

ments on carbon dioxide and ethane by Reamer et al. (5, 6). Over most of the region, agreement between the two sets of data is very close.

Nomenclature

B, C = second and third virial refractivity coefficients, respectively
 ρ = density, g/cc
 M = molecular weight
 n = refractive index at 6328Å relative to vacuum
 R_{LL} = Lorentz-Lorenz molar refractivity, cc/g-mol
 R_{LL}^0 = zero density limit of the molar refractivity at 6328Å
 V = molar volume, cc/g-mol

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Vapor Pressure of α -Samarium and α -Ytterbium

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The torsion-effusion method was used to determine the vapor pressure of α -samarium and α -ytterbium in the temperature range 1043–1179K and 775–907K, respectively. The proposed heat of sublimation at 298K, obtained as an estimated average between our second- and third-law values, was 49.56 ± 0.50 and 37.20 ± 0.40 kcal/mol for α -samarium and α -ytterbium, respectively.

Few data on the vapor pressure of α -samarium and α -ytterbium are reported in the literature (3, 4, 6, 9, 10). A new series of tensimetric data, obtained by the Knudsen torsion-effusion method, is given in this paper. The basis of the method and the experimental apparatus have been described elsewhere (7, 8). Vapor pressures were calculated from the torsion-effusion data by means of the equation

$$P = 2 K \beta / (a_1 d_1 f_1 + a_2 d_2 f_2) \quad (1)$$

where P is the pressure; β the deflection; K the torsion constant of the suspension; a_1 , a_2 , d_1 , and d_2 the orifice area and distances from the axis of rotation; and f_1 and f_2 the Freeman and Searcy (1) correction factor for orifice geometry.

The metals were vaporized from tantalum cells placed in the constant-temperature zone of the furnace. The samarium and ytterbium samples were from Koch-Light Lab certified to be at least 99% pure with respect to total impurities. The loading of the cell was carried out with samples (~1 gram) mechanically cleaned and reduced to small pieces (~2 mm) to increase the evaporating surface. Loading in inert atmosphere was not necessary (4). An ambient vacuum less than 10^{-5} mm Hg was maintained during the runs. The temperature of the operating cell was taken to be the temperature determined by a calibrated iron-constantan thermocouple placed inside an identical but empty cell located directly beneath the operating cell. This procedure was tested putting a second thermocouple in the operating cell and measuring the differences in emf values. All the temperature uncertainties were estimated to be $\pm 2^\circ\text{C}$ at about 1200K. The effusion cell was suspended on a 30- μ diam

tungsten wire, 33.0 cm long, with a torsion constant of 0.358 ± 0.004 dyn cm/rad. The details of the effusion cells are given as a footnote in Table I.

The vapor pressures of α -samarium and α -ytterbium, determined in the temperature range 1043–1179K and 775–907K, respectively, are reported in Table I, considering the vapor constituted by a monoatomic species only (10). The corresponding values of ΔH_{298}° (subl) of both elements, calculated using the free energy function, $(G_T^\circ - H_{298}^\circ)/T$, (fef), selected by Hultgren et al. (5), are reported in the same table. The average third-law ΔH_{298}° (subl) values for Sm and Yb are 49.60 ± 0.20 and 37.01 ± 0.11 kcal/mol, respectively, where the associated errors are standard deviations. The least-squares lines through the pressure data over the experimental temperature range are given by the equations:

$\log P$ (atm) =

$$5.33 \pm 0.19 - \frac{(10.39 \mp 0.21) \times 10^3}{T}, \text{ samarium} \quad (2)$$

$\log P$ (atm) =

$$5.61 \pm 0.17 - \frac{(7.97 \mp 0.14) \times 10^3}{T}, \text{ ytterbium} \quad (3)$$

The lines are drawn in Figure 1 and the relative slopes give the sublimation enthalpy values, ΔH_{298}° (Sm) =

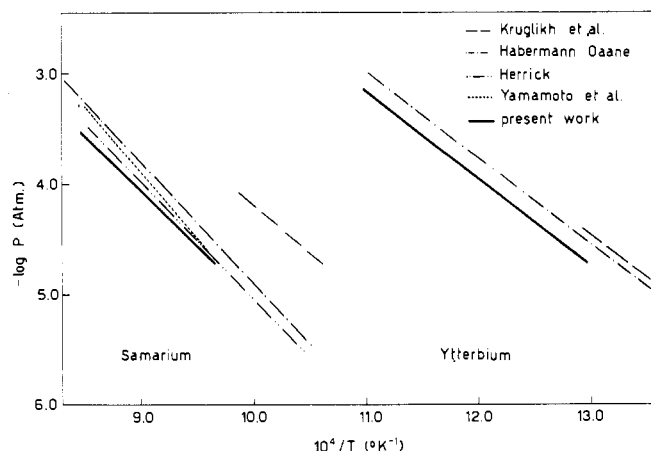


Figure 1. Vapor pressure of solid samarium and ytterbium

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Table I. Vapor Pressure and ΔH_{298}° (subl) Values for Samarium and Ytterbium^a

