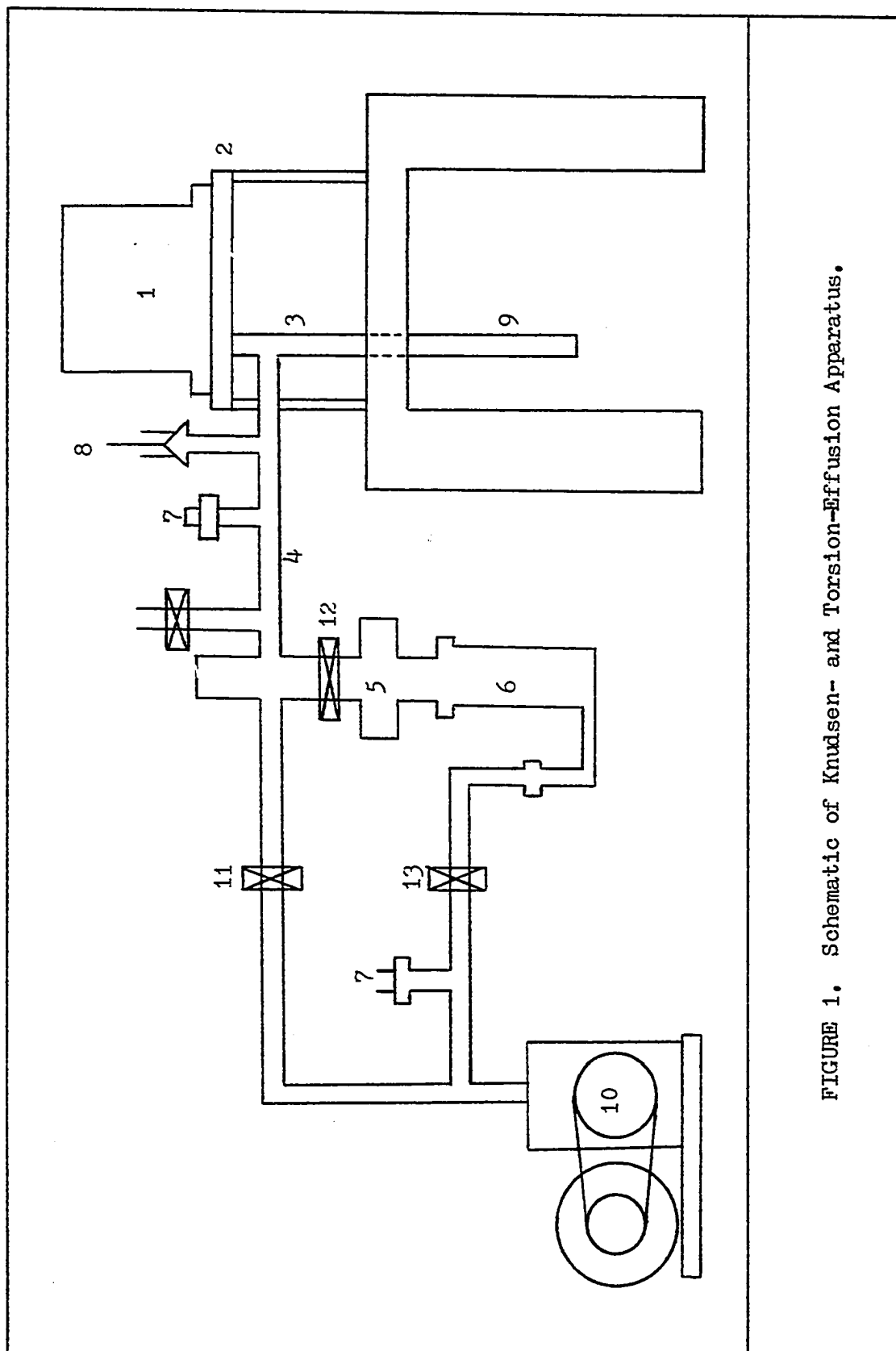
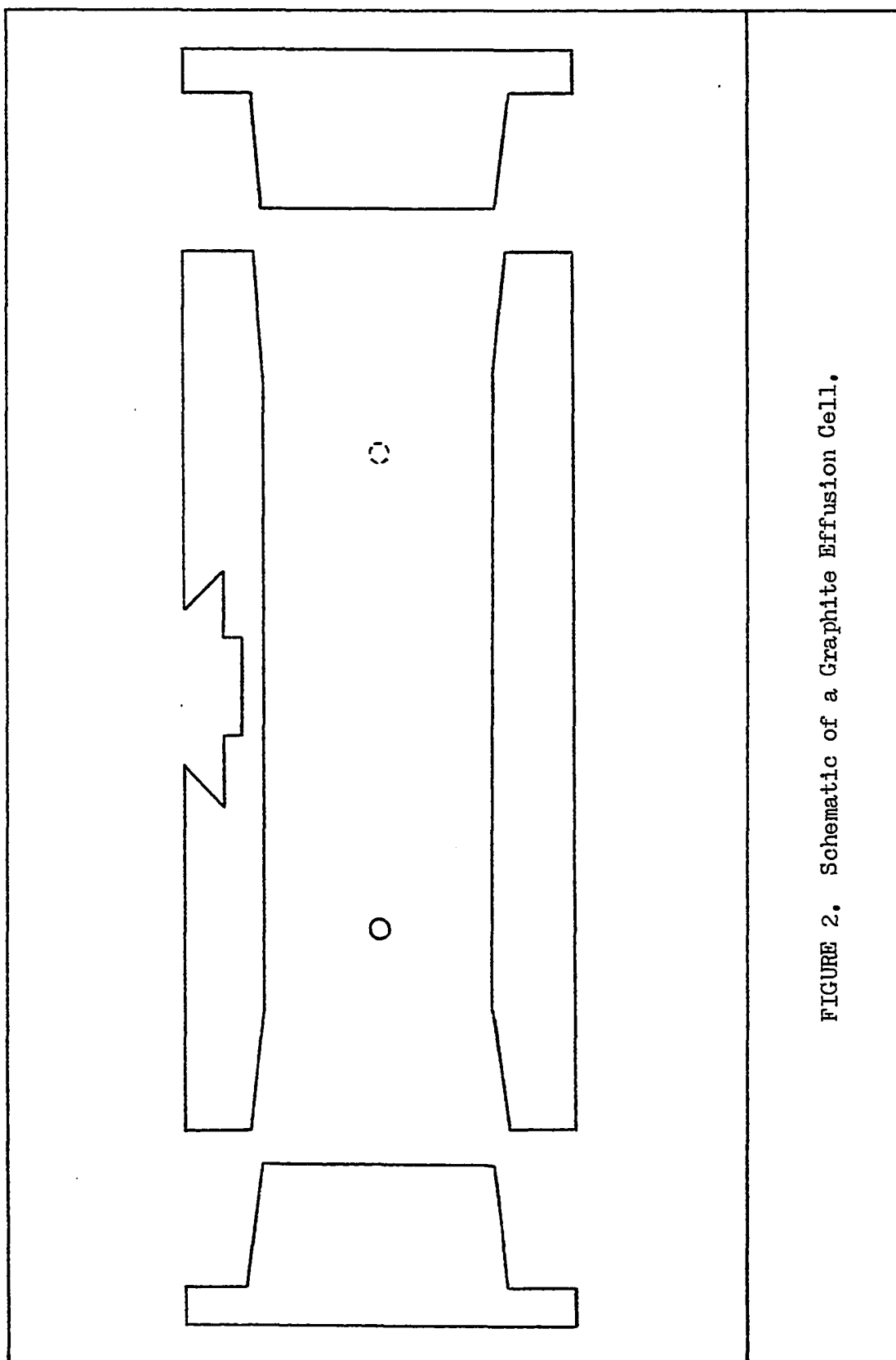


FIGURE 1. Schematic of Knudsen- and Torsion-Effusion Apparatus.



The Heating Chamber

The tapered lower end of the brass extension tube connects the balance to the heating chamber. The heating chamber is a pyrex tube with a matching tapered glass joint (71/60) at its open end. It is shaped like a test tube and has a thermocouple well at the bottom (4.33 cm long and 1 cm in diameter) which terminates 0.48 cm below the cell. The dimensions of the heating chamber are: 46.36 cm long and 6.93 cm outside diameter.

The Furnace and Temperature-Control and Measurement

The furnace and temperature control

Heating was produced by a furnace constructed of two Lindberg semi-cylindrical heating units (model 50332) with additional windings at the ends to compensate for radiation loss. The temperature was controlled by a time proportioning controller.

Temperature measurement

Temperatures of the sample in the effusion cell were measured by a calibrated chromel-alumel thermocouple located inside the thermocouple well, in the heating chamber.

Calibrations

Calibrations of the thermocouples

Since the measuring thermocouple must be outside the cell it was necessary to calibrate it with respect to a measuring thermocouple located inside the cell. The reference thermocouple is of the same composition as the measuring thermocouple and was calibrated by Kana'an²³, according to procedures described by McCreary and Thorn²⁴,

at the freezing points of benzoic acid, phthalic anhydride, pyrene, p-anisic acid, anthracene and carbazole. The reference junction of the thermocouple was maintained at 0°C by an Ice-Point Reference Standard (Model RCS4-Joseph Kaye and Company, Inc.).

The temperature of the sample in the cell is related to the potential, in millivolts, of the measuring thermocouple in the heating chamber by:

$$T(K) = (273.91_2 \pm 0.45_6) + (25.98_2 \pm 0.06_6) \times mv \quad (III-1)$$

The propagated error in the constants of equation (III-1) and the estimated precision of the thermocouple output yield an estimated error of ± 0.8 K which is consistent with the average deviation of the temperature over the period of mass effusion measurement at a given temperature setting.

Calibration of the torsion filament

The torsion constant, τ , of the tungsten filament was determined by a torsional pendulum (a cylindrical ring mounted on a crossbar). The crossbar is connected to the torsion assembly in place of the cell. In this arrangement, the torsion assembly and the crossbar (or the crossbar and the ring) function as a torsional pendulum and measurements can be made of the period of oscillation. The torsion constant is related to the moment of inertia of the cylindrical ring, I , and to the periods of oscillation of the pendulum, with and without the ring on the bar, T_1 and T_2 respectively, according to:

$$\tau = \frac{4\pi^2 I}{(T_1^2 - T_2^2)} \quad (III-2)$$

The ring and crossbar were made of aluminum. The moment of inertia of the ring is related to its dimensions according to²⁵:

$$I = \frac{m_r}{8} (D_1^2 + D_2^2) \quad (\text{III-3})$$

where m_r is the mass of the ring, D_1 is the inside diameter and D_2 is the outside diameter. In a calibration experiment, the number of oscillations during a given time are counted by an electric counter activated by a relay in a circuit incorporating a photocell. The optical-lever system is utilized in the torsion constant calibration where the light beam reflected from the mirror is intercepted by the photocell twice for each oscillation and eventually the counter registers two counts per single oscillation. The data of a typical calibration are shown in Table I. Values for the torsion constant of the filament, used in this work, are shown in Table II.

Values of the torsion constant for the filament have been found to vary slightly from experiment to experiment. The maximum fluctuation was 0.07% which corresponds to approximately $0.0006 \text{ dyn cm rad}^{-1}$. The propagated error in the value of τ , arising from uncertainties in the individual errors in mass, diameter and time, estimated from the precision of their respective measurements, is $\pm 0.03\%$ which corresponds to approximately $0.0003 \text{ dyn cm rad}^{-1}$. The variation in the torsion constant, τ , from experiment to experiment was averaged to be $\pm 0.06\%$ or $0.0005 \text{ dyn cm rad}^{-1}$.

TABLE I.

Sample of Data of Torsion-Constant Calibration

Pendulum of Suspension System with Aluminum Crossbar

No.	Counts	Time/s	Oscillations	T_2/s
1	20	184.0	10	18.40
2	26	239.2	13	18.40
3	32	294.5	16	18.41
4	38	349.7	19	18.41
5	44	404.9	22	18.40

Average $T_2 = (18.40 \pm 0.01) \text{ s}$

Pendulum of Suspension System with Aluminum Crossbar and Ring

No.	Counts	Time/s	Oscillations	T_1/s
1	8	268.2	4	67.05
2	12	402.4	6	67.07
3	16	536.5	8	67.06
4	20	670.6	10	67.06
5	24	804.7	12	67.06

Average $T_1 = (67.06 \pm 0.01) \text{ s}$

TABLE II.

