Light Metal Amides and Imides
For
Hydrogen Storage
by
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A thesis submitted to the University of Birmingham for
the Degree of Doctor of Philosophy
The School of Chemistry
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The University of Birmingham
September 2011
ABSTRACT

The thermal decomposition of mixed cation amides, Li$_3$Na(NH$_2$)$_4$ and LiNa$_2$(NH$_2$)$_3$, with light metal hydrides, lithium hydride, sodium hydride and magnesium hydride, was investigated and hydrogen gas was identified as the major desorption product in all cases. Minimal ammonia was detected and therefore the mixed cation amides could be considered as hydrogen storage materials. The reactions were found to be similar to previously studied light metal amide-hydride systems like lithium amide/lithium hydride and lithium amide/magnesium hydride. Magnesium hydride caused the hydrogen desorption from the mixed cation amides to occur at a lower temperature than when they were heated with lithium hydride. The hydrogen desorption was also at a lower temperature than LiNH$_2$ + LiH and 2LiNH$_2$ + MgH$_2$. Although hydrogen was desorbed when the mixed cation amides were heated with NaH, the amount was much smaller than for LiH and MgH$_2$, therefore making it less suitable as a hydrogen storage material.

Reactions in various ratios between NaNH$_2$ and MgH$_2$ were investigated to intermediate temperatures up to 350 °C. Thermal decomposition, Raman spectroscopy and thermogravimetric analysis were all employed to explore the decomposition and reaction pathways of these reactions. It was found that the products were analogous to those formed by lithium amide heated with magnesium hydride in similar ratios. The more hydride included in the reaction, the greater the hydrogen loss for the products. Three new phases were identified and each was attempted to be made pure in order to characterise them. Evidence for the formation of a mixed Na-Mg amide, Na-Mg imide and Na-Mg nitride, under different temperatures and reaction conditions, was obtained. Attempts to rehydrogenate the Na-Mg imide were successful, reforming magnesium amide and sodium hydride.

Sodium amide (NaNH$_2$) has been relatively neglected in the literature and so an examination of its decomposition products and reaction with sodium hydride, as a comparison to LiNH$_2$-LiH, were carried out. Using Raman and thermal decomposition techniques, it was proposed that a sodium imide may be formed, possibly with the same variable stoichiometry as observed for LiNH$_2$-Li$_2$NH. Rehydrogenation was attempted on this phase, but was unsuccessful.
ACKNOWLEDGEMENTS

I have many people to thank for their help in getting this thesis finished. First and foremost many thanks to my supervisor Paul Anderson for allowing me to do a PhD in the first place. Also, thanks to Phil Chater for all his help, advice, suggestions and cider on a Friday night. Thanks to rest of Paul’s group: Jim Prendergast, Matt Turnbull, Alvaro Mayoral Garcia, Ian Evans, David Hewett, Chao Zhao and Tom Carey for the opinions, ideas and comedy times. Thanks to all members of floor 5, past and present, for all the chats and procrastination. For all the equipment time I’ve hogged in materials, thanks to David Book, Allan Walton, Vicky Mann and especially Dan Reed for also explaining all the intricacies of the TGA, DSC and Raman.

Thank you to my parents for allowing me the freedom to be a student all this time and for letting me return home to write up. Thanks to Rachel and Simon for giving me a place to get away from everything when it got a bit overwhelming and to Ben for baby cuddles. And of course, thanks to Rich... anyone that can put up with me whilst I write a thesis is worth their weight in gold.
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<th>Description</th>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>ESRF</td>
<td>European Synchrotron Radiation Facility</td>
</tr>
<tr>
<td>FCC</td>
<td>Face Centred Cubic</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infra Red Spectroscopy</td>
</tr>
<tr>
<td>IGA</td>
<td>Intelligent Gravimetric Analysis</td>
</tr>
<tr>
<td>MIM</td>
<td>Multiple Ion Monitoring</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton Exchange Membrane</td>
</tr>
<tr>
<td>PSD</td>
<td>Position Sensitive Detector</td>
</tr>
<tr>
<td>PTC</td>
<td>Positive Temperature Coefficient</td>
</tr>
<tr>
<td>QPA</td>
<td>Quantitative Phase Analysis</td>
</tr>
<tr>
<td>RGA</td>
<td>Residual Gas Analysis</td>
</tr>
<tr>
<td>RMM</td>
<td>Relative Molecular Mass</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
</tr>
<tr>
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<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TG-DTA</td>
<td>Thermogravimetric-Differential Thermal Analysis</td>
</tr>
<tr>
<td>TPA</td>
<td>Temperature Programmed Absorption</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
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<td>XRD</td>
<td>X-ray Diffraction</td>
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1. INTRODUCTION

1. Hydrogen Economy

Hydrogen is the most abundant element in the universe; however, it does not exist in its elemental form. It is in this form that it is needed to be used as an energy vector. Therefore, hydrogen in its elemental form must be produced. At present, hydrogen is mostly produced from fossil fuels via steam reformation and the water gas shift reactions:

\[
\begin{align*}
\text{Equation 1-1} & \quad -\text{(CH}_2\text{)}_n + \text{H}_2\text{O} \rightarrow \text{CO} + (n + 1)\text{H}_2 \\
\text{Equation 1-2} & \quad \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]

Unfortunately, in gathering hydrogen from these reactions fossil fuels are used and CO\textsubscript{2} is released from these reactions and therefore the disadvantages outweigh the benefits. The ideal production of hydrogen would be independent from fossil fuels, from a limitless energy source and without the release of CO\textsubscript{2}. Electrolysis is one way of producing hydrogen cleanly, but this depends on the source of electricity. Electricity produced from renewable energy sources, such as photovoltaics, wind turbines and hydroelectricity provide the limitless ‘green’ energy required. Nuclear power can also provide electricity without the CO\textsubscript{2} release, however there are harmful by-products from the radioactive waste and is therefore not ideal as a long term replacement for fossil fuels. In the short to medium term though, it can help meet our growing energy needs.
Hydrogen is important as fossil fuels are depleting and by burning them they are releasing CO$_2$, that was locked away underground, into the atmosphere. CO$_2$ is a greenhouse gas and has been linked to global climate change.$^1$

The use of hydrogen is dependent on the challenges associated with production, storage and use. Storage is arguably the biggest challenge faced when considering the hydrogen economy.

Hydrogen can be combusted cleanly to give just water as the only product when burnt in oxygen. Hydrogen can also be used electrochemically in a fuel cell to produce electrical power. There are different types of fuel cell depending on their electrolyte: alkaline, phosphoric acid, molten carbonate, solid oxide and proton exchange membrane (PEM). PEM fuel cells have fast start up times, high efficiency from 65 °C and are good for mobile applications.

PEM fuel cells are, however, bad with contaminants in the hydrogen supply. With only 30 ppm NH$_3$ in the hydrogen supply there is a rapid drop in fuel cell performance that is not recoverable when the NH$_3$ is removed.

Hydrogen gas in its natural state fills a volume of 11 m$^3$ kg$^{-1}$. This is massive and requires reduction to a more usable volumetric density. The usual ways of fulfilling this is through compression or liquefaction. This comes at the expense of the gravimetric density, that is the storage vessels in order to hold hydrogen at greater pressure than ambient reduce the gravimetric capacity of the system as a whole. Ideally, a compromise between the gravimetric and volumetric density would be reached. Here, we look at the storage of hydrogen within light metal amides and hydrides. The targets for the ideal hydrogen storage system have been outlined by the US Department of Energy (DOE).$^2$
The original targets suggested by the US DOE have been replaced by more realistic goals. The current target for gravimetric capacity of a hydrogen storage system is 5.5 wt% in the year 2015 and ultimately 7.5 wt%. The delivery temperature target has been set at −40 to 85 °C with a delivery pressure of 5 bar for fuel cell applications. Recharging would ideally take no more than 2.5 minutes, it would need to be rapidly reversible to same standard throughout, withstand 1500 de/rehydrogenation cycles and be of low enough cost for widespread acceptance.

So far, there has been no single system which meets all the demanding criteria.

2. Using Hydrogen

Research into using hydrogen as an energy vector has expanded exponentially during the past few years. One of the most promising hydrogen storage media for use for a vehicular application is that of storing hydrogen in the solid state with light metals and non-metals. These metals and non-metals include lithium, sodium, magnesium, aluminium, boron and nitrogen in various combinations. Complex hydrides in particular demonstrate excellent hydrogen storage potential by their ability to contain within them high hydrogen mass (Table 1-1). Unfortunately, the reversibility (the ability to recombine the products after dehydrogenation with hydrogen) of these is poor.
Table 1-1 Selected complex hydrides and their hydrogen weight%.³

<table>
<thead>
<tr>
<th>Hydride</th>
<th>Wt%</th>
<th>Availability or Synthetic Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH₄</td>
<td>18.2</td>
<td>Commercially Available</td>
</tr>
<tr>
<td>LiAlH₄</td>
<td>10.5</td>
<td>Commercially Available</td>
</tr>
<tr>
<td>Al(BH₄)₃</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>LiAlH₂(BH₄)₂</td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>Mg(AlH₄)₂</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>Mg(BH₄)₂</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>Ca(AlH₄)₂</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>Ca(BH₄)₂</td>
<td>11.4</td>
<td>Synthetic procedure to be developed</td>
</tr>
<tr>
<td>NaAlH₄</td>
<td>7.5</td>
<td>Commercially Available</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>10.5</td>
<td>Commercially Available</td>
</tr>
<tr>
<td>Ti(BH₄)₃</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>Ti(AlH₄)₄</td>
<td>9.3</td>
<td>Synthetic procedure to be developed</td>
</tr>
<tr>
<td>Zr(BH₄)₃</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>Fe(BH₄)₃</td>
<td>11.9</td>
<td>Synthetic procedure to be developed</td>
</tr>
</tbody>
</table>

Light metal amides have recently shown better prospect of reversibility whilst maintaining a modest hydrogen weight%. Light metal amides have an additional problem of the possibility of ammonia release along with hydrogen. The challenge is now to utilise the maximum amount of hydrogen release with the minimal amount of ammonia release along with reasonable reversing conditions.

The reaction of lithium nitride (Li₃N) with hydrogen was originally investigated for hydrogen storage in 2002¹⁰ and this system was found to reversibly absorb 11.5 wt% hydrogen (Equation 1-3). This made lithium amide (LiNH₂) reacted with LiH a realistic hydrogen storage system, as when heated alone LiNH₂ decomposes to lithium imide (Li₂NH) with the release of ammonia (Equation 1-4).
Equation 1-3 \[ \text{Li}_3\text{N} + 2\text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + 2\text{LiH} \]

Equation 1-4 \[ 2\text{LiNH}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{NH}_3 \]

Unfortunately, the reversing conditions are too harsh for the first part of Equation 1-3 to be practical, however the lithium amide-lithium imide conversion stores 6.5 wt% H\(_2\) (1.85 hydrogen atoms) under 300 °C with favourable thermodynamics (\(\Delta H = -45 \text{ kJ mol}^{-1}\)).\(^{10}\) The hydrogen desorption is thought to occur by one of two possible mechanisms. In the first, when \(\text{LiNH}_2\) is heated with lithium hydride (LiH) it decomposes to lithium imide (\(\text{Li}_2\text{NH}\)) and ammonia (\(\text{NH}_3\)) (Equation 1-4) (\(\Delta H = +84 \text{ kJ mol}^{-1}\) \(\text{NH}_3\)).\(^{11}\) The \(\text{NH}_3\) then reacts with LiH to form \(\text{LiNH}_2\) with the release of hydrogen (\(\text{H}_2\)) (Equation 1-5). The enthalpy change was found to be \(-42 \text{ kJ mol}^{-1}\) \(\text{H}_2\).\(^{11}\)

Equation 1-5 \[ \text{LiH} + \text{NH}_3 \rightarrow \text{LiNH}_2 + \text{H}_2 \]

These reactions continue until all the starting materials are used up.\(^{12,13}\)

The second mechanism involves the direct reaction between \(\text{LiNH}_2\) and LiH by the \(\text{H}^+\) of \(\text{LiNH}_2\) and \(\text{H}^-\) of LiH. This reaction forms hydrogen and the release of hydrogen is the driving force behind the reaction (Equation 1-6).\(^{14,15}\)

Equation 1-6 \[ \text{H}^+ + \text{H}^- \rightarrow \text{H}_2 \]
The unit cell of LiNH₂ is shown in Figure 1-1. LiNH₂ has a tetragonal unit cell with lattice parameters $a = 5.03$ Å and $c = 10.25$ Å. It has been drawn with Li atoms on the unit cell edges and nitrogen forming N₄ tetragonal clusters.

Figure 1-1 Crystal structure of LiNH₂. Nitrogen is shown in blue, lithium in red and hydrogen in grey. The unit cell is shown in black.¹⁶

The structure of Li₂NH is shown in Figure 1-2. It has cubic unit cell with lattice parameters of $a = 5.057$ Å. It is drawn as an anti-fluorite structure with nitrogen atoms on a face-centered cubic lattice.

Figure 1-2 Crystal structure of Li₂NH. Nitrogen is shown in blue, lithium in red and hydrogen in grey. The unit cell is shown in black.¹⁷
Although LiNH$_2$ + LiH releases hydrogen without the desorption of ammonia, the temperature of 300 °C is still too high to be practical for a PEM fuel cell. Further improvements can be made to the LiNH$_2$-Li$_2$NH system have been found by substituting some lithium ions in the system for magnesium.

3. Li-Mg-N-H System

The decomposition temperature of LiH is 550 °C, whereas that of MgH$_2$ is much lower at around 280 °C. This shows LiH alone cannot be considered in this instance as a good hydrogen storage medium. MgH$_2$ alone (7.6 wt% H$_2$) has been investigated as a hydrogen storage material, but is still somewhat inadequate due to slow kinetics\(^\text{\textsuperscript{18}}\) as well as being fundamentally flawed by bad thermodynamics. \(\Delta H_f\) (MgH$_2$) is \(-75\) kJ mol\(^{-1}\) which means it will always be difficult (if not impossible) to remove the hydrogen below 280 °C.\(^\text{\textsuperscript{19}}\)

The lower stability of MgH$_2$ is due to magnesium hydride being partially ionic and partially covalent in its bonding, whereas lithium hydride is fully ionic, therefore much research has been conducted reacting LiNH$_2$ with MgH$_2$ in place of LiH.

The reaction between LiNH$_2$ and MgH$_2$ for hydrogen storage was first carried out in 2004 concurrently by 4 groups.\(^\text{\textsuperscript{20,21,22,23}}\) They all investigated slightly different factors in the reaction including different ratios between amide and hydride and variations using Mg(NH$_2$)$_2$ with LiH.
1. 2LiNH₂ + MgH₂

Xiong *et al.*\(^{20}\) heated lithium amide and magnesium hydride in a 2:1 ratio up to 350 °C in order that there was one amide unit for each hydrogen on the hydride. As with LiNH₂ and LiH only hydrogen, without any ammonia, was desorbed when lithium amide and magnesium hydride were reacted. It was found that the desorption temperatures, both onset and peak, of the hydrogen release were lower than for LiNH₂ + LiH. Powder X-ray Diffraction (XRD) was carried out on the sample after heating and comprised of peaks that did not match any previously identified Li-N-(H) compound. The sample was identified as Li₂MgN₂H₂ (Equation 1-7), with a cubic lattice with \(a = 10.03\) Å.

Equation 1-7  
\[
2\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{Li}_2\text{MgN}_2\text{H}_2 + 2\text{H}_2
\]

The sample was rehydrogenated under H₂ pressure at 90 bar and 180 °C. When the sample was hydrogenated completely it was found the temperature of this was dramatically reduced in comparison to the lithium system. The sample was cycled in order to assess the stability of the system. Little change in the temperature and intensity of hydrogen desorption/absorption showed a stable and reversible system. The XRD pattern showed the products of rehydrogenation to be Mg(NH₂)₂ and LiH rather than the original starting materials LiNH₂ and MgH₂ (Equation 1-8).

Equation 1-8  
\[
2\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{Li}_2\text{MgN}_2\text{H}_2 + 2\text{H}_2 \leftrightarrow \text{Mg(NH}_2)_2 + 2\text{LiH}
\]
Xiong et al.\textsuperscript{20} mention that amides of alkali and alkali earth metals consist of positively charged hydrogen ions bonded to N ions and conversely, the hydrogen in ionic hydrides is negatively charged. They suggested the high enthalpy of the reaction between these two opposing charged hydrogen ions could possibly drive the reaction between amides and hydrides (Equation 1-6).

At the same time, Luo\textsuperscript{21} also published work on $2\text{LiNH}_2 + \text{MgH}_2$, directly comparing the absorption and desorption of $2\text{LiNH}_2 + \text{MgH}_2$ with $\text{LiNH}_2 + \text{LiH}$. Samples were ball-milled for 2 hours and heated to 300 °C for $\text{LiNH}_2 + \text{LiH}$ and 240 °C for $2\text{LiNH}_2 + \text{MgH}_2$. Hydrogen desorption started at 160 °C for the lithium only sample, whereas the Li-Mg sample started releasing at 100 °C. The samples were then subjected to pressure-composition isotherm measurements. The lithium only sample was compared to that of Chen et al.\textsuperscript{10} and found to be similar, with any differences attributed to sample composition and preparation. The hydrogen pressure was found to be 1 bar at 280 °C. The Li-Mg sample was found to desorb a much higher H\textsubscript{2} wt% and therefore a greater pressure of 1.6 bar H\textsubscript{2} at 220 °C. The XRD pattern after dehydrogenation found there to be no Li\textsubscript{2}NH or MgNH present and so Luo et al. concluded Li\textsubscript{2}MgNH\textsubscript{2}H\textsubscript{2} was present, via Equation 1-7.

The Li-Mg-N-H sample was cycled 9 times and no degradation in desorption capacity was observed, which is important for hydrogen storage applications.

Yong Chen et al.\textsuperscript{24} investigated the reaction of $2\text{LiNH}_2 + \text{MgH}_2$ ball-milled. They initially looked at the dehydriding profiles of the first 4 cycles of $2\text{LiNH}_2 + \text{MgH}_2$. It was seen that the first dehydrogenation profile was significantly slower than the subsequent 3. This was thought to be due to the first cycle being the interaction between LiNH\textsubscript{2} and MgH\textsubscript{2}, whereas later cycles, as investigated by Luo and Sickafoose\textsuperscript{25}, were found to be reactions between
Mg(NH$_2$)$_2$ and LiH. Chen et al.\textsuperscript{24} looked into the optimum dehydriding temperature for the starting reaction. It was found that 200 °C had substantially faster kinetics compared to 160 °C or 180 °C. Chen et al. suggested that in order to improve the kinetics of the lower temperature reactions, a suitable dopant to catalyze the reaction was necessary.

Luo et al.\textsuperscript{26} looked into quantification of NH$_3$ release from the reaction of 2LiNH$_2$ + MgH$_2$. The cycling of the Li-Mg-N-H system at 180 °C was found to have less capacity deterioration than the same reaction at 240 °C. This was due to less Mg(NH$_2$)$_2$ self-decomposition to MgNH at 180 °C.

Markmaitree et al.\textsuperscript{27} found the reaction kinetics of 2LiNH$_2$ + MgH$_2$ were more sluggish than LiNH$_2$ + LiH as it took longer for the former to reach equilibrium pressure. The two reactions were carried out with and without ball-milling. The 2LiNH$_2$ + MgH$_2$ reaction always had more NH$_3$ desorbed from it, showing an overall poorer performance in terms of clean H$_2$ desorption. They confirmed the slow reaction between MgH$_2$ and NH$_3$, as suggested by Nakamori.\textsuperscript{23} The more the samples were ball-milled, the less NH$_3$ was detected. This was thought to be due to smaller particle size and larger surface area of the MgH$_2$ and so greater opportunity for the NH$_3$ and MgH$_2$ to react, although not sufficient to alleviate the problem entirely. 2LiNH$_2$ + MgH$_2$ heated to 210 °C for 5 hours formed MgNH and Li$_2$Mg(NH)$_2$ along with LiNH$_2$ and MgH$_2$ starting materials. There was no Mg(NH$_2$)$_2$ identified either by XRD or FTIR which is in conflict with Luo and Sickafoose who suggested a metathesis reaction occurred before the main reaction.\textsuperscript{25} After heating for 10 hours, LiNH$_2$ had mostly disappeared as had MgNH; there was still a small amount of MgH$_2$ present as well as an increased amount of Li$_2$Mg(NH)$_2$. Li$_2$Mg(NH)$_2$ was characterised as being identical to the product formed by Luo and Sickafoose.\textsuperscript{25} The suggested reaction scheme for this reaction
was the decomposition of lithium amide to imide and NH₃ (Equation 1-4), followed by the reaction of MgH₂ with NH₃ (Equation 1-9).

Equation 1-9  \[ \text{MgH}_2 + 2\text{NH}_3 \rightarrow \text{Mg(NH}_2)_2 + 2\text{H}_2 \]

The reaction between MgH₂ and NH₃ was found to be very slow. The magnesium amide formed then goes on to decompose to MgNH with the release of NH₃ (first part of Equation 1-10). This occurs at a reasonable rate from 250 °C. The ammonia recently formed then further reacts with MgH₂ and the reaction cycle continued. The products from this cycle were MgNH and Li₂NH. These would then react to form Li₂MgN₂H₂ (Equation 1-11).

