Heat capacity from 5 to 350 K and thermodynamic properties of cesium nitrate to 725 K [a]

H. E. FLOTOW,[b] P. A. G. O'HARE,

Chemistry Division, Argonne National Laboratory,
Argonne, Illinois 60439, U.S.A.

and JULIANA BOERIO-GOATES

Chemistry Department, The University of Michigan,
Ann Arbor, Michigan 48109, U.S.A.

The low-temperature heat capacity (5 to 350 K) of $CsNO_3$ was determined by adiabatic calorimetry. No anomalies were observed in this temperature region, the curve of heat capacity against temperature having the normal sigmoid shape. These measurements yielded the thermodynamic properties at 298.15 K:

$$C_p^\circ = (96.47 \pm 0.19) \text{ J K}^{-1} \text{ mol}^{-1};$$
$$S^\circ = (153.95 \pm 0.31) \text{ J K}^{-1} \text{ mol}^{-1};$$
$$\{H^\circ(T) - H^\circ(0)\} = (20046 \pm 40) \text{ J mol}^{-1},$$
$$\{G^\circ(T) - H^\circ(0)\}/T = -(86.71 \pm 0.17) \text{ J K}^{-1} \text{ mol}^{-1}.$$

These measurements have been combined with published high-temperature heat capacities to give the thermodynamic properties of $CsNO_3$ to 725 K.

1. Introduction

Because cesium is found as a major fission product in irradiated nuclear fuels, much attention has been given recently to its chemistry. This interest has stimulated a considerable amount of research into the thermodynamics of interactions of cesium with various nuclear materials and this, in turn, required reliable thermodynamic information for many compounds of cesium. From this Laboratory, for example, calorimetric studies of the chromates,[1] molybdates,[2] and uranates[3] of cesium have been reported within the past few years.

As a result of these and other similar research activities, reliable thermodynamic quantities are now available for a variety of complex cesium compounds.[4] There still are, however, relatively simple cesium compounds for which the published thermochemical values are scanty or of questionable calibre. Thus, several years ago

[b] To whom correspondence concerning this paper should be addressed.

we concluded that the standard enthalpy of formation ΔH_f of cesium nitrate, $CsNO_3$, needed to be redetermined. Our literature search at that time also revealed that neither the low-temperature heat capacity nor the standard entropy at 298.15 K had been reported for $CsNO_3$. The thermodynamics of this salt, a 1-1 electrolyte, are important from a fundamental as well as from a technological point of view. For example, $CsNO_3$ plays an important role in radioactive waste management.[5]

In order to establish accurate and precise thermochemical quantities for $CsNO_3$, we measured the enthalpy of solution in water[6] and derived ΔH_f. In the same publication, we estimated the standard entropy S at 298.15 K, based on a standard Gibbs energy of solution calculated from activity coefficients.

This investigation describes adiabatic-calorimetric measurements from 5 to 350 K of the heat capacity C_p of a high-purity specimen of $CsNO_3$ and the derivation of other thermodynamic functions such as S. We have, in addition, re-examined the high-temperature heat capacities reported for $CsNO_3$,[7] and this has enabled us to include in the present paper a set of recommended thermodynamic functions to 725 K.

2. Experimental

CHARACTERIZATION OF SAMPLE

The cesium nitrate (Batch No. S.82821A) was a Johnson Matthey "Puratronic" material specially formulated for electronic applications. As received, the sample appeared to be damp. It was therefore heated at 400 K for 70 h in a vacuum oven and then stored in a desiccator. Spectrographic analysis showed the presence of Ca, K, Rb, and Na at levels no greater than 0.005 mass per cent, and these impurities were assumed to have a negligible effect on the measured heat capacities. The X-ray diffraction pattern agreed with that described in the literature for the hexagonal modification.[8] A d.s.c.-d.t.a. analysis of the material showed a solid-to-solid transition at 424 K and the melting temperature was found to be 679 K. Both temperatures are very close to those selected in a recent critical evaluation.[9] At the lower transition point, the structure changes from hexagonal to cubic.