Measurement of the Torsion Constant

Parameters of the Ring of the Torsion Pendulum

Inside Diameter (D_2 /cm)	5.398
Outside Diameter (D_1 /cm)	5.716
Mass (m_r /g)	11.9608
Moment of Inertia (I /g cm ²)	92.408

Calibration Measurements of Tungsten Wire of 3.8×10^{-2} mm in Diameter and 34.6 cm in Length

Experiment	T_2 /s	T_1 /s	τ /dyn cm rad ⁻¹	τ_{avg} (for an Experiment)
Si-42 ^b	18.41	67.09	0.8765	
Si-42 ^a	18.41	67.07	0.8770	0.8768
Si-43 ^a	18.41	67.09	0.8763	0.8767
Si-44 ^b	18.41	67.09	0.8765	
Si-44 ^a	18.40	67.07	0.8764	0.8765
Si-62 ^b	18.40	67.07	0.8767	
Si-62 ^a	18.40	67.05	0.8775	0.8771
Si-63 ^a	18.40	67.06	0.8773	0.8774
Si-64 ^a	18.41	67.06	0.8773	0.8773

a) Measurement after experiment; b) Measurement before experiment.

Characteristics of the Effusion Cell

A traveller microscope (UNITRON TMD 3621) with micrometer drums reading to 0.001 mm was used to measure the orifice diameters and moment arms. For orifice diameter measurements, the cell was positioned in five different orientations. In each orientation the cell was rotated 45° relative to the preceeding one. Twelve readings were taken for each orientation: six in one direction and six 180° relative to the preceeding direction. The uncertainty of the orifice diameter is $\pm 1.25\%$ and the uncertainty in the moment arm is $\pm 0.1\%$. The corresponding uncertainty in the orifice area is $\pm 2.43\%$. The depth of the orifices was measured using a vernier caliper which could be read to ± 0.001 inches. The depth to radius ratio, $\frac{1}{r}$, was used to determine the Clausing factor and the pressure factor. The characteristics of the cell are tabulated in Table III.

Operational Procedure

Prior to an experiment with a given compound, the cell was out-gassed under vacuum at 840 K. Each experiment was started with the calibration of the torsion filament. Next, the suspension system was weighed for further check on any possible deposition of the sublimate during the course of an experiment. Then, the cell was loaded with 0.8-0.9 grams of sample and attached to the suspension system using the dovetail connection. The torsion assembly, including the loaded cell, was weighed again. The zero point for the angular-displacement measurements was checked and adjusted when necessary. The entire system was sealed after placing the pyrex tube in the proper position. The

TABLE III.

Parameters of the Knudsen Cell

	Orifice A	Orifice B
Diameter ($\text{cm} \times 10^2$)	4.79	4.28
Area ($\text{cm}^2 \times 10^3$)	1.80	1.44
Moment arm ($\text{cm} \times 10$)	9.027	8.996
Depth ($\text{cm} \times 10^2$)	3.493	3.493
Depth to radius ratio	1.46	1.63
Clausing factor	0.5881 ₃	0.5626 ₃
Pressure factor	0.6490 ₆	0.6228 ₆

furnace was put into position and the mechanical pump was started to evacuate the system to a pressure of 10^{-2} Torr. At this point, the oil-diffusion pump was turned on. After a pressure of 10^{-6} Torr was established, the zero point on the optical-lever system was recorded and the system was outgassed, for at least 48 hours, at 110°C .

At the beginning of a series of vapor pressure determinations, at various temperatures, the zero point was checked and recorded. This was followed by raising the temperature to a point just above the highest temperature desired for the sublimation study. Approximately 100 mg of sample were sublimed at this temperature before the first datum point was recorded. Once equilibrium was achieved, at a given temperature, the mass loss, angular displacement and the temperature were recorded every 3-5 min (more often at high temperatures and less frequently at low temperatures). The establishment of equilibrium was ascertained by constancy of the temperature, of the rate of mass effusion and of the angular displacement of the reflected beam on the scale of the optical-lever system.

For each of a succession of effusion measurements in an experiment, the temperatures were selected at random. Usually one experiment was completed in two to three days from the time of the first point. At the end of each day, the experiment was interrupted by lowering the temperature to 110°C overnight with continuous pumping. At the beginning of each day, the zero point on the optical-lever system and the pressure of the vacuum system were recorded prior to resumption of heating and measurements of the experiment parameters.

When the experiment was completed, the sample was cooled down

and a final reading of the angular displacement zero point was recorded. Then, the diffusion pump was turned off, allowed to cool and the balance and the heating chamber were isolated from the vacuum pumps. Argon was introduced into the system through the bleeding valve in order to bring the system to atmospheric pressure. After the furnace and heating chamber were removed, the cell was disconnected, and finally, the suspension system was weighed to check for any possible change as a result of sublimate deposition. The experiment was concluded by a second calibration of the torsion filament.

CHAPTER IV

VAPOR PRESSURE AND THERMODYNAMIC PROPERTIES OF TETRAPHENYL SILANE

Literature Review

Only one investigation of the temperature dependence of the vapor pressure of tetraphenyl silane has been reported while the present study was in progress. McCauley and Smith²⁶ measured the sublimation pressures of SiPh_4 in the temperature range 428 to 489 K using a differential manometer. Their results were expressed by:

$$\ln P(\text{Torr}) = 11.830 - 6130.6 T^{-1} \quad (\text{IV-1})$$

with a corresponding mean enthalpy of sublimation equal to (12.2 ± 1) kcal_{th} mol⁻¹ in this temperature range.

Material

The tetraphenyl silane sample, used in this work, was obtained from Pierce Chemical Company. The commercial sample was recrystallized from hot benzene solution, and dried under vacuum in presence of P_2O_5 for about one week at 110°C prior to use. The melting point of the purified sample was 235–237°C compared with the literature value 235–237°C²⁷.

Analysis (Midwest Microlab. Inc.). Found: C, 84.48; H, 6.08; Si, 6.50. Calculated for $\text{C}_{24}\text{H}_{20}\text{Si}$: C, 85.66; H, 5.99; Si, 8.35.

Experimental Measurements

Vapor pressure measurements were performed by the apparatus and according to the procedure described in Chapter III. Prior to effusion-

rate and torsion-deflection measurements, the loaded cell was heated, after degassing under vacuum at 110°C for 48 hours, to about 466 K. After a weight loss of about 70-90 mg the first datum point at the highest temperature was recorded. Successive points were recorded at lower temperatures, down to the lowest temperature point. A new set of measurements was recorded over the same temperature range, starting at the lowest temperature. The weight loss during an experiment was between 350 to 400 mg. The pressure inside the heating chamber was maintained at 10^{-6} Torr.

Results

The saturated vapor pressures in equilibrium with solid SiPh_4 were determined from simultaneous measurements of the rate of mass effusion and torsional recoil in five experiments using the same graphite cell and the same torsion filament. Only data from three experiments were considered for calculation purposes since the first experiment was exploratory and the last one was a check run. Equations (II-5) and (II-10) were used to calculate the vapor pressure assuming the monomeric vapor species of molecular weight $336.513 \text{ g mol}^{-1}$ for equation (II-5).

Clausius-Clapeyron equations,

$$\log_{10} P(\text{atm}) = A - BT^{-1} \quad (\text{IV-2})$$

with the parameters, A and B, established by least-squares analyses were obtained using a PDP-10 computer. The experimental data and the computed vapor pressures are tabulated in Tables IV to VI and presented graphically in Figures 3 to 5.

TABLE IV.

Knudsen- and Torsion-Effusion Results for SiPh_4 , Experiment No. Si-42

No.	T/K	$10^3 m/g$	t/min	$10^5 P_K/\text{atm}$	$-\log_{10} P_K$	S/inch	$10^5 P_T/\text{atm}$	$-\log_{10} P_T$
1	446.2	9.70	40.00	5.6138	4.2507	4.90	6.3323	4.1984
2	432.7	9.77	132.50	1.6809	4.7745	1.42	1.8351	4.7363
3	439.3	10.90	85.00	2.9458	4.5308	2.54	3.2825	4.4838
4	427.0	5.35	122.50	0.9890	5.0048	0.82	1.0597	4.9748
5	420.1	2.52	112.50	0.5032	5.2983	0.42	0.5428	5.2654
6	413.6	1.83	138.75	0.2940	5.5317	0.26	0.3360	5.4737
7	407.6	1.38	195.00	0.1566	5.8052			
8	452.3	10.62	27.50	9.0009	4.0457	8.04	10.390	3.9834
9	458.5	15.23	25.00	14.296	3.8448	13.36	17.265	3.7628
10	464.8	20.35	22.50	21.369	3.6702	20.90	27.009	3.5685

$$\log_{10} P_K(\text{atm}) = (11.790 \pm 0.142) - (7169 \pm 62) T^{-1}$$

$$\log_{10} P_T(\text{atm}) = (12.246 \pm 0.190) - (7345 \pm 83) T^{-1}$$

m is the mass loss, t the time of effusion, and P_K the pressure in the Knudsen experiments; S is the displacement and P_T the pressure in the torsional experiments; $\text{atm} = 101,325 \text{ N m}^{-2}$.

TABLE V.

Knudsen- and Torsion-Effusion Results for SiPh_4 , Experiment No. Si-43

No.	T/K	$10^3 m/g$	t/min	$10^5 P_K/\text{atm}$	$-\log_{10} P_K$	S/inch	$10^5 P_T/\text{atm}$	$-\log_{10} P_T$
1	465.2	17.27	17.50	23.327	3.6321	21.81	28.182	3.5500
2	439.5	6.87	57.50	2.7451	4.5614			
3	433.1	3.87	56.25	1.5691	4.8044			
4	427.1	5.14	132.50	0.8786	5.0562			
5	415.2	2.83	195.00	0.3241	5.4893			
6	421.8	3.17	120.00	0.5946	5.2258			
7	447.1	5.05	20.00	5.8512	4.2328	4.95	6.3662	4.1941
8	446.6	4.89	20.00	5.6625	4.2470	4.77	6.1636	4.2102
9	445.6	5.18	22.50	5.3264	4.2736	4.45	5.7501	4.2403
10	451.6	7.72	20.00	8.9894	4.0463	7.92	10.234	3.9900
11	457.2	14.25	25.00	13.358	3.8743	12.00	15.506	3.8095
12	461.3	21.18	26.25	18.992	3.7214	17.19	22.212	3.6534
13	466.1	13.50	12.50	25.555	3.5925	23.52	30.392	3.5172

$$\log_{10} P_K = (12.236 \pm 0.202) - (7369 \pm 89) T^{-1}$$

$$\log_{10} P_T = (12.380 \pm 0.342) - (7404 \pm 155) T^{-1}$$

Notation is similar to Table IV.

TABLE VI.

Knudsen- and Torsion-Effusion Results for SiPh_4 , Experiment No. Si-44

No.	T/K	$10^3 m/g$	t/min	$10^5 P_K/\text{atm}$	$-\log_{10} P_T$	S/inch	$10^5 P_T/\text{atm}$	$-\log_{10} P_T$
1.	465.8	36.76	25.00	34.781	3.4587			
2	452.8	27.00	52.50	11.994	3.9210	10.14	13.100	3.8827
3	440.8	14.12	80.00	4.0613	4.3913	3.23	4.1727	4.3796
4	427.2	2.88	57.50	1.1346	4.9452	0.90	1.1627	4.9345
5	434.0	11.18	118.75	2.1496	4.6676	1.67	2.1574	4.6661
6	437.2	9.59	75.00	2.9303	4.5331	2.32	2.9971	4.5233
7	443.4	13.60	62.50	5.0218	4.2991	4.13	5.3354	4.2728
8	447.3	13.71	45.00	7.0615	4.1511	5.91	7.6350	4.1172
9	450.3	14.87	37.50	9.2220	4.0352	7.86	10.154	3.9934
10	456.1	33.61	51.25	15.350	3.8139	13.54	17.492	3.7572

$$\log_{10} P_K(\text{atm}) = (12.988 \pm 0.086) - (7662 \pm 38) T^{-1}$$

$$\log_{10} P_T(\text{atm}) = (13.752 \pm 0.163) - (7989 \pm 72) T^{-1}$$

Notation is similar to Table IV.

