

Thermodynamic Properties of Cerium Gas

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Values of C_p° , $H_f^\circ - H_{298.15}^\circ$, $S_f^\circ - S_{298.15}^\circ$, and $(G_f^\circ - H_{298.15}^\circ)/T$ 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} .

FEBER and Herrick (2), in their calculation of ideal gas thermodynamic functions for lanthanide elements, had access to only 15 energy levels for cerium. Recently, Martin (4) 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 for 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 C_p° , $H_f^\circ - H_{298.15}^\circ$, $S_f^\circ - S_{298.15}^\circ$, and the Gibbs energy function, $(G_f^\circ - H_{298.15}^\circ)/T$, from 298.15° to 6000° K. The results are presented in Table I. (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.)

The ground state of cerium has been designated $4f5d6s^2(^1G_0)$. The physical constants used are those given by the National Academy of Sciences and adopted by the National Bureau of Standards (5), 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 $^{-1}$

Table I. Thermodynamic Properties of Cerium Gas

$H_{298.15}^\circ - H_0^\circ = 1593.6$ cal. mole $^{-1}$ $S_{298.15}^\circ = 45.8072$ cal. deg. $^{-1}$ mole $^{-1}$									
Cal. Deg. $^{-1}$ Mole $^{-1}$					Cal. Deg. $^{-1}$ Mole $^{-1}$				
$T, ^\circ\text{K.}$	$H_f^\circ - H_{298.15}^\circ$ Cal. Mole $^{-1}$	C_p°	$S_f^\circ - S_{298.15}^\circ$	$(G_f^\circ - H_{298.15}^\circ)/T$	$T, ^\circ\text{K.}$	$H_f^\circ - H_{298.15}^\circ$ Cal. Mole $^{-1}$	C_p°	$S_f^\circ - S_{298.15}^\circ$	$(G_f^\circ - H_{298.15}^\circ)/T$
298.15	0.0	5.5150	0.0000	-45.8072					
300	10.2	5.5190	0.0341	-45.8073	3200	25221.2	9.0328	18.9456	-56.8712
400	577.9	5.8756	1.6648	-46.0273	3300	26123.7	9.0174	19.2233	-57.1143
500	1190.9	6.4006	3.0305	-46.4559	3400	27024.6	8.9998	19.4923	-57.3511
600	1859.4	6.9710	4.2478	-46.9560	3500	27923.6	8.9797	19.7529	-57.5819
					3600	28820.4	8.9568	20.0055	-57.8071
700	2584.2	7.5168	5.3640	-47.4795					
800	3360.7	8.0016	6.4002	-48.0065	3700	29714.8	8.9309	20.2506	-58.0268
900	4181.9	8.4082	7.3669	-48.5276	3800	30606.5	8.9019	20.4884	-58.2413
1000	5039.6	8.7313	8.2703	-49.0379	3900	31495.1	8.8699	20.7192	-58.4508
1100	5925.5	8.9742	9.1144	-49.5348	4000	32380.4	8.8348	20.9433	-58.6555
					4100	33262.0	8.7968	21.1610	-58.8556
1200	6832.1	9.1457	9.9031	-50.0170					
1300	7752.7	9.2574	10.6399	-50.4836	4200	34139.6	8.7560	21.3725	-59.0513
1400	8682.0	9.3217	11.3286	-50.9344	4300	35013.1	8.7125	21.5780	-59.2427
1500	9615.8	9.3504	11.9729	-51.3696	4400	35882.0	8.6666	21.7778	-59.4300
1600	10551.2	9.3535	12.5766	-51.7893	4500	36746.3	8.6185	21.9720	-59.6134
					4600	37605.7	8.5683	22.1609	-59.7930
1700	11485.9	9.3394	13.1432	-52.1941					
1800	12418.7	9.3149	13.6764	-52.5844	4700	38459.9	8.5163	22.3446	-59.9689
1900	13348.7	9.2848	14.1793	-52.9608	4800	39308.9	8.4628	22.5234	-60.1413
2000	14275.6	9.2530	14.6547	-53.3241	4900	40152.4	8.4079	22.6973	-60.3102
2100	15199.4	9.2218	15.1054	-53.6748	5000	40990.4	8.3520	22.8666	-60.4758
					5100	41822.8	8.2951	23.0314	-60.6381
2200	16120.1	9.1929	15.5337	-54.0136					
2300	17038.0	9.1671	15.9418	-54.3412	5200	42649.4	8.2374	23.1920	-60.7974
2400	17953.6	9.1447	16.3314	-54.6580	5300	43470.3	8.1793	23.3483	-60.9536
2500	18867.1	9.1255	16.7043	-54.9647	5400	44285.3	8.1209	23.5007	-61.1069
2600	19778.8	9.1091	17.0619	-55.2619	5500	45094.4	8.0622	23.6491	-61.2574
					5600	45897.7	8.0035	23.7939	-61.4051
2700	20689.0	9.0949	17.4054	-55.5501					
2800	21597.8	9.0823	17.7360	-55.8297	5700	46695.1	7.9450	23.9350	-61.5501
2900	22505.5	9.0705	18.0545	-56.1012	5800	47486.7	7.8867	24.0727	-61.6926
3000	23411.9	9.0587	18.3618	-56.3650	5900	48272.5	7.8287	24.2070	-61.8325
3100	24317.2	9.0464	18.6586	-56.6216	6000	49052.5	7.7712	24.3381	-61.9699

