Derived Results. Using the heat of formation of water and carbon dioxide reported in the National Bureau of Standards tables (*9*) gives $\Delta Hf^\circ(\mathrm{c}) = -103.51 \pm 0.30$ kcal-mol^{-1}. Measurement of the heat of sublimation was made in this laboratory using the Knudsen method which yielded a value of 13.7 ± 1.0 kcal-mol^{-1}. This result is based on five determinations of the rate of effusion at 100°C and three experiments at 195°C; both sets of experiments were carried out at a pressure of about 10^{-6} torr. The heat of sublimation was calculated from a combined form of the Clausius-Clapeyron equation. Combination of $\Delta Hf^\circ(\mathrm{c})$ and ΔH_{subl} gives $\Delta Hf^\circ(\mathrm{g}) = -89.8 \pm 1.0$ kcal-mol^{-1}.

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Vaporization of Zn_3As_2

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The sublimation of $Zn_3As_2(c)$ has been investigated by the torsion effusion method over a range of temperature from 613–853K. Vaporization occurs by congruent decomposition, and the total pressure in effusion cells is dependent on orifice dimensions. Equations are given for the temperature dependences of the total pressure of vapor in equilibrium with $Zn_3As_2(c)$ and for the equilibrium constant for the decomposition reaction $Zn_3As_2(c) \rightleftharpoons 3Zn(g) + {}^1/_2P_4(g)$. At the mean temperature in the range covered by this work the enthalpy change for the decomposition reaction is 123.8 ± 6 kcal/mol. Other thermodynamic and kinetic data related to the vaporization of zinc arsenide are presented and discussed.

Metal nitrides, phosphides, and arsenides have interesting electrical properties. Zn_3As_2 is a *p*-type semiconductor and its preparation and properties have been previously studied (*21, 24*). As a result of semiconducting and electroluminescent properties, there is general interest in the thermal stabilities of II–V and III–V compounds. Panish (*12, 13*) has noted the importance of zinc arsenides and phosphides in the interpretation of the gallium–arsenic–zinc and gallium–phosphorus–zinc ternary-phase diagrams. In a recent analysis of the diffusion of zinc in gallium arsenide from an invariant ternary source, Casey and Panish (*2*) did not have necessary thermodynamic data for Zn_3As_2.

We have previously reported the results of studies on the thermodynamics and kinetics of vaporization of metal nitrides (*17*) and phosphides (*10, 19, 20*). A pattern of vaporization by decomposition with low-vaporization coefficients has been established. In several cases, the low-vaporization coefficient appears to be due, in part at least, to an enthalpy of activation which exceeds the equilibrium enthalpy of vaporization.

The present study was initiated to provide thermodynamic data on thermal stability for a system which is of considerable interest and importance and to extend the investigation of vaporization kinetics to see whether previously established patterns represent general behavior.

EXPERIMENTAL

The torsion effusion apparatus and high-density graphite torque cells have been previously described along with a general discussion of the technique (*10, 17, 20*). The experimental work reported here extended over many months, and many different samples of finely powdered, crystalline Zn_3As_2 were used. Samples of Zn_3As_2 (from Ventron Div., Alfa Inorganics, Beverly, Mass.) with an assay of 99+% were used for most of the runs. However, the data were checked by making several runs with a zinc arsenide sample which had a purity reported to be 99.999% (Sevac Grade Zn_3As_2 from Semi-elements, Inc., Saxonburg, Pa.). Several tungsten torsion fibers of 0.0025- and 0.0051-cm diameter were employed together with three conventional, double-orifice, torque cells. Geometrical factors for the effusion cells are listed in Table I.

