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SIMULTANEOUS KNUDSEN- AND TORSION-EFFUSION MEASUREMENTS OF THE
VAPOR PRESSURES OF TRIPHENYL ALUMINUM AND TRIPHENYL BORON

by

Steven Wayne Govorchin

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

Western Michigan University
Kalamazoo, Michigan
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SIMULTANEOUS KNUDSEN- AND TORSION-EFFUSION MEASUREMENTS OF THE
VAPOR PRESSURES OF TRIPHENYL ALUMINUM AND TRIPHENYL BORON

Steven Wayne Govorchin, M.A.

Western Michigan University, 1986

The sublimation pressures of triphenyl aluminum and triphenyl boron have been determined from simultaneous measurements of the rate of mass effusion and torsional recoil. For triphenyl aluminum the measured vapor pressures are expressed by the equations:

$$\log_{10} (P_k/p^\circ) = (12.76 \pm 1.25) - (8214 \pm 572) (K/T)$$

$$\log_{10} (P_\tau/p^\circ) = (12.83 \pm 1.34) - (8206 \pm 615) (K/T)$$

where P_k and P_τ are the pressures measured by the Knudsen-effusion and torsional-recoil techniques, respectively, and $p^\circ = 101.325 \text{ kPa}$. For triphenyl boron the measured vapor pressures are expressed by the equations:

$$\log_{10} (P_k/p^\circ) = (9.39 \pm 0.13) - (5274 \pm 46) (K/T)$$

$$\log_{10} (P_\tau/p^\circ) = (10.00 \pm 0.07) - (5489 \pm 27) (K/T)$$

where the same notation applies. The standard molar enthalpies and entropies, of sublimation of triphenyl aluminum monomer: $\text{Al}(\text{C}_6\text{H}_5)_3(\text{cr}) \rightarrow \text{Al}(\text{C}_6\text{H}_5)_3(\text{g})$, and dissociation of the solid dimer: $\{\text{Al}(\text{C}_6\text{H}_5)_3\}_2(\text{cr}) \rightarrow 2\text{Al}(\text{C}_6\text{H}_5)_3(\text{cr})$ are estimated. The standard molar heat of formation of gaseous triphenyl boron: $\Delta_f H_m^\circ\{\text{B}(\text{C}_6\text{H}_5)_3, \text{g}, 363 \text{ K}\}$ and the mean molar bond-dissociation enthalpy $\langle D \rangle(\text{B}-\text{C}_6\text{H}_5)$ are calculated.

ACKNOWLEDGEMENTS

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Steven Wayne Govorchin

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DEDICATION

To A. S. Kana'an

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CHAPTER 1

INTRODUCTION

Thermodynamic data such as the vapor pressures, enthalpies, and entropies of sublimation of a series of analogous compounds are essential for deductions of structural information about such compounds. Also, information about bond strengths or bond energies may be determined when such thermodynamic data are combined with other data, namely, enthalpies of combustion or solution and enthalpies of formation of reactants and products of these processes.

The primary objective of this research has been to acquire vapor pressure data for the sublimation of triphenyl boron, $B(C_6H_5)_3$, and triphenyl aluminum, $Al(C_6H_5)_3$, in temperature ranges suitable for these compounds. The temperature range for a given compound depends on its volatility and thermal stability. An optimum temperature range is determined from preliminary sublimation studies.

Vapor pressures were determined from simultaneous measurements of the rate of mass effusion (Knudsen effusion) and the torsional recoil. Such simultaneous measurements provide information about the mode of sublimation which neither method alone could provide. Several compounds do not simply sublime to a monomer in the gas phase. The equilibrium vapor over some compounds may be dimeric, or perhaps polymeric, within a temperature range. Other compounds may decompose upon sublimation into fragments of molar masses smaller than the molar mass of the condensed phase. Correlation of the data from these two

methods allows information about the nature of the equilibrium vapors to be inferred.

Vapor pressure data derived from Knudsen-effusion experiments on triphenyl compounds of Group IIIA elements has been reported in the literature.¹ In their study, Greenwood et al.¹ noted an anomaly in the trend of enthalpies of sublimation of triphenyl compounds of Group IIIA as a function of atomic mass of the central atom. Specifically, with the exception of triphenyl aluminum, the molar enthalpy of sublimation, ΔH_{sub} , increased gradually in the series from triphenyl boron to triphenyl indium. The ΔH_{sub} as determined for triphenyl aluminum was even greater than that of triphenyl indium. Some conjecture about the crystal structure was offered to explain this, but at the time of that study, the various crystal structures had not been determined.

CHAPTER II

THEORY

The Knudsen-Effusion Method

The Knudsen-effusion method is a technique for determining equilibrium vapor pressures and dissociation pressures in the range 10^{-2} to 10^{-6} torr. The kinetic molecular theory of dilute gases² provides a basis for Knudsen-effusion. According to this theory for gaseous molecules in equilibrium with a condensed phase, the rate of mass effusion, w/t , of vapor molecules from a pinhole of orifice area, A_0 , in the sample enclosure is related to the vapor density, ρ , and the mean velocity of the gas molecules, \bar{C} , by:

$$\frac{w}{tA_0} = \frac{1}{4} \rho \bar{C} \quad (\text{II-1})$$

According to the kinetic molecular theory of gases, the mean velocity, \bar{C} , is related to molar mass, M , by:

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

The density, ρ , of an ideal gas is expressed by:

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

Substitution of \bar{C} and ρ into equation (II-1) yields the molecular effusion equation³:

$$P_k = \frac{w}{tA_o} \left(\frac{2\pi RT}{M} \right)^{\frac{1}{2}} \quad (\text{II-4})$$

where P_k is the equilibrium vapor pressure. In application of equation (II-4) in the Knudsen-effusion experiment, it is assumed that the vapor results from simple sublimation of the condensed phase so that the molar mass of the vapor is the molar mass of the condensed phase.

In a hypothetical ideal Knudsen-effusion experiment,⁴⁻⁶ the following conditions must be valid:

1. The sample enclosure is an inert cell which contains the condensed and vapor phases in equilibrium with each other.
2. Effusion is under thermal equilibrium where the system is maintained at constant uniform temperature.
3. Vapor molecules effuse through a small, thin edged orifice in the cell wall into an outer enclosure maintained at reduced pressure.
4. Collisions within the orifice between vapor molecules and the orifice walls or with each other are negligible.
5. The number of molecules which strike the orifice edges and return to the cell must be negligible.
6. Only a negligible number of molecules may deposit on the external surface of the cell or any part of the suspension system which attaches the cell to the weighing balance.

The phase and thermal equilibria conditions may be satisfied by designing and machining the orifice to be small in relation to the

surface area inside the cell and allowing sufficient time at a given temperature. The third condition is attained by using a vacuum system to maintain a reduced pressure 10^{-6} torr outside the sample cell. The fourth condition remains in effect as long as the vapor pressures being measured are below a certain maximum.

To satisfy the fifth condition, the cell orifice(s) must be completely round and infinitely thin. In practice, an orifice has a finite thickness within which collisions are not negligible and the reflections of molecules into the cell is not likely to be eliminated. A correction factor, which is essentially a transmission coefficient (fraction of molecules entering the orifice which exit the cell) may be applied. Clausing^{7,8} developed a correction factor scheme based on the dimensions of the orifice. Later, DeMarcus and Hopper⁹ reported a more accurate derivation of the correction factors. The theoretical justification for the correction factor or Clausing factor, W_0 , is summarized by Carlson.¹⁰ The theory considers cell geometry, including orifice geometry, vapor phase molecular collisions, and vapor-solid boundary interactions.

The explanation of the effect of the geometry of the cell on the rate of mass effusion is that not all of the molecules evaporating or subliming from the sample surface enter the orifice. Some vapor molecules are reflected back by the interior wall of the cell. The geometry of the orifice affects the flow of the vapor molecules passing through it where some molecules are reflected back into the cell by the orifice walls. The ratio of the orifice length to the orifice radius, L/r , is the function which determines the fraction of

molecules that effuse after having entered the orifice. The Clausing factor, W_0 , is a function of this ratio. The Knudsen-effusion equation is modified to:

$$P_k = \frac{W}{t A_0 W_0} \left(\frac{2\pi RT}{M} \right)^{\frac{1}{2}} \quad (\text{II-5})$$

The sixth condition may be met by proper arrangements of radiation shields which provide a proper surface for effusate condensation.

The Torsion-Effusion Method

The torsion-effusion method for determining the vapor pressure uses a suspended cell as a torsion pendulum. In the earliest application of the torsion-effusion method, Volmer¹¹ combined it with the Knudsen-effusion method, although the torsion-effusion method has been used separately.¹² Freeman¹³ discussed the details of the construction of the practical torsion-effusion apparatus. A hollow cylindrical (or rectangular) cell is suspended horizontally by means of a fine filament. The cell is positioned on the filament so that the point of attachment precisely coincides with the geometric center of the cell. The two orifices are located on opposite sides, 180° out of phase to each other and close to the ends of the cell to permit the effusing vapor molecules to exert a torque generated by the recoil force produced by effusion. The orifices are centered about the plane which bisects the cell top and bottom. Each orifice is equally distant from the center of the cell and suspension axis.

When thermal and phase equilibria conditions are achieved, the rate of molecular effusion, and therefore the rate of momentum transfer, becomes constant. The effusion of molecules through an orifice constitutes a transfer of momentum across the plane of the orifices. The transfer of momentum indicates the presence of a force and a counterbalancing recoil force. The pressure, P_τ , is directly related to the recoil force, F , and the orifice area, A_o , by:

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

The torque, T_r , exerted by the recoil force depends on the moment arm, d , of the cell orifice as:

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

The moment arm of the cell orifice, d , is the distance from the geometric center of the orifice to the axis of rotation. Effusion from each of the two orifices contributes to the total torque thus, by:

$$T_r = F_1d_1 + F_2d_2 \quad (\text{II-8})$$

The recoil torque causes the cell to rotate by an angle, θ , and the suspension filament to twist, exerting a torsional recoil torque, T_w , which counterbalances the recoil torque:

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

The torsion constant, τ , is a property of the filament. It has the units of torque per angular displacement (newton·meter·radian⁻¹).

Equation (II-6) must be corrected to allow for the partial collimation of velocities of the effusing molecules by the orifice as well as for the tendency of a real orifice to reflect some of the molecules back into the cell. This latter effect can be accounted for by means of the Clausing factor. In practice, both effects are corrected for with a combined factor which depends on L/r . This factor is called the "recoil force factor" or "pressure factor," f_1 (the ratio of the recoil force arising from effusion through a real orifice to the recoil force from an infinitesimally thin orifice). Values for the pressure factor as a function of L/r are available.¹⁴⁻¹⁵ For effusion from two orifices in a torsion-effusion experiment, the vapor pressure is given by substitution of equations (II-8) and (II-9) into equation (II-6) and introduction of the pressure factor, f_1 , where:

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

Correlation between Knudsen- and Torsion-Effusion Methods

Calculation of vapor pressure according to the Knudsen equation (II-5) assumes that the molar mass of the vapor species is known. In

the case of simple sublimation, the molar mass of the vapor is that of the sample. However, if the vapor exists as a polymer or if it is the product(s) of a decomposition process, its molar mass will differ from that of the sample. It is possible to determine the effective molar mass of the vapor by means of mass spectrometry or other analytical techniques. Since the torsional-recoil method provides direct determination of the vapor pressure and does not require a knowledge of the effusate molar mass, it is possible to deduce the molar mass of the effusate by combining equations (II-5) and (II-10) as follows:

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

The calculated molar mass, M^* , from simultaneous measurements of the rate of mass effusion and torsional recoil can be expressed as a weighted average of the molar mass of the various components (polymer, monomer, molecular fragments) as follows:¹³

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

Where m_i is the mass fraction of the vapor species i and M_i is the molar mass of that species.