Equation 1-10  \[ 3\text{Mg(NH}_2)_2 \rightarrow 3\text{MgNH} + 3\text{NH}_3 \rightarrow \text{Mg}_3\text{N}_2 + 4\text{NH}_3 \]

Equation 1-11  \[ \text{MgNH} + \text{Li}_2\text{NH} \rightarrow \text{Li}_2\text{MgN}_2\text{H}_2 \]

This paper was the first to suggest the reaction between the two imides led to the mixed imide. FTIR gave no indication of Mg(NH₂)₂ being present at any time. This was ascribed to the reaction in Equation 1-9 being slow.

Rijssenbeek investigated the phase composition of Li₂Mg(NH)₂. 2LiNH₂ + MgH₂ were ball-milled between 8 and 24 hours. There was no evidence of Mg(NH₂)₂ after milling, but a small amount of LiH was detected. The LiH was most likely present from metathesis between LiNH₂ and MgH₂, but Mg(NH₂)₂ did not appear as it is known to be non-crystalline after ball-milling. Li₂Mg(NH)₂ first appeared after heating the starting materials to 280 °C. The desorption of H₂ and NH₃ was evidenced at this temperature. No further changes were
observed up to 330 °C. This was then labelled as $\alpha$-Li$_2$Mg(NH)$_2$ (Figure 1-3). Complete hydrogen absorption was observed for $\alpha$-Li$_2$Mg(NH)$_2$ and this reverted to Mg(NH)$_2$ and LiH. The $\alpha$-Li$_2$Mg(NH)$_2$ was cycled. During the dehydrogenation phases of the cycling process, NH$_3$ was still evidenced, although in lesser amounts than the first desorption.

![Crystal structure](image)

Figure 1-3 Crystal structure of $\alpha$-Li$_2$Mg(NH)$_2$. Nitrogen is shown in blue, mixed lithium and magnesium sites in red and hydrogen in grey. The unit cell is shown in black.\(^{37}\)

The XRD pattern observed at 330 °C was indexed to an orthorhombic unit cell, with space group \textit{Iba2} or \textit{Ibam} with lattice parameters of $a \approx 10$ Å, $b \approx 5$ Å and $c \approx 5$ Å.\(^{37}\) This structure is similar to that reported by Xiong \textit{et al.}\(^{33}\) using Mg(NH$_2$)$_2$-LiH (1:1) at 330 °C, whereas the 1:2 Mg(NH$_2$)$_2$ + LiH ratio at 250 °C gave only a cubic structure. Heating 2LiNH$_2$ + MgH$_2$ to 350 °C caused a phase change to a primitive cubic phase, $\beta$-Li$_2$Mg(NH)$_2$.\(^{37}\) Another transition occurred at 500 °C to a face centred cubic structure, $\gamma$-Li$_2$Mg(NH)$_2$. On cooling $\gamma$-Li$_2$Mg(NH)$_2$ reverted back to $\beta$-Li$_2$Mg(NH)$_2$, but $\alpha$-Li$_2$Mg(NH)$_2$ was only formed from rehydrogenation followed by dehydrogenation at 280 °C. It was noted that using Mg(NH$_2$)$_2$ and LiH as starting
materials also formed the 3 phases of Li$_2$Mg(NH)$_2$, but the $\alpha$-Li$_2$Mg(NH)$_2$ was sometimes difficult to detect and $\beta$-Li$_2$Mg(NH)$_2$ appeared at a lower temperature. A small amount of Mg$_3$N$_2$ was detected during some reactions at higher temperatures.

A fourth polymorph of Li$_2$Mg(NH)$_2$ was seen under different conditions. Under high-pressure hydrogen (137 bar) and high temperatures (290 °C) $\delta$-Li$_2$Mg(NH)$_2$ was formed with a tetragonal unit cell $a \approx 5.16$ Å, $c \approx 9.60$ Å (very close to $\alpha$-Li$_2$Mg(NH)$_2$). However, when the temperature was cooled to below 280 °C, $\delta$-Li$_2$Mg(NH)$_2$ reverted back to Mg(NH)$_2$ and LiH.

Full structural refinement was carried out for $\alpha$-Li$_2$Mg(NH)$_2$. Space group $Iba2$ was used and lattice parameters of $a = 9.78$ Å, $b = 4.99$ Å, $c = 5.20$ Å were refined. $\beta$-Li$_2$Mg(NH)$_2$ was refined to a primitive cubic unit cell with space group $P-4_3m$ and a lattice parameter of $a = 5.03$ Å. Xiong et al. also reported a cubic structure, but with a unit cell with twice the lattice parameter. Rijssenbeek attempted to index $\gamma$-Li$_2$Mg(NH)$_2$, but the XRD pattern was very similar to high temperature Li$_2$NH. It was indexed to a FCC cell with space group $Fm-3m$ and $a \approx 5$ Å.

2. Mg(NH)$_2$ + 2LiH

Work was carried out by Xiong et al. in 2005. This consisted of combining Mg(NH)$_2$ with 2LiH (the crystal structure of Mg(NH)$_2$ is shown in Figure 1-4). The reactants were ball-milled together for 2 days and then dehydrogenated by heating to 250 °C. The same Li$_2$Mg(NH)$_2$ phase as found the year before was formed. The sample was then rehydrogenated under 90 bar H$_2$ up to 250 °C. This was found to reform Mg(NH)$_2$ and LiH. The hydrogen uptake started at 90 °C and became more rapid above 110 °C. Approximately 5.0 wt% H$_2$ was up taken below 200 °C in less than 50 minutes. The last of the hydrogen took
over 1 hour to be absorbed. The desorption occurred above 100 °C and more than 4.5 wt% was desorbed as the temperature reached 200 °C. The rest of the hydrogen desorbed much more slowly. For both the hydrogenation and dehydrogenation, the kinetics became slower towards completion of the reaction. As the hydrogen remained in the reaction vessel with the sample, the overpressure of hydrogen may suppress the last of the hydrogen release, therefore higher temperatures or gas removal system like a flowing line are required to complete the dehydrogenation more quickly.

Xiong et al.\textsuperscript{31} also investigated this reaction by DSC. They found the hydrogen desorption started at around 100 °C and peaked at 200 °C. The $\Delta H_{\text{desorption}}$ was 44.1 kJ mol\textsuperscript{−1} H\textsubscript{2}.

Figure 1-5 shows the reaction mechanism published by Xiong et al.\textsuperscript{31} The mechanism shows the attraction between a H\textsuperscript{δ+} on the Mg(NH\textsubscript{2})\textsubscript{2} and H\textsuperscript{δ−} on LiH. This forms bonds concertedly between the H\textsuperscript{δ+} and H\textsuperscript{δ−} and the Li\textsuperscript{δ+} and N\textsuperscript{δ−}. The bonds within lithium hydride and the nitrogen and hydrogen of Mg(NH\textsubscript{2})\textsubscript{2} break leaving an intermediate of ‘LiMgN\textsubscript{2}H\textsubscript{3}’ and H\textsubscript{2}. As this mechanism involves H\textsuperscript{δ+} and H\textsuperscript{δ−} (Equation 1-6) it was similar to that suggested by Chen.
et al.\textsuperscript{14} and Aguey-Zinsou et al.\textsuperscript{15} for hydrogen release from LiNH\textsubscript{2} + LiH. For Mg(NH\textsubscript{2})\textsubscript{2} and LiH, Xiong et al. concluded that to decrease the activation energy of the reaction there needs to be a way of forming a greater attraction between H\textsuperscript{+} and H\textsuperscript{−} of the amide and hydride respectively (Equation 1-6), or else weakening the Li-N and N-H bonds for rehydrogenation. This mechanism is not ammonia mediated, unlike the mechanisms proposed for much of the research previously discussed.

\[
\text{H} \quad \text{N-Mg-N} \quad \text{H} \quad + \quad \text{H-Li} \quad \rightarrow \quad \text{H} \quad \text{N-Mg-N} \quad \text{H} \quad \quad \quad \quad \text{H-Li} \quad \rightarrow \quad \text{H} \quad \text{N-Mg-N} \quad \text{H} \quad + \quad \text{H}_2
\]

Figure 1-5 Possible reaction mechanism for the hydrogen desorption from Mg(NH\textsubscript{2})\textsubscript{2} + 2LiH.\textsuperscript{31}

Xiong et al.\textsuperscript{33} investigated Mg(NH\textsubscript{2})\textsubscript{2} + 2LiH, alongside 1:1 and 1:3 ratios. The reactants were ball-milled together for 20 h. The 1:2 mixture had better desorption characteristics than the 1:1 or 1:3 ratios. The hydrogen release was much greater than the 1:1 ratio and almost all the NH\textsubscript{3} desorption was suppressed. After cycling this mixture, all ammonia release was eliminated.

The 1:2 mixture was found to form Li\textsubscript{2}Mg(NH)\textsubscript{2} at 250 °C, with a similar structure as previously reported by the same authors.\textsuperscript{20,33} Mg\textsubscript{3}N\textsubscript{2} was formed at 500 °C, but less than for the 1:1 ratio. The 1:3 mixture produced a Li-Mg-N-H complex at 240 °C similar to that in the 1:2 reaction mixture. Mg\textsubscript{3}N\textsubscript{2} was again observed towards 500 °C.

The gas release from the 1:2 and 1:3 reactions were analysed quantitatively\textsuperscript{33} using a gas reaction controller and applying soak and release modes. They both started to desorb
hydrogen at \( \sim 120 \, ^\circ \text{C} \). Between 160–170 \( ^\circ \text{C} \) the rate of desorption increased, matching with temperature programmed desorption (TPD) data. Overall, the higher hydride content did not appear to increase the hydrogen desorption temperature. The 1:2 mixture gave 5 wt% \( \text{H}_2 \) by 230 \( ^\circ \text{C} \), whereas the 1:3 reaction released 5.1 wt% \( \text{H}_2 \) by 330 \( ^\circ \text{C} \). The hydrogen desorbed remained in the sample chamber and therefore provided a hydrogen over pressure which explained the lack of complete hydrogen desorption from the 1:3 mixture. Higher temperatures were required to remove more \( \text{H}_2 \).

The 1:2 mixture was more rapid than 1:3 for rehydrogenation at 70 bar.\(^{33}\) At 100 \( ^\circ \text{C} \) the kinetics of adsorption were much quicker than 1:3. The slow kinetics of the 1:3 reaction mixture were blamed on possible sintering due to high temperature desorption or else the additional Li present in the sample.

Chen \textit{et al.}\(^{29}\) compared the reaction of \( \text{Mg(NH}_2\text{)}_2 + 2\text{LiH} \) with that of \( \text{Mg(NH}_2\text{)}_2 \) alone. They found the activation energies of the two reactions to be 88.1 kJ mol\(^{-1}\) and 130 kJ mol\(^{-1}\) respectively. This showed \( \text{Mg(NH}_2\text{)}_2 \) had a much larger kinetic barrier to overcome in order to liberate \( \text{NH}_3 \).

Chen \textit{et al.}\(^{29}\) commented that as the reaction rate is determined by the rate-determining step, the reaction between \( \text{Mg(NH}_2\text{)}_2 \) and \( \text{LiH} \) is unlikely to be started by the thermal decomposition of \( \text{Mg(NH}_2\text{)}_2 \). Isotopic exchange, of D for H, was also investigated and found to occur with relative ease which was supportive of a coordinated mechanism.

Liu \textit{et al.}\(^{34}\) investigated the effect of sodium compounds upon the Li-Mg-N-H system with partial substitution of \( \text{Mg(NH}_2\text{)}_2 \) for \( \text{NaNH}_2 \) and \( \text{LiH} \) for \( \text{NaH} \). It was found that the hydrogen desorption kinetics of the Na containing reactions were markedly improved. \( \text{NH}_3 \) desorption was also reduced. The activation energies of the three samples, \( \text{Mg(NH}_2\text{)}_2 + 2\text{LiH}, \text{Mg(NH}_2\text{)}_2 + \)
1.6LiH + 0.4NaH and 0.8Mg(NH$_2$)$_2$ + 0.4NaNH$_2$ + 2LiH, were 105.5, 97.7, and 92.5 kJ mol$^{-1}$ respectively. The Na-containing reactions desorbed their hydrogen quicker due to their lower activation energies. Unfortunately, less hydrogen was desorbed/adsorbed. The dehydrogenation products were different depending on the molar ratios between Li, Mg and Na.

NaH was added into the Mg(NH$_2$)$_2$-LiH mix [Mg(NH$_2$)$_2$-1.6LiH-0.4NaH]. There was no reaction when the starting materials were ball-milled together; therefore the starting materials were already in their lowest energy configuration or the activation energy for any reaction was not overcome. On heating it was observed that H$_2$ desorption started at 80 °C and peaked at 220 °C. The initial hydrogen loss was due to the formation of the mixed Li-Mg imide. The peak at 220 °C was thought to be from the reaction between Mg(NH$_2$)$_2$ and NaH. The products after hydrogen desorption were a Li$_2$MgN$_2$H$_2$-like phase, NaH and NaNH$_2$. On rehydrogenation Mg(NH$_2$)$_2$, LiH and NaH were all present.

When NaNH$_2$ was added to the Mg(NH$_2$)$_2$-LiH mix [0.8Mg(NH$_2$)$_2$-0.4NaNH$_2$-2LiH] the products after ball milling were found to be Mg(NH$_2$)$_2$, LiH, NaH and LiNH$_2$. This revealed a salt metathesis reaction had occurred (Equation 1-12). The desorption started at 80 °C as before, but peaked at 230 °C. Again, the initial desorption was thought to be due to the reaction of Mg(NH$_2$)$_2$ and LiH. The peak was thought to be from LiNH$_2$ + NaH. The products after dehydrogenation were a cubic imide, NaH and NaNH$_2$. After rehydrogenation Mg(NH$_2$)$_2$, LiH, NaH, NaNH$_2$ and LiNH$_2$ were all present.

Equation 1-12

\[ \text{NaNH}_2 + \text{LiH} \rightarrow \text{LiNH}_2 + \text{NaH} \]
Sudik et al.\textsuperscript{35} investigated Mg(NH\textsubscript{2})\textsubscript{2} + 2LiH both unseeded and seeded with pre-decomposed Li\textsubscript{2}Mg(NH\textsubscript{2}) added in excess to the reaction (5 wt%, 10 wt% and 15 wt%). All samples were ball-milled whether unseeded or with the seeded excess. It was found the 10 wt% Li\textsubscript{2}Mg(NH\textsubscript{2}) lowered the desorption temperature by 40 °C, from 220 °C (for 0 wt% seeding) to 180 °C. The desorption curves indicated a two-step hydrogen release, the second stage being closer to the unseeded desorption curve. This suggested that not all the sample was exposed to the kinetically enhanced product seed. The activation energy of the seeded sample was lowered by 13% from 88.0 kJ mol\textsuperscript{−1} to 76.2 kJ mol\textsuperscript{−1} relative to the unseeded sample. The lowering of the desorption temperature aided the suppression of NH\textsubscript{3}, although the temperature of NH\textsubscript{3} desorption was also lowered. Cycling the seeded sample continued to give lower temperatures of desorption although at 10 °C higher than on the first cycle. The relative desorption kinetics were found to be much quicker for the seeded sample than for the unseeded. At 220 °C the unseeded sample took an order of magnitude longer to fully desorb.

Liu et al.\textsuperscript{36} looked at sintering their starting materials, Mg(NH\textsubscript{2})\textsubscript{2} + 2LiNH\textsubscript{2}, in order to reduce particle size and increase mixing between the starting materials. The starting materials were first ball-milled for 36 hours, followed by heating to 315 °C under pure nitrogen gas. Li\textsubscript{2}Mg(NH\textsubscript{2}) was formed along with the release of ammonia (Equation 1-13).

\textbf{Equation 1-13} \hspace{1cm} Mg(NH\textsubscript{2})\textsubscript{2} + 2LiNH\textsubscript{2} \rightarrow Li\textsubscript{2}Mg(NH\textsubscript{2}) + 2NH\textsubscript{3}
3 samples were then prepared from the sintered starting materials. The first was Li$_2$Mg(NH)$_2$ hand-milled for 2 minutes. Samples 2 and 3 were ball-milled for 3 and 36 hours respectively.

The hydrogen uptake of all 3 samples was measured by heating them to 210 °C under 100 bar H$_2$. All samples absorbed about 5 wt% H$_2$. The onset of absorption was reduced by the ball-milling (particularly 36 h). The onset temperature for the hand-milled sample was 180 °C. By 180 °C the 36 hours ball-milled sample had already absorbed 3 wt% H$_2$.

The samples after their milling treatments were investigated via powder XRD and FTIR. The hand-milled sample showed the presence of both orthorhombic α-Li$_2$Mg(NH)$_2$ and cubic β-Li$_2$Mg(NH)$_2$. All the diffraction peaks were sharp indicating a well-ordered crystalline phase. By contrast, the ball-milled samples showed only the main peaks of β-Li$_2$Mg(NH)$_2$ and those were broad and less intense indicating a much less well-ordered state. The 2 ball-milled samples looked very similar, only that the sample milled for 36 hours had broader XRD peaks. The crystallite sizes for all 3 samples were calculated using the Scherrer equation and found to be about 41, 29 and 25 nm, respectively. The dramatic reduction in particle sizes between samples 1 and 2 explained the difference in the XRD patterns.

The FTIR spectra for the hand-milled sample showed the presence of 2 peaks in the imide region as well as very weak intensity absorbances from unreacted LiNH$_2$ (Figure 1-6). The 2 peaks in the imide region were most likely from the two forms of Li$_2$Mg(NH)$_2$ present. The two ball-milled samples both had one peak in the imide region: this concurred with the XRD results for these samples. After rehydrogenation at 210 °C, the samples were dehydrided again. The kinetics of all the samples were very similar to their first dehydrogenation.
At the same time as Xiong et al.\textsuperscript{31} above, Luo and Sickafoose\textsuperscript{25} were examining the structural characteristics of the Li-Mg-N-H system. As it was already known that the reaction between LiNH\textsubscript{2} and MgH\textsubscript{2} was reversible back to Mg(NH\textsubscript{2})\textsubscript{2} and LiH (Equation 1-8), initially comparisons between desorption isotherms of 2LiNH\textsubscript{2} + MgH\textsubscript{2} and Mg(NH\textsubscript{2})\textsubscript{2} + 2LiH were carried out.

The desorption isotherms for 2LiNH\textsubscript{2} + MgH\textsubscript{2} and Mg(NH\textsubscript{2})\textsubscript{2} + 2LiH were virtually identical with any variations attributed to experimental error (Figure 1-7). Luo et al. were troubled as to why they should be so close in isothermal characteristics. XRD patterns of the milled LiNH\textsubscript{2} and MgH\textsubscript{2} mixture showed no reaction during ball-milling. The 2LiNH\textsubscript{2} + MgH\textsubscript{2} mixture was heated to 220 °C under 100 bar H\textsubscript{2} for 2 h in order to establish which mechanism may be present. No desorption activity was expected under those conditions. The XRD after this experiment showed the presence of Mg(NH\textsubscript{2})\textsubscript{2} and LiH, as well as the starting materials LiNH\textsubscript{2} and MgH\textsubscript{2}. This gave evidence of an incomplete salt metathesis reaction.
Figure 1-7 Desorption pressure-composition isotherms at 220 °C for the first and third desorption of the (2LiNH₂ + MgH₂) sample. Desorption isotherm for (Mg(NH₂)₂ + 2LiH) is included.²⁵

Fourier transform infrared (FTIR) spectroscopy was used in this paper²⁵ to provide evidence on the makeup of the system throughout the hydriding/dehydriding cycle. The sample started in its dehydrided state. FTIR evidence showed the first dehydrided sample contained no –NH₂ bands and so was identified as an imide. The imide bands did not match MgNH or Li₂NH (as confirmed by XRD) and so were most likely from Li₂Mg(NH)₂. From XRD it was seen that the peak positions were slightly different at the start of hydriding to a short time after. The FTIR showed –NH₂ bands attached to Li, not Mg, without evidence for a new phase. Therefore, the following reaction was suggested:

Equation 1-14 \[ \text{Li}_2\text{MgN}_2\text{H}_2 + 0.6\text{H}_2 \rightarrow \text{Li}_2\text{MgN}_2\text{H}_{3.2} \]

The authors chose this stoichiometry due to their observations above.
After rehydrogenation, there was evidence of Mg(NH$_2$)$_2$ and LiH in the XRD results. FTIR confirmed the presence of Mg(NH$_2$)$_2$. The following reaction was suggested for this region:

Equation 1-15

$$\text{Li}_2\text{MgN}_2\text{H}_{3.2} + 1.4\text{H}_2 \leftrightarrow \text{Mg(NH)}_2 + 2\text{LiH}$$

As the new phases of Mg(NH$_2$)$_2$ and LiH were formed gradually during absorption, the plateau observed during sorption isotherms was explained. The authors propose a pathway for the rehydriding reactions (Figure 1-8).

![Figure 1-8 Proposed pathway for the sorption reaction of Li$_2$Mg(NH)$_2$ + 2H$_2$.]

