Thermochimica Acta, 237 (1994) 247–252
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01672-P

Heat capacity and thermodynamic properties of alkali metal compounds. Part 8. Cesium and rubidium halides

Rajiv Kohli
Environmental Systems and Technology Division, Battelle Memorial Institute, 505 King Avenue, Columbus, OH 43201-2693, USA

(Received 25 October 1993; accepted 10 December 1993)

Abstract

The heat capacities of cesium and rubidium bromides and rubidium iodide have been measured by differential scanning calorimetry (DSC) in the temperature range 310–780 K. These values have been combined with measured and estimated values for the standard entropy and enthalpy of formation for CsBr, RbBr, and RbI to obtain thermodynamic functions up to 800 K.

INTRODUCTION

The alkali metals cesium and rubidium are volatile, and are present as high-yield fission products in nuclear reactor fuel rods. These elements are also highly reactive and they thus tend to form very stable compounds with the fuel and with other fission products such as the halogens. This suggests that the chemical activity of the halogens will be determined by cesium and rubidium during irradiation.

Elemental iodine and bromine can cause embrittlement of the zircaloy cladding of UO_2 fuel rods. However, the fission yields of the alkali metals are 10–20 times the fission yields of the halogens, and all of the fission product iodine and bromine should be tied up as Cs and Rb halides. These halides are highly volatile and will migrate through the hot fuel to the cooler regions of the cladding. In regions of contact between the fuel and the zircaloy cladding, the presence of the alkali halides could lead to the formation of cesium and rubidium zirconates, which might generate sufficiently large halogen pressures to cause failure of the cladding by halogen stress corrosion cracking.

To define the thermochemical conditions under which such interactions will occur, high temperature thermodynamic data on the alkali metal halides are needed. The thermodynamic properties of CsI have been reviewed in detail by Cordfunke and Konings [1], and reliable data to 2000 K are available. Brönsted [2], Kirkham and Yates [3], Sorai et al. [4], Paukov et al. [5] and Robbins and Marshall [6] have measured the heat capacity of CsBr in the range 1.5–307 K. For the rubidium compounds, Rollefson and Peressini [7] and Ho and Dandekar [8] have measured the heat capacities in the range 0.1–24 K. Brönsted reported the heat capacities for RbBr and RbI at a single temperature, 283 K, and Clausius et al. [9] measured the heat capacities for these compounds in the range 10.5–276.9 K.

This paper, which is the eighth in a series on the thermodynamic properties of alkali metal compounds, presents the results of heat capacity measurements on solid CsBr, RbBr, and RbI from 310 to 780 K.

EXPERIMENTAL

Sample preparation and characterization

The salts used in this work were purchased from commercial sources as high purity materials (99.9 mol% nominal purity). Each salt was recrystallized from distilled water and dried in vacuo at 480 K for 4 h. X-ray, chemical, and spectrographic analyses showed the samples to be better than 99.9% pure.

Calorimetric technique

The experimental techniques employed have been described previously [10]. All handling of the samples was carried out in an argon-filled glove box. The measurements were carried out on a Perkin-Elmer DSC II instrument from 310 to 780 K with a heating rate of 10 K min^{-1} and a sensitivity of 5 mcal s^{-1} full scale deflection. As reference material, ground NBS sapphire was sealed in a gas-tight pan; its mass was so chosen as to give a heat capacity similar to those of the samples.

The heat capacity was determined in the usual way by measurements on an empty pan (baseline), the samples, and the reference material against an empty pan. The heat capacities were calculated from the expression

$$[C_p^\circ]_{\text{sample}} = [C_p^\circ]_{\text{sapphire}} \times \frac{[m]_{\text{sapphire}} \cdot [d]_{\text{sample}}}{[m]_{\text{sapphire}} \cdot [d]_{\text{sample}}} \quad (1)$$

where $[m]$ = mass, $[d]$ = recorded thermal effect, and $[C_p^\circ]$ = heat capacity.

