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MASTER

Sm and Gd

VAPOR PRESSURES OF SAMARIUM AND GADOLINIUM

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DISCLAIMER

ABSTRACT

The vapor pressures of solid samarium and liquid gadolinium were determined in the temperature range of 1033 to 1302°K and 1623 to 1784°K, respectively. Employed in this investigation was the Knudsen effusion method in which the weight-loss data of the effusion cells were used to calculate the vapor pressures. The data are represented as follows:

$$\alpha\text{-Sm } (1033\text{-}1173^{\circ}\text{K}) \qquad \log_{10} P_{(\text{mm Hg})} = -\frac{11{,}900 \pm 300}{T} + 9.71 \pm 0.24$$

$$\beta\text{-Sm } (1202\text{-}1302^{\circ}\text{K}) \qquad \log_{10} P_{(\text{mm Hg})} = -\frac{11{,}400 \pm 200}{T} + 9.30 \pm 0.21$$

$$\text{Liquid Gd } (1623\text{-}1784^{\circ}\text{K}) \qquad \log_{10} P_{(\text{mm Hg})} = -\frac{14{,}740 \pm 424}{T} + 8.51 \pm 0.25$$

The heats of sublimation for samarium were obtained from the slopes of the above equations. For alpha-samarium the heat of sublimation is 54.45 ± 1.37 kcal/mole and for beta-samarium, 52.17 ± 0.92 kcal/mole. The average ΔH°_{298} values for alpha- and beta-samarium, computed using the third law method, are 48.92 ± 0.09 and 48.10 ± 0.11 kcal/mole, respectively. The heat of transition for the metal is thus 820 cal/mole.

The heat of vaporization for liquid gadolinium obtained similarly is 67.45 ± 1.9 kcal/mole.

INTRODUCTION

In conjunction with a thermodynamic study of the samarium-gadolinium alloy system, a knowledge of the vapor pressures of the two component metals, samarium and gadolinium was required. However, a literature survey revealed very little direct experimental data are available for either metal, although vapor pressure data based on theoretical thermodynamic calculations exist for gadolinium (1, 2) and samarium (2). Vapor pressure data for samarium were quoted by Hultgren, et al. (3) who evaluated and computed the mass spectrometric results reported by Savage and his colleagues (4). More recently, scanty experimental data for gadolinium by the Knudsen effusion method appeared in an Annual Research Report, Ames Laboratory, Iowa State University, Ames, Iowa (5). Therefore, it was imperative to undertake more comprehensive determinations of the vapor pressures of these two metals. The vapor pressure data for samarium and gadolinium were obtained in the temperature ranges from 1350 to 1511°K and from 1623 to 1784°K, respectively.

EXPERIMENTAL

Both samarium and gadolinium metals of special high-purity grade were purchased from the Ames Laboratory, Iowa State University, Ames, Iowa. The metals were purified by vacuum distillation, and their chemical analysis data furnished by the supplier are given in Table I.

Knudsen effusion cell charges were prepared by carefully sectioning and, if necessary, filing the supplied metals into a few large pieces to fit in the tantalum crucible immediately prior to welding of the lid. The effusion cell would subsequently be placed in the effusion apparatus under vacuum in the order of 4×10^{-7} mm Hg for about 12 hours before the first melting.

The Knudsen effusion cells were made of tantalum. The design of the cells is described elsewhere (6). The notable exception to the previous design is that tungsten lids had to be used for determining the vapor pressure of gadolinium. It was found earlier that the gadolinium vapor attacked the lids made of tantalum rather readily. However, the tungsten lids were resistant to the reaction with the vapor, and their knife-edged orifices were intact throughout the experiment. Only one orifice size, 0.0523 cm in diam, was employed in the vapor pressure measurements for the solid samarium while two different sized orifices, 0.0973 and 0.0706 cm in diam, were used for determination of the liquid gadolinium vapor pressure.

