Vapor Pressure of Dysprosium and Erbium

JAMES M. McCORMACK[1], PETER R. PLATT[2], and RICHARD K. SAXER
Department of Engineering Mechanics, U. S. Air Force Academy, Colo.

The Knudsen effusion technique was used to determine the equilibrium vapor pressure of solid high-purity dysprosium in the temperature range 1239–1534° K and the vapor pressure of solid high-purity erbium in the range 1352–1587° K. The average heat of sublimation of 298° K was calculated to be 69,600 ± 140 cal/mole for dysprosium and 75,510 ± 130 cal/mole for erbium.

Vapor pressure data for dysprosium and erbium in the recent literature show discrepancies between reported values. The present work, based on the Knudsen effusion technique, was undertaken to resolve some of the conflicts in the reported data. The vapor pressures obtained during this study are in excellent agreement with the previous findings of Habermann and Daane (*7*) and extend the range of reliable data to lower temperatures.

Experimental Equipment Procedure. The Knudsen effusion method, developed from statistical thermodynamics and kinetic theory, postulates that the rate of effusion from an enclosed cell through an orifice into a vacuum is related to the vapor pressure of the metal within the cell. This relationship (*9, 15*) is expressed as

$$P = (W/At)(2\pi RT/M)^{1/2} = \dot{m}\, 2.258 \times 10^{-2}\, (T/M)^{1/2} \qquad (1)$$

In these expressions, P is the vapor pressure, atm; W is the weight loss in grams during the effusion time interval; A is the orifice area, cm^2; R is the universal gas constant in cgs units; T is the temperature, ° K; t is the total effective time at temperature T; M is the molecular weight of the effusant; and $\dot{m}$ is the effusion rate in grams/sec/cm^2. A monatomic vapor specie was assumed (*22*).

In Equation 1, the orifice is assumed to be ideal—i.e., zero thickness. In actual practice, the orifice does have measurable thickness and approximates a short tube or channel. Speiser (*18*) has compiled factors based on orifice geometry to correct for this condition. In this work, the need for correction was avoided by reaming the orifice with a machinist's bit to a knife edge of 30° included angle. Calculations based on Balson's derivation (*1*) indicated that the orifice was nearly ideal.

Tantalum was selected as the cell material to avoid problems of cell-specimen reaction (*4*). Cell bases and lids were die-formed from 0.010-in. thick tantalum sheet and welded to the tubular body. Welding was done in an argon atmosphere to preclude oxidation. The orifice diameters used in this study were 0.1514 cm for dysprosium and 0.1660 cm for erbium. Measurements were made with the microscope and micrometer stage of a microhardness tester.

The water-cooled vacuum chamber was constructed from a 6-in. diameter stainless steel cylinder. A mechanical forepump, oil diffusion pump, and liquid nitrogen cold trap were used to create an operating vacuum of at least 1 × 10^{-6} torr.

A molybdenum wire-wound resistance-type furnace provided operating temperatures. Tantalum radiation shields surrounded the furnace to improve thermal isolation. Power was supplied to the furnace by means of a constant voltage transformer.

Temperatures were measured with a Leeds and Northrup disappearing filament-type optical pyrometer in preference to a thermocouple system. All measurements were made at the orifice of the cell, which is effectively a "hohlraum," to eliminate the need for cell emissivity corrections. The pyrometer was calibrated against a Bureau of Standards pyrometer by means of a tungsten ribbon filament lamp. The calibration was performed with viewing window in place to avoid corrections for window transmissibility. A manually controlled rotary shutter shielded the viewing window from the vapor source. Periods with open shutter were kept short to minimize vapor deposition. The absence of any apparent drift to lower observed temperatures after equilibrium was attained indicated that vapor condensation on the window was not a problem. Temperature measurements with a thermocouple in contact with the cell also were tried, but proved unsatisfactory. The thermocouple leads acted as a heat short to conduct heat away from the hot junction. The apparent temperature seen at the hot junction was consistently low by 40–60° C when compared to pyrometer readings. These results indicate thermocouple measurements made in small furnaces tend to be unreliable unless extreme care is taken to avoid shorts (by increasing the lead length in the furnace hot zone) or unless the thermocouple is recalibrated in situ.

