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Published in Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 3, 923-929

ECN-W--08-001 JUNE 2008

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INVESTIGATION OF THERMODYNAMIC PROPERTIES OF MAGNESIUM CHLORIDE AMINES BY HPDSC AND TG

For application in a high-lift high-temperature chemical heat pump

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The formation as well as the decomposition of magnesium chloride ammonia complexes was studied by high-pressure differential scanning calorimetry (HPDSC) and thermogravimetric analysis (TG). HPDSC runs were performed under constant ammonia pressure conditions to determine the transition temperatures and stability regions of the ammonia complexes. The TG technique has been employed to examine the stoichiometry of the complexes. The hexa-, di- and mono-ammines are proven to exist under our experimental conditions. The decomposition of the mono ammine to pure $MgCl_2$ occurs most probably in two steps.

Keywords: *ammonia, chemical heat pump, DSC, magnesium chloride, stability diagram, TG, thermodynamic properties*

Introduction

In recent years, the subject of energy saving has come under close examination. One of the options being investigated is a high-lift high-temperature chemical heat pump (CHP), which should make it possible to upgrade industrial waste heat, which is usually released at a temperature range of 80–150°C. Useful heat for the industry should be available at approximately 230°C (middle pressure steam utility). The principle of such a CHP [1, 2] is based on the reversible reactions between a salt and a gas, commonly being a metal chloride and ammonia gas, respectively. A CHP always uses two carefully selected materials, a low-temperature salt (LTS) and a high-temperature salt (HTS) that are contained in separate reactors of the CHP, to achieve a cyclic heat pumping process.

$MgCl_2$ is considered as a good candidate [3] for the use as a high-temperature salt in the CHP under investigation, because the transitions are in the right *p–T* area and the potential temperature lift is sufficient. Although the thermodynamic properties of the magnesium chloride ammonia complexes have been the subject of several studies [4–6], recently as well as in the past, the outcome of these studies appeared to be ambiguous. According to the literature several magnesium chloride ammonia complexes have been determined, namely the hexa-, tetra-, di- and mono-ammonia complexes. This implies that the following reactions are possible:

$$Mg(NH_3)_6Cl_2 \leftrightarrows Mg(NH_3)_4Cl_2 + 2NH_3 \qquad (1)$$

$$Mg(NH_3)_4Cl_2 \leftrightarrows Mg(NH_3)_2Cl_2 + 2NH_3 \qquad (2)$$

$$Mg(NH_3)_2Cl_2 \leftrightarrows Mg(NH_3)Cl_2 + NH_3 \qquad (3)$$

$$Mg(NH_3)Cl_2 \leftrightarrows MgCl_2 + NH_3 \qquad (4)$$

The different literature sources are only consistent about the existence of the hexa-ammonia complex and of the pure anhydrous magnesium chloride.

In the present paper, therefore, the thermodynamic properties, such as transition temperatures and heats of transition, formation and decomposition, of the magnesium chloride ammonia complexes are investigated in a pressures range from 1 to 6 bar. Due to the discordance in the literature another reason to perform this study is to establish which are the stable ammonia complexes under our experimental process conditions.

The reactions under investigation are assumed to be monovariant under thermodynamic equilibrium. However, under the process circumstances used for our experiments, formation and decomposition of the complexes were observed at different temperatures. This implies that an area of pseudo equilibrium exists [7] where the overall reaction rate appears to be zero. Trudel *et al.* [8] postulated two possible reasons for this appearance. The first explanation is that the hysteresis may be caused by an activation barrier necessary to expand the material (work of expansion that is not recovered on contraction). The second explanation, and perhaps a more likely one, is that the observed hysteresis can be found in the fact that there

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1388–6150/$20.00

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could be a temperature difference between the gas and the crystalline complex caused by the (exothermic/endothermic) heat effect of the reaction.

