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Note

HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF ALKALI METAL COMPOUNDS. III. ESTIMATION OF THE THERMODYNAMIC PROPERTIES OF CESIUM AND RUBIDIUM CHALCOGENIDES

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For thermochemical calculations involving the reactions of the relatively abundant fission products cesium, rubidium, tellurium, and selenium, reliable thermodynamic data are required. As reported previously [1,2], we have initiated an experimental program to acquire high temperature thermodynamic data on various cesium and rubidium compounds. While these measurements are in progress, we are also exploring methods for estimating the thermodynamic properties of the compounds for which experimental data are unavailable. In the third paper in this series, we briefly present methods for estimating the standard enthalpies of formation and the standard entropies of cesium and rubidium chalcogenides, M_2X (M = Cs, Rb; X = Te, Se).

STANDARD ENTHALPY OF FORMATION, ΔH_f^0

Cesium chalcogenides, Cs_2Te and Cs_2Se

If the values for the corresponding sulfide and any other alkali metal chalcogenides are known, one can estimate $\Delta H_f^0(M_2X)$ from the expression

$$\Delta H_f^0(M_2X) = \frac{\Delta H_f^0(M_2S) \cdot \Delta H_f^0(N_2X)}{\Delta H_f^0(N_2S)} \quad (1)$$

where N is any alkali metal other than cesium and rubidium.

Available experimental ΔH_f^0 values [3,4] are listed in Table 1. Using the values for the appropriate lithium and sodium compounds and K_2S in eqn. (1), we first estimated ΔH_f^0 for K_2Te:

$\Delta H_f^0(K_2Te) = -299.53$ kJ mole^{-1} with N = Li (KI)

$\Delta H_f^0(K_2Te) = -364.59$ kJ mole^{-1} with N = Na (KII)

Mills [4] estimates a value of -344.72 kJ mole^{-1} which is also the value

TABLE 1

Experimental ΔH_f^0 values

Compound	$-\Delta H_f^0$ (kJ mole^{-1})	Ref.
Li_2S	441.41	3
Li_2Se	419.24	3
Li_2Te	347.27	4
Na_2S	364.85	3
Na_2Se	341.41	3
Na_2Te	349.36	3
K_2S	380.74	3
K_2Se	394.97	3
Rb_2S	360.66	3
Cs_2S	359.82	3

listed by Lindemer et al. [5]. Each of these values can, in turn, be used to estimate $\Delta H_f^0(Cs_2Te)$ from eqn. (1):

$\Delta H_f^0(Cs_2Te) = -283.07$ kJ mole^{-1} with KI

$\Delta H_f^0(Cs_2Te) = -344.56$ kJ mole^{-1} with KII

$\Delta H_f^0(Cs_2Te) = -316.33$ kJ mole^{-1} with Mills' value

The comparison with lithium appears to be inappropriate since the values of the lithium compounds (Li_2S, Li_2Se) are consistently different from the other alkali metal compounds. Also, Mills' estimated value for $\Delta H_f^0(K_2Se)$ is based on older data. Hence, the best selected value is $\Delta H_f^0(Cs_2Te) = -344.56$ kJ mole^{-1}. This value can be compared with other estimates for $\Delta H_f^0(Cs_2Te)$ in the literature. Gotzmann [6] and Adamson et al. [7] list estimated values of -314 kJ mole^{-1} and -294 kJ mole^{-1}, respectively, but they provide no details of either their estimation methods or the data base they used. Lindemer et al. [5] estimate a value of -284.5 kJ mole^{-1} based on values for the analogous compounds listed by Mills [4]. As noted above, Mills' data should be superseded by newer data compiled in the recent NBS monograph [3].