Effective times at temperature were calculated to compensate for heating and cooling periods. The effective time was calculated from the following equation (*12*):

$$t_{\text{eff}} = \sum \Delta t_i [e^{-\Delta H_T / RT_A} + \Delta H_T / RT_R] \qquad (2)$$

where Δt_i is the real time interval between any two successive temperature measurements, T_A is the average temperature during that interval, T_R is the temperature of the experimental run, ΔH_T is the heat of sublimation of the metal specimen. Equation 2 is used to convert a real time interval at a T_A not equal to T_R, to an effective time interval at T_R. For example, 60 sec real time at T_A = 1426° K is equivalent to 36 sec effective time at T_R = 1457° K. The effect of time correction was minimized by maintaining short heating and cooling periods relative to the length of time where T_A was identical to T_R.

The analysis of the dysprosium and erbium used in this work is given in Table I. The specimens were placed directly in the tantalum cell. Alumina crucibles reacted severely with the rare earth specimens in preliminary trials and were not used in subsequent work. Weight losses were obtained from direct weighings on an Ainsworth balance before and after each test. No surface diffusion at the orifice was observed that could effect weight loss.

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[1] To whom correspondence should be addressed.

[2] Present address, Columbus AFB, Miss.

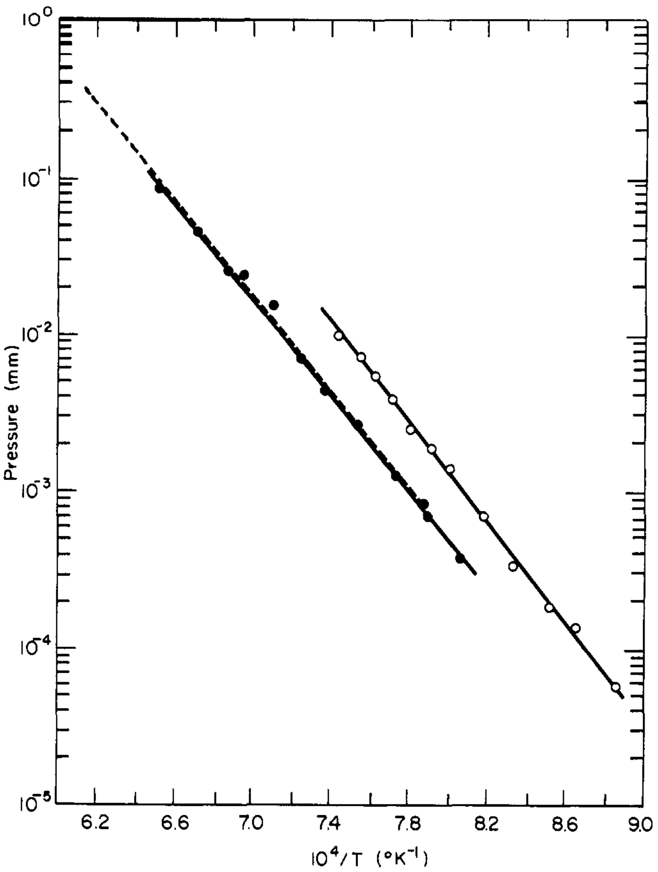

Figure 1. Vapor pressure of solid dysprosium

-●- This work
----- Habermann and Daane (*7*)
-○- Kovtun et al. (*10*)

Vapor pressure calculations and least-square curve fitting of data to an equation of the form

$$\ln P = -A/T + B \qquad (3)$$

were preformed on a Burroughs B5500 digital computer. Initial ΔH_T values used in effective time calculations were 68,200 and 67,000 cal/mole for dysprosium and erbium, respectively. Iterative calculations with refined values of ΔH_T were made of effective times, vapor pressures, and least-square curve adjustments until the ΔH_T obtained from the slope of ln P vs. $1/T$ was insignificantly different from the refined value used in computations.

Experimental data were determined to the following accuracy: weight loss, ±0.05 mg; temperature, ±4° C; effective time, ±60 sec; orifice diameter, ±0.0004 cm. Orifice dimensions were corrected for thermal expansion (*2*) in the computer program. The uncertainty in these measurements create an error of 1.1% in vapor pressure.

Experimental Results and Discussion. The vapor pressures of solid dysprosium in the range 1239–1534° K are given in Table II and plotted in Figure 1. The relation obtained from the least-square treatment of data is

$$\ln P_{\text{mm}} = -(35{,}170 \pm 160)/T + (20.56 \pm 0.12) \qquad (4)$$

The data for erbium in the range 1352–1587° K given in Table II and plotted in Figure 2 can be expressed by the relationship

$$\ln P_{\text{mm}} = -(37{,}060 \pm 340)/T + (19.65 \pm 0.23) \qquad (5)$$

The probable error of the measured values of −ln P is 0.0262 for dysprosium and 0.0402 for erbium. These equate to errors in P of about 2.6 and 6%, respectively. The experimental results reveal a slightly larger measure of scatter than would have been expected from the probable experimental uncertainties. The heats of sublimation were determined from the slope of the log plot in accordance with the Clausius-Clapeyron equation. The ΔH_T is 69,880 ± 320 cal/mole for dysprosium and 73,640 ± 680 cal/mole for erbium.