CALORIMETER

The calorimeter was cylindrical. It was made from OFHC-grade copper, was gold-plated on the outside, and had a central re-entrant well which accommodated a bifilarly-wound Evanohm heater and an encapsulated platinum resistance thermometer. Its mass and internal volume were 49.606 g and 34.23 cm³, respectively.

The $CsNO_3$ was loaded into the calorimeter in a glovebox filled with dry purified helium, and the calorimeter was then sealed as previously described.[10] In order to provide efficient transfer of heat between the sample and calorimeter, a small amount of He, 1.01×10^{-4} mol, was included in the sealed calorimeter. The mass of $CsNO_3$ was 29.9103 g and its density at 298.15 K was taken to be 3.635 g cm⁻³.[8]

TECHNIQUES

The adiabatic calorimeter and the measurement techniques have been described in detail in other publications.[11,12] The agreement between the calibrated platinum resistance thermometer used in the measurements and thermodynamic temperatures is believed to be within 0.1 K from 3 to 14 K, within 0.03 K from 14 to 90 K, and within 0.05 K between 90 and 373 K. Temperature differences are reliable to 0.01 K at 4.2 K, to 0.0008 K at 14 K, to 0.0001 K from 25 to 58 K, and to 0.001 K above 58 K. Our standards of electrical potential difference, resistance, and mass were calibrated against standards traceable to the U.S. National Bureau of Standards. The Wang electronic timer used to determine the heating intervals was checked against signals from station WWV.

Two series of measurements, one on the empty calorimeter and the other on the calorimeter plus sample, were made over the temperature range 5 to 350 K. The heat capacity of $CsNO_3$ was obtained as the difference between the two series after minor heat-capacity corrections had been applied for different amounts of helium, Apiezon T grease, copper, and gold associated with the empty and with the loaded calorimeter. A small curvature correction equal to $-(d^2 C_p/dT^2)(\Delta T)^2/24$ was applied to each heat-capacity value.

The sample heat capacity was about 79 per cent of the total near 10 K, and decreased to approximately 40 per cent over the temperature range from 100 K to 350 K.

3. Heat-capacity results

The experimental heat capacities are given in table 1. The temperature rises in the experiments were about 2 K below 20 K, about $0.1\langle T\rangle$ between 20 and 100 K, and

TABLE 1. Molar heat capacity C_p of $CsNO_3$ at constant pressure [a]

$\langle T\rangle$	C_p	$\langle T\rangle$	C_p	$\langle T\rangle$	C_p	$\langle T\rangle$	C_p
K	J K^{-1} mol^{-1}	K	J K^{-1} mol^{-1}	K	J K^{-1} mol^{-1}	K	J K^{-1} mol^{-1}
5.33	0.1890	21.91	14.36	78.11	58.87	213.92	84.48
5.56	0.2253	22.72	15.32	86.17	61.86	223.92	85.96
6.76	0.4783	24.23	17.08	88.67	62.65	233.95	87.36
7.45	0.6846	24.91	17.89	94.81	64.51	243.99	88.76
8.05	0.9004	26.68	19.97	97.20	65.03	254.00	90.16
9.45	1.565	29.29	23.00	106.26	67.18	263.75	91.53
9.86	1.801	31.52	25.51	116.23	69.41	273.59	92.87
11.61	3.051	32.41	26.48	126.63	71.49	283.61	94.40
12.06	3.440	34.78	29.02	136.83	73.31	293.62	95.85
13.66	4.935	38.14	32.44	146.94	74.94	303.62	97.25
14.19	5.499	42.25	36.34	157.01	76.53	313.63	98.82
15.70	7.131	47.19	40.63	163.59	77.51	323.59	100.33
16.31	7.835	52.80	45.09	167.03	78.00	333.63	101.96
17.73	9.475	58.34	48.90	173.81	79.04	341.43	103.12
18.43	10.29	58.39	48.93	184.02	80.51	347.06	104.15
19.76	11.85	64.17	52.32	193.91	81.83		
20.57	12.80	70.78	55.72	203.90	83.20		

[a] The molar mass of $CsNO_3$ was taken to be 194.9103 g mol^{-1}.

about 10 K above 100 K. The heat capacities in table 1 are uncertain by about 5 per cent near 6 K, by about 1 per cent near 14 K, and by about 0.2 per cent above 25 K. No corrections were deemed necessary for the trace metal impurities in the sample.