In one series of runs the amount of the initial charge of zinc arsenide in the effusion cells was varied over a wide range, while in another series of runs the fraction of the sample which vaporized was varied. X-ray diffraction studies were made on

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Table I. Geometrical Factors for Torsion Effusion Cells[a]

	Cell					
	1		2		3	
	Left	Right	Left	Right	Left	Right
d, cm	0.230	0.230	0.121	0.121	0.080	0.082
q, cm	0.940	0.920	0.900	0.870	0.895	0.900
L, cm	0.155	0.125	0.065	0.070	0.050	0.053
f	0.669	0.717	0.720	0.704	0.686	0.679
$\overline{Wa}/A'$	0.036		0.010		0.0045	

[a] d, orifice diameter; q, torque arm; L, minimum thickness of orifice; f, Searcy-Freeman factor (*3*); $\bar{W}$, Clausing factor; $\bar{a}$, average orifice area; A', cross-sectional area of sample chamber.

fresh samples and on samples from which various percentages of the initial charge had vaporized. Torque-cell temperature was calibrated against the temperature of a graphite block located directly below the cell. Temperature calibration runs were made before and after vaporization experiments, and the calibration was reproducible over a period of months. The uncertainty in the temperature of the torque cell is estimated to have been ±2°C. Calculations were made on the Oberlin College IBM 360/44 computer.

THEORY

In a torsion effusion experiment, the total pressure, p_t, due to all vaporizing species in the torque cell, is related to angular deflection, θ, torsion constant, τ, and geometrical factors through Equation 1:

$$p_t = \frac{2\,\tau\theta}{\Sigma\, afq} \tag{1}$$

If the vaporization coefficient is small compared to unity, the total pressure in an effusion cell may depend on the size of the orifice. It has been demonstrated (*6*, *19*, *20*) that an equation of the type of Equation 2:

$$\frac{1}{p_t} = M(\overline{Wa}) + 1/p_e \tag{2}$$

is useful for determination of the equilibrium pressure, p_e, by linear extrapolation of measured pressures, p_t, in a series of effusion cells with different effective orifice areas, $\overline{Wa}$. Motzfeld (*11*) and Rosenblatt (*15*) have examined the theoretical significance of equations of the type of Equation 2, and they have discussed the assumptions which make it possible to relate M, the slope of a plot of $1/p_t$ vs. $\overline{Wa}$, to the condensation or vaporization coefficient.

The vaporization of Zn_3As_2 proceeds according to Equation 3:

$$Zn_3As_2(c) \rightleftharpoons 3Zn(g) + \underset{\displaystyle As_2(g)}{\overset{}{{}^1\!/_2As_4(g)}\atop \upharpoonleft\!\downharpoonright} \tag{3}$$

and for such a process Equations 4–6 are applicable. These equations permit determination of the partial pressures of all major species in the vapor over Zn_3As_2(c).