The results for dysprosium (Figure 1) are in excellent agreement with those obtained by Habermann and Daane who used the Knudsen technique in conjunction with a quartz fiber microbalance. They report a ΔH_T of 69,040 ± 240 cal/mole. The vapor pressure data of Kovtun (*10*) appear to be too high. A ΔH_T value of 72,400 cal/mole was reported by Kovtun. The mass spectrometric measure-

Table I. Specimen Analysis

Impurity	Ppm[a]
Dysprosium	
Er	88
Ho	ND < 50
Yb	65
Y	100
Si	250
Ca	80
Zn	ND < 10
Erbium	
Ho	P < 10
Yb	ND < 10
Dy	ND < 100
Sm	ND < 100
Si	P < 1
Y	P < 10
Ca	63
Zn	25

[a] P = present, ND = not detected, < = less than.

Table II. Vapor Pressure of Solid Dysprosium and Erbium

Temp, °K	Time, sec	Wt loss, grams	Press., mm	Press., mm[a]
Dysprosium				
1239	21,728	0.00320	3.827×10^{-4}	4.005×10^{-4}
1265	21,170	0.00567	7.029×10^{-4}	7.177×10^{-4}
1270	23,178	0.00738	8.393×10^{-4}	8.008×10^{-4}
1292	20,064	0.00952	1.258×10^{-3}	1.283×10^{-3}
1325	20,377	0.01989	2.620×10^{-3}	2.528×10^{-3}
1354	15,667	0.02566	4.441×10^{-3}	4.463×10^{-3}
1377	9,627	0.02497	7.089×10^{-3}	6.888×10^{-3}
1406[b]	9,484	0.05188	1.510×10^{-2}	1.167×10^{-2}
1436[b]	8,232	0.07123	2.413×10^{-2}	1.967×10^{-2}
1453	9,457	0.08665	2.569×10^{-2}	2.620×10^{-2}
1485	6,442	0.10599	4.662×10^{-2}	4.414×10^{-2}
1534	2,713	0.08268	8.792×10^{-2}	9.404×10^{-2}
Erbium				
1352	19,579	0.00386	4.380×10^{-4}	4.230×10^{-4}
1375	11,175	0.00334	6.699×10^{-4}	6.737×10^{-4}
1407	8,655	0.00461	1.206×10^{-3}	1.244×10^{-3}
1437	8,249	0.00732	2.030×10^{-3}	2.155×10^{-3}
1457	4,529	0.00644	3.274×10^{-3}	3.071×10^{-3}
1477	10,124	0.01750	4.006×10^{-3}	4.333×10^{-3}
1497	4,329	0.01227	6.581×10^{-3}	6.059×10^{-3}
1526	6,285	0.02404	9.005×10^{-3}	9.699×10^{-3}
1551	6,130	0.03921	1.518×10^{-2}	1.435×10^{-2}
1586	1,709	0.01826	2.562×10^{-2}	2.431×10^{-2}
1587	3,445	0.03293	2.293×10^{-2}	2.467×10^{-2}

[a] Calculated from the relation ln $P = -(35{,}170 \pm 160)/T + (20.56 \pm 0.12)$ for dysprosium; ln $P = -(37{,}060 \pm 340)/T + (19.65 \pm 0.23)$ for erbium. [b] Not included in subsequent calculations due to large random errors in P greater than five times the probable error.

ment of ΔH_T by Savage et al. (*16*) is in agreement with the results of the present work. White et al. (*22*) report a much lower value.

The erbium data obtained in this investigation do not closely agree with any previous work. (See Figure 2.) The results tend to support the findings of Habermann and Daane who report vapor pressures about 20% lower at high temperatures and a ΔH_T of 79,280 ± 270 cal/mole. The data of Kruglykh et al. (*11*) appear to be too high. The results of Savitskii et al. (*17*) appear to be, low. Kruglykh and Savitskii report values for ΔH_T as 60,530 and 64,750 ± 2150 cal/mole, respectively. The ΔH_T value of 73,180 ± 340 obtained by Trulson et al. (*20*) from mass spectrometric measurements is in excellent agreement with the results of the present investigation.