A plot of C_p° against $\langle T \rangle$ exhibited the normal sigmoid shape; no anomalies were observed.

TABLE 2. Thermodynamic functions of CsNO₃ to 350 K [a]

T	$C_p^\circ(T)$	$S^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$-\{G^\circ(T) - H^\circ(0)\}/T$
K	J K⁻¹ mol⁻¹	J K⁻¹ mol⁻¹	J mol⁻¹	J K⁻¹ mol⁻¹
5	0.149	(0.0448)	(0.1755)	(0.0097)
10	1.888	0.5377	4.207	0.1170
15	6.364	2.067	23.82	0.4790
20	12.12	4.680	69.92	1.184
25	18.01	8.016	145.2	2.207
30	23.79	11.81	249.8	3.487
35	29.24	15.90	382.5	4.965
40	34.26	20.13	541.5	6.595
45	38.82	24.44	724.4	8.338
50	42.93	28.74	929.0	10.16
60	49.90	37.21	1394	13.97
70	55.38	45.33	1922	17.87
80	59.66	53.02	2498	21.79
90	63.03	60.25	3112	25.67
100	65.77	67.04	3757	29.47
110	68.10	73.42	4426	33.18
120	70.18	79.43	5118	36.78
130	72.07	85.12	5829	40.28
140	73.82	90.53	6559	43.68
150	75.46	95.68	7305	46.98
160	77.00	100.60	8068	50.18
170	78.47	105.31	8845	53.28
180	79.89	109.84	9637	56.30
190	81.28	114.19	10443	59.23
200	82.66	118.40	11262	62.09
210	84.03	122.46	12096	64.87
220	85.40	126.41	12943	67.57
230	86.78	130.23	13804	70.21
240	88.18	133.95	14679	72.79
250	89.58	137.58	15567	75.31
260	91.00	141.12	16470	77.78
270	92.43	144.58	17387	80.19
280	93.85	147.97	18319	82.55
290	95.29	151.29	19264	84.86
300	96.74	154.55	20225	87.13
310	98.25	157.74	21200	89.36
320	99.79	160.89	22190	91.54
330	101.36	163.98	23196	93.69
340	102.94	167.03	24217	95.80
350	104.58	170.04	25255	97.88
273.15	92.88	145.66	17679	80.94
298.15	96.47	153.95	20046	86.71
	±0.19	±0.31	±40	±0.17

[a] The molar mass of CsNO₃ was taken to be 194.9103 g mol⁻¹.

4. Derived thermodynamic results

A weighted least-squares procedure was used to fit the heat capacities in table 1 to two polynomial expressions in T, one covering the region to 40 K and the other the region above 20 K. The standard deviations of the experimental heat capacities from the calculated curves were 0.18 and 0.07 per cent, respectively. The heat capacities above 5 K (table 2) have been calculated from these polynomials.

A plot of C_p°/T against T^2 of the nine lowest experimental points was linear from about 13 to 7 K and then curved smoothly downwards to $T \to 0$. The heat capacity at 5 K in table 2 was read from this curve and S° (5 K) and $\{H^\circ(5\ K) - H^\circ(0)\}$ were computed by integrating under the curve. Above 5 K, the functions given in table 2 were obtained by integrating the two polynomials referred to above.

5. Discussion

In this paper, we report the first experimental determination of the low-temperature heat capacity of $CsNO_3$. As mentioned earlier, we previously estimated $S^\circ(CsNO_3)$ at 298.15 K based on enthalpy-of-solution and density measurements, and published activity coefficients. That value, $(155.2 \pm 0.8)\ J\ K^{-1}\ mol^{-1}$,[6] is close to the new experimental result $(153.95 \pm 0.31)\ J\ K^{-1}\ mol^{-1}$, and this lends support to the enthalpy-of-solution results which have, in the meantime, also been confirmed by Lovetskaya et al.[13]

