JOURNAL OF SOLID STATE CHEMISTRY **53**, 113–119 (1984)

Thermodynamic Properties of Two Metal-Rich Tantalum Sulfides: Ta_2S and Ta_6S

B. U. HARBRECHT, S. R. SCHMIDT, AND H. F. FRANZEN*

Ames Laboratory-DOE and Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Received November 22, 1983; in revised form January 16, 1984

The incongruent vaporization reactions of Ta_2S and Ta_6S have been investigated by mass-loss effusion in the temperature range 1576 to 1902 K. By extrapolation of P_S(obs) to equilibrium the enthalpies of the reactions $\frac{3}{2}$ $Ta_2S(s) = \frac{1}{2} Ta_6S(s) + S(g)$ and $Ta_6S = 6\ Ta(s) + S(g)$ were found to be $\Delta H^0_{298}/R = 53.0(0.3) \times 10^3$ K and $\Delta H^0_{298}/R = 58.1(0.4) \times 10^3$ K, respectively. Comparison between the above values, determined by a 2nd law treatment, and 3rd law values was used to derive fef ("free energy function") values for Ta and S in the compounds. These postulated fef's, which apply only to the elements as present in the compounds measured, are compared to tabulated quantities for the pure solid elements to provide a criterion for 2nd and 3rd law evaluation.

Introduction

A reinvestigation of the Ta/S system by Jellinek (*1*) confirmed the existence of three compounds: TaS_3, pentamorphic TaS_2, and non-stoichiometric $Ta_{1-x}S_2$ $(0.2 < x < 0.35)$ occurring in three modifications. 2H-$Ta_{1.35}S_2$ was considered to be the phase coexisting with tantalum. The application of high-temperature preparative techniques at temperatures above 1600 K led to synthesis of Ta_2S (*2*) and Ta_6S (*3*), two metal-rich phases exhibiting unusual structural features.

Existing evidence indicated that measurable incongruent vaporization of the solid phase occurs in about the same temperature range in which the compounds are formed. Our purpose in this study was to identify the vaporizing species, determine the thermal stability of the solid phases by measuring the effusion of these species, and then to relate the obtained thermodynamic properties to the corresponding decomposition reactions. These reactions differ considerably in a crystal-chemical sense; Ta_2S decomposes to structurally related Ta_6S which in turn rearranges to *bcc* Ta on further loss of S.

Experimental

Sample Preparation and Phase Analysis

X-Ray-pure samples of Ta_2S were prepared in two steps. The reactions of granular tantalum (Alpha Products, 60 mesh, 99.98%) with stoichiometric amounts of sulfur (Alpha Products 99.9999%) were performed in evacuated quartz glass ampules at 1120 K for 4 days. Subsequently the sam-

---

* To whom correspondence should be addressed.

0022-4596/84 $3.00

ples were compressed and then inductively heated in closed tungsten crucibles under vacuum (ca. 10^{-5} Torr) to a final temperature of 1800 K which was maintained for several hours. By varying starting molar ratios the following phases were similarly formed: Ta_6S, $2H\text{-}Ta_{1.35}S_2/Ta_2S$, Ta_2S/Ta_6S, and Ta_6S/Ta.

The Guinier powder X-ray diffraction technique was employed for phase analysis. Comparison of the lattice parameters of Ta_2S and Ta_6S determined from the two phase mixtures suggested negligible phase width for each compound. Powder patterns of samples of Ta_6S which had been annealed below 1850 ± 20 K pointed to the existence of a second modification whose structure is not yet identified.