Each box above (Figure 1-8) represents the sample at various times during the rehydrogenation. Box 1 shows the starting materials for rehydrogenation- Li$_2$MgN$_2$H$_2$ and H$_2$. Box 2 shows the addition of one hydrogen to the imide forming the previously suggested Li$_2$MgN$_2$H$_{3.2}$ (Equation 1-14). The authors suggest the similarity in crystal structure between Li$_2$MgN$_2$H$_2$ and Li$_2$MgN$_2$H$_{3.2}$ in boxes 1 and 2 above could account for the similarity in the XRD patterns observed for both phases. The ringed section also highlights the presence of Li$^+$-NH$_2^-$, although still part of the mixed imide. The FTIR shows us that NH$_2^-$ ions were coordinated to Li$^+$, which the authors have called LiNH$_2$, but these were still present as part of the mixed Li-Mg-imide-amide phase/phases, not as crystalline LiNH$_2$. Once the reaction is
complete (box 1 to 2), more hydrogen is added to form the bonds between Li and H and N and H of Mg(NH$_2$)$_2$. The transition from box 2 to 3 is not really a mechanistic progression, more a jump from the proposed intermediate to the fully hydrided phase.

This pathway (Figure 1-8$^{25}$) is in contrast to Xiong et al.$^{31}$ who presented a possible mechanism for the dehydrogenation (Figure 1-5). Xiong et al. acknowledge the possible instability of the intermediate, but it is along the same mechanistic lines as Luo and Sickafoose.$^{25}$

Janot et al.$^{38}$ compared the reactions Mg(NH$_2$)$_2$ + 2LiH and 2LiNH$_2$ + MgH$_2$. They attempted to gather preliminary data on the crystallographic unit cell of Li$_2$Mg(NH)$_2$ and found a cubic antifluorite structure, $a = 10.06(1)$ Å. This was roughly twice the value of that suggested by Xiong et al.$^{20,33}$

3. 3Mg(NH$_2$)$_2$ + 8LiH

Concurrent with Xiong et al.$^{20}$ and Luo,$^{21}$ Leng et al.$^{22}$ also investigated the Li-Mg-N-H system. Leng et al.,$^{22}$ however, looked directly at the reaction between magnesium amide and lithium hydride in a 3:8 ratio. This indicated a product of Mg$_3$N$_2$ may be possible due to the addition of extra Mg(NH$_2$)$_2$ compared to the reactions seen previously. They suspected that the reaction between the Mg(NH$_2$)$_2$ and LiH would go via an NH$_3$-mediated solid-gas reaction like LiNH$_2$ + LiH (Equation 1-4 and Equation 1-5).

The mixture of Mg(NH$_2$)$_2$ (made by ball-milling MgH$_2$ under a pure NH$_3$ gas atmosphere of 4 bar) and LiH was ball milled under hydrogen gas for 2 h and then heated up to 400 °C.$^{22}$ A large amount of hydrogen desorption was observed. The temperature of desorption and the amount of hydrogen desorbed were both higher than the LiNH$_2$ + LiH reaction (as seen
Leng et al. attributed this to Mg\((\text{NH}_2)_2\) being less stable and more easily decomposed to imide and nitride than LiNH\(_2\) (smaller enthalpy, larger entropy). The products after heating to 400 °C were characterised by XRD and found to be \(\text{Mg}_3\text{N}_2\) and \(\text{Li}_2\text{NH}\) (Equation 1-16).

\[
\text{Equation 1-16} \quad 3\text{Mg(\text{NH}_2)_2} + 8\text{LiH} \rightarrow \text{Mg}_3\text{N}_2 + 4\text{Li}_2\text{NH} + 8\text{H}_2
\]

This reaction had a theoretical hydrogen capacity of about 7 wt% (in comparison to \(2\text{LiNH}_2 + \text{MgH}_2\), 5.35 wt% \(\text{H}_2\)) and this was mirrored experimentally. In order to investigate the reversibility, the dehydrogenated sample was heated at 200 °C under 30 bar \(\text{H}_2\). The starting materials were reproduced after rehydrogenation/dehydrogenation cycling, which indicated complete reversibility.

Leng et al.\(^{22}\) suggested the reaction went by three elementary reactions:

1. The decomposition of \(\text{Mg(\text{NH}_2)_2}\) to \(\text{MgNH}\) and \(\text{NH}_3\). This continues to \(\text{Mg}_3\text{N}_2\) at higher temperatures (Equation 1-10).

2. The \(\text{NH}_3\) desorbed reacts with LiH present to form \(\text{LiNH}_2 + \text{H}_2\) (Equation 1-5).

3. The newly formed \(\text{LiNH}_2\) decomposes to \(\text{Li}_2\text{NH}\) and further \(\text{NH}_3\) (Equation 1-4). The \(\text{NH}_3\) then reacts with more LiH, forming further \(\text{LiNH}_2\) and undergoing further decomposition (Equation 1-5).

The products from the reaction carried out by Leng et al.\(^{22}\) do not suggest \(\text{Li}_2\text{Mg(\text{NH})}_2\) was ever formed. The additional \(\text{Mg(\text{NH}_2)_2}\) present pushed the reaction through to the most hydrogen deficient magnesium species, \(\text{Mg}_3\text{N}_2\).
The rehydrogenation process could not simply follow the reverse of the suggested dehydrogenation reaction, as \( \text{Li}_2\text{NH} \) when rehydrogenated forms \( \text{LiNH}_2 \) and \( \text{LiH} \). However, \( \text{Mg}_3\text{N}_2 \) does not rehydrogenate to \( \text{Mg(NH}_2)_2 \) and \( \text{MgH}_2 \)\(^{39}\) (or any other products). Rehydrogenation of \( \text{Mg}_3\text{N}_2 \) to \( \text{Mg(NH}_2)_2 \) and \( \text{MgH}_2 \) was however shown to occur by Nakamori et al. when mixed with \( \text{Li}_3\text{N} \)\(^{40}\).

4. **\( \text{Mg(NH}_2)_2 + 4\text{LiH} \)**

Nakamori *et al.*\(^{23}\) investigated \( \text{Mg(NH}_2)_2 + 4\text{LiH} \) to compare with the desorption characteristics of \( \text{Mg(NH}_2)_2 \) alone and when reacted with \( \text{MgH}_2 \). They found the decomposition of the two magnesium based reactions to be very similar in that they both desorbed \( \text{NH}_3 \) as a majority gas, possibly with a small amount of hydrogen. This indicated to them that the addition of \( \text{MgH}_2 \) to \( \text{Mg(NH}_2)_2 \) did not suppress the desorption of ammonia from \( \text{Mg(NH}_2)_2 \) as the addition of \( \text{LiH} \) does compared to \( \text{LiNH}_2 \) heated alone. It was concluded this was due to the reaction between \( \text{LiH} \) and \( \text{NH}_3 \) being “ultrafast”,\(^{41}\) whereas the analogous reaction between \( \text{MgH}_2 \) and \( \text{NH}_3 \) took in the region of a day to go to completion.

\( \text{Mg(NH}_2)_2 + 4\text{LiH} \) were heated up to 600 °C. Mass loss began at approximately 150 °C; by 600 °C 6.5 wt% loss had been observed. This was less than the theoretical mass loss (9.1 wt% \( \text{H}_2 \)) using Equation 1-17. It was seen from thermogravimetric-differential thermal analysis (TG-DTA) that more than 2 steps occurred during desorption (Figure 1-9). Only \( \text{Mg}_3\text{N}_2 \) and \( \text{Li}_3\text{N} \) were observed after dehydrogenation in a vacuum at 477 °C. The gas desorbed from the reaction was confirmed to be only hydrogen with no ammonia release observed. In comparison to the gas desorption temperature of \( \text{LiNH}_2 \) with \( \text{LiH} \), Equation
Equation 1-17 occurred at over 100 °C lower. Nakamori *et al.*\textsuperscript{23} put this down to the lower decomposition temperature of Mg(NH$_2$)$_2$ compared to LiNH$_2$.

![Figure 1-9 TG-DTA of the mixture of Mg(NH$_2$)$_2$ + 4LiH in argon flow at 0.1 MPa with a heating rate of 10 °C min$^{-1}$. The inset shows the powder XRD profile after dehydriding reaction of the mixture of Mg(NH$_2$)$_2$ + 4LiH. The closed diamonds and open circles show the peak positions of Mg$_3$N$_2$ and Li$_3$N.\textsuperscript{23}]

Equation 1-17 \hspace{1cm} 3Mg(NH$_2$)$_2$ + 12LiH $\leftrightarrow$ Mg$_3$N$_2$ + 4Li$_3$N + 12H$_2$

Equation 1-18 \hspace{1cm} LiNH$_2$ + LiH $\leftrightarrow$ Li$_2$NH + H$_2$

Aoki *et al.*\textsuperscript{42} focused on 3Mg(NH$_2$)$_2$ + 12LiH due to the high hydrogen storage capacity of 9 wt%. The full reaction is seen in Equation 1-17. Up to 250 °C, only half the hydrogen was desorbed. The similarities noticed between the isotherms of 3Mg(NH$_2$)$_2$ + 12LiH and Mg(NH$_2$)$_2$ + 2LiH imply the dehydrogenation reactions are similar. After dehydrogenation of the 3:12 mixture, two new phases were identified. One indexed with a tetragonal lattice, the other orthorhombic. The orthorhombic unit cell increased throughout hydrogen loss. (This is
different from interstitial hydrides.) Lattice parameters of the tetragonal and orthorhombic phases observed are shown in

Table 1-2 1–2.

Table 1-2 Lattice parameters of the tetragonal and orthorhombic phases observed (from Aoki et al.42).

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>Tetragonal 3.1</th>
<th>Orthorhombic 3.5</th>
<th>Orthorhombic 4.0</th>
<th>Orthorhombic 4.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b$/ Å</td>
<td>5.141</td>
<td>5.011</td>
<td>5.000</td>
<td>5.004</td>
</tr>
<tr>
<td>$c$/ Å</td>
<td>5.141</td>
<td>5.187</td>
<td>5.191</td>
<td>5.201</td>
</tr>
</tbody>
</table>

The tetragonal and orthorhombic phases corresponded to Li$_4$Mg$_3$(NH$_2$)$_2$(NH)$_4$ and Li$_{4+x}$Mg$_3$(NH$_2$)$_{2-x}$(NH)$_{4+x}$ ($x = 0.4, 1, 2$) respectively.42 Li$_4$Mg$_3$(NH$_2$)$_2$(NH)$_4$, Mg(NH$_2$)$_2$ and LiH were all thought to coexist and the molar ratio of Li$_4$Mg$_3$(NH$_2$)$_2$(NH)$_4$ increased whilst the others decreased, throughout the plateau of the isotherm. The orthorhombic phase, Li$_{4+x}$Mg$_3$(NH$_2$)$_{2-x}$(NH)$_{4+x}$, formed at the sloping part of the isotherm. The final products were Li$_2$MgN$_2$H$_2$ and LiH. The authors suggest the temperature at 250 °C was the reason for the lack of continued reaction of the products.

5. Mg(NH$_2$)$_2$ + LiH

Xiong et al.33 investigated Mg(NH$_2$)$_2$ and LiH in a 1:1 ratio. The reactants were ball-milled together for 20 h. The mixture started to desorb hydrogen at approximately 200 °C. There was less hydrogen comparatively than when compared to 1:2 and 1:3 mixtures also investigated by Xiong et al. A considerable amount of ammonia was also detected, starting at 150 °C and peaking at 270 °C. It was noted how the reaction between Mg(NH$_2$)$_2$ and $x$LiH
gave a lower decomposition temperature than the decomposition temperature of Mg(NH$_2$)$_2$ alone (~360 °C). It was suggested, therefore, that the NH$_3$ was not from the unreacted Mg(NH$_2$)$_2$ but from another –NH containing intermediate. Above 370 °C another large desorption of NH$_3$ was present. This may have been due to Mg(NH$_2$)$_2$ decomposition.

Powder XRD was then used in order to characterise the structural changes occurring.$^{33}$ The 1:1 mixture was examined by XRD after heating to 220 °C. The result was an XRD pattern that indicated a cubic structure with $a = 5.033$ Å (Figure 1-10). This is analogous to the structures noted by Xiong et al.$^{20}$ No Mg(NH$_2$)$_2$ or LiH was present. The ammonia released at higher temperature was suggested to have been the result of the Li-Mg-N-H structure decomposing. The decomposed structure (after heating to 370 °C) was tetragonal; $a = 5.131$ Å, $c = 9.626$ Å. By 500 °C, Mg$_3$N$_2$ had appeared as well as a post 220 °C compound, but with lower symmetry than the tetragonal phase.
Figure 1-10 X-ray diffraction patterns of sample M-I after TPD test stopping at 220, 330 and 500 °C. Broad peaks at around 43.0 and 62.5° belong to MgO. Li$_2$O has diffraction peaks positioned at 33.6 and 56.4°; LiOH at 20.5, 32.6 and 35.8°.

By gravimetric methods the gas desorbed from the 1:1 ratio was found to be $\frac{1}{2}$ NH$_3$ and $\frac{1}{2}$ H$_2$ at 310 °C however, this did not match the equation Xiong et al. suggested (Equation 1-19).

Equation 1-19

$$2\text{Mg(NH}_2\text{)}_2 + 2\text{LiH} \rightarrow \text{Li}_2\text{Mg}_2\text{N}_3\text{H}_3 + \text{NH}_3 + 2\text{H}_2$$
The Li$_2$Mg$_2$N$_3$H$_3$ phase here (Equation 1-19) was previously characterised by Juza and Eberius, in 1962.\textsuperscript{43} It was formed by reacting LiMgN with ammonia at 320–400 °C. Juza et al. indexed the phase to a tetragonal structure with $a = 5.15$ Å and $c = 9.67$ Å. Xiong et al.\textsuperscript{33} formed this phase below 350 °C. The rehydrogenation of Li$_2$Mg$_2$N$_3$H$_3$ by Xiong et al. achieved an uptake of only 0.5 wt% between 70 and 210 °C. The structure has since been fully characterised and indexed in space group $I-42m$ with lattice parameters $a = 5.130$ Å and $c = 9.619$ Å.\textsuperscript{44}

6. LiNH$_2$ + MgH$_2$

Osborn et al.\textsuperscript{45} combined LiNH$_2$ and MgH$_2$ in a 1:1 ratio. The DFT work of Alapati et al.\textsuperscript{46} inspired this investigation due to a favourable thermodynamic driving force for the theoretical equation:

Equation 1-20 LiNH$_2$ + MgH$_2$ → LiMgN + 2H$_2$

This reaction has a theoretical 8.2 wt% H$_2$ compared to 5.4 wt% for a 2:1 ratio. Their reaction relies on the decomposition of LiNH$_2$ to imide and ammonia (Equation 1-4) and then the reaction of ammonia with MgH$_2$ to Mg(NH$_2$)$_2$ and H$_2$ (Equation 1-9).

Unfortunately, a high concentration of ammonia was detected. A maximum of 3.4 wt% H$_2$ was desorbed. XRD after heating to 210 °C showed the presence of remaining MgH$_2$, newly formed LiH and Li$_2$Mg$_2$(NH)$_3$ as previously formed by Xiong et al. above.\textsuperscript{33} None of the expected LiMgN was formed. The actual reaction scheme occurring was proposed to be:
Equation 1-21 gives a theoretical 4.1 wt% H₂ release, much closer to the 3.4 wt% H₂ measured. The reaction overall was less promising for hydrogen storage purposes due to less H₂ being stored in the 1:1 system, ammonia desorption alongside hydrogen and unreacted starting material present. The proposed reaction of MgH₂ with NH₃ led to the unrealistic expectations of the authors.

Liu et al.⁴⁷ investigated the reaction of LiNH₂ + MgH₂ (1:1) using ball-milling and no external heat. The reactants were ball-milled together and hydrogen was released. As the starting materials did not desorb hydrogen when ball-milled alone this showed the reaction was occurring between the starting materials when ball-milled together. After 24 hours of ball-milling, Mg(NH₂)₂ was identified using FTIR. The powder XRD patterns taken at that time showed evidence of LiH. This showed further evidence of a metathesis reaction occurring to form Mg(NH₂)₂ and LiH.²⁵ Upon prolonged ball-milling (36 h), the Mg(NH₂)₂ XRD peaks started to diminish and new imide peak in its place began to be formed. XRD identified the new peaks as MgNH. No Li₂Mg₂(NH)₃ was detected at any time. This was put down to the different ball-milling time (36 h) used in comparison to Osborne et al. (3 h).⁴⁵ At 270 °C Mg₃N₂ was seen in XRD. This was quite a low temperature for the appearance of Mg₃N₂. After heating to 390 °C, Mg₃N₂, Li₂Mg(NH)₂ and LiH were all identified. Upon heating under hydrogen pressure (81 bar), the products were Mg₃N₂, LiH and Mg(NH₂)₂. The continued presence of Mg₃N₂ after attempted rehydriding gives further weight to the experiments of Kojima et al.,³⁹ whilst disagreeing with Nakamori et al.⁴⁰ and Leng et al.²² As Nakamori et al.

Equation 1-21  
\[ \text{LiNH}_2 + \text{MgH}_2 \rightarrow \frac{1}{3}\text{Li}_2\text{Mg}_2(\text{NH})_3 + \frac{2}{3}\text{MgH}_2 + \frac{1}{3}\text{LiH} + \text{H}_2 \]
had Li$_3$N present and Leng et al. had Li$_2$NH present in the rehydrogenation reactants the lithium products may be necessary for Mg$_3$N$_2$ to rehydride.

7. $3\text{Mg(NH}_2\text{)}_2 + 2\text{Li}_3\text{N}$

Ma et al.$^{48}$ investigated the reaction between $3\text{Mg(NH}_2\text{)}_2$ and $2\text{Li}_3\text{N}$ in hope of enhancing capacity and mitigating NH$_3$ desorption. The reaction was heated to 240 °C under dynamic vacuum. $\alpha$-Li$_2$Mg(NH)$_2$ was formed. Only NH$_3$ was desorbed (Equation 1-22).

$$\text{Equation 1-22} \quad 3\text{Mg(NH}_2\text{)}_2 + 2\text{Li}_3\text{N} \rightarrow 3\text{Li}_2\text{Mg(NH)}_2 + 2\text{NH}_3$$

It was suggested this reaction had occurred via a 3-step mechanism. Firstly the Mg(NH$_2$)$_2$ decomposed to MgNH and NH$_3$ (Equation 1-10). The NH$_3$ then reacted with Li$_3$N to form Li$_2$NH (Equation 1-23).

$$\text{Equation 1-23} \quad 2\text{Li}_3\text{N} + \text{NH}_3 \rightarrow 3\text{Li}_2\text{NH}$$

The two imides then combined to form Li$_2$Mg(NH)$_2$ (Equation 1-11). Upon hydrogenation, the mixed imide hydried back to Mg(NH$_2$)$_2$ and LiH (Equation 1-8).

