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Heat capacities and enthalpies of transition of $AgNO_3$

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Abstract

The heat capacities of $AgNO_3$ in the solid and liquid phases and the related enthalpies of transition have been measured by differential scanning calorimetry. A review of the literature data and a comparison with the present results are presented.

Keywords: DSC; Silver nitrate; Thermodynamics

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1. Introduction

Some experimental thermodynamic data are available in the literature. Several studies concerning phase equilibria between monovalent nitrates in the condensed phases have been published with the aim of the establishment of data banks [1–3]. A number of experimental investigations are related to pure nitrates. The heat capacities and the enthalpies of transition have already been measured by various methods. The drop method and adiabatic calorimetry have been used since the beginning of the twentieth century. In the seventies, the differential scanning calorimetry appeared, and its increasing success with experimentalists is principally due to its relative ease in carrying out the experiment. In the case of $AgNO_3$, most of the data have been published before 1967 [4–16]. The recent results of Asahina [17] disagree with the previous ones.

As a part of a more complete thermodynamic study of the $NaNO_3$–KNO_3–$AgNO_3$ system, the thermodynamic properties of pure silver nitrate which represents one of the basic elements of the binary and the ternary mixtures of the system has first been reinvestigated. In this paper, new measurements of the enthalpies of transition and of fusion are presented, together with the heat capacities in the solid and liquid phases by differential scanning calorimetry in the 340–520 K temperature range. A review of the literature is also given. The aim of this review is to determine the most reliable thermodynamic data which will be introduced in the further computer optimization of the ternary system.

2. Experimental

The calorimeter is a DSC4 Perkin–Elmer which has already been used in similar measurements [18]. The main difficulty is to reproduce identical thermal conditions during the various runs. Particularly, the

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thermal resistance between the sample and the measurement cell must be as low and as reproducible as possible.

The silver nitrate is purchased from Aldrich (99.995% purity). To prevent chemical contamination, the samples are melted in covered pure platinum crucibles which are used in the calorimeter cell. Each sample of ca. 50 mg is weighed with electronic scales, accurately to ±0.01 mg. Before each run, the sample is held at 380 K in the measurement crucible during 24 h at least and then slowly cooled to room temperature. Curves are recorded between 340 and 520 K at a 5 K min^{-1} heating rate. Pure argon is used as the purge gas.

The heat capacities are calculated from the difference between both the base lines recorded with the empty crucible and with the sample. Before each set of runs, the apparatus is calibrated on a pure α-alumina sample, the heat capacity of which is well known [18].

The enthalpies of transition are measured by the areas under the recorded DSC curves. The calorimeter is calibrated with phase transformations whose enthalpies are well known. In the present study, the calibration is performed by melting 0.19 mmol of indium of 99.999% purity. This transition is recommended in the definition of the ITS-90 at 429.7485 K [19] and the corresponding enthalpy is given at 3263.52 J mol^{-1} [20].

The measured curves are treated by a computer and the thermodynamic data automatically deduced.

3. Results and discussion

The heat capacity measurements are presented in Table 1 and Fig. 1. The results of the measurements of

Table 1
Heat capacity measurements of $AgNO_3$

T/K	C_p/(J mol^{-1} K^{-1})	T/K	C_p/(J mol^{-1} K^{-1})	T/K	C_p/(J mol^{-1} K^{-1})
343	98.5	378	105	418	111
344	99.0	379	105	419	111
345	99.6	380	105	421	112
346	99.8	381	106	422	112
347	100	382	106	423	112
348	101	383	106	424	112
349	101	384	106	424	112
352	101	387	106	425	112
353	102	388	107	427	112
354	102	389	107	428	113
355	102	390	107	429	113
358	102	393	107	430	113
359	102	395	108	431	114
360	103	396	108	433	114
361	103	397	108		
362	103	399	108	474	123
363	103	400	108	475	123
365	103	401	109	476	123
366	103	403	109	477	123
367	104	404	109		
368	104	405	109	514	138
369	104	406	109	515	138
370	104	407	110	516	138
371	104	410	110	517	138
373	104	411	110		
374	105	412	111		
375	105	414	111		
376	105	415	111		
377	105	417	111		