$$p_t = p_{Zn} + p_{As_4} + p_{As_2} \tag{4}$$

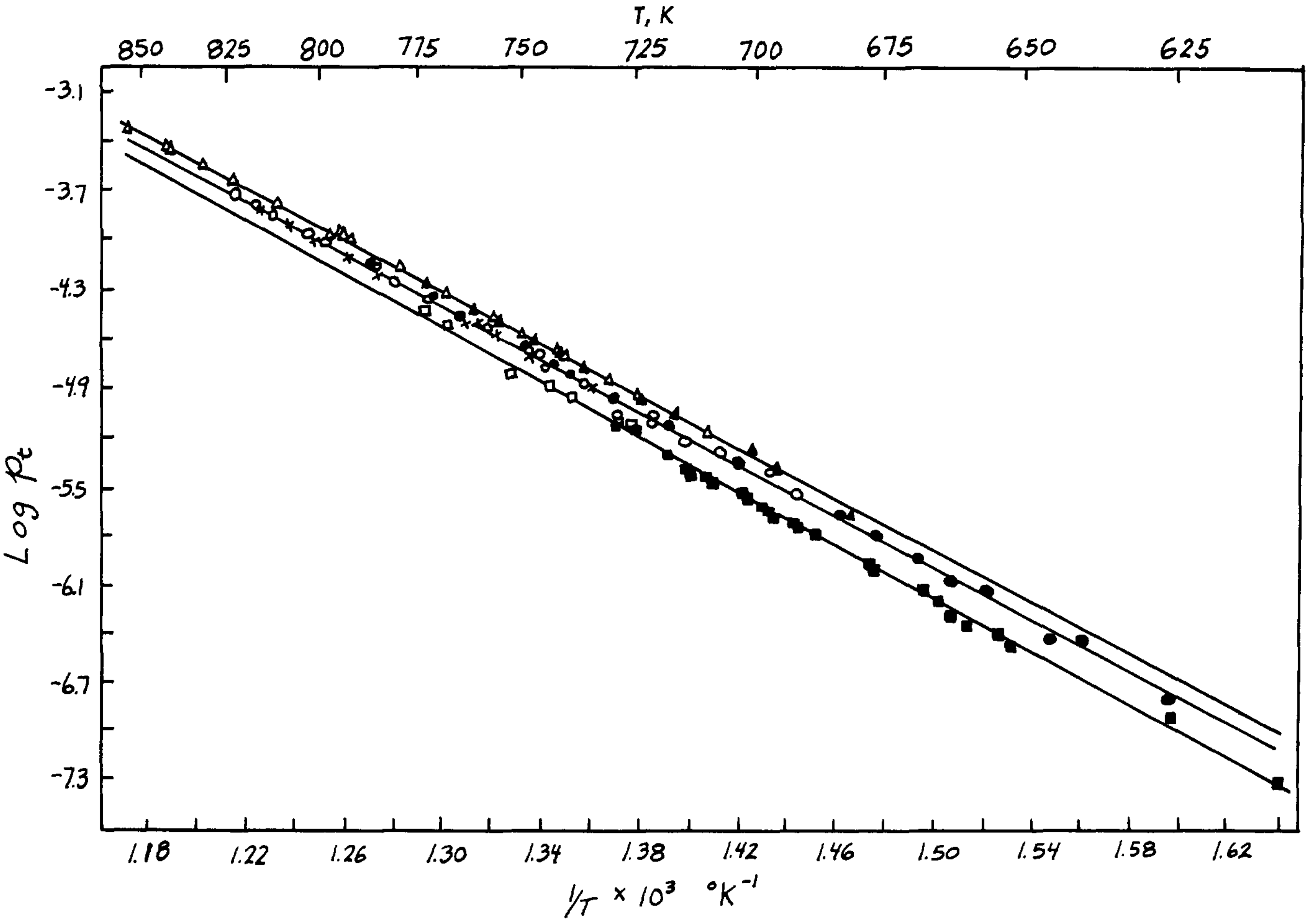

Figure 1. Logarithm of the total pressure in effusion cells vs. reciprocal temperature

Cell 1 ■, □; cell 2 ●, ○, ×; cell 3 ▲, △; 0.0025-cm diameter torsion fibers ■, ●, ▲; 0.0051-cm torsion fibers □, ○, △; ultrapure sample, 0.0025-cm torsion fiber ×

$$p_{\mathrm{As}_2}{}^2/p_{\mathrm{As}_4} = \mathrm{K}_{\mathrm{equil}} \tag{5}$$

$$\begin{cases} \dfrac{p_{\mathrm{Zn}}}{(M_{\mathrm{Zn}})^{1/2}} = \dfrac{6p_{\mathrm{As}_4}}{(M_{\mathrm{As}_4})^{1/2}} + \dfrac{3p_{\mathrm{As}_2}}{(M_{\mathrm{As}_2})^{1/2}} & (6) \\ p_{\mathrm{Zn}} = 6p_{\mathrm{As}_4} + 3p_{\mathrm{As}_2} & (6') \end{cases}$$

M_i is the mass of the ith vapor species. Equations 6 and 6′ are required by the constraint which is imposed by congruence of the vaporization process. Equation 6′ is applicable under true equilibrium conditions when p_t in Equation 4 is replaced by p_e while Equations 4–6 apply to steady-state effusion.