Varying of the ratio between the two starting materials ($x\text{Li}_3\text{N} + 3\text{Mg(NH}_2\text{)}_2$, $x = 2, 2.1, 2.3, 2.5, 3$) was also investigated. It was found that when heated to 200 °C for 120 minutes the 2.3:3 mixture desorbed 4.9 wt% H$_2$. Further increase in the amount of Li$_3$N reduced the amount of H$_2$ desorbed down to 4.25 wt%. The cycling stability was found to be very good and less ammonia was detected with this sample. Upon rehydrogenation the products were
Mg(NH$_2$)$_2$, LiNH$_2$ and LiH. During rehydrogenation Li$_2$NH may have been formed, but due to its structural similarity to Li$_2$Mg(NH)$_2$ this was difficult to ascertain. When the products from rehydrogenation were dehydrided again, Li$_2$Mg(NH)$_2$ was formed from the reaction of Mg(NH)$_2$$_2$ and LiH, however LiNH$_2$ and the remaining LiH were stable at the temperatures tested. No difference in the desorption mechanism was encountered with the use of more Li$_3$N. This was different to the various ratios of Mg(NH$_2$)$_2$/LiH investigated by others.\textsuperscript{20,21,22,23} LiNH$_2$ is thought to be an important intermediate in the formation of Li$_2$Mg(NH)$_2$. The LiNH$_2$ may provide favourable nucleation/growth sites. This is thought to be similar to the effect of product seeding.
8. Conclusions

Table 1-3 Summary of the Li-(Mg-)N-H systems discussed above.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNH₂ + LiH</td>
<td>Possible 11.5 wt% hydrogen release, 6.5 wt% hydrogen release below 300 °C</td>
</tr>
<tr>
<td>2LiNH₂ + MgH₂</td>
<td>Lower H₂ desorption temperature than LiNH₂-LiH system, Li₂Mg(NH)₂ formed, rehydrogenated at 180 °C under 90 bar H₂, temperature, stability on cycling with products: Mg(NH₂)₂ + 2LiH, more ball milling = less NH₃</td>
</tr>
<tr>
<td>Mg(NH₂)₂ + 2LiH</td>
<td>α-, β-, γ-, δ-Li₂Mg(NH)₂ formed, rehydrogenated under 90 bar H₂ and 250 °C, reformed Mg(NH₂)₂ and LiH, rapid hydrogen uptake above 110 °C, 5 wt% uptake below 200 °C, remaining H₂ desorbed slower, seeding with Li₂Mg(NH)₂ decreased desorption temperature</td>
</tr>
<tr>
<td>3Mg(NH₂)₂ + 8LiH</td>
<td>Desorption temperature higher than LiNH₂-LiH, Mg₃N₂ and Li₂NH formed, 7 wt% H₂ desorbed, rehydrogenated under 30 bar H₂ and 200 °C</td>
</tr>
<tr>
<td>Mg(NH₂)₂ + 4LiH</td>
<td>Up to 250 °C 4.5 wt% loss, up to 600 °C 6.5 wt% H₂ loss (theoretical 9.1 wt%), Mg₃N₂ and Li₃N as products, Li₄Mg₃(NH)₂(NH)₄ and Li₄ₓMg₃(NH)₂ₓ(NH)₄ₓ (x = 0.4, 1, 2) intermediates identified</td>
</tr>
<tr>
<td>Mg(NH₂)₂ + LiH</td>
<td>Started to desorb H₂ at 200 °C, less H₂ desorbed than 1:2 or 1:3, ammonia detected from 150 °C, Li₂Mg₂N₃H₃ formed, only 0.5 wt% H₂ uptake up to 210 °C on rehydriding</td>
</tr>
<tr>
<td>LiNH₂ + MgH₂</td>
<td>3.4 wt% H₂ desorbed on heating, ammonia detected, Li₂Mg₂(NH)₃ formed, when ball-milled with no heating H₂ desorbed, no ammonia, Mg(NH₂)₂ and LiH formed after 24 h rehydriding, MgNH formed after 36 h</td>
</tr>
<tr>
<td>3Mg(NH₂)₂ + 2Li₃N</td>
<td>Heated to 240 °C under dynamic vacuum, Li₂Mg(NH)₂ formed, NH₃ desorbed, no hydrogen, 2.3:3 ratio of starting materials gave 4.9 wt% H₂ after 120 mins at 200 °C</td>
</tr>
</tbody>
</table>

In conclusion, it can be seen that the Li-Mg-N-H system overall seems to have kinetics and thermodynamics more promising for hydrogen storage than the LiNH₂-LiH system, in particular Mg(NH₂)₂/LiH starting materials after undergoing ball-milling to reduce particle
size. Mg(NH$_2$)$_2$/LiH would also be better starting materials than LiNH$_2$/MgH$_2$ as Mg(NH$_2$)$_2$ is less reactive with the atmosphere than LiNH$_2$. Using Mg(NH$_2$)$_2$ and LiH is also of benefit as LiH has a greater reactivity with NH$_3$ than MgH$_2$. The best ratio of Mg(NH$_2$)$_2$:LiH was 3:8. This desorbed 7 wt% H$_2$ on heating at 400 °C after 2 hours ball-milling under hydrogen. It appeared the best rehydriding conditions used were 30 bar H$_2$ and 200 °C for this reaction. Although the desorption temperature was higher than other literature published, the higher hydrogen content and lower hydrogen pressure required to reverse back to starting materials was most promising in comparison to other systems reviewed here.

The partial substitution of lithium for magnesium in the lithium amide lattice appears to destabilise the system and encourages hydrogen desorption at a lower temperature than for LiNH$_2$/LiH.

4. Aims

The aims of the research carried out within this thesis concerns the reactions of light metal hydrides with various light metal amides reactions not previously studied. The mixed cation amides Li$_3$Na(NH$_2$)$_4$ and LiNa$_2$(NH$_2$)$_3$ were heated with LiH, NaH and MgH$_2$ in order to establish whether hydrogen was desorbed and if so whether the mixed cations within the amides destabilised the temperature at which the reactions desorbed hydrogen in comparison to LiNH$_2$ and NaNH$_2$ respectively.

The reactions of NaNH$_2$ and MgH$_2$ in various ratios were investigated using thermal decomposition, Raman spectroscopy and thermogravimetric analysis in order to establish whether there was a similar reaction mechanism to that of LiNH$_2$ and MgH$_2$. The products
from heating NaNH$_2$ + MgH$_2$ were then put under a hydrogen atmosphere in order to attempt rehydrogenation.

Finally, it was realised that the decomposition characteristics of NaNH$_2$ had been relatively neglected in the literature and so an examination of its decomposition products and reaction with sodium hydride, as a comparison to LiNH$_2$/LiH, were carried out, using Raman and thermal decomposition techniques.

1. T. M. Letcher, Climate Change - Observed Impacts on Planet Earth, Elsevier, 2009
5. British Patents 840,572 and 863,491
43 R. Juza, E. Eberius, Naturwissenschaften, 49 (1962) 104
2. EXPERIMENTAL

1. Crystallography

Crystallography describes the arrangement of atoms in the solid state (although not all solids are crystalline). Atoms in the solid state form a regular arrangement in 3 dimensions. A ‘unit cell’ is the smallest regular, repeating unit of atoms which completely describes the atomic arrangement and symmetry of the crystal structure. This is present in all ideal crystals and demonstrates the full symmetry of the crystal structure. By translating the unit cell it is possible to form the full crystal lattice. The lattice is defined by locating equivalent positions, which are known as lattice points. The unit cell can be described by the three lengths of the edges (a, b and c), as well as the angles between them (α, β and γ). These are known as lattice parameters (Figure 2-1).

![Figure 2-1 General three-dimensional unit cell definition.](image)

The lattice parameters may take any values and therefore Figure 2-1 shows a cell with no symmetry. As the symmetry increases, the unit cell develops relationships between various
cell parameters and seven primitive (P) crystal systems can be formed. Primitive cells have only one lattice point. 14 lattice types can be formed if body centring (I) and face centring (F and C) are introduced. The body centred lattice has an additional lattice point at the centre of the unit cell and face centred lattices have lattice points at the centre of every unit cell face (F-centring only). These additional F and C, as well as P lattices are known as the 14 Bravais lattices (Table 2-1).

Table 2-1 Dimensions and essential symmetry features of the seven crystal systems.

<table>
<thead>
<tr>
<th>7 Lattice Systems</th>
<th>Unit Cell Dimensions</th>
<th>Essential Symmetry</th>
<th>Allowed Lattices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>a=b=c; α=β=γ=90 °</td>
<td>Four threefold axes</td>
<td>P, I, F</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>a=b≠c; α=β=γ=90 °</td>
<td>One fourfold axis</td>
<td>P, I</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>a≠b≠c; α=β=γ=90 °</td>
<td>Three twofold axes</td>
<td>P, I, F, C</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>a=b≠c; α=β=γ=90 °</td>
<td>One sixfold axes</td>
<td>P</td>
</tr>
<tr>
<td>Trigonal</td>
<td>a=b=c; α=β=γ=90 °</td>
<td>One threefold axis</td>
<td>R</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>a≠b≠c; α=γ=90 °, β≠90 °</td>
<td>One twofold axis</td>
<td>P, C</td>
</tr>
<tr>
<td>Triclinic</td>
<td>a≠b≠c; α≠β≠γ≠90 °</td>
<td>None</td>
<td>P</td>
</tr>
</tbody>
</table>

1. Crystal Structures

The lattice parameters, atomic positions within the unit cell and the internal symmetry of the unit cell can completely describe the crystal structure of a material. Atomic positions are described as fractional coordinates in each direction along the unit cell from one corner of the cell. With the inclusion of atoms to the unit cell, further translational symmetry elements to those required for the description of Bravais lattices must be considered. The arrangement of the atoms can give rise to screw axes and glide planes. 230 ‘spaces groups’ can be derived when all of the possible 3-D symmetry arrangements are combined. Space groups completely describe the symmetry of the crystal structure.
2. Lattice Vectors, Planes and Miller Indices

An unambiguous description of the directions and planes of crystals is very important in
diffraction and crystallography. The directional vectors in a lattice must pass through the
origin. Any point on a vector can be described as fractions of unit cell lengths \(a\), \(b\) and \(c\).
These fractions, in turn, are multiplied up to whole numbers to give the conventional form
\([uvw]\). Any directional coordinate going in the opposite direction is identified by a negative,
e.g. \([\bar{u}\bar{v}\bar{w}]\) (Figure 2-2).

Figure 2-2 Examples of lattice vectors.

Figure 2-3 Lattice planes with different Miller indices.
A lattice plane (Figure 2-3) is formed by the connection of several lattice points in 3-D. Each lattice point must sit on a lattice plane. A lattice plane is defined by how it intersects the unit cell vectors, $a$, $b$ and $c$. This is described by Miller indices. For each of $a$, $b$ and $c$, there is an equivalent Miller index $h$, $k$ and $l$ respectively. The reciprocals of the fractions along $a$, $b$ or $c$ are written as $(hkl)$. Therefore, any equivalent lattice plane will have the same $(hkl)$ value. The perpendicular distance that separates equivalent lattice planes is known by $d$-spacing ($d_{hkl}$). $d$ can be derived for a cubic system by Equation 2-1.

Equation 2-1

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

3. Bragg’s Law

Bragg’s treatment of the diffraction of X-rays was based on considering crystals as layers of atoms which behave as reflecting planes, where the angle of incidence equals the angle of reflection. (These layers of atoms may be regarded as lying in planes, which are described by the Miller indices, as described above.) Some X-rays are considered to be reflected by the first planes of atoms, those that are not continue travelling through the crystal until reflected by another plane (Equation 2-2). The reflections are observed only when $n$ is an integer, that is, when completely constructive interference occurs between the waves of X-rays (Figure 2-4 and Equation 2-3). All other values of $n$ destroy the scattering, therefore do not result in any peaks.
Equation 2-2 \( (xy + yz) = (d_{hkl} \sin \theta + d_{hkl} \sin \theta) = 2d_{hkl} \sin \theta \)

For completely constructive interference, the change in phase of the reflected (or diffracted) wave must be equal to an integer multiple of the wavelength:

Equation 2-3 \( n\lambda = 2d_{hkl} \sin \theta_n \)

where \( n \) is an integer. While in theory \( n \) can take any integer value, in practice the diffracted intensity falls off rapidly with increasing \( n \) (higher order reflections), so the Bragg equation is frequently simplified further to:

Equation 2-4 \( \lambda = 2d_{hkl} \sin \theta_n \)
Only scattering events where $n$ is an integer will give rise to $n$ observed diffracted intensity, with all other values giving rise to completely destructive interference when summed over all scattering events. The angle of the observed diffracted beam gives the separation of the planes of atoms giving rise to that diffracted beam (known as the $d$-spacing), whereas the intensity of the beam gives information on the properties of the scatterers.

2. X-ray Diffraction

An X-ray diffraction (XRD) experiment comprises shining a monochromatic source of radiation onto a sample, with a movable detector placed in a defined geometry relative to the source and sample. It is generally a non-destructive technique which reveals information regarding the crystallographic structure and chemical composition of materials.

In a laboratory setting, X-rays are produced when a beam of electrons are accelerated and collide with a metal anode target inside a vacuum tube. These electrons induce electronic transitions within the atoms of the target. When these atoms relax, well defined electronic transitions within the atoms lead to the emission of radiation of characteristic wavelengths. In this study, a Cu target was exclusively used, but others including Mo, Cr, Fe and Co can be used.

The X-rays emitted from the metal anode source form a divergent beam containing a spectrum of X-rays. The spectrum comprises characteristic discrete wavelengths, which correspond to the energy of atomic transitions of the metal target and a background spectrum known as Bremsstrahlung. Bremsstrahlung (brake radiation) is produced from the deceleration of a charged particle (electron) when deflected by another charged particle, for
an electron usually an atomic nucleus (target). As the moving particle loses kinetic energy, a photon (X-ray) is produced (due to conservation of energy). The total X-ray spectrum is continuous with additional peaks at certain energies which are characteristic of the target material. For the experiments here a copper radiation source was used, as shown in Figure 2-5.

![Cu X-ray emission spectrum](image)

Figure 2-5 Cu X-ray emission spectrum.

A single, intense beam of radiation is required for X-ray diffraction. Monochromation is necessary to select the single most intense part of the spectrum. There are two types of monochromation often used in laboratory X-ray sources. The first is a crystal monochromator. This is a single crystal set at a specific orientation, $\theta_m$, so that the Bragg equation is satisfied:

\[ \lambda = 2d_{hkl}\sin\theta_m \]

Equation 2-5

where $d_{hkl}$ is the d-spacing of an intense Bragg reflection.
Crystal monochromators are typically made from Si, Ge, quartz or graphite. A single wavelength can be selected using this method of monochromation. The second type of monochromator is a Göbel mirror. This is formed from curved multi-layer crystals made up of alternating strongly and weakly scattering materials. The multi-layer spacing determines the wavelength of the radiation that is reflected. This produces a parallel X-ray beam. Göbel mirrors are unable to monochromate the radiation adequately to differentiate between the two strongest types of Cu radiation: $K\alpha_1$ and $K\alpha_2$ (shown in Figure 2-5).

Scintillation counters are the most common form of X-ray detectors. A phosphorescent crystal fluoresces when struck by the photons emitted by the X-rays. A photomultiplier tube then detects and amplifies the fluorescence from the crystal. The signal is directly proportional to the number of photons hitting the crystal. This is a point detector as only data from a single $2\theta$ angle can be measured at any time. Position sensitive detectors (PSD) are becoming more popular as they can collect data over a $2\theta$ range to reduce data collection time. The detector records the $2\theta$ angle at which each X-ray is detected.

Accurate relative positioning between the X-ray beam, sample and detector is essential in diffraction. A goniometer is used to measure the relative angles between the components. There are two common geometries of diffractometers: reflection (Bragg-Brentano) and transmission (Debye-Scherrer).

1. Synchrotron X-ray Diffraction

A synchrotron is a particle accelerator in which a magnetic field and electric field are synchronised to produce a high energy, focussed beam of charged particles. Synchrotron radiation is emitted when charged particles change their velocity (or direction). Many
wavelengths are emitted and can be selected using monochromation. Synchrotron X-ray sources have the advantage of being very intense, perfectly polarised sources of X-ray radiation.

Powder synchrotron X-ray diffraction data were collected on beam line ID31 at the European Synchrotron Radiation Facility (ESRF), in Grenoble, France, at a wavelength and step-size of 0.79986916 Å and 0.003 ° respectively. Borosilicate capillaries of 0.9 mm were filled in a glove bag under flowing nitrogen. Once the samples were tightly packed, the capillary was sealed with 0.7 mm diameter glass rod, removed from the glove bag and sealed with a gas torch. No signs of oxidation of samples from the loading and sealing processes were observed.

The sealed capillaries were spun at 100 r.p.m. perpendicular to the X-ray beam to improve randomisation of the individual crystal orientations. Reflections from a silicon standard were used to determine the exact wavelength and zero point. The samples were scanned for 15 minutes and in this time no noticeable radiation damage, in the form of anisotropic peak shift or broadening, was observed.

Powder synchrotron X-ray data were also collected on beam line I11 at the Diamond Light Source, in Didcot, UK at a wavelength and step-size of 0.825594 Å and 0.002 °, respectively.

2. Laboratory X-ray Diffraction

Laboratory powder X-ray data were collected on a Siemens D5000 diffractometer in transmission mode. A copper X-ray source was monochromated using a germanium monochromator. This gave Cu K\(\alpha_1\) radiation with a wavelength of 1.54056 Å. Samples were
prepared by grinding in an argon filled glove box and sealed on a metal disc between two layers of Scotch® Magic™ tape. Samples were rotated perpendicular to the X-ray beam. Samples were also collected on a Bruker AXS D8 diffractometer in transmission mode. A copper X-ray source was monochromated using a germanium monochromator. This gave Cu Kα₁ radiation with a wavelength of 1.54056 Å. Samples were prepared as above.

3. Rietveld Analysis

It is not always possible to grow large single crystals in order to gain structural information. Rietveld analysis can be used on powder diffraction samples. The conventional problem with powder diffraction is the inability to differentiate between overlapping peaks. The Rietveld method creates virtual separation of the overlapping peaks, thereby allowing accurate determination of the structure. Rietveld analysis requires the unit cell size and shape, atomic positions, occupancies and thermal motion parameters in order to build a structural model. Experimental parameters such as peak profile and background shape are then combined with the structural model to calculate a diffraction pattern. A least-squares method is used to vary these parameters until the difference between the measured and calculated diffraction profiles is at a minimum. The $S_y$ function is minimised during the least squares refinement:

$$S_y = \sum_i w_i (y_i - y_{ci})^2$$

where

$$w_i = \frac{1}{\sigma_i^2},$$

$y_i = \text{observed intensity at the } ith \text{ step}$,

$y_{ci} = \text{calculated intensity at the } ith \text{ step, and the sum is over all data points.}^{1,2}$
The Rietveld method is used to refine the structural model as opposed to structure solution, therefore the best starting model as possible is necessary. However, the Rietveld method can be used in structure solution, as well as being vital in the last step of structure determination, when the final refinement of the structural determination is performed. Crystal structure determination is carried out in a number of steps. Firstly, the diffraction pattern is indexed and the crystal system and lattice parameters are determined. The space group, followed by approximate structure are then identified. Finally the Rietveld method is used to refine the structure.

In carrying out a Rietveld refinement the observed pattern along with a calculated pattern and the difference line are produced. Ideally the difference line would be straight for a perfect fit. However, in order to assess how different variations affect the calculated pattern, a series of statistics are produced. These give a numerical indication as to how good the fit is. The statistical value based on the fitting of the complete calculated pattern to that of the observed pattern is known as the ‘$R$-weighted pattern’, $R_{wp}$ (Equation 2-7).

\[
R_{wp} = \left[ \frac{\sum w_i(y_i^{(obs)} - y_i^{(calc)})^2}{\sum w_i[y_i^{(obs)}]^2} \right]^{1/2}
\]

This equation includes the $S_y$ value being minimised and therefore is a good indication as to how the refinement is progressing. The $R_{wp}$ value can appear artificially high if not all peaks in the pattern are accounted for. This, however, can be easily identified by viewing the difference line. The value may appear too low if the background is high as it is easier to fit
well to slow changing background, than to peaks. It is therefore possible to find a background corrected version of this and other $R$-values can be calculated (Equation 2-8).

\[
R_{wp} = \sqrt{\frac{\sum w_i |y_i(\text{obs}) - y_i(\text{calc})|^2}{\sum w_i |y_i(\text{obs}) - Bkg|^2}}^{1/2}
\]

The $R_{wp}$ finally reached should agree with the statistically expected $R$-value, $R_{\text{exp}}$ (Equation 2-9), which gives the best possible $R$-value based upon the quality of the data.

\[
R_{\text{exp}} = \left(\frac{N-P-C}{\sum w_i |y_i(\text{obs})|^2}\right)^{1/2}
\]

where

- $N = \text{number of observables}$,
- $P = \text{number of parameters}$,
- $C = \text{number of constraints used}$.

The calculation to work out the statistical significance of the difference between $R_{wp}$ and $R_{\text{exp}}$ is given by Equation 2-10. $\chi^2$ is the square of the ratio between $R_{wp}$ and $R_{\text{exp}}$; the lower the value of $\chi^2$, the better the fit. $\chi^2$ includes the number of refined parameters and is therefore a useful statistic as the fit to the observed data tends to increase as the number of refined parameters increases. If the $\chi^2$ value is very small it can indicate that poor quality data outweighs the errors associated with the structural model and a high background, (which is easily modelled and significantly reduce the $\chi^2$ value).
It is also very important to consider the quality of the structural model in terms of chemical sense. The atomic distances between bonding and non-bonding atoms must be sensible as well as the bonding angles. Fractional occupancies should also be reasonable for the suggested chemical composition of the sample.

4. Quantitative Phase Analysis

Rietveld analysis has been shown to provide very accurate estimates of the relative and/or absolute amounts of constituent phases in the mixture. X-ray and neutron diffraction have shown the effectiveness of this technique, known as quantitative phase analysis (QPA). QPA is reliant on the following equation:

Equation 2-11

\[ W_p = \frac{S_p(ZMV)_p}{\sum_{i=1}^{n} S_i(ZMV)_i} \]

where \( W \) is the relative weight fraction of phase \( p \) in a mixture of \( n \) phases, and \( S, Z, M \) and \( V \) are the Rietveld scale factor, the number of formula units per unit cell, the mass of the formula unit (in atomic mass units) and the unit cell volume (in Å³), respectively. If an internal standard phase, \( s \), is added to the phase mixture in the weight fraction \( W_s \), then the absolute weight fractions of the other identified components, \( p \), are given by:
A reduction from unity of the sum of the determined weight fractions of the \( n \) identified constituents can provide an estimate as to the amount of non-crystalline or amorphous material present in the sample.

The intensity of Bragg peaks can be affected by preferred orientation, extinction, micro-absorption and sample representability. Preferred orientation can cause the most deviation. It arises when there is a stronger tendency for the crystallites in a powder to be oriented more one way then all others. Rapidly spinning the sample during data collection essentially removes the possible effects of preferred orientation. This can cause a deviation of the determined weight fractions from their true values. Extinction effects are most pronounced when mixture components have radically different crystallite and grain sizes. Micro-absorption is most prominent when phases present have very different absorption coefficients. One advantage of QPA is that the effects of preferred orientation and extinction effects can be taken into account.