Thermodynamic Measurements

Thermochemical properties of Ta_2S and Ta_6S were determined by measuring rates of mass loss (ranging from 2.3×10^{-4} mg/min at 1576 K to 3.4×10^{-2} mg/min at 1902 K) via vaporization from samples (ca. 400 mg) whose initial composition was, in each case, Ta_2S. The apparatus, which is essentially a tungsten Knudsen effusion cell suspended from a microbalance, was previously described in detail (*4*). Mass spectrometry indicated that S and S_2 were the only important vapor species. An effusion cell of differing orifice size was used in each of three separate experiments to gauge the extent of deviation from equilibrium, suspected due to the incongruent vaporization. Each measurement proceeded until mass was lost at an immeasurably small rate even at 2000 K. The abrupt decrease in decomposition rate just before this point suggested there is no appreciable solubility of sulfur in tantalum, in agreement with evidence from X-ray powder diffraction.

The temperatures used in calculating thermodynamic quantities were arrived at by adjusting observed temperatures according to a calibration. This correction was based on a comparison of readings from identical W–5%Re/W–26%Re thermocouples, one positioned as during a measurement (nearly in contact with the outside of the crucible), and another inserted to the center of an empty crucible resembling the experimental cell. This compensated for errors due to placement of the thermocouple junction at other than the exact location of the sample being measured.

Raw data—temperature in degrees K, mass loss in milligrams, time in minutes, pressure of sulfur (monomer) in atmospheres for each experiment and from the extrapolation to equilibrium are available upon request from the authors.

Data Analysis and Results

The partial pressure due to a vapor species of molar mass M, effusing through an orifice of area A, is related to rate of mass loss by the Knudsen equation (*5*)

$$P = \left(\frac{\Delta m}{\Delta t}\right)\left(\frac{1}{A}\right)\left(\frac{2\pi RT}{M}\right)^{1/2} \qquad (1)$$

To calculate partial pressures of both species from a single measured $\Delta m/\Delta t$ we assume monomer/dimer equilibrium (although the actual process of equilibration does not necessarily occur in the gas phase alone):

$$S_2(g) = 2\,S(g) \qquad (2a)$$

$$K_P = \frac{P_S^2}{P_{S_2}} \qquad (2b)$$

Incorporating (2b) in (1) yields

$$P_S = \frac{K_P}{2\sqrt{2}}\left[\left(1 + \left(\frac{4\sqrt{2}}{K_p}\right)\left(\frac{\Delta m}{\Delta t}\right)\left(\frac{(2\pi RT/M_S)^{1/2}}{A}\right)\right)^{1/2} - 1\right]. \qquad (3)$$

K_P at each measured T_i was generated from results of a linear least-squares fit to tabulated values (*6*) of ($-R \ln K_P - \Delta$fef) vs $1/T$. (Δfef, change in the "free energy func-

TABLE I

RESULTS OF 2ND AND 3RD LAW CALCULATIONS OF $\Delta H^0_{\mathrm{vap},298}/R$ USING DERIVED fef VALUES

	$10^7 \times A$ (m^2)			
Reaction, Method	12.5	7.5	1.53	0.00
$\frac{3}{2}$ Ta_2S = $\frac{1}{2}$ Ta_6S + S				
2nd	54.9(0.3)	55.7(0.3)	53.9(0.5)	53.0(0.3)
3rd	54.5(0.1)	54.2(0.1)	53.4(0.1)	
Ta_6S = 6 Ta + S				
2nd	58.2(0.3)	58.1(0.5)	58.2(1.0)	58.1(0.4)
3rd	59.7(0.1)	59.4(0.1)	58.6(0.3)	

Note. A = area of orifice. Numbers in parentheses are std. deviations.

