THE HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF THE THERMAL TRANSITIONS OF STRONTIUM HEXAAMMINE

L.V. COULTER⁽¹⁾, A. MITCHELL⁽²⁾, S. LEE-BECHTOLD⁽³⁾ and J.K. GIBSON⁽⁴⁾

Department of Chemistry, Boston University, Boston, MA 02215, U.S.A.

Abstract - The heat capacity, transition temperatures and the corresponding enthalpy changes of a 6.51 MPM $\text{Sr}(\text{NH}_3)_6/\text{NH}_3$ system have been measured from 80 K to 190 K by means of adiabatic calorimetry. From 85 K to 145 K the heat capacity of the solid ammine is approximately linear and displays a modest pretransition increase from ~145 K to 175.74 K where a solid-solid transition occurs for which $\Delta H = 1181 \pm 10 \text{ cal mole}^{-1}$ of $\text{Sr}(\text{NH}_3)_6$ and $\Delta S_{\text{tr}} = 7.61 \text{ cal mole}^{-1} \text{ K}^{-1}$ after correction for a pretransition effect of $0.89 \text{ cal mole}^{-1} \text{ K}^{-1}$. From ~80 K to ~140 K our Cp data are about midway between others' results reported earlier for two different samples of the hexaammine which differed ~40% at 100 K. The enthalpy change we have observed is ~ double that reported by others using differential thermal analysis. For the eutectic transition, we estimate $\Delta S_{\text{tr}} \approx 5.28 \text{ kcal mole}^{-1} \text{ K}^{-1}$ of hexaammine melting. An exploratory investigation of the effect of ND_3 substitution for NH_3 in the hexaammine indicated that the S-S transition was elevated 6.34 K from 175.74 K to 182.08 K; and that the eutectic transition was increased by 5.17 K from 185.37 K to 190.54 K. The ΔS_{tr} for the S-S transition, which we take to be an order-disorder transition, is in line with ΔS_{tr} for similar transitions that occur in the $\text{M}(\text{NH}_3)_6\text{I}_2$ salts in which "revised" ΔS_{tr} 's are $\approx R \ln 32$ which also approximates the experimental ΔS for $\text{Ca}(\text{NH}_3)_6\text{I}_2$ as well as for $\text{Sr}(\text{NH}_3)_6$ - both of which contain comparably large M^{+2} .

1. **Introduction:** The paucity of low temperature calorimetric thermodynamic data for the alkaline earth hexaammines and the general as well as specific utility of such information stimulated the extension of our earlier calorimetric studies of the lithium-ammonia systems [1] to the characterization of the heat capacity and transition enthalpies of a Sr/NH_3 system in the 80 K-185 K range. Aspects of these measurements, which were completed over a decade ago, were communicated briefly during the discussion period of the paper by Jacobs, Major and McCormick [2] at Colloque Weyl VI in 1983 on the heat capacity of calcium and strontium hexaammines in the 2 K-140 K range. Prior to that time some relevant information regarding the transition enthalpies of Sr/NH_3 Systems had been obtained by differential thermal analysis (DTA) techniques and reported by Mehta and Mammano [3], and will be introduced later.

The following account will be confined to the results we obtained for a single 6.514 MPM system of strontium and ammonia although some preliminary measurements on a lower MPM system have been completed. In addition, transition temperatures for a Sr/ND_3 system will be included.

2. **Experimental:** The heat capacity and enthalpy measurements were made in an adiabatically controlled cryostat and used a stainless steel calorimeter within which the strontium-ammonia systems were prepared as previously described [1]. Samples of strontium metal (99.5% by wt., Atomergic Chemical Co.) were prepared free of surface oxidation and transferred to and from weighing ampoules and into the calorimeter within a polyethylene glove bag containing dry argon gas. Samples of metal were stored and weighed in evacuated glass ampoules. 0.1124 and 0.01460 moles of metal were used for the NH_3 and the ND_3 studies, respectively.

The ND_3 was prepared according to the directions given by Schindewolf [4]. Analysis by NMR techniques indicated the presence of 0.76% H. High purity Matheson NH_3 and the preparation of ND_3 were further purified and introduced into the calorimeter in a manner as previously described [1]. For

⁽¹⁾Present Address: 14 Fox Hill St., Westwood, MA 02090, U.S.A.