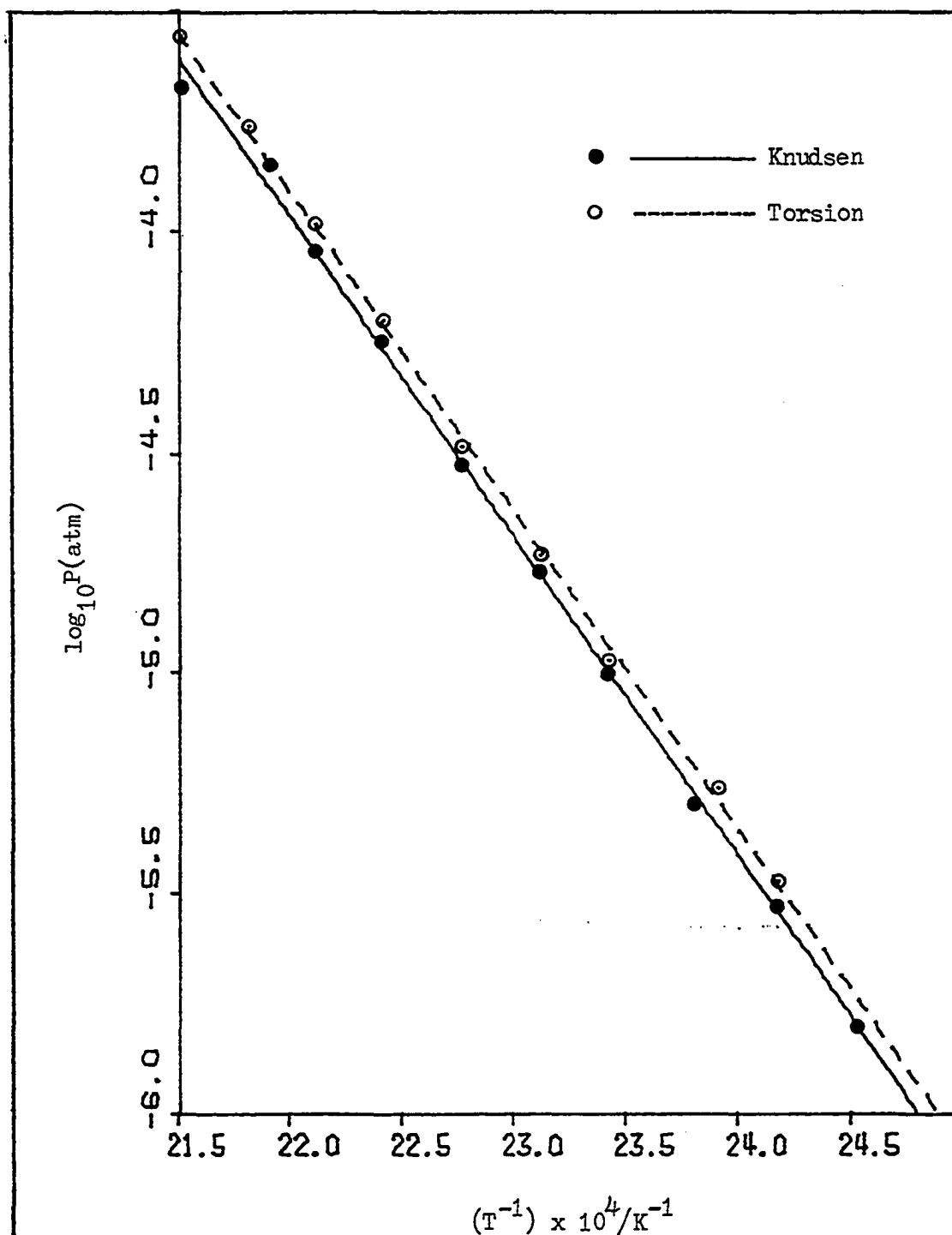
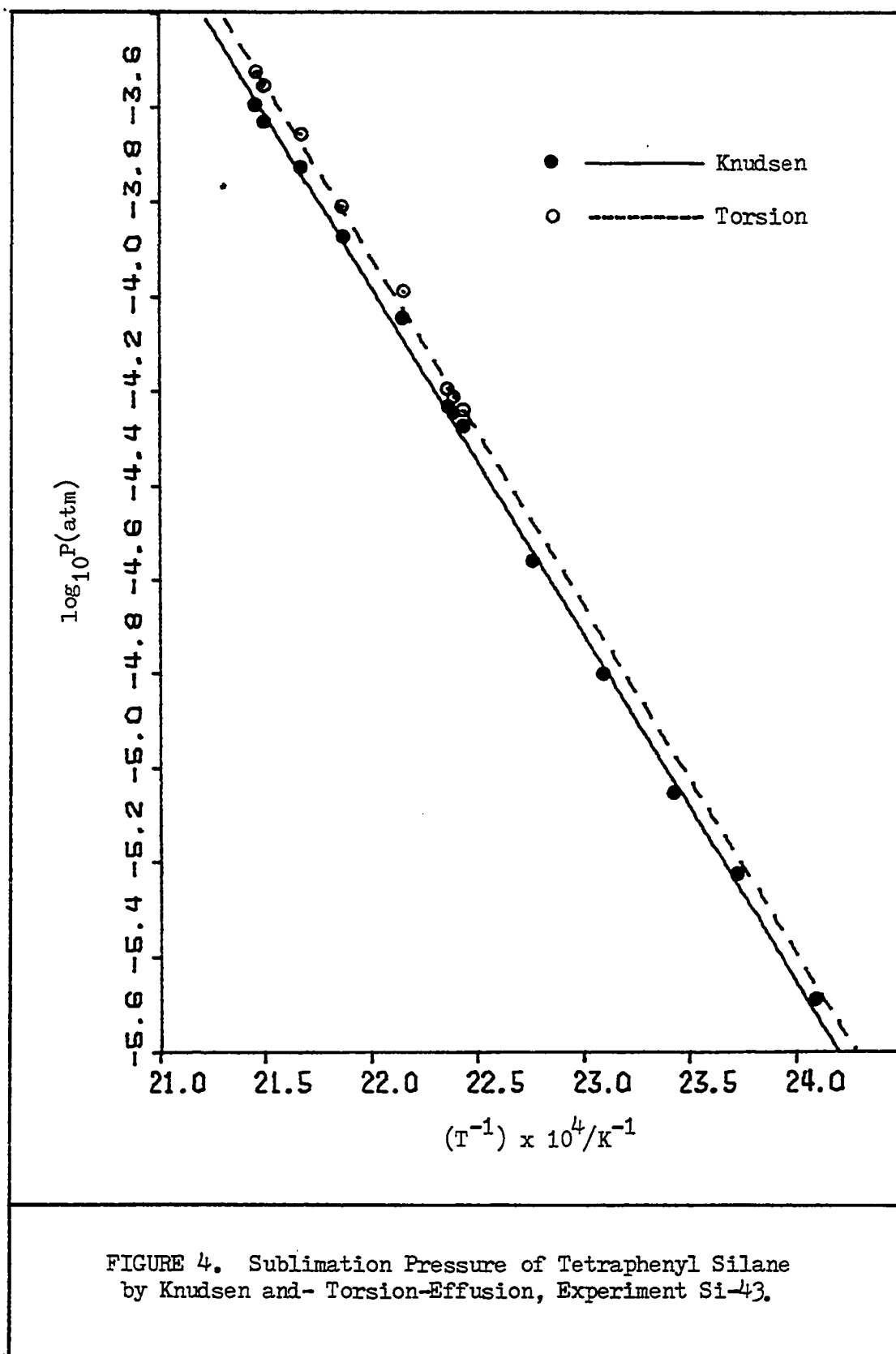


FIGURE 3. Sublimation Pressure of Tetraphenyl Silane by Knudsen- and Torsion-Effusion, Experiment Si-42.



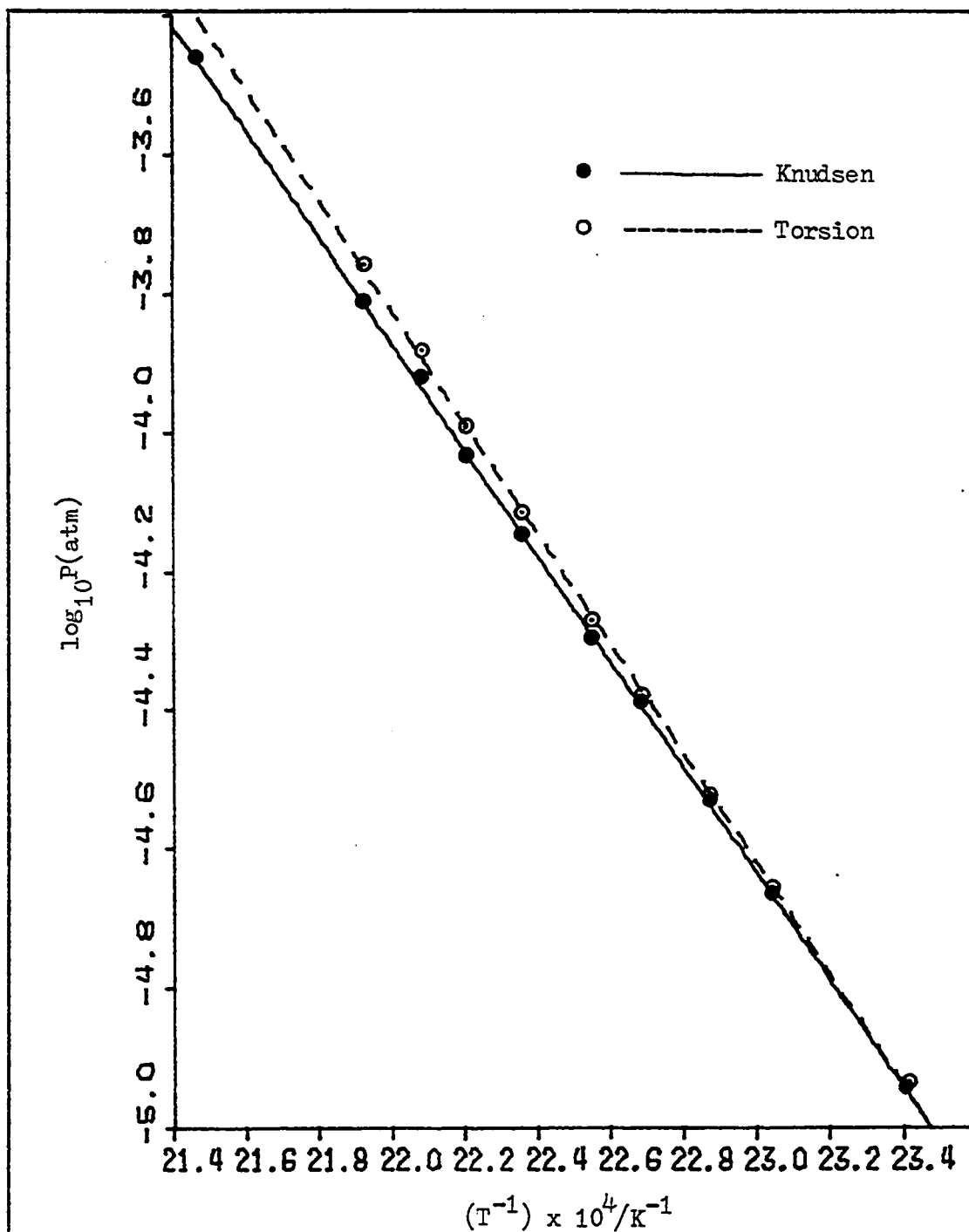


FIGURE 5. Sublimation Pressure of Tetraphenyl Silane by Knudsen- and Torsion-Effusion, Experiment Si-44.

The second-law enthalpies and entropies of sublimation obtained from the above treatment and the vapor pressure values at the mid-temperature of 440 K are summarized in Table VII. The uncertainties listed therein are standard deviations. Also listed in Table VII are the results of a composite least-squares analysis of all points of $\log_{10} P_K$ versus T^{-1} and of $\log_{10} P_T$ versus T^{-1} . A graphical presentation of these results is shown in Figure 6.

Comparison of Simultaneous Measurements Via Torsional Recoil and Mass Effusion

Comparisons of P_T and P_K , derived from the least-squares analyses at the mid-temperature of 440 K indicate that the average ratio P_T/P_K is (1.12 ± 0.06) . This lack of agreement between P_T and P_K has been observed in reported investigations²⁸⁻³² of such simultaneous measurements on substances known to vaporize as monomers. Thus the deviation of P_T/P_K from unity is not due to decomposition of SiPh_4 ; see p 10.

Error Analyses

Uncertainty in the vapor pressure from Knudsen-effusion measurements may result from uncertainties in the variables: the mass loss, areas of orifices and temperature. The propagated error in the Knudsen vapor pressures, arising from these uncertainties, is of a value of $\pm 2.2\%$ at low pressures, $\pm 2.0\%$ at intermediate pressures and $\pm 2.2\%$ at high pressures.

Uncertainties in the vapor pressure from torsion-effusion measurements arise from uncertainties in the following variables: the filament

TABLE VII.