The reliability of the vapor pressure data can be established by the constancy and temperature dependence of ΔH°_{298}, the heat of sublimation at 298° K. Values of ΔH°_{298} were calculated by the third-law method by use of the expression

$$R \ln P_{\text{atm}} = \left(\frac{F^\circ - H^\circ_{298}}{T}\right)_{\text{solid}} - \left(\frac{F^\circ - H^\circ_{298}}{T}\right)_{\text{vapor}} - \frac{\Delta H^\circ_{298}}{T} \tag{6}$$

The terms in parentheses are the free energy functions of solid and gaseous dysprosium or erbium. In Equation 6, an ideal vapor phase is assumed. The free energy functions for the vapor phase were interpolated from the recent data of Feber and Herrick (*5*, *6*). Data for the solid phase were taken from the tabulated values of Stull and Sinke (*19*). Values of ΔH°_{298} were calculated at each test temperature and averaged to obtain 69,600 ± 140 cal/mole for dysprosium and 75,510 ± 130 cal/mole for erbium (Table III). A very slight trend toward decreasing ΔH°_{298} values with increasing temperature is apparent at lower temperatures for dysprosium, but none is apparent in the erbium data. The values of ΔH°_{298} were consistent within the accuracy of this work, and the absence of any significant trend with temperature indicates there were no serious systematic errors. The free energy function data were made available subsequent to the reporting of the prior works. In the present study, the third-law treatment was applied to these works, as well, to provide an additional basis for comparison. A significant trend of ΔH°_{298} values with temperature was detected in Kovtun's work. Similar observations were noted in the erbium data of Savitskii and of Kruglykh. A very slight trend was detected in the treatment of raw data obtained from Daane (*3*) which was not included in the published work (*7*). The ΔH°_{298} value obtained from Daane's dysprosium data is in excellent agreement with the present work.

Third-law values for ΔH°_{298} may be checked by calculating a second value of ΔH°_{298} from ΔH_T and thermal function data at the average temperature of the investigation. This calculation also was performed for the previous works. Enthalpy values are summarized in Table IV for comparison. Included are values for mass spectrometric work. A large disparity between second- and third-law enthalpies indicates a poor reliability in the data. Significant differences in enthalpies may also occur if the vapor is not ideal (*8*). At the low vapor pressures encountered in this investigation, deviations from ideality are considered to be negligible.

Interpretation and comparison of the experimental results were complicated by the discovery of residue traces found in the cell after a series of tests. Analysis of erbium cell contents revealed traces of a pink deposit, suspected as being an erbium oxide. Emission spectrographic analysis indicated erbium as the only metal present in the deposit. X-Ray diffraction failed to confirm the presence of Er_2O_3, the only known oxide (*21*). The traces of dark gray matter found in the dysprosium cell were identified as Dy_2O_3. No TaC was detected that may have resulted from cell reaction with diffusion pump oil. The origin of the residue cannot be positively established. Rare earths are known to oxidize easily (*14*). Oxidation of dysprosium has been

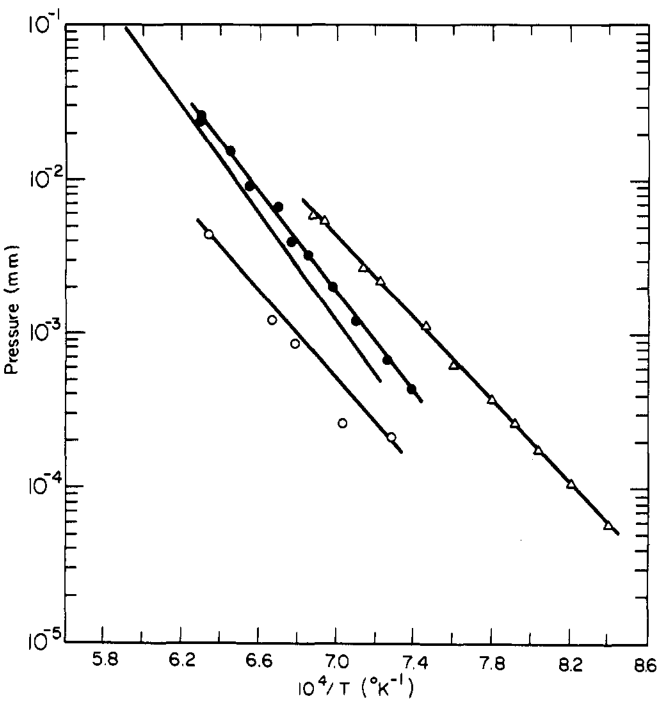

Figure 2. Vapor pressure of solid erbium

- ● This work
- —— Habermann and Daane (*7*)
- △ Kruglykh et al. (*11*)
- ○ Savitskii et al. (*17*)