⁽²⁾Present Address: A.T. and T. Bell Laboratories, Murray Hill, NJ 07974, U.S.A.

⁽³⁾Present Address: Washington College, Chestertown, MD, U.S.A.

⁽⁴⁾Present Address: Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN 37830, U.S.A.

the Sr-NH₃ system 1.6130 moles of NH₃ were employed which gave a 6.514 MPM system. For the Sr-ND₃ system, 0.2363 moles of ND₃ were added to the Sr which gave a 5.819 MPM system.

Continuous monitoring of the cryostat and calorimeter containing the refrigerated metal ammonia systems after preparation gave no evidence of a decomposition reaction over many months during which the measurements were completed. Transition temperatures were determined by warming curves into the transitions as previously described [1c] and also by measurements of equilibrium temperatures following the introduction of appropriate amounts of energy to produce the desired fraction of the transition.

3. Results: The molar heat capacity of Sr(NH₃)₆ was calculated from the measured values of the total heat capacity of the calorimeter and contents from which the heat capacity of the calorimeter and excess NH₃ have been subtracted. We have assumed (1) that all of the Sr exists in the form of Sr(NH₃)₆ below the eutectic point (2) that below the eutectic temperature excess NH₃ appears as pure solid NH₃ and (3) that, in accordance with the phase diagram [5], solid NH₃ is present in diminishing amount as the temperature of the eutectic mixture (7.0 MPM) is increased above the eutectic temperature on the NH₃ rich side of the phase diagram.

The molar heat capacities of Sr(NH₃)₆ from 80 K to 186 K are listed in Table 1 and are presented graphically for the solid system in figure 1. From ~85 K to ~150 K Cp slowly increases linearly followed by a more rapid rise in the 150 K-175 K range which precedes an isothermal solid-solid transition at (175.74 ± 0.02) K. Between the solid-solid transition and the eutectic point, Cp exceeds the pretransition value by ~60 cal mole⁻¹ K⁻¹ followed by the eutectic transition at (185.37 ± 0.03) K.

The Cp data in figure 1 consist of several series of measurements, each of which is designated by a number, above or below the Cp curves, that relates the chronology of the measurements which covered a total period of many months. Thus, all four of the Cp values in series 20 were determined consecutively and preceded series 21 which consisted of two Cp consecutive measurements.

In some regions the Cp data display considerable scatter - up to 2-3% - which we attribute to poor thermal equilibration that was frequently encountered.

The dashed line in figure 1 represents the total calculated heat capacity of one mole of Sr metal [6] and six moles of solid NH₃ [7] for comparison with the measured molar heat capacity of Sr(NH₃)₆. Although the measured Cp of the hexaammine exceeds the additive heat capacity from ~80 K to ~115 K, in line with expectations for an expanded metal structure, the values for the 115 K to 175 K range are less than the additive values with the exception of two Cp values obtained in preliminary measurements. This behavior contrasts sharply with the observations on Li/NH₃ systems [1a] for which the measured Cp exceeded the additive values substantially in the entire temperature range of the measurements.

Figure 1 Cp of Sr(NH₃)₆. Insert at top is on an expanded scale; Curves A and B [2]; dashed line ----, calculated Cp of one mole Sr and 6 moles NH₃(s); S-S, solid-solid transition; E.U., eutectic transition. Numbers at top and bottom give relative chronological order of measurements.

Figure 2 ΔS_{tr} vs. Radius of M^{+2} in $M(NH_3)_6X_2$ salt and Sr^{+2} in $Sr(NH_3)_6$; ΔS_{tr} values [5]; ionic radii, L. Pauling, "Nature of the Chemical Bond" (Cornell University Press, Ithaca, NY (1940), pp. 345-350).