5. TOPAS

The powder diffraction data was analysed using the computer program Topas.\(^3\) Initially the diffraction patterns of pure samples of the constituent phases were used. The lattice parameters, atomic positions, thermal parameters and pseudo-Voigt peak shape parameters were refined for each phase, as well as using a suitable emission profile and Lorentz-
polarisation factor with sample height error included. The background was described with a Chebyshev polynomial. Once the observed diffraction data of the pure phases gave a good Rietveld refinement, the atomic positions and thermal parameters were fixed.

In Figure 2-6 a typical powder XRD pattern as produced by Topas is shown. The $2\theta$ value is on the $x$-axis, the counts are on the $y$-axis. The identified products are in the key in the top right hand corner. They are listed as Rietveld refined phases first, with the weight% value included. This is only established from the Rietveld phases. The phases with 0 wt% are Pawley refined and therefore have no wt% value given. The observed powder XRD pattern is shown by the black line, with the fitting for both Rietveld and Pawley phases with the red line to the observed phases, in this example, of NaNH$_2$ (blue tick marks), NaH (black tick marks) and Mg$_{0.5}$Na$_{0.5}$(NH) (green tick marks). The difference line between the experimental and calculated X-ray patterns is shown in grey. There are unidentified peaks present which have not been fitted by the red line. At $\sim$51° the red line is not fitted to the observed powder XRD at all. This is due to the region being excluded to stop the fitting to an inappropriate peak.

The weight% given here for NaNH$_2$ and NaH can be converted to mole% by dividing the weight% by the RMM of the phase.
3. Solid State Synthesis

The starting materials used react with atmospheric water and oxygen. This required all manipulations of the starting materials to be carried out under inert conditions. All samples were prepared in an argon filled glove box (MBraun, Unilab, <1 ppm O₂, 0.1 ppm H₂O), using an analytical balance (up to ±0.1 mg accuracy) to weigh out the samples in the desired molar ratios.

The starting materials were intimately ground together using a mortar and pestle. Once ground, they were transferred into a quartz reaction tube (½" O/D) and sealed with a Young’s tap via an Ultra-Torr® fitting, before being removed from the glove box. The T-piece was specially designed in order that gas may be passed through the top of the T-piece, allowing purging of the line, before opening the Young’s tap so the sample was kept at atmospheric pressure whilst maintaining an inert atmosphere (Figure 2-7(a)).

The preparation of the reactions occurred under an inert atmosphere, specifically flowing argon gas. The Young’s taps were attached to plastic tubing which was connected to sulphuric acid bubblers. The argon passed over the samples went via these bubblers on the
inlet and outlet in order that any moisture present in the gas stream would dissolve in the acid, therefore not contaminating the samples.

The reaction tube was then clamped into place inside a vertical furnace (Lenton Furnaces, LTF 12/25/250 fitted with a Eurotherm 3216P1 controller and an insulating plug at the base of the work tube to improve thermal uniformity), ensuring the reaction mixture was within the centre of the hot zone of the furnace (Figure 2-7(b)). The reactions were heated at a ramp rate of $2 \, ^\circ\text{C} \, \text{min}^{-1}$ in order to ensure heating of the sample did not overshoot the desired temperature. Reaction mixtures were typically heated for 12 hours before the power was turned off and the reaction products allowed to cool naturally at approximately $3 \, ^\circ\text{C} \, \text{min}^{-1}$.

Figure 2-7 Solid state synthesis set-up of (a) breakdown of components of T-piece and (b) whole T-piece in tube furnace.

A = Young’s tap
B = Glass T-piece
C = Ultra-Torr® fitting
D = Quartz reaction tube
E = Whole T-piece
F = Tube Furnace
G = Furnace stand
4. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC, Figure 2-8) measures the heat flow into or out of a sample in relation to a reference whilst heating the sample with a linear temperature ramp. Information regarding exothermic and endothermic events such as melting, crystallisation and reactions can be gleaned from using DSC. Quantitative and qualitative information can also be garnered. DSC is an experimental technique that involves measuring the energy required in order to keep a near-zero temperature difference between a test substance (S) and an inert reference material (R) while the samples are subjected to an identical temperature programme. The reference material is usually an empty sample pan and lid. There is a direct relationship between the difference in energy supplied to the sample (S) and reference (R) and the enthalpy of the reaction or phase change giving rise to the energy difference.

DSC is a more advanced version of differential thermal analysis (DTA). DTA involves looking at the temperature difference, ΔT, when a sample and inert reference material are subjected to the same heating programme. The temperature is monitored by thermocouples. ΔT is then plotted against time or furnace temperature. If the sample were to undergo an endothermic event, the temperature of the sample would lag behind that of the reference material, until the melting is completed and normal heating can resume. DSC looks at the difference in energy required in order to keep both the sample and the reference material at the same temperature when heated or cooled. This enables DSC to be fully quantitative, whereas DTA is at best semi-quantitative.

For DSC experiments presented in this thesis, heat-flux DSC was used. The test sample and reference material are enclosed within the same heating block with high thermal
conductivity in order to establish good heat flow between S and R. The enthalpy changes that occur to S cause a temperature difference between S and R. This results in heat flow between S and R (due to good thermal contact). The temperature difference between S and R is recorded and by using calibration experiments can be further related to the enthalpy change of the specimen.

In heat-flux DSC, the energy required to maintain a constant temperature of both S and R is a measure of the energy changes in S relative to R. DSC can detect very small energy changes between S and R as long as both S and R are subject to the same temperature programme (Figure 2-8). The data from DSC can be quantifiable so long as the sample mass is carefully measured and careful calibration is undertaken.

DSC measurements were performed on a calibrated Netzsch DSC 204 HP Phoenix, which was housed inside a flowing argon glove box. Samples of approximately 8 mg were loaded into a shallow aluminium pan and fitted with an aluminium lid, edges turned up. A hole was pierced in the top of the lid prior to it being transferred into the glove box. This was to allow any gas desorbed to escape. The sample was spread evenly over the base of the pan in order to allow uniform heating of the sample. The sample mass was measured to 0.001 mg accuracy. The reference was another Al pan and lid. An argon atmosphere of 3 bar was maintained inside the DSC at 100 ml min⁻¹ flow rate. Typical experiments involved a ramp at 2 min⁻¹ to 250 or 350 °C, a dwell time of 20 minutes followed by cooling at 2 °C min⁻¹ to room temperature. The wobble at the start of traces is caused by an initial start-up deflection.
5. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a thermal analysis technique used to analyse the mass loss of a sample with respect to a change in temperature under a controlled atmosphere. It can be used with mass spectrometry (MS) in order to monitor the gases desorbed from the sample during heating and therefore assign specific mass losses to specific gaseous products (Figure 2-9).

TGA is reliant on precise measurements of weight, temperature and rate of temperature change. A baseline measurement must be carried out before experiments are conducted. Temperature gradients, air buoyancy, convection currents within the furnace tube and other factors contribute to a buoyancy effect, that is: when a sample is heated under argon, the apparent weight changes with the increase in temperature. This is due to the change in...
weight of the displaced gas. The sample therefore appears to gain weight on heating. This affect can be removed by heating the empty crucible under the same conditions as the samples would be. This baseline is then subtracted from the experimental run.

The TGA (Netzsch TG209) was contained within an argon filled flowing glovebox. Two calibration runs were conducted by heating the empty crucible pan at 2 °C min\(^{-1}\) to 350 °C with one heated with an isothermal heating run at 350 °C for 1 hour, the other with immediate cooling. All experiments were cooled at 2 °C min\(^{-1}\) to room temperature. The experiments in this study were carried out under argon gas at 1 bar pressure. Samples of approximately 20 mg were loaded into an alumina crucible pan and the lid (with a small hole in the top) was placed on top (as used for the baseline measurement).

![Block diagram of thermogravimetric analyser.](image)

Figure 2-9 Block diagram of thermogravimetric analyser.
6. Raman Spectroscopy

Raman spectroscopy is a technique used to study vibrational, rotational and other low-frequency modes in a system. It involves the scattering of monochromatic light from infrared to ultraviolet which is used to irradiate the sample. The incident light interacts with the molecule polarising the electron cloud surrounding the constituent nuclei to form a short-lived “virtual state”. The virtual state is unstable and on relaxing back to the ground state emits a photon. Usually the difference in energy between the emitted and absorbed photons is very small and so the process can be treated as elastic scattering, also known as Rayleigh scattering (Figure 2-10). Occasionally nuclear motion can be induced in the molecule. In this event, a significant amount of energy is transferred between the photon and the molecule. This is inelastic Raman scattering of which there are two types, Stokes and anti-Stokes scattering. Stokes scattering involves the emitted photon having less energy than the absorbed photon. This is caused by the molecule being excited from its ground vibrational state to a higher energy vibrational state. Anti-Stokes scattering involves the emitted photon having more energy than the absorbed photon. This is caused by the molecule starting in a higher vibrational state. If this energy is transferred to the absorbed photon, the photon is emitted with more energy than the photon absorbed. At room temperature most molecules are in their ground state and therefore a Stokes shift is observed most often. As the temperature of the sample is increased, so does the ratio of anti-Stokes to Stokes scattering. In order for the molecule to exhibit Raman scattering a change in the molecular polarisation potential with respect to the vibrational coordinate is required. The amount of polarisability change will determine the intensity of the Raman scattering. The most intense bands
observed in Raman spectra are usually symmetric vibrations. The symmetry of the molecule determines the vibrations which will be active.

Raman spectra in this study were collected on a Renishaw InVia Raman microscope using an Ar ion laser at a wavelength of 488 nm. Samples were loaded in an Instec sample cell in an argon filled glove box. The sample cell was then transferred to the microscope and argon gas was flowed over the sample at 1 bar pressure during data collection.

Figure 2-10 Diagram of Raman scattering processes. The incident energy and scattered energy are represented in purple and green respectively.
7. Temperature Programmed Desorption

Temperature programmed desorption (TPD) is a generic term used to describe an apparatus set-up that can control the heating rate and atmospheric conditions of a solid sample. The gaseous products are monitored in relation to the temperature of the sample (Figure 2-11). In this study, TPD was carried out under flowing argon and products were monitored using mass spectrometry (TPD-MS). A mass flow controller (Hastings 200 Series, Teledyne) was used to control a constant rate of argon at 100 ml min\(^{-1}\) flowing over the sample. The sample (~0.1 g) was weighed into a quartz reaction tube (7 mm O/D, 4 mm I/D) inside an argon filled glove box and sealed upright in the reaction chamber. The sealed reaction chamber was then transferred onto the TPD apparatus without exposing the sample to the atmosphere. A barrel heater was placed around the reaction chamber. The barrel heater was controlled by an internal thermocouple that was placed within the sample. As the thermocouple was in contact with the sample it was sometimes possible to see endothermic and exothermic events within the temperature trace of the TPD. The gaseous desorption products were monitored using a quadrupole mass spectrometer (HPR-20, Hiden Analytical) using a Faraday cup detector.
1. Calibration

In order to determine the true total sensitivity of the mass spectrometer towards hydrogen and ammonia, a calibration gas was used (BOC Speciality Gases, 4736 ppm H₂, 4898 ppm NH₃, balance Ar). Determining NH₃ in a mass spectrometer is problematic as the NH₃⁺ mass fragment has the same m/z value as OH⁺ fragment of water, which is frequently present in high vacuum systems such as mass spectrometers. Therefore, the NH₂⁺ fragment of NH₃ was used to determine the true amount of NH₃. NH₂⁺ is approximately 80% of the intensity of the NH₃⁺ fragment.

The calibration gas was connected to the TPD apparatus under the control of the mass flow controller in the same way as for the argon carrier gas described above. The mass flow for the calibration gas was 20 ml min⁻¹. The observed partial pressures (Pₚ) for mass channels (m/z) 2 (H₂⁺), 16 (NH₂⁺), 17 (NH₃⁺/OH⁺), 18 (H₂O⁺), 28 (N₂⁺), 32 (O₂⁺), and 40 (Ar⁺) were recorded until a constant signal was reached. In order to determine the background levels of
mass channels 2 ($H_2^{++}$) and 16 ($NH_2^{++}$), the equivalent mass spectrum data were also collected for the pure argon carrier gas.

The observed partial pressure signals of $H_2$ and $NH_2$ ($P_2$ and $P_{16}$) were converted to fractions ($\chi_2$ and $\chi_{16}$) of the observed argon signal ($P_{40}$):

\begin{equation}
\chi_2 = \frac{P_2}{P_{40}} \quad \chi_{16} = \frac{P_{16}}{P_{40}}
\end{equation}

The observed fractional signals determined for $H_2$ and $NH_2$ for the pure argon carrier gas ($\chi_2^0$ and $\chi_{16}^0$) were deducted from the respective fractional signals from the calibration gas. This gave background subtracted fractional signals. These fractional signals were then divided by the true molar fraction as provided by the calibration gas certificate, to give the relative sensitivity, $RS$, values for $H_2$ and $NH_3$ (Equation 2-14):

\begin{equation}
R_{H_2} = \frac{\chi_2 - \chi_2^0}{4.736 \times 10^{-3}} \quad R_{NH_3} = \frac{\chi_{16} - \chi_{16}^0}{4.890 \times 10^{-3}}
\end{equation}

The observed values for $H_2^{+}$ and $NH_2^{+}$ from the TPD-MS experiments could then be corrected to true values by using these determined relative sensitivity values.

When collecting TPD-MS data the same mass channels were recorded as for the calibration using the same data collection routine. The background signals for mass channels 2 ($H_2^{+}$) and 16 ($NH_2^{+}$) were determined by allowing the MS to collect data for an appropriate period of time before the TPD-MS experiment was started. The data collected were then converted to a fraction of the argon signal ($\chi_2$ and $\chi_{16}$, Equation 2-13). For the $m/z$ 2 and 16 mass
channels, the background signal determined before starting the experiment was then subtracted from the following signals. The corrected fractional signal was then divided by the determined RS value to give the corrected molar fractions of H\textsubscript{2} and NH\textsubscript{3} in the gas stream, given by $\chi^*_\text{H}_2$ and $\chi^*_\text{NH}_3$ (Equation 2-15).

\begin{equation}
\chi^*_\text{H}_2 = \frac{\chi_2 - \chi^0_2}{R_{\text{H}_2}} \quad \chi^*_\text{NH}_3 = \frac{\chi_{16}-\chi^0_{16}}{R_{\text{NH}_3}}
\end{equation}

Accurate values for the relative amounts of H\textsubscript{2} and NH\textsubscript{3} released could then be established from this corrected TPD-MS data.

Pseudo-gravimetric data could be produced by using a mass flow controller in the TPD-MS experiment to control the flowing gas stream. The molar fractions of H\textsubscript{2} and NH\textsubscript{3} at t, ($\chi^*_\text{H}_2(t)$ and $\chi^*_\text{NH}_3(t)$) were by the corrected MS data at regular time intervals ($\delta t$) determined by the rate of the MS data collection (approximately one spectrum every 20 seconds). The volume of each gas ($V_{\text{H}_2}$ and $V_{\text{NH}_3}$) released during the timescale for one MS spectrum could be determined by knowing the flow rate of the argon carrier gas (100 ml min\textsuperscript{-1}). The total volume (ml) of each gas desorbed during a certain time interval, $V(t)$ could therefore also be deduced (Equation 2-16).

\begin{equation}
V_{\text{H}_2}(t) = \sum_{t=0}^{t} 100 \times \delta t \times \chi^*_\text{H}_2(t) \quad V_{\text{NH}_3}(t) = \sum_{t=0}^{t} 100 \times \delta t \times \chi^*_\text{NH}_3(t)
\end{equation}

The molar volumes of H\textsubscript{2} and NH\textsubscript{3} at room temperature and pressure are 24.804 l mol\textsuperscript{-1} and 24.532 l mol\textsuperscript{-1} respectively.\textsuperscript{5}
Once the volume of gas released had been calculated it could be multiplied by 4.032 x 10^{-5} \text{mol ml}^{-1} and 4.076 x 10^{-5} \text{mol ml}^{-1}, respectively, in order to estimate the number of moles of H\textsubscript{2} and NH\textsubscript{3} released. If the starting mass of the sample and molecular mass were known, the number of moles of each gas released could be expressed in terms of the number of moles of the starting sample.

A simulated mass of each gas released could be calculated by multiplying the molecular mass of the gas by the calculated number of moles of the gas released (Equation 2-17 and Equation 2-18). The calculated mass of gas released could then be subtracted from the initial sample mass (m\textsubscript{s}, grams) and expressed as a percentage of the starting mass. Therefore, a simulated gravimetric plot could be plotted.

\textbf{Equation 2-17}
\[
\text{wt\%}(t) = 100 \times \frac{m_s - \sum_{t=0}^{T} V_{H_2}(t) \times 4.032 \times 10^{-5} \times 2.02}{m_s}
\]

\textbf{Equation 2-18}
\[
\text{wt\%}(t) = 100 \times \frac{m_s - \sum_{t=0}^{T} V_{NH_3}(t) \times 4.076 \times 10^{-5} \times 16.02}{m_s}
\]

This form of data analysis allows for a more complete examination of the desorbed gases in relation to the starting sample despite it being a complex method. Much more information can be deduced from the TPD-MS set-up than merely identification of desorbed gases.

\section*{8. Mass Spectrometry}

TPD apparatus described above was coupled to a quadrupole mass spectrometer (MS) (HPR-20, Hiden Analytical). The detection limit of the MS was approximately 5 ppm in the argon carrier gas stream.
MS is an analytical technique used to measure the mass to charge \((m/z)\) ratio of charged particles. Mass spectrometers can scan across a range of \(m/z\) values and establish the relative amount of each observed. Specific \(m/z\) ratios can be monitored in order to determine the amount of any given analyte. Species are ionised and then electromagnetic fields manipulate the ions differently depending on their \(m/z\) ratio. MS must be carried out at low pressure in order to stop the ions colliding with other species and losing their charge. MS consists of three main processes: ionisation, separation and detection.\(^6\)

1. Ionisation

Ionisation of species can occur in many different ways. In this study, electron ionisation (EI, formerly known as electron impact) is the only ionisation method used. Ionisation converts atoms/molecules into gas-phase ionic species by the removal or addition of an electron or proton (Equation 2-19).

Equation 2-19 \[ M + e^- \rightarrow M^{++} + 2e^- \]

where

\(M = \text{analyte molecule being ionised,}\)
\(e^- = \text{electron,}\)
\(M^{++} = \text{resulting ion.}\)

The electrons are produced from thermionic emission by heating a wire filament that has an electric current running through it. The neutral analyte molecules are introduced to the ion source in a direction perpendicular to the electron beam. The electron beam knocks an electron from atoms to create a singly charged cation. Some double ionisation does occur but these ions are discarded by the analyser. As the species are monitored by their \(m/z\) ratio,
singly charged species are preferable. The energy of the electron beam is usually tuned to avoid multiple ionisations. The radical cation products are then accelerated towards the mass analyser by a repeller electrode. The ionisation process can give rise to fragmentation of larger molecules, as excess ionisation energy can cause the ionised species to break up into smaller fragments. These smaller species will also be detected by their $m/z$ ratio. For larger, organic samples, this fragmentation pattern can be useful for phase identification and can give important structural information about the analyte.

2. Separation

The ionic species are separated according to their $m/z$ ratio by an analyser. A quadrupole mass analyser is the most common type of mass analyser now used in MS (Figure 2-12). Originally species were separated by bending their flight radius depending on their $m/z$ ratio. The frequency of the oscillation is chosen in order to selectively stabilise one $m/z$ ratio, and therefore this ratio reaches the detector at the expense of the other $m/z$ ratios. The other ionic species get scattered or neutralised in collisions and are therefore not detected.

Figure 2-12 Schematic diagram of a quadrupole mass spectrum analyser.
3. Detection

The detector records the ion current produced when an ion hits a surface. The signal is then amplified and the data output as a mass spectrum. A Faraday cup detector was used in this study to collect and measure the separated ions. A Faraday cup is a conductive cup designed to catch charged particles in vacuum. The current resulting from the impact can be measured. The current is directly proportional to the number of ions hitting the surface.

4. Overview

The analyte is contained in an argon carrier gas which is sampled through a heated capillary. The gas then passes into the vacuum system of the mass spectrometer via the capillary. The capillary has a small diameter in order to restrict the amount of gas entering the system so the low pressure required can be maintained. The vacuum system is heated in order to reduce the water concentration present in the system as water is ever-present (in low concentrations) in high vacuum appliances (Figure 2-13).

Here, the mass spectrum was first collected over the \( m/z \) range of 1 to 50 to identify which species were present. Multiple ion monitoring mode (MIM) was then used to detect only the ions of interest. This enabled an increase in the rate of data collection.
Figure 2-13 Schematic diagram of a mass spectrometer with the principal components labelled.