Computation of the ratio P_{τ}/P_k yields information about the mode of sublimation. With P_k calculated from equation (II-5) and the molar mass, M , set equal to the molar mass of the condensed phase, the P_{τ}/P_k may be expressed by:

$$\frac{P_{\tau}}{P_k} = \left(\frac{M}{M^*} \right)^{\frac{1}{2}} \quad (\text{II-13})$$

Three cases may arise:

Case 1. If P_{τ}/P_k is equal to unity, then M is equal to M^* . This implies that the vapor phase consists of a simple monomer.

Case 2. If P_{τ}/P_k is less than unity, then M is less than M^* . This implies that the vapor phase is polymerized to some degree.

Case 3. If P_{τ}/P_k is greater than unity, then M is greater than M^* . This implies that some or all of the vapor phase molecules may be the products of decomposition.

The result predicted for substances known to sublime simply as monomers is not, in fact, obtained in the simultaneous measurement of the two vapor pressures. The P_{τ}/P_k is generally slightly larger than unity. A possible explanation for this might be that some of the effusate reflects off the walls of the enclosure which contains the cell and impacts on the outer cell surface. The additional momentum from the rebounding molecules exaggerates the measured P_{τ} .

The ratio P_{τ}/P_k , used in conjunction with other chemical information about a given system, may be used to calculate or estimate relative concentrations of the various components of the vapor phase. Freeman¹³ and Taylor¹⁶ discussed such an approach.

CHAPTER III

EXPERIMENTAL

Description of the Apparatus

The apparatus used for simultaneous Knudsen-effusion and torsional-recoil measurements is a combination of components. A full description of the apparatus has been discussed by Keiser.¹⁷ The description which follows is intended to cover only those features which are pertinent to this study.

An Overview of the Apparatus

Figure 1 is a schematic of the apparatus. The effusion cell and its suspension system are enclosed in a pyrex tube which is positioned directly beneath a semimicro balance. The balance is connected to a chart recorder which records mass changes as a function of time. The effusion cell, its suspension system, and the balance are evacuated by a mechanical pump and a diffusion pump vacuum system.

The Torsion-Effusion Assembly

The torsional-recoil system

Figure 2 shows the torsion-effusion assembly. Angular displacement of the torsion assembly due to the vapor effusing from the cell is measured by visually noting the distance traversed along a

KEY TO FIGURE 1

Schematic of Knudsen- and Torsion-Effusion Apparatus

1. Vacuum recording balance
2. Balance stand
3. Brass evacuation line
4. Brass extension tube
5. Liquid nitrogen trap
6. Oil-diffusion pump
7. Thermocouple guage
8. Ionization guage
9. Pyrex tube
10. Mechanical pump
11. Roughing valve
12. Main-gate valve
13. Fore-line vacuum valve
14. Light source of optical lever system
15. Stripchart recorder

KEY TO FIGURE 2

Schematic of Torsion-Effusion Assembly

1. Lamp
2. Ruled arc
3. Window port
4. Brass extension tube
5. Mirror
6. Tungsten filament
7. Rod
8. Cell
9. Balance

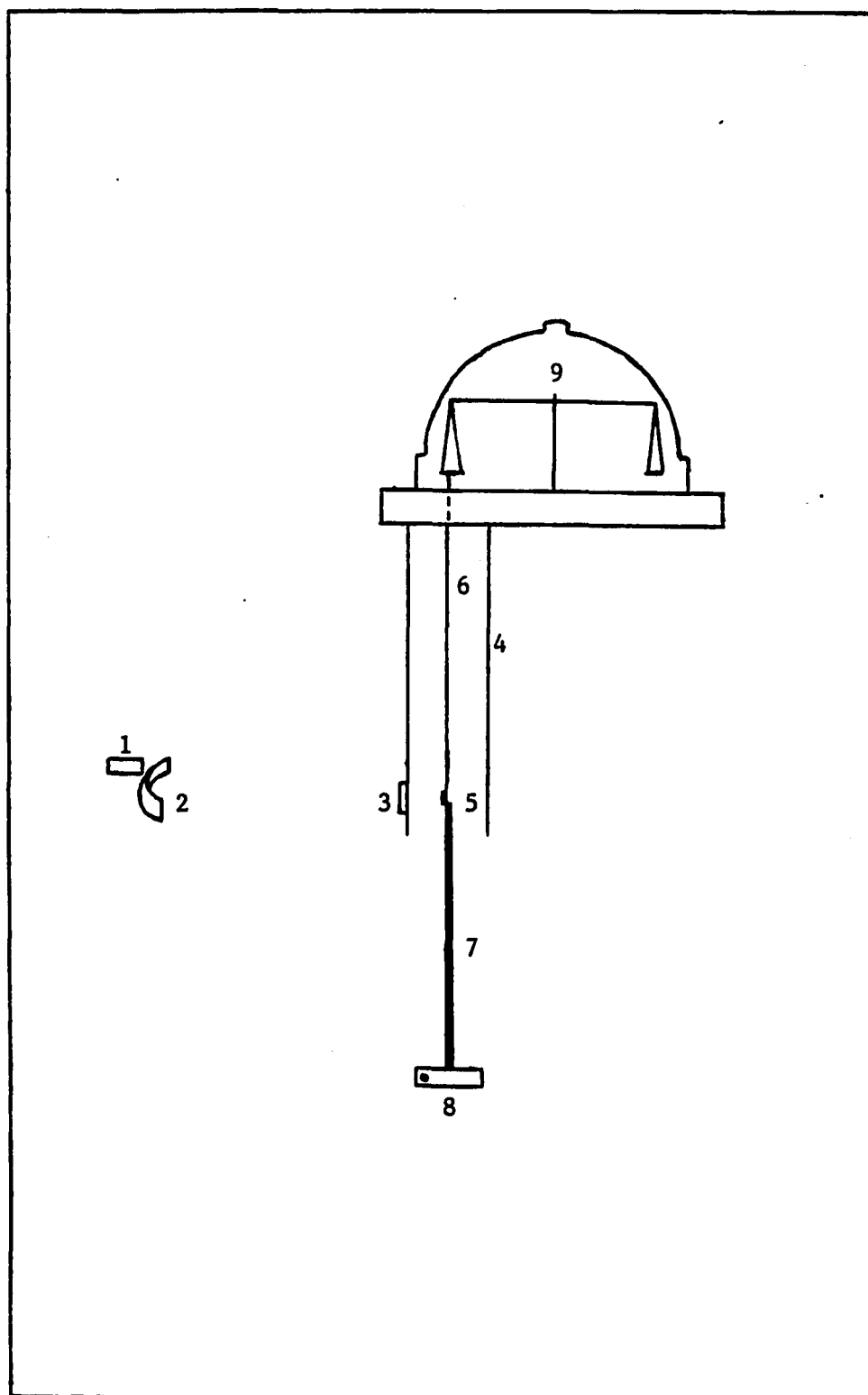


Figure 2. Schematic of Torsion-Effusion Assembly.

ruled arc by a beam of light reflected from a mirror positioned at the center of the suspension system.

The torsion filament was an annealed, high-purity tungsten wire, 3.8×10^{-2} mm in diameter and 35 cm long.

The effusion cell

One cell, designated "21-83," was used for all experiments in this study. The cell, machined from spectroscopic graphite, has two orifices, located on opposite sides of the cell along its horizontal axis, such that a line connecting the orifices would pass through the cell vertical axis. The cell is connected to the suspension system by a dovetail connector which lines the cell vertical axis with the vertical axis of the suspension system. Tapered graphite plugs, fitted to the ends of the cell allow for loading the sample. A diagram, showing the cell dimensions from which the orifice depth was calculated, is given in Figure 3.

The orifice diameter and moment arm were measured with a traveller microscope (UNITRON TMD 3621) having micrometer drums of precision of 0.001 mm. The diameter of each orifice was measured in eight different orientations of the cell on the microscope rotating table. The parameters of the cell are given in Table 1. The cited uncertainties of the radii and areas are standard deviations of the actual measurements. The Clausing and pressure factors were arrived at by means of the depth to radius ratio, L/r .^{9,15}

Table 1
Parameters of the Effusion Cell 21-83

	Orifice 1	Orifice 2
Radius (cm x 10 ²)	4.07 ± 0.03	4.05 ± 0.05
Area (cm ² x 10 ³)	5.20 ± 0.08	5.15 ± 0.13
Moment arm (cm x 10)	11.09 ± 0.01	10.91 ± 0.01
Depth (cm x 10 ²)	1.84 ± 0.03	1.84 ± 0.03
Depth to radius ratio	0.452 ± 0.018	0.454 ± 0.020
Clausing factor	0.817 ± 0.006	0.816 ± 0.007
Pressure factor	0.864 ± 0.005	0.864 ± 0.006

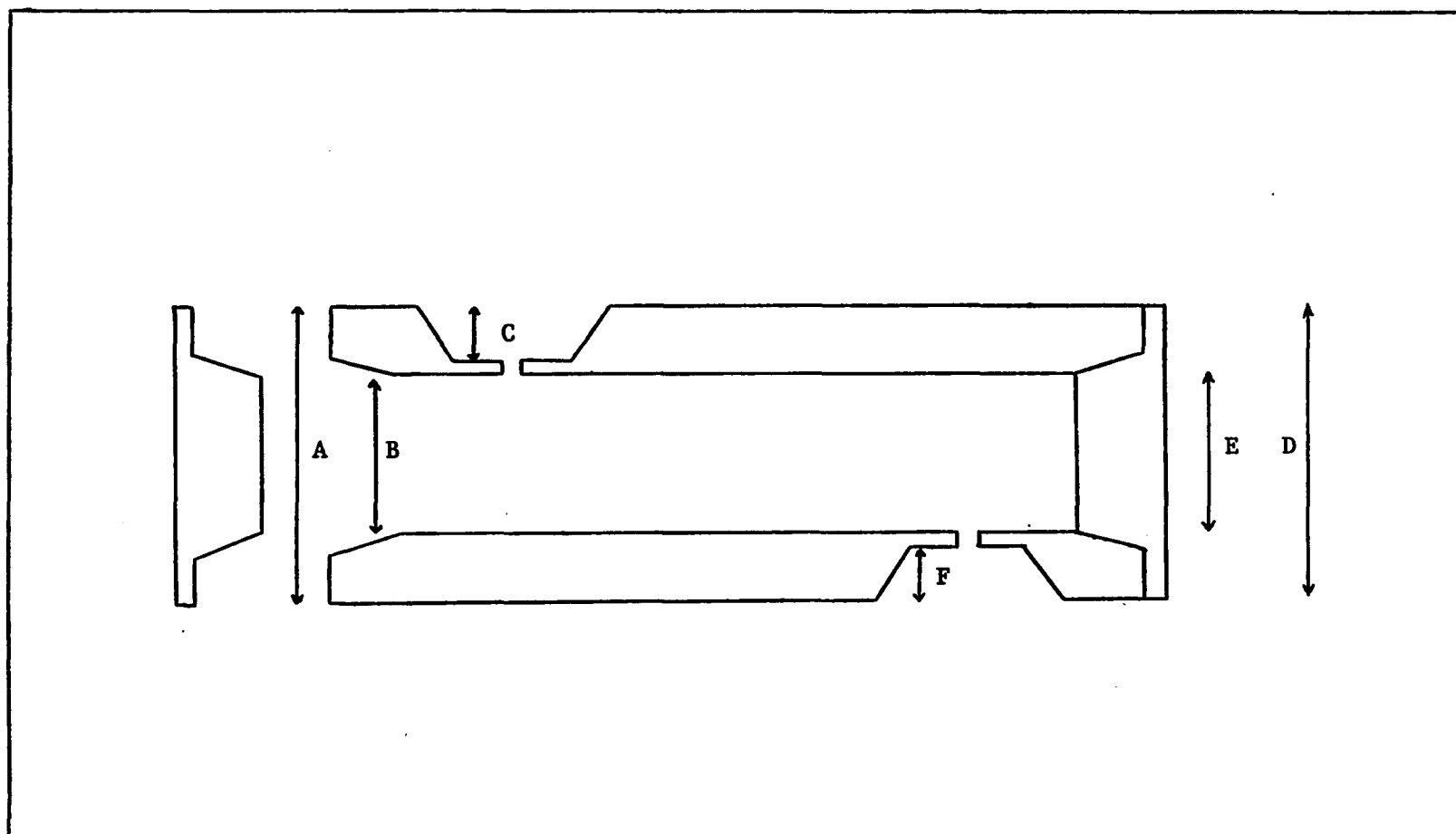


Figure 3. Schematic of a Graphite Effusion Cell. The parameters A through F of cell 21-83 in cm are 1.58, 0.96, 0.29, 1.59, 0.96, and 0.29, respectively.