Table 1 Cp of $\text{Sr}(\text{NH}_3)_6$ cal mole⁻¹K⁻¹

Series	T/K	Cp	Series	T/K	Cp	Series	T/K	Cp	Series	T/K	Cp
9	80.85	40.47	10	95.80	45.94	11	132.30	51.78	14	163.92	62.28
16	81.19	42.36	7	97.96	45.04	21	134.52	51.08	3	166.93	67.54
15	82.48	42.11	19	99.97	46.82	12	136.17	52.16	24	167.92	63.48
18	82.79	43.19	7	104.78	46.23	21	140.46	51.34	13	171.98	75.27
17	83.20	41.99	19	105.62	47.78	12	142.23	53.30	24	172.72	68.15
9	85.76	44.24	7	111.14	48.20	22	146.56	53.65	2	178.21	105.27
16	86.72	44.63	20	112.23	48.72	13	147.21	52.33	1	181.07	104.57
15	87.94	44.26	8	113.58	48.49	23	149.78	54.73	2	182.25	98.52
18	88.70	44.89	20	117.98	49.33	22	153.19	54.78	1	183.45	97.04
17	88.92	45.08	8	119.80	49.73	13	153.42	55.76	3	187.61	107.13
9	90.57	44.50	20	123.39	50.56	23	155.96	56.92	4	192.15	211.2
10	90.89	45.02	8	126.29	49.49	14	158.43	58.62	4	192.51	171.80
19	94.15	45.11	11	126.68	50.22	24	162.34	57.16	4	197.72	152.24
18	94.73	46.08	20	128.86	51.00	23	162.41	60.78			

Table 2 $\Delta H/\text{mole Sr}(\text{NH}_3)_6$ for the Solid-Solid Transition at $(175.74 \pm .02)$ K

Temperature Interval, K	Heat Input cal	$T_1 \int_{T_1}^{T_2} \text{Cpdt}$	ΔH cal
173.81 - 179.64	298.03	163.97	1192.7
175.58 - 176.99	174.35	41.39	1182.9
175.26 - 177.30	190.56	58.89	1171.4
174.86 - 179.97	279.95	147.53	1178.1
ΔS (at 175.74K) ≈ 6.72 cal/mole K			Mean 1181.3 ± 10

"Pretransition entropy correction": $\Delta S_{\text{cor}} = 0.89$ cal mole⁻¹ K⁻¹

Total entropy change for S-S transition = $\Delta S_{\text{tot}} = 7.61$ cal mole⁻¹ K⁻¹

Table 3 $\Delta H/\text{mole of Sr}(\text{NH}_3)_6$ Melting at the Eutectic Temperature $(185.37 \pm .02)$ K

Temperature Interval, K	Energy Input	$\int \text{Cpdt}$ cal	ΔH cal
184.54 - 185.97	672.28	63.29	5418
184.11 - 186.29	689.43	95.04	5288
183.96 - 186.27	700.18	99.19	5347
184.94 - 186.46	654.0	83.50	5076
			Mean 5.28 $\pm .2$ kcal

We have also included in figure 1 the heat capacity curves for two different samples (A and B) of $\text{Sr}(\text{NH}_3)_6$ which were determined by Jacobs et al. [2] and reported previously at Colloque Weyl VI at which time aspects of this research were briefly mentioned during the discussion of their communication. Although the heat capacities for samples A and B differ substantially in the temperature range in which the Jacobs et al. data overlap with the data obtained in this research, it should be mentioned that their curves for A and B merge at ~ 20 K to 2 K after displaying an anomalous hump in the heat capacity in the 25 K-50 K range. As indicated in figure 1, our results lie between the Cp curves of samples A and B. However, our data extrapolate smoothly from 85 K and higher into the Cp curve for sample A at ~ 65 K.

The measured enthalpy changes for the S-S transition at 175.74 K are given in the last column of Table 2 after subtraction of the appropriate pre and post-transition $\int_{T_1}^{T_2} \text{Cp dT}$ from the total energy input. For ΔH_{tr} at 175.74 K we have obtained $1,181 \text{ cal mole}^{-1}$. The corresponding ΔS_{tr} is $6.72 \text{ cal mole}^{-1} \text{ K}^{-1}$. However, in view of the rise in Cp before the transition at 175.74 K, we make the common assumption that the total transition event should include an appropriate pretransition contribution, $\int \text{Cp dln T}$, above a base line which appears to be a simple linear extrapolation from ~ 135 K to the transition temperature. The uncertainties associated with ΔH_{tr} and ΔS_{tr} are probably to be attributed principally to the poorly defined values for Cp in the pretransition as well as the posttransition temperature range. As is to be seen in figure 1, the two Cp's designated #3 are 6-10% above the last measurements (#24) which define the Cp curve as drawn in the pretransition region of figure 1. Accordingly, there is some uncertainty about the correct Cp curve to employ.