Mustajoki in 1957[7] reported values for the heat capacity of $CsNO_3$ in the temperature region from 323 to 723 K. His measurements were performed with an adiabatic calorimeter similar in design to that described by Moser.[14] An accuracy of 0.05 per cent was claimed for this apparatus. However, between 323 and 350 K where our measurements overlap those of Mustajoki, there is a difference of about 4 per cent between the two sets of heat capacities, ours being lower. We believe the present heat capacities to be more reliable. Accordingly, we have smoothly extrapolated $(C_p^\circ$ against T graph) our values to 425 K, the temperature of the hexagonal-to-cubic transformation. A second-degree polynomial in T was used to represent the extrapolated heat capacities and gave the first three C_p° values and, thence, the corresponding thermodynamic functions in table 3.

For the hexagonal-to-cubic transformation at 425 K, we have taken $\Delta S = 8.7\ J\ K^{-1}\ mol^{-1}$ and $\Delta H = 3.7\ kJ\ mol^{-1}$ as selected by Stern[9] from Mustajoki's results. A linear equation in T was fitted by the method of least squares to the heat capacities of Mustajoki from 425 K to the melting temperature and this polynomial was used to obtain the heat capacities and the derived thermodynamic properties in the central section of table 3.

For the cubic-to-liquid transformation, we have taken Stern's[9] selected values, based on Mustajoki's experiments: $\Delta S = 20.8\ J\ K^{-1}\ mol^{-1}$ and $\Delta H = 14.1\ kJ\ mol^{-1}$. Again, an equation linear in T was used to represent the heat capacities of Mustajoki for $CsNO_3(l)$, and the values in the lower part of table 3 and the corresponding thermodynamic functions were calculated in the usual way.

TABLE 3. Thermodynamic functions of CsNO$_3$ (375 to 725 K)

T K	C_p ^{a} J K^{-1} mol^{-1}	S ^{a} J K^{-1} mol^{-1}	$H(T)-H(0)^a$ kJ mol^{-1}	$-\{G(T)-H(0)\}/T$ J K^{-1} mol^{-1}
375	108.73	177.40	27.92	102.94
400	113.02	184.55	30.69	107.82
425^b	117.47	191.53 ± 0.50	33.57	112.54
425^b	131.92	200.2 ± 0.7	37.27	112.54
450	135.55	207.9	40.62	117.62
475	139.18	215.3	44.05	122.56
500	142.81	222.5	47.58	127.38
525	146.44	229.6	51.19	132.08
550	150.07	236.5 ± 2.0	54.90	136.67
575	153.70	243.2	58.69	141.16
600	157.33	249.9	62.58	145.55
625	160.96	256.3	66.56	149.85
650	164.59	262.7	70.63	154.07
675	168.22	269.0	74.79	158.21
679^b	168.80	270.0 ± 4.0	75.46	158.87
679^b	169.87	290.8 ± 5.0	89.56	158.87
700	172.84	296.0	93.16	162.94
725	176.37	302.2 ± 6.0	97.53	167.63

^{a} We estimate the heat capacities to have a probable error of 5 per cent above 425 K. There are corresponding uncertainties in the *incremental* values for the other functions. The resultant overall uncertainties have been tabulated for S only at selected temperatures.

^{b} Broken lines denote a hexagonal-to-cubic transformation at 425 K and a cubic-to-liquid transformation at 679 K.

Finally for the formation at 298.15 K of CsNO$_3$ from its elements according to the equation:

$$Cs(c) + \tfrac{1}{2}N_2(g) + \tfrac{3}{2}O_2(g) = CsNO_3(c), \qquad (1)$$
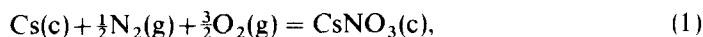
we recommend the following values:

$$\Delta H_f^\circ = -(505.8 \pm 0.5)\,\text{kJ mol}^{-1},[6]$$

$$\Delta S_f^\circ = -(334.59 \pm 0.51)\,\text{J K}^{-1}\,\text{mol}^{-1},$$

and

$$\Delta G_f^\circ = -(406.0 \pm 0.5)\,\text{kJ mol}^{-1}.$$

For the calculation of ΔS_f°, standard entropies: (85.23 ± 0.40), (191.50 ± 0.03), (205.04 ± 0.03), and (153.95 ± 0.31) J K^{-1} mol^{-1} were taken from the CODATA selection[15] and from this work for Cs, N$_2$, O$_2$, and CsNO$_3$, respectively.