For the transformation of solid ammonia complexes according to the chemical equation:

$$A(s) \leftrightarrows B(s)+xC(g) \tag{5}$$

the change of the Gibbs energy $\Delta_r G$ is equal to zero at equilibrium:

$$\Delta_r G(T)=\Delta_r G^0(T)+xRT\ln p(NH_3)=0 \tag{6}$$

where ΔG^0 is the standard Gibbs energy change, x the amount of compound C (mole), R the gas constant (R=8.3144472 J mol^{-1} K^{-1}) and $p(NH_3)$ represents the equilibrium pressure of ammonia (bar). When taken into account the relation with the enthalpy (H) and entropy (S) as follows:

$$\Delta_r G^0=\Delta_r H^0-T\Delta_r S^0 \tag{7}$$

the Clausius–Clapeyron equation can be formulated:

$$\ln\frac{p(T)}{p_0}=-\left(\frac{\Delta_r H^0}{xR}\right)\left(\frac{1}{T}\right)+\frac{\Delta_r S^0(T)}{xR} \tag{8}$$

The slope of a Clausius–Clapeyron diagram, ln$p$ *vs.* $1/T$, equals minus the enthalpy effect of the reaction per mole of C divided by the gas constant.

Experimental

Materials and methods

Sample preparation

The anhydrous magnesium chloride was obtained from Merck (CAS 7786-30-3). The assay of this product was indicated as ≥98%. Because of the hygroscopic character of magnesium chloride the sample was first dehydrated in a Mettler-Toledo DSC821^e in a nitrogen atmosphere (obtained by the vaporization of liquid nitrogen, Hoekloos). After this drying procedure the sample was quickly weighed and introduced into the Mettler-Toledo DSC27HP (the uncertainty in the sample mass has been estimated as 2.5%). To remove a possible small amount of water that may have absorbed during the transfer to the HPDSC, first the sample was heated again under nitrogen atmosphere. Hereafter the atmosphere was changed from nitrogen to ammonia (Hoekloos, ammonia purity higher than 99.98%), at this point the sample is ready to be measured.

For the thermogravimetric (TG) experiments the magnesium chloride ammonia complex was prepared by using a glass tube (Fig. 1). Inside the tube the magnesium chloride (A) was placed on top of a glass filter (B). Then after sealing the tube by using a teflon ring, a vacuum was created inside the tube. The atmosphere was controlled by using a pressure controller (at the outlet of the setting) as well as a flow controller (at the inlet). After creating a vacuum the pressure was slowly increased by using an ammonia gas flow of 50 mL min^{-1} while the pressure controller was set at 1.4 bar. When this pressure was reached, the sample was kept overnight in the glass-tube to accomplish complete formation of the magnesium ammonia complex. The preparation took place at ambient temperature.

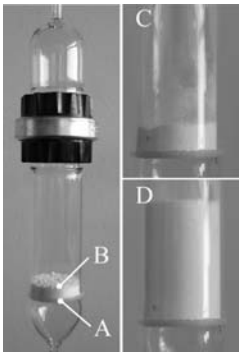

Fig. 1 Glass-tube, A – holding the glass filter which support the B – dry magnesium chloride. Magnesium chloride C – before and D – after the adsorption of ammonia

Thermal analysis

The HPDSC measurements were carried out in a Mettler-Toledo DSC27HP. The atmosphere was regulated by using Brooks Instruments pressure and flow controllers, type 5866 and 5850S, respectively. The ammonia gas flow for these measurements was set at a constant rate of 50 mL min^{-1}. Each formation as well as decomposition experiment was performed at a given constant pressure while the sample (3.65 mg), placed in a 40 μL golden pan, covered with a lid in which a hole was drilled, was submitted to a temperature program with a constant heating or cooling rate of 1.0 K min^{-1}.

The system was calibrated prior to the measurements using indium, tin and lead. It was interesting that we found that the temperature calibration parameters depend on pressure [9].