tion,'' means the difference in the quantity $\sum_i \nu_i(G^0_{i,T} - H^0_{i,T\mathrm{ref}})/T$ from products to reactants). Hereafter, calculations refer to the reactions

$$\tfrac{3}{2}\, Ta_2S(s) = \tfrac{1}{2}\, Ta_6S(s) + S(g) \qquad (4)$$

$$Ta_6S(s) = 6\, Ta(s) + S(g) \qquad (5)$$

The enthalpies of (4) and (5) were calculated for the experimental temperature range by applying the 2nd law method, and for 298 K by both the 2nd and 3rd law methods. In a 2nd law treatment one fits a linear equation to $-\ln K_P$ vs $1/T$ to give $\Delta H^0_{T\mathrm{med}}/R$ or $(-\ln K_P - \Delta\mathrm{fef}/R)$ vs $1/T$ to give $\Delta H^0_{T\mathrm{ref}}/R$. ($T$med signifies the median temperature in the experimental range.) By contrast, $\Delta H^0_{T\mathrm{ref}}/R$ may also be calculated from each data point as $T(-\ln K_P - \Delta\mathrm{fef}/R)$ according to the 3rd law method.

Our criterion for evaluating the (T,P)-measurements is the reasonableness of the numerical results for fef's which were determined by comparison of the 2nd and 3rd law expressions for $\Delta H^0_{298}/R$ (see Appendix A.) By using our derived set of fef values for the components of $Ta_2S(s)$ and $Ta_6S(s)$ (as opposed to fef's corresponding to various combinations of tabulated $\mathrm{fef}_{Ta(s)}$ and $\mathrm{fef}_{S(s)}$), we could force agreement between the 2nd and 3rd law enthalpies. The fact that (as discussed below) the derived and tabulated partial fefs coincide within the limits expected for phase changes, and differ in the directions anticipated for these refractory, close-packed compounds, satisfies the most stringent criterion for 2nd law-to-3rd law comparison currently available for this system.

Table I summarizes the results for all experiments. The last column lists enthalpies extrapolated to $A = 0$ according to the slight orifice-dependent trend in P_S(obs) (see Appendix B for details); a single value is listed here because the 2nd and 3rd law expressions were equated for purposes of determining fef values. Plots representing the 2nd law treatment before and after this extrapolation are seen in Figs. 1a to 1d. The derived T-dependences of the monomer pressure P_S(equ) for the reactions are

Ta_2S/Ta_6S

$$\ln K_P = -\frac{51.7(3) \times 10^3}{T} + 16.0(1) \qquad (6)$$

Ta_6S/Ta

$$\ln K_P = -\frac{57.4(4) \times 10^3}{T} + 18.3(3) \qquad (7)$$

Table II lists enthalpies of formation and atomization (divided by R) in 10^3 K for

TABLE II

ENTHALPIES OF FORMATION (f) AND ATOMIZATION (at) $\Delta H^0_{298}/R$ IN 10^3 K

Phase (solid)	$\Delta H^0_{f,298}/R$ (in 10^3 K)	$\Delta H^0_{at,298}/R$ (in 10^3 K)	References
S	0	33.6(0.3)	(*6*)
TaS_3	−45.3(2.5)	60.0(0.7)	(*8*)
	−43.3(5.0)	59.5(1.3)	(*9*)
TaS_2			
(2nd)	−36.7(3.0)	66.0(1.0)	(*10*)
(3rd)	−42.6(2.0)	67.9(0.7)	
$Ta_{1+x}S_2$			
x = 0.2	−48.8(3.8)	71.5(1.2)	Estim.
x = 0.35	−50.5(4.0)	73.0(1.2)	Estim.
Ta_2S (2nd)	−21.0(0.3)	80.9(0.2)	This work
Ta_6S (2nd)	−24.5(0.5)	88.9(0.3)	This work
Ta	0	94.0(0.3)	(*7*)