The direct crucible-weighing method was used in this study to calculate the vapor pressures of both solid samarium and liquid gadolinium. The weights of the Knudsen effusion cells before and after each run was determined using a Mettler microbalance with the reported accuracy of ± 0.1 mg.

Since the furnace assembly, temperature control, temperature measurements with the tungsten/tungsten-25% rhenium thermocouples and the vacuum attainable were reported in detail at the Second Conference on Rare-Earth Research (6), only the pertinent information is given in this paper.

The fluctuations at the experimental temperatures were less than ± 3°C, and temperature drifts observed in the long-term runs were in the order of 0.5°C/hr. The accuracy of the tungsten/tungsten-25% rhenium thermocouples was less than ± 3°C over the calibrated temperature range from 700 to 1500°C. Integrity of the thermocouple was checked after each vapor-pressure determination whenever the thermal arrests due to melting, transformation or both could be observed. The vacuum observed at the experimental temperatures was in the order of 1 to 4 x 10^{-7} mm Hg.

RESULTS AND DISCUSSION

The vapor pressures of solid samarium and liquid gadolinium were determined by the Knudsen effusion method in which the weight-loss data of the effusion crucibles and the well known Knudsen relation (6) were used. The vaporizing species of samarium and gadolinium were considered as monatomic. The vapor pressure data combined with free energy functions taken from the compilation by Hultgren and his colleagues allow computation of the third law heats of vaporization at 298°K.

The vapor pressure data for samarium are tabulated in Table 2. Because of its high volatility, determination of the vapor pressures of the solid metal was made possible in both the low-temperature modification (α) and high-temperature modification (β). Seven data points were obtained in the low-temperature allotropic phase while six points were determined in the high-temperature phase using a single effusion cell. The plot of $\log_{10} P_{(\text{mm Hg})}$ vs. $1/T$ (°K) for alpha- and beta-samarium is shown in Figure 1. A least-squares treatment of the data gives the following equations in the two temperature ranges as indicated:

$$\alpha\text{-Sm } (1033\text{-}1173^\circ\text{K}) \qquad \log_{10} P_{(\text{mm Hg})} = -\frac{11{,}900 \pm 300}{T} + (9.71 \pm 0.24) \tag{1}$$

$$\beta\text{-Sm } (1202\text{-}1302^\circ\text{K}) \qquad \log_{10} P_{(\text{mm Hg})} = -\frac{11{,}400 \pm 200}{T} + (9.30 \pm 0.21) \tag{2}$$

The known experimental and theoretical vapor pressure data for samarium are compared below:

Pressure mm Hg	Temperature, °C		
	L. C. Beavis (2)	This Study	Savage et al. (4)
1.0	957	954	974
10^{-1}	827	838	844
10^{-2}	727	738	742

It is obvious that all three data are in good agreement.

The heats of sublimation were calculated from the slopes of Equations 1 and 2. The values obtained for α- and β-samarium are 54.46 ± 1.37 and 52.17 ± 0.92 kcal/mole, respectively. The average ΔH^{0}_{298} values computed using the third law method for α- and β-samarium, are 48.92 ± 0.09 and 48.10 ± 0.11 kcal/mole. These values compare favorably with 49.56 ± 0.6 kcal/mole in the temperature range from 798 to 833°K, selected by Hultgren et al. (3) from the mass spectrometric data reported by Savage, Hudson and Spedding (4) and also with 46 kcal/mole presented by Spedding and Daane (7).

The intercept of the slopes of Equations 1 and 2 gives the transition temperature of α- to β-samarium as 946.3°C. The transition temperature determined by thermal analysis in this study was 911.5°C. Spedding, McKeown and Daane (8) report the transition temperature of samarium to be 917°C.