RESULTS

Figure 1 is a composite of the results of measurements for many effusion runs made over a period of several months with several different torsion fibers of 0.0025- or 0.0051-cm diameter combined with the torque cells described in Table I loaded with various amounts of powdered samples of Zn_3As_2. Steady-state pressures were attained rapidly and were independent of the initial amount of sample and the fraction vaporized over the range investigated. Equation 1 was used to convert angular deflection of the torque cell to total pressure. The data for each of the torque cells were smoothed by a least-squares procedure, and total pressures were calculated from the appropriate equations, Table II, for each cell at 10° intervals over the temperature range 613–853K. Equation 2 was used for linear extrapolation of the measured total pressure to zero effective orifice area to provide values for the total pressure of vapor in equilibrium with solid zinc phosphide. Figure 2 shows a typical linear extrapolation, Equation 2, at 623K, and Figure 3 shows the equilibrium vapor pressure from which Equation 7 is derived by a least-squares analysis:

$$\mathrm{Log}\ p_e(\mathrm{atm}) = \frac{-7728.8}{T} + 5.739 \tag{7}$$

Table II. Log p_t (atm) = $-(A/T) + B$[a]

Cell	A	B
1	8345.8	6.301
2	7952.1	5.919
3	7903.0	5.948

[a] $p_t = p_{\mathrm{Zn}} + p_{\mathrm{As}_4} + p_{\mathrm{As}_2}$.

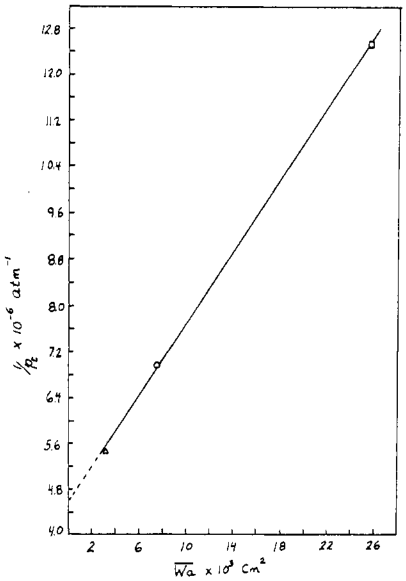

Figure 2. Linear extrapolation of $1/p_t$ to zero effective orifice area at 623K

□, ○, △. Cells 1, 2, 3, respectively

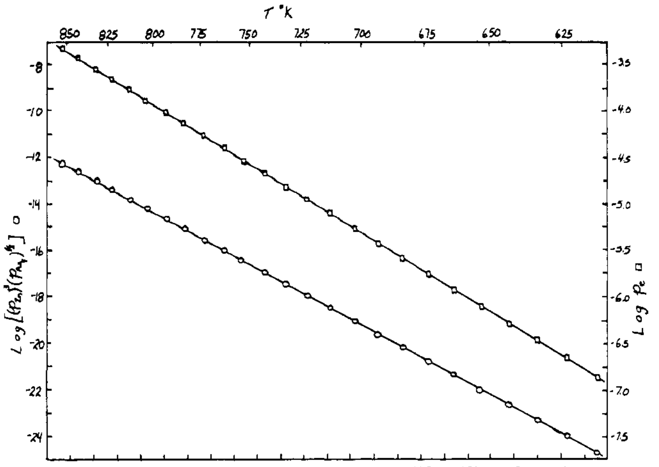

Figure 3. Logarithm of total pressure at equilibrium and logarithm of K_p vs. reciprocal temperature for $Zn_3As_2(c) \rightleftharpoons 3Zn(g) + {}^1/_2As_4(g)$

K_p, ○; p_e, □

If we wish to utilize the total equilibrium pressures for a thermodynamic analysis of the vaporization process we must know the mode of vaporization. There is ample evidence from mass spectrometric studies of analogous systems, Zn_3P_2 (*20*), Cd_3P_2 (*19*), and Cd_3As_2 (*26*) to suggest that Zn_3As_2 vaporizes congruently by decomposition. In this study, vaporization by decomposition was suggested by repeated observations during and after runs of arsenic and metallic zinc on cool parts of the apparatus. Congruent vaporization is implied by the identity of X-ray diffraction spectra for fresh samples of Zn_3As_2 and residues from several runs that varied widely in percent decomposition. The X-ray diffraction spectra in all cases were in good agreement with published data (*22*) for crystalline Zn_3As_2. Diffraction patterns corresponding to $ZnAs_2$, Zn, As, and ZnO were not observed. Equations 4, 5, and 6′ may be used with equilibrium pressures determined from the effusion measurements and thermodynamic data for arsenic from Stull and Sinke (*23*) to calculate the partial pressures and equilibrium constants in Table III.