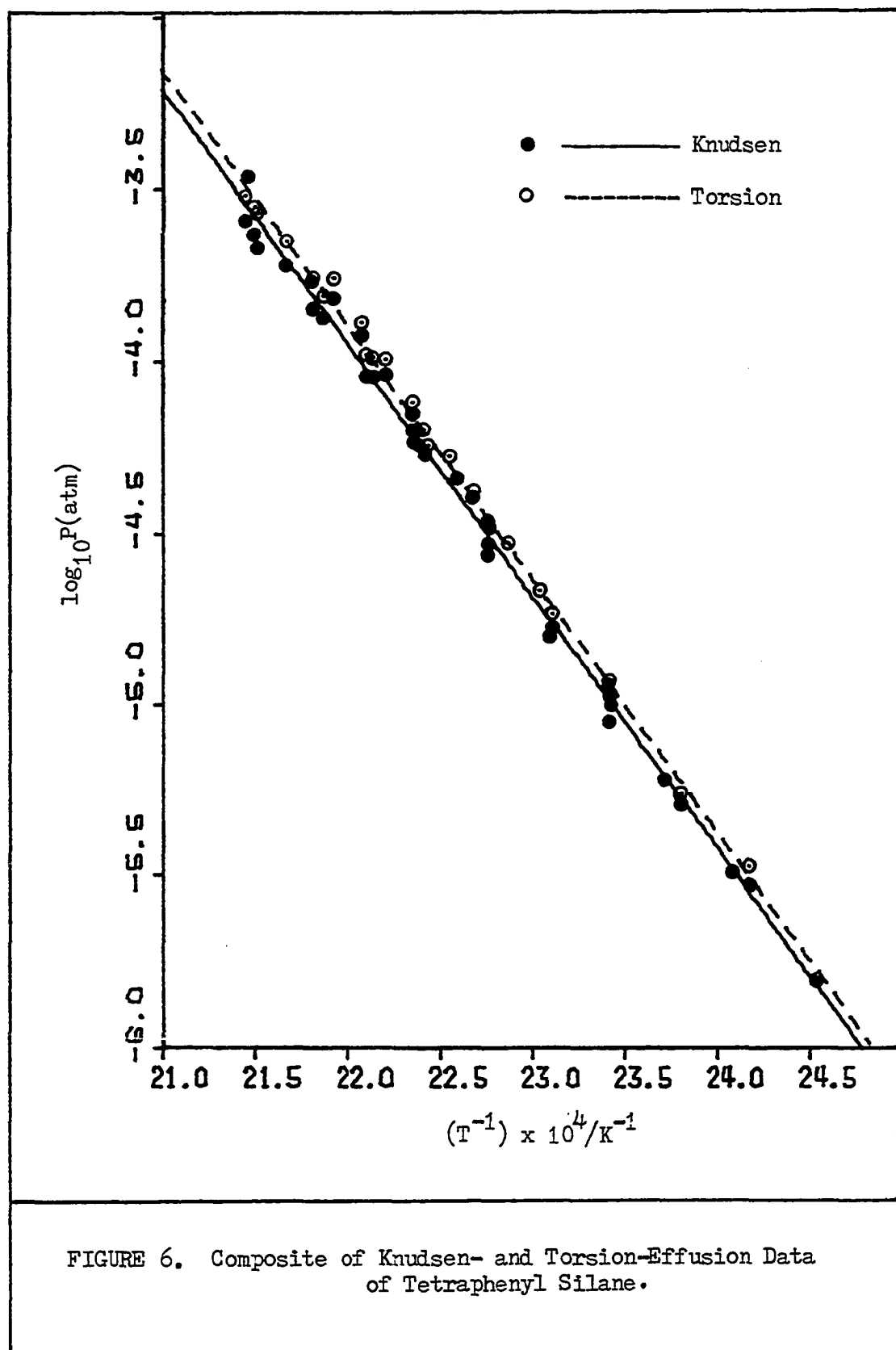
Sublimation Results for SiPh₄

Exp. No.	Method	A	B	T ₁ K	T ₂ K	10 ⁵ P(440) atm	ΔH _{sub} ^o kcal _{th} mol ⁻¹	ΔS _{sub} ^o cal _{th} K ⁻¹ mol ⁻¹
Si-42	Knudsen	11.790 ± 0.142	7169 ± 62	408	465	3.1392	32.81 ± 0.28	53.95 ± 0.65
	Torsion	12.246 ± 0.190	7345 ± 83	414	465	3.5712	33.61 ± 0.38	56.04 ± 0.87
Si-43	Knudsen	12.236 ± 0.202	7369 ± 89	415	466	3.0780	33.72 ± 0.41	55.99 ± 0.92
	Torsion	12.380 ± 0.342	7404 ± 155	447	466	3.5705	33.88 ± 0.71	56.65 ± 1.56
Si-44	Knudsen	12.988 ± 0.086	7662 ± 38	427	466	3.7529	35.06 ± 0.18	59.43 ± 0.39
	Torsion	13.752 ± 0.163	7989 ± 72	427	456	3.9371	36.56 ± 0.33	62.92 ± 0.75
Combined	Knudsen	12.299 ± 0.161	7383 ± 71	408	466	3.3072	33.78 ± 0.32	56.28 ± 0.74
	Torsion	12.424 ± 0.150	7416 ± 67	414	466	3.7107	33.93 ± 0.31	56.85 ± 0.69

The coefficients A and B are for the equation

$$\log_{10} P(\text{atm}) = A - BT^{-1}$$

P is the vapor pressure; T₁ and T₂ are the bounds of the temperature range and P(440) is the vapor pressure at the mid-temperature in K; cal_{th} = 4.184 J; atm = 101,325 N m⁻².



constant, the torsional deflection, the areas and the moment arms of the cell orifices. These uncertainties lead to a propagated error in the torsion vapor pressure of $\pm 3.4\%$ at low pressures, $\pm 1.9\%$ at intermediate pressures and ± 2.2 at high pressures. The corresponding uncertainties from the least-squares treatment are of the order of $\pm 3.1\%$ for P_K and $\pm 2.8\%$ for P_T .

Derived Thermodynamic Properties

Thermochemical data listed in Table VIII and thermodynamic properties derived from the measurements associated with the sublimation process, have been used to calculate the enthalpy of formation of $\text{SiPh}_4(\text{g})$ and the mean bond dissociation energy $\langle D \rangle(\text{Si-Ph})$.

Enthalpy of formation of $\text{SiPh}_4(\text{s})$

The enthalpy of combustion of $\text{SiPh}_4(\text{s})$ ³³ and the standard enthalpies of formation of $\text{CO}_2(\text{g})$ ³⁴, $\text{H}_2\text{O}(\text{l})$ ³⁴ and $\text{SiO}_2(\text{c, quartz})$ ³⁵ have been used to calculate the standard enthalpy of formation of crystalline SiPh_4 as:

$$\Delta H_f^\circ(\text{SiPh}_4, \text{c}, 298.15 \text{ K}) = (67 \pm 3) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

Enthalpy of formation of $\text{SiPh}_4(\text{g})$

The average standard enthalpy of sublimation at the mid-temperature of 440 K was calculated to be $(33.86 \pm 0.22) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. This value was corrected to 298.15 K by allowing an increment of approximately 0.3 $\text{kcal}_{\text{th}} \text{ mol}^{-1}$ per 25 K decrease. The corrected value is:

$$\Delta H_{\text{sub}}^\circ(\text{SiPh}_4, \text{c}, 298.15 \text{ K}) = (35.7 \pm 0.4) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

Combination of this corrected value and the standard enthalpy of formation

TABLE VIII.

Thermochemical Data

Thermodynamic Property	kcal _{th} mol ⁻¹	Reference
$\Delta H_c^\circ(\text{SiPh}_4, \text{c}, 298.15 \text{ K})$	-3225. ± 3	33
$\Delta H_f^\circ(\text{CO}_2, \text{g}, 298.15 \text{ K})$	-94.051	34
$\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}, 298.15 \text{ K})$	-68.315	34
$\Delta H_f^\circ(\text{SiO}_2, \text{c, quartz}, 298.15 \text{ K})$	-217.5 ± 0.5	35
$\Delta H_f^\circ(\text{Si}, \text{g}, 298.15 \text{ K})$	107.7 ± 1	36
$\Delta H_f^\circ(\text{Ph.}, \text{g}, 298.15 \text{ K})$	77.7	37

of the crystalline compound lead to the standard enthalpy of formation of the vapor as:

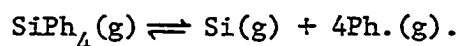
$$\Delta H_f^{\circ}(\text{SiPh}_4, \text{g}, 298.15 \text{ K}) = (103 \pm 3) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

The mean bond dissociation energy of (Si-Ph) in SiPh₄

The mean bond dissociation energy $\langle D \rangle (\text{Si-C})_{\text{SiPh}_4}$ is expressed by:

$$\langle D \rangle (\text{Si-Ph}) = \frac{1}{4} \left[\Delta H_f^{\circ}(\text{Si}, \text{g}) + 4\Delta H_f^{\circ}(\text{Ph.}, \text{g}) - \Delta H_f^{\circ}(\text{SiPh}_4, \text{g}) \right] \quad (\text{IV-3})$$

for the dissociation process:



Using the values for the standard enthalpies of formation of Si(g)³⁶ and Ph.(g)³⁷ listed in Table VIII and the calculated standard enthalpy of formation of SiPh₄(g), the mean bond dissociation energy $\langle D \rangle (\text{Si-Ph})$ was calculated to be:

$$\langle D \rangle (\text{Si-Ph})_{\text{SiPh}_4} = (79 \pm 2) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

Discussion

The Clausius-Clapeyron equation for the sublimation pressures of SiPh₄ in the temperature range 428 to 489 K, reported by McCauley and Smith²⁶ is:

$$\log_{10} P(\text{atm}) = 2.257 - 2662.5 \text{ T}^{-1} \quad (\text{IV-4})$$

This equation leads to a value of $(12.2 \pm 1) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ for the enthalpy of sublimation of SiPh₄ in the above temperature range. This value is rather low relative to the value of $(33.86 \pm 0.22) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ obtained from the present work. A comparison of Clausius-Clapeyron

plots based on the work of McCauley and Smith and on the present work is presented in Figure 7. Also shown in this figure are the calculated vapor pressures at the mid-temperature of 440 K. The discrepancy between the two sets of data is significant, specially at low temperatures. The relatively high vapor pressures reported by McCauley and Smith may be attributed to incomplete degassing of the sample.

The value for the standard enthalpy of sublimation of SiPh_4 obtained from the present investigation is consistent with the reported values of the standard enthalpies of sublimation of tetraphenyl compounds of group IV elements. The reported values are: (33.65 ± 0.60) $\text{kcal}_{\text{th}} \text{mol}^{-1}$, (37.5 ± 1) $\text{kcal}_{\text{th}} \text{mol}^{-1}$ and (36.3 ± 0.3) $\text{kcal}_{\text{th}} \text{mol}^{-1}$ for CPh_4 ²⁸, GePh_4 ²⁹ and SnPh_4 ³⁰ respectively.

Further support for the reliability of the data from this work follows from the additivity rule for lattice energy of organic crystals³⁸ and the additivity of the enthalpy of sublimation in terms of uniquely defined group increments³⁹. According to the first rule, the phenyl group contribution to the enthalpy of sublimation is $9.0 \text{ kcal}_{\text{th}} \text{mol}^{-1}$. The second rule suggests a contribution of $10 \text{ kcal}_{\text{th}} \text{mol}^{-1}$ by each phenyl group and $-0.60 \text{ kcal}_{\text{th}} \text{mol}^{-1}$ by tetravalent silicon. According to Bondi³⁹ the second rule errs consistently on the high side. A sharp decrease in the phenyl contribution is expected with increasing size of the molecule. Combination of these two rules lead to an estimated value of 35.4 to $39.4 \text{ kcal}_{\text{th}} \text{mol}^{-1}$ for the enthalpy of sublimation of SiPh_4 , which is in close agreement with the value obtained from this work.

