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James Joseph Dudash

M. S. Thesis

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ABSTRACT

The melting point of stannous fluoride was determined to be 488.2° ± .5°K.

The vapor pressure of stannous fluoride was measured in the temperature range 532° to 670°K by the torsion effusion method. The equilibrium pressure is represented by the expression

$$\log_{10} P_{atm} = -(6.951 \pm .033) \frac{10^3}{T} + 6.726 \pm .055$$

where the quoted errors are the standard deviations from the least squares fit. With use of this expression for the total pressure and the relative pressures measured by K. Zmbov, J. W. Hastie and J. L. Margrave, heats of vaporization at 600°K for the monomer, dimer, and trimer were found to be 31.8 ± 3, 30.3 ± 3, and 42.0 ± 5 kcal/mole, respectively.

I. INTRODUCTION

Despite several investigations of the thermochemical properties of stannous fluoride,[1-3] the melting point and vapor pressure are still not well known. Melting points have been reported by Nebergall, Muhler and Day[1] and Zmbov, Hastie and Margrave[2] to be about 488°K with an uncertainty of about 3 degrees.

The vapor pressure of stannous fluoride has been determined over the temperature range 769° to 1100°K by Fischer and Petzel[3] using the "Bell method". Zmbov, et al.[2] have measured the relative intensities of $SnF_2(g)$, $Sn_2F_4(g)$ and $Sn_3F_6(g)$ with a mass spectrometer and have used the information with an extrapolation of Fischer and Petzel's data to calculate the partial pressures of the vaporizing species.

This paper reports measurements of the melting point of stannous fluoride and of the equilibrium vapor pressure at 532° to 670°K. From the vapor pressure measurements and the relative intensity measurements of Zmbov et al., the heat of sublimation for each species was calculated at 600°K.

II. EXPERIMENTAL

The stannous fluoride used in this study was obtained from K and K Laboratories Incorporated. Xray diffraction analysis showed SnF_2 to be the major constituent and spectrographic analysis showed .06% of iron to be the major metallic impurity.

The melting point of stannous fluoride was measured by heating and cooling curve methods with a chromel-alumel thermocouple. For the measurements, samples of about 50 gm were heated in closed graphite crucibles in a vertical tube furnace. A 2 inch diameter alumina tube with 3/8 inch wall thickness and 6 inches of alumina bubble insulation gave the furnace a relatively high heat capacity. The thermocouple was standardized both before and after the stannous fluoride runs by determining the melting points of tin and cadmium in the same furnace using similar crucibles. These calibrations established the fact that the thermocouple temperature was correct to 0.1°K at the melting point of stannous fluoride.

The torsion-effusion technique, which was used to study the vapor pressure of SnF_2, is fully described by Freeman.[4] In brief, the method yields values of the pressure in a torsion effusion cell from the following relationship:

$$P = \frac{2\theta D}{\Sigma\, q_i a_i f_i}$$

where θ is the angle through which the cell is twisted, D is the torsion constant of the fiber from which the cell is suspended, q_i is the moment arm of orifice i from the suspending fiber, a_i is the area of orifice

i and f_i is the Freeman-Searcy[8,9] correction factor for the finite channel length of an orifice.

The apparatus used in the present study had previously been used by B. Blank.[10] The system was modified by replacement of the pyrex column which had enclosed the suspension system with a copper column and by the insertion inside the heating elements of a copper can 2-1/2 inches in diameter and 3-1/2 inches long to enclose the dummy and effusion cells. The can improved the temperature uniformity in the zone of the cells.

Tungsten suspension wires 30 cm long and 1.5 and 2 mills in diameter were used. Torsion constants were approximately 1.12 and 3.00 dyne-cm/rad. respectively, with an estimated error of ±0.5%.

The torsion cells which were about 3.0 cm in length, 1.3 cm in width, and 1.9 cm in height, were made of National Carbon 2T 101 grade graphite. Table I gives orifice dimensions and correction factors.

The angle of cell rotation was determined by a null technique. A modified goniometer was used to rotate the upper part of the suspension in the direction opposite to that of the cell rotation and the measure the angle of twist necessary to return the cell to its position before heating.

