Liquid Praseodymium Heat Content by Levitation Calorimetry

Lawrence A. Stretz[1] **and Renato G. Bautista**[2]
Ames Laboratory and the Department of Chemical Engineering, Iowa State University, Ames, Iowa 50010

The high-temperature heat content of liquid praseodymium was measured experimentally by the levitation calorimetry technique. The samples, ranging in size from 0.5 to 1.5 g, were simultaneously levitated and heated by a radiofrequency generator in an argon–helium mixture prior to being dropped into a conventional copper block drop calorimeter. Corrections were made for the convection and radiation losses during the fall of the sample from the levitation chamber into the calorimeter. The praseodymium data, from 1460 to 2289K, were fitted by the following equation where the indicated errors represent the average deviation of the experimental value from the value predicted by the equation: $H_T - H_{298.15} = \{41.57 \pm 0.29\}(T - 1208) + \{41733 \pm 197\}$ J/mol.

The increasing use of materials at very high temperatures has highlighted the need for accurate high-temperature thermodynamic data derived from either experimental or theoretical considerations. Experimental data for liquid metals, when available, are often meager. The available theories of liquids are presently unable to provide the estimates of properties needed for thermodynamic considerations.

The development by Bonnell (*4*), Chaudhuri et al. (*5*), and Treverton and Margrave (*16, 17*) of simultaneously levitating and heating a metal sample before being dropped into a drop calorimeter has made possible the direct measurement of the heat content of liquid metals up to around 3000K. Using the same technique, Stretz and Bautista (*13–15*) have extended the measurement of the heat content of liquid yttrium from 1800 to 2360K and that of liquid lanthanum from 1250 to 2420K.

A levitation calorimetry system was built by coupling a levitation melting apparatus powered by a high-frequency generator with a conventional copper block calorimeter. The simultaneous levitation and melting of the sample in an inert atmosphere make possible the attainment of these very high temperatures without contact between the sample and any container material. A higher degree of accuracy in the measurement of the heat content of the reactive liquid metals can be expected since sample reaction with the container is eliminated.

The heat content of praseodymium has been reported by McKeown (*9*) from 374 to 1150K and by Berg et al. (*2, 3*) from 373 to 1373K. The only experimental data previously available above the melting point of praseodymium, 1204K, were the three points reported by Berg et al. The lack of more data in the liquid phase could be attributed to the reactivity of the liquid rare earth metals with container materials such as tantalum and tungsten (*6, 7*).

Experimental Technique

The complete description of the experimental setup, procedures, and calculation technique for the levitation calorimetry method has been reported by Stretz and Bautista (*13, 14*). A brief description of the experimental aspect of this work follows.

The experimental equipment essentially consists of the levitation chamber, drop tube, copper block calorimeter, the Leeds and Northrup automatic recording optical pyrometer, the Hewlett-Parkard quartz thermometer, and a 15 kV-A, 450 kHz Lepel radiofrequency generator.

The calorimeter block was calibrated by passing a measured quantity of electrical energy through a heater and by following the temperature response of the block. The uncorrected calorimeter constant of 2025.75 J/K obtained is in good agreement with the calculated value of 2030 J/K based on the approximate mass of the calorimeter block. The corrected calorimeter block constant is 1976.68 J/K.

The praseodymium sample was prepared at the Ames Laboratory (*11*) in the form of 0.635 cm diameter by 0.635-cm length cylinders. The praseodymium sample is 99.97% pure, and an analysis of its impurities is given in Table I. The samples were electropolished and stored under vacuum prior to use. Once the sample is placed in the levitation chamber, the system is flushed with the purified argon–helium mixture for at least 2 hr before a run is made.

Results and Discussion

The experimental technique and equipment performance were checked by determining the heat content of liquid copper from 1358 to 2061K. Liquid copper was chosen as a standard because of the ease of levitation and the availability of liquid copper heat content data. The results were in excellent agreement with the values reported in the literature (*5, 8, 12, 14*).

The levitation coil successfully used for praseodymium for work below 1900K was done with a solenoid type coil with three turns of 0.953 cm diameter in the lower section and two reverse turns of 1.905 cm diameter in the upper section. A gap of 0.635 cm was set between the upper and lower sections. A solenoid coil 0.953 cm in diameter with three turns in the lower section and three reverse turns in the upper section with a gap of 0.635 cm was used for levitation work above 1900K.