The average bond dissociation energy, $\langle D \rangle (\text{Si-Ph})_{\text{SiPh}_4} = (79 \pm 2)$ $\text{kcal}_{\text{th}} \text{mol}^{-1}$, is in conformity with the established trend for the com-

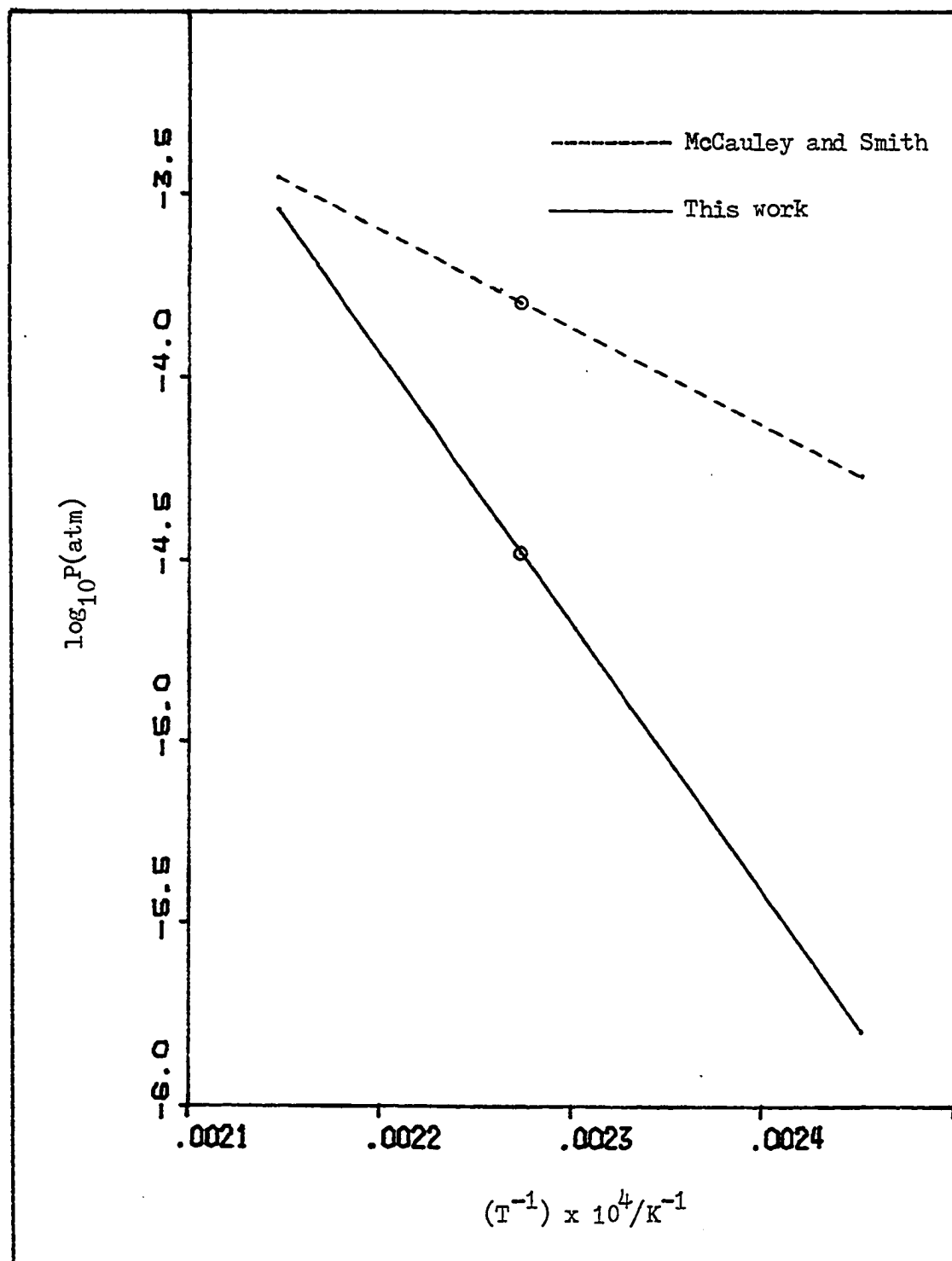


FIGURE 7. Comparison of the Vapor Pressure Data for Tetraphenyl Silane.

pounds SiR_4 where $\langle D \rangle(\text{Si-R})$ falls progressively when R is changed from Ph to Me to Et³⁵. Cottrel⁴⁰ cited a value of $72 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ for $\langle D \rangle(\text{Si-Me})$ in SiMe_4 . The corresponding value $\langle D \rangle(\text{Si-Et})$ in SiEt_4 reported by Tel'noi and Rabinovich³³ is $(63 \pm 2) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$.

In addition to the above trend the results of this study confirm that in the series of carbon, silicon, germanium and tin the average bond dissociation energy $\langle D \rangle(\text{M-Ph})$ in the tetraphenyl compounds decreases with increase in atomic the weight of M. The corresponding values are (98.8 ± 0.5) for C²⁸, (79 ± 2) for Si, (73.7 ± 0.8) for Ge²⁹, and $(61.6 \pm 0.5) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ for Sn³⁰.

Summary

Vapor pressure measurements of tetraphenyl silane in the temperature range 408 to 466 K lead to the following Clausius-Clapeyron equations from Knudsen-effusion and torsional-recoil respectively:

$$\log_{10} P_K(\text{atm}) = (12.299 \pm 0.161) - (7383 \pm 71) T^{-1} \quad (\text{IV-4})$$

$$\log_{10} P_T(\text{atm}) = (12.424 \pm 0.150) - (7416 \pm 67) T^{-1} \quad (\text{IV-5})$$

The enthalpy and entropy of sublimation derived from the least-squares analyses of the results are:

$$\Delta H_{\text{sub}}^{\circ}(\text{SiPh}_4, c, 440 \text{ K}) = (33.86 \pm 0.22) \text{ kcal}_{\text{th}} \text{ mol}^{-1},$$

$$\Delta S_{\text{sub}}^{\circ}(\text{SiPh}_4, c, 440 \text{ K}) = (56.57 \pm 0.51) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}.$$

The corrected value for the standard enthalpy of sublimation at 298.15 K is:

$$\Delta H_{\text{sub}}^{\circ}(\text{SiPh}_4, c, 298.15 \text{ K}) = (35.7 \pm 0.4) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

The standard enthalpy of formation of the gas based on the standard enthalpy of formation of the solid and on the standard enthalpy of sublimation is

$$\Delta H_f^\circ(\text{SiPh}_4, \text{g}, 298.15 \text{ K}) = (103 \pm 3) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

The calculated average bond dissociation energy is

$$\langle D \rangle(\text{Si-Ph})_{\text{SiPh}_4} = (79 \pm 2) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

CHAPTER V

VAPOR PRESSURE AND THERMODYNAMIC PROPERTIES OF HEXAPHENYL DISILANE

Literature Review

The vapor pressure of hexaphenyl disilane and its temperature dependence have not been reported in the literature.

Material

Hexaphenyl disilane, used in this work, was a sample of the commercially available compound from CPR. Prior to use the sample was recrystallized from hot benzene solution and dried under vacuum in presence of P_2O_5 at $110^\circ C$ for at least forty eight hours. Recrystallization gave a purified sample which melts at $365-367^\circ C$ compared with the literature melting point of $366-370^\circ C$ ⁴¹. Analysis of sample (Midwest Microlab, Inc.). Found: C, 82.86; H, 5.89; Si, 8.35. Analysis of the sublimate. Found: C, 83.00; H, 5.86; Si, 10.70. Calculated for $C_{36}H_{30}Si_2$: C, 83.34; H, 5.83; Si, 10.828.

Experimental Measurements

Vapor pressure measurements were carried out by the same procedure as for tetraphenyl silane except for heating the loaded cell to 551 K prior to measurements in the temperature range 511 to 551 K.

Results

The saturated vapor pressures in equilibrium with solid hexaphenyl disilane were determined from simultaneous measurements of the rate of mass-effusion and torsional-recoil in four experiments using the same graphite cell and the same filament used in the studies of tetraphenyl silane. Only data from three experiments were considered for calculation purposes since the first experiment was exploratory. The vapor pressures were calculated according to equations (II-5) and (II-10) assuming the monomeric vapor species of molecular weight $518.82 \text{ g mol}^{-1}$ for the mass-effusion equation. All calculations and least-squares analyses were made using a PDP-10 computer. The experimental data, the computed vapor pressures and Clausius-Clapeyron equations are listed in Tables IX and XI and presented graphically in Figures 8 to 10. The second-law enthalpies and entropies of sublimation as well as the vapor pressure values at the mid-temperature of 530 K are summarized in Table XII. Also listed in this table are the standard deviations. Composite least squares-analyses of all points of $\log_{10} P_K$ versus T^{-1} and of $\log_{10} P_T$ versus T^{-1} were performed. The resulting Clausius-Clapeyron equations are presented graphically in Figure 11.

TABLE IX.

Knudsen- and Torsion-Effusion Results for Si_2Ph_6 , Experiment No. Si-62

No.	T/K	$10^3 m/g$	t/min	$10^5 P_K/\text{atm}$	$-\log_{10} P_K$	S/inch	$10^5 P_T/\text{atm}$	$-\log_{10} P_T$
1	548.8	12.53	10.00	25.909	3.5866	24.46	31.621	3.5000
2	542.8	25.38	30.00	17.398	3.7595	15.86	20.503	3.6882
3	536.6	24.40	46.25	10.786	3.9671	9.50	12.281	3.9108
4	530.2	9.73	31.25	6.3278	4.1987	5.36	6.9292	4.1593
5	523.6	18.62	102.50	3.6690	4.4355	2.98	3.8524	4.4143
6	511.0	7.88	122.50	1.2834	4.8916	0.86	1.1118	4.9540
7	513.4	4.35	58.75	1.4808	4.8295	1.00	1.2928	4.8885
8	518.3	8.89	78.75	2.2685	4.6443	1.68	2.1718	4.6632
9	522.3	9.53	61.25	3.1385	4.5033	2.42	3.1285	4.5047
10	526.2	11.63	53.75	4.3809	4.3584	3.50	4.5247	4.3444
11	535.0	22.68	51.25	9.0342	4.0441	7.78	10.058	3.9975
12	540.5	10.32	15.00	14.118	3.8502	12.64	16.340	3.7867
13	548.6	24.81	18.75	27.357	3.5629	25.60	33.095	3.4802

$$\log_{10} P_K(\text{atm}) = (14.567 \pm 0.153) - (9953 \pm 81) T^{-1}$$

$$\log_{10} P_T(\text{atm}) = (16.632 \pm 0.215) - (11034 \pm 114) T^{-1}$$

Notation is similar to Table IV.

TABLE X.

Knudsen- and Torsion-Effusion Results for Si_2Ph_6 , Experiment No. Si-63

No.	T/K	$10^3 m/g$	t/min	$10^5 P_K/\text{atm}$	$-\log_{10} P_K$	s/inch	$10^5 P_T/\text{atm}$	$-\log_{10} P_T$
1	551.2	21.03	15.00	29.053	3.5368			
2	545.2	25.39	26.25	19.934	3.7004	18.66	24.131	3.6174
3	539.3	14.43	23.75	12.453	3.9047	11.55	14.936	3.8258
4	531.9	18.48	55.00	6.8397	4.1650	6.18	7.9920	4.0973
5	526.0	7.22	35.00	4.1758	4.3793	3.76	4.8624	4.3131
6	519.0	8.81	73.75	2.4021	4.6194	2.15	2.7804	4.5559
7	513.4	9.24	125.00	1.4784	4.8302	1.38	1.7846	4.7485
8	515.0	7.28	93.75	1.5555	4.8081	1.50	1.9398	4.7122
9	527.8	11.52	51.25	4.5580	4.3412	4.13	5.3409	4.2724
10	539.6	22.52	38.75	11.915	3.9239	11.04	14.277	3.8454
11	548.1	7.12	6.25	23.541	3.6282	22.29	28.825	3.5402
12	547.4	24.55	22.50	22.532	3.6472	21.60	27.933	3.5539

$$\log_{10} P_K(\text{atm}) = (14.420 \pm 0.197) - (9890 \pm 105) T^{-1}$$

$$\log_{10} P_T(\text{atm}) = (14.709 \pm 0.214) - (10002 \pm 114) T^{-1}$$

notation is similar to Table IV.

TABLE XI.

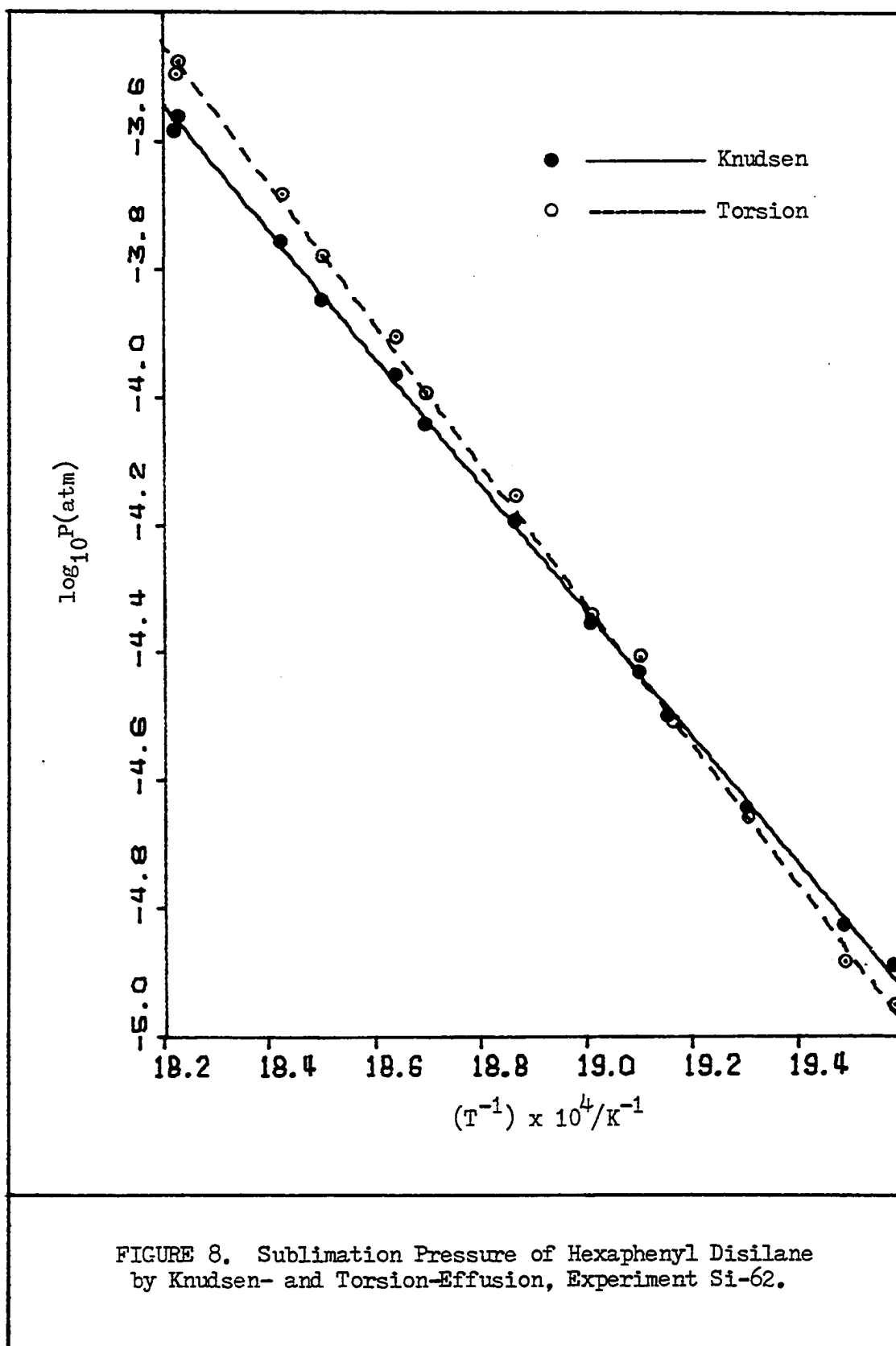
Knudsen- and Torsion-Effusion Results for Si_2Ph_6 , Experiment No. Si-64