The Heating Chamber

Surrounding the cell and its suspension system is the heating chamber, a pyrex tube with a thermocouple well penetrating up into the tube from its bottom. The heating chamber has a tapered glass joint at its open (top) end by which it is connected to the tapered lower end of the brass extension tube at the balance base. The inner diameter of the tube used in the triphenyl aluminum effusion study was 6.5 cm; for the triphenyl boron study, a tube with an inner diameter of 8.5 cm was used. The height of both tubes was 46.5 cm.

The Furnace and Temperature-Control and Measurement

The furnace and temperature control

For the effusion study of triphenyl aluminum, a heavy metal-encased resistive furnace was used. To improve accuracy in temperature control and to reduce the time to attain a desired operating temperature, a cyclindrical heating mantle was used in the triphenyl boron effusion study. A time-proportioning controller provided temperature control.

Temperature measurement

A calibrated chromel-alumel thermocouple was located inside the thermocouple well of the heating chamber for measurement of the sample temperature during an experiment.

Calibrations

Calibrations of the thermocouples

Since, during an experiment the measuring thermocouple was positioned in the thermocouple well outside the cell, it was necessary to calibrate it with respect to the temperature of the sample inside the cell. Thus, a reference thermocouple positioned inside a cell, identical in construction, material, and location, in the heating chamber to the cell of effusion measurement, was used for calibration¹⁸ of the experimental thermocouple outside the cell. The relationships of the calibrated experimental thermocouple output and the reference temperature inside the cell are:¹⁹

$$T(K) = (279.713 \pm 1.582) + (25.207 \pm 0.152) \times \text{mV} \quad (\text{III-1})$$

for the triphenyl aluminum experiments, and

$$T(K) = (269.635 \pm 1.352) + (25.442 \pm 0.164) \times \text{mV} \quad (\text{III-2})$$

for the triphenyl boron experiments. The propagated errors in the calculated temperatures from the uncertainties in the parameters of equations (III-1) and (III-2), and from the precision of measurement on the potentiometer are ± 2.0 and ± 1.8 K, respectively.

Calibration of the torsion filament

The torsion constant, τ , of the filament was determined from measurement of the period of oscillation of a torsional pendulum according to the procedure described by Calle.²⁰ The torsion constant is defined as:

$$\tau = \frac{4\pi^2 I}{(T_1^2 - T_2^2)} \quad (\text{III-3})$$

where T_1 and T_2 are the periods of oscillation of the pendulum with and without an aluminum ring, respectively. The moment of inertia, I , is defined by:

$$I = \frac{M_r (D_1^2 + D_2^2)}{8} \quad (\text{III-4})$$

where M_r is the mass of the aluminum ring and D_1 and D_2 are the inner and outer diameters of the same ring, respectively. Two calibrations, one prior to an experiment and another after an experiment were performed. The average value of the two calibrations was used for the torsion constant for that experiment. Table 2 shows sample data from a torsion filament calibration. Values for the torsion constant for that filament used in the experiments are listed in Table 3.

The torsion constant varied over the duration of this study, but no trend is observed. Between experiments the greatest variation in

Table 2

Sample of Torsion-Constant Calibration Data

Torsion Pendulum of Suspension System with Aluminum Crossbar

No.	Counts	Times/s	Oscillations	T_1/S per period
1	20	189.4	10	18.94
2	26	246.1	13	18.93
3	32	303.2	16	18.95
4	38	359.1	19	18.90
5	44	416.7	22	18.94
6	50	470.7	25	18.83

Average (18.93 ± 0.01) s

Torsion Pendulum of Suspension System with Aluminum Crossbar and Ring

No.	Counts	Times/s	Oscillations	T_1/S per period
1	8	269.0	4	67.25
2	10	335.7	5	67.14
3	12	403.3	6	67.22
4	14	470.3	7	67.19
5	16	536.8	8	67.10
6	18	604.4	9	67.16

Average (67.18 ± 0.04) s

Table 3

Measurement of the Torsion Constant Parameters
of the Aluminum Ring of the Torsion Pendulum

Inside Diameter (D_2 /cm)	5.402
Outside Diameter (D_1 /cm)	5.730
Mass (M_r /g)	11.9616
Moment of Inertia (I /g cm ²)	92.716

Calibration of Measurements of Tungsten Wire,
 3.8×10^{-2} in Diameter and 35 cm in Length

Experiment	T_2/S	T_1/S	$\tau/\text{dyn}\cdot\text{cm rad}^{-1}$	$\tau/\text{avg (for exp)}$
Al-2 ^b	67.10	18.98	0.8837	0.8834
Al-3 ^b	67.13	19.03	0.8832	0.8826
Al-4 ^b	67.13	19.00	0.8820	0.8825
Al-4 ^a	67.13	19.00	0.8830	0.8825
B-1 ^b	67.10	19.00	0.8838	0.8838
B-2 ^b	67.10	19.00	0.8838	0.8837
B-3 ^b	67.10	18.98	0.8837	0.8846
B-3 ^a	67.01	19.00	0.8855	0.8846

a) Measurement after experiment; b) Measurement before experiment

the value of the torsion constant was 0.018 dyn·cm. This is appropriately 0.20%. The average variation for all of the experiments in this study was 0.0007 dyn·cm or 0.08%. Uncertainties in the precision of measurement of time, ring diameter, and mass result in a propagated error in the value of the torsion constant of about 0.0003 dyn·cm.

Operational Procedure

The procedure for loading the cell with a sample, evacuating the system, recording data, and interrupting the data-acquisition process at day's end was based on the procedure described by Calle.²¹

The cell was outgassed under vacuum at 840 K before use in an effusion study of a particular compound. Prior to a given experiment the torsion filament was calibrated. The suspension system was weighed to check the possibility of sublimate deposit during an experiment so that a correction be made, if necessary. The cell was loaded with 0.7-0.8 g of sample in a dry nitrogen-atmosphere dry box. The cell orifices were sealed inside the dry box with fused naphthalene to protect the sample from oxygen and moisture in the laboratory atmosphere. The cell was then attached to the suspension system and a second weighing of the assembly including the loaded cell was made. The zero point for angular-displacement measurements was checked and, if necessary, adjusted to insure that the reflected light beam is intercepted on the ruled arc at a point which permits covering the deflection range within the arc ends. The pyrex tube was positioned around the cell and its suspension system so that a vacuum

could be applied. After a pressure of 10^{-6} torr was attained, the zero point of the optical-lever system was recorded.

The sample was outgassed under vacuum for at least 48 hours. For the triphenyl aluminum experiments, the temperature during outgassing was 400 K. For triphenyl boron, due to its low melting temperature, the initial outgassing was at room temperature.

At the start of a series of daily measurements, the zero point on the optical-lever system was recorded. The sample temperature was raised to the desired point and thermal equilibrium was established before recording mass loss, temperature, and angular displacement. The three criteria used to ascertain whether thermal equilibrium had been established were constancy of the temperature, of the rate of mass loss and of the angular displacement. At thermal equilibrium, the angular displacement and temperature were measured every three to five minutes while the rate of mass loss was recorded continuously as a function of time.

No systematic temperature selection was employed although care was taken to choose equal temperature intervals. The duration of a typical experiment was from two to four days from the time the first point was started. The zero point on the optical-lever system, the pressure of the system, the temperature and the available mass of the sample to the nearest 10 mg were recorded at the beginning of each day. At the end of a given day, the experiment was interrupted by lowering the temperature overnight to 100°C and room temperature for triphenyl aluminum and triphenyl boron, respectively.

After the experiment was concluded, the sample temperature was lowered to room temperature and the zero point was again recorded. The balance and heating chamber were then isolated from the vacuum pumps and, using argon, the system was restored to atmospheric pressure. Next, the furnace and heating chamber were removed and the cell was detached from the suspension system. To check for a sublimate deposit, the suspension system was reweighed. Finally, the torsion filament was recalibrated.

CHAPTER IV

VAPOR PRESSURE AND THERMODYNAMIC PROPERTIES OF TRIPHENYL ALUMINUM

Literature Review

Only one investigation of the sublimation of triphenyl aluminum was reported in the literature. Greenwood et al.¹ studied the sublimation of triphenyl compounds of Group III elements to establish their enthalpies of sublimation. From their sublimation study of triphenyl aluminum in the temperature range 450 to 475 K, they reported an enthalpy of sublimation of $(145.6 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$. However, absolute vapor pressures were not reported.

Material

The triphenyl aluminum sample used was obtained commercially from Pfaltz and Bauer, Inc., with a specified purity of 98 mole percent or better. It was used without further purification. The melting temperature ranged between 507-511 K, as compared with the literature values of 514 K,²² 512-514 K²³ and 510 K.^{24,25}

Experimental Measurements

Approximately 0.8 g of triphenyl aluminum was loaded into the cell for each experiment. The cell containing sample was outgassed under vacuum in the effusion apparatus at 400 K for at least 48 hours prior to recording the first point in an experiment. The sample was

heated to about 475 K where a few exploratory points were taken. The remainder of the data were recorded successively upward starting from the lowest temperature (around 430 K). The measurements of the rate of mass effusion (Knudsen-effusion) and torsional recoil (torsion-effusion) were performed according to the procedure described in Chapter III. Approximately 200 mg were sublimed in an experiment. A pressure of 10^{-6} torr was maintained by the vacuum system in the heating pyrex enclosure of the cell and the effusion apparatus.

Results

Four experiments were performed to determine the sublimation pressures in equilibrium with solid triphenyl aluminum. The first experiment was exploratory, where only the rate of mass loss by Knudsen-effusion was measured to establish a reasonable temperature range for the investigation. Torsional recoil measurements were not feasible since a nickel cell was used. The cell was affected by external magnetic fields which interfered with the angular displacement of the torsion assembly. The other three experiments were conducted using the same graphite cell described in Chapter III. Only data from the last three experiment are used in the calculation of the thermodynamic properties associated with the sublimation.

Equation (II-5) was used to calculate the equilibrium vapor pressure from Knudsen-effusion measurements. The molar mass of $\text{Al}(\text{C}_6\text{H}_5)_3$ ($258.30175 \text{ g}\cdot\text{mol}^{-1}$) was used in the calculation of the Knudsen pressure, P_k . The torsion pressure was calculated using the equation (II-10).

Linear least-squares analyses of the experimental data yielded the parameters A and B of the Clausius-Clapeyron equation:

$$\text{Log}_{10}(p/p^{\circ}) = A - B (K/T) \quad (\text{IV-1})$$

The experimental data and calculated vapor pressures are presented in Tables 4 to 7. Arrhenius plots of the temperature dependence of the vapor pressures are presented in Figures 4 to 6. A summary of the sublimation results is given in Table 8. The standard molar enthalpy and entropy of sublimation were calculated from the parameters B and A, respectively, of equation (IV-1). The cited uncertainties are the standard deviations obtained from the linear least-squares analyses. Also listed in Table 8 are the results of linear least-squares analysis of the combined points of three experiments.