Table I. Impurities in Praseodymium Sample in Ppm Atomic

Impurity	Praseodymium initial	Final[a]
Na	30	
Cl	15	
Fe	19	
Ta	40	
W	8	
Pt	6	
Hg	7	
Y	7.7	
La	14	
Nd	10	
Gd	<1	
Tb	5	
Lu	<0.2	
H[b]	1.4	76
N[b]	92	89
O[b]	48	252
C[b]	48	

[a] Vacuum fusion on sample after simulated run. [b] Ppm by weight.

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[1] Present address, El Paso Natural Gas Co., El Paso, Tex.
[2] To whom correspondence should be addressed.

Table II. Results of Runs Using Praseodymium Samples[a]

Run	Brightness T, K	True T, K	% He in He–Ar, atm	Corrections		Heat content		Dev %
				Convection ΔH_c, J/mol	Radiation ΔH_r, J/mol	Exptl $\Delta H\}_{298.15}^{T}$, J/mol	Smoothed $\Delta H\}_{298.15}^{T}$, J/mol	
36	1345	1460	100	1549	632	52261	52209	0.10
31	1390	1512	100	1503	636	54740	54370	0.68
30	1424	1551	100	1507	687	56174	55990	0.33
28	1462	1596	90	1290	749	58146	57862	0.49
26	1506	1650	90	1310	837	59740	60107	−0.61
25	1543	1693	70	1017	934	62143	61895	0.40
24	1577	1734	70	1009	996	63345	63599	−0.40
21	1595	1757	50	754	1034	64115	64554	−0.68
35	1643	1815	50	783	1168	66738	66966	−0.34
22	1688	1870	50	724	1231	68892	69252	−0.52
14	1719	1908	90	1277	1294	70859	70831	0.04
2	1756	1954	90	1403	1465	72893	72740	0.21
3	1802	2011	60	934	1641	75321	75111	0.28
13	1826	2041	50	833	1746	76177	76360	−0.24
1	1831	2047	60	950	1750	76787	76611	0.23
4	1873	2099	50	862	1938	78722	78772	0.00
12	1873	2100	30	641	1943	78306	78810	−0.64
18	1908	2144	30	661	2114	80980	80641	0.42
5	1943	2189	30	687	2294	82653	82513	0.17
7	1956	2205	30	678	2332	82871	83179	−0.37
11	1989	2247	20	607	2537	85205	84925	0.33
8	1992	2250	30	708	2541	85099	85048	0.06
9	2022	2289	20	574	2613	86791	86670	0.14
							Av % deviation	0.34

[a] C_p = 41.57 ± 0.25 J/mol K. ϵ_{ht} = 0.350 (hemispherical total emittance). $\epsilon_{n\lambda}$ = 0.294 (normal spectral emittance). ρ = 6.10 g/cm³. M = 140.91 g/mol. X = 36 cm (drop distance).

Table III. Comparison of Results for Liquid Praseodymium with Literature Values

Temp, K	Exptl[a] $H\}_{298.15}^{T}$, J/mol	Berg et al.[b] $H\}_{298.15}^{T}$, J/mol	Dev	Dev %
1208	41733	41360	373	0.88
1225	42440	42093	347	0.81
1250	43478	43169	309	0.71
1275	44517	44244	273	0.61
1300	45554	45316	238	0.52
1325	46593	46392	201	0.43
1350	47631	47468	163	0.34
1375	48673	48543	130	0.26

[a] Extrapolated below experimental temperature range.
[b] Refs. *2* and *3*.

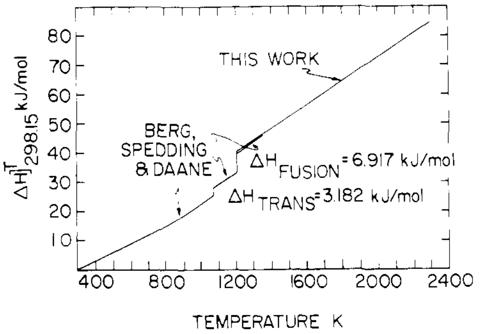

Figure 1. Heat content of praseodymium from 298.15 to 2289K

The determination of the true temperature of the sample is considered to be the largest source of error in the heat content calculation. The normal spectral emittance, $\epsilon_{n\lambda}$, of praseodymium has been found by Moscowitz et al. (*10*), using a black body comparison technique to be 0.294. The hemispherical total emittance, ϵ_{ht}, needed for the calculation of the true temperature was estimated from the normal spectral emittance as described by Baria and Bautista (*1*). The hemispherical total emittance of praseodymium was 0.350.