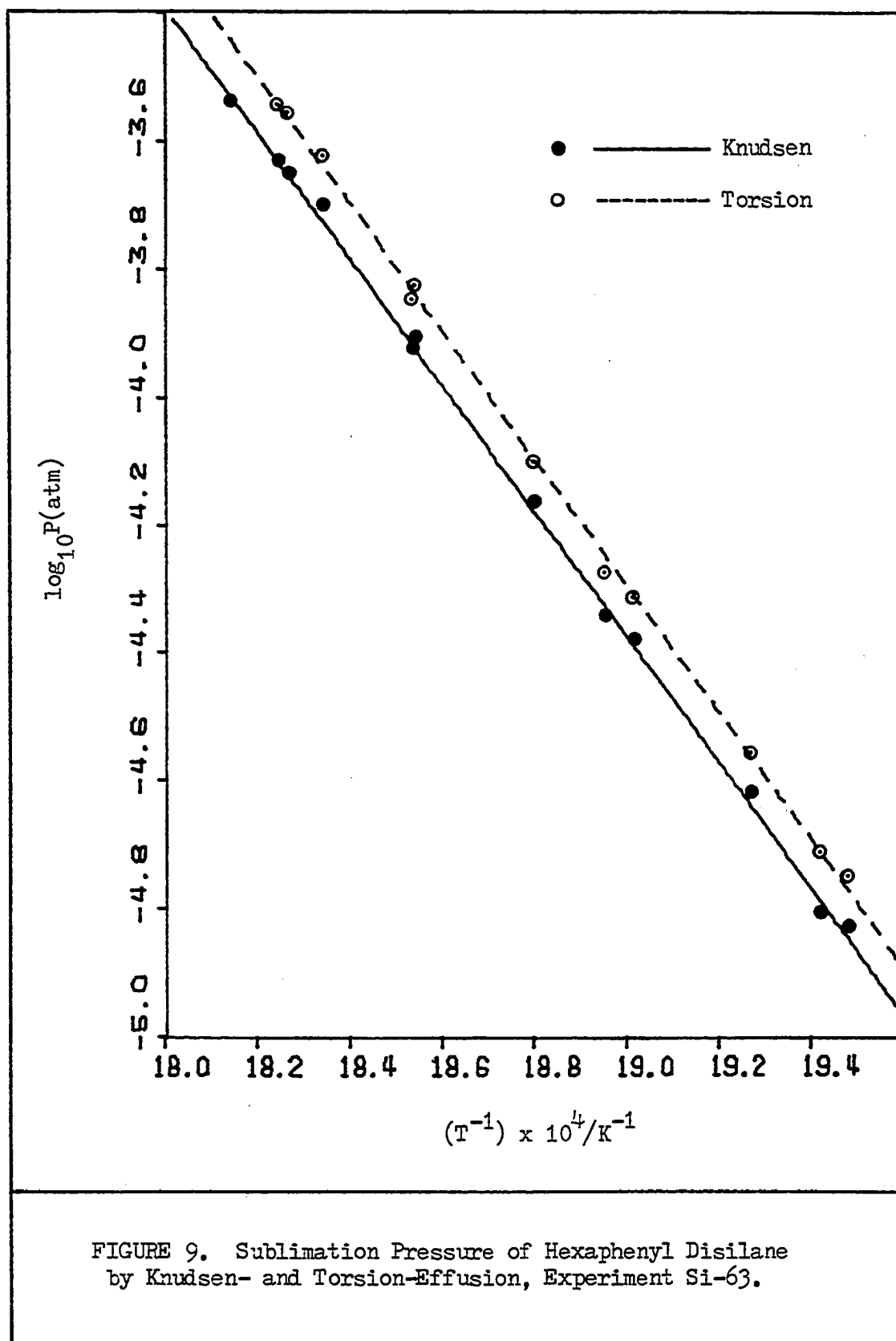
No.	T/K	$10^3 m/g$	t/min	$10^5 P_K/\text{atm}$	$-\log_{10} P_K$	S/inch	$10^5 P_T/\text{atm}$	$-\log_{10} P_T$
1	550.9	23.50	16.25	29.960	3.5234			
2	543.7	16.70	20.00	17.185	3.7449	15.57	20.133	3.6961
3	537.8	16.46	31.25	10.781	3.9673	9.17	11.857	3.9260
4	531.0	14.48	48.75	6.0411	4.2189	5.15	6.6592	4.1766
5	525.5	13.28	71.25	3.7712	4.4235	3.09	3.9955	4.3984
6	513.6	4.72	70.00	1.3488	4.8701			
7	518.8	7.93	75.00	2.1257	4.6725			
8	522.8	8.23	56.25	2.9528	4.5298	2.29	2.9611	4.5285
9	526.9	8.48	41.25	4.1651	4.3804	3.35	4.3317	4.3633
10	535.2	11.03	27.50	8.1901	4.0867	7.20	9.3100	4.0311
11	540.2	14.68	23.75	12.681	3.8969	11.36	14.689	3.8330
12	549.5	9.67	7.50	26.677	3.5739	25.38	32.818	3.4839

$$\log_{10} P_K(\text{atm}) = (15.074 \pm 0.109) - (10246 \pm 58) T^{-1}$$

$$\log_{10} P_T(\text{atm}) = (16.858 \pm 0.196) - (11177 \pm 105) T^{-1}$$

Notation is similar to Table IV.





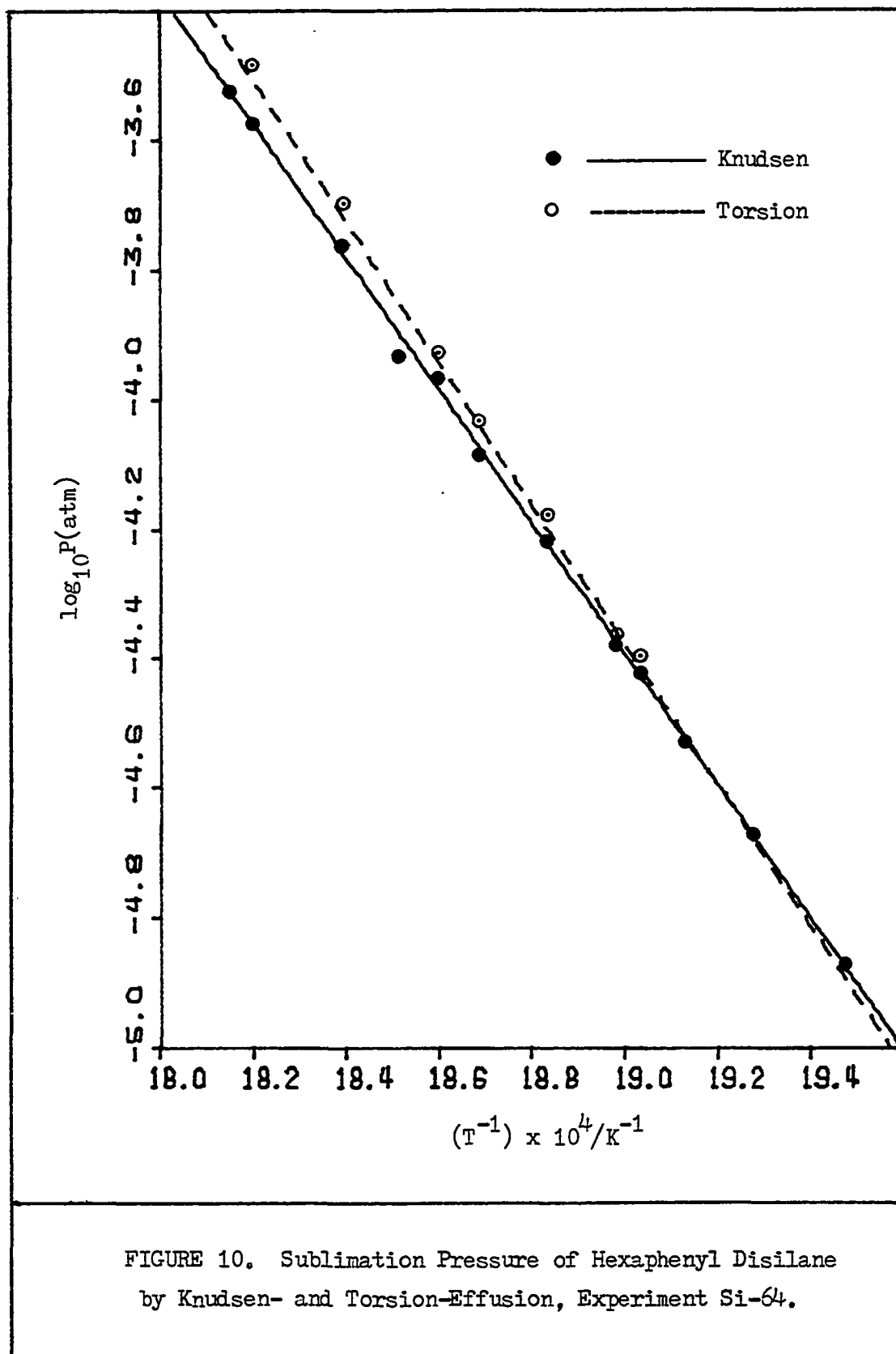


TABLE XII.

Sublimation Results for Si_2Ph_6

Exp. No.	Method	A	B	T_1 K	T_2 K	$10^5 P(530)$ atm	$\Delta H_{\text{sub}}^\circ$ kcal _{th} mol ⁻¹	$\Delta S_{\text{sub}}^\circ$ cal _{th} K ⁻¹ mol ⁻¹
Si-62	Knudsen	14.567 ± 0.153	9953 ± 81	511	549	6.1342	45.54 ± 0.37	66.65 ± 0.70
	Torsion	16.632 ± 0.215	11034 ± 114	511	549	6.5033	50.49 ± 0.52	76.10 ± 0.98
Si-63	Knudsen	14.420 ± 0.197	9890 ± 105	513	551	5.7494	45.25 ± 0.48	65.98 ± 0.90
	Torsion	14.709 ± 0.214	10002 ± 114	513	548	6.9054	45.76 ± 0.52	67.30 ± 0.98
Si-64	Knudsen	15.074 ± 0.109	10246 ± 58	514	551	5.5198	46.88 ± 0.27	68.97 ± 0.50
	Torsion	16.858 ± 0.196	11177 ± 105	523	550	5.7986	51.14 ± 0.48	77.14 ± 0.90
Combined	Knudsen	14.579 ± 0.119	9972 ± 63	511	551	5.8064	45.63 ± 0.29	66.70 ± 0.54
	Torsion	15.803 ± 0.195	10596 ± 104	511	550	6.4647	48.48 ± 0.48	72.31 ± 0.89

The coefficients A and B are for the equation

$$\log_{10} P(\text{atm}) = A - BT^{-1}$$

P is the vapor pressure; T_1 and T_2 are the bounds of the temperature range and $P(530)$ is the vapor pressure at the mid-temperature in K; cal_{th} = 4.184 J; atm = 101,325 N m⁻².

