Thermodynamic Properties of Metal Amides Determined by Ammonia Pressure-Composition Isotherms

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Abstract

Thermodynamic properties of Mg(NH\textsubscript{2})\textsubscript{2} and LiNH\textsubscript{2} were investigated by measurements of NH\textsubscript{3} pressure-composition isotherms (PCI). Van’t Hoff plot of plateau pressures of PCI for decomposition of Mg(NH\textsubscript{2})\textsubscript{2} indicated the standard enthalpy and entropy change of the reactions were $\Delta H^o = (120 \pm 11)$ kJ\textperiodcentered mol\textsuperscript{-1} (per unit amount of NH\textsubscript{3}) and $\Delta S^o = (182 \pm 19)$ J\textperiodcentered mol\textsuperscript{-1}\textperiodcentered K\textsuperscript{-1} for the reaction: Mg(NH\textsubscript{2})\textsubscript{2} $\rightarrow$ MgNH + NH\textsubscript{3}, and $\Delta H^o = 112$ kJ\textperiodcentered mol\textsuperscript{-1} and $\Delta S^o = 157$ J\textperiodcentered mol\textsuperscript{-1}\textperiodcentered K\textsuperscript{-1} for the reaction: MgNH $\rightarrow$ (1/3)Mg\textsubscript{3}N\textsubscript{2} + (1/3)NH\textsubscript{3}. PCI measurements for formation of LiNH\textsubscript{2} were carried out, and temperature dependence of plateau pressures indicated $\Delta H^o = (-108 \pm 15)$ kJ\textperiodcentered mol\textsuperscript{-1} and $\Delta S^o = (-143 \pm 25)$ J\textperiodcentered mol\textsuperscript{-1}\textperiodcentered K\textsuperscript{-1} for the reaction: Li\textsubscript{2}NH + NH\textsubscript{3} $\rightarrow$ 2LiNH\textsubscript{2}.

Keywords: Hydrogen storage materials; Pressure-composition isotherms; Gas-solid reactions; van’t Hoff plot; Heat of formation
1. Introduction

Thermodynamic properties of metal amides were estimated from ammonia \( \text{NH}_3 \) Pressure-Composition (\( p-C \)) isotherms (PCI) for decomposition and formation of metal amides. Metal amides react with metal hydrides to desorb hydrogen and these reactions have been paid attention as new hydrogen storage systems since Chen et al.’s report [1]. Hydrogen desorbed from these compounds contaminated by a small amount of \( \text{NH}_3 \) originated from decomposition of the amides themselves, which would be a problem for an application of these systems [2, 3]. Therefore, thermodynamic properties of the metal amides are important, and the thermodynamics of metal-N-H system should be discussed by taking account of the thermodynamics of elementary reactions.

The chemistry of the alkali and alkaline earth metal amides has been the subject of a large number of investigations [4, 5]. Thermal decomposition properties of metal amides under inert gas flow (or in vacuum) have been investigated. Magnesium amide \( \text{Mg(NH}_2\text{)}_2 \) decomposes to magnesium imide \( \text{MgNH} \) and \( \text{NH}_3 \) by heating to \( T = 573 - 673 \text{ K} \) through the following reaction [6]:

\[
\text{Mg(NH}_2\text{)}_2 \rightarrow \text{MgNH} + \text{NH}_3. \quad (1)
\]

Then, magnesium imide decomposes into magnesium nitride \( \text{Mg}_3\text{N}_2 \) with \( \text{NH}_3 \) release at more than \( T = 623 \text{ K} \) as follows:

\[
\text{MgNH} \rightarrow (1/3)\text{Mg}_3\text{N}_2 + (1/3)\text{NH}_3. \quad (2)
\]

Lithium amide \( \text{LiNH}_2 \) decomposes to lithium imide \( \text{Li}_2\text{NH} \) and \( \text{NH}_3 \) at temperatures of \( 573 - 673 \text{ K} \) [7, 8] :

\[
2\text{LiNH}_2 \rightarrow \text{Li}_2\text{NH} + \text{NH}_3, \quad (3)
\]

and imide decomposes into lithium nitride at higher temperatures. In addition, the enthalpies of formation of \( \text{LiNH}_2 \) and \( \text{Li}_2\text{NH} \) have been reported from the measurements of the heat of dissolution [9].