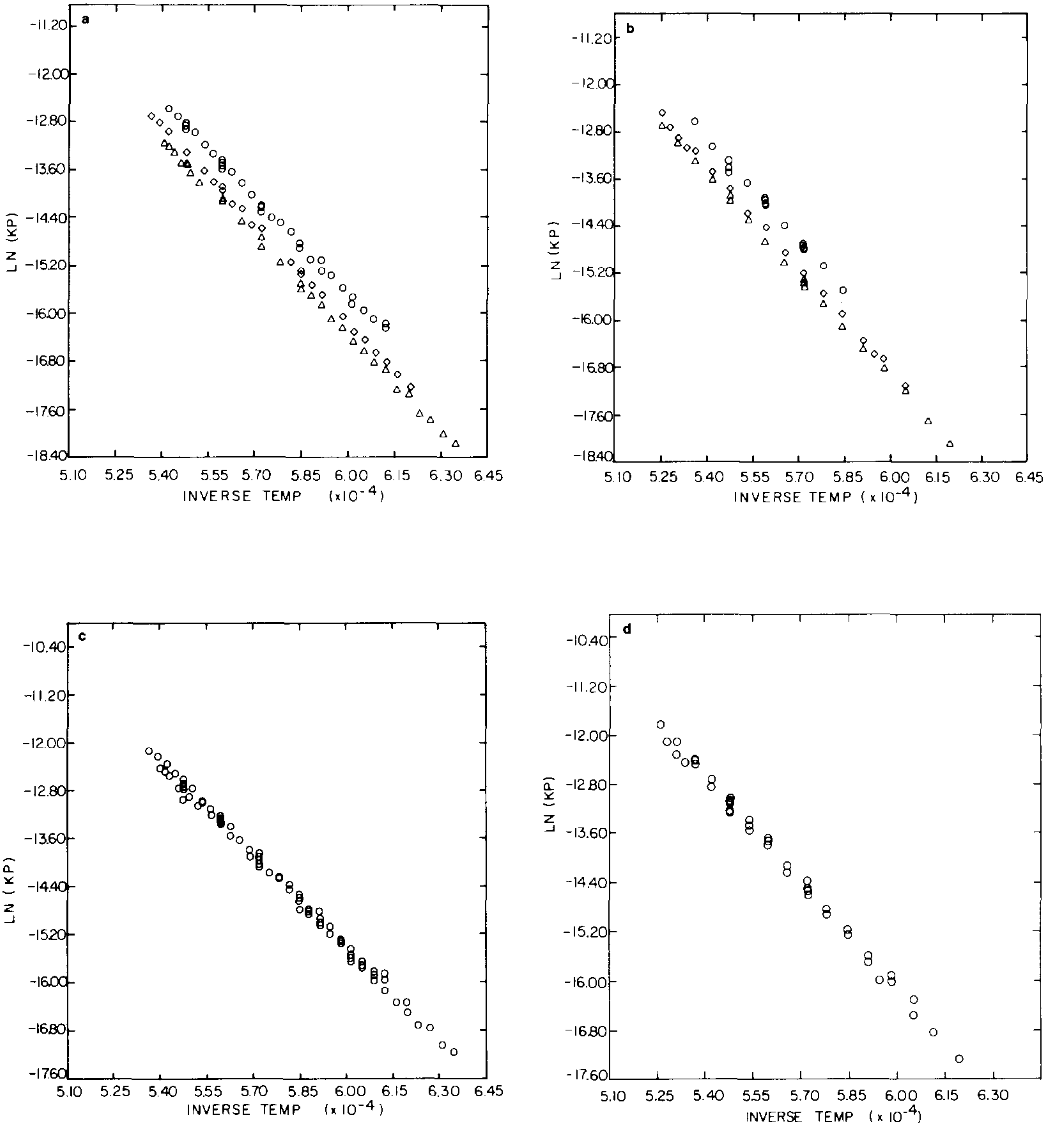

FIG. 1a. Plots ln K_p vs $1/T$ of the reaction $\frac{3}{2}\,Ta_2S(s) = \frac{1}{2}\,Ta_6S(s) + S(g)$ for three different Knudsen cell orifice sites. Key:

Symbol (Figs. 1a,1b)	Expt. No. (cf. Table I)	Orifice area (10^{-7} m^2)
○	1	1.53
△	2	12.5
◇	3	7.50

(b) ln K_p vs $1/T$ plots of the reaction $Ta_6S(s) = 6\,Ta(s) + S(g)$ for three different Knudsen cell orifice sites. (c) Results of adjusting data of Fig. 1a by extrapolating to equilibrium pressures. (d) Results of adjusting data of Fig. 1b by extrapolating to equilibrium pressures.