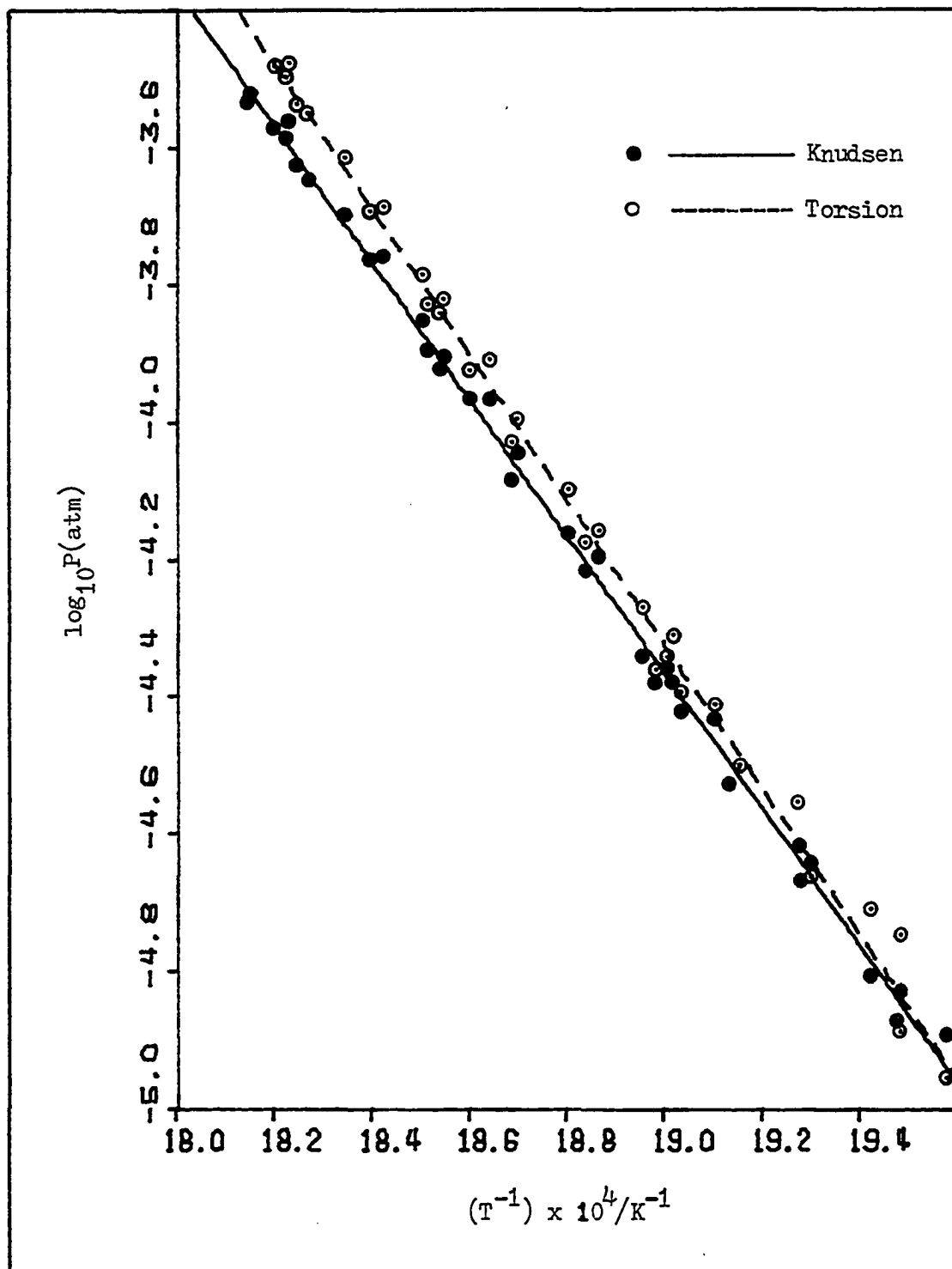


FIGURE 11. Composite of Knudsen- and Torsion-Effusion Data of Hexaphenyl Disilane.

Comparison of Simultaneous Measurements via Torsional Recoil and Mass Effusion

Comparison of P_T and P_K , derived from the least-squares treatment at the mid-temperature of 530 K indicates that the average P_T/P_K ratio is (1.10 ± 0.08) . The same remark, mentioned on p. 30, regarding the deviation of this ratio from unity is applicable.

Error Analyses

The same error analyses presented in chapter IV for tetraphenyl silane are also true for hexaphenyl disilane. The corresponding uncertainties in the calculated vapor pressures from the least-squares analyses are: $\pm 2.28\%$ in P_K and $\pm 2.44\%$ in P_T .

Derived Thermodynamic Properties

Standard enthalpy of sublimation of $\text{Si}_2\text{Ph}_6(\text{s})$

The average enthalpy of sublimation at the mid-temperature of 530 K was calculated to be $(45.628 \pm 0.288) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ from Knudsen-effusion measurements and $(48.484 \pm 0.476) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ from torsional-recoil measurements. The corresponding values corrected to 298.15 K are:

$$\Delta H_{\text{sub}}^{\circ}(\text{Si}_2\text{Ph}_6, \text{c}, 298.15 \text{ K}) = (48.3 \pm 0.6) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$$

$$\Delta H_{\text{sub}}^{\circ}(\text{Si}_2\text{Ph}_6, \text{c}, 298.15 \text{ K}) = (51.6 \pm 0.7) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

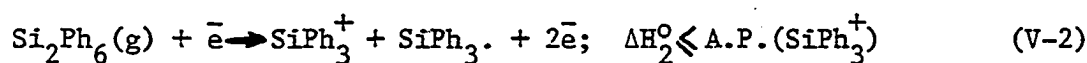
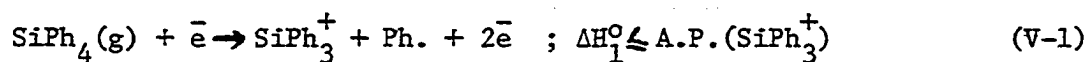
Enthalpy of formation of $\text{Si}_2\text{Ph}_6(\text{g})$

To calculate the standard enthalpy of formation of gaseous Si_2Ph_6 the standard enthalpy of combustion is needed. Unfortunately such

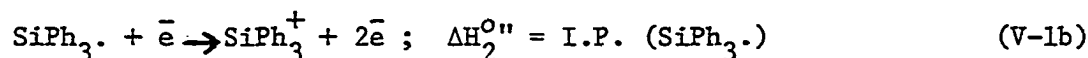
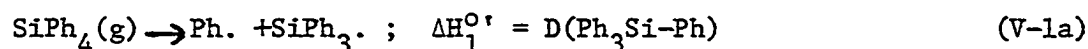
information is not available. Without this minimum information it is not possible to utilize the sublimation data directly for this purpose as well as for evaluation of the average bond dissociation energy $\langle D \rangle$ (Si-Ph) in Si_2Ph_6 and the bond dissociation energy $D(\text{Ph}_3\text{Si-SiPh}_3)$.

Mass spectrometric data and derived thermochemical properties

An alternate approach is to use mass spectrometric data, namely, the appearance potential, A.P., and ionization potential, I.P., of SiPh_3^+ and $\text{SiPh}_3\cdot$ respectively. The appearance potential of an ion, A.P. (ion), measures the heat of reaction by which the ion is formed. Thus, the SiPh_3^+ ion can be formed by the processes:



Reaction (V-1) may be expressed as the sum of the following reactions:



From these equations the following relation is obtained for A.P.

(SiPh_3^+) from $\text{SiPh}_4(\text{g})$ as a parent molecule:

$$\text{A.P.}(\text{SiPh}_3^+) \geq D(\text{Ph}_3\text{Si-Ph}) + \text{I.P.}(\text{SiPh}_3\cdot) \quad (\text{V-3})$$

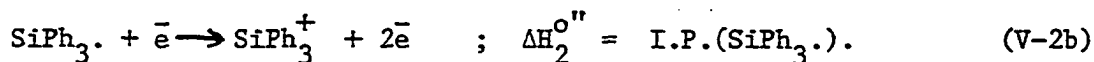
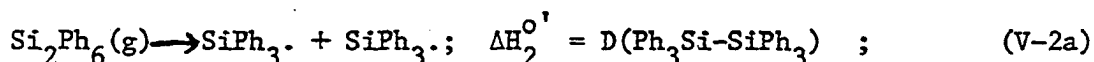
The bond dissociation energy $D(\text{Ph}_3\text{Si-Ph})$ of the first Carbon-Silicon bond in SiPh_4 is defined by

$$D(\text{Ph}_3\text{Si-Ph}) = \Delta H_f^0(\text{SiPh}_3\cdot) + \Delta H_f^0(\text{Ph}\cdot) - \Delta H_f^0(\text{SiPh}_4\cdot\text{g}) \quad (\text{V-4})$$

Thus from mass spectrometric data and the standard enthalpy of formation of $\text{Ph}\cdot(\text{g})$ and $\text{SiPh}_4(\text{g})$ it is possible to calculate $\Delta H_f^0(\text{SiPh}_3\cdot, \text{g})$

by the proper substitutions into equations (V-3) and (V-4). It should be pointed out that in equation (V-3) the excess energy of the fragments is neglected. To the extent that the excess energy is nonzero, the calculated ΔH_f^O will be an upper limit.

Reaction (V-2) is equivalent to the sum of the following reactions:



Thus the A.P. (SiPh_3^+) from Si_2Ph_6 as a parent molecule is expressed by:

$$\text{A.P.}(\text{SiPh}_3^+) \triangleq D(\text{Ph}_3\text{Si-SiPh}_3) + \text{I.P.}(\text{SiPh}_3\cdot) \quad (\text{V-5})$$

where

$$D(\text{Ph}_3\text{Si-SiPh}_3) = 2\Delta H_f^O(\text{SiPh}_3\cdot) - \Delta H_f^O(\text{Si}_2\text{Ph}_6, \text{g}). \quad (\text{V-6})$$

By substitution for proper quantities into equations (V-5) and (V-6) the standard enthalpy of formation of gaseous Si_2Ph_6 may be evaluated.

The needed mass spectrometric data for SiPh_4 and Si_2Ph_6 have been reported by Gaidis et.al.⁴² and are tabulated in Table XIII. The derived thermodynamical properties are listed below:

Bond dissociation energies:

$$D(\text{Ph}_3\text{Si-Ph}) = (95 \pm 7) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$$

$$D(\text{Ph}_3\text{Si-SiPh}_3) = (88 \pm 7) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

Standard enthalpies of formation:

$$\Delta H_f^O(\text{SiPh}_3\cdot) = (121 \pm 8) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$$

$$\Delta H_f^O(\text{Si}_2\text{Ph}_6, \text{g}) = (153 \pm 18) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

TABLE XIII.

Thermochemical and Mass Spectrometric Data

Mass Spectrometric Data

Parent Molecule	A.P. (SiPh_3^+) $\text{kcal}_{\text{th}} \text{mol}^{-1}$	I.P. ($\text{SiPh}_3\cdot$) $\text{kcal}_{\text{th}} \text{mol}^{-1}$	Reference
SiPh_4	229+2	134+7	42
Si_2Ph_6	222+2	134+7	42

Enthalpies of formation $(\Delta H_f^\circ, \text{g}, 298.15 \text{ K})$

Species	$\text{kcal}_{\text{th}} \text{mol}^{-1}$	Reference
Si_2	141 +3	36
Ph.	77.7	37

The mean bond dissociation energy of (Si-Ph) in Si_2Ph_6

The mean bond dissociation energy $\langle D \rangle$ (Si-Ph) for the reactions:



may be expressed by:

$$\langle D \rangle (\text{Si-Ph}) = \left[\frac{1}{6} \Delta H_f^\circ (\text{Si}_2, \text{g}) + 6\Delta H_f^\circ (\text{Ph} \cdot, \text{g}) - \Delta H_f^\circ (\text{Si}_2\text{Ph}_6, \text{g}) \right] \quad (\text{V-8})$$

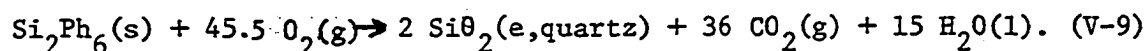
Using the values for $\Delta H_f^\circ (\text{Si}_2, \text{g})$ and $\Delta H_f^\circ (\text{Ph} \cdot, \text{g})$ from Table XIII, and $\Delta H_f^\circ (\text{Si}_2\text{Ph}_6, \text{g})$ derived above the mean bond dissociation energy $\langle D \rangle$ (Si-Ph) in Si_2Ph_6 is calculated to be $(76 \pm 4) \text{ kcal}_{\text{th}} \text{mol}^{-1}$.