A Mettler-Toledo TGA/SDTA 851^e used to follow the decomposition of the reaction product depicted in Fig. 1. The sample (15.27 mg) was placed in a 100 μL aluminium crucible with pierced lid (50-μm hole). Reason for the use of perforated lids is that this leads to much narrower decomposition peaks. The measurements were performed in a flow of nitrogen (Hoekloos, purity higher than 99.9%) of 50 mL min^{-1} from 300.15 up to 873.15 K with a heating rate 5.0 K min^{-1}.

Results and discussion

DSC experiments

High-pressure differential scanning calorimetry was used to measure the heat of decomposition as well as

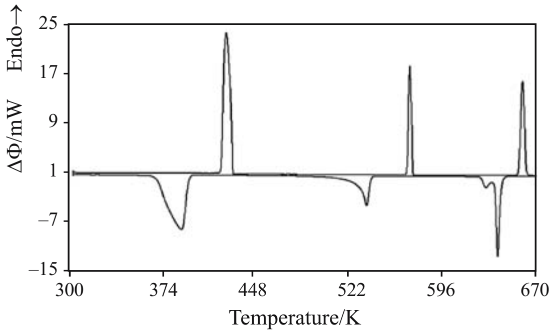

Fig. 2 Typical example of the transitions of $MgCl_2$ and NH_3 at $p=1$ bar, endothermic effects plotted upwards

the heat of formation at partial ammonia pressures between 1 and 6 bar, using heating and cooling rates of 1 K min^{-1}.

Figure 2 represents a typical result of these HPDSC measurements. On heating as well as on cooling three effects were observed, corresponding to decomposition and formation reactions, respectively.

The thermal effects at low temperature are caused by the decomposition (upward) and formation (downward) of the ammonia complex containing the highest amount of NH_3 (i.e. the hexa-ammonia complex). The effects at higher temperatures are associated to the complexes containing smaller amounts of NH_3. The thermal effects will be further on assigned as 'low-, middle- and high-temperature transition', respectively.

For the low-temperature transition the measured heat effects are greater than those for the other two transitions. Furthermore the formation reaction at high temperature appears to take place in two steps at a pressure below 2.0 bar. When a cycle is performed at higher pressure, namely 6.0 bar (Fig. 3a), the formation reaction at low temperature as well as the decomposition at high temperature appears to take place in two steps (Fig. 3b, subdivision II). Contrary to the splitting up of the high-temperature formation reaction at 1 bar, the formation at 6 bar appears to be a single step (Fig. 3b, subdivision III). From the shape of the high-temperature formation peak it appears that the formation of the ammonia complex occurs instantaneously. As a consequence of such a fast formation reaction the data collection of the HPDSC is not sufficiently fast enough to reproduce a reliable reflection of the evolution of the reaction. Because the reaction rate is so high the corresponding calculated heat of transition will be continually lower than it should be. Therefore the heat of this transition can not be considered as reliable and will not be included in the data reporting.

The experimental transition temperatures at different pressures are plotted in a Clausius–Clapeyron diagram (Fig. 4).

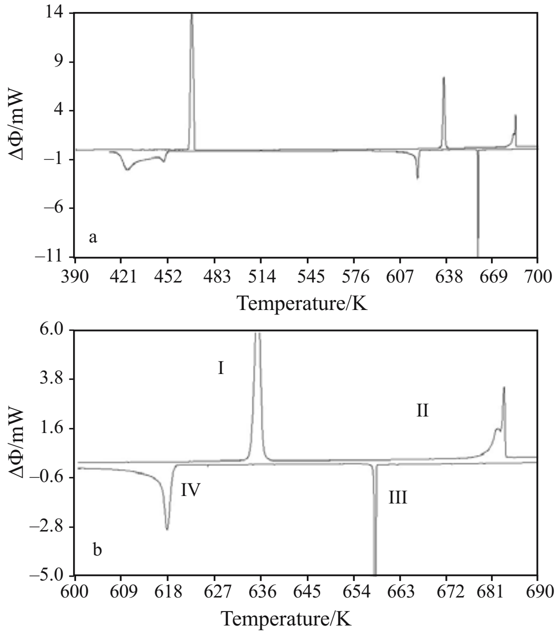

Fig. 3 Example of the splitting up of the thermal effects at a – $p=$ 6.0 bar, b – middle- and high-temperature transitions enlarged, endothermic effects plotted upwards