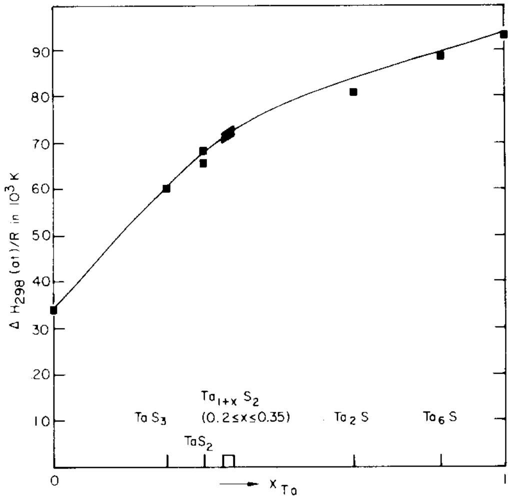

FIG. 2. Intercomparison of enthalpies of atomization in the Ta/S system.

phases in the Ta/S system. The cohesive energies are of the general form $1/(x + y)$ $Ta_xS_y(s) = x/(x + y)\,Ta(g) + y/(x + y)\,S(g)$.

Intercomparison of these quantities is seen in Fig. 2. The values for $Ta_{1-x}S_2$ represent lower limits estimated on the basis that the enthalpies for TaS_3 and TaS_2 (3rd law value) are reliable and that this nonstoichiometric phase is not metastable at 298 K.

Discussion

The calculations of new fef values for Ta and S as components of Ta_6S and Ta_2S involves two implicit assumptions. First, it forces agreement between $\Delta H^0_{298}(\text{3rd})/R$ and $\Delta H^0_{298}(\text{2nd})/R$ (at A extrapolated to 0), therein postulating that use of varying values for Δfef is the primary cause for agreement or disagreement of 2nd and 3rd law enthalpies, to obtain Δfef for the reactions. That this is appropriate, and does not inadvertently compensate for errors in measuring P_S is seen by noting that the correction for orifice-dependence in P_S(obs) (less than approximately a factor of 2) adjusts $\Delta H^0_{298}(\text{3rd})/R$ by only 1.5×10^3 K (cf. 8×10^3 if tabulated fef's used). Second, confidence is placed in $\Delta H^0_{T\text{med}}$ as a basis for these calculations; this is done both because that result is derived using only measured quantities (e.g., no fef assumptions), and because the raw data in turn show reasonable reproducibility and small random statistical error within a given experimental run. For both Ta_2S and Ta_6S, standard deviations in $\Delta H^0_{298}/R$ are generally <500 K.

In comparing the derived and tabulated (elemental) listings for fef_{Ta} and fef_S (Table III) it is seen that for the approximate T range of measurement, $\text{fef}_{Ta}(\text{der})/R$ is smaller in magnitude than $\text{fef}_{Ta}(\text{tab})/R$ by 0.4. This is of about the same size as the fef difference between *hcp* and *bcc* structures for Ti, Hf, and Ca metals. Ta in fact exhibits only the *bcc* type. The still larger discrepancy for S, $[\text{fef(tab)} - \text{fef(der)}]/R \approx 1$, seems physically reasonable if S atoms in Ta_6S or Ta_2S are considered more rigidly bonded than S atoms in orthorhombic S_8. The relatively close agreement between fef(der) and fef(tab) is taken as verification that serious temperature measurement errors do not enter into the 2nd law results. It might be overly optimistic to assume that the derived fef's are substantially correct, but the rationalizations for their magnitudes given above suggest that they are reasonable approximations.