For the process

$$Zn_3As_2(c) \rightleftharpoons 3Zn(g) + {}^1/_2As_4(g) \tag{8}$$

$K_p = p_{\mathrm{Zn}}{}^3 p_{\mathrm{As}_4}{}^{1/2}$ and Figure 3 shows a plot of log K_p vs. reciprocal temperature from which $\Delta H_{733}° = 123.8 \pm 6$ kcal may be determined. The value for the enthalpy change for Equation 8 may be combined with $\Delta H_T°$ for $As_2(g) \rightleftharpoons {}^1/_2As_4(g)$ (*23*) to give $\Delta H_{733}° = 154.1 \pm 6$ kcal/mol for Equation 9:

$$Zn_3As_2(c) \rightleftharpoons 3Zn(g) + As_2(g) \tag{9}$$

Combination of $\Delta G_T°$ and $\Delta H_T°$ gives $\Delta S_{733}° = 89.1$ e.u. for Equation 8 and this value together with tabulated entropy data (*8, 9*) gives a value of $S_{733}°$ [$ZnAs_2(c)$] = 86.1 e.u. When pressures are in atmospheres, K_p for Equation 8 is well represented over the temperature interval 613–853K by Equation 10:

$$\mathrm{Log}\ K_p = \frac{-27{,}054}{T} + 19.4652 \tag{10}$$

To determine the standard heat of formation for zinc arsenide

$$2As(c) + 3Zn(c) \rightleftharpoons Zn_3As_2(c) \tag{11}$$

Table III. Thermodynamic Data for the Decomposition of Zinc Arsenide

T, K	p_e	p_{Zn}	p_{As_2}	p_{As_4}	$K_p = p_{Zn}^3 p_{As_4}^{1/2}$
613	1.36×10^{-7}	1.17×10^{-7}	2.76×10^{-11}	1.94×10^{-8}	2.21×10^{-25}
633	3.37×10^{-7}	2.89×10^{-7}	9.56×10^{-11}	4.81×10^{-8}	5.29×10^{-24}
653	8.06×10^{-7}	6.91×10^{-7}	3.10×10^{-10}	1.15×10^{-7}	1.12×10^{-22}
673	1.80×10^{-6}	1.53×10^{-6}	9.29×10^{-10}	2.56×10^{-7}	1.84×10^{-21}
693	3.86×10^{-6}	3.31×10^{-6}	2.62×10^{-9}	5.50×10^{-7}	2.68×10^{-20}
713	8.01×10^{-6}	6.86×10^{-6}	7.00×10^{-9}	1.14×10^{-6}	3.45×10^{-19}
733	1.57×10^{-5}	1.35×10^{-5}	1.76×10^{-8}	2.24×10^{-6}	3.67×10^{-18}
753	2.99×10^{-5}	2.56×10^{-5}	4.21×10^{-8}	4.24×10^{-6}	3.45×10^{-17}
773	5.47×10^{-5}	4.69×10^{-5}	9.62×10^{-8}	7.76×10^{-6}	2.87×10^{-16}
793	9.84×10^{-5}	8.43×10^{-5}	2.12×10^{-7}	1.39×10^{-5}	2.24×10^{-15}
813	1.71×10^{-4}	1.46×10^{-4}	4.47×10^{-7}	2.42×10^{-5}	1.54×10^{-14}
833	2.86×10^{-4}	2.45×10^{-4}	9.06×10^{-7}	4.04×10^{-5}	9.35×10^{-14}
853	4.80×10^{-4}	4.10×10^{-4}	1.80×10^{-6}	6.75×10^{-5}	5.68×10^{-13}

[a] All pressures are in atmospheres.