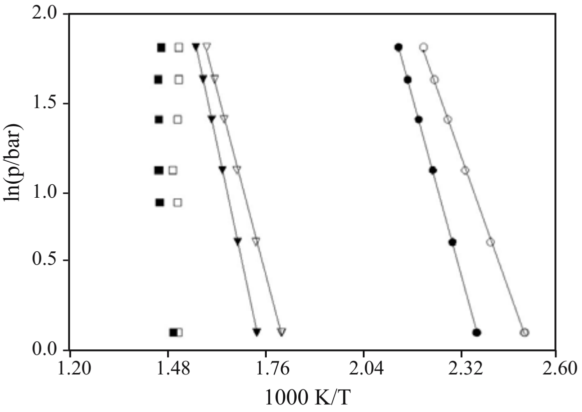

Fig. 4 Results of the low-temperature transition of $MgCl_2$ ○ – formation, ● – decomposition, middle-temperature transition ▽ – formation, ▼ – decomposition and the high-temperature transition, □ – formation, ■ – decomposition

Table 1 collects the extrapolated onset temperatures together with the measured heats of reaction of the exothermic and endothermic events observed in the HPDSC during the cycles at different pressures. The presented transition temperatures as well as the heats of transition were obtained by averaging the measured values by the number of cycles reported in the table. Due to the high precision of the instrument the use of two decimals for the temperatures is justified. The heats, Q, are given with respect to one gram of magnesium chloride. Note that due to the instantaneously occurrence of the reaction the heat of transition of the high-temperature formation transition are not included.

Table 1 Experimental results of all transitions of magnesium chloride

Pressure/bar	Formation: Transition temperature/K	Formation: $-Q$/J g^{-1}	Decomposition: Transition temperature/K	Decomposition: Q/J g^{-1}	Number of measurements
Low-temperature transition					
1.20	398.87±0.27	1783	421.11±0.05	1786	13
2.00	414.48±0.04	1551	433.86±0.06	1549	6
3.00	427.24±0.09	1374	444.65±0.05	1374	8
4.00	436.40±0.08	1084	452.67±0.02	1090	6
5.00	443.70±0.05	866	459.10±0.02	876	5
6.00	449.84±0.05	643	464.62±0.15	662	4
1.20	398.35±0.32	362	421.35±0.27	414	8
Middle-temperature transition					
1.20	548.80±0.10	656	570.89±0.05	656	13
2.00	571.59±0.15	542	589.01±0.03	553	6
3.00	589.94±0.08	455	604.18±0.02	484	8
4.00	602.79±0.12	344	615.53±0.01	378	6
5.00	612.82±0.03	258	624.88±0.01	301	5
6.00	621.14±0.02	184	633.43±0.10	226	4
1.20	549.36±0.24	130	571.10±0.09	145	8
High-temperature transition					
1.20	653.77	–	659.48	680	13
2.00	654.53	–	676.98	552	6
3.00	660.41	–	679.14	442	8
4.00	654.77	–	678.14	360	6
5.00	652.87	–	678.62	286	5
6.00	652.97	–	675.12	159	4