The determination of ΔH for the eutectic transition at 185.37 K could not be made with much accuracy and should be regarded as an estimate because of very poor equilibration of the calorimeter and the heterogeneous Sr/NH_3 system in the post-transition region. For the 6.514 MPM system studied in this research, the phase diagram for the Sr/NH_3 system indicates that solid NH_3 or a solid solution of $\text{Sr}(\text{NH}_3)_6$ in solid NH_3 , if the phase diagram proposed by Mehta and Mammano [3] is correct, would be present at temperatures just above the eutectic temperature. Accordingly, since the density of solid NH_3 is probably greater than the density of the liquid solution at the eutectic temperature, it is likely that the crystals of solid NH_3 would be located at the bottom of the calorimeter, and as a consequence the heterogeneous system would require a long period of time to achieve an overall equilibrium both with respect to composition as well as temperature following the energy input and melting of the eutectic mix. The results of our attempts to evaluate $\Delta H \text{ mole}^{-1}$ of $\text{Sr}(\text{NH}_3)_6$ melting $[\text{Sr}(\text{NH}_3)_6(\text{s}) + \chi \text{NH}_3(\text{s}) \rightarrow \text{Sat'd Sol'n (7\% Sr)}]$ at the eutectic point (185.37 ± 0.03 K), are given in Table 3. For ΔH per mole of $\text{Sr}(\text{NH}_3)_6(\text{s})$ melting we have obtained $(5.28 \pm 0.2) \text{ kcal}$.

For $\text{Sr}(\text{ND}_3)_6$ we found by warming curves that the order-disorder transition occurred at $(182.08 \pm 0.03) \text{ K}$ and the eutectic transition at $(190.54 \pm 0.03) \text{ K}$.

4. Discussion of Results: The reasons for the deviation of the Cp of Jacobs et al. [2] samples A and B from one another, as well as the divergence of their Cp values from those of this research are not obvious. However, it may be, as suggested by Jacobs et al. [2], that "the variation in the data between the two samples of the same compound was due to different amounts of the metastable, supercooled high temperature phase in the samples." which could occur as a consequence of variations in the thermal histories of the samples.

The enthalpy changes which we have found for the transitions are substantially larger than the corresponding values, reported by Mehta and Mammano [3] who, by means of differential thermal analysis measurements, found the temperatures of the solid-solid and eutectic transitions to be 175 K and 184 K - in reasonably good agreement with our observations - but report much lower values for the corresponding ΔH 's. For the solid-solid transition Mehta and Mammano [3] found a maximum value of $623 \text{ cal mole}^{-1}$ of Sr at a composition of 7.0 MPM (the eutectic composition) and a maximum value of $3843 \text{ cal mole}^{-1}$ for the eutectic transition also at 7.0 MPM. These values are $\sim 53\%$ and $\sim 73\%$ of the corresponding values we have observed in this research. Moreover, Mehta and Mammano [3] also observed that for NH_3 rich systems < 7 MPM the heat effects decreased toward zero with decreasing MPM and, as a consequence, they invoked solid solution formation of $\text{Sr}(\text{NH}_3)_6$ in NH_3 to account for their results. However, it is to be noted that DTA measurements on the Li/NH_3 systems by David et al. [8] also exhibited an unexpected decreasing heat effect for Li/NH_3 systems below 16 MPM in contrast to a constant heat effect observed by Mammano and Coulter [1a,b] for the eutectic and solid-solid transitions for two systems < 20 mole % Li in NH_3 . At the present, an acceptable explanation for the disagreement between DTA and adiabatic calorimetric measurements is wanting.