Vapor pressure data for gadolinium are as meager and incomplete in the literature as those for samarium. This investigation produced thirteen data points in the temperature range from 1623 to 1784°K which are tabulated in Table 3. Two cells with tungsten lids of 0.0973 and 0.0706 cm orifices were used in the study. A plot of these data are also shown in Figure 2. Equation 3 represents the vapor pressure of liquid gadolinium obtained after treating the data with a least-squares method:

$$\text{Liquid Gd } (1623\text{-}1784^{\circ}\text{K}) \quad \log_{10} P_{(\text{mm Hg})} = -\frac{14{,}740 \pm 424}{T} + (8.51 \pm 0.25) \qquad (3)$$

The comparison is made among the vapor pressure data, experimental and theoretical, as follows:

Pressure mm Hg	Temperature, °C L. C. Beavis (2)	 This study	 Ames Lab. (5)
10^{-2}	1327	1457	1595
10^{-3}	1178	1277	1433
10^{-4}	1077	--	1295

As can be seen from the above, the vapor pressure data for gadolinium are in wide disagreement. The three data are apart approximately by one order of magnitude.

Second-law treatment of the data gives the heat of vaporization of 67.45 ± 1.9 kcal/mole. This is quite smaller than 89.5 kcal/mole reported by Ames Laboratory (5) but is in fair agreement with 72 kcal/mole quoted by Spedding and Daane (7). Lack of the reliable free energy functions for gadolinium did not permit a third-law calculation of ΔH^{o}_{298}. However, the following ΔH^{o}_{298} values are found in the literature : 83.6 kcal/mole (9) and 81.2 kcal/mole (10).

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TABLE 1

Impurity	Sm	Gd
C	30 ppm	150 ppm
N_2	<25 ppm	100 ppm
O_2	--	--
F	<17 ppm	800 ppm
Ti	--	--
Fe	0.002%	0.01%
Y	VW	--
Pr	--	--
Nd	≦ 0.02%	--
Sm	--	--
Eu	≦ 0.01%	--
Gd	≦ 0.01%	--
Yb	VFT	--
Ca	0.05%	<0.005%
Si	--	<0.025%
Mg	--	≦0.02%
Ta	--	<0.05%

No other rare
earth metals
were detected

TABLE 2

Samarium Vapor Pressure Data

Temperature °K	Time min	Weight Loss mg	-log P(atm)	ΔH^{o}_{298} Kcal/mole
		β-Samarium		
1302.2	19.28	182.8	2.319	47.71
1270.2	33.01	185.7	2.559	47.95
1243.2	46.60	174.8	2.738	47.96
1228.2	59.50	162.1	2.866	48.20
1213.2	70.58	138.2	3.015	48.45
1202.2	83.10	147.9	3.070	48.33
			Avg.	48.10
			S.D.	±0.11
		α-Samarium		
1173.2	82.50	77.7	3.346	48.70
1148.2	78.90	48.1	3.526	48.64
1125.2	101.16	40.6	3.721	48.71
1117.2	109.48	31.9	3.852	49.06
1097.2	108.50	22.6	4.002	48.95
1075.2	184.00	23.2	4.234	49.15
1033.2	214.32	10.5	4.649	49.26
			Avg.	48.92
			S.D.	±0.09

TABLE 3

Liquid Gadolinium Vapor Pressure Data

Temperature °K	Time min	Weight Loss mg	Orifice Diameter at Room Temp., cm	$-\log P_{(atm)}$
1784.2	61.76	4.6	7.061×10^{-2}	4.625
1774.2	66.61	4.0	7.061×10^{-2}	4.720
1753.7	91.53	4.7	7.061×10^{-2}	4.790
1721.2	93.51	3.4	7.061×10^{-2}	4.944
1681.2	130.80	3.2	7.061×10^{-2}	5.121
1651.2	180.93	3.2	7.061×10^{-2}	5.266
1642.2	175.10	2.5	7.061×10^{-2}	5.360
1764.2	160.00	19.7	9.728×10^{-2}	4.686
1740.2	181.41	16.8	9.728×10^{-2}	4.813
1703.2	188.90	11.8	9.728×10^{-2}	4.988
1671.7	254.05	10.2	9.728×10^{-2}	5.184
1624.2	415.50	9.9	9.728×10^{-2}	5.417
1623.2	95.00	1.9	9.728×10^{-2}	5.493