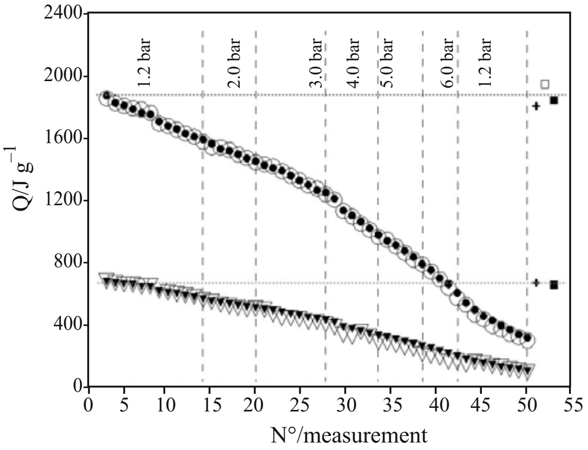

Fig. 5 Summary of the number of measurement performed against the elapse of the heats of transitions concerning the low-temperature transition ○ – formation, ● – decomposition and the middle-temperature transition, ▽ – formation, ▼ – decomposition regarding all data presented in Table 2. Additionally the first measurements of new sequences starting at a pressure of + – 1.01, ■ – 2.00 and □ – 7.00 bar with fresh magnesium chloride

When the heats of transition are closely inspected it is noticeable that the heats of transitions are decreasing correspondingly to increasing number of performed measurements (Fig. 5) for the formation as well as for the decomposition reactions.

Figure 5 shows this downward trend. The decline of the measured heat effects appears not to be influenced by the applied pressure, since also the last measurements at one pressure show the same decline.

From this observation the assumption is made that the first heat effect measured in the sequence of each transition, approaches the actual heat of transition, and therefore is to be used in further calculation and interpretation. This assumption is confirmed by additional measurements with fresh magnesium chloride as starting material and at different starting pressures. The ΔH and ΔS deduced in terms of Eq. (8) are given in Table 2, together with the heats of transition of the first measurement in the sequence, in contrast to the average heat of transition in Table 1, obtained via the HPDSC measurements. Note that the enthalpy and entropy obtained via the C–C diagram are given with respect to one mole ammonia. The C–C analysis for the high-temperature transitions can not be calculated: the slope is close to infinity.

TG experiments

The thermal stability of the magnesium chloride ammonia complexes was examined by measuring its decomposition as a function of increasing temperature. The TG curve, as shown in Fig. 6a, shows a substantial mass loss between 347 and 463 K and a smaller

Table 2 Survey of the outcome of our investigation

Transition		Q/J g^{-1}	ΔH from HPDSC curve/kJ mol^{-1}	ΔH from C–C diagram/J mol^{-1}	ΔS from C–C diagram/J K^{-1} mol^{-1}
Low-temperature	formation	1935	184.3	46677	118.53
	decomposition	1954	186.1	60456	145.06
Middle-temperature	formation	719	68.4	62876	115.92
	decomposition	714	67.9	78089	138.31
High-temperature	decomposition	737	70.2		

Table 3 Survey of the thermal decomposition data of magnesium chloride ammonia complexes

Stage number	Temperature range/K	Peak value DTA/K	Presupposed released ammonia	Theoretical mass loss at each stage/%	Mass loss measured by TG/%
I	347–463	431.04	$4NH_3$	34.51	32.73±0.08
II	490–575	567.67	NH_3	13.17	14.81±0.05
III	583–653	646.17	NH_3	15.17	18.09±0.24
IV	653–708	693.22			
I–IV	–	–	$6NH_3$	51.77	53.06±0.11

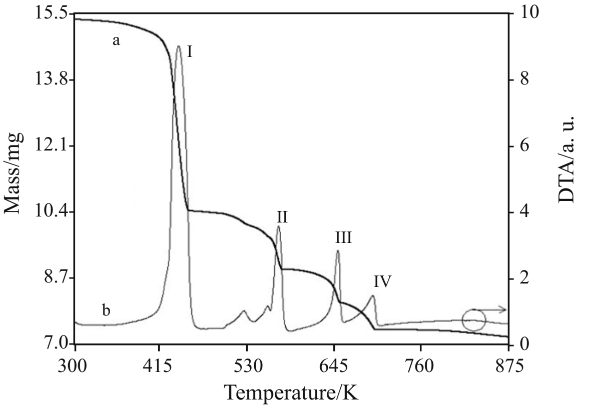

Fig. 6 a – TG curve and b – DTA signal of the decomposition of the magnesium chloride ammonia complexes

mass loss between 490 and 575 K. At temperatures above 583 K two mass loss steps are noticed which are not completely separated from each other; this is also visible in the recorded DTA signal (Fig. 6b). Therefore these mass losses are calculated as one step (Table 3). As shown in Fig. 6, four decomposition steps were observed. TG analysis shows that the high-temperature transition is subdivided into two steps (stages III and IV).