9. Intelligent Gravimetric Analysis

An Intelligent Gravimetric Analyser (IGA, Hiden Analytical) is a pressure controlled thermo-gravimetric balance with complete control of the environment. The sample is loaded into a crucible (quartz crucibles were made in-house for this study) and placed on a hang-down attached to a microbalance head. The weight of the sample is then monitored under different environmental conditions so that weight changes can be observed with changing temperature and pressure. The temperature of the sample is controlled by using an external furnace which surrounds the reaction tube accommodating the sample hang-down. The sample temperature is monitored using a positive temperature coefficient (PTC) sensor placed next to the sample (Figure 2-14).
1. Pressure Control Mode

The IGA used in this study had stepping motors on the gas inlet and outlet so the pressure inside the reactor could be controlled precisely from 50 mbar to 20 bar. An assortment of gases can be connected to the inlet, but here only Ar and H\textsubscript{2} were used. In pressure control mode, pressure is set and a ramp rate selected. The IGA then admits gas up to the desired pressure by continually admitting small amounts of gas \textit{via} the inlet stepping motor. The pressure is then maintained at the set-point value by continually allowing gas in whilst monitoring the sample mass. The outlet is connected to a vacuum system and the pressure is reduced by continually bleeding small amounts of gas out into the vacuum system. The pressure control mode was used to observe the hydrogenation of samples under a hydrogen atmosphere.
2. Inert Sample Loading

The sample was able to be loaded without contact with the atmosphere by using a portable glove box. The dry mass of the sample crucible was weighed and recorded, before being taken into a glove box where the sample was loaded into it. The sample and crucible were removed from the glove box, sealed in a sample cartridge. The sample cartridge was inserted into the portable glove box whilst it was attached to the IGA. The portable glove box was then purged of air by cycling with argon between 1050 mbar and 1250 mbar 100 times. After this, the sample cartridge was opened and the sample crucible was transferred to the hang-down using a mechanical arm.

10. High Pressure Rig

The high pressure rig allows samples to be exposed to high temperature and pressures of various gases. For these experiments argon and hydrogen gases were connected (Figure 2–15).

The high pressure rig is capable of hydrogenating samples at pressures of up to 100 bar and temperatures up to 640 °C. Samples of ~0.1 g were loaded into a quartz reaction tube (7 mm O/D, 4 mm I/D) in an argon filled glove box. Up to four of these were then loaded into the high pressure cell. The bolts on this were tightened to 60 Nm in the glove box before removing and tightening further to 90 Nm. The cell was supported inside a vertical furnace and connected to the control manifold. The manifold was purged of air by cycling with argon and then the whole system, including the high pressure cell, was purged of argon with 100% hydrogen. The system was cycled with hydrogen at ~3 bar and down to rough vacuum
(\sim 1 \times 10^{-3} \text{ mbar}). The argon was used as an intermediate gas in order to eliminate the risk of explosion between air and hydrogen gas, if air was purged directly with hydrogen. The system was then pressurised to the desired pressure with hydrogen. The pressure in the cell increases with the increase in temperature and the initial pressure was set to ensure the final pressure was as desired (under heating). The sample was heated to the desired set point inside a vertical slit furnace. The temperature was monitored using an internal thermocouple.

Once the reactor was cool, it was vented to \sim 3 \text{ bar} before evacuating and cycling between \sim 3 \text{ bar} argon and rough vacuum. The high pressure cell was then returned to the argon glove box to remove and weigh the samples. The pressure was measured to \sim \pm 5 \text{ bar} on an analogue pressure gauge.

![Diagram of high pressure rig]

A = Vent to fumehood  
B = Pressure Release Valve  
C = Analogue Pressure Gauge

Figure 2-15 Schematic diagram of high pressure rig.
3 Topas, general profile and structure analysis software for powder diffraction data. A. A. Coelho; Bruker AXS, Karlsruhe, Germany, 3.0 ed., 2004.
3. Li$_3$Na(NH$_2$)$_4$ and LiNa$_2$(NH$_2$)$_3$

1. Introduction

The mixed amides Li$_3$Na(NH$_2$)$_4$, Li$_3$Na(NH$_2$)$_6$ and Li$_5$Na$_2$(NH$_2$)$_3$ were first synthesised by Harbrecht and Jacobs, in 1982,\textsuperscript{1} using supercritical ammonia and the lithium and sodium metals in molar ratios from 1:3 to 3:1 (Equation 3-1 and Equation 3-2). The ammonia was between 1.7 and 4.3 kbar in an autoclave at 157–197 °C for between 4 and 20 days.

\begin{align*}
\text{Equation 3-1} & \quad 8\text{Li} + 2\text{Na} + 10\text{NH}_3 \rightarrow \text{Li}_3\text{Na(NH}_2\text{)}_4 + \text{Li}_5\text{Na(NH}_2\text{)}_6 + 5\text{H}_2 \\
\text{Equation 3-2} & \quad 2\text{Li} + 4\text{Na} + 6\text{NH}_3 \rightarrow 2\text{LiNa}_2\text{(NH}_2\text{)}_3 + 3\text{H}_2
\end{align*}

The lattice parameters for the three mixed amides are given in Table 3-1. The LiNa$_2$(NH$_2$)$_3$ and Li$_3$Na(NH$_2$)$_4$ lattice parameters were backed up by single crystal X-ray structure determination, however Li$_5$Na(NH$_2$)$_6$ lattice parameters were determined by Weissenberg and precession photographs.

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>LiNa$_2$(NH$_2$)$_3$</th>
<th>Li$_3$Na(NH$_2$)$_4$</th>
<th>Li$_5$Na(NH$_2$)$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$/ Å</td>
<td>6.278(2)</td>
<td>5.072(4)</td>
<td>5.072(3)</td>
</tr>
<tr>
<td>$c$/ Å</td>
<td>11.142(4)</td>
<td>11.478(5)</td>
<td>34.36(1)</td>
</tr>
<tr>
<td>Space group</td>
<td>$P4_2/m$</td>
<td>$I-4$</td>
<td>$I-4$</td>
</tr>
</tbody>
</table>

Table 3-1 Lattice parameters of LiNa$_2$(NH$_2$)$_3$, Li$_3$Na(NH$_2$)$_4$ and Li$_5$Na(NH$_2$)$_6$ (from Jacobs et al.\textsuperscript{1})

These mixed amides are important because of their high hydrogen content (LiNa$_2$(NH$_2$)$_3$ 6.0 wt%; Li$_3$Na(NH$_2$)$_4$ 7.5 wt%; Li$_5$Na(NH$_2$)$_6$ 7.9 wt%) although the addition of sodium
decreases gravimetric content compared to LiNH$_2$. It is however possible that the mixing of the cations might cause destabilisation of the amide, which with the addition of a light metal hydride could cause the material to release hydrogen, at a lower temperature than lithium amide under the same conditions. This can be compared to LiNH$_2$ which is known to be destabilised by the addition of Mg (from MgH$_2$) into the lattice and therefore reduce the temperature at which hydrogen is desorbed.$^2$

Equation 3-3 and Equation 3-4 were carried out in the solid state by Lowton et al.$^3$ in 2008. Lattice parameters have been confirmed for both Li$_3$Na(NH$_2$)$_4$ and LiNa$_2$(NH$_2$)$_3$ (Table 3–2).

Equation 3-3  
3LiNH$_2$ + NaNH$_2$ → Li$_3$Na(NH$_2$)$_4$

Equation 3-4  
LiNH$_2$ + 2NaNH$_2$ → LiNa$_2$(NH$_2$)$_3$

Table 3-2 Lattice parameters of LiNa$_2$(NH$_2$)$_3$ and Li$_3$Na(NH$_2$)$_4$ (from Lowton et al.$^3$)

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>LiNa$_2$(NH$_2$)$_3$</th>
<th>Li$_3$Na(NH$_2$)$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a/ Å</td>
<td>6.2838(1)</td>
<td>5.081(1)</td>
</tr>
<tr>
<td>c/ Å</td>
<td>11.1485(2)</td>
<td>11.511(5)</td>
</tr>
<tr>
<td>Space Group</td>
<td>P4$_2$/m</td>
<td>I-4</td>
</tr>
</tbody>
</table>

We decided to prepare the mixed amides and study their reactions with common light metal hydrides. The light metal hydrides chosen were: LiH, NaH and MgH$_2$. Alone, these hydrides are not practical because, as previously mentioned, LiH decomposes above 550 °C, which is too high. Similarly, NaH decomposes at 425 °C and MgH$_2$, although a light and cheap material, suffers from slow desorption kinetics.
2. Results

1. Preparation of Li$_3$Na(NH$_2$)$_4$

Li$_3$Na(NH$_2$)$_4$ was prepared in house from heating 3LiNH$_2$ (Sigma-Aldrich, hydrogen storage grade) + NaNH$_2$ (Sigma-Aldrich, hydrogen storage grade) to 200 °C for 12 hours. The powder XRD pattern produced is shown below (Figure 3-1). The lattice parameters were tetragonal $a = 5.08124$ Å, $c = 11.506$ Å. These parameters compare well with the literature values published by Lowton et al.$^3$ of $a = 5.081$ Å, $c = 11.511$ Å.

![Figure 3-1 Li$_3$Na(NH$_2$)$_4$, formed in house from 3LiNH$_2$ + NaNH$_2$ heated to 200 °C for 12 hours. $R_{wp} = 11.425$, $R_{exp} = 6.833$, $\chi^2 = 2.8$.](image)

It was found on heating Li$_3$Na(NH$_2$)$_4$ alone to 350 °C for 1 hour that LiNa$_2$(NH$_2$)$_3$ and LiNH$_2$ were the products, along with remaining Li$_3$Na(NH$_2$)$_4$ (Equation 3-5 and Figure 3-2).

Equation 3-5 \[ 2\text{Li}_3\text{Na}(\text{NH}_2)_4 \rightarrow \text{LiNa}_2(\text{NH}_2)_3 + 5\text{LiNH}_2 \]

After 4 hours, heating the LiNH$_2$ previously present in the products had disappeared (Figure 3-3).
Figure 3-2 Powder XRD pattern of Li₃Na(NH₂)₄, heated to 350 °C for 1 hour on a flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li₃Na(NH₂)₄ (blue tick marks), LiNa₂(NH₂)₃ (black tick marks), LiNH₂ (green tick marks) and Li₂O (pink tick marks). \( R_{wp} = 7.000, \ R_{exp} = 5.020, \ \chi^2 = 1.9. \)

Figure 3-3 Powder XRD pattern of Li₃Na(NH₂)₄, heated to 350 °C for 4 hours on a flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li₃Na(NH₂)₄ (blue tick marks), LiNa₂(NH₂)₃ (black tick marks) and Li₂O (green tick marks). \( R_{wp} = 7.348, \ R_{exp} = 4.914, \ \chi^2 = 2.2. \)

2. Preparation of LiNa₂(NH₂)₃

LiNa₂(NH₂)₃ was formed in house from heating LiNH₂ + 2NaNH₂ to 200 °C for 12 hours (Figure 3-4). The LiNa₂(NH₂)₃ was characterised by using the lattice parameters published by Lowton et al.³ The lattice parameters of our tetragonal LiNa₂(NH₂)₃ starting material were found to be \( a = 6.30 \) Å and \( c = 11.19 \) Å. This was in comparison to Lowton et al. lattice parameters of \( a = 6.28 \) Å and \( c = 11.15 \) Å.
Figure 3-4 LiNa$_2$(NH$_2$)$_3$, formed in house from LiNH$_2$ + 2NaNH$_2$ heated to 200 °C for 12 hours. $R_{wp} = 15.575$, $R_{exp} = 8.985$, $X^2 = 3.0$.

On heating LiNa$_2$(NH$_2$)$_3$ for 1 hour at 350 °C, the products were a mix of LiNa$_2$(NH$_2$)$_3$ starting material and Li$_3$Na(NH$_2$)$_4$ (Figure 3-5). The lattice parameters of Li$_3$Na(NH$_2$)$_4$ were larger than in the literature.\textsuperscript{3} This suggested there was less Li and more Na present in the unit cell. This may account for the lack of NaNH$_2$ present as it could be expected that:

Equation 3-6 \[ 3\text{LiNa}_2(\text{NH}_2)_3 \rightarrow \text{Li}_3\text{Na}(\text{NH}_2)_4 + 5\text{NaNH}_2 \]

Figure 3-5 Powder XRD pattern of LiNa$_2$(NH$_2$)$_3$, heated to 350 °C for 1 hour on a flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_3$Na(NH$_2$)$_4$ (blue tick marks), LiNa$_2$(NH$_2$)$_3$ (black tick marks) and Li$_2$O (green tick marks). $R_{wp} = 6.737$, $R_{exp} = 5.005$, $X^2 = 1.8$. 

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No gas was desorbed from either mixed cation amide when heated alone. It seemed the two mixed cation amides formed an equilibrium between them.

3. \( \text{Li}_3\text{Na(NH}_2\text{)}_4 + 4\text{LiH} \)

\( \text{Li}_3\text{Na(NH}_2\text{)}_4 \) was heated with \( \text{LiH} \) (Sigma-Aldrich, 95%) in a 1:4 ratio. This ratio was chosen in order to react one mole of amide with one mole of hydride, as with the \( \text{LiNH}_2 – \text{LiH} \) system.

1. *Temperature Programmed Desorption-Mass Spectrometry*

The reaction was carried out on a TPD-MS apparatus at a heating rate of 2 °C min\(^{-1} \) to 350 °C. As can be seen from Figure 3-6, the reaction predominantly gave off hydrogen with a very small amount of ammonia desorbed at the peak of hydrogen desorption. The hydrogen desorption proceeded slowly as soon as heating started. At 235 °C the rate of hydrogen desorption increased and peaked at 315 °C, before rapidly decreasing back to the background level of hydrogen release. This drop off in hydrogen release occurred concurrently with the isothermal heating of the sample. The shape of the hydrogen desorption appears to be that of two separate hydrogen desorption reactions. The first being the slow desorption up to 235 °C, the second above 235 °C. The products after heating were analysed by powder XRD and identified as \( \text{Li}_2\text{NH} \) and \( \text{NaH} \).
Figure 3-6 Thermal decomposition analysis of Li$_3$Na(NH$_2$)$_4$ + 4LiH in a TPD-MS apparatus. The temperature trace is shown in black and the mole percent of H$_2$ and NH$_3$ released are shown in red and green respectively.

When the Li$_3$Na(NH$_2$)$_4$ + 4LiH mixture was heated on the flowing line at 350 °C for 12 hours the products were Li$_2$NH, LiNa$_2$(NH$_2$)$_3$ and Na, together with a significant amount of lithium oxide (Figure 3-7). The oxide present in XRD patterns was most likely from the reaction of the sample with the Scotch® Magic™ tape used to make up the sample for XRD.

The XRD pattern includes the weight percent (wt%) of the known phases that have been refined by the Rietveld method, using computer program Topas.$^4$
The weight percents calculated by Topas can be converted to mole percents by dividing the weight percent by the relative molecular mass (RMM). The mole fraction can in turn be
calculated by summing the mole percents and dividing the individual mole percents by the sum total for Rietveld phases in each XRD.

Figure 3-7 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 4LiH, heated to 350 °C for 12 hours under flowing argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_2$NH (blue tick marks), LiNa$_2$(NH$_2$)$_3$ (black tick marks), Na (green tick marks and Li$_2$O (pink tick marks). $R_{wp} = 11.034$, $R_{exp} = 5.503$, $\chi^2 = 4.0$.

There was no NaH present under these reaction conditions in comparison to TPD-MS results. However, Na metal was present instead. Under these conditions it is known NaH decomposes to Na with the release of hydrogen (Equation 3-7). This should account for the tail of hydrogen present during the isothermal heating.

Equation 3-7  

\[
2\text{NaH} \rightarrow 2\text{Na} + \text{H}_2
\]

The majority product under both these conditions was Li$_2$NH, however on heating under argon for 12 hours, LiNa$_2$(NH$_2$)$_3$ was also present.
2. Discussion

For the reaction to have gone to completion only imide, not amide as present here, should have been present in the products. As it was LiNa$_2$(NH$_2$)$_3$ that was present in the products, not the Li$_3$Na(NH$_2$)$_4$ starting material, it is suggested that LiNa$_2$(NH$_2$)$_3$ is more stable.

We concluded that the Li$_3$Na(NH$_2$)$_4$ + 4LiH stoichiometry was not correct to maximise the hydrogen from this system. In order for the reaction to go stoichiometrically, more LiH was needed. Therefore, we investigated:

Equation 3-8 \[ \text{Li}_3\text{Na(NH}_2\text{)}_4 + 5\text{LiH} \rightarrow 4\text{Li}_2\text{NH + NaH + 4H}_2 \]

4. Li$_3$Na(NH$_2$)$_4$ + 5LiH

1. Temperature Programmed Desorption-Mass Spectrometry

As before, the reaction was first carried out on TPD-MS apparatus. From Figure 3-8, it can be seen hydrogen was the only gas desorbed from this reaction. There was a slow rise in hydrogen desorption from heating onset and the peak of the hydrogen desorption was still at nearly 350 °C with a similar desorption profile as the 1:4 mixture. Figure 3-8 also shows a comparison between the hydrogen release from Li$_3$Na(NH$_2$)$_4$ + 5LiH to Li$_3$Na(NH$_2$)$_4$ heated with 4NaH and 2MgH$_2$, sections 3.2.6 and 3.2.7 respectively.
Figure 3-8 Thermal decomposition analysis of hydrogen release from Li$_3$Na(NH$_2$)$_4$ + 5LiH (red trace) in a TPD-MS apparatus in comparison to Li$_3$Na(NH$_2$)$_4$ + 4LiH (purple trace), Li$_3$Na(NH$_2$)$_4$ + 4NaH (blue trace) and Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$ (green trace). The temperature trace is shown in black.

The solid products present after TPD-MS, identified by their powder XRD pattern were Li$_2$NH and NaH (Figure 3-9). As no mixed cation amides were present in the products this implied that the reaction had gone to completion with the additional mole of LiH. Also, any further dehydrogenation would come from the decomposition pathways of the individual products.
Figure 3-9 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 5LiH, after TPD-MS to 350 °C. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_2$NH (blue tick marks), NaH (black tick marks) and Li$_2$O (green tick marks). $R_{wp} = 13.806$, $R_{exp} = 4.784$, $\chi^2 = 8.3$.

These results from heating Li$_3$Na(NH$_2$)$_4$ with 5LiH were consistent with the products of Equation 3-8.

2. Thermogravimetric Analysis

The starting materials, Li$_3$Na(NH$_2$)$_4$ + 5LiH, were heated to 350 °C on TGA-MS apparatus, at a rate of 2 °C min$^{-1}$ to 350 °C where heating ceased (Figure 3-10). It was found that only hydrogen gas was desorbed. No ammonia was seen above the detection limit of the mass spectrometer. The hydrogen was desorbed in one main release with two peaks. The desorption started at ~190 °C and the peaks occurred at ~270 and ~330 °C. The desorption started at a slightly lower temperature than when the reaction was heated on TPD-MS apparatus. The first peak of the hydrogen desorption on TGA-MS apparatus was at a lower temperature than for TPD-MS apparatus.

The overall mass loss from this experiment was 4.3 wt%. This was in comparison to a theoretical mass loss of 5.5 wt% for the products NaH and Li$_2$NH, Equation 3-8.
Figure 3-10 TGA-MS of the Li$_3$Na(NH$_2$)$_4$ + 5LiH reaction. The H$_2$ release is shown in red and the percentage mass loss is shown in black.

3. Flowing Line Reactions

In order to establish the reaction pathway from reactants to products, the same reaction was carried out under different conditions. The Li$_3$Na(NH$_2$)$_4$ + 5LiH starting materials were heated to 150 °C for 12 and 24 hours, 200 °C for 12 and 24 hours and 250 °C, 300 °C and 350 °C for 12 hours on the flowing line.

After heating to 150 °C for 12 hours, the products were Li$_2$NH, LiNa$_2$(NH$_2$)$_3$ and NaH (Figure 3-11) with the Li$_3$Na(NH$_2$)$_4$ and LiH starting materials as the majority phases present. There was approximately twice as much LiNa$_2$(NH$_2$)$_3$ present after heating for 24 hours (Figure 3-12) compared to 12 hours heating.
Figure 3-11 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 5LiH, heated to 150 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_3$Na(NH$_2$)$_4$ (blue tick marks), LiH (black tick marks), Li$_2$NH (green tick marks), LiNa$_2$(NH$_2$)$_3$ (pink tick marks), NaH (purple tick marks) and Li$_2$O (light green tick marks). $R_{wp} = 8.888$, $R_{exp} = 6.469$, $X^2 = 1.9$.

Figure 3-12 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 5LiH, heated to 150 °C for 24 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_3$Na(NH$_2$)$_4$ (blue tick marks), LiH (black tick marks), LiNa$_2$(NH$_2$)$_3$ (green tick marks), Li$_2$NH (pink tick marks), NaH (purple tick marks) and Li$_2$O (light green tick marks). $R_{wp} = 8.627$, $R_{exp} = 6.411$, $X^2 = 1.8$.

Li$_3$Na(NH$_2$)$_4$ + 5LiH was heated to 200 °C for 12 (Figure 3-13) and 24 hours. The products for both were the same: LiNH$_2$, Li$_2$NH and NaH, along with remaining Li$_3$Na(NH$_2$)$_4$ and LiH.
Figure 3-13 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 5LiH, heated to 200 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_3$Na(NH$_2$)$_4$ (blue tick marks), LiH (black tick marks), Li$_2$NH (green tick marks), LiNa$_2$(NH$_2$)$_3$ (pink tick marks), NaH (purple tick marks) and Li$_2$O (light green tick marks). $R_{wp} = 8.231$, $R_{exp} = 6.881$, $\chi^2 = 1.4$.