Temperature measurements were made with a chromel-alumel thermocouple placed in a dummy cell directly below the effusion cell. Temperatures of the dummy cell had been calibrated against temperatures of an effusion cell into which a thermocouple had been inserted. All thermocouples were calibrated by heating and cooling through cadmium

and antimony melting points.

When a run was started, the sample was initially heated to about 500°K for several hours to remove water of hydration and was then slowly heated to at least fifty degrees above the highest point at which data would be taken in order to remove volatile impurities. The sample was then cooled and reheated keeping pressures below 2×10^{-5} torr while measurements were made. Eighty five readings were taken in ten separate runs.

The equilibrium vapor pressure of zinc was measured to test for any systematic errors. From 21 measurements at 588° to 706°K, the third law heat of sublimation of zinc at 298°K was determined as $\Delta H^{o}_{298} = -31.15 \pm .19$ kcal/mole. The value selected by Hultgren et al.[11] from collected studies is $\Delta H^{o}_{298} = -31.2$ kcal/mole.

III. RESULTS AND DISCUSSION

Difficulty was encountered in obtaining an arrest in the heating or cooling curves of SnF_2, probably because of low heat conductivity through the sample and because the material readily supercooled. Supercooling of 10° was easily observed. To reduce these problems, heating and cooling rates were decreased to approximately 2° per minute, and melts were seeded when they had cooled to the apparent melting point.

Heating curves with clear arrests were never obtained. The melting point was determined from cooling curves which supercooled no more than 0.5° and then gave a constant reading for periods of 0.5 to 1.5 minutes. The melting point was found to be 488.2 ± .15°K where the error is the standard deviation. Data are summarized in Table II. With allowance for errors in standardization and for sample impurities, a total uncertainty of 0.5° is estimated. The value previously reported was 488 ± 3°K.[1]

The results of the Knudsen equilibrium vapor pressure data collected in the range 432.1° to 670.5°K yielded the equation

$$\log_{10} P_{atm} = -(6.951 \pm 0.033)\,\frac{10^3}{T} + (6.726 \pm .055)$$

where the errors are standard deviations. Figure 1 is a plot of pressure versus 1/T and the experimental data are presented in Tables III, IV and V.

Molecular flow conditions of a gas through an orifice have been shown to apply only when the mean free path of the vapor is greater than some critical value depending on the effusion orifice dimensions.[12,13]

In order to insure molecular flow conditions, data points with values of the mean free path to orifice diameter, τ/d, less than 0.5, as calculated by the hard sphere approximation,[14] were not included in the final calculations. No deviations were found by Mar and Searcy[6] with τ/d ratios as low as 0.4. In the present study, pressures obtained under conditions for which τ/d was calculated to be less than 0.2 to 0.3 fell above the extrapolated pressure curve by more than the calculated standard deviation (c.f. Fig. 1).

The heat of vaporization to the equilibrium mixture of vapor species was calculated to be 31.80 ± 0.15 kcal/mole at 600°K by the second law method.[15]

Experimental errors in orifice and cell measurements, determinations of torsion constants and of deflection angles lead to an estimated error of 1% in ΔH_T. Assumption of a maximum systematic temperature error of +4° at the upper end and -4° at the lower end of the temperature range leads to a calculated error of 1.6 kcal/mole for the second law calculation. The heat of vaporization at 600°K can therefore be estimated to be correct within ±3 kcal/mole.

Using the equation

$$P_{SnF_2} = P_T \left[\frac{\dfrac{I(SnF_2^+)}{\sigma}}{\dfrac{I(SnF_2^+)}{\sigma} + \dfrac{I(Sn_2F_4^+)}{\sigma} + \dfrac{I(Sn_3F_6^+)}{\sigma}} \right]$$

where P_T is the total pressure determined in this work and I is the relative intensity of the ions from Zmbov, et al.[2] The pressures and second law heats were calculated for the monomer, dimer and trimer.

A comparison of the temperature dependence for the total pressures was made by applying to the data of Zmbov, et al., the equation

$$P \alpha \frac{I^{+}T}{\sigma \nu} \left(\frac{A}{E-A}\right)$$

where I^{+} is the ion current, A is the appearance potential for the ion, E is the electron energy at which the measurement was made, σ is the cross section for the ion and γ is the multiplier efficiency taken here as one. The cross section was calculated using values from Otvos and Stevenson.[16] Values of I^{+}, T, A and E from Zmbov, et al. were used to calculate relative pressures of the species, which were then summed to give a value for the total pressure.