we must know ΔH_{f298}° and $[H_{733}^\circ - H_{298}^\circ]$ for Zn(g) and As_4(g) and $[H_{733}^\circ - H_{298}^\circ]$ for Zn_3As_2(c). All the necessary data are available (*7, 8, 23*) except $[H_{733}^\circ - H_{298}^\circ]$ for Zn_3As_2(c). Several methods of approximation have been investigated: (1) $[H_{733}^\circ - H_{298}^\circ] \approx 14.1$ kcal/mol, a value derived from application of Kopp's rule (*14*); (2) $[H_{733}^\circ - H_{298}^\circ] \approx 15.2$ kcal/mol, the tabulated value for Zr_3N_2 (*8*); (3) $[H_{733}^\circ - H_{298}^\circ] \approx 13.3$ kcal/mol, the tabulated value for Zn_3N_2 (*8*). These three approximations give values for ΔH_{f298}° $[Zn_3As_2(c)]$ of -16.1, -17.3, and -15.3 kcal/mol, respectively. We believe that the first value is preferable and we estimate an uncertainty of ± 8 kcal/mol.

From the slope, M, of a plot of $1/p_t$ vs. effective orifice area, Equation 2 and Figure 2, it is possible to place upper limits on the gross vaporization coefficient for Zn_3As_2(c). In the derivation of equations of the type of Equation 2, the assumption is made that the condensation and vaporization coefficients, α_c and α_v, are equal. An additional set of simple assumptions (*15*) leads to $M = 1/\alpha p_e A$ where A is the area from which vaporization occurs in an effusion cell. In general, the cross-sectional area, A', of the sample well in the torque cell is a lower limit for the unknown surface from which vaporization occurs for a finely powdered sample which covers the bottom of the effusion cell chamber. Thus, $\alpha \lesssim 1/Mp_eA'$. Upper limits for the gross vaporization coefficient calculated from values of M in Equation 2 are listed in Table IV.

DISCUSSION

Zn_3P_2, Cd_3P_2, and Zn_3As_2 all have the same crystal structure (*4*). They all vaporize by congruent decomposition in the temperature range around 700K and all have low gross coefficients for condensation on, or vaporization from, the M_3P_2 crystal surface. In all of these compounds, the vaporization coefficient appears to be temperature-dependent which suggests that the deviation of α from unity is caused, in part at least, by an enthalpy barrier to activation for vaporization which exceeds the equilibrium enthalpy change. As noted previously (*19, 20*), the low vaporization coefficient may be the result of an excess enthalpy of activation associated with rearrangement of bond distances and angles in formation of X_4 units which do not exist in the crystal. Rosenblatt and co-workers (*16*) suggested a similar explanation for a low coefficient for vaporization of As_4(g) from crystalline arsenic.

Table IV. Upper Limits for Vaporization Coefficient of Zinc Arsenide

T, K	α_v	*T*, K	α_v	*T*, K	α_v
613	0.020	713	0.035	813	0.056
663	0.027	763	0.046	853	0.075

Apparently similar behavior has been encountered in the vaporization of red phosphorus (*1*). Zinc arsenide is like zinc phosphide but unlike cadmium phosphide in that the vaporization is well behaved—i.e., steady-state effusion rates are attained rapidly and are independent of the amount of sample initially placed in the effusion cell and the fraction decomposed. The reproducibility of the data for the Zn_3As_2 system, Figure 1, is remarkable. Extensive studies of the vaporization of ultrapure Cd_3As_2 (*18*) have shown that it is a badly behaved system like Cd_3P_2 and that it is difficult to obtain reproducible, reliable data.

The work of Ward (*25*) and co-workers raises questions concerning the effusion method and its reliability. Among others, Hildenbrand (*6*), Schoonmaker and Rubinson (*19*), and Hilden and Gregory (*5*) have shown that thermodynamic data obtained from effusion studies on systems which vaporize by decomposition compare favorably with data obtained by other methods—e.g., static pressure measurements, calorimetry, and third law calculations. The foregoing results together with the length of the temperature range covered, the reproducibility of data, and the relatively short extrapolation to obtain equilibrium pressures in the present work provide a measure of confidence in the assumptions which have been made in interpreting the effusion data and the results derived from them.