Table III. Sublimation Data at 298° K

Temp, °K	$-R \ln P$ cal/mole-deg	$-\left(\frac{F^\circ - H^\circ_{298}}{T}\right)^a$	$-\left(\frac{F^\circ - H^\circ_{298}}{T}\right)^b$	ΔH°_{298} cal/mole
		Dysprosium		
1239	28.815	22.48	50.111	69,936
1265	27.607	22.59	50.191	69,838
1270	27.255	22.62	50.207	69,649
1292	26.450	22.71	50.275	69,787
1325	24.993	22.86	50.373	69,569
1354	23.944	22.98	50.458	69,625
1377	23.014	23.07	50.526	69,497
1453	20.456	23.39	50.742	69,465
1485	19.272	23.52	50.832	69,177
1534	18.011	23.71	50.966	69,439
			Av value	69,600
			Probable error	±140
		Erbium		
1352	28.547	22.69	49.993	75,509
1375	27.703	22.79	50.060	75,584
1407	26.534	22.93	50.152	75,640
1437	25.499	23.05	50.235	75,701
1457	24.549	23.13	50.292	75,341
1477	24.148	23.22	50.347	75,741
1497	23.162	23.30	50.403	75,239
1526	22.539	23.41	50.481	75,705
1551	21.501	23.51	50.548	75,286
1586	20.462	23.65	50.641	75,256
1587	20.682	23.66	50.644	75,646
			Av value	75,510
			Probable error	±130

[a] Solid. [b] Vapor.

Table IV. Comparison of Sublimation Enthalpies

Reference	Temp, °K	ΔH_T, cal/mole	ΔH°_{298} (2nd),[a] cal/mole	ΔH°_{298} (3rd), cal/mole
		Dysprosium		
This work	1239–1534	69,880 ± 320	72,420	69,600 ± 140
Habermann (*7*)	1257–1690	69,050 ± 240	71,920	69,390 ± 130
Kovtun (*10*)	1125–1346	72,400	74,510	67,490 ± 230
Savage (*16*)	1080–1400	69,300 ± 600	71,420	. . .
White (*22*)	1278–1566	60,100 ± 300	62,740	. . .
		Erbium		
This work	1352–1587	73,640 ± 680	76,580	75,510 ± 130
Habermann (*7*)	1392–1790	79,280 ± 270	82,660	75,820 ± 350
Kruglykh (*11*)	1188–1453	60,530	63,030	72,350 ± 430
Savitskii (*17*)	1373–1573	64,750 ± 2150	67,620	80,280 ± 670
Trulson (*20*)	1208	73,180 ± 340	75,350	. . .
White (*22*)	1349–1743	64,500 ± 600	67,660	. . .

[a] Calculated at the average temperature from ΔH_T and thermal functions.

studied by Pethe et al. (*13*) but not at low oxygen pressures. The residue weights correspond to those estimated to occur from a specimen reaction with dissolved oxygen in the tantalum cell. The accuracy of the measured vapor pressures suggests the formation of oxide residue from sources within the cell and not to a "getter" type reaction. If the oxide sources were external to the cell, the dysprosium and erbium vapor pressures would only be in error by approximately 1.0% and 6.0%, respectively. The significant differences between this work and that of Habermann and Daane occur at the lower temperatures where pyrometric temperature measurement is most subject to error.

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Correlation Equation for Solubility of Carbon Dioxide in Water, Seawater, and Seawater Concentrates

PREM MUNJAL[1] and PAUL B. STEWART[2]
Sea Water Conversion Laboratory and Department of Mechanical Engineering,
University of California, Berkeley, Calif. 94720

The solubility of carbon dioxide in pure water, synthetic seawater, and synthetic seawater concentrates with three- and five-times normal salts content, in the temperature range of −5° to 25° C, and from 1 to 45 atm pressure has been determined experimentally and reported elsewhere in tabular and graphical form (*7-9*).

The gas solubility is a function of temperature, pressure, and solvent composition, as is to be expected. Since both phases are nonideal, this functional relationship is not a simple one. The solubility isobars for pure water, Figure 4 in ref. 9 and for synthetic seawater and its concentrates, Figure 1 in this paper, lead one to suspect that empirical

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[1] Present address, System Development Corp., 2500 Colorado Avenue, Santa Monica, Calif. 90406.
[2] To whom correspondence should be addressed.