Results of the three separate vapor pressure studies are compared in Figure 2 and Table VI. Fischer and Petzel's extrapolated pressures are about a factor of 2 higher than measured in this work. Zmbov, et al. used the measured temperature dependences of Fischer and Petzel rather than their own considerably steeper temperature dependences in calculating partial pressures from their mass spectrometer intensities, presumably because their own temperature calibrations were somewhat uncertain.

Because of the high reproducibility of data collected in the present study with cells of different orifice areas and with wires of different torsion constants and especially because of the very careful temperature calibrations, the total pressure data obtained should be the best now available. The most reliable estimates of partial pressures should be those given by combining the total pressures of this study with the

relative pressure data of Zmbov, Hastie and Margrave. Some support to this assertion is provided by the close agreement between the measured entropy of the reaction $SnF_2(l) = SnF_2(g)$ at 600°K and the value 33.5 ± 6 eu estimated by adopting $\Delta S_{298} = 46.4$ for $SnF_2(s) = SnF_2(g)$[17] and estimating that the entropy of fusion is 6 eu and ΔCp for vaporization of both solid and liquid SnF_2 is -10 cal/deg. On the assumption that the entropy of the reaction $2SnF_2(g) = Sn_2F_4(g)$ at 600°K is the same as estimated[18] for $2\ BF_2(g) = B_2F_4(g)$ at 600°, the entropy of sublimation to Sn_2F_4 is calculated to be 25.5 ± 10 found also to agree well with the experimental value.

Table I. Orifice dimensions

Cell	Orifice Diameter (mm)		Channel Length (mm)		Correction Factors	
	(a)	(b)	(a)	(b)	(a)	(b)
1	1.010	1.018	1.516	1.555	.4720	.4676
2	2.011	2.013	.972	.988	.6795	.6761

Table II. Melting point data

Run	Average Thermocouple Readings at Arrest (Millivolts)
1	8.735
2	8.739
3	8.753
4	8.747
5	8.748
6	8.739

8.744 ± .006 M.V. = 488.3° ± 0.16°K

Corrected Value 488.2 ± 0.16°K

Table III. Temperature and pressure data for 1 mm orifice and 2 mill wire

Temperature (°K)	Pressure (atm)
606.7	1.893×10^{-5}
613.5	2.675×10^{-5}
614.5	2.545×10^{-5}
619.7	3.228×10^{-5}
623.0	3.673×10^{-5}
628.6	4.649×10^{-5}
632.7	5.408×10^{-5}
635.7	6.115×10^{-5}
638.6	7.432×10^{-5}
639.5	7.029×10^{-5}
645.5	9.037×10^{-5}
647.5	9.541×10^{-5}
649.0	1.037×10^{-4}
652.7	1.200×10^{-4}
657.2	1.411×10^{-4}
657.2	1.405×10^{-4}
659.0	1.669×10^{-4}
664.0	2.038×10^{-4}
668.7	2.158×10^{-4}
670.5	2.322×10^{-4}
676.2*	2.903×10^{-4}
677.7*	3.039×10^{-4}
679.7*	3.238×10^{-4}
686.0*	4.169×10^{-4}
688.2*	4.433×10^{-4}
690.7*	5.034×10^{-4}
690.7*	5.521×10^{-4}
693.2*	5.521×10^{-4}
694.5*	6.270×10^{-4}

*$\lambda/d > .5$, not used to calculate heats

Table IV. Temperature and pressure data for 2 mm orifice and 2 mill wire

Temperature (°K)	Pressure (atm)
574.2	4.396×10^{-6}
580.7	5.474×10^{-6}
584.7	6.691×10^{-6}
588.2	7.978×10^{-6}
590.0	9.237×10^{-6}
594.0	1.037×10^{-5}
595.6	1.259×10^{-5}
597.2	1.187×10^{-5}
600.5	1.352×10^{-5}
603.0	1.543×10^{-5}
607.2	1.831×10^{-5}
607.8	2.156×10^{-5}
609.0	1.960×10^{-5}
613.0	2.291×10^{-5}
614.0	2.560×10^{-5}
615.2	2.918×10^{-5}
617.6	2.783×10^{-5}
619.0	2.984×10^{-5}
619.2	3.439×10^{-5}
620.7	3.192×10^{-5}
622.5	3.469×10^{-5}
624.2	3.739×10^{-5}
629.5	4.590×10^{-5}
633.0	5.270×10^{-5}
634.5	5.652×10^{-5}
636.7	6.186×10^{-5}
637.2	6.376×10^{-5}
638.2	6.660×10^{-5}
639.2	6.988×10^{-5}
640.0	7.147×10^{-5}

