Inorganica Chimica Acta, 54 (1981) L31–L33
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Determination of the Heat Capacity of Calcium Chloride Octa- and Tetraammines

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Received February 4, 1981

The thermodynamic behavior of calcium chloride ammines was initially investigated in the latter part of the 19th century and at the beginning of the 20th century by Isambert [1], Bonnefoi [2], Ephraim [3], Hüttig [4], Biltz [5], Clark [6], Linge [7] and Hart and Partington [8]. The existence of the following complexes

$$CaCl_2 \cdot nNH_{3(s)} \text{ (where n = 1, 2, 4 or 8)} \quad (1)$$

was established and confirmed by the equilibrium vapor pressure measurements for the stable systems:

$$CaCl_{2(s)} + NH_{3(g)} \Leftrightarrow CaCl_2 \cdot NH_{3(s)} \quad (2)$$

$$CaCl_2 \cdot NH_{3(s)} + NH_{3(g)} \Leftrightarrow CaCl_2 \cdot 2NH_{3(s)} \quad (3)$$

$$CaCl_2 \cdot 2NH_{3(s)} + 2NH_{3(g)} \Leftrightarrow CaCl_2 \cdot 4NH_{3(s)} \quad (4)$$

$$CaCl_2 \cdot 4NH_{3(s)} + 4NH_{3(g)} \Leftrightarrow CaCl_2 \cdot 8NH_{3(s)} \quad (5)$$

The pressure–temperature (P–T) measurements, performed mostly within a limited temperature range, yielded approximate ΔH and ΔS values for the equilibria (2–5). As concerns thermal data, the heat of reaction was measured calorimetrically by Isambert [9] for the reactions (2–4) and Linge for (4 & 5).

Recently, the $CaCl_2 \cdot 8/4NH_{3(s)}$ system has come under widespread investigation as a possible medium for thermal energy storage due to its favorable P–T characteristics, reasonably high energy density and its low cost. Modern investigations have confirmed most of the preexisting results [10, 11], although new techniques have been applied [12–14], and technical [15, 16] and other aspects [17–19] given due regard.

In the present paper, we would like to report the results of a differential scanning calorimetry (DSC) determination of the heat capacity values for the tetra- and octaammines of calcium chloride, which are the most important from an energy storage point of view. Because of the significance of these values, both from theoretical and practical viewpoints [20, 21], they had to be estimated [22, 23], but were never determined experimentally, presumably due to difficulties in handling volatile and reactive samples. In this respect, the technique chosen here, DSC, was found to be suitable, especially since it provided a means to check the absence of sample decomposition.

Experimental

Calcium chloride dihydrate (Merck, *p.a.*) was dried at 160 °C under vacuum with a liquid nitrogen trap for three days prior to use. Each individual sample, after weighing, was transferred to a cylindrical pyrex reaction flask and attached to a pyrex vacuum manifold system by means of glass-to-glass o-ring seals. The reaction flask could be isolated from the manifold system using teflon stopcocks. The salt was further dried to insure no water absorption upon weighing by placing the reaction flask in a thermostated temperature bath at 70 °C and pumping on the salt through a liquid nitrogen trap for at least on hour. At this point, the salt was sealed under vacuum, and ammonia gas (AGA, 99.999%) was introduced into the manifold system. From the knowledge of the pressure–temperature characteristics of the calcium chloride ammines, the sample size and the manifold volumes, the amount of $NH_{3(g)}$ needed to synthesize the desired ammine could be determined. The salt was then exposed to $NH_{3(g)}$ and allowed to equilibrate (2 days for the octaammine and 4 days for the tetraammine). Final stoichiometries were $CaCl_2 \cdot 8.0\ NH_{3(s)}$ ($\pm 0.1\ NH_3$) and $CaCl_2 \cdot 4.0\ NH_{3(s)}$ ($\pm 0.1\ NH_3$).