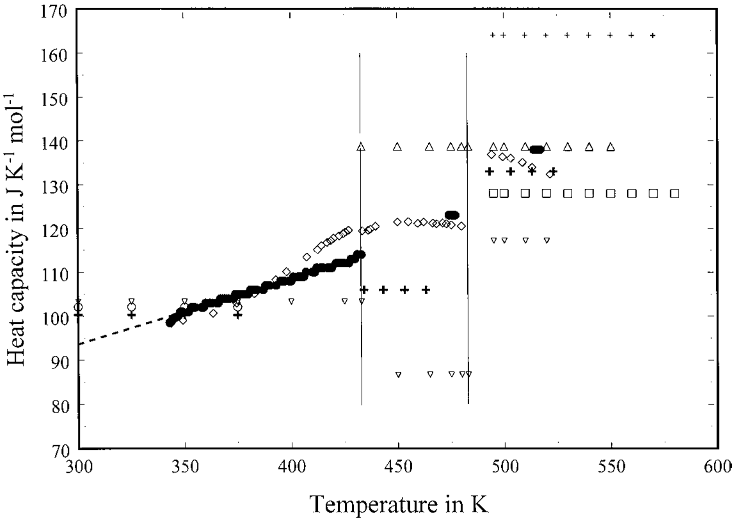

Fig. 1. Heat capacity of $AgNO_3$. (○) [4], (+) [5], (△) [6], (□) [10], (▽) [13], (◇) [16], (+) [17], (●) [this work], and (—) [9].

Table 2
Thermodynamic data of the solid–solid transition and of the fusion of $AgNO_3$

T_{tr}/K	T_f/K	$\Delta_{tr}H$/(J mol^{-1})	$\Delta_f H$/(J mol^{-1})	Method	References
432	481	3485	12 518	[a] and [e]	[5]
—	491	—	10 795	[c]	[6]
433	—	2405	—	[b]	[7]
—	—	—	11 606	[e]	[8]
—	483	—	12 385	[c]	[11]
—	—	2481	—	[e]	[12]
433	483	2510	12 501	[c]	[13]
—	483	—	12 075±34	[g]	[14]
433	483	2347	12 092	[d]	[16]
433	484	2390±4%	12 300±4%	[f]	this work

[a] Mixing method.
[b] Volume discontinuity method.
[c] Drop calorimetry.
[d] Adiabatic calorimetry.
[e] Near adiabatic conditions (for more details see the original publication).
[f] Differential scanning calorimetry.
[g] Dissolution calorimetry.

the temperatures and the enthalpies of transition and fusion are reported in Table 2. A fit of the heat capacity data is reported in Table 3.

On comparing with the literature data, no systematic error due to the methods of measurement of the enthalpies of transitions or the heat capacities has been detected. Nevertheless, the drop method seems less reliable in revealing low variations of the heat capacity as compared to adiabatic calorimetry or differential scanning calorimetry.

3.1. Solid–solid transition

Both solid phases of the silver nitrate crystallize in the rhombohedral form. The parameters are for the low temperature α form: a=6.342 Å, α=47° 49′ and

Table 3
Heat capacities of $AgNO_3$ in the solid and liquid phases (in J/K mol; temperature range in brackets)

α-solid	β-solid	liquid	Methods	References
102.1(273–373K)	—	—	[a]	[4]
100.3(273–432 K)	106(432–481 K)	133(481–525 K)	[a]	[5]
—	138.9(441–474 K)	138.8(493–541 K)	[b]	[6]
—	—	128.0(490–543 K)	[b]	[10]
103.3(424–433 K)	86.7(433–483 K)	117.1(483–574 K)	[b]	[13]
$1.650+0.275T$(343–431 K)	$107.7+0.0285T$(434–481 K)	$219.3-0.166T$(495–522 K)	[c]	[16]
—	—	$164+0.0022(T-T_f)$(495–570 K)	[c]	[17]
$47.39+0.153T$(343–433 K)	122.6(473–478 K)	138.0(514–516 K)	[d]	this work

[a] Mixing method.
[b] Drop calorimetry.
[c] Adiabatic calorimetry.
[d] Differential scanning calorimetry.

for the high temperature β form: a=6.411 Å, α=47° 36′ [21]. Table 2 presents the various data published in the literature with the corresponding type of method which has been used.