Table V. Temperature and pressure data for 2 mm orifice and 1.5 mill wire

Temperature (°K)	Pressure (atm)
532.1	4.824×10^{-7}
534.5	5.118×10^{-7}
535.0	4.836×10^{-7}
538.5	5.381×10^{-7}
539.2	7.189×10^{-7}
541.7	7.741×10^{-7}
542.2	7.287×10^{-7}
543.7	8.090×10^{-7}
547.5	1.074×10^{-6}
550.5	1.226×10^{-6}
550.7	1.180×10^{-6}
554.2	1.755×10^{-6}
556.5	1.624×10^{-6}
558.5	1.840×10^{-6}
559.0	2.442×10^{-6}
563.0	2.566×10^{-6}
565.0	3.213×10^{-6}
568.5	3.490×10^{-6}
571.2	4.086×10^{-6}
575.4	4.972×10^{-6}
577.2	5.261×10^{-6}
581.0	6.090×10^{-6}
584.2	7.148×10^{-6}
589.0	8.446×10^{-6}
593.2	9.977×10^{-6}
600.7	1.350×10^{-5}

Table VI. Heats of Sublimation for Reactions Involving SnF_2

Reaction	Zmbov et al. °K	Zmbov et al. ΔH_T(kcal/mole)	This Work °K	This Work ΔH_T(kcal/mole)	This Work ΔS(eu)	Estimated ΔS(eu)
$SnF_2(l) \rightarrow SnF_2(g)$	570	38.8 ± 0.6	600	31.9 ± 3	30.7 ± 3	33.5 ± 5
$2SnF_2(l) \rightarrow Sn_2F_4(g)$	570	38.5 ± 0.6	600	30.0 ± 3	23.6 ± 3	25.5 ± 10
$2SnF_2(l) \rightarrow Sn_3F_6(g)$	610	49.0 ± 5	600	41.8 ± 5	37.7 ± 5	

Total Pressure	ΔH at 600°K	ΔS at 600°K
Fischer & Petzel	27.4	24.8
This Work	31.8 ± 3	30.9 ± 3
Zmbov et al.	40.3	45.0*