Comparison of Simultaneous Measurements by the Two Methods

Simultaneous determination of the torsion pressure, P_{τ} , and the Knudsen pressure, P_k , of species known to sublime as monomers show²⁷⁻³¹ a ratio, P_{τ}/P_k , which is slightly but consistently higher than unity. This can be explained in terms of the effects of reflection from the enclosure wall by effusate molecules. Reflection back into the orifice would result in a value for P_k lower than the true value, while the additional torque from reflected effusate

Table 4

Effusion Results for Triphenyl Aluminum, Experiment Al-1:
 m is the Mass, t is the Time of Effusion, and P_k ,
 the Pressure as Determined by the Knudsen-Effusion Method

No.	T/K	$10^3 m/g$	t/s	$10^3 P_k/kPa$
1	447.7	3.64	4500	0.33221
2	458.0	10.04	4500	0.92677
3	463.5	11.64	3000	1.6213
4	467.6	5.00	900	2.3319
5	470.0	6.59	900	3.0812
6	468.3	6.29	900	2.9357
7	472.4	16.35	1800	3.8320
8	477.8	25.88	1800	6.1004
9	434.1	1.00	5400	0.074891
10	444.6	3.41	6300	0.22153
11	453.6	8.67	6300	0.56893

Table 5

Effusion Results for Triphenyl Aluminum, Experiment Al-2:
 m is the Mass, the Time of Effusion, and P_k , the Pressure
 in the Knudsen Experiments; S is the Displacement and
 P_t , the Pressure in the Torsion Experiments

No	T/K	$10^3 m/g$	t/s	$10^3 P_k/kPa$	S/cm	$10^3 P_t/kPa$
1	477.5	8.04	600	4.9226	57.73	5.6663
2	475.6	7.26	600	4.4364	51.99	5.1029
3	476.8	3.96	300	4.8459	57.07	5.6015
4	471.8	18.45	2100	3.2083	37.46	3.6670
5	431.6	0.56	3600	0.05433		
6	434.8	1.45	6900	0.07366		
7	437.9	1.60	5400	0.10424		
8	446.2	3.30	5400	0.21701	2.24	0.21938
9	449.3	1.65	1800	0.32667	3.45	0.33903
10	447.8	1.21	1500	0.28699	3.02	0.29665
11	446.1	0.84	1200	0.24856	2.57	0.25178
12	449.9	4.72	5100	0.33004	3.48	0.34153
13	454.4	7.46	5100	0.52418	5.66	0.55591
14	458.2	7.45	3600	0.74476	8.38	0.82266
15	463.1	11.30	3300	1.2389	14.27	1.4010
16	467.2	11.42	2100	1.9760	23.06	2.2635
17	472.0	16.85	2100	2.9306	32.41	3.1809

Table 6

Effusion Results for Triphenyl Aluminum, Experiment Al-3:
 m is the Mass, t the Time of Effusion, and P_k the Pressure
 in the Knudsen Experiments; S is the Displacement and
 P_τ the Pressure in the Torsion Experiments

No.	T/K	$10^3 m/g$	t/s	$10^3 P_k/kPa$	S/cm	$10^3 P_\tau/kPa$
1	474.6	4.63	300	5.6525	66.95	6.5653
2	471.9	3.56	300	4.3340	52.12	5.1107
3	471.3	6.40	600	3.8931	46.58	4.5677
4	471.5	6.80	600	4.1375	49.78	4.8815
5	467.4	6.82	900	2.7541	33.12	3.2478
6	433.3	1.76	6600	0.09332	1.12	0.10958
7	436.6	2.05	5400	0.13336	1.63	0.15939
8	440.5	3.21	6000	0.18878	2.29	0.22415
9	444.7	3.77	4500	0.29701	3.51	0.34370
10	449.4	3.34	2400	0.49601	5.64	0.55291
11	451.5	1.46	900	0.57949	6.78	0.66500
12	452.3	6.65	3900	0.60965	7.24	0.70982
13	457.0	5.13	1800	1.0243	11.25	1.1033
14	460.7	11.15	2700	1.4902	17.70	1.7359
15	465.2	15.86	2400	2.3961	28.58	2.8019
16	466.8	11.21	1500	2.7146	32.74	3.2104
17	466.9	6.85	900	2.7650	32.99	3.2353
18	467.0	9.13	1200	2.7640	32.94	3.2303

Table 7

Effusion Results for Triphenyl Aluminum, Experiment Al-4:
 m is the Mass, t the Time of Effusion, and P_k the Pressure
 in the Knudsen Experiments; S is the Displacement and
 P_τ the Pressure in the Torsion Experiments

No.	T/K	$10^3 m/g$	t/s	$10^3 P_k/kPa$	S/cm	$10^3 P_\tau/kPa$
1	478.3	7.38	1500	1.8090	20.93	2.0519
2	480.7	8.30	1500	2.0397	24.69	2.4206
3	473.8	9.52	3000	1.1613	13.59	1.3323
4	438.8	0.33	3600	0.032284	0.4064	0.039844
5	444.0	0.80	5100	0.055567	0.6350	0.062256
6	448.8	1.20	4800	0.089038	1.067	0.10459
7	453.4	2.17	5700	0.13629		
8	464.5	6.10	5400	0.40930		
9	467.5	12.37	7800	0.57649		
10	470.6	11.45	4800	0.87000	10.21	1.0011
11	476.3	7.64	1800	1.5574	18.75	1.8378
12	487.1	18.75	1800	3.8650	48.23	4.7381
13	474.4				15.49	1.5191

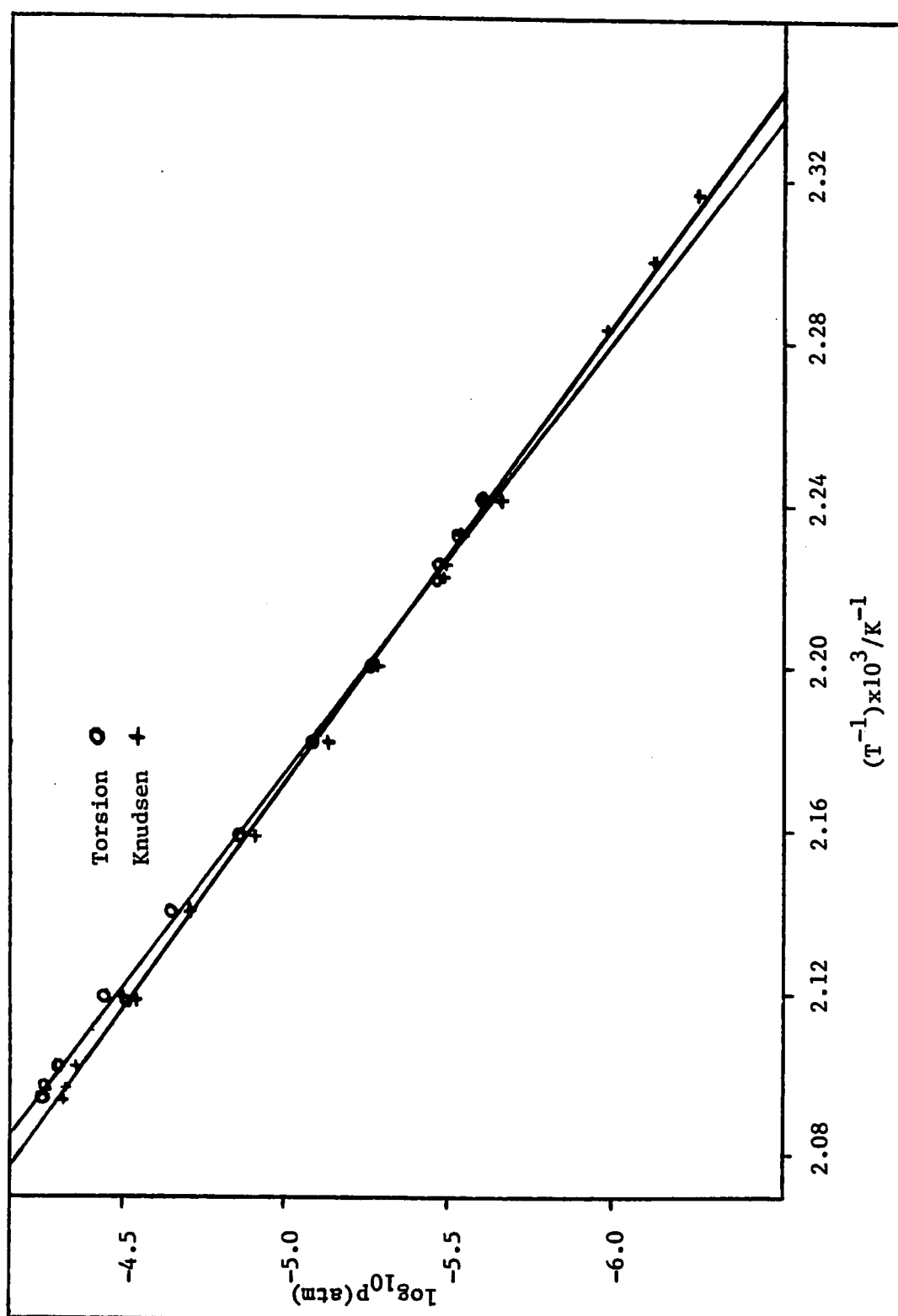


Figure 4. Sublimation Pressure of Triphenyl Aluminum by Knudsen- and Torsion-Effusion, Exp. Al-2.

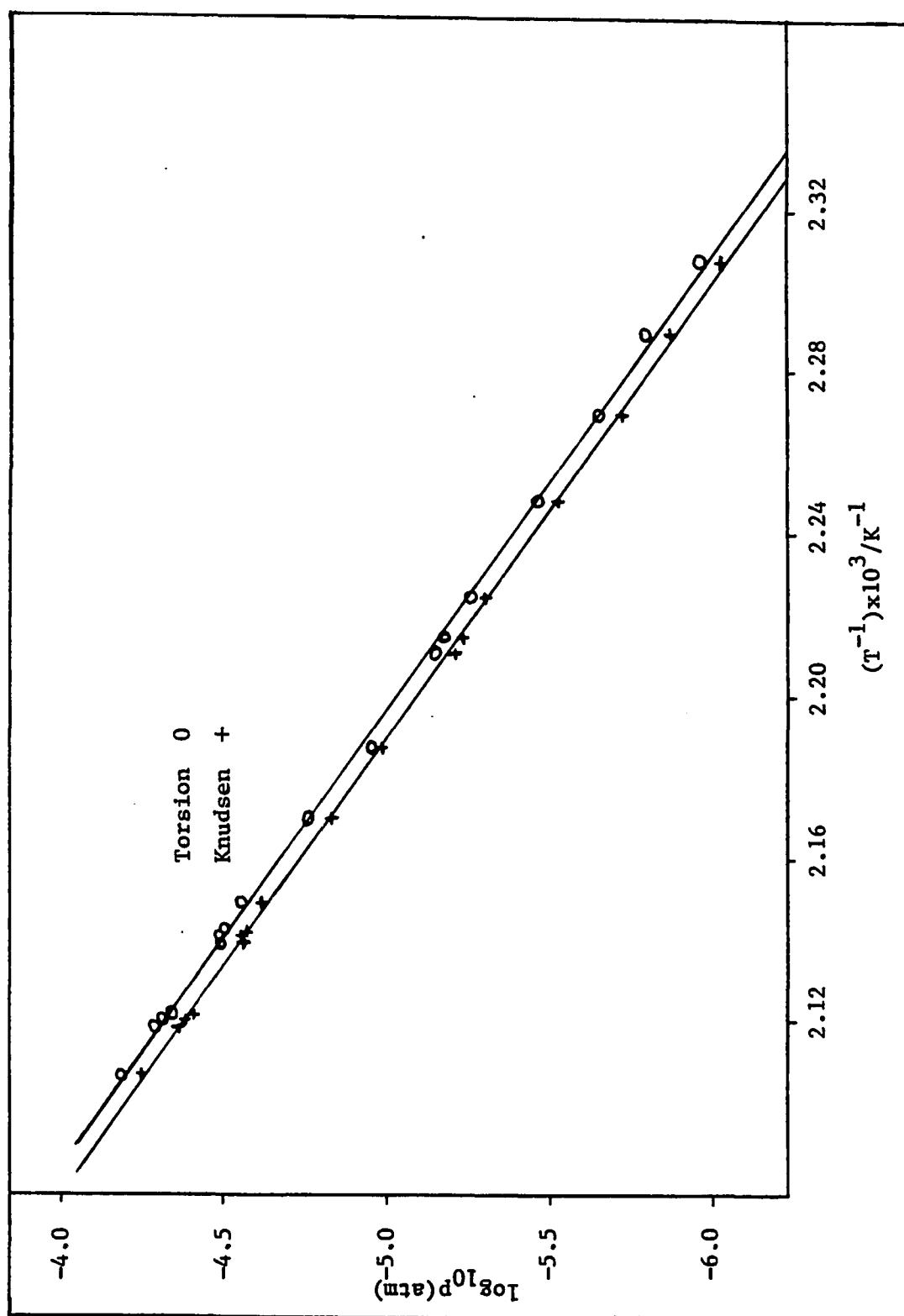


Figure 5. Sublimation Pressure of Triphenyl Aluminum by Knudsen- and Torsion-Effusion, Exp. Al-3.

