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Thermodynamic Properties of Cerium Gas

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ABSTRACT

Values of Cp°, $H^\circ_T - H^\circ_{298.15}$, $S^\circ_T - S^\circ_{298.15}$, and $\frac{G^\circ_T - H^\circ_{298.15}}{T}$ for cerium gas are calculated in the temperature range from 298.15° to 6000°K from 391 spectroscopic energy levels up to 20,000 $cm.^{-1}$.

INTRODUCTION

Feber and Herrick[1], in their calculation of ideal gas thermodynamic functions for lanthanide elements, had access to only 15 energy levels for cerium. Recently, Martin[2] has interpreted most of the neutral cerium spectrum. So far he has identified 391 levels, up to 20,000 $cm.^{-1}$, estimating that up to 30 levels, all above 13,000 $cm.^{-1}$, remain to be found below 20,000 $cm.^{-1}$. A more complete assignment of energy levels is not expected to be available for several years. Although several hundred levels have been found above 20,000 $cm.^{-1}$, the above data are sufficient to calculate the thermodynamic properties of cerium as an ideal monatomic gas with far greater accuracy than was possible by Feber and Herrick.

The method of calculating thermodynamic properties from spectroscopic energy levels has been detailed in many textbooks, such as that by Lewis, Randall, Pitzer, and Brewer[3]. A CDC 6400 computer was programmed to calculate and print values of Cp°, $H^\circ_T - H^\circ_{298.15}$, $S^\circ_T - S^\circ_{298.15}$, and the Gibbs energy function, $\frac{G^\circ_T - H^\circ_{298.15}}{T}$ from 298.15° to 6000°K. The results are presented in Table I.*

The ground state of cerium has been designated $4f5d6s^2(^1G^\circ_4)$. The physical constants used are those given by the National Academy of Sciences and adopted by the National Bureau of Standards[4], as follows:

R = gas constant = 1.98717 cal. deg.$^{-1}$ mole^{-1}

h = Planck's constant = 6.62560×10^{-27} erg sec.

k = Boltzmann constant = 1.38054×10^{-16} erg deg.$^{-1}$

c = speed of light = 2.997925×10^{10} cm. sec.$^{-1}$

N = Avogadro's number = 6.02252×10^{23} molecules mole^{-1}.

The atomic weight of cerium, 140.12, was taken from Cameron and Wichers.[5]

DISCUSSION

Values are tabulated to the nearest 0.0001 cal. deg.$^{-1}$ mole^{-1} in order to facilitate rounding to 3 decimal places. Uncertainties in the multiplicities of 21 of the higher energy levels results in an uncertainty of 0.0034 cal. deg.$^{-1}$ mole^{-1} in the Gibbs energy function and 30 cal. mole^{-1} in the heat content at 6000°K. This uncertainty becomes insignificant below about 1500°K.

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*A list of the energy levels used in the calculation may be obtained on request from W. C. Martin, Spectroscopy Section, Atomic Physics Division, National Bureau of Standards, Washington, D. C., 20234.

By comparing the results obtained when the 47 energy levels between 19,000 and 20,000 cm.$^{-1}$ were omitted, with the tabulated values, it was found that omission of the levels introduced a lowering of 3% in C_p° at 6000°K, and less at lower temperatures. The possibly 30 missing levels below 20,000 cm.$^{-1}$ should have less of an effect than this. The present values differ significantly from those calculated by Feber and Herrick because of the contributions of the many higher levels unavailable to them.

ACKNOWLEDGMENT

We are indebted to W.C. Martin for kindly supplying us with his unpublished energy level data from work in progress and to Ralph Hultgren for helpful assistance. This work was supported by the U.S. Atomic Energy Commission.