For $\Delta H_f^0(Cs_2Se)$, we have used the experimental data for lithium, sodium, and potassium compounds in eqn. (1) to estimate the following values:

$\Delta H_f^0(Cs_2Se) = -341.75$ kJ mole^{-1} with N = Li

$\Delta H_f^0(Cs_2Se) = -336.70$ kJ mole^{-1} with N = Na

$\Delta H_f^0(Cs_2Se) = -373.27$ kJ mole^{-1} with N = K

Clearly, the value estimated by comparison with potassium is considerably lower, since the ratio $\Delta H_f^0(K_2Se)/\Delta H_f^0(K_2S)$ is greater than unity. Hence, this value is rejected. The best estimated value selected is $\Delta H_f^0(Cs_2Se) = -339.92$ kJ mole^{-1}. By comparison, Lindemer et al. [5] estimate $\Delta H_f^0(Cs_2Se) = -313.7$ kJ mole^{-1}.

Rubidium chalcogenides, Rb_2Te and Rb_2Se

As before, we used the experimental values for the appropriate lithium and sodium compounds and the previously estimated value of K_2Te in eqn. (1) to obtain the following values for $\Delta H_f^0(Rb_2Te)$ shown in Table 2. Again, the value estimated by comparing with lithium is rejected and the best estimated value selected is $\Delta H_f^0(Rb_2Te) = -345.35$ kJ mole^{-1}.

For $\Delta H_f^0(Rb_2Se)$, we obtain the values given in Table 3. Here again the comparison with potassium is rejected. The best estimated value selected is $\Delta H_f^0(Rb_2Se) = -340.02$ kJ mole^{-1}. By comparison, Lindemer et al. [5]

TABLE 2

$\Delta H_f^0(Rb_2Te)$ values

N	$-\Delta H_f^0(Rb_2Te)$ (kJ mole^{-1})
Li	283.74
Na	345.35
K	345.36

TABLE 3

$\Delta H_f^0(Rb_2Se)$ values

N	$-\Delta H_f^0(Rb_2Se)$ (kJ mole^{-1})
Li	342.55
Na	337.49
K	374.14

TABLE 4

A comparison of the S^0 values estimated in the present work with those estimated by Lindemer et al. [5]

Compound	S^0(J mole^{-1})	
	This work	Lindemer et al. [5]
Cs_2Te	159.41	174.4
Cs_2Se	156.06	166.5
Rb_2Te	145.19	157.7
Rb_2Se	141.84	149.7

estimated ΔH_f^0 values of -301.2 kJ mole^{-1} and -330.5 kJ mole^{-1} for Rb_2Te and Rb_2Se, respectively.

STANDARD ENTROPY, S^0

The standard entropies of these compounds were estimated by a Latimer scheme using revised values of the entropies of the cations and anions listed by Kubaschewski and Alcock [8]. The estimated values are compared with the values estimated by Lindemer et al. [5] in Table 4.

FUTURE WORK

The experimental program to measure the heat capacities of the alkali metal compounds, including the chalcogenides, is currently underway. The results will be reported as they become available.

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REFERENCES

1 R. Kohli and W. Lacom, Thermochim. Acta, 57 (1982) 155.
2 R. Kohli, Thermochim. Acta, 65 (1983) 285.
3 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm and R.L. Nuttall, Natl. Bur. Stand. (U.S.), Tech. Note 270-8, May 1981.
4 K.C. Mills, Thermodynamic Data for Sulphides, Selenides and Tellurides, Butterworths, London, 1974.
5 T.B. Lindemer, T.M. Besmann and C.E. Johnson, J. Nucl. Mater., 100 (1981) 178.
6 O. Götzmann, J. Nucl. Mater., 84 (1979) 39.
7 M.G. Adamson, E.A. Aitken, R.W. Caputi, P.E. Potter and M.A. Mignanelli, Proc. Symp. Thermodyn. Nucl. Mater., 1979, Vol. I, IAEA, Vienna, 1980, p. 503.
8 O. Kubaschewski and C.B. Alcock, Metallurgical Thermochemistry, Pergamon Press, New York, 5th edn., 1979.