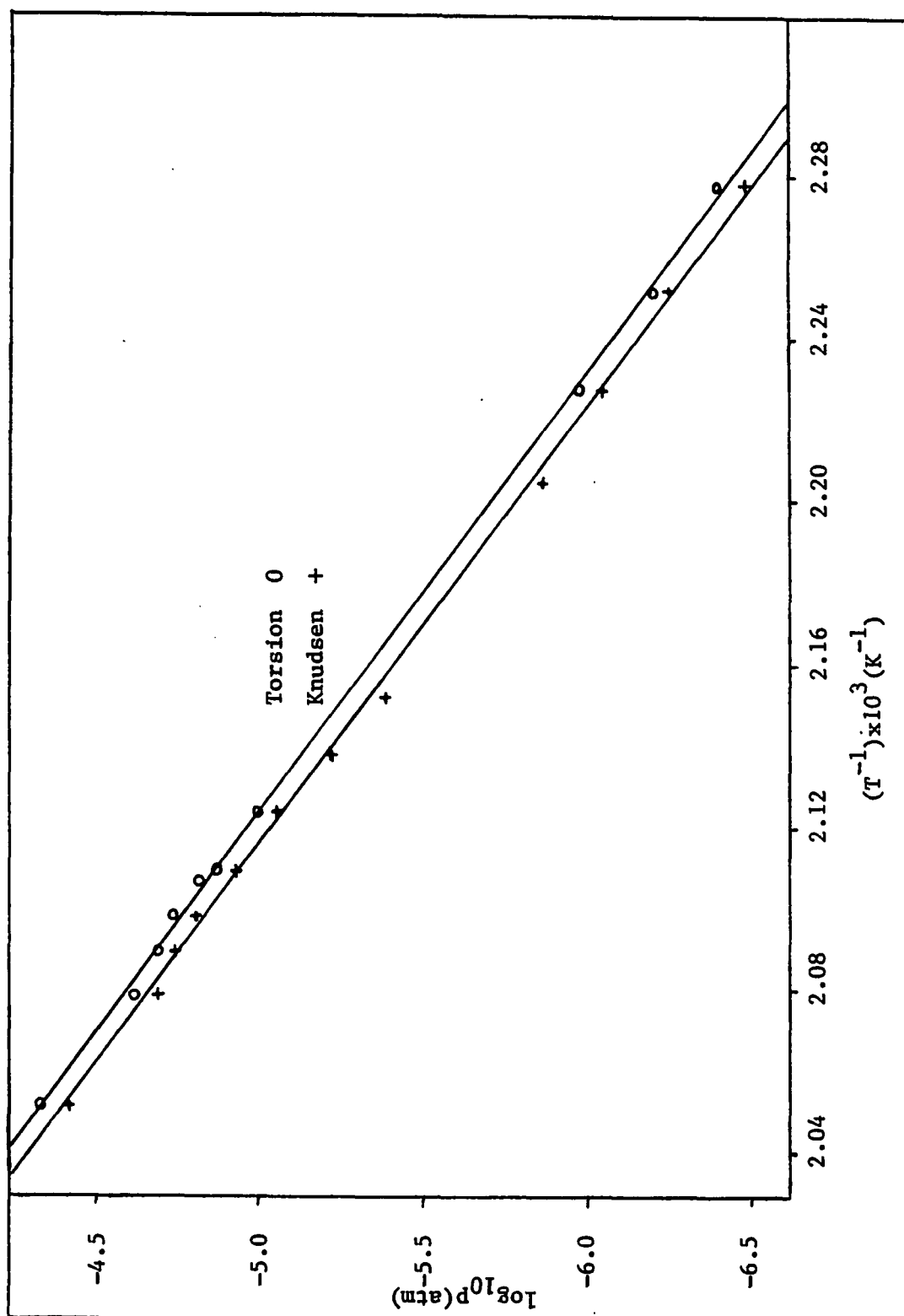


Figure 6. Sublimation Pressure of Triphenyl Aluminum by Knudsen- and Torsion-Effusion, Exp. Al-4.

Table 8
Sublimation Results for Triphenyl Aluminum

Exp No.	Cell Material	Method	A	B	T ₁	T ₂	10 ⁶ P(460K) atm	$\Delta_{\text{sub}}H_m^{\circ}$ kJ·mol ⁻¹	$\Delta_{\text{sub}}S_m^{\circ}$ J·K ⁻¹ ·mol ⁻¹
Al-1	Nickel	Knudsen	15.08±0.24	9213±112	434	478	11.511	176.4±2.1	289±4.6
Al-2	Graphite	Knudsen	14.46±0.19	8959±85	446	477	9.6929	171.5±1.6	277±3.8
		Torsion	15.71±0.25	9522±116	446	477	10.405	182.3±2.2	301±5.0
Al-3	Graphite	Knudsen	14.48±0.12	8897±55	433	475	14.042	170.3±1.0	277±2.1
		Torsion	14.56±0.16	8904±74	433	475	16.338	170.5±1.4	279±2.9
Al-4	Graphite	Knudsen	14.71±0.25	9315±116	439	487	2.9132	178.4±2.2	282±4.6
		Torsion	14.74±0.21	9291±97	439	487	3.5328	177.9±1.8	282±4.2

Notation given on next page.

Table 8 (continued)

Exp No.	Cell Material	Method	A	B	T ₁	T ₂	10 ⁶ P(460K) atm	$\Delta_{\text{sub}}H_m^\circ$ kJ·mol ⁻¹	$\Delta_{\text{sub}}S_m^\circ$ J·K ⁻¹ ·mol ⁻¹
Combined Al-2-3-4	Graphite	Knudsen	12.76±1.25	8214±572	433	487	8.1783	157.3±11.0	244±24
		Torsion	12.83±1.34	8206±615	433	487	9.8950	157.2±11.8	246±26
Combined Al-2-3	Graphite	Knudsen	14.66±0.48	9015±217	433	477	11.539	172.6±4.2	281±9.1
		Torsion	14.56±0.68	8950±311	433	477	12.690	171.3±5.9	279±13.0

The coefficients A and B are for the equation: $\log_{10} (P/P^\circ) = A - B(K/T)$

P is the vapor pressure; T₁ and T₂ are the bounds of temperature range and P(460 K) is the vapor pressure at the midpoint of temperature in K; cal_{th} = 4.1840 J; P° is the standard pressure, 101.325 kPa.

molecules exerted preferentially on the same side of the cell from which they came would result in a value for P_T higher than the true value. A sublimation study of cadmium carried out prior to, and using the same cell enclosure (inner diameter 65 mm) as was used in the triphenyl aluminum experiments resulted in a P_T/P_K ratio of (1.17 ± 0.05) . This ratio decreased to (1.06 ± 0.03) in a similar study of cadmium carried out prior to, and using the same cell enclosure (inner diameter 85 mm) as was used in, the triphenyl boron experiments of Chapter V. Apparently, as the diameter of the cell enclosure increases, the effects of the reflecting effusate molecules diminish and the experimentally determined P_T/P_K approaches the true value.

The average P_T/P_K for the three experiments is (1.15 ± 0.05) at the approximate midpoint temperature. Since this is close to the ratio observed in the control experiment on cadmium, it is established that triphenyl aluminum sublimes to monomeric vapor.

Error Analyses

Uncertainties in the measurement of temperature, mass loss and orifice areas give rise to a propagated error in the calculated Knudsen vapor pressure. At high pressures the error is $\pm 1.9\%$, at intermediate pressures $\pm 2.6\%$, and at low pressure $\pm 4.2\%$.

Uncertainties in the measurement of the torsion filament constant, the torsional deflection, and the cell orifices and moment arms result in a propagated error for the torsion-effusion vapor pressure of $\pm 1.6\%$, $\pm 2.2\%$, and $\pm 9.9\%$ at high, intermediate, and low pressures, respectively.

Two computer programs were used to calculate the vapor pressures and standard molar enthalpies and entropies of sublimation from the experimental data. The programs also listed the relative percent errors between the observed vapor pressures and those calculated by linear least-squares analysis for each datum point. Typically the mean percent error between observed and calculated vapor pressures was $\pm 2.7\%$ for Knudsen experiments and $\pm 3.0\%$ for torsion-effusion experiments.

Discussion

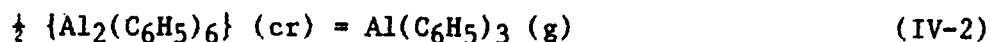
Relationship of structure to thermochemical quantities

The steric interference of phenyl rings is expected to affect the enthalpy of sublimation of a given compound. If a molecule has all the phenyl carbon atoms in the same plane with the central atom, the enthalpy of sublimation is expected to be greater than for a non-planar structure.

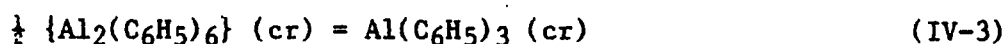
The study by Greenwood et al.¹ on the triphenyl compounds of Group III elements showed good agreement with these expectations. The gallium and indium compounds were reported to have high molar sublimation enthalpies (approximately $7.73 \text{ kJ}\cdot\text{mol}^{-1}$ per carbon atom) as compared with the lower value ($6.18 \text{ kJ}\cdot\text{mol}^{-1}$ per carbon atom) for the boron analogue. The larger central atoms of Ga and In presumably separate the phenyl rings enough to eliminate steric interference which might make the respective molecules nonplanar. Boron is much smaller and does not prevent such steric interferences, resulting in a non-planar geometry. Triphenyl aluminum is a dimer³² in the solid

phase and, as its anomalously high enthalpy of sublimation suggests, it must be considered separately.

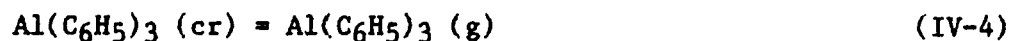
Triphenyl aluminum sublimes according to:



which is the sum of the two contributing reactions:



and



The observed molar enthalpy of sublimation of the dimer is related to the molar enthalpy of sublimation of the monomer by:

$$\begin{aligned} \frac{1}{2} \Delta_{\text{sub}}^{\circ} H_m \{ \text{Al}_2(\text{C}_6\text{H}_5)_6 \} &= \Delta_{\text{sub}}^{\circ} H_m \{ \text{Al}(\text{C}_6\text{H}_5)_3 \} \\ &+ \Delta_{\text{diss}}^{\circ} H_m \{ \text{Al}_2(\text{C}_6\text{H}_5)_6 \} \end{aligned} \quad (\text{IV-5})$$

Since both of the experimental methods for measuring the vapor pressure of triphenyl aluminum in this study apply only to the overall reaction represented by equation (IV-2), the enthalpies associated with the individual equilibria (IV-3) and (IV-4) can only be estimated. Table 9 shows the values of the sublimation enthalpies of the monomer based on the additivity rules^{1,29} for the two possible

geometries of the monomer (planar or non-planar). Two different values for the dissociation enthalpy of the solid dimer, depending on the possible geometry of the monomer, are given in Table 9. Although the dissociation enthalpy calculated assuming a planar solid monomer is more consistent with the $68.2 \pm 6.3 \text{ kJ}\cdot\text{mol}^{-1}$ dissociation enthalpy for $\text{Al}(\text{CH}_3)_3$ reported by Hay et al.,³³ the true geometry of the $\text{Al}(\text{C}_6\text{H}_5)_3$ monomer is not established firmly.