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Table I. Thermodynamic Properties of Cerium Gas

$$H^\circ_{298.15} - H^\circ_0 = 1593.6 \text{ cal mole}^{-1}$$

$$S^\circ_{298.15} = 45.8072 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

		cal deg^{-1} mole^{-1}		
T, °K	$H^\circ_T - H^\circ_{298.15}$ cal mole^{-1}	Cp°	$S^\circ_T - S^\circ_{298.15}$	$\frac{G^\circ_T - H^\circ_{298.15}}{T}$
298.15	0.0	5.5150	0.0000	-45.8072
300	10.2	5.5190	0.0341	-45.8073
400	577.9	5.8756	1.6648	-46.0273
500	1190.9	6.4006	3.0305	-46.4559
600	1859.4	6.9710	4.2478	-46.9560
700	2584.2	7.5168	5.3640	-47.4795
800	3360.7	8.0016	6.4002	-48.0065
900	4181.9	8.4082	7.3669	-48.5276
1000	5039.6	8.7313	8.2703	-49.0379
1100	5925.5	8.9742	9.1144	-49.5348
1200	6832.1	9.1457	9.9031	-50.0170
1300	7752.7	9.2574	10.6399	-50.4836
1400	8682.0	9.3217	11.3286	-50.9344
1500	9615.8	9.3504	11.9729	-51.3696
1600	10551.2	9.3535	12.5766	-51.7893
1700	11485.9	9.3394	13.1432	-52.1941
1800	12418.7	9.3149	13.6764	-52.5844
1900	13348.7	9.2848	14.1793	-52.9608
2000	14275.6	9.2530	14.6547	-53.3241
2100	15199.4	9.2218	15.1054	-53.6748
2200	16120.1	9.1929	15.5337	-54.0136
2300	17038.0	9.1671	15.9418	-54.3412
2400	17953.6	9.1447	16.3314	-54.6580
2500	18867.1	9.1255	16.7043	-54.9647
2600	19778.8	9.1091	17.0619	-55.2619
2700	20689.0	9.0949	17.4054	-55.5501
2800	21597.8	9.0823	17.7360	-55.8297
2900	22505.5	9.0705	18.0545	-56.1012
3000	23411.9	9.0587	18.3618	-56.3650
3100	24317.2	9.0464	18.6586	-56.6216
3200	25221.2	9.0328	18.9456	-56.8712
3300	26123.7	9.0174	19.2233	-57.1143
3400	27024.6	8.9998	19.4923	-57.3511

Table I. (continued)

T, °K	$H^\circ_T - H^\circ_{298.15}$	Cp°	$S^\circ_T - S^\circ_{298.15}$	$\frac{G^\circ_T - H^\circ_{298.15}}{T}$
3500	27923.6	8.9797	19.7529	-57.5819
3600	28820.4	8.9568	20.0055	-57.8071
3700	29714.8	8.9309	20.2506	-58.0268
3800	30606.5	8.9019	20.4884	-58.2413
3900	31495.1	8.8699	20.7192	-58.4508
4000	32380.4	8.8348	20.9433	-58.6555
4100	33262.0	8.7968	21.1610	-58.8556
4200	34139.6	8.7560	21.3725	-59.0513
4300	35013.1	8.7125	21.5780	-59.2427
4400	35882.0	8.6666	21.7778	-59.4300
4500	36746.3	8.6185	21.9720	-59.6134
4600	37605.7	8.5683	22.1609	-59.7930
4700	38459.9	8.5163	22.3446	-59.9689
4800	39308.9	8.4628	22.5234	-60.1413
4900	40152.4	8.4079	22.6973	-60.3102
5000	40990.4	8.3520	22.8666	-60.4758
5100	41822.8	8.2951	23.0314	-60.6381
5200	42649.4	8.2374	23.1920	-60.7974
5300	43470.3	8.1793	23.3483	-60.9536
5400	44285.3	8.1209	23.5007	-61.1069
5500	45094.4	8.0622	23.6491	-61.2574
5600	45897.7	8.0035	23.7939	-61.4051
5700	46695.1	7.9450	23.9350	-61.5501
5800	47486.7	7.8867	24.0727	-61.6926
5900	48272.5	7.8287	24.2070	-61.8325
6000	49052.5	7.7712	24.3381	-61.9699

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