As stated earlier, the goal of this research is to obtain the transition temperatures, heats of transition and more certainty about the stoichiometry of the magnesium chloride ammonia complexes. Therefore this section will be divided accordingly.

Transition temperatures

The transition temperatures for the formation as well as for the decomposition reactions have been determined. As shown in Table 1, the temperatures are obtained with high accuracy, despite the presence of pseudo equilibrium regions. When comparing these temperatures with the ones obtained by TG, there is a perceptible similarity. A reason for the small difference between these data may be the difference in the used heating rate and the partial NH_3 pressure.

From Fig. 4 it can be observed that the slope of the high-temperature transition is close to infinity, meaning that the reaction appears to be independent of the partial ammonia pressure. Two extreme assumptions can be considered for this behaviour. Firstly, the enthalpy of reaction is infinitely large. Secondly, there are no molecules of ammonia involved in this transition. Considering the mass losses measured by TG and the fact that the reaction is reversible, the latter explanation is highly unlikely. Although it is visible in Fig. 3 (subdivision III) that during the formation of this transition the complex is instantaneously formed, this could not be the explanation of this phenomenon. Owing to the complexity of the system, a simple and straightforward explanation for this phenomenon is not easily given. The figure also shows that the existence of the earlier stated pseudo equilibrium is consistent with the experimental results. Even though some of the reactions proceed slower than the other ones, the onset temperatures of both formation and decomposition reactions should result in a single C–C line. Deviation from this ideal behaviour has been reported in many cases [7, 8]. Differences in formation and decomposition kinetics are the main reason for the existence of this pseudo equilibrium area in which the overall reaction rate is zero. Of course the actual thermodynamic equilibrium temperatures lie in between the measured temperatures for formation and decomposition. Contrary to the high-temperature transition the low- and middle-temperature transitions do not show any deviant behaviour concerning the C–C diagram.

Heats of transition

Figure 5 reveals an obvious decline of the measured heats of transition. Various series of experiments, each with another fresh magnesium chloride sample as starting material, reveals the same decline even though the sequence of the applied pressure on the fresh samples dissimilar.

Two possible reasons can be postulated concerning this decline. First due to chemical reactions there may be a significant structural modification at every transition the host, magnesium chloride, undergoes. This may result in a transition from a crystalline structure towards an amorphous one. The latter structure is less capable of absorbing ammonia, which is reflected in the experimental results. When this mechanism recurs at every subsequent cycle the active crystalline mass, is decreasing resulting in a lower heat effect.

A second explanation for this occurrence may be that the instrument does not measure the heat effect to its full extent, as noticed in previous research [10]. It can be learned from Fig. 1 that there is an enormous increase in volume (decrease in density upon absorption of ammonia); the salt will change in a more porous structure resulting in a decreased contact area with the pan, which may lead to a lower recorded heat of transition. In other words, because of the poor heat conductivity of the expanded magnesium chloride ammonia complex the true heat effect may not be measured to its full extent by the HPDSC sensor. This effect can hardly be expected to increase after the first few cycles.

Furthermore due to the observation that despite the decreasing heat effect the same transition temperature is repeatedly recorded, it may be assumed that the first explanation is most likely to be correct.