The same arguments apply to the entropy of sublimation. Contributions to the entropy of sublimation for the process in equation (IV-2) result from the entropies of the two equilibria (IV-3) and (IV-4). An estimate of the contribution per phenyl ring to the molar entropy of sublimation of analogous non-planar monomers, namely, tetraphenyl compounds of group IV, has been reported³⁴ as $63 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. No similar estimate is available for planar analogue molecules. Hence, the molar entropies of sublimation listed in Table 9 include a value for the process in equation (IV-2) and for the processes of equations (IV-3) and IV-4) assuming non-planar $\text{Al}(\text{C}_6\text{H}_5)_3$ monomer only. Since the absolute vapor pressures observed in the last experiment, Al-4, were much lower than those for the other experiments, it is suspected that different conditions were in effect for Al-4. For this reason, Tables 8 and 9 also include entrees of results and thermochemical quantities calculated using experiments Al-2 and Al-3 only.

Table 9

Summary of Thermochemical Quantities at T = 460 K:
Sublimation and Dissociation of Triphenyl Aluminum

	$\Delta_{\text{sub}} H_m^\circ$		$\Delta_{\text{sub}} S_m^\circ$	
	$\text{kJ} \cdot \text{mol}^{-1}$		$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	
	combined Al-2-3-4	combined Al-2-3	combined Al-2-3-4	combined Al-2-3
Sublimation, observed*	157	172	245	280
Sublimation of monomer				
planar	132	132		
non-planar	105	105	188	188
Dissociation of solid dimer to monomer:				
planar	50	80		
non-planar	104	134	114	184

$$* \Delta_{\text{sub}} H_m^\circ = \frac{1}{2} \Delta_{\text{sub}} H_m^\circ \{ \text{Al}(\text{C}_6\text{H}_5)_3 \}_2.$$

Comparison of thermochemical quantities with literature values

The standard molar enthalpy of sublimation of $\text{Al}(\text{C}_6\text{H}_5)_3$ reported by Greenwood et al.¹ is $(145.6 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$ over the temperature range 450 to 475 K. Their explanation of this high value was based on the (correct)³² assumption that triphenyl aluminum is a dimer in the solid phase as it was known to be in certain solutions.³³ However, in their study, they made no attempt to establish the absolute sublimation pressures or calculate the sublimation entropy.

The standard molar enthalpies of sublimation for equation (IV-2) from the present study are $(157.28 \pm 10.96) \text{ kJ}\cdot\text{mol}^{-1}$ from Knudsen-effusion and $(157.17 \pm 11.80) \text{ kJ}\cdot\text{mol}^{-1}$ by torsional recoil measurements. Although these two values are accompanied by relatively high uncertainties, they are consistent with each other. The large relative errors arise from combining data from three experiments of differing absolute sublimation pressures. The reason for the difference in absolute pressures from the three experiments is not known. Yet Table 8 shows that the Knudsen-effusion and torsional recoil results of a given experiment are consistent, and the relative errors are small.

Summary

Linear least-squares analysis of the combined data from three experiments of sublimation of triphenyl aluminum in the temperature range 433 to 487 K has resulted in the following Clausius-Clapeyron equations for Knudsen-effusion and torsional recoil, respectively:

$$\log_{10} (P_K/P^\circ) = (12.76 \pm 1.25) - (8214 \pm 572) (K/T) \quad (\text{IV-6})$$

$$\log_{10} (P_T/P^\circ) = (12.83 \pm 1.34) - (8206 \pm 615) (K/T) \quad (\text{IV-7})$$

Reference to the Clausius-Clapeyron parameters A and B of the contributing experiments, given in Table 8 casts suspicion on the validity of the procedure of combining data from experiments having disparate absolute vapor pressures. Similar suspicion surrounds the enthalpy and entropy of sublimation results derived from the linear least-squares analyses:

$$\Delta_{\text{sub}} H_m^\circ \{ \text{Al}(\text{C}_6\text{H}_5)_3, \text{ cr, 460 K} \} = (157.2 \pm 16.1) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{sub}} S_m^\circ \{ \text{Al}(\text{C}_6\text{H}_5)_3, \text{ cr, 460 K} \} = (245 \pm 35) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

It is established that dimeric crystalline triphenyl aluminum sublimates to form a monomer in the vapor phase. However, without knowing the conformation of the monomer, the thermochemical quantities associated with dissociation of the dimer and sublimation of the monomer may only be estimated.

CHAPTER V

VAPOR PRESSURE AND THERMODYNAMIC PROPERTIES OF TRIPHENYL BORON

Literature Review

The only report in the literature on the vapor pressure of triphenyl boron at the time of the present study has been that by Greenwood et al.¹ Their study utilized the Knudsen-effusion method to establish the enthalpy of sublimation over the temperature range 352.8 to 383.4 K as $(111.3 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$. The absolute vapor pressures were not reported.

Material

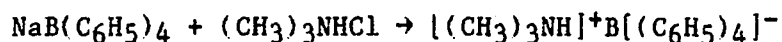
Because triphenyl boron undergoes rapid autodecomposition even when stored under nitrogen, no acceptable sample could be obtained commercially. A synthesis was carried out based on the procedure of Raff and Wittig³⁵ to insure that a fresh sample would be available for the start of each experiment.

The synthesis consisted of three main steps. First a solution of trimethylammonium chloride was prepared by mixing dilute solution of hydrochloric acid and trimethylamine:



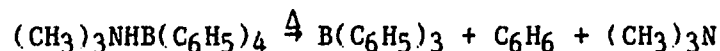
Trimethyl ammonium chloride is water soluble and nonvolatile in aqueous solution. Second, an aqueous solution of sodium tetraphenyl-

borate was dripped through the bottom of a filter flask into the trimethylammonium chloride solution to precipitate the pure white trimethylammonium tetraphenyl borate:



The trimethylammonium tetraphenylborate was then filtered, washed with water, and thoroughly dried in a vacuum desiccator at room temperature.

The third step was the thermal decomposition at 473 to 483 K of trimethylammonium tetraphenylborate under nitrogen to give triphenyl boron:



where benzene and trimethylamine are waste products. Under a slow and steady stream of dry-grade nitrogen, the starting material was heated in a roundbottom flask to approximately 453 K, at which temperature decomposition began, and then finally to about 473 K. After several hours of heating, the temperature was reduced, the flow of nitrogen was halted, and the decomposition apparatus (sealed from the atmosphere) was placed in a nitrogen-atmosphere dry box.

A purification procedure was implemented to remove any undecomposed starting material remaining in the roundbottom flask with the triphenyl boron. First, the contents of the flask (a crusty brownish residue) were recrystallized from hexane to yield

yellow-white needles of triphenyl boron. Second, the yellow-white needles were vacuum sublimed to give a white crystalline powder of triphenyl boron which melted between 408 and 416 K. The literature values are 411 to 413 K³⁶ and 415 to 416 K.³⁷ The entire purification process was carried out in a nitrogen-atmosphere dry box.

A 60 MHz proton nmr scan on the purified sample of triphenyl boron in carbon tetrachloride showed only the expected multiplet centered about 7.4 δ , which provides reassurance that the sample had been successfully prepared.

Experimental Measurements

The same general procedure used for effusion studies of triphenyl aluminum was applied in the triphenyl boron experiments with one exception. Since triphenyl boron has a melting point of only 415 K, the loaded cell was outgassed at room temperature.

Results

Three experiments of simultaneous Knudsen-effusion and torsion-effusion measurements were performed. The same graphite cell and tungsten filament used in the effusion studies of triphenyl aluminum were used. The vapor pressures were calculated according to the Knudsen equation (II-5) and the torsion-effusion equation (II-10). The mass, $M[B(C_6H_5)_3]$ of $242.131 \text{ g}\cdot\text{mol}^{-1}$ was used in the calculation of the Knudsen pressure, P_k . Linear least-squares analyses of P_k and P_t for the experimental data yielded the parameters A and B of the Clausius-Clapeyron equation (IV-1). Tables

10 to 12 list the experimental data and calculated vapor pressures. These results are displayed graphically in Figures 7 to 9.

The results, in standard molar enthalpies and entropies of sublimation and vapor pressures at the temperature range midpoint, are given in Table 13. The cited errors are the standard deviations obtained in the linear least-squares analyses. Also, listed in Table 13 are the linear least-squares analyses of the combined points of the experiments.

Comparison of Simultaneous Measurements by the Two Methods

The average ratio, P_T/P_K , derived from the linear least-squares analyses at the mid-temperature of 363 K is (1.03 ± 0.05) . This is sufficiently close to unity to conclude that triphenyl boron sublimes as a simple monomer.

A ratio, P_T/P_K , which is greater than unity even for a substance known to sublime as a monomer, can be explained in terms of the effects of reflection from the enclosure wall by effusate molecules, as discussed in Chapter IV.

Error Analyses

Uncertainties in the measured parameters result in propagated errors in the calculated vapor pressures. These propagated errors amount to $\pm 1.7\%$ at a high pressure, $\pm 3.3\%$ at an intermediate pressure, and $\pm 5.3\%$ at a low pressure for P_K . For P_T the propagated errors are $\pm 1.6\%$, $\pm 2.8\%$, and $\pm 5.1\%$ at the respective pressures.

Table 10

Effusion Results for Triphenyl Boron, Experiment B-1:
 m is the Mass, t the Time of Effusion, and P_k the Pressure
 in the Knudsen Experiments; S is the Displacement and
 P_τ the Pressure in the Torsion Experiments.

No.	T/K	$10^3 m/g$	t/s	$10^3 P_k/kPa$	S/cm	$10^3 P_\tau/kPa$
1	382.0	18.05	1500	4.084	49.07	4.818
2	378.7	11.32	1200	3.188	35.97	3.532
3	375.2	12.60	1800	2.354	25.55	2.509
4	372.5	10.13	1800	1.886	19.61	1.925
5	370.2	9.50	2100	1.511	15.70	1.541
6	353.6	3.40	2700	0.4112	3.45	0.3392
7	349.5	1.43	1800	0.2579	2.29	0.2245
8	348.6	1.42	1800	0.2557	2.08	0.2045
9	344.9				1.52	0.1496
10	366.3	8.07	2400	1.118	11.23	1.102
11	362.1	5.35	2400	0.7365	7.26	0.7133
12	358.6	9.33	5700	0.5382	5.18	0.5088
13	356.9				4.42	0.4339

Table 11

Effusion Results for Triphenyl Boron, Experiment B-2:
 m is the Mass, 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 Torsion Experiments.

No.	T/K	$10^3 m/g$	t/s	$10^3 P_k/kPa$	S/cm	$10^3 P_t/kPa$
1	339.8	1.48	6000	0.0790	0.76	0.0748
2	343.8	0.93	2700	0.1109	1.07	0.1047
3	344.6	0.87	2400	0.1169	1.17	0.1147
4	345.2	0.70	1800	0.1255	1.27	0.1247
5	351.7	1.72	2400	0.2334	2.44	0.2394
6	352.3	0.90	1200	0.2444	2.59	0.2544
7	350.2	2.50	3900	0.2083	2.18	0.2144
8	354.0	1.50	1800	0.2722	2.95	0.2893
9	358.0	1.90	1500	0.4162	4.52	0.4439
10	360.3	4.37	2700	0.5335	5.64	0.5536
11	361.5	2.80	1500	0.6163	6.45	0.6334
12	365.3	3.28	1200	0.9071	9.75	0.9576
13	368.6	3.27	900	1.211	12.95	1.272

Table is continued on next page.

Table 11 - Continued

No.	T/K	$10^3 m/g$	t/s	$10^3 P_k/kPa$	S/cm	$10^3 P_\tau/kPa$
14	365.9	6.83	2400	0.9452	10.01	0.9825
15	369.9	4.95	1200	1.378	14.99	1.471
16	370.7	2.65	600	1.477	16.10	1.581
17	371.5	2.80	600	1.562	17.22	1.691
18	372.6	3.18	600	1.776	19.46	1.910
19	373.5	8.57	1500	1.917	21.39	2.100
20	375.0	14.00	2100	2.242	24.43	2.399
21	374.5	3.77	600	2.111	23.37	2.294
22	376.9	11.68	1500	2.625	29.31	2.878
23	377.5	14.37	1800	2.693	30.53	2.997
24	341.9	0.25	900	0.0892	0.97	0.0948
25	342.6	0.52	1800	0.0928	0.97	0.0948
26	343.3	0.98	3000	0.1051	1.07	0.1047

TABLE 12

Effusion Results for Triphenyl Boron, Experiment B-3:
 m is the Mass, t the Time of Effusion, and P_k the Pressure
 in the Knudsen Experiments; S is displacement and P_τ the
 Pressure in the Torsion Experiments.