After heating to 250 °C, there was still a mix of LiNH$_2$ and Li$_2$NH present (Figure 3-14) alongside NaH. There was also LiH present, but this was a smaller amount than observed after reaction at 200 °C. Li$_3$Na(NH$_2$)$_4$ was no longer present at 250 °C. Between 200 and 250 °C the most significant hydrogen desorption started (Figure 3-8).

Figure 3-14 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 5LiH, heated to 250 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_2$NH (blue tick marks), LiNH$_2$ (black tick marks), NaH (green tick marks), LiH (pink tick marks) and Li$_2$O (purple tick marks). $R_{wp} = 11.734$, $R_{exp} = 7.161$, $\chi^2 = 2.7$. 

After heating to 300 °C for 12 hours the imide forming reaction had gone to completion and only Li$_2$NH, NaH and Li$_2$O were present in the products (Equation 3-8 and Figure 3-15).

Figure 3-15 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 5LiH, heated to 300 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_2$NH (blue tick marks), NaH (black tick marks) and Li$_2$O (green tick marks). $R_{wp} = 13.758$, $R_{exp} = 7.051$, $\chi^2 = 3.8$.

The starting materials were then heated to 350 °C for 12 hours. The majority products were Li$_2$NH and NaH as for 300 °C, but with the addition of Na from the decomposition NaH (Equation 3-7).

Figure 3-16 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 5LiH, heated to 350 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_2$NH (blue tick marks), NaH (black tick marks), Na (green tick marks) and Li$_2$O (pink tick marks). $R_{wp} = 11.404$, $R_{exp} = 8.461$, $\chi^2 = 1.8$. 
The full reaction can be described as:

Equation 3-9 \[ 2\text{Li}_3\text{Na(NH}_2\text{)}_4 + 10\text{LiH} \rightarrow 8\text{Li}_2\text{NH} + (2-x)\text{NaH} + x\text{Na} + (8+\frac{1}{2}x)\text{H}_2 \]

4. Rehydrogenation

The products from \( \text{Li}_3\text{Na(NH}_2\text{)}_4 + 5\text{LiH} \) heated at 350 °C for 12 hours (Figure 3-16) were subjected to rehydrogenation in order to establish whether the reaction was reversible. After heating the previously formed products \([\text{Li}_2\text{NH} \text{and NaH}]\) under hydrogen gas at 100 bar, 200 °C for 48 hours, the new, post-hydrogenation products were examined by XRD and found to be \( \text{LiNH}_2, \text{LiH and NaH} \) (present before hydriding) (Figure 3-17).

![Figure 3-17 Powder XRD pattern of products from \( \text{Li}_3\text{Na(NH}_2\text{)}_4 + 5\text{LiH} \) (heated to 350 °C, 12 hours) rehydrogenated under 200 °C, 100 bar \( \text{H}_2 \), 48 hours. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases \( \text{LiNH}_2 \) (blue tick marks), \( \text{LiH} \) (black tick marks), \( \text{NaH} \) (green tick marks) and \( \text{Li}_2\text{O} \) (pink tick marks). \( R_{\text{wp}} = 9.430, R_{\text{exp}} = 6.724, \chi^2 = 2.0 \).](image)

5. Discussion

From Figure 3-8, it was shown that up to 240 °C there was slow but significant hydrogen desorption. At these temperatures it would be unlikely \( \text{Li}_2\text{NH} \) would form due to a reaction
between LiNH₂ and LiH as this known not to occur below 275 °C under these conditions (Equation 3-10). An alternative reason for the hydrogen release could be the diffusion of Li⁺ ions, from LiH, into Li₃Na(NH₂)₄ and H⁺ diffusing out. The H⁺ diffusing out could combine with the H⁻ remaining from LiH, forming H₂. This would result in ‘Li₃ₓNa(NH₂)₄ₓNHₓ’ forming along with H₂. When \( x = 2\frac{1}{2} \), \( \text{Li}_{6\frac{1}{2}}\text{Na}(\text{NH}_2)_{1\frac{1}{2}}(\text{NH})_{2\frac{1}{2}} \) would be formed. This can be rewritten as 5Li₂NH + LiNa₂(NH₂)₃. As this diffusion process was likely to be slow, this would account for the small amount of H₂ desorbed and also the small amount of LiNa₂(NH₂)₃ formed. The wt% calculated by Topas of the Li₂NH and LiNa₂(NH₂)₃ were found to be in a 5:1 mole ratio (Figure 3-12). Although the amount of hydrogen appeared small (0.2 wt%), it was very much below the temperature of hydrogen desorption traditionally attributed to amide-hydride hydrogen release of about 300 °C.

The presence of LiNH₂ as well as Li₂NH within the products after heating the starting materials to 200 °C suggested that a second pathway may be present. Significant hydrogen release from this reaction was observed under these conditions from 225 °C.

Equation 3-10

\[
\text{LiNH}_2 + \text{LiH} \rightarrow \text{Li}_2\text{NH} + \text{H}_2
\]

The presence of LiNH₂ may have resulted from a metathesis occurring between the Li₃Na(NH₂)₄ and LiH. If Li⁺ were to diffuse into Li₃Na(NH₂)₄ (as before) and Na⁺ were to diffuse out and combine with H⁻ (from LiH), the products would be LiNH₂ and NaH. Obviously Na⁺ is much larger than H⁺; therefore the rate of diffusion was likely to be much slower than the other suggested pathway at 150 °C whereas any increase in temperature would also assist the diffusion of Na⁺ out of Li₃Na(NH₂)₄. The structural similarity between Li₃Na(NH₂)₄ and
LiNH$_2$ (both tetragonal with space group I-4) may cause a topotactic reaction to occur between them. The N atoms would remain in the same place and Li$^+$ and Na$^+$ ions would diffuse around them. This would aid the ease of which Li$^+$ and Na$^+$ can diffuse into and out of the structure respectively.

The main desorption would most likely to be due to the formation of Li$_2$NH from LiNH$_2$. In forming Li$_2$NH, NH$_3$ is also desorbed. The NH$_3$ then reacts with LiH forming more LiNH$_2$ (this reaction is known to be ultra-fast$^5$). This would continue until all the LiH was exhausted (Equation 3-11). This reaction uses up the excess LiH present.

\[
\text{Equation 3-11} \quad \text{LiNH}_2 \rightarrow \frac{1}{2}\text{Li}_2\text{NH} + \frac{1}{2}\text{NH}_3 \rightarrow \frac{1}{2}\text{NH}_3 + \frac{1}{2}\text{LiH} \rightarrow \frac{1}{2}\text{LiNH}_2
\]

An overall reaction scheme is shown in Table 3-3. This shows the temperatures at which each product was formed.

<table>
<thead>
<tr>
<th>Temp/ °C</th>
<th>Reaction Scheme</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset of heating–235</td>
<td>2Li$_3$Na(NH$_2$)$_4$ + 2½Li$^+$ – H$^+$</td>
<td>2Li$_{5\frac{1}{3}}$Na(NH$_2$)$<em>4$(NH)$</em>{2\frac{1}{3}}$, H$_2$</td>
</tr>
<tr>
<td>150–235</td>
<td>Li$_3$Na(NH$_2$)$_4$ + Li$^+$ – Na$^+$</td>
<td>Li$_4$(NH$_2$)$_4$, NaH</td>
</tr>
<tr>
<td>225–315</td>
<td>LiNH$_2$ + LiH</td>
<td>Li$_2$NH, H$_2$</td>
</tr>
<tr>
<td>350</td>
<td>NaH</td>
<td>Na, H$_2$</td>
</tr>
</tbody>
</table>

The products present after rehydriding were LiNH$_2$ and LiH along with NaH that was present before. The method for the main hydrogen desorption from Li$_3$Na(NH$_2$)$_4$ + 5LiH was one of
Li\(^+\) diffusion into Li\(_3\)Na(NH\(_2\))\(_4\) and Na\(^+\) diffusion out. Due to the stability of LiNH\(_2\) and NaH, it would be unlikely to be thermodynamically preferable to reform Li\(_3\)Na(NH\(_2\))\(_4\) by reverse diffusion and only the rehydrogenation of the individual products to their fully hydrogenated state was possible (Equation 3-12).

Equation 3-12  
\[
4\text{Li}_2\text{NH} + \text{Na} + 4\frac{1}{2}\text{H}_2 \rightarrow 4\text{LiNH}_2 + 4\text{LiH} + \text{NaH}
\]

5. Li\(_3\)Na(NH\(_2\))\(_4\) + 3LiH

In order to clarify the pathways of the reactions occurring within the dehydrogenation of Li\(_3\)Na(NH\(_2\))\(_4\) + 5LiH, Li\(_3\)Na(NH\(_2\))\(_4\) + 3LiH was investigated at 350 °C.

Heating to 350 °C for 12 hours under argon produced the powder XRD pattern shown in Figure 3-18. The products were Li\(_2\)NH, LiNa\(_2\)(NH\(_2\))\(_3\), Na and NaH. These products back up the results from Li\(_3\)Na(NH\(_2\))\(_4\) + 4LiH in that LiNa\(_2\)(NH\(_2\))\(_3\) was formed if not enough LiH was present. We can presume both mechanisms discussed above are at work here as LiNa\(_2\)(NH\(_2\))\(_3\) and NaH/Na were both present, although much more LiNa\(_2\)(NH\(_2\))\(_3\) was present than NaH/Na. This indicated the Li\(^+\)/H\(^+\) diffusion may predominate, due to the lack of LiH available to diffuse at higher temperatures.
Figure 3-18 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 3LiH, heated to 350 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_2$NH (blue tick marks), LiNa$_2$(NH$_2$)$_3$ (black tick marks), Na (green tick marks), NaH (pink tick marks) and Li$_2$O (purple tick marks). $R_{wp} = 12.337$, $R_{exp} = 5.436$, $\chi^2 = 5.2$.

6. Li$_3$Na(NH$_2$)$_4$ + 4NaH

Li$_3$Na(NH$_2$)$_4$ was heated with NaH (Sigma-Aldrich, 95%) in a 1:4 ratio. This ratio was chosen in order to react one mole of amide with one mole of hydride, as with the LiNH$_2$-LiH system.

1. Temperature Programmed Desorption-Mass Spectrometry

The reaction was carried out on a TPD-MS apparatus at a heating rate of 2 °C min$^{-1}$ up to 350 °C (Figure 3-19). The TPD-MS trace showed a small amount of H$_2$ was desorbed from this reaction. No other gases were desorbed during heating. The release of hydrogen started soon after heating was started, 60 °C. At 160 °C the rate at which hydrogen was desorbed increased rapidly. This desorption peaked at 195 °C and then rapidly fell away to background hydrogen desorption levels. At 300 °C the rate of desorption increased again. This peaked at 350 °C before decreasing as isothermal heating took place. In the furnace power at 190 °C there was a very small endotherm; this coincided with the peak of the first hydrogen
desorption. The comparison between this hydrogen desorption and that of \( \text{Li}_3\text{Na(NH}_2\text{)}_4 + 4\text{LiH}, \text{Li}_3\text{Na(NH}_2\text{)}_4 + 5\text{LiH} \) and \( \text{Li}_3\text{Na(NH}_2\text{)}_4 + 2\text{MgH}_2 \) is shown in Figure 3-8.

![Figure 3-19 TPD-MS analysis of the \( \text{Li}_3\text{Na(NH}_2\text{)}_4 + 4\text{NaH} \) reaction. The temperature trace is shown in black and the mole percents of \( \text{H}_2 \) and \( \text{NH}_3 \) released are shown in red and green respectively.](image)

2. **Flowing Line Reactions**

The reaction was then heated up to intermediate temperatures in an attempt to establish the pathway for desorption. \( \text{Li}_3\text{Na(NH}_2\text{)}_4 + 4\text{NaH} \) was first heated up to 150 °C for 12 hours and the products analysed using powder XRD (Figure 3-20). The products from this reaction were newly formed \( \text{NaNH}_2 \) and \( \text{LiNa}_2(\text{NH}_2)_3 \) and a large amount of \( \text{Li}_2\text{O} \), as well as \( \text{Li}_3\text{Na(NH}_2\text{)}_4 \) and \( \text{NaH} \) starting materials.
Figure 3-20 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 4NaH, after heating 150 °C for 12 hours. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaH (blue tick marks), LiNa$_2$(NH$_2$)$_3$ (black tick marks), NaNH$_2$ (green tick marks), Li$_3$Na(NH$_2$)$_4$ (pink tick marks) and Li$_2$O (purple tick marks). $R_{wp} = 11.379$, $R_{exp} = 8.587$, $\chi^2 = 1.8$.

The products after heating the starting materials to 250 °C were LiNa$_2$(NH$_2$)$_3$ and NaNH$_2$ as for heating to 150 °C, along with the continued presence of NaH and Li$_2$O (Figure 3-21). There was a hydrogen desorption at 200 °C, but no hydrogen deficient species were present upon heating to 250 °C. (Although in the context of other desorptions, this one was very small, 0.5 wt%)

Figure 3-21 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 4NaH, after heating 250 °C for 12 hours. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases LiNa$_2$(NH$_2$)$_3$ (blue tick marks), NaH (black tick marks), NaNH$_2$ (green tick marks) and Li$_2$O (pink tick marks). $R_{wp} = 12.116$, $R_{exp} = 8.799$, $\chi^2 = 1.9$. 
The starting materials were heated together to 350 °C for 20 minutes. The products after analysing using powder XRD were LiNa$_2$(NH$_2$)$_3$ and a very small amount of sodium metal (Figure 3-22) and remaining starting materials. It was clear that starting materials were still present, particularly NaH.

Figure 3-22 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 4NaH, after heating 350 °C for 20 minutes. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases LiNa$_2$(NH$_2$)$_3$ (blue tick marks), NaH (black tick marks), Li$_3$Na(NH$_2$)$_4$ (green tick marks), Na (pink tick marks) and Li$_2$O (purple tick marks). $R_{wp} = 8.217$, $R_{exp} = 6.613$, $\chi^2 = 1.5$.

After heating to 350 °C for 12 hours the products were NaNH$_2$, LiNa$_2$(NH$_2$)$_3$, Na and a small amount of NaH (starting material) (Figure 3-23). The Na present was most likely from the decomposition of NaH (Equation 3-7).
Figure 3-23 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 4NaH, after heating 350 °C for 12 hours. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaNH$_2$ (blue tick marks), LiNa$_2$(NH$_2$)$_3$ (black tick marks), Na (green tick marks), NaH (pink tick marks) and Li$_2$O (purple tick marks). $R_{wp} = 15.245$, $R_{exp} = 8.631$, $\chi^2 = 3.1$.

3. Discussion

The amount of Li$_3$Na(NH$_2$)$_4$ starting material had decreased after heating to 150 °C and exhausted by 250 °C. Its presence at 350 °C, upon heating for 20 minutes, was most probably due to the reaction time shortened. NaNH$_2$ was present upon heating for 12 hours at 150, 250 and 350 °C, but not heated for 20 minutes at 350 °C. This indicated the NaNH$_2$ required hours in which to form. The NaNH$_2$ may have been formed from the Li$_3$Na(NH$_2$)$_4$, therefore explaining the inverse relationship between their presence in the products.

NaH was present up to 350 °C when it was found to decompose to Na metal and hydrogen gas (Equation 3-7). It appeared that all the NaH did not partake in the reaction and merely decomposed to Na when the reaction temperature was high enough. This would coincide with the second hydrogen desorption in Figure 3-19.

It could be tentatively suggested that the oxidation of Li$_3$Na(NH$_2$)$_4$ could form Li$_2$O and LiNa$_2$(NH$_2$)$_3$. If the Li$^+$ from Li$_3$Na(NH$_2$)$_4$ were to diffuse out in order to form Li$_2$O and Na$^+$ from NaH were to diffuse into Li$_3$$_{3-x}$Na$_{1+x}$(NH$_2$)$_4$, when $x = 2$, LiNa$_3$(NH$_2$)$_4$ would form. This can
be rewritten as LiNa$_2$(NH$_2$)$_3$ + NaNH$_2$. The remaining NaH would then go on to decompose to its constituent elements (Equation 3-7). An overall equation for the products is suggested in Equation 3-13.

Equation 3-13 when $x = 2$;

\[
\begin{align*}
\text{Li}_{3-x}\text{Na}_{1+x}(\text{NH}_2)_4 + (4-x)\text{NaNH}_2 + x/4\text{O}_2 & \rightarrow \text{LiNa}_3(\text{NH}_2)_4 + 2\text{NaNH}_2 + x/2\text{Li}_2\text{O} + \text{H}_2 \\
& \rightarrow \text{LiNa}_2(\text{NH}_2)_3 + \text{NaNH}_2 + (2-y)\text{NaNH}_2 + y\text{Na} + x/2\text{Li}_2\text{O} + (1+\frac{1}{2}y)\text{H}_2
\end{align*}
\]

The reaction gave a hydrogen loss of 0.5 wt%. If only NaH was responsible for the hydrogen desorbed then there was a theoretical mass loss of 2.0 wt% H$_2$.

7. Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$

Li$_3$Na(NH$_2$)$_4$ was heated with MgH$_2$ (Alfa Aesar, 98%) in a 1:2 ratio. This ratio was used in order to keep the amide and hydride in a 1:1 ratio.

1. *Temperature Programmed Desorption-Mass Spectrometry*

Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$ was first examined on a TPD-MS apparatus at a heating rate of 2 °C min$^{-1}$ up to 350 °C. In Figure 3-24, it can be seen that hydrogen was the predominant gas desorbed, but a very small amount of ammonia also appeared to be released. The hydrogen desorption started at a slow rate at 115 °C. The rate increased steeply at 180 °C. The desorption peaked quickly at 215 °C and slowly dropped whilst maintaining a broad desorption. The desorption dropped back to almost background levels by 350 °C, although a small tail of desorption continued to be observed. At 215 °C there was a fluctuation in the
temperature trace. When comparing the temperature trace to the furnace power it can be seen there was a drop in power followed by a rise at the same temperature (Figure 3-25). The mass loss on heating Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$ for 300 minutes was calculated to be 2.8 wt%. The products after heating Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$ to 350 °C on the TPD-MS apparatus were α-Li$_2$Mg(NH)$_2$, β-Li$_2$Mg(NH)$_2$ and Na as well as some unidentified peaks (Figure 3-26). The comparison between this hydrogen desorption and that of Li$_3$Na(NH$_2$)$_4$ + 4LiH, Li$_3$Na(NH$_2$)$_4$ + 5LiH and Li$_3$Na(NH$_2$)$_4$ + 4NaH is shown in Figure 3-8.

Figure 3-24 TPD-MS analysis of Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$. The temperature trace is shown in black and the mole percentages of H$_2$ and NH$_3$ released are shown in red and green respectively.
Figure 3-25 Furnace power during the TPD-MS analysis of Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$. The furnace power and temperature are shown in blue and black respectively.

2. **Flowing Line Reactions**

The reaction was then carried out at 300 °C for 12 hours on a flowing line. The products from this reaction were α-Li$_2$Mg(NH)$_2$ and NaH as well as the same unidentified peaks as present.
after TPD-MS, but in a smaller amount (Figure 3-27). The reaction was then carried out at 350 °C for 20 minutes (Figure 3-28) and repeated for 12 hours (Figure 3-29). The products at 350 °C after 20 minutes were the same as for 300 °C heated for 12 hours, with the addition of some Li$_2$NH and NaNH$_2$ (Figure 3-28). $\alpha$-Li$_2$Mg(NH)$_2$ was the majority product in both reactions.

Figure 3-27 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$, heated to 300 °C for 12 hours on a flowing line under argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases $\alpha$-Li$_2$Mg(NH)$_2$ (blue tick marks), NaH (black tick marks), MgO (green tick marks) and Li$_2$O (pink tick marks). $R_{wp} = 18.841$, $R_{exp} = 9.101$, $\chi^2 = 4.3$.

Figure 3-28 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$, heated to 350 °C for 20 minutes on a flowing line under argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases $\alpha$-Li$_2$Mg(NH)$_2$ (blue tick marks), NaH (black tick marks), Li$_2$NH (green tick marks), NaNH$_2$ (pink tick marks), LiNa$_2$(NH$_2$)$_3$ (purple tick marks) and MgO (light green tick marks). $R_{wp} = 13.052$, $R_{exp} = 9.791$, $\chi^2 = 1.8$. 
Upon heating $\text{Li}_3\text{Na(NH}_2\text{)}_4 + 2\text{MgH}_2$ to 350 °C for 12 hours $\beta$-$\text{Li}_2\text{Mg(NH)}_2$ appeared as a product alongside a much smaller amount of $\alpha$-$\text{Li}_2\text{Mg(NH)}_2$ (Figure 3-29). This was consistent with the post TPD XRD results.