RESULTS AND DISCUSSION

Cesium bromide

The experimental heat capacities for CsBr are listed in Table 1. The method of least squares was used to fit these values to the following polynomial for the heat capacity in the range 310–800 K

TABLE 1

Measured molar heat capacity of CsBr. Molar mass of CsBr = 212.814 g mol^{-1}

Temperature/K	C_p°/(J K^{-1} mol^{-1})	Temperature/K	C_p°/(J K^{-1} mol^{-1})
310	52.20	550	55.71
330	52.54	580	56.10
350	52.82	600	56.37
380	53.21	630	56.75
400	53.59	650	56.95
430	53.90	680	57.35
450	54.32	700	57.61
480	54.76	730	57.99
500	55.01	750	58.21
530	55.40	780	58.55

$$C_p^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 49.2145 + 1.2218 \times 10^{-2}T - 8.11557 \times 10^4 \times T^{-2} \quad (2)$$

As noted earlier, several authors [2–5] have measured the heat capacities of CsBr. Comparing their results at 283 K, the data of Kirkham and Yates [3] and Sorai et al. [4] are indistinguishable, and Brönsted's [2] heat capacity value is 0.36% lower; the value of Paukov et al. [5] is approx. 1.3–1.65% higher than those of the other authors. The present results merge smoothly with the low temperature data of Kirkham and Yates [3] and Sorai et al. [4].

Entropy and enthalpy values for CsBr were calculated from appropriate integrals of eqn. (2). These values were combined with published entropies and standard enthalpies at 298.15 K to obtain the thermal functions listed in Table 2. The thermodynamic properties of cesium and bromine used in the calculations were obtained from refs. 11–14.

TABLE 2

Thermodynamic properties of cesium bromide to 800 K

Temperature/K	C_p° /(J K^{-1} mol^{-1})	$S^\circ(T)$ /(J K^{-1} mol^{-1})	$H^\circ(T) - H^\circ(298)$ /(kJ mol^{-1})	$-[G^\circ(T) - H^\circ(298)]/T$ /(J K^{-1} mol^{-1})	$-\Delta H_f^\circ$ /(kJ mol^{-1})	$-\Delta G_f^\circ$ /(kJ mol^{-1})
298.15	52.928	113.052	0	113.052	405.806	361.996
300	52.021	113.374	0.096	113.053	405.808	361.726
350	52.846	121.456	2.718	113.689	407.925	354.084
400	53.599	128.562	5.380	115.113	407.894	346.427
450	54.309	134.917	8.077	116.967	407.811	338.772
500	54.993	140.674	10.810	119.054	407.683	331.127
550	55.660	145.947	13.576	121.263	407.512	323.496
600	56.315	150.818	16.376	123.525	407.301	315.880
650	56.962	155.351	19.208	125.801	407.054	308.283
700	57.603	159.596	22.072	128.065	406.774	300.705
750	58.240	163.592	24.968	130.301	406.463	293.147
800	58.873	167.371	27.896	132.501	406.122	285.611

TABLE 3

Measured molar heat capacity of RbBr. Molar mass of RbBr = 165.377 g mol^{-1}

Temperature/K	$C_p^\circ/(J\ K^{-1}\ mol^{-1})$	Temperature/K	$C_p^\circ/(J\ K^{-1}\ mol^{-1})$
310	52.92	550	55.15
330	53.11	580	55.41
350	53.30	600	55.60
380	53.64	630	55.81
400	53.77	650	55.93
430	54.11	680	56.19
450	54.28	700	56.34
480	54.61	730	56.56
500	54.72	750	56.68
530	54.96	780	56.89

TABLE 4

Measured molar heat capacity of RbI. Molar mass of RbI = 212.372 g mol^{-1}

Temperature/K	$C_p^\circ/(J\ K^{-1}\ mol^{-1})$	Temperature/K	$C_p^\circ/(J\ K^{-1}\ mol^{-1})$
310	53.22	550	55.73
330	53.48	580	56.04
350	53.71	600	56.23
380	54.01	630	56.55
400	54.19	650	56.81
430	54.50	680	56.98
450	54.78	700	57.23
480	55.03	730	57.57
500	55.21	750	57.73
530	55.52	780	58.01