The heat of formation at 298K for zinc arsenide, $\Delta H_{f298}^\circ = -16.1 \pm 8$ kcal/mol, may be compared to values of -39.5 and -29.5 kcal/mol for Zn_3P_2(c) and Cd_3P_2(c). The large uncertainty in the present result arises because the enthalpy of formation at 298K is derived by taking the difference between two large numbers, each of which involves an uncertainty of about $\pm$4–6 kcal/mol. Application of Kopp's rule provides a method for converting S_{733}° for Zn_3As_2(c), derived in this work, to S_{298}° $[Zn_3As_2(c)] = 59$ e.u. which may be compared to $S_{298}^\circ = 63.6$ e.u. (*9*) for Zn_3Sb_2(c).

Previously observed patterns of vaporization for Zn_3P_2(c) and Cd_3P_2(c) are followed for Zn_3As_2(c). Congruent vaporization by decomposition with low vaporization coefficients appears to be characteristic of the II–V compounds.

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Vapor Pressure of Tantalum Pentachloride

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The gas transpiration method was used to measure the equilibrium vapor pressure of tantalum pentachloride over the range 431–73°K. The second law enthalpy of sublimation was calculated to be $\Delta H_T^\circ = 21.1 + 0.2$ kcal/g-mol. Third-law estimates of the enthalpy and entropy of sublimation at 298°K are $\Delta H_{298}^\circ = 22.1$ kcal/g-mol and $\Delta S_{298}^\circ = 44.8$ eu, respectively, based on estimated heat capacities. The data were fit by $\log_{10} P_{\mathrm{mm}} = (12.03 \pm 1.86) - (4604 \pm 40)/T$.

Reported vapor pressures of tantalum pentachloride (*1*, *3*, *4*, *7*, *8*) differ appreciably at temperatures below the melting point (216.5°C). Data were obtained in this work using the gas transpiration method under carefully controlled anhydrous conditions. The vapor pressure data obtained compared favorably with the literature values of Saeki et al. (*4*), whereas the heat of sublimation is more consistent with the calculated values reported by Schafer and Kahlenberg (*5*) as obtained from prior published data.

EXPERIMENTAL

The apparatus used in this experimental work consisted of a pyrex sublimation chamber which was maintained isothermal by a fused salt bath, a connecting hot line, and a condenser which was connected to the hot line by a ball and socket joint. The equipment and experimental technique are essentially the same as those used and described by Joung and Stevenson (*2*). Resublimed tantalum pentachloride was obtained in sealed ampuls from Alfa Inorganics, Inc. (lot No. 06871) and contained no detectable quantities of niobium according to spectroscopic analysis. Other impurities were less than 0.02%. The $TaCl_5$ was loaded into the sublimation chamber within an inert atmosphere dry box having fewer than 0.5 ppm H_2O content. The sublimer was sealed (fused) into the system under dry inert gas purged to prevent any contamination by atmospheric moisture.

Measurements were made after the helium carrier gas flow rate and salt bath temperatures had stabilized. The sublimed $TaCl_5$ was condensed from the gas phase for a measured period of time and weighed to determine the gas composition. Flow rates were measured before and after each run using a soap film flow meter and appropriately corrected to standard conditions. Flow rates could be determined to within about 0.002 cc/sec in this way. Temperatures were measured by a calibrated chromel-alumel thermocouple placed in the salt bath next to the sublimer. The temperature of the salt bath in the vicinity of the sublimer was thus established to within approximately ±0.2°C.

Vapor pressures were calculated from the expression

$$P_{\mathrm{TaCl_5}} = P/(1 + Mvt/22{,}400\, w)$$

where

$P_{\mathrm{TaCl_5}}$ = vapor pressure of $TaCl_5$ in mm Hg
P = system pressure, mm Hg
M = mol wt of $TaCl_5$
v = flow rate of the carrier gas, std. cc/sec
t = time, sec
w = weight of $TaCl_5$ condensed in grams

Partial pressures of $TaCl_5$ were calculated from the above equation for flow rates between 0.15 and 0.9 std cc/sec to

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