The amminated salts were transferred to a glove bag where loading of the DSC sample containers took place. The sample cells were constructed of a stainless steel (304) top and bottom, closed with an o-ring seal by means of a press. The cells, designated LVCs (large volume capsules), of 75 μl internal volume were filled to approximately 3/4 capacity with the salt, then sealed. The octaammine was transferred in a pure $NH_{3(q)}$ atmosphere, since the salt was saturated and no further absorption should have occurred. The tetraammine was transferred in a $NH_{3(g)}/N_{2(g)}$ atmosphere, with the partial pressure of $NH_{3(g)}$ estimated to be near the equilibrium pressure of the salt. In either case, the loading was accomplished in under one minute, thus minimizing any possible stoichiometry change.

Each sample was placed in the heating block of a Perkin-Elmer DSC-2, and temperature scans were run at 10 °C/min from 268 to 333 K, using an established procedure [24, 25]. The instrument was calibrated prior to each run using Al_2O_3 (Fisher), whose heat capacity is accurately known throughout a wide temperature range [26].

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TABLE I. Heat Capacity of $CaCl_2 \cdot 8NH_{3(s)}$.[a]

Temp. (K)	C_v^{obs} (J/K Mol)	C_v^{cal} (J/K Mol)	$C_v^{obs} - C_v^{cal}$
268.0	465	467	−2
273.0	473	473	0
278.0	481	479	2
283.0	489	487	2
288.0	495	495	0
293.0	505	504	1
298.0	512	515	−3
303.0	525	526	−1
308.0	538	537	1
313.0	550	550	0
318.0	562	563	−1
323.0	576	577	−1
328.0	590	591	−1
333.0	609	606	3

[a] C_v(J/K Mol) = $-(2.98 \pm 0.22) \times 10^3 + (6.92 \pm 0.37)T + (4.26 \pm 0.33) \times 10^5/T$ (T in K).

TABLE II. Heat Capacity of $CaCl_2 \cdot 4NH_{3(s)}$.[a]

Temp. (K)	C_v^{obs} (J/K Mol)	C_v^{cal} (J/K Mol)	$C_v^{obs} - C_v^{cal}$
268.0	257	259	−2
273.0	260	260	0
278.0	263	262	1
283.0	265	264	1
288.0	268	267	1
293.0	271	271	0
298.0	276	276	0
303.0	280	281	−1
308.0	286	287	−1
313.0	292	293	−1
318.0	301	300	1
323.0	307	308	−1
328.0	316	316	0
333.0	327	325	2

[a] C_v(J/K Mol) = $-(2.35 \pm 0.18) \times 10^3 + (4.90 \pm 0.30)T + (3.47 \pm 0.27) \times 10^5/T$ (T in K).

Results and Discussion

The experimental results are summarized in Tables I and II, giving the determined heat capacity (C_v^{obs}) in five degree increments from 268 to 333 K for both ammines. The values listed are the average of two separate samples synthesized concurrently, with each sample being scanned at least twice. The reproducibility differed by less than 2%. The results obtained from another sample synthesized independently were also in good agreement, and we estimate the overall experimental accuracy to be within ±5%. It should be added that the heat capacity of $NH_{3(g)}$ inside the capsule was calculated and found to be negligible with respect to the measured heat capacity.

The experimental data were fitted by a least squares method to an equation of the form

$$C_v = a + bT + c/T \tag{6}$$

The results of this procedure and the values so generated (C_v^{cal}) are also given in the tables.

Before attempting to discuss the experimental results, a brief mention of the isothermal lines obtained before and after temperature scanning in the DSC runs is necessary. The importance of these lines and their alignment in heat capacity measurements has been stressed [25]. We would like to add that while handling volatile substances such as the octa- and tetraammines of calcium chloride, the alignment of these isothermal lines serves as a check on the absence of sample decomposition. Had they decomposed completely or partially before the end of the scan, a peak would have been obtained; if they decompose during heating (temperature scanning) and continue to do so even at the end of the scan, naturally the isothermal line at the higher temperature will not immediately align with the previously established isothermal line at the lower initial temperature. In all our experiments no peak was obtained and both isothermal lines were identical with respect to those of the runs with empty crucibles (base line) and with the reference sample (Al_2O_3). Furthermore, the cooling mode curve for the octaammine agreed within experimental error with that obtained in the heating mode.