TABLE 5

Thermodynamic properties of rubidium bromide to 800 K

Temperature/K	C_p° /(J K^{-1} mol^{-1})	$S^\circ(T)$ /(J K^{-1} mol^{-1})	$H^\circ(T) - H^\circ(298)$ /(kJ mol^{-1})	$-[G^\circ(T) - H^\circ(298)]/T$ /(J K^{-1} mol^{-1})	$-\Delta H_f^\circ$ /(kJ mol^{-1})	$-\Delta G_f^\circ$ /(kJ mol^{-1})
298.15	52.844	109.956	0	109.956	394.593	352.253
300	52.793	110.282	0.098	109.957	394.591	352.092
350	53.351	118.464	2.752	110.602	396.769	344.790
400	53.482	125.620	5.432	112.041	396.719	337.399
450	54.295	131.988	8.135	113.910	396.631	330.014
500	54.725	137.731	10.861	116.010	396.509	322.638
550	55.138	142.967	13.607	118.226	396.358	315.274
600	55.541	147.782	16.374	120.491	396.180	307.923
650	55.937	152.243	19.161	122.764	395.978	300.588
700	56.327	156.403	21.968	125.020	395.755	293.268
750	56.713	160.302	24.794	127.243	395.514	285.964
800	57.096	163.975	27.639	129.425	395.257	278.676

TABLE 6

Thermodynamic properties of rubidium iodide to 800 K

Temperature/ K	C_p° /(J K^{-1} mol^{-1})	$S^\circ(T)$ /(J K^{-1} mol^{-1})	$H^\circ(T) - H^\circ(298)$ /(kJ mol^{-1})	$-[G^\circ(T) - H^\circ(298)]/T$ /(J K^{-1} mol^{-1})	$-\Delta H_f^\circ$ /(kJ mol^{-1})	$-\Delta G_f^\circ$ /(kJ mol^{-1})
298.15	53.179	118.407	0	118.407	333.794	346.222
300	53.160	118.736	0.098	118.408	333.797	292.095
350	53.694	126.971	2.770	119.057	335.958	284.884
400	54.213	134.175	5.467	120.506	335.893	277.592
450	54.725	140.590	8.191	122.387	335.788	270.310
500	55.232	146.382	10.940	124.502	335.644	263.042
550	55.736	151.670	13.714	126.735	335.464	255.791
600	56.237	156.541	16.513	129.018	335.250	248.557
650	56.737	161.062	19.338	131.311	335.004	241.342
700	57.326	165.285	22.187	133.589	334.729	234.147
750	57.734	169.251	25.061	135.835	334.427	226.973
800	58.232	172.993	27.961	138.042	334.100	219.820

Rubidium halides

Tables 3 and 4 list the experimental values for the heat capacities of RbBr and RbI, respectively, which were fitted to the following polynomials for the heat capacity of each compound from 310 to 800 K

$$\text{RbBr: } C_p^\circ/(\text{J K}^{-1}\text{mol}^{-1}) = 51.4248 + 0.7223 \times 10^{-2}T - 7.61764 \times 10^4 \times T^{-2} \quad (3)$$

$$\text{RbI: } C_p^\circ/(\text{J K}^{-1}\text{ mol}^{-1}) = 50.4174 + 0.9799 \times 10^{-2}T - 2.01628 \times 10^4 \times T^{-2} \quad (4)$$

Our high temperature data join smoothly with the low temperature heat capacities of Clausius et al. [10] extrapolated to room temperature for both rubidium compounds.

Appropriate integrals of eqns. (3) and (4) were used to calculate the entropy and enthalpy values for the rubidium compounds. These values were combined with published entropies and standard enthalpies for RbBr and RbI at 298.15 K to obtain the thermodynamic properties for those compounds listed in Tables 5 and 6. The thermodynamic properties of rubidium, bromine, and iodine used in the calculations were obtained from refs. 11–14.

ACKNOWLEDGMENTS

The author is grateful to Paul Tomlin for assistance with the experimental work. He also thanks Claire Matthews for very useful discussions and Karen Rush for assistance in manuscript preparation. Dr. Malcolm Chase at the National Institute of Standards and Technology kindly provided us with the review of the thermodynamic properties of the alkali metals in advance of publication.

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