REFERENCES

1. (a) Kim, K.-Y.; Johnson, G. K.; Johnson, C. E.; Flotow. H. E.; Appelman, E. H.; O'Hare, P. A. G. *J. Chem. Thermodynamics*, in press.
   (b) Lyon, W. G.; Osborne, D. W.; Flotow, H. E. *J. Chem. Thermodynamics* **1975**, 7, 1189.
   (c) O'Hare. P. A. G.; Boerio, J. *J. Chem. Thermodynamics* **1975**, 7, 1195.
   (d) Fredrickson, D. R.; Johnson, G. K.; O'Hare, P. A. G. *J. Chem. Thermodynamics* **1980**, 12, 801.
   (e) O'Hare, P. A. G.; Boerio, J.; Jensen, K. J. *J. Chem. Thermodynamics* **1976**, 8, 381.
2. (a) O'Hare, P. A. G.; Hoekstra, H. R. *J. Chem. Thermodynamics* **1975**, 7, 279.
   (b) Osborne, D. W.; Flotow, H. E.; Hoekstra, H. R. *J. Chem. Thermodynamics* **1974**, 6, 179.
   (c) Fredrickson, D. R.; Chasanov, M. G. *Analytical Calorimetry*, Vol. 3. Porter. R. S.; Johnson, J. F.; Editors. Plenum Publishing Corp.: New York. **1974**, p. 723.
   (d) O'Hare. P. A. G.; Hoekstra, H. R. *J. Chem. Thermodynamics* **1973**, 5, 851.
3. (a) O'Hare. P. A. G.; Hoekstra, H. R.. *J. Chem. Thermodynamics* **1974**, 6, 251.
   (b) Osborne. D. W.; Brletic, P. A.; Hoekstra, H. R.; Flotow, H. E. *J. Chem. Thermodynamics* **1976**, 8, 361.
   (c) O'Hare, P. A. G.; Hoekstra, H. R. *J. Chem. Thermodynamics* **1975**, 7, 831.
   (d) Fredrickson, D. R.; O'Hare, P. A. G. *J. Chem. Thermodynamics* **1976**, 8, 353.
4. Cordfunke, E. H. P.; O'Hare, P. A. G. *The Chemical Thermodynamics of Actinide Elements and Compounds, Part 3. Miscellaneous Actinide Compounds.* International Atomic Energy Agency: Vienna, Austria. **1978**.
5. Chun, K. S. *U.K. At. Energy Res. Establ. Rep.* AERE R8735. **1977**.
6. O'Hare. P. A. G.; Boerio, J. *J. Chem. Thermodynamics* **1975**, 7, 937.
7. Mustajoki, A. *Ann. Acad. Sci. Fenn. Ser. A, VI, Physica* **1957**, 7.
8. Swanson, H. E.; Cook, M. I.; Isaacs, T.; Evans, E. H. *Standard X-Ray Diffraction Powder Patterns.* Natl Bur. Stand. (U.S.) Circular 539, **1960**, 9, 25.
9. Stern, K. H. *J. Phys. Chem. Ref. Data* **1972**, 1, 747.
10. Flotow, H. E.; Klocek, E. E. *Rev. Sci. Instrum.* **1968**, 39, 1578.
11. Osborne, D. W.; Flotow, H. E. *J. Chem. Thermodynamics* **1972**, 4, 411.
12. Osborne, D. W.; Schreiner, F.; Flotow, H. E.; Malm, J. G. *J. Chem. Phys.* **1972**, 57, 3401. Additional references concerning techniques and temperature scale are given in this publication.
13. Lovetskaya, G. A.; Kuznetsova, G. P.; Stepin, B. D. *Zh. Fiz. Khim.* **1975**, 49, 1601.
14. Moser, H. *Physik. Zeit.* **1936**, 37, 737.
15. CODATA recommended key values for thermodynamics, 1977. *J. Chem. Thermodynamics* **1978**, 10, 903.