Recent research [11] did not reveal a decline of the heats of transition of the magnesium chloride ammonia complexes after more than 50 cycles. A plausible reason for the different outcome may be that in the research by Haije *et al.* magnesium chloride, obtained via crystallization from a solution in ethanol, is impregnated into a metallic foam. By impregnating the salt into the foam with subsequent evaporation of the solvent firstly a much better heat conduction is obtained, and secondly the evaporation of the alcohol might have pre-expanded the structure leading to less mechanical strain and thence tendency to amorphise.

Stoichiometry

From the obtained diagrams it may be concluded that the formation of the magnesium ammonia complex is a rather slow process compared to the decomposition of the complex (with the exception of the high-temperature formation). Furthermore the difference in magnitude between the directly measured enthalpy values (via HPDSC) and the ones derived from the C–C diagram for the formation is calculated to be 3.64. Moreover when the value of the low-temperature transition is divided by that of the middle-temperature-transition the quotient is 4.02. This infers that there are 4 times more ammonia molecules involved in the low-temperature transition than there are in the middle-temperature transition. When assuming that the starting material represents the hexa-ammonia complex, it is easily calculated what the theoretical mass loss should be, Table 3. The difference between the theoretical mass losses and the ones measured by TG could be explained by the fact that the TG measurements were not performed under a partial ammonia pressure. Under certain ammonia pressure the complex is stable but when an ammonia pressure is not present the bonded ammonia from the complex could already be desorbed during the introduction in the TG. This will result in a lower measured mass loss for the low-temperature decomposition, as shown in Table 3. After the decomposition of the hexa-ammonia complex there will be a build up ammonia pressure. The larger measured mass losses compared with the theoretical ones for stages II, III and IV could arise from adsorbed water during the preparation and the introduction in the TG. These ammoniates are quite hygroscopic.

The study of Lastra [4] provides the evidence of the existence of a stable tetra-ammonia complex. Our data reported in Table 3, cannot confirm the existence of a stable tetra-ammonia complex under our experimental conditions.

The splitting up of the low-temperature formation (Fig. 3a) suggests that the low-temperature transition consist of two overlapping steps, which basically embraces the results stated by Hummelshøj *et al.* [12]. According to Hummelshøj the binding energy of the first two NH_3 molecules to desorb is almost the same energy as the following two NH_3 molecules. In other words, the desorption of the first two NH_3 molecules are almost immediately followed by the next two molecules. The phenomenon that only the formation is subdivided into two peaks can be explained by the fact that the formation reaction is an exothermal effect and thus heat will be released and so slow down the cooling of the sample, and therefore also slow down the reaction. In other words, the sample is too warm regarding to its equilibrium position and the adsorption fails to occur at actual equilibrium.

Conclusions

The equilibrium relation between the ammonia pressure and the temperature of the transitions was established for magnesium chloride by means of HPDSC, in the range of 1.20 to 6.0 bar in pressure, as well as by TG, from 300 up to 873 K in temperature. Under the applied experimental circumstances, our results indicate that the following reactions occur;

$$MgCl_2+NH_3\leftrightarrows Mg(NH_3)Cl_2 \qquad (9)$$

$$Mg(NH_3)Cl_2+NH_3\leftrightarrows Mg(NH_3)_2Cl_2 \qquad (10)$$

$$Mg(NH_3)_2Cl_2+4NH_3\leftrightarrows Mg(NH_3)_6Cl_2 \qquad (11)$$

It should be noted that reaction (9) occurs in two partially overlapping steps. The TG results suggest that the transition occurs in two about equal steps, involving the reaction with about half a mole of ammonia each.

When the results of the HPDSC and TG measurements are combined it may be concluded that the existence of the stable tetra-ammonia complex could not be confirmed.

For the utilisation of the $MgCl_2$–NH_3 system as a working pair in a solid-sorption type chemical heat pump, the operation window has been established. Although the low-temperature transition is in the right *p–T* area for application as a high-temperature salt in a CHP, the decline of the measured heat effect after each cycle may impose a problem for its application.

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Received: November 7, 2006
Accepted: March 8, 2007

DOI: 10.1007/s10973-006-8247-1