As mentioned above, the heat capacities of $CaCl_2 \cdot 8NH_{3(s)}$ and $CaCl_2 \cdot 4NH_{3(s)}$ have previously been estimated. This was done by, *e.g.*, assuming an additivity of the heat capacities of solid (or liquid) ammonia and calcium chloride [22, 23]. A comparison shows that these estimates were approximately twice as high as the experimental values given here.

An estimate of the variation of ΔH with temperature of reaction (5) is possible from the relation

$$\int d(\Delta H) = \int \Delta C_p dT \tag{7}$$

with the now known heat capacities of $CaCl_2 \cdot 8NH_{3(s)}$ and $CaCl_2 \cdot 4NH_{3(s)}$ and that of $NH_{3(g)}$ [27] (without pressure dependent terms which are negligible in our P–T range) calculated from

$$C_p(\text{J/K Mol}) = 19.17 + 4.05 \times 10^{-2}T + 1.31 \times 10^3/T \tag{8}$$

The variation of C_p of the products and reactants with temperature can be taken into account by feeding the functions $C_p = f(T)$ directly into eqn. (7), which after integration between T_1 and T_2 ($>T_1$) gives the following:

$$\Delta(\Delta H) = 7.07 \times 10^2(T_2 - T_1) - 9.29 \times 10^{-1}(T_2^2 - T_1^2) - 7.38 \times 10^4 \ln(T_2/T_1) \tag{9}$$

Note that since these ammines are solids, we have taken $C_p = C_v$ for the purpose of this calculation.

TABLE III. Temperature Dependence of ΔH for the Reaction $CaCl_2 \cdot 8NH_{3(s)} \Longleftrightarrow CaCl_2 \cdot 4NH_{3(s)} + 4NH_{3(g)}$.

T_1 (K)	T_2 (K)	Δ(ΔH) in Joules/Mol Ammine		
		This Work	Calculated from Previous Work	Reference
268	333	−6362	–	–
273	333	−6020	−6196	7
293	333	−4426	−4354	7
			−14400	13

Comparisons can be made with two previous works that dealt with direct determinations of ΔH. Linge [7] had been able to quantitatively estimate ΔH at temperatures up to 100 °C by using the following equation:

$$\Delta H = APV_{NH_3} \frac{B}{T} - C \qquad (10)$$

where A, B and C are empirical constants. This equation was obtained by combining an empirical non-linear equation, describing his experimental P–T behavior in the temperature range 20–95 °C, with the Clapeyron equation. The value calculated from eqn. (10) was also found to agree with his calorimetrically determined ΔH of 165 kJ/Mol ammine at 20 °C. A comparison between our values calculated from eqn. (9) and Linge's from eqn. (10) is given in Table III, and shows excellent agreement for the two chosen temperature intervals.

Furrer [13] had measured the enthalpy change for reaction (5) by DTA techniques at six different temperatures from 45 to 95 °C. He fitted its variation to a linear equation and obtained $\Delta C_p = [\Delta(\Delta H)/\Delta T]$ as 360 J/K Mol ammine. Our calculations, see Table III, confirm his judgment that this value is too high. On the other hand, Furrer's estimate of ΔC_p, obtained from a procedure [28] employing the Nernst equation, is very close to our value at 20 °C.

Acknowledgements

The authors are indebted to the people of Televerket, in particular J. Björkman and L. Köszegi, who have graciously allowed us the use of their DSC instrument for this work. We would also like to thank Dr. S. Seetharaman, from the Institute of Theoretical Metallurgy, for his valuable suggestions. The grants from the Swedish National Council for Technical Development (STU) and the Swedish Natural Science Research Council (NFR) are gratefully acknowledged.

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