No.	T/K	$10^3 m/g$	t/s	$10^3 P_k/kPa$	S/cm	$10^3 P_\tau/kPa$
1	368.7	7.72	2400	1.072	12.19	1.198
2	369.4	8.40	2400	1.168	13.31	1.308
3	368.8	5.95	1800	1.102	12.50	1.228
4	375.6	19.20	3000	2.154	25.55	2.511
5	377.9	12.15	1500	2.734	32.00	3.145
6	380.4	12.23	1200	3.452	40.69	3.999
7	350.0	3.45	5100	0.2198	2.29	0.2247
8	360.2	1.49	900	0.5456	5.99	0.5891
9	357.2	1.19	900	0.4339	4.52	0.4443
10	357.9	1.60	1200	0.4380	4.67	0.4593
11	357.2	2.29	1800	0.4175	4.39	0.4318
12	364.3	4.36	1800	0.8028	8.69	0.8537
13	372.0	1.41	300	1.574	17.81	1.750
14	371.0	2.61	600	1.455	16.48	1.620
15	364.1	2.02	900	0.7436	8.33	0.8187
16	363.7	7.20	3300	0.7225	8.03	0.7888

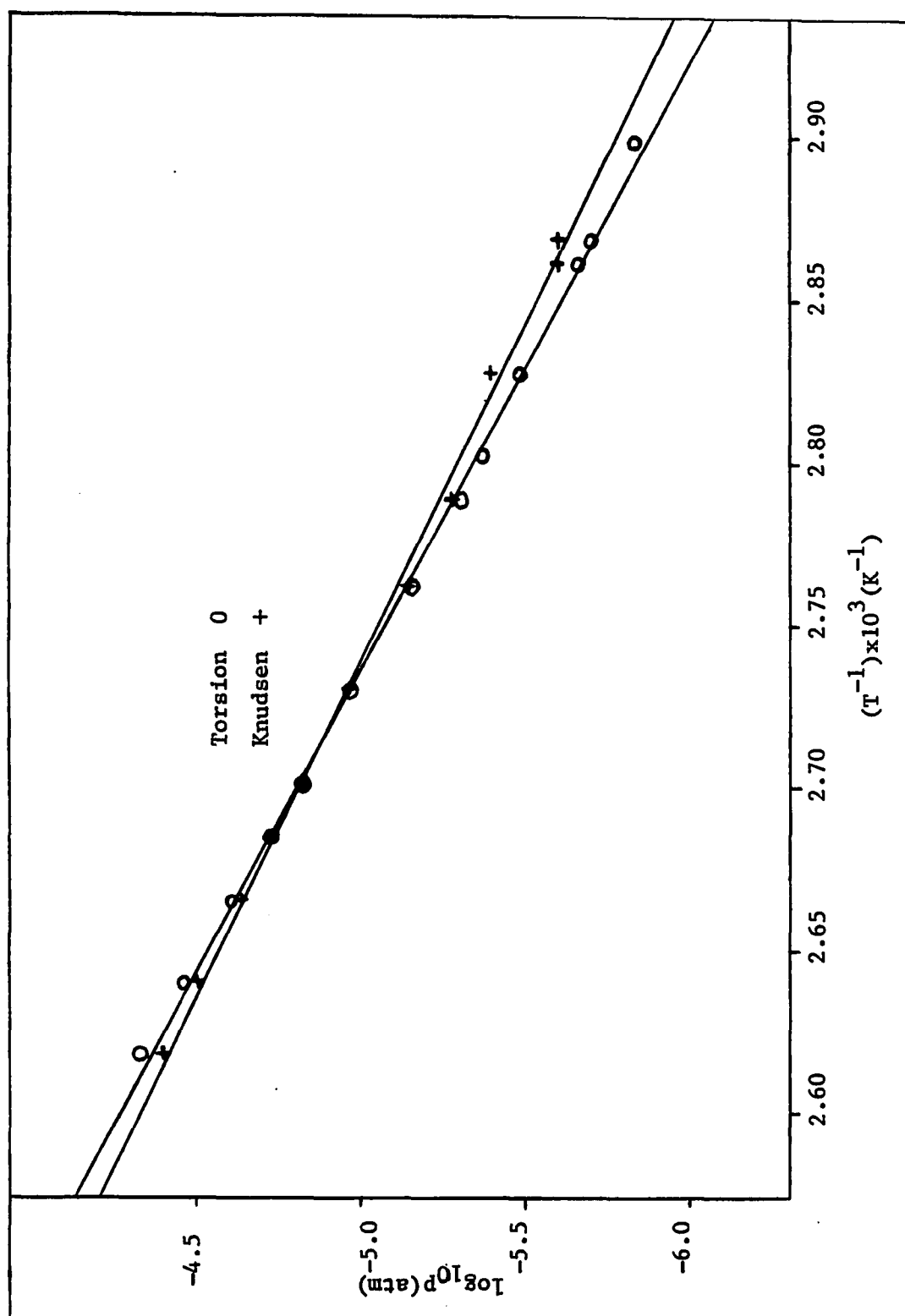


Figure 7. Sublimation Pressure of Triphenyl Boron by Knudsen- and Torsion-Effusion, Exp. B-1.

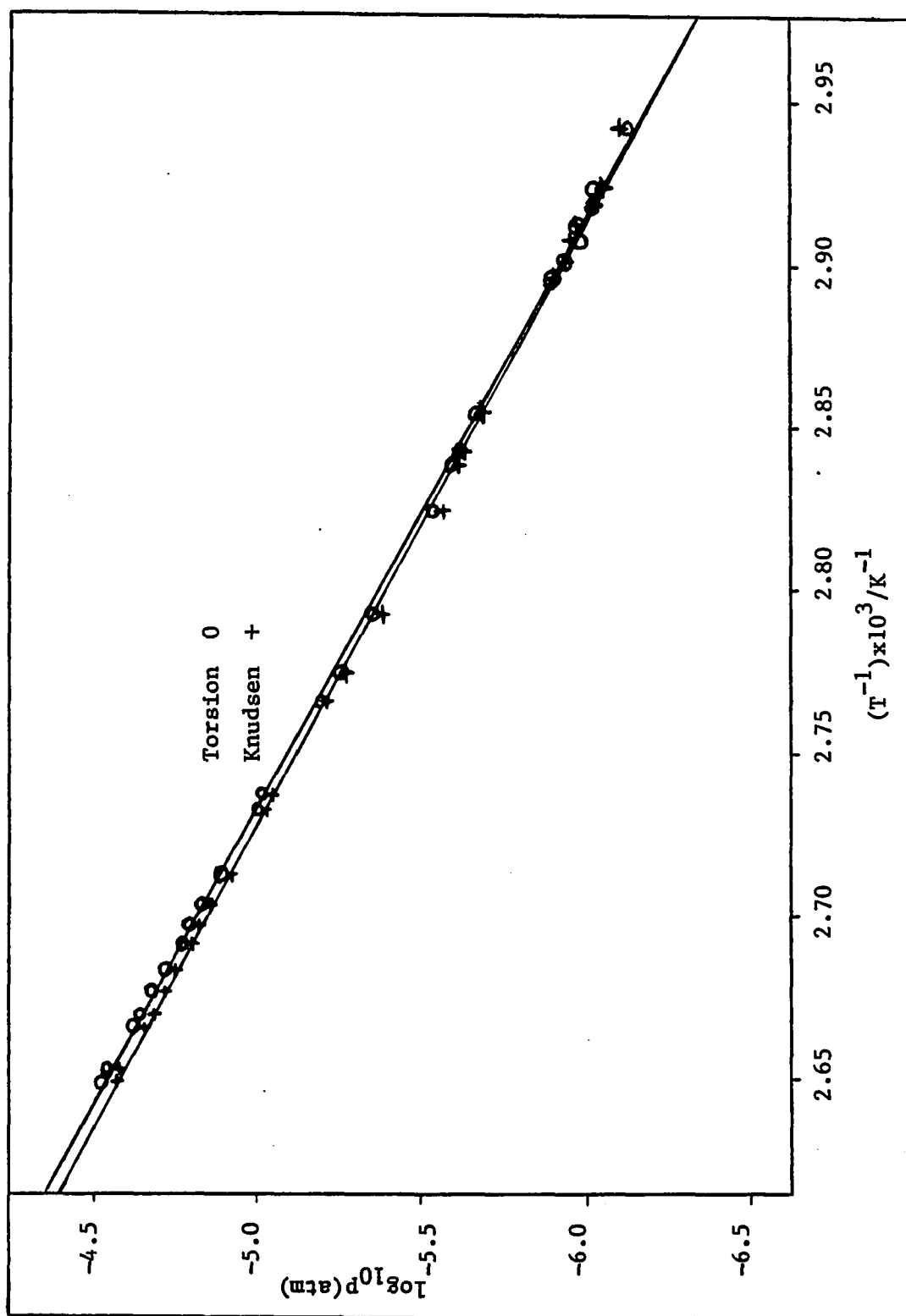


Figure 8. Sublimation Pressure of Triphenyl Boron by Knudsen- and Torsion-Effusion, Exp. B-2.

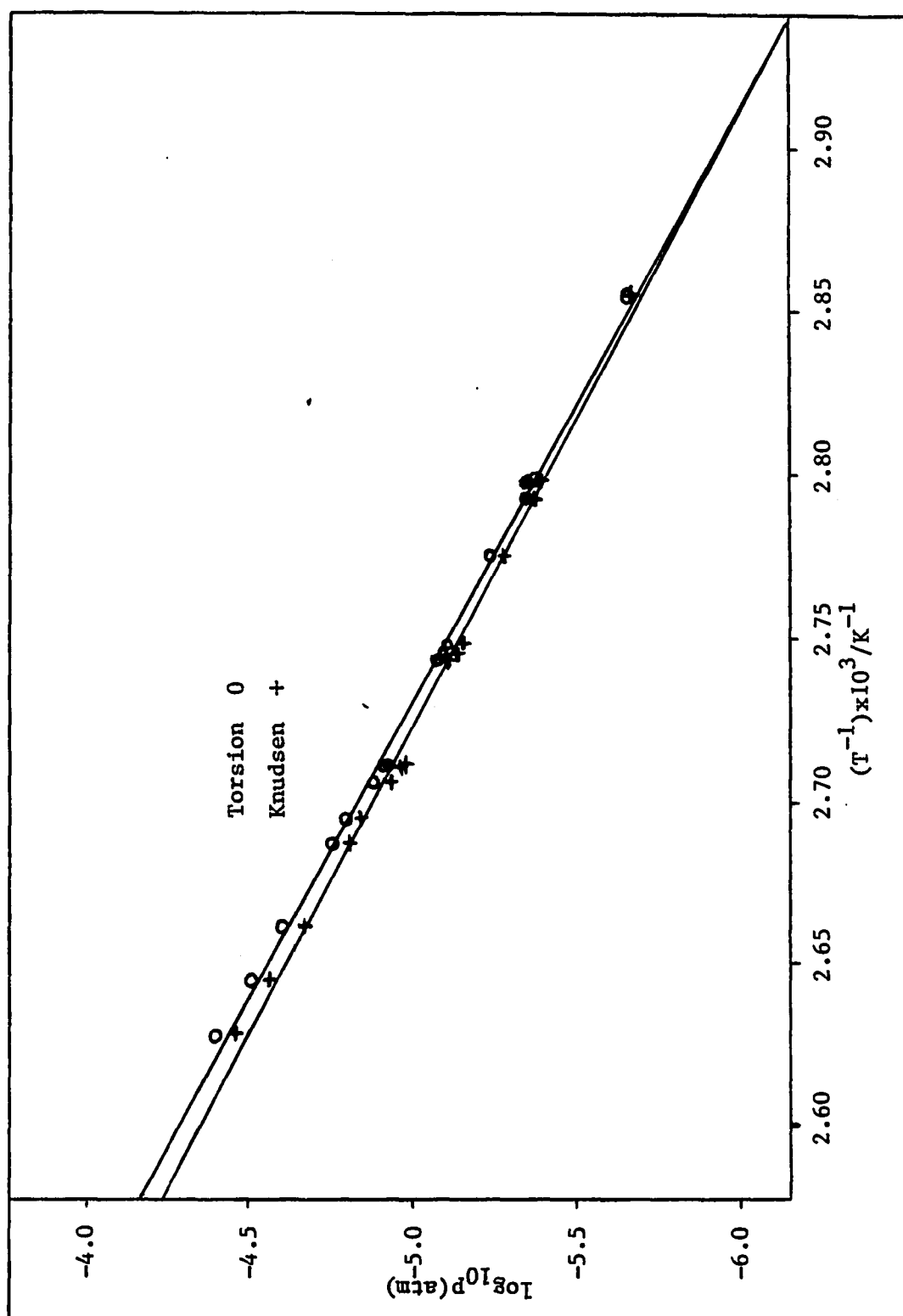


Figure 9. Sublimation Pressure of Triphenyl Boron by Knudsen- and Torsion-Effusion, Exp. B-3.