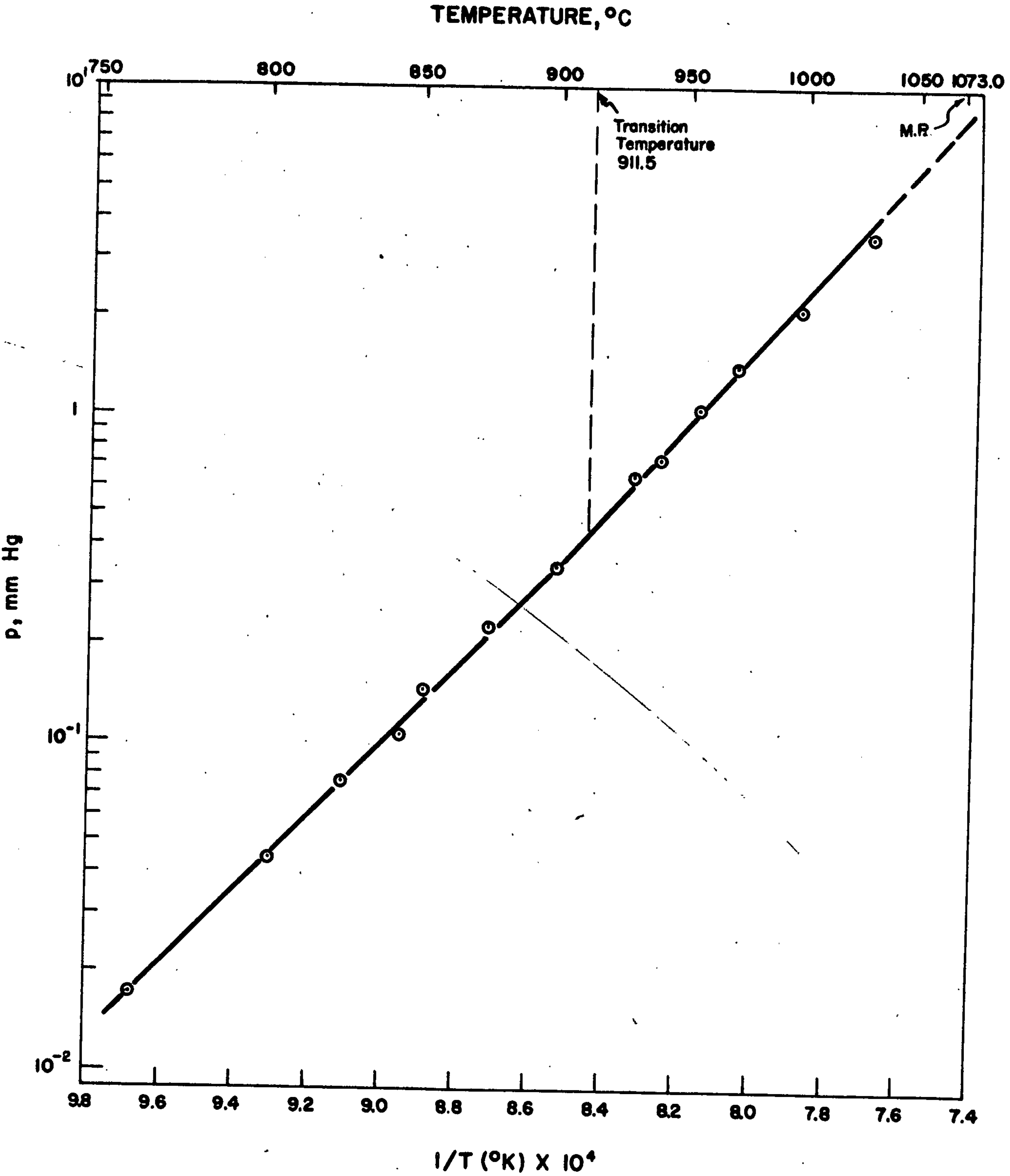

Figure 1. Log_{10} P vs. 1/T for Samarium