It is of interest to consider the thermal properties of $\text{Sr}(\text{NH}_3)_6$ in the context of these properties of metal hexaammine salts of divalent metals, $\text{M}(\text{NH}_3)_6 \text{X}_2$. The presence of the $\text{M}(\text{NH}_3)_6^{++}$ cluster in all cases appears to impart the common feature of a principal order-disorder transition which has been attributed to an orientation disordering of the hexaammine clusters and the NH_3 molecules about their trigonal axes in moving through the transition. Presumably, this involves the change of hindered rotation of NH_3 molecules that have been confined by barriers to a single, or very few, orientations of lowest energy to a state in which the barriers to rotation are cooperatively surmounted and a redistribution of

molecules and clusters into several inter- and intra- additional configurations results. This would, in turn, result in a more symmetrical phase above the transition temperature [9,10].

In pursuing this notion Klaaijsen et al. [9] have measured the heat capacities and heats of transition of several metal hexaammines iodides from which they have calculated the corresponding entropy changes for the transitions. It is of interest to view their results as a function of the radii of the dipositive metal ions which we show graphically in figure 2. We have also included the ΔS for the solid-solid transition of $\text{Sr}(\text{NH}_3)_6$ determined in this research. Although the correlation of the ΔS values with ionic radii is admittedly qualitative, it would appear that the disordering effect on the entropy change becomes larger for large ions and that ΔS for the transition in $\text{Sr}(\text{NH}_3)_6$ follows qualitatively the behavior of the $\text{M}(\text{NH}_3)_6\text{I}_2$ compounds.

However, Klaaijsen et al. [9] have regarded the experimental transition entropies as somewhat superficial and have calculated "revised" values based on considering the NH_3 molecules as restricted rotators and accordingly contributing differently to the lattice heat capacity in the several iodides. This along with suitable Debye and Einstein contributions were subtracted from the total measured heat capacity and enabled them to compute the "revised" ΔS_{tr} . Although details of the calculation are not given by them, it appears that their procedure is in lieu of the usual estimate of the basic lattice contribution to the entropy which involves estimating a base curve from below to above the transition which serves to establish the entropy contribution to ΔS_{tr} of the measured Cp above the base line. As a consequence of their procedure, they obtained for ΔS_{tr} values "nearly the same amount of entropy $\Delta S_{\text{tr}} = R \ln 32$ for most of the samples" [9] and have proposed that the order-disorder transition, $\Delta S_{\text{tr}} \geq R \ln 32$, arises from a change of presumably one to possibly "32 low energy inter-cluster configurations of the NH_3 octahedral clusters throughout the whole crystal" [9] which qualitatively would be in accord with the theoretical approach of Bates and Stevens [10] for the hexaammine nickel halides. Although we have not attempted to obtain a "revised" ΔS_{tr} for the transition in $\text{Sr}(\text{NH}_3)_6$ in order to justify a direct comparison with the $\Delta S = R \ln 32$ value, it seems likely that the value, $\Delta S_{\text{tr}} = 7.61 \text{ cal mole}^{-1} \text{ K}^{-1}$, we have obtained will not be modified to any great extent in view of the relatively small revision of the ΔS_{tr} values for the larger ions - calcium in particular.

In addition to the common existence of the primary transition in the iodide salts and $\text{Sr}(\text{NH}_3)_6$, several of these systems also exhibit breaks in the slopes of the Cp/temperature curves. For $\text{Sr}(\text{NH}_3)_6$ this occurs at $(38.6 \pm 0.2) \text{ K}$ - 137 K below the primary transition [2]. For $\text{Cd}(\text{NH}_3)_6$ [9] a bump occurs in the curve 1.7 K below the transition at 32.6 K and a shoulder to the transition occurs in the case of $\text{Ni}(\text{NH}_3)_6\text{I}_2$ [11], 1.7 K below the transition at 19.78 K. Similar behavior is also exhibited in $\text{Ni}(\text{NH}_3)_6(\text{BF}_4)_2$ [12] as a bump in the Cp curve at $\sim 112.9 \text{ K}$, $\sim 27 \text{ K}$ below the transition at $(140.1 \pm 0.2) \text{ K}$, and in $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$ [13] at 143K, 30 K below the primary transition at 173.05 K. To what extent these secondary anomalies are also a part of an order-disorder transition involving the +2 cluster ion or some other phenomenon (such as disordering of the polyatomic negative ions) is not clear, although in those cases where the anomaly is only a few degrees below the primary transition, the contribution to the ΔS_{tr} has already been included in the calculations of ΔS for the transition and is obviously a part of the transition event.