Thermodynamic properties (e.g. standard enthalpy or entropy change of reaction, \( \Delta H^o \) and \( \Delta S^o \)) of metal-hydrogen systems have been investigated by measuring \( p-C \) isotherms [10]. The \( p-C \) isotherms of decomposition (and formation) of \( \text{LiNH}_2 \) to (from) \( \text{Li}_2\text{NH} \) at \( T = 573 \text{ K} \) and \( T = 673 \text{ K} \) have been reported in 1951 [8]. Liu et al. [11] has reported the results of \( p-C \) isotherms of decompositions of \( \text{LiNH}_2 \) and \( \text{Mg(NH}_2\text{)}_2 \).

These measurements were performed above the melting point of \( \text{LiNH}_2 \) (\( T = 653 \text{ K} \)) and \( \text{Mg(NH}_2\text{)}_2 \) (\( T = 633 \text{ K} \)). \( \text{LiNH}_2 \) volatilizes around \( T = 673 \text{ K} \) and may be sublimed under pressure in an ammonia atmosphere [12], which may prevent accurate determination of equilibrium pressures. In the present work, all \( p-C \) isotherms were carried out below the melting point of the metal amides. Temperature dependences of plateau pressures \( p \) were measured to determine \( \Delta H^o \) and \( \Delta S^o \) of the reactions for the decomposition or
formation of the metal amides from van’t Hoff equation \((\ln (p/p^o) = -\Delta F^o/RT + \Delta S^o/R)\), where \(p^o\) is standard pressure 0.1 MPa, \(R\) the gas constant and \(T\) absolute temperature.

Decomposition reaction of ammonia to nitrogen and hydrogen \((2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2)\) should be considered during the \(\text{NH}_3\) PCI measurements. In the viewpoint of thermodynamics, equilibrium \(\text{NH}_3\) conversion to \(\text{N}_2\) and \(\text{H}_2\) is >90% above \(T = 573\) K under normal pressure [13]. Therefore, amounts of generated \(\text{H}_2\) were measured by gas chromatography (GC), and net \(\text{NH}_3\) pressures were evaluated.

2. Experimental

\(\text{Mg(NH}_2\text{)}_2\) was synthesized by reacting \(\text{MgH}_2\) under gaseous \(\text{NH}_3\) flow \((p = 0.5\) MPa, at a flow rate of \(25\) ml-min\(^{-1}\)) at \(T = 473\) K for 14 days \((\text{MgH}_2 + 2\text{NH}_3 \rightarrow \text{Mg(NH}_2\text{)}_2 + 2\text{H}_2)\). \(\text{LiNH}_2\) (Sigma-Aldrich Co., 95%) was heated up to \(T = 723\) K under vacuum for 10 h to derive \(\text{Li}_2\text{NH}\). \(\text{Li}_2\text{NH}\) was activated by ball-milling (Fritsch, P7) under Ar atmosphere for 2 h and was provided for PCI measurement of formation of \(\text{LiNH}_2\). All handling of chemicals took place in a glove box filled with purified Ar.

\(\text{NH}_3\) \(p-C\) isotherms were measured using a Sieverts type apparatus. Prior to the sample measurement, blank \(p-C\) isotherms were measured, and as a result, the total pressure was found to increase slightly due to the \(\text{NH}_3\) decomposition.

Desorption PCI: ~100 mg sample was loaded in a sample holder (10ml volume). The system was evacuated, and sufficient amount of \(\text{NH}_3\) (5N) gas was introduced into the system. The sample cell was heated up to a measurement temperature with a heating rate of 5 K-min\(^{-1}\) and the temperature was held constant. Pressure change was monitored by a pressure transducer (GE Druck, PDCR-4000) and data acquisition system. After stabilizing the pressure (waiting time: 1-12 h), gas in the reservoir (61 or 14 ml volume) was introduced to a gas chromatograph (GC-14B, Shimadzu Corp.) to determine \(\text{H}_2\) and \(\text{N}_2\) amounts from GC peak intensities. Pure \(\text{H}_2\) (7N) and \(\text{N}_2\) (99.99995%) gases are used for calibration of the GC peak area and gas pressure. Net \(\text{NH}_3\) equilibrium pressure and the amount of decomposed ammonia were estimated by subtracting \(\text{H}_2\) and \(\text{N}_2\) pressures from total pressure, as a result, one data point of PCI curve was derived. Stepwise decrease in \(\text{NH}_3\) pressure followed by waiting for equilibrium and GC measurement were continued. In the case of waiting time exceeded 12 h, measurement went next step, because such slow pressure increase may be caused by \(\text{NH}_3\) decomposition.