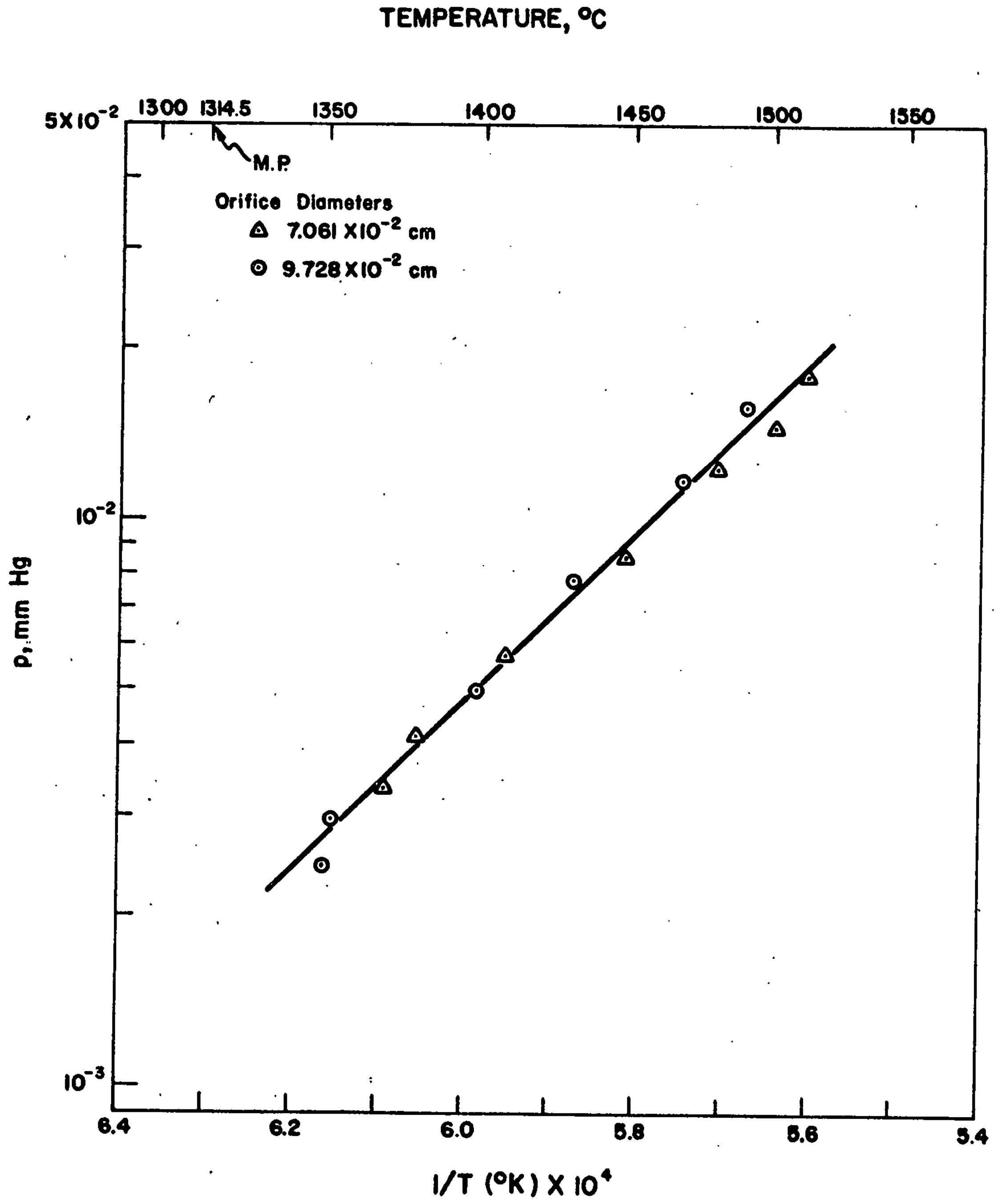

Figure 2. Log_{10} P vs. 1/T for Gadolinium