TABLE III

COMPARISON OF DERIVED (der) AND TABULATED (tab) VALUES FOR fef_{Ta}/R AND fef_S/R IN THE SOLIDS

T (K)	fef_{Ta}/R (der)	fef_{Ta}/R (tab)	fef_S/R (der)	fef_S/R (tab)	$\Delta\text{fef}_4/R$	$\Delta\text{fef}_5/R$
1400	−7.02	−7.403	−5.68	−6.723	−16.56	−18.87
1500	−7.20	−7.583	−5.87	−6.984	−16.52	−18.83
1600	−7.37	−7.754	−6.03	7.241	−16.49	−18.80
1700	−7.53	−7.918	−6.19	−7.494	−16.46	−18.77
1800	−7.69	−8.076	6.35	−7.744	−16.43	−18.75
1900	−7.84	−8.225	−6.49	−7.991	16.41	−18.73
2000	−7.99	−8.374	−6.62	−8.235	16.39	18.70

Note. The Δfef/*R* for reactions (4) and (5) employed for the derivation are also listed.

As depicted in Fig. 2, ΔH^0_{298}(at) per atom for the metal-rich compounds is larger than that for sulfur-rich compounds of the same system. By contrast the stability of Ta_2S or Ta_6S with respect to the elements, represented by the vertical distance between the straight line (Ta to S) and the curved line (passing through stable compounds) is smaller than for compounds to their left. It may also be seen that Ta_2S and Ta_6S are metastable at room temperature (as they fall below the straight line connecting adjacent phases), i.e., thermodynamics alone predicts each should disproportionate into the neighboring phases. However, annealing at above 1270 K for 3 days did not convert Ta_2S into $Ta_{1.35}S_2$ + Ta. The kinetic barrier allowing for the metastability of Ta_6S could be overcome in a separate experiment, by using I_2 as a transport agent. In this test X-ray powder patterns showed the presence of $Ta_{1.35}S_2$ and Ta after the reaction of Ta_6S with I_2 at 1220 K for 2 days.

Although Ta_2S decomposes to a phase whose metal substructure is quite similar (Ta_6S), and Ta_6S in turn rearranges to a quite dissimilar metal structure (*bcc* Ta), there is not a remarkable difference in $\Delta H^0_{298}/R$ for the two reactions.

Our suggestions for possibly useful further studies include: (i) measurement of the heat capacity for Ta_2S and Ta_6S to provide corroboration for the fef(T) results described herein, (ii) verification of and determination of crystal structure for the postulated second (lower T) modification of Ta_6S, which could help to complete the Ta-rich region of the phase diagram, and (iii) determination of ΔH^0_{298} for $Ta_{1.35}S_2$, which to date has been only estimated, in order to strengthen our knowledge of relative stabilities of compounds in the system.

Appendix A

To obtain fef's for Ta and S as components of Ta_2S and Ta_6S such that 2nd and 3rd law results agree, we have done the following:

(i) Write expressions for 2nd and 3rd law T-dependence of ΔG

$$\Delta G^0_T/R = \Delta H^0_{T\text{med}}/R - T\Delta S^0_{T\text{med}}/R \qquad \text{2nd law} \quad \text{(A1)}$$

in which $\Delta H^0_{T\text{med}}/R$ and $\Delta S^0_{T\text{med}}/R$ are the slope and intercept, respectively, resulting from a linear least-squares fit

$$\begin{aligned}\Delta G^0_T &= \Delta H^0_{T\text{ref}} - T\Delta \text{fef}_T \\ &= \Delta H^0_{T\text{med}} + \int_{T\text{med}}^{T\text{ref}} \Delta C^0_p \, dT + T\Delta\text{fef}_T \end{aligned} \qquad \text{3rd law.} \quad \text{(A2)}$$