Absorption PCI: ~50 mg sample was loaded in the sample holder and the system was evacuated and then heated. The \(\text{NH}_3\) gas was introduced to apply stepwise increase in the pressure. At each pressure, waiting time of 15 min was adopted to realize
the equilibrium state, because the absorption reaction showed fast kinetics. It was difficult to perform the GC measurement for the analysis of the gas composition, since equilibrium pressures were very low.

Powder X-ray diffraction (RINT-2500V, Rigaku, Cu-Kα radiation) measurement was carried out at room temperature to identify phases before and after the PCI measurements.

3. Results and Discussion

The $p$-$C$ isotherms of the decomposition of Mg(NH$_2$)$_2$ to MgNH were measured at lower temperatures than the melting point of Mg(NH$_2$)$_2$, i.e. $T = 633$ K. Total pressure gradually increased during the desorption measurement with a rate of 0.2 - 1 kPa·h$^{-1}$, which may be caused by decomposition of NH$_3$ itself. Therefore, the GC measurement was carried out to subtract H$_2$ and N$_2$ contribution to the total pressure and actual NH$_3$ pressure was estimated. Fig. 1 shows NH$_3$ $p$-$C$ isotherms of decomposition of Mg(NH$_2$)$_2$ at $T = (583, 603$ and 623) K. Plateau regions which corresponded to the decomposition of amide phase to imide phase appeared, and the plateau pressures, i.e., the values of the pressures at the midpoint of the plateau, are $p = (6.0, 15.6$ and 29.4) kPa at $T = (583, 603, 623)$ K, respectively. Plateau region of the decomposition of MgNH to Mg$_3$N$_2$ was not observed, therefore, the plateau pressure of the decomposition of imide to nitride phase may be too low at these temperatures. For the isotherms at temperatures of 623 and 583 K, the lengths of the plateau regions did not reach a theoretical value (25%). It could be caused by decrease in surface or bulk activity of a part of the powder sample by long time sintering. We suppose a small amount of deactivated powders have no significant effect for the plateau pressure. XRD profiles of the sample after desorption PCI measurement at $T = 603$ K are shown in Fig. 2(a), which shows the presence of MgNH phase after the PCI measurement.

Higher temperature was applied to measure $p$-$C$ isotherms of decomposition of MgNH to Mg$_3$N$_2$. Fig. 3 shows the PCI curves of the reaction (2) at $T = (663, 683$ and 693) K. The plateau regions which corresponded to the decomposition of imide phase to nitride phase appeared for the measurements at temperatures of 663 K and 683 K, and the values of the plateau pressures are $p = 8.0$ kPa at $T = 663$ K, $p = 14.9$ kPa at $T = 683$K. After the desorption PCI measurement at $T = 693$ K, main phase was Mg$_3$N$_2$ in XRD profile as shown in Fig. 2(b).

The NH$_3$ desorption plateau pressures in van’t Hoff plot (ln $(p/p^0)$ vs. $T^{-1}$) are shown in Fig. 4(a,b). The slope of ln $(p/p^0)$ and the intercept corresponds to $\Delta H^0$ and $\Delta S^0$, respectively. The results are $\Delta H^0 = (120 \pm 11)$ kJ·mol$^{-1}$ and $\Delta S^0 = (182 \pm 19)$
J·mol⁻¹·K⁻¹ for the reaction (1), and \( \Delta H^0 = 112 \text{ kJ} \cdot \text{mol}^{-1} \) and \( \Delta S^0 = 157 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \) for the reaction (2). Here, we define the unit as per mole amount of NH₃ for the reactions. Liu et al. [11] have reported much higher NH₃ equilibrium pressure (\( p = \text{ca. 200 kPa at } T = 623 \text{ K} \)) for the decomposition of Mg(NH₂)₂ to MgNH in the temperature range of \( T = 613 - 643 \text{ K} \), and calculated smaller enthalpy change of NH₃ generation (\( \Delta H^0_{\text{ref}} = 40.8 \text{ kJ} \cdot \text{mol}^{-1} \)). Such high pressures could come from the decomposition of NH₃ to H₂ and N₂, and van’t Hoff plot of the total pressures could not show \( \Delta H^0 \) of the decomposition of the amide. In our work, the partial pressures of H₂ and N₂ were calculated by the GC measurement.