Table 13

Sublimation Results for Triphenyl Boron

Exp No.	Cell Material	Method	A	B	T ₁	T ₂	10 ⁶ P(363K) atm	$\Delta_{\text{sub}}H_m^\circ$ kJ·mol ⁻¹	$\Delta_{\text{sub}}S_m^\circ$ J·K ⁻¹ ·mol ⁻¹
B-1	Graphite	Knudsen	8.27 ± 0.24	4844 ± 86	349	382	8.2831	92.7 ± 1.7	158.4 ± 4.5
		Torsion	9.70 ± 0.19	5370 ± 68	345	328	7.9316	102.8 ± 1.3	185.8 ± 3.6
B-2	Graphite	Knudsen	9.68 ± 0.10	5381 ± 37	340	378	6.9438	103.0 ± 0.7	185.2 ± 2.0
		Torsion	10.11 ± 0.09	5531 ± 33	340	378	7.3089	105.9 ± 0.6	193.6 ± 1.8
B-3	Graphite	Knudsen	9.15 ± 0.25	5194 ± 93	350	380	6.7844	99.4 ± 1.8	175.2 ± 4.9
		Torsion	9.95 ± 0.23	5472 ± 85	350	380	7.3061	104.8 ± 1.6	190.4 ± 4.4
Combined B-1-2-3	Graphite	Knudsen	9.39 ± 0.13	5274 ± 46	340	382	7.0982	101.0 ± 0.9	179.8 ± 2.4
		Torsion	10.00 ± 0.07	5489 ± 27	340	382	7.4365	105.1 ± 0.5	191.5 ± 1.4
Combined B-2-3	Graphite	Knudsen	9.52 ± 0.07	5326 ± 26	340	380	7.0441	102.0 ± 0.5	182.2 ± 1.4
		Torsion	10.08 ± 0.06	5518 ± 22	340	380	7.5666	105.6 ± 0.4	192.9 ± 1.1

The coefficients A and B are for the equation: $\log_{10} (P/P^\circ) = A - B (K/T)$

P is the vapor pressure; T₁ and T₂ are the bound of the temperature range and P (363 K) is the vapor pressure at the midpoint of temperature in K; cal_{th} = 4.1840J; P° is the standard pressure, 101.325 kPa.

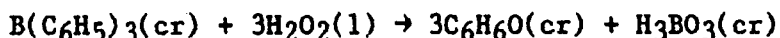
The relative percent errors between the observed vapor pressures and those calculated by linear least-squares analyses, for each datum point are $\pm 2.8\%$ and $\pm 2.9\%$ for Knudsen- and torsion-effusion, respectively.

Discussion

Derived thermodynamic quantities

By combining the results of the present study with previously compiled thermodynamic data, it is possible to calculate additional thermodynamic quantities. Two such quantities are the standard molar enthalpy of formation of gaseous triphenyl boron and the mean molar bond-dissociation enthalpy $\langle D \rangle$ (B-C₆H₅).

The standard molar enthalpy of formation of gaseous triphenyl boron is obtained by calculating the standard molar enthalpy of formation of the crystal and adding this to standard molar enthalpy of sublimation. The standard molar enthalpy of the reaction:



at 298.15 K was reported³⁸ to be $\Delta_f H_m^\circ = -(1074.5 \pm 7.5) \text{ kJ}\cdot\text{mol}^{-1}$.

Using this and the enthalpies of formation³⁹ data in Table 13, the standard molar enthalpy of formation of the crystal is calculated to be $\Delta_f H_m^\circ\{\text{B}(\text{C}_6\text{H}_5)_3, \text{cr}, 298.15 \text{ K}\} = (48.4 \pm 7.8) \text{ kJ}\cdot\text{mol}^{-1}$. The average standard molar enthalpy of sublimation at 363 K from Table 14, when corrected to 298.15 K, gives $\Delta_{\text{sub}} H_m^\circ\{\text{B}(\text{C}_6\text{H}_5)_3, \text{cr}, 298.15 \text{ K}\} =$

Table 14
Thermochemical Data

Thermodynamic Property	$\text{kJ}\cdot\text{mol}^{-1}$	Reference
$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{H}_2\text{O}_2, \text{l}, 298.15 \text{ K})$	$-(187.8 \pm 0.0)$	38
$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{H}_3\text{BO}_3, \text{cr}, 298.15 \text{ K})$	$-(1094.5 \pm 0.5)$	38
$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{C}_6\text{H}_5\text{O}, \text{cr}, 298.15 \text{ K})$	$-(165.0 \pm 0.7)$	38
$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{C}_6\text{H}_5, \text{g}, 298.15 \text{ K})$	(324.3 ± 10.5)	39
$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{B}, \text{g}, 298.15 \text{ K})$	(559.8 ± 12.6)	40

$(105.6 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$. Thus, the standard molar enthalpy of formation of the vapor is $\Delta_f H_m^\circ\{\text{B}(\text{C}_6\text{H}_5)_3, \text{g}, 298.15 \text{ K}\} = (153.9 \pm 7.9) \text{ kJ}\cdot\text{mol}^{-1}$.

The mean molar boron-phenyl bond-dissociation enthalpy, $(459.6 \pm 23.5) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated from the expression:

$$\langle D \rangle(\text{B}-\text{C}_6\text{H}_5) = 1/3[\Delta_f H_m^\circ(\text{B}, \text{g}) + 3\Delta_f H_m^\circ(\text{C}_6\text{H}_5, \text{g}) - \Delta_f H_m^\circ\{\text{B}(\text{C}_6\text{H}_5)_3, \text{g}\}]$$

and the corresponding standard molar enthalpies of formation data^{40,41} in Table 14.

Comparison of thermodynamic properties with literature values

The average value of the standard molar enthalpy of sublimation of triphenyl boron, derived from the linear least-squares treatment of the combined points of Knudsen- and torsion-effusion measurements individually is $\Delta_{\text{sub}} H_m^\circ\{\text{B}(\text{C}_6\text{H}_5)_3, \text{cr}, 363 \text{ K}\} = (103.0 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$. This value, when corrected to 298.15 K, is consistent with the additivity contribution²⁹ which assigns a contribution of 5.86 $\text{kJ}\cdot\text{mol}^{-1}$ to the standard molar enthalpy of sublimation by each carbon atom in a non-planar phenyl-substituted molecule. Greenwood et al.¹ reported the standard molar enthalpy of sublimation as $(111.3 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$, which, though higher than the value obtained by the present study, still supports their notion that the three phenyl rings of triphenyl boron are not coplanar with the B-C skeleton due to mutual steric interference. As suggested by Greenwood et al.,¹ larger central atoms of triphenyl gallium and triphenyl indium probably

permit the rings to be coplanar with the M-C skeleton. In this case, the crystal packing of molecules is more efficient, and the molar enthalpy of sublimation is expected to be higher, as it was in the case of their study.

The average value of the standard molar entropy of sublimation, also computed from the linear least-squares treatment of combined points, is: $\Delta_{\text{sub}} S_m^\circ \{B(C_6H_5)_3, \text{cr}, 363 \text{ K}\} = (185.6 \pm 2.8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. This is consistent with an assignment of $10.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for each carbon atom for the entropies of sublimation of tetraphenyl compounds of Group IV.³⁴ No value for the standard molar entropy of sublimation had been reported in the literature previously.

The mean molar bond-dissociation enthalpy $\langle D \rangle (B-C_6H_5)$ is greater than the analogous enthalpies $\langle D \rangle (M-C_6H_5)$ of the tetraphenyl compounds of Group IV,³⁴ and the triphenyl compounds of Group V.⁴² At present there are not enough thermodynamic results available to compare $\langle D \rangle (M-C_6H_5)$ among the triphenyl compounds of Group III. Since there is no apparent continuity among the triphenyl compounds of Group III with regard to structure, it is not possible to make predictions about how the bond-dissociation enthalpy may vary within the group.

Summary

Linear least-squares analysis of the combined data from three experiments of sublimation of triphenyl boron in the temperature range 339.8 to 382.0 K has resulted in the following Clausius-Claypeyron equations for Knudsen-effusion and torsional recoil, respectively:

$$\log_{10} (P_k/P^\circ) = (9.39 \pm 0.13) - (5274 \pm 46) (K/T) \quad (V-1)$$

$$\log_{10} (P_t/P^\circ) = (10.00 \pm 0.07) - (5489 \pm 27) (K/T) \quad (V-2)$$

The average values for the standard molar enthalpy and entropy of sublimation derived from the linear least-squares analyses of the results are:

$$\Delta_{\text{sub}} H_m^\circ \{B(C_6H_5)_3, \text{ cr, } 363 \text{ K}\} = (103.0 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1},$$

$$\Delta_{\text{sub}} S_m^\circ \{B(C_6H_5)_3, \text{ cr, } 363 \text{ K}\} = (185.6 \pm 2.8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

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

$$\Delta_{\text{sub}} H_m^\circ \{B(C_6H_5)_3, \text{ cr, } 298.15 \text{ K}\} = (105.6 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}.$$

The standard molar enthalpy of formation of gaseous triphenyl boron calculated from the standard molar enthalpy of formation of the solid and the standard molar enthalpy of sublimation is

$$\Delta_f H_m^\circ \{B(C_6H_5)_3, \text{ g, } 298.15 \text{ K}\} = (153.9 \pm 7.9) \text{ kJ} \cdot \text{mol}^{-1}.$$

The calculated average average bond dissociation enthalpy is:

$$\langle D \rangle (\text{B-C}_6\text{H}_5) = (459.6 \pm 23.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

Because the absolute pressures observed in the first experiment are different from those observed in the other two experiments, Table 13 also includes results from the combined points of the second and third experiments.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE WORK

This study has improved upon earlier work¹ involving sublimation of the triphenyl compounds of boron and aluminum. To complete the study of the triphenyl compounds of the Group III elements it is recommended that triphenyl gallium and triphenyl indium be studied by simultaneous Knudsen- and torsion-effusion processes.

Two improvements in the apparatus should be made to enhance experimental reproducibility: (1) The sample cell should be made deeper to insure that it can hold an adequate amount of sample and still provide enough inner capacity for satisfying the requirement¹⁰ that the mean free path of the vapor molecules be large compared to the orifice diameter. (2) With the ruled metal arc for reading angular displacement replaced by a traversing photocell system the entire process of taking data could be controlled by a microprocessor. Currently efforts to accomplish this are underway.

The true structure of the gaseous triphenyl aluminum monomer should be determined by photoelectron spectroscopy so that more accurate estimates of the thermochemical quantities associated with the dissociation of the dimer and sublimation of the monomer can be made. Also, combustion studies should be carried out on triphenyl aluminum so that, in combination with the enthalpies of sublimation determined in this study, the bond-dissociation energy of Al-C may be calculated.

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