*Normalized using the total pressure found in this work at 600°K

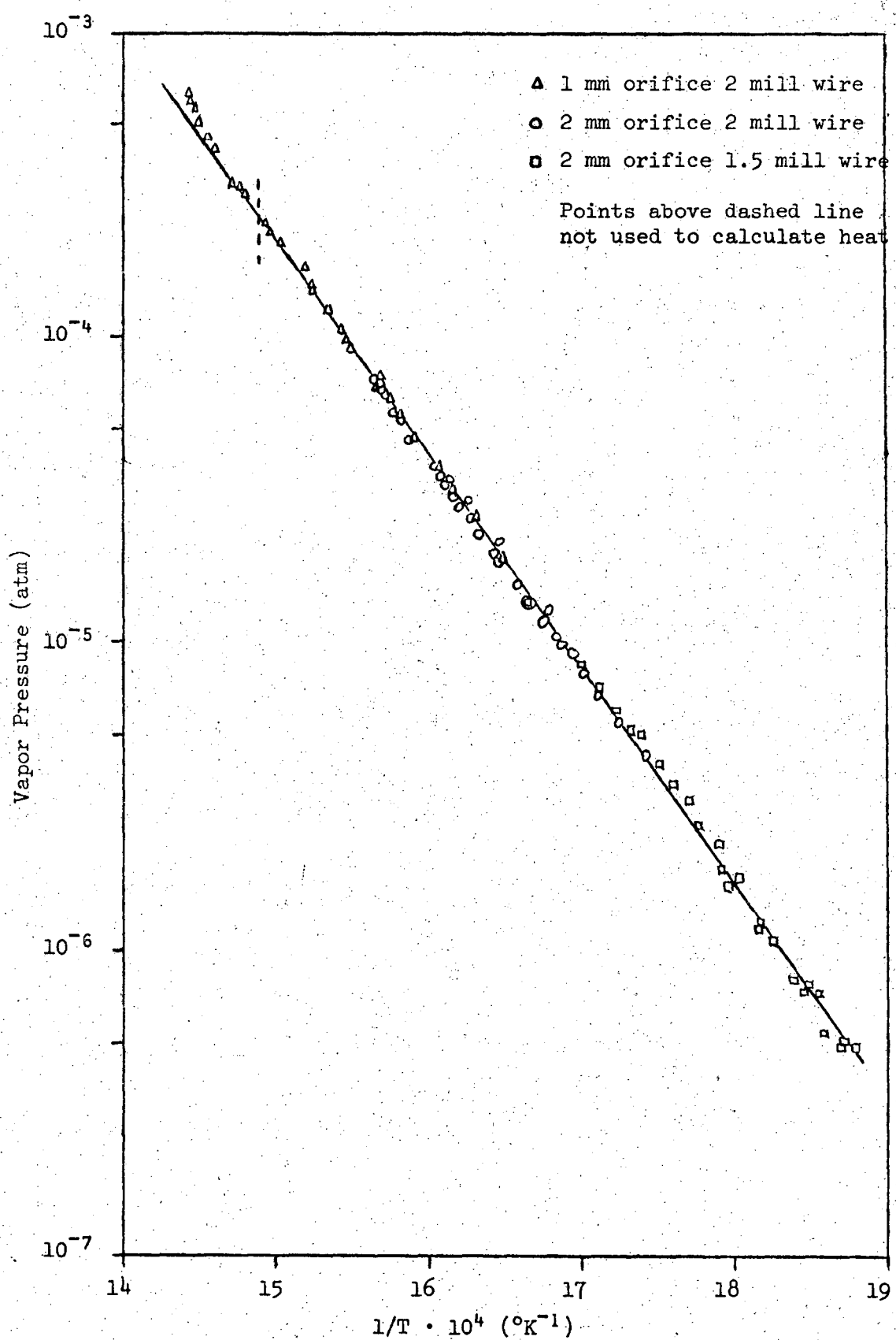

Figure 1. Vaporization data for SnF_2

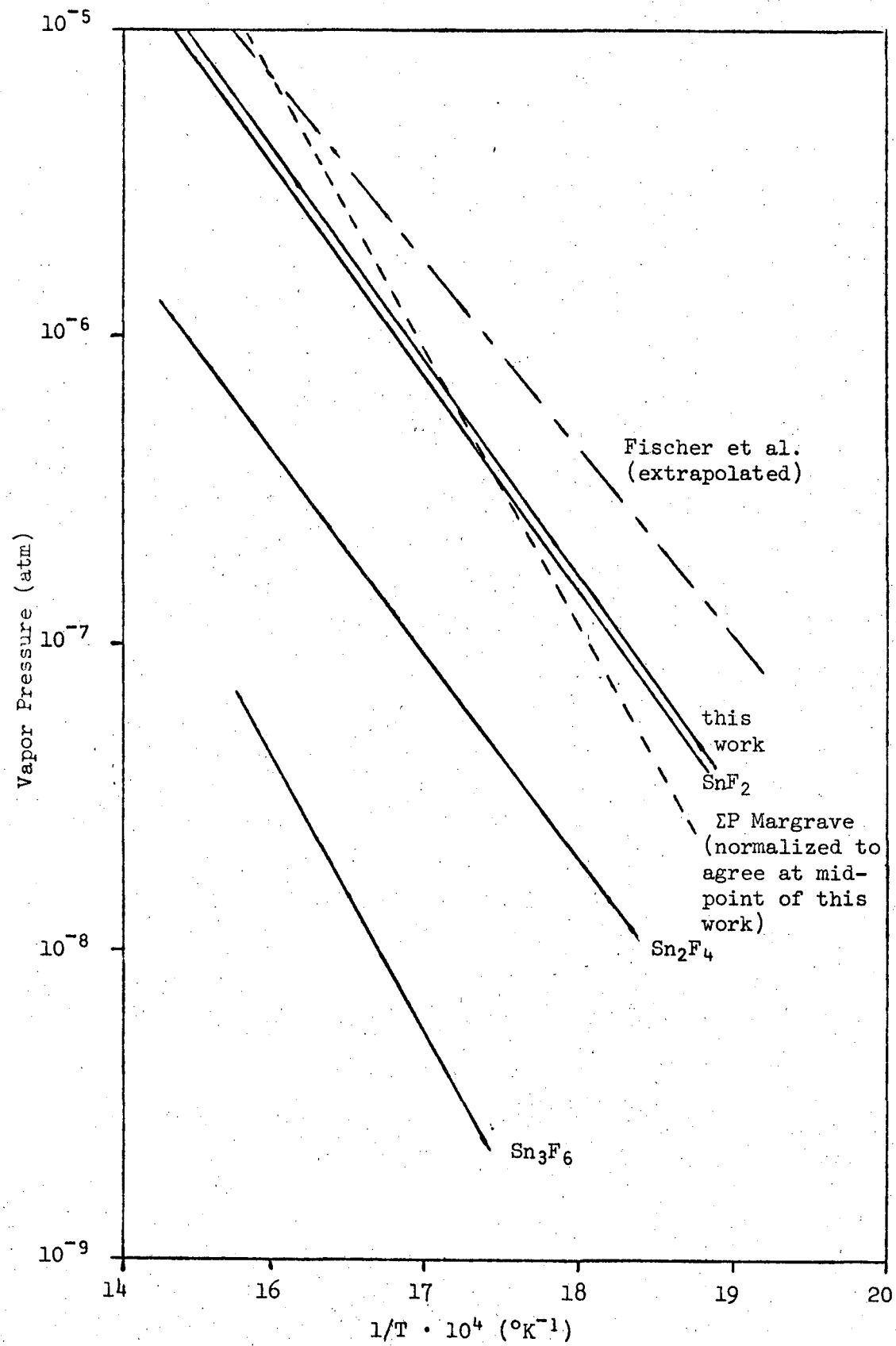

Figure 2. Comparison of slopes, total and partial pressures

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REFERENCES

1. W. H. Nebergall, J. C. Muhler, H. G. Day, J. Amer. Chem. Soc., 74, 1604 (1952).

2. K. Zmbov, J. W. Hastie, J. O. Margrave, Thermodynamics of Vaporization of SnF_2 and PlF_2 and the Dissociation Energies of SnF_2 and PbF_2, preprint of paper presented at the Third International Symposium on High Temperature Technology at Asilomar, Calif., Sept. (1967).

3. V. W. Fischer and T. Petzel, Z. Anorg. Allg. Chem., 333, 226 (1967).

4. R. D. Freeman, in The Characterization of High Temperature Vapors, J. L. Margrave, Ed., (John Wiley and Sons, Inc., New York, 1967).

5. M. J. Lim and A. W. Searcy, J. Phys. Chem. 70, 1762 (1966).

6. R. W. Mar and A. W. Searcy, J. Phys. Chem. 71, 888 (1967).