The limits of error recognized by the National Bureau of Standards for optical pyrometers could introduce around ±1.00% error in the heat content values.

In Table I are shown the impurity levels in the praseodymium sample as well as the H, N, and O analyses before and after a simulated run. The sizable increase in both H and O probably occurred during the handling of the sample in air rather than during a run. Taking into account all other possible sources of error results in a maximum estimated error of ±2.5% for the levitation calorimetry technique.

Variation of *sample size, inert atmosphere composition*, and high-frequency generator power allowed measurements at temperatures down to 1500K. Below this temperature the levitation of the samples was unstable, and the samples often struck the coil or fell from the field. One successful measurement was obtained at 1460K, but attempts to obtain measurements at lower temperatures were unsuccessful. The upper temperature limit was due to sample vaporization and formation of metal smoke rather than a temperature limitation of the levitation system. The maximum temperature at which data were taken was 2289K.

The results of the work on praseodymium, including the correction for convection and radiation heat losses during the sample drop, are given in Table II. A linear fit to the data resulted in Equation 1 as a representation of the heat content of liquid praseodymium:

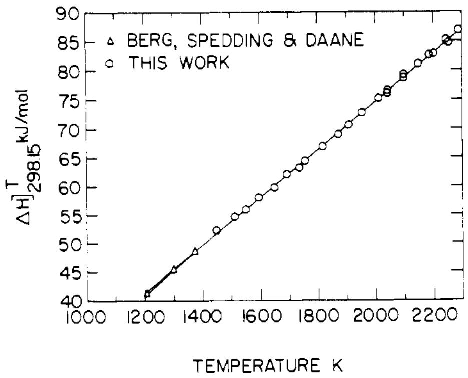

Figure 2. Heat content of praseodymium from melting point, 1208, up to 2289K

Table IV. Thermodynamic Functions of Liquid Praseodymium (J/mol K)

T, K	C_p	$S^\circ_T - S^\circ_O$	$\frac{H^\circ_T - H^\circ_{298.15}}{T}$	$\frac{-G^\circ_T - H^\circ_{298.15}}{T}$
1208	41.57	127.07	34.55	92.53
1250	41.57	128.50	34.78	93.72
1300	41.57	130.13	35.05	95.09
1350	41.57	131.70	35.29	96.41
1400	41.57	133.21	35.51	97.70
1450	41.57	134.66	35.72	98.95
1500	41.57	136.07	35.91	100.16
1550	41.57	137.43	36.10	101.34
1600	41.57	138.75	36.27	102.49
1650	41.57	140.03	36.43	103.61
1700	41.57	141.27	36.58	104.70
1750	41.57	142.48	36.72	105.76
1800	41.57	143.65	36.85	106.80
1850	41.57	144.78	36.98	107.81
1900	41.57	145.89	37.10	108.80
1950	41.57	147.02	37.22	109.76
2000	41.57	148.02	37.32	110.71
2050	41.57	149.05	37.43	111.63
2100	41.57	150.05	37.53	112.53
2150	41.57	151.03	37.62	113.42
2200	41.57	151.98	37.71	114.28
2250	41.57	152.92	37.79	115.13
2300	41.57	153.83	37.87	115.96

$$H_T - H_{298.15} = \{41.57 \pm 0.29\}(T - 1208) + \{41733 \pm 197\}\ \text{J/mol} \qquad (1)$$

$$1460 < T < 2289\text{K}$$

The heat capacity value of 41.57 J/mol K compares to the value reported by Berg et al. (*2, 3*) of 43.00 J/mol K. Table III gives a comparison of Berg et al.'s data to values obtained from this work by extrapolation of Equation 1 back to the melting point. The comparison is also shown in Figure 1 which displays Berg et al.'s data from 298 to 1373K and the results of this work from the melting point, 1208, up to 2289K. Figure 2 shows the liquid range of Figure 1 in more detail.

Values of the thermodynamic functions of praseodymium were calculated at 50° intervals from the melting point up to 2300K and are tabulated in Table IV.

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