Enthalpy of formation of $\text{Si}_2\text{Ph}_6(\text{s})$

The standard enthalpy of formation of $\text{Si}_2\text{Ph}_6(\text{s})$ may be evaluated from the average standard enthalpy of sublimation $\Delta H_{\text{sub}}^\circ (\text{Si}_2\text{Ph}_6, \text{c}, 298.15 \text{ K}) = (50.0 \pm 0.5) \text{ kcal}_{\text{th}} \text{mol}^{-1}$ and the derived standard enthalpy of formation of the vapor $\Delta H_f^\circ (\text{Si}_2\text{Ph}_6, \text{g}, 298.15 \text{ K}) = (153 \pm 18) \text{ kcal}_{\text{th}} \text{mol}^{-1}$. A value of $\Delta H_f^\circ (\text{Si}_2\text{Ph}_6, \text{s}, 298.15 \text{ K}) = (103 \pm 18) \text{ kcal}_{\text{th}} \text{mol}^{-1}$ is obtained.

Estimation of the enthalpy of combustion of $\text{Si}_2\text{Ph}_6(\text{s})$

An estimated value for the enthalpy of combustion of $\text{Si}_2\text{Ph}_6(\text{s})$ may be obtained according to:



Using the above value for the enthalpy of formation of $\text{Si}_2\text{Ph}_6(\text{s})$ and the values for the enthalpies of formation of the combustion products presented in Table VIII, the estimated value for $\Delta H_c^\circ (\text{Si}_2\text{Ph}_6, \text{c}, 298.15 \text{ K})$ is $-(4949 \pm 18) \text{ kcal}_{\text{th}} \text{mol}^{-1}$.

Discussion and Conclusion

The average value for the standard enthalpy of sublimation of hexaphenyl disilane corrected to 298.15 K, $\Delta H_{\text{sub}}^{\circ} = (50.0 \pm 0.5)$ kcal_{th} mol⁻¹, seems to be consistent with the reported values of (44.95 ± 0.65) kcal_{th} mol⁻¹ and (50 ± 1) kcal_{th} mol⁻¹ for Sn₂Ph₆³⁰ and Ge₂Ph₆²⁹, respectively. Application of the additivity rules mentioned in the previous chapter lead to an estimated value of 52.8 to 58.8 kcal_{th} mol⁻¹ for the standard enthalpy of sublimation of Si₂Ph₆. The same remark regarding the high value obtained from the additivity rule of Bondi, mentioned in the previous chapter, is valid in the case of Si₂Ph₆. This agreement with the additivity rules lends further support to the validity of the sublimation data of this work.

The large uncertainty in the estimated value for the standard enthalpy of formation of gaseous Si₂Ph₆, $\Delta H_{\text{f}}^{\circ}(\text{Si}_2\text{Ph}_6, \text{g}, 298.15 \text{ K}) = (158 \pm 18)$ kcal_{th} mol⁻¹ results from the uncertainties in the ionization potential of SiPh₃., I.P. (SiPh₃.) = (134 ± 7) kcal_{th} mol⁻¹. Gaidis et. al.⁴² calculated $\Delta H_{\text{f}}^{\circ}(\text{Si}_2\text{Ph}_6, \text{g})$ to be 142.0 kcal_{th} mol⁻¹, using a bond energy scheme for group contributions to the enthalpies of formation of a number of substituted disilanes. Their scheme seems to lead to lower values for the enthalpies of formation. For example their value for $\Delta H_{\text{f}}^{\circ}(\text{SiPh}_4, \text{g}) = 95.8$ kcal_{th} mol⁻¹ compared with (103 ± 3) kcal_{th} mol⁻¹ as derived from the sublimation data of SiPh₄. Similarly the estimated value for $D(\text{Ph}_3\text{Si-SiPh}_3) = (88 \pm 7)$ kcal_{th} mol⁻¹

is lower than the value of $(90 \pm 6) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ calculated by Gaidis et. al.⁴². However the corresponding bond dissociation energies $D(\text{R}_3\text{Si-SiR}_3)$ where R is Me or Et are lower than for R = Ph. Steele et. al.⁴³ reported the following values $D(\text{Me}_3\text{Si-SiMe}_3) = 81.3 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ and Tel'noi and Rabinovitch³³ reported $D(\text{Et}_3\text{Si-SiEt}_3) = (70 \pm 10) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. Thus the trend that $D(\text{R}_3\text{Si-SiR}_3)$ is higher for the phenyl compound as compared with the alkyl disilanes is established. An additional trend seems to be established with regard to the decrease in the bond dissociation energy $D(\text{R}_3\text{M-MR}_3)$ as the atomic weight increases in group IV.

Summary

Vapor pressure measurements of hexaphenyl disilane in the temperature range 511 to 551 K, lead to the following Clausius-Clapeyron equations from Knudsen-effusion and torsional-recoil respectively:

$$\log_{10} P_{\text{T}}(\text{atm}) = (14.579 \pm 0.119) - (9972 \pm 63) T^{-1} \quad (\text{V-10})$$

$$\log_{10} P_{\text{K}}(\text{atm}) = (15.803 \pm 0.195) - (10596 \pm 104) T^{-1}. \quad (\text{V-11})$$

The standard enthalpy and entropy of sublimation derived from the least-squares analyses of the results are:

$$\Delta H_{\text{sub}}^{\circ}(\text{Si}_2\text{Ph}_6, \text{c}, 530 \text{ K}) = (47.06 \pm 0.28) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$$

$$\Delta S_{\text{sub}}^{\circ}(\text{Si}_2\text{Ph}_6, \text{c}, 530 \text{ K}) = (69.50 \pm 0.52) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}.$$

The corrected value for the standard enthalpy of sublimation at 298.15 K is:

$$\Delta H_{\text{sub}}^{\circ}(\text{Si}_2\text{Ph}_6, \text{c}, 298.15 \text{ K}) = (50.0 \pm 0.5) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$$

The estimated standard enthalpy of formation of the vapor is:

$$\Delta H_f^\circ(\text{Si}_2\text{Ph}_6, \text{g}, 298.15 \text{ K}) = (153 \pm 18) \text{ kcal}_{\text{th}}\text{mol}^{-1}.$$

The calculated bond dissociation energies are:

$$\langle D \rangle(\text{Si-Ph})_{\text{Si}_2\text{Ph}_6} = (76 \pm 4) \text{ kcal}_{\text{th}}\text{mol}^{-1}$$

$$D(\text{Ph}_3\text{Si-SiPh}_3) = (88 \pm 7) \text{ kcal}_{\text{th}}\text{mol}^{-1}.$$

The estimated standard enthalpy of combustion of $\text{Si}_2\text{Ph}_6(\text{s})$ is:

$$\Delta H_c^\circ(\text{Si}_2\text{Ph}_6, \text{s}, 298.15 \text{ K}) = -(4949 \pm 18) \text{ kcal}_{\text{th}}\text{mol}^{-1}.$$

CHAPTER VI

RECOMMENDATIONS FOR FUTURE WORK

The difficulty in performing the calculations leading to the attainment of values for the average bond dissociation energy of silicon to carbon and the bond dissociation energy of silicon to silicon from equilibrium vapor pressure measurements arises mainly from the non-availability of enthalpy of combustion data for substituted silanes and disilanes. Therefore, combustion studies of these compounds are recommended. Upon attaining enthalpy of combustion data for such compounds sublimation studies should be performed.

To complete the systematic study of the sublimation of polyphenyl compounds of group IV elements it is recommended that vapor pressure measurements of PbPh_4 and Pb_2Ph_6 be made.

Certain improvements in the apparatus are desirable to permit better reproducibility of the experimental data and to facilitate ease of operation. The following improvements are recommended:

1. Replacement of the light source of the optical lever system by a laser. A laser should provide a more intense light beam thus allowing easy readability of the angular displacement even in a well illuminated laboratory.
2. Replacement of the concave mirror of the torsion assembly by a cubic mirror with four reflecting surfaces. This should allow an increase in the range of vapor pressures measurable by the present

system.

3. Replacement of the present scale for reading angular displacement by photocells incorporated in an electric circuit. Such arrangement may be adaptable for automation and recording of the angular displacement.

4. The present connections between the components of the torsion assembly system might be responsible for the slight shift in the zero point of the torsional displacement. A check of these connections is recommended specifically with regard to possible loosening under the conditions of high temperatures.

BIBLIOGRAPHY

1. Mortimer, C. T., Reaction Heats and Bond Strengths, Addison Wesley Publishing Co., Inc., Reading, Mass., 1962, p 4.
2. Sears, F. W., Introduction to Thermodynamics, The Kinetic Theory of Cases and Statistical Mechanics, Addison Wesley Publishing Co., Inc., Cambridge, Mass., 1953, pp 200-220.
3. Hertz, H., Ann. Physik, 17, 177 (1882).
4. Knudsen, M., Ann. Physik, 28, 75 (1909).
5. loc. cit., p 999.
6. Knudsen, M., Ann. Physik, 29, 179 (1909).
7. Clausing, P., Physica, 9, 65 (1929).
8. Clausing, P., Ann. Physik, 12(5), 961 (1932).
9. DeMarcus, W. C. and Hopper, E. H., J. Chem. Phys., 23, 1344 (1955).
10. Carlson, K. D., in The Characterization of High Temperature Vapors, Margrave, J. L. (Ed.), John Wiley and Sons, Inc., New York, N.Y., 1967, pp 115-129.
11. Volmer, M. C., Z. Physik. Chem., Bodenstein Festband, 863 (1931).
12. Neumann, K. and Volker, E., Z. Physik. Chem., (Leipzig), A161, 33 (1932).
13. Freeman, R. D., in The Characterization of High Temperature Vapors, Margrave, J. L. (Ed.), John Wiley and Sons, Inc., New York, N.Y., 1967, pp 152-192.
14. Searcy, A. W. and Freeman, R. D., J. Am. Chem. Soc., 76, 5229 (1954).
15. Schulz, D. A. and Searcy, A. W., J. Chem. Phys., 36, 3099 (1962).

16. Taylor, W. J., J. Chem. Phys., 38, 779 (1963).
17. Whitman, C. I., J. Chem. Phys., 20, 161 (1952).
18. Whitman, C. I., J. Chem. Phys., 21, 1407 (1953).
19. Motzfeldt, K., J. Phys. Chem., 59, 139 (1955).
20. Speiser, R. and Spretnak, J. W., Vacuum Metallurgy, The Electrochemical Society, New York, N.Y., 1955, pp 151-191.
21. Paule, R. C. and Margrave, J. L. in The Characterization of High Temperature Vapors, Margrave, J. L. (Ed.), John Wiley and Sons, Inc., New York, N.Y., 1967, pp 130-151.
22. Keiser, D., Simultaneous Knudsen- and Torsion-Effusion Measurements of the Vapor Pressures of Tetraphenyltin and Hexaphenylditin.
Unpublished Master's Thesis, Western Michigan University, Kalamazoo, Michigan, June 1969, pp.11-22.
23. Kana'an, A. S., (unpublished work).
24. McCreary, J. R. and Thorn, R. J., J. Chem. Phys., 48, 3290 (1968).
25. Myles, K. M., Trans AIME, 230, 736 (1969).
26. McCauley, J. A. and Smith, N. O., J. Chem. Thermodynamics, 5, 31 (1973).
27. Kaufman, H. C., Handbook of Organometallic Compounds, D. Van Nostrand Company, Inc., Princeton, N.J., 1961, p 548.
28. Kana'an, A. S., J. Chem. Thermodynamics, 4, 893 (1972).
29. Kana'an, A. S., J. Chem. Thermodynamics, (in press).
30. Keiser, D. and Kana'an, A. S., J. Phys. Chem., 73, 4264 (1969).
31. McCreary, J. R. and Thorn, R. J., High Temp. Sci., 3, 300 (1971).
32. Cancaya, K., Pretzer, W. R., Livingston, W. A. and Kana'an, A. S., High Temp. Sci., 2, 322 (1970).

33. Tel'noi, V. I. and Rabinovitch, I. B., Russ. J. Phys. Chem., 40, 842 (1966).
34. Wagman, D. D., Evans, W. H., Hallow, I., Parker, V. B., Bayley, S. M. and Schumm, R. H., Natl. Bur. Stand. (U.S.) Tech. Note, 270-3 (1968).
35. Skinner, H. A., in Advances in Organometallic Chemistry, Skinner, H. A., Stone, F. G. A. and West. R. (Ed.), Academic Press, New York, N.Y., 1964, Vol. II, p 73.
36. JANAF Thermochemical Tables, Dow Chemical Company, Midland, Michigan, 2nd Addendum, PB 168, 370-2, 1967.
37. Chamberlain, G. A. and Whittle, E., Trans. Farad. Soc., 67, 2077 (1971).
38. Aihara, A., Bull. Chem. Soc. Jap., 32, 1242 (1959).
39. Bondi, A., J. Chem. Eng. Data, 8, 371 (1963).
40. Cottrell, T. L., The Strength of Chemical Bonds, Butterworths Scientific Publications, London, 1958, p 275.
41. Kaufman, op. Cit., p 399.
42. Gaidis, J. M., Briggs, P. R. and Shannon, T. W., J. Phys. Chem., 75, 974 (1971).
43. Steel, W. C. and Stone, F. G. A., J. Amer. Chem. Soc., 84, 3599 (1962).