7. H. B. Skinner, Lawrence Radiation Laboratory Report, UCRL-17804, Sept. 1967.

8. R. D. Freeman and A. W. Searcy, J. Chem. Phys. 22, 762 (1954).

9. D. A. Schulz and A. W. Searcy, J. Chem. Phys. 36, 11 (1962).

10. B. Blank, Lawrence Radiation Laboratory Report UCRL-16018, July, 1967.

11. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, (John Wiley and Sons, Inc., New York, 1963).

12. A. W. Searcy and D. A. Schulz, J. Chem. Phys. 38, 722 (1963).

13. K. D. Carlson, P. W. Gilles and R. J. Thorn, J. Chem. Phys., 38 2064 (1963).

14. S. Dushman, Scientific Foundations of Vacuum Technique, (John Wiley and Sons, Inc., New York, 1949).

15. G. N. Lewis, M. Randall, K. S. Pitzer and L. Brewer, Thermocynamics, Revised Edition, (McGraw-Hill Book Co., Inc., New York, 1961).

16. J. W. Otvos and D. P. Stevenson, J. Amer. Chem. Soc., 78, 546 (1956).

17. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Rev. 63, 111 (1963).

18. JANAF Thermochemical Data, Dow Chemical Company, Midland, Michigan (1964).

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