The atomic weight of cerium, 140.12, was taken from Cameron and Wichers (1).

DISCUSSION

Values are tabulated to the nearest 0.0001 cal. deg.⁻¹ mole⁻¹ in order to facilitate rounding to three decimal places. Uncertainties in the multiplicities of 21 of the higher energy levels result 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.

By comparing with the tabulated values, the results obtained when the 47 energy levels between 19,000 and 20,000 cm.⁻¹ were omitted, 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 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.

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Particle Size Distribution in Compacts of Solids

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Knowledge of particle size distribution in compacts is useful in studies of porous beds and catalysts. Compacts of 2 cm. diameter of calcite, sand, quartz, barytes, marble, and soapstone in the initial particle size range of -0.200, +0.125 to -0.050, +0.040 cm. are prepared by application of pressures of 93 to 3153 kg. per sq. cm. and disintegrated into individual particles by acetone. The sizes of the disintegrated particles are determined by sieve analysis. The particle size distributions are given using a modified upper limit equation. The standard deviation is characteristic of the material. An equation relating mean diameter of size distribution to the initial particle size and surface energy of material, diameter of compact, and pressure of compaction is presented on the basis of dimensional analysis and experimental data.

COMPACTION is a technique of size enlargement of small particles of materials by compressing them into a coherent mass. It is used extensively for briquetting peats, lignites, and bituminous coals, tableting of pharmaceuticals, compacting metal powders, and pelleting of catalysts. The most important macroscopic characteristic of compacts which has been studied is porosity (1, 4, 5, 7, 10).

From the results of an experimental study of porosities of compacts of six materials of different initial particle sizes compacted at the pressures given in Table I, the porosity of compacts is correlated (10) by

$$\epsilon_0^2 = k \left(\frac{\nu}{Pd_{av}} \right)^m \quad (1)$$

The exponent m is equal to 0.1 of the coefficient of internal friction (Table II), but the porosity data do not give an idea about the size distribution of particles within the compact, which is necessary in studies of porous beds and catalysts, as compacts of same porosity may have different surface areas. This study, which seems to be the first of its kind reported, relates the size distribution to

the physical properties of material and the conditions of compaction.

The particles from which the compact is made may be presumed to be subjected to certain basic processes, resulting in particle disintegration and size distribution within the compact. Under small loads, the particles may be pushed into the void spaces, causing consolidation which may progress until the individual void size is less than the particle size. As the load increases, the particles bearing the load may yield and the resulting smaller particles may fill the void spaces. This process may continue until the applied load is balanced by the bearing capacity of the particles. However, the actual compaction process may be complicated by the shape and orientation of the particles and simultaneous occurrence of consolidation and disintegration. These observations are for brittle materials. For plastic materials, these processes are further complicated since the voidage may also be reduced owing to plastic deformation and subsequent fusion of the particles.

The literature on particle size distributions within compacts is limited and most references deal with the types of packings of regular and irregular shaped particles of