Using \( \Delta H^0 \) and \( \Delta S^0 \) values above and literature values of the standard enthalpy \( \Delta f H^0 \) of formation and standard entropy \( S^0 \) for Mg₃N₂ and NH₃ [14], one can derive \( \Delta f H^0 \) and \( S^0 \) of Mg(NH₂)₂ and MgNH as shown in Table 1. Hu et al. [15] reported the standard enthalpy of formation of Mg(NH₂)₂ measured by differential scanning calorimetry (DSC) and dissolution calorimetry as −325 and −351 kJ·mol⁻¹, respectively. We suspect the contributions of gas phase NH₃ to the DSC signal (such as heat capacity and heat of evaporation) may not be sufficiently treated, while, the \( \Delta f H^0 \) value measured from the heat of dissolution of Mg(NH₂)₂ is in reasonable agreement with our result.

The \( p-C \) isotherms of the formation of LiNH₂ from Li₂NH were measured at lower temperatures than the melting point of LiNH₂, i.e. \( T = 643 \text{ K} \). Fig. 5 shows NH₃ \( p-C \) isotherms of formation of LiNH₂ at \( T = (583, 603 \text{ and } 623) \text{ K} \). The plateau regions which corresponded to the formation of amide phase from imide phase appeared, the plateau pressures are \( p = (0.7, 1.2 \text{ and } 2.8) \text{ kPa at } T = (583, 603 \text{ K and } 623) \text{ K}, \) respectively. The isotherms ended around 80 % of NH₃ absorption, which could be caused by partial deactivation of the powder sample. XRD profiles of the samples before and after the absorption PCI measurement at \( T = 583 \text{ K} \) are shown in Fig. 2(c, d), which indicated main phase is LiNH₂ after the PCI measurement.

The plateau pressures in van’t Hoff plot (\( \ln (p/p^0) \) vs. \( T^{-1} \)) are shown in Fig. 4(c). Least-squares fit of the plot gives \( \Delta H^0 \) and \( \Delta S^0 \). The results are \( \Delta H^0 = (108 \pm 15) \text{ kJ} \cdot \text{mol}^{-1} \) and \( \Delta S^0 = (143 \pm 25) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \). Liu et al. [15] have measured NH₃ equilibrium pressures for the decomposition of LiNH₂ in the temperature range of \( T = 633 - 678 \text{ K} \), and calculated enthalpy change of NH₃ generation to be 43.4 kJ·mol⁻¹. (They have described the unit as kJ·mol⁻¹ per unit amount of LiNH₂, however it should be kJ·mol⁻¹ per unit amount of NH₃). This \( \Delta H^0_{\text{ref}} \) value is about half of the value derived by the present work, and the values of equilibrium pressure are much higher than the extrapolated values of our work at high temperatures. The NH₃ decomposition could result in these high pressures, if they have measured the equilibrium pressure by directly
using a pressure transducer. If the NH₃ partial pressures have been calculated from ion concentrations in the gaseous phase, the high pressures could be caused by sublimed LiNH₂. We also noted, above the melting point of the amides, Δ_H⁰ and Δ_S⁰ of the amide decomposition reactions would be smaller than those values measured below the melting point. Because Δ_H⁰ and Δ_S⁰ of solid phase should be smaller than those of liquid phase for the metal amides. Therefore, our measurements were carried out below the melting point of the amides. Using reported Δ_H⁰ values (LiNH₂: −186.3 kJ⋅mol⁻¹) in our previous work [16] and in the literature [14] (NH₃: −45.9 kJ⋅mol⁻¹), one obtains Δ_H⁰ value of Li₂NH as Δ_H⁰(Li₂NH) = (−219 ± 24) kJ⋅mol⁻¹. This value is in good agreement with the literature [9] (Δ_H⁰ ref(Li₂NH) = −220 kJ⋅mol⁻¹).