Our results agree very well with the solid-state transition temperature which is given in the literature at a remarkably constant value (432–433 K), whatever the determination method. Four direct determinations [7,12,13,16] of the heat of transition lie between 2347 and 2510 J mol^{-1} (mean value 2426 J mol^{-1}). The indirect determination of Franzosini and Sinistri [15] in the K–Ag diagram at 2343 J mol^{-1} agrees well with these data. The old result of Guinchant [5] seems to be 40% too high. The value of 5.6 J K^{-1} mol^{-1} for the entropy of transition can be proposed with good confidence.

3.2. Solid–liquid transitions

The melting temperature of silver nitrate has been measured four times at 483 K (Table 2) [11,13,14,16]. Our result at 484 K and that of Guinchant [5] at 481 K agree well with these values. Only the data of Goodwin and Kalmus (491 K) [6] differ markedly from the previous results, which can be retained for further optimization. The values of enthalpy of fusion lie in the [12075–12518 J mol^{-1}] range for the five determinations carried out [5,11,13,14,16], which includes also our result. The value obtained by the indirect method by Franzosini and Sinistri [15] (12552 J mol^{-1}) is in good agreement. Only, the values obtained by Goodwin [6] using drop calorimetry, and by Magnus [8] using adiabatic calorimetry, are ca. 12% lower than the mean value 12314 J mol^{-1}. An entropy of melting of 25.5 J K^{-1} mol^{-1} can then be deduced.

3.3. Heat capacities

The present results are gathered with the literature data in Table 3 and Fig. 1. Three authors [4,5,13] give a constant mean heat capacity of the α phase included in the narrow range [100–104 J K^{-1} mol^{-1}] over the [300–375 K] temperature range. In the 350–375 K range, all these data added to our results agree within an interval of ±2.5%. Between 375 K and the temperature of the solid–solid transition, two sets of values are available. Janz and Kelly [13] give a constant value all over the α phase range. Our results agree very well up to 400 K with those of Reinsborough and Wetmore [16], obtained by adiabatic calorimetry. At 483 K, the data of these latter authors are 5% higher than ours. A very good agreement is found between the present data and the extrapolation of a linear fit of the results of Smith et al., between 180 and 300 K [9]. In principal, it is for this reason that our value is being now recommended.

The β phase is stable only in a narrow temperature range around 50 K. The heat capacity measurements are then not easy. Both the determinations by drop calorimetry give values differing by 60% [6,13]. The data of Goodwin and Kalmus [6] are identical in the solid β and in the liquid state. Our results agree well with those of Reinsborough et al. [16] within an interval of ±1.5% error range. The results of Guinchant [5] are 14% lower than these present results. We propose for that phase a constant heat capacity of 121±3 J K^{-1} mol^{-1}.

In the liquid state, the heat capacity remains constant over a 50–100 K temperature range, except for Reinsborough and Wetmore [16] who observed a decrease of 4% up to 40 K above the melting point. Like previously shown for $NaNO_3$, KNO_3 and $CsNO_3$ [18], the heat capacities in the liquid nitrates seem to be constant just above the melting point. Four determinations are included in the 128–139 J K^{-1} mol^{-1} range [5,6,10,16]. Our results lie at the upper limit of this range. The recent results of Asahina et al. [17] are 19% higher than 139 J K^{-1} mol^{-1} and those of Janz and Kelly [13], 9% lower than 128 J K^{-1} mol^{-1}.

4. Conclusion

The present results agree well for the temperature and enthalpies of transition with most of the data of the literature. The present heat capacity data are very close to those of Reinsborough and Wetmore [16].

For a further optimization of phase diagrams, the following set of values can be proposed.

α–β transition temperature: (433±1) K
temperature of fusion: (483±1) K
enthalpy of the α–β transition: (2427±90) J mol^{-1}
enthalpy of fusion: (12312±240) J mol^{-1}
entropy of the α–β transition: (5.61±0.22) J K^{-1} mol^{-1}
entropy of fusion: (25.5±0.6) J K^{-1} mol^{-1}
heat capacity in the α state (350–433 K): $(47.4+0.153\,T\pm0.6)$ J K^{-1} mol^{-1}
heat capacity in the β state (433–483 K): (121±3) J K^{-1} mol^{-1}
heat capacity in the liquid state (483–583 K): (135±7) J K^{-1} mol^{-1}

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