(ii) Approximate ΔC^0_p by $C^0_{p\text{S(g)}} - C^0_{p\text{Ta(s)}}$ (6) for both reactions (4) and (5), let Tref = 298 K and Tmed = 1720 K and equate (A1) with (A2) to yield

$$\Delta\text{fef} = -1/T \int_{T\text{med}}^{T\text{ref}} [C^0_{p\text{S(g)}} - C^0_{p\text{Ta(s)}}] \, dT - \Delta S^0 \quad \text{(A3)}$$

(this was done by graphical integration using tabulated $C^0_{p\text{Ta(s)}}$ values, yielding

$$\int_{T\text{med}}^{T\text{ref}} \Delta C^0_p \, dT/R = 0.77 \times 10^3 \, K).$$

(iii) Write expressions for Δfef corresponding to (4) and (5) in terms of both tabulated and unknown values for species

$$\Delta\text{fef} = \text{fef}_{\text{S(g)}} - y \quad \text{(A4)}$$

$$\Delta\text{fef} = 6 \times [\text{fef}_{\text{Ta(s)}} - x] + \text{fef}_{\text{S(g)}} - y. \quad \text{(A5)}$$

Here x is the unknown fef for Ta as a component in the solid compounds and y signifies the same property of S.

(iv) Evaluate (A3) for both reactions (4) and (5) at temperatures spanning 1400 to 2000 K in increments of 100 K, then equate these numerical results with corresponding expressions according to (A4) and (A5), yielding two equations which can be solved for x and y at each T. Both x and y are listed as "fef_{Ta}(der)" and "fef_{S}(der)" in Table IV, where we compare the results to related published values.

Appendix B

We account for the orifice dependence of P_S(obs) by postulating a relationship between rate of vaporization and deviation from equilibrium P_S(equ)

$$P_S(\text{obs}) = P_S(\text{equ}) - a(dm/dt) \quad \text{(B1)}$$

in which we neglect higher order terms in the expansion of P_S(obs) in dm/dt, the differential form of rate-of-mass-loss. Substituting (2) for dm/dt yields

$$P_S(\text{obs}) = P_S(\text{equ}) - a'A[P_S(\text{obs}) + \sqrt{2}P_S^2(\text{obs})/K_P] \quad \text{(B2)}$$

where $a' = a(2\pi RT/M_S)^{-1/2}$. The a' is determined at each of five selected experimental T_i spanning the measured range by fitting (B2) to $\{A[P_S(\text{obs}) + \sqrt{2}P_S^2(\text{obs})/K_P], P_S(\text{obs})\}$ data pairs. The T-dependence of a' is found by fitting a straight line to a' vs $T_i^{-1/2}$. The extrapolated value P_S(equ) for each temperature is then calculated from the fitting equation mentioned above.

Acknowledgments

The Ames Laboratory-DOE is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Material Sciences Division.

References

1. F. Jellinek, *J. Less-Common Met.* **4**, 9 (1962).
2. H. F. Franzen and J. G. Smeggil, *Acta Crystallogr. Sect. B* **25**, 1736 (1969).
3. H. F. Franzen and J. G. Smeggil, *Acta Crystallogr. Sect. B* **26**, 125 (1970).
4. R. A. Schiffman, H. F. Franzen, and R. J. Ziegler, *High Temp. Sci.* **15**, 69 (1982).
5. M. Knudsen, *Ann. Phys.* **29**, 179 (1909).
6. "JANAF Thermochemical Tables" (D. R. Stull and H. Prophet, Eds.) (1971).
7. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleisser, K. K. Kelley, and D. D. Wagman, "Selected Values of the Thermodynamic Properties of the Elements," Metals Park, Ohio (1973).
8. W. Biltz and A. Köcher, *Z. Anorg. Allg. Chem.* **238**, 81 (1938).
9. D. Kubaschewki, E. U. Evans, and C. B. Alcock, "Metallurgical Thermochemistry," p. 220, Pergamon, Oxford (1967).
10. H. R. Larson and J. F. Elliott, *Trans. AIME* **239**, 1713 (1967).