4. Conclusions

NH₃ pressure-composition isotherms for decomposition of Mg(NH₂)₂ and formation of LiNH₂ were measured at lower temperatures than melting points of the metal amides. During the decomposition isotherms of Mg(NH₂)₂, H₂ and N₂ generation due to NH₃ decomposition was observed by gas chromatography. Temperature dependences of NH₃ plateau pressures gave Δ_H⁰ and Δ_S⁰ values for the decomposition or formation of the metal amides. The results are Δ_H⁰ = (120 ± 11) kJ⋅mol⁻¹ and Δ_S⁰ = (182 ± 19) J⋅mol⁻¹⋅K⁻¹ for the reaction Mg(NH₂)₂ → MgNH + NH₃, Δ_H⁰ = 112 kJ⋅mol⁻¹ and Δ_S⁰ = 157 J⋅mol⁻¹⋅K⁻¹ for the reaction MgNH → (1/3)Mg₃N₂ + (1/3)NH₃, and, Δ_H⁰ = (−108 ± 15) kJ⋅mol⁻¹ and Δ_S⁰ = (−143 ± 25) J⋅mol⁻¹⋅K⁻¹ for the reaction Li₂NH + NH₃ → LiNH₂. The standard enthalpy Δ_H⁰ of formation and standard entropy S⁰ were derived as follows: Δ_H⁰(Mg(NH₂)₂) = (−374 ± 11) kJ⋅mol⁻¹, S⁰(Mg(NH₂)₂) = (52 ± 19) J⋅mol⁻¹⋅K⁻¹, Δ_H⁰(MgNH) = −208 kJ⋅mol⁻¹, S⁰(MgNH) = 41 J⋅mol⁻¹⋅K⁻¹, Δ_H⁰(Li₂NH) = (−219 ± 24) kJ⋅mol⁻¹.

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References

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Figure legends

Table 1. Thermodynamic functions of reactions and compounds. The units are defined as per mole amount of NH$_3$ and each compounds for the reactions and compounds, respectively.

Fig.1 Pressure-composition isotherms for decomposition of Mg(NH$_2$)$_2$ at $T = 583$ K (○), $T = 603$ K (∆), and $T = 623$ K (□). The horizontal axis shows the percent of ammonia left to desorb, where $x$NH$_3$ desorbs through the following reaction: Mg(NH$_2$)$_2$ (100%) $\rightarrow$ MgNH (25%) + NH$_3$ $\rightarrow$ (1/3)Mg$_3$N$_2$ (0%) + (4/3)NH$_3$.

Fig.2 Powder X-ray diffraction profiles (intensities $I$ in arbitrary units) before and after pressure-composition isotherms (PCI): (a) after decomposition PCI of Mg(NH$_2$)$_2$ at $T = 603$ K, (b) after decomposition PCI of MgNH at $T = 693$ K, (c) before and (d) after formation PCI of LiNH$_2$ at $T = 583$ K. The peak positions of the typical reflections in the ICDD powder diffraction files are included for comparison: Mg(NH$_2$)$_2$ (#72-0786), MgNH (#23-0391), Mg$_3$N$_2$ (#35-0778), Li$_2$NH (#75-0050), LiNH$_2$ (#71-1616).

Fig.3 Pressure-composition isotherms for decomposition of MgNH at $T = 663$ K (○), $T = 683$ K (∆), and $T = 693$ K (□). The horizontal axis shows the percent of ammonia left to desorb, where $x$NH$_3$ desorbs through the following reaction: Mg(NH$_2$)$_2$ (100%) $\rightarrow$ MgNH (25%) + NH$_3$ $\rightarrow$ (1/3)Mg$_3$N$_2$ (0%) + (4/3)NH$_3$.

Fig.4 Van’t Hoff plot of plateau pressures for: (a) decomposition of Mg(NH$_2$)$_2$ to MgNH, (b) decomposition of MgNH to Mg$_3$N$_2$, (c) formation of LiNH$_2$ from Li$_2$NH.

Fig.5 Pressure-composition isotherms for formation of LiNH$_2$ at $T = 583$ K (○), $T = 603$ K (∆), and $T = 623$ K (□). The horizontal axis shows the percent of absorbed ammonia ($x$NH$_3$) through the following reaction: Li$_2$NH (0%) + NH$_3$ $\rightarrow$ 2LiNH$_2$ (100%).
Table 1. Thermodynamic functions of reactions and compounds. The units are defined as per mole amount of NH$_3$ and each compounds for the reactions and compounds, respectively.