T, K	P, atm	$-\Delta[\text{fef}], \text{e.u.}$	$\Delta H_{298}^{\circ}, \text{kcal/mol}$	T, K	P, atm	$-\Delta[\text{fef}], \text{e.u.}$	$\Delta H_{298}^{\circ}, \text{kcal/mol}$
Samarium				Ytterbium			
Cell A				Cell A			
1076	5.22×10^{-5}	26.34	49.42	791	3.85×10^{-5}	26.39	36.85
1098	8.10×10^{-5}	26.31	49.44	807	5.66×10^{-5}	26.36	36.96
1103	9.21×10^{-5}	26.30	49.38	810	6.15×10^{-5}	26.36	36.96
1113	1.11×10^{-4}	26.28	49.39	810	5.94×10^{-5}	26.36	37.01
1121	1.03×10^{-4}	26.27	49.91	815	6.51×10^{-5}	26.35	37.09
1130	1.57×10^{-4}	26.26	49.34	827	1.04×10^{-4}	26.34	36.85
1131	1.66×10^{-4}	26.25	49.25	831	1.01×10^{-4}	26.33	37.07
1141	1.93×10^{-4}	26.24	49.34	836	1.23×10^{-4}	26.32	36.97
1153	1.91×10^{-4}	26.22	49.85	846	1.58×10^{-4}	26.30	36.96
1153	1.90×10^{-4}	26.22	49.86	851	1.73×10^{-4}	26.30	37.02
1154	1.94×10^{-4}	26.22	49.86	853	1.99×10^{-4}	26.29	36.87
1154	2.21×10^{-4}	25.22	49.56	857	2.06×10^{-4}	26.29	36.99
1159	2.23×10^{-4}	26.21	49.74	858	2.19×10^{-4}	26.29	36.93
1160	2.76×10^{-4}	26.21	49.28	860	2.16×10^{-4}	26.28	37.02
1170	2.79×10^{-4}	26.19	49.67	860	2.22×10^{-4}	26.28	36.98
1171	2.83×10^{-4}	26.19	49.68	874	3.01×10^{-4}	26.20	37.03
				875	3.02×10^{-4}	26.26	37.07
				877	3.03×10^{-4}	26.25	36.99
				885	3.55×10^{-4}	26.24	37.19
				885	3.43×10^{-4}	26.24	37.25
				889	4.15×10^{-4}	26.24	37.08
				905	6.42×10^{-4}	26.21	36.93
				907	6.44×10^{-4}	26.21	37.01
Cell B				Cell B			
1043	2.18×10^{-5}	26.39	49.77	775	2.08×10^{-5}	26.42	37.08
1050	3.01×10^{-5}	26.38	49.43	789	2.93×10^{-5}	26.40	37.19
1057	3.15×10^{-5}	26.37	49.65	798	3.65×10^{-5}	26.38	37.25
1063	3.15×10^{-5}	26.36	49.92	799	3.86×10^{-5}	26.38	37.21
1077	4.66×10^{-5}	26.34	49.72	801	3.94×10^{-5}	26.38	37.27
1081	5.01×10^{-5}	26.33	49.73	829	1.15×10^{-4}	26.33	36.78
1085	5.96×10^{-5}	26.33	49.55	839	1.44×10^{-4}	26.32	36.83
1086	5.81×10^{-5}	26.33	49.64	839	1.39×10^{-4}	26.32	36.89
1092	6.52×10^{-5}	26.31	49.64	848	1.75×10^{-4}	26.30	36.88
1109	9.81×10^{-5}	26.29	49.49	863	2.51×10^{-4}	26.28	36.90
1111	9.65×10^{-5}	26.29	49.62	863	2.48×10^{-4}	26.28	36.91
1114	9.65×10^{-5}	26.28	49.74	879	2.98×10^{-4}	26.25	37.21
1120	1.07×10^{-4}	26.27	49.78				
1120	1.22×10^{-4}	26.27	49.48				
1123	1.22×10^{-4}	26.27	49.62				
1137	1.77×10^{-4}	26.24	49.36				
1179	3.33×10^{-4}	26.18	49.63				

Av value 49.60 ± 0.20

Av value 37.01 ± 0.11

^a Physical constants of the cells: A, effusion holes area ($\text{cm}^2 \times 10^{-3}$): 13.2 and 12.3; moment arm (cm): 1.05 and 1.04; correction factor: 0.646 and 0.651. B, effusion holes area ($\text{cm}^2 \times 10^{-3}$): 14.3 and 13.5; moment arm (cm): 1.06 and 1.07; correction factor: 0.631 and 0.643.

49.49 ± 0.96 kcal/mol and ΔH_{298}° (Yb) = 37.62 ± 0.66 kcal/mol, corrected to 298K using the heat content reported in literature (5).

The estimated average values between our second- and third-law values, $\Delta H_{298}^{\circ} = 49.56 \pm 0.50$ kcal/mol for Sm and $\Delta H_{298}^{\circ} = 37.20 \pm 0.40$ kcal/mol for Yb, are proposed considering more reliable the third-law value. A comparison with the selected values by Hultgren et al. (5), $\Delta H_{298}^{\circ} = 49.400 \pm 0.500$ kcal/mol and $\Delta H_{298}^{\circ} = 36.350 \pm 0.200$ kcal/mol shows a good agreement especially for samarium. As concerns ytterbium, we believe that the selected value is slightly low; this seems supported by the comparison with the recent mass spectrometric value $\Delta H_{298}^{\circ} = 36.9 \pm 0.7$ kcal/mol deduced from $\Delta H_0^{\circ} = 37.0 \pm 0.7$ kcal/mol, reported by Guido and Balducci (2).

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