Finally, it is to be noted that the effect of substitution of ND_3 for NH_3 in $\text{Sr}(\text{NH}_3)_6$ produced an increase in the temperatures of both the order-disorder and the eutectic transitions. The former was increased 6.34 K from 175.74 K to 182.08 K and the eutectic temperature was elevated 5.17 K from 185.37 K to 190.54 K. A similar effect has been reported, as is to be expected, for substitution of ND_3 for NH_3 in $\text{Ni}(\text{ND}_3)_6\text{I}_2$ [14] in which the order-disorder transition occurs at 26.5 K, 7.0 K above T_{tr} at 19.5 K in $\text{Ni}(\text{NH}_3)_6\text{I}_2$. Although ND_3 substitution for NH_3 in $\text{Li}(\text{NH}_3)_4$ appears to increase the order-disorder transition in the tetraammine from 82.23 K into the eutectic transition (i.e., the order-disorder transition and the eutectic melting occur simultaneously at the eutectic point) at 88.37 K in $\text{Li}(\text{ND}_3)_4$ [1d] the eutectic temperature is surprisingly lowered by $\sim 0.4 \text{ K}$ from 88.80 K in $\text{Li}(\text{NH}_3)_4$.

In summary we find aspects of the thermal properties of $\text{Sr}(\text{NH}_3)_6$ and $\text{Sr}(\text{ND}_3)_6$ systems that can also be identified in the hexaammine M^{+2} salts presumably because of the presence of the common cluster entity, $\text{M}(\text{NH}_3)_6^{+2}$ which displays properties common to both types of systems.

References:

- [1] (a) N. Mammano and L. V. Coulter, *J. Chem. Phys.* **47**, 1564 (1967); (b) N. Mammano and L. V. Coulter, *J. Chem. Phys.* **50**, 393 (1969); (c) L. V. Coulter, S. Lee-Bechtold, V. Madhvaraja and J. K. Gibson, *Chem. Thermodyn.* **13**, 815 (1981); (d) L. V. Coulter, J. K. Gibson and N. Mammano, *J. Phys. Chem.* **88**, 3896 (1984).
- [2] D. A. Jacobs, T. J. Major and W. E. M. McCormick, *J. Phys. Chem.* **88**, 3877 (1984).
- [3] K. Mehta and N. Mammano, *Jour. Sol. State Chem.* **8**, 348 (1973).
- [4] U. Schindewolf, "Metal Ammonia Solutions: Colloque Weyl II, J. J. Lagowski and M. I. Sienko, Eds., Butterworths, London, 1970, p. 495.
- [5] A. J. Birch and D. K. C. MacDonald, *Trans. Faraday Soc.* **44**, 735 (1948).
- [6] J. Boerio and E. F. Westrum, *J. Chem. Thermodynamics* **10**, 1 (1978).

- [7] R. Overstreet and W. F. Giaque, J. Am. Chem. Soc. 59, 254 (1937).
- [8] T. David, W. Glaunsinger, S. Zolotov and M. Sienko, "Electrons in Fluids," J. Jortner and N. R. Kestner, Eds., Springer-Verlag, Berlin, 1973, p. 323.
- [9] F. W. Klaaijsen, H. Sugu and Z. Dokoupkil, Physica 51, 630 (1971).
- [10] A. R. Bates and K. W. H. Stevens, J. Phys. C.: Solid State. Phys. 2, 1573 (1969); A. R. Bates, J. Phys. C.: Solid State. Phys. 3, 1825 (1970).
- [11] R. D. Worswick, J. C. Corvell and L. A. K. Stavely, Jour. Chem. Soc. I 70 (9), 1590 (1975).
- [12] T. Grzybek, J. A. Janik, M. Mayer, G. Pytasz, M. Rachwalska and T. Waluga, Phys. Stat. Sol. (a) 16, K165 (1973).
- [13] M. Rachwalska, J. M. Janik, J. A. Janik, G. Pytasz and T. Waluga, Phys. Stat. Sol. (a) 30, K81 (1975).
- [14] H. Van Kempen, T. Sarofano, A.R. Miedema and W. J. Huiskamp, Physica 31, 1096 (1965).