<table>
<thead>
<tr>
<th>reaction or compound</th>
<th>this work</th>
<th>lit.</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg(NH}_2\text{)} \rightarrow \text{MgNH + NH}_3 )</td>
<td>( \Delta H^{\circ} / \text{kJ-mol}^{-1} )</td>
<td>( \Delta S^{\circ} / \text{J-mol}^{-1} \cdot \text{K}^{-1} )</td>
<td>( \Delta H^{\circ} / \text{kJ-mol}^{-1} )</td>
</tr>
<tr>
<td>Mg(NH$_2$)$_2$</td>
<td>120 ± 11</td>
<td>182 ± 19</td>
<td>40.8</td>
</tr>
<tr>
<td>MgNH → (1/3)Mg$_3$N$_2$ + (1/3)NH$_3$</td>
<td>112</td>
<td>157</td>
<td></td>
</tr>
<tr>
<td>2LiNH$_2$ → Li$_2$NH + NH$_3$</td>
<td>108 ± 15</td>
<td>143 ± 25</td>
<td>43.4</td>
</tr>
</tbody>
</table>

| reaction or compound | \( \Delta \tilde{H}^{\circ} / \text{kJ-mol}^{-1} \) | \( S^{\circ} / \text{J-mol}^{-1} \cdot \text{K}^{-1} \) | \( \Delta \tilde{H}^{\circ} / \text{kJ-mol}^{-1} \) | \( S^{\circ} / \text{J-mol}^{-1} \cdot \text{K}^{-1} \) | |
|----------------------|-----------|------|------|------|
| Mg(NH$_3$)$_2$ | -374 ± 11 | 52 ± 19 | -325, -351 | | [13] |
| MgNH | -208 | 41 | | | |
| Li$_2$NH | -219 ± 24 | | -220 | | [7] |
| NH$_3$ (gas) | | | -45.9 | 192.77 | [12] |
| Mg$_3$N$_2$ | | | -461.08 | 87.86 | [12] |
| LiNH$_2$ | | | -186.3 ± 9.1 | | [14] |
Fig. 1 Pressure-composition isotherms for decomposition of Mg(NH₃)₂ at T = 583 K (○), T = 603 K (△), and T = 623 K (□). The horizontal axis shows the percent of ammonia left to desorb, where xNH₃ desorbs through the following reaction: Mg(NH₂)₂ (100%) → MgNH (25%) + NH₃ → (1/3)Mg₃N₂ (0%) + (4/3)NH₃.
Fig. 2  Powder X-ray diffraction profiles (intensities $I$ in arbitrary units) before and after pressure-composition isotherms (PCI): (a) after decomposition PCI of Mg(NH$_2$)$_2$ at $T = 603$ K, (b) after decomposition PCI of MgNH at $T = 693$ K, (c) before and (d) after formation PCI of LiNH$_2$ at $T = 583$ K. The peak positions of the typical reflections in the ICDD powder diffraction files are included for comparison: Mg(NH$_2$)$_2$ (#72-0786), MgNH (#23-0391), Mg$_3$N$_2$ (#35-0778), Li$_2$NH (#75-0050), LiNH$_2$ (#71-1616).
Fig. 3 Pressure-composition isotherms for decomposition of MgNH at $T = 663$ K ($\circ$), $T = 683$ K ($\triangle$), and $T = 693$ K ($\square$). The horizontal axis shows the percent of ammonia left to desorb, where $x$NH$_3$ desorbs through the following reaction: Mg(NH$_2$)$_2$ (100%) $\rightarrow$ MgNH (25%) + NH$_3$ $\rightarrow$ $\frac{1}{3}$Mg$_3$N$_2$ (0%) + $\frac{4}{3}$NH$_3$. 
Fig. 4 Van’t Hoff plot of plateau pressures for: (a) decomposition of Mg(NH$_2$)$_2$ to MgNH, (b) decomposition of MgNH to Mg$_3$N$_2$, (c) formation of LiNH$_2$ from Li$_2$NH.
Fig. 5  Pressure-composition isotherms for formation of LiNH$_2$ at $T = 583$ K (○), $T = 603$ K (△), and $T = 623$ K (□). The horizontal axis shows the percent of absorbed ammonia ($x$NH$_3$) through the following reaction: Li$_2$NH (0%) + NH$_3$ → 2LiNH$_2$ (100%).