![XRD pattern](image)

Figure 3-29 Powder XRD pattern of $\text{Li}_3\text{Na(NH}_2\text{)}_4 + 2\text{MgH}_2$, heated to 350 °C for 12 hours on flowing line under argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases $\beta$-$\text{Li}_2\text{Mg(NH)}_2$ (blue tick marks), $\alpha$-$\text{Li}_2\text{Mg(NH)}_2$ (black tick marks), NaNH$_2$ (green tick marks), Na$_2$O (pink tick marks), MgO (purple tick marks) and Li$_2$O (light green tick marks). $R_{wp} = 17.386$, $R_{exp} = 7.315$, $\chi^2 = 3.7$.

The starting materials were heated to 550 °C for 4 hours. The products were Li$_3$NH, Mg$_3$N$_2$ and $\beta$-$\text{Li}_2\text{Mg(NH)}_2$ (Figure 3-30).
Figure 3-30 Powder XRD pattern of Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$, heated to 550 °C for 4 hours on a flowing line under argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_2$NH (blue tick marks), Mg$_3$N$_2$ (black tick marks), β-Li$_2$Mg(NH)$_2$ (green tick marks), MgO (pink tick marks) and Li$_2$O (purple tick marks). $R_{wp} = 11.416$, $R_{exp} = 7.001$, $\chi^2 = 2.7$.

3. Discussion

The fluctuation in the temperature trace (Figure 3-24) accompanied by the drop in the furnace power followed quickly by a rise (Figure 3-25), was indicative of an exothermic event occurring in the sample. As this coincided with the hydrogen desorption peak the exotherm can be assigned to the sudden increase in loss of hydrogen. This is not ideal for a hydrogen storage medium as the hydrogen loss would need to be endothermic in order to be thermodynamically reversible.

The products from heating on a TPD-MS apparatus were α-Li$_2$Mg(NH)$_2$, β-Li$_2$Mg(NH)$_2$ and a very small amount of NaNH$_2$, as well as the unidentified peaks. The lack of sodium present in the known products implied sodium would be part of the compound(s) giving rise to the unidentified peaks. The lattice parameters of the mixed Li-Mg imides were as expected and so it appeared no partial substitution of sodium into the mixed Li-Mg imides had occurred.

The presence of β-Li$_2$Mg(NH)$_2$ at 350 °C (Figure 3-29) was expected as β-Li$_2$Mg(NH)$_2$ transforms from α-Li$_2$Mg(NH)$_2$ at around 350 °C. The heating of the starting materials for
12 hours enabled $\beta$-Li$_2$Mg(NH)$_2$ to form, whereas heating at 350 °C for 20 minutes (Figure 3-28) was not prolonged enough for $\alpha$-Li$_2$Mg(NH)$_2$ to transform.

The products after heating to 350 °C for 12 hours were consistent with those after heating on TPD-MS. The products after heating to 300 °C for 12 hours gave no NaNH$_2$, but there was NaH. After heating to 350 °C for 20 minutes there was the presence of both NaNH$_2$ and NaH and after prolonged heating for 12 hours, only NaH was present, with no NaNH$_2$. The longer heating time at 350 °C completed the conversion of NaNH$_2$ to NaH. This may not have been a direct conversion as no ammonia was seen to be desorbed (Figure 3-24).

The products after heating the sample to 550 °C for 4 hours were all identified and completely devoid of sodium. The other products: Li$_2$NH, Mg$_3$N$_2$ and $\beta$-Li$_2$Mg(NH)$_2$ were hydrogen deficient. A possible equation could be suggested (Equation 3-14). At heating to 550 °C it was possible that ammonia was desorbed (although we had no evidence for this as the TPD-MS was not carried out up to 550 °C). The lack of sodium present in the known products on heating to above 350 °C was most probably due to the NaH formed (Figure 3-28) decomposing to Na (Equation 3-7) and the Na metal then vaporising off.

Equation 3-14  

$$2\text{Li}_3\text{Na(NH}2\text{)}_4 + 4\text{MgH}2 \rightarrow 2\text{Li}_2\text{NH} + \text{Li}_2\text{Mg(NH}2\text{)}_2 + 2\text{Na} + \text{Mg}_3\text{N}2 + 7\text{H}2 + 2\text{NH}3$$

Products from Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$ could be compared with those from 2LiNH$_2$ + MgH$_2$. On heating Li$_3$Na(NH$_2$)$_4$ + 2MgH$_2$ up to 350 °C the known products were $\alpha$-Li$_2$Mg(NH)$_2$, $\beta$-Li$_2$Mg(NH)$_2$, a small amount of NaNH$_2$ and hydrogen. In comparison, 2LiNH$_2$ + MgH$_2$ heated to 350 °C gives the products of $\alpha$-Li$_2$Mg(NH)$_2$ and $\beta$-Li$_2$Mg(NH)$_2$ and accompanied by hydrogen release.
The products are very similar to each other. The presence of sodium within the $\text{Li}_3\text{Na(NH}_2\text{)}_4 + 2\text{MgH}_2$ reaction appeared to form $\text{NaNH}_2$ and be part of the compound(s) giving rise to the unidentified peaks. The lithium and magnesium form the mixed Li-Mg imide as if sodium was not present. The $\text{NaNH}_2$ had metathesised with both LiH and $\text{MgH}_2$ to form NaH (pages 82 and 152). This suggested that here the mixed Li-Mg imides were more stable than NaH.

8. $\text{LiNa}_2(\text{NH}_2)_3 + 3\text{LiH}$

$\text{LiNa}_2(\text{NH}_2)_3$ was originally heated with LiH in the ratio 1:3. This was in order to maintain a 1:1 ratio between amide and hydride- as with $\text{LiNH}_2$-LiH system.

1. *Temperature Programmed Desorption-Mass Spectrometry*

It can be seen from the TPD-MS data that only hydrogen was desorbed from the reaction (Figure 3-31). There was no evidence of ammonia desorption. There were two main hydrogen desorption regions. The lower temperature desorption started at about 50 °C with a slow release. An endothermic event occurred at 100 °C, although this was not reflected in the furnace power. Shortly after this, the rate of hydrogen desorption increased and formed an isolated desorption that decreased at 230 °C. There was a ‘blip’ in the desorption trace at 190 °C. This was present when the reaction was repeated. The fluctuation was accompanied by an exotherm in the temperature trace. Closer inspection of the furnace power (Figure 3-32) showed a drop in power followed by a rise. This confirmed the presence of an exothermic reaction in the sample. The main hydrogen desorption started at about 240 °C, peaking at 310 °C, before decreasing and then slowly tailing off. This was a much greater hydrogen desorption compared to the first desorption. At the peak of the hydrogen
desorption a small endotherm in the temperature trace was seen. This was confirmed by an increase in furnace power.

Figure 3-31 Thermal decomposition analysis of LiNa$_2$(NH$_2$)$_3$ + 3LiH in a TPD-MS apparatus. The temperature trace is shown in black and the mole percents of H$_2$ and NH$_3$ released are shown in red and green respectively.
Figure 3-32 Furnace power during the TPD-MS analysis of LiNa$_2$(NH$_2$)$_3$ + 3LiH. The furnace power and temperature are shown in blue and black respectively.

The products after heating the reaction on TPD-MS were Li$_2$NH, NaNH$_2$, Na, a very small amount of NaH and remaining LiNa$_2$(NH$_2$)$_3$ starting material (Figure 3-33).

The equation for this reaction could be written as:

Equation 3-15  
\[
\text{LiNa}_2(\text{NH}_2)_3 + 3\text{LiH} \rightarrow 2\text{Li}_2\text{NH} + \text{NaNH}_2 + (1-x)\text{NaH} + x\text{Na} + (2\frac{1}{2}+x)\text{H}_2
\]

A total of 3.3 wt% H$_2$ was desorbed in comparison to 4.0 wt% theoretically possible from this reaction when heated up to 350 °C for 300 minutes. This was the equivalent of 2 moles of H$_2$ released.
Figure 3-33 Powder XRD pattern of LiNa$_2$(NH$_2$)$_3$ + 3LiH heated to 350 °C on TPD-MS apparatus. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases LiNa$_2$(NH$_2$)$_3$ (blue tick marks), Li$_2$NH (black tick marks), Na (green tick marks), NaNH$_2$ (pink tick marks), NaH (purple tick marks) and Li$_2$O (light green tick marks). $R_{wp} = 9.962$, $R_{exp} = 7.396$, $\chi^2 = 1.8$.

There was still amide starting material present in the products suggesting the reaction had not gone to completion. Therefore, more LiH was required in order to complete the dehydrogenation of LiNa$_2$(NH$_2$)$_3$ to Li$_2$NH and other products. LiNa$_2$(NH$_2$)$_3$ + 5LiH was then investigated on the TPD-MS apparatus.

9. LiNa$_2$(NH$_2$)$_3$ + 5LiH

1. Temperature Programmed Desorption-Mass Spectrometry

The hydrogen desorption curve from TPD-MS was very similar to LiNa$_2$(NH$_2$)$_3$ + 3LiH, but there was slightly more hydrogen desorbed in the major peak (Figure 3-34). Figure 3-34 also shows the comparison of hydrogen desorption from LiNa$_2$(NH$_2$)$_3$ + 5LiH, LiNa$_2$(NH$_2$)$_3$ + 3LiH, LiNa$_2$(NH$_2$)$_3$ + 3NaH and 2LiNa$_2$(NH$_2$)$_3$ + 3MgH$_2$. Again, there was a fluctuation in the temperature trace at 190 °C.
Figure 3-34 Thermal decomposition analysis of hydrogen release from LiNa$_2$(NH$_2$)$_3$ + 5LiH (red trace) in a TPD-MS apparatus in comparison to LiNa$_2$(NH$_2$)$_3$ + 3LiH (purple trace), LiNa$_2$(NH$_2$)$_3$ + 3NaH (blue trace) and 2LiNa$_2$(NH$_2$)$_3$ + 3MgH$_2$ (green trace). The temperature trace is shown in black.

The products from this reaction were Li$_2$NH, NaH and Na (Figure 3-35). As no LiNa$_2$(NH$_2$)$_3$ remained, it appeared the amide to imide reaction had gone to completion. It could be seen that the additional two moles of LiH was necessary to complete the reaction. The complete reaction can be written as:

Equation 3-16 \[ \text{LiNa}_2\text{(NH}_2\text{)}_3 + 5\text{LiH} \rightarrow 3\text{Li}_2\text{NH} + (2-x)\text{NaH} + x\text{Na} + (3+\frac{1}{2}x)\text{H}_2 \]

4.0 wt% H$_2$ total was desorbed from this reaction when heated for 300 minutes; 2.8 moles of H$_2$. The theoretical mass loss is 5.7 wt%.
Figure 3-35 Powder XRD of LiNa$_2$(NH$_2$)$_3$ + 5LiH heated to 350 °C on a TPD-MS apparatus. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_2$NH (blue tick marks), NaH (black tick marks), Na (green tick marks) and Li$_2$O (pink tick marks). $R_{wp} = 8.031$, $R_{exp} = 4.737$, $X^2 = 2.9$.

2. **Flowing Line Reactions**

The starting materials were then heated to intermediate temperatures in order to establish the mechanism of desorption occurring. The starting materials were initially heated to 150 °C and held for 12 hours. 150 °C was part way through the first desorption (Figure 3-34). The products from the reaction after powder XRD were found to be Li$_3$Na(NH$_2$)$_4$, NaH, Li$_2$NH and a very small amount of NaNH$_2$, as well as LiNa$_2$(NH$_2$)$_3$ and LiH starting materials (Figure 3-36).
Figure 3-36 Powder XRD pattern of LiNa$_2$(NH$_2$)$_3$ + 5LiH, heated to 150 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases LiNa$_2$(NH$_2$)$_3$ (blue tick marks), LiH (black tick marks), Li$_3$Na(NH$_2$)$_4$ (green tick marks), Li$_2$NH (pink tick marks), NaH (purple tick marks), NaNH$_2$ (light green tick marks) and Li$_2$O (brown tick marks). $R_{wp} = 13.080$, $R_{exp} = 8.612$, $\chi^2 = 2.3$.

The reaction was then carried out at 200 °C. This was towards the end of the first desorption (Figure 3-34) and also shortly after the endothermic event occurring at 190 °C. The products were found to be LiH starting material along with LiNH$_2$, Li$_3$Na(NH$_2$)$_4$, NaH and Li$_3$NH. LiNa$_2$(NH$_2$)$_3$, starting material, had been consumed by this temperature (Figure 3-37). The hydrogen desorption may be in some way related to the consumption of the LiNa$_2$(NH$_2$)$_3$.

Figure 3-37 Powder XRD pattern of LiNa$_2$(NH$_2$)$_3$ + 5LiH, heated to 200 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Li$_3$Na(NH$_2$)$_4$ (blue tick marks), LiNH$_2$ (black tick marks), LiH (green tick marks), NaH (pink tick marks), Li$_2$NH (purple tick marks) and Li$_2$O (light green tick marks). $R_{wp} = 11.627$, $R_{exp} = 8.814$, $\chi^2 = 1.7$. 
The reaction carried out at 250 °C coincided with the very start of the second, major desorption (Figure 3-34). Neither mixed cation amide was present in the products. LiH starting material was present as well as LiNH₂, NaH and Li₂NH (Figure 3-38). It appeared that the second hydrogen peak was due to the reaction between LiNH₂ and LiH.

Figure 3-38 Powder XRD pattern of LiNa₂(NH₂)₃ + 5LiH, heated to 250 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases LiNH₂ (blue tick marks), NaH (black tick marks), Li₂NH (green tick marks), LiH (pink tick marks) and Li₂O (purple tick marks). $R_{wp} = 12.071$, $R_{exp} = 9.153$, $\chi^2 = 1.7$.

3. Discussion

NaNH₂ was only visible in the products from the reaction carried out to 150 °C, with the additional LiH. It had been expected that more NaNH₂ would be observed throughout the reaction at different temperatures, if the same mechanism of Li⁺ and H⁺ diffusion took part here. NaNH₂ should still be formed by the low temperature Li⁺/H⁺ diffusion. However, further work carried out below showed it was possible for NaNH₂ to react with LiH to form LiNH₂ and NaH in a metathesis reaction (Equation 3-17).

Hu et al.⁶ investigated improvements to the Li-Mg-N-H hydrogen storage system. They used NaNH₂ as an additive in order to improve kinetics of hydrogen desorption. Mg(NH₂)₂, LiH and NaNH₂ were ball-milled together. For 0.8Mg(NH₂)₂–0.4NaNH₂–2LiH, the powder XRD pattern
post milling showed the presence of Mg(NH$_2$)$_2$, LiH, NaH, and LiNH$_2$. It was noted that a metathesis reaction had occurred between the NaNH$_2$ and LiH in order to form the LiNH$_2$ and NaH present post milling (Equation 3-17).

The standard formation enthalpies of NaNH$_2$, LiH, LiNH$_2$, and NaH are $-123.8$, $-90.5$, $-179.5$, and $-56.3$ kJ mol$^{-1}$, respectively. The enthalpy change of Equation 3-17 was calculated to be $-21.5$ kJ mol$^{-1}$.

The possible metathesis between NaNH$_2$ and LiH was investigated under the same conditions as here. The starting materials were heated together to 350 °C for 2 hours. The products were LiNH$_2$ (2 moles) and NaH (2 moles) (Figure 3-39), as hypothesised. There was no evidence of Li$_2$NH from a reaction between LiNH$_2$ and LiH (Equation 3-10).

Figure 3-39 Powder XRD pattern of NaNH$_2$ + LiH, heated to 350 °C for 2 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases LiNH$_2$ (blue tick marks), NaH (black tick marks) and NaOH (green tick marks). $R_{wp} = 11.904$, $R_{exp} = 5.026$, $\chi^2 = 5.6$.

The metathesis would explain the lack of NaNH$_2$ observed in the products from the reaction of LiNa$_2$(NH$_2$)$_3$ + 5LiH.

Equation 3-17  
NaNH$_2$ + LiH $\rightarrow$ LiNH$_2$ + NaH
NaNH$_2$ was present in the products of LiNa$_2$(NH$_2$)$_3$ + 3LiH, Equation 3-15, as not enough LiH was added to the reaction to perform a metathesis reaction with the NaNH$_2$ (only 3 moles). The LiNH$_2$ formed from both the Li$^+$/Na$^+$ diffusion discussed previously (section 3.4.5) and as a result of Equation 3-17 could then go on to further react with LiH present to form Li$_2$NH (Equation 3-10). This would result in the large hydrogen desorption starting at 240 °C (Figure 3-34).

There was both NaH and NaNH$_2$ present in the products of both LiNa$_2$(NH$_2$)$_3$ + 3LiH and LiNa$_2$(NH$_2$)$_3$ + 5LiH. This suggested similar pathways to those discussed in section 3.2.4 were occurring in these reactions. This was due to NaH and NaNH$_2$ each being the product of one of the pathways. The first, thought to predominate at lower temperatures, involved the diffusion of Li$^+$ ions into and diffusion of H$^+$ ions out of LiNa$_2$(NH$_2$)$_3$. The H$^+$ combined with H$^-$ remaining from LiH to form H$_2$ which was the cause of the low temperature H$_2$ desorption. This pathway may be more prominent here, in comparison to Li$_3$Na(NH$_2$)$_4$ + xLiH, as a much greater hydrogen peak was present in the lower temperature heating region (up to 240 °C).

LiNa$_2$(NH$_2$)$_3$ with H$^+$ diffusing out and Li$^+$ diffusing in would form Li$_{1+x}$Na$_2$(NH$_2$)$_{3-x}$(NH)$_x$ (0 ≤ x ≤ 1). When x = 1, ‘Li$_2$Na$_2$(NH$_2$)$_2$NH’ would form. This can be rewritten as Li$_2$NH + ‘Na$_2$(NH$_2$)$_2$’, which in turn can be rewritten as Li$_2$NH + 2NaNH$_2$.

At higher temperatures the LiH may again (as per section 3.2.4) be able to undergo a metathesis with LiNa$_2$(NH$_2$)$_3$ with Li$^+$ diffusing into the LiNa$_2$(NH$_2$)$_3$ which would be accompanied by Na$^+$ diffusing out of the sample. This would form Li$_{1+x}$Na$_{3-x}$(NH$_2$)$_3$. When x = 2, Li$_3$(NH$_2$)$_3$ + 2NaH would be formed. This can be rewritten as 3LiH$_2$ + 2NaH. The LiNH$_2$ present can then further react with LiH to form Li$_2$NH (Equation 3-10). Na was present in the products instead of NaH, due to NaH decomposing to Na and H$_2$ (Equation 3-7). The H$_2$ from
the decomposition of NaH would most likely be the cause of the tail of hydrogen visible during the isothermal heating. The greater size of Na$^+$ ions hinders their ionic mobility and therefore this pathway would be assisted by higher temperatures. The overall reaction scheme is shown in Table 3-4. The products from each temperature are shown.

Table 3-4 Overall reaction scheme $\text{LiNa}_2(\text{NH}_2)_3 + 5\text{LiH}$ of heated to various temperatures. The products from each temperature are shown.

<table>
<thead>
<tr>
<th>Temp/ °C</th>
<th>Reaction Scheme</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset of heating–240</td>
<td>$\text{LiNa}_2(\text{NH}_2)_3 + \text{Li}^+ - \text{H}^+ \rightarrow \text{Li}_2\text{Na}_2(\text{NH}_2)_2(\text{NH}), \frac{1}{2}\text{H}_2$</td>
<td>$\text{Li}_2\text{NH} + \text{Na}_2(\text{NH}_2)_2$ (2$\text{NaNH}_2$)</td>
</tr>
<tr>
<td>Throughout heating</td>
<td>$\text{NaNH}_2 + \text{LiH} \rightarrow \text{LiNH}_2 + \text{NaH}$</td>
<td></td>
</tr>
<tr>
<td>200–350</td>
<td>$\text{LiNa}_2(\text{NH}_2)_3 + 2\text{Li}^+ - 2\text{Na}^+ \rightarrow \text{Li}_3\text{Na}_2(\text{NH}_2)_3 \rightarrow \text{Li}_3(\text{NH}_2)_3$ (3$\text{LiNH}_2$) + 2$\text{NaH}$</td>
<td></td>
</tr>
<tr>
<td>240–350</td>
<td>$\text{LiNH}_2 + \text{LiH} \rightarrow \text{Li}_2\text{NH}, \text{H}_2$</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>$\text{NaH} \rightarrow \text{Na}, \frac{1}{2}\text{H}_2$</td>
<td></td>
</tr>
</tbody>
</table>

It is interesting to note that at no time is an unidentified phase present. An unidentified phase could have suggested the presence of a mixed Li-Na imide i.e. ‘$\text{Li}_3\text{Na}(\text{NH})_2$’ or ‘$\text{Li}_2\text{Na}_4(\text{NH})_3$’ forming. As the structure of $\text{Li}_3\text{Na}(\text{NH}_2)_4$ is based on $\text{LiNH}_2$ units it is possible the structure of $\text{Li}_3\text{Na}(\text{NH}_2)_4$ would still be maintained if less H were present (cf. $\text{LiNH}_2 \rightarrow \text{Li}_2\text{NH}$).

It would theoretically also result in the loss of ammonia (Equation 3-18).

\[ \text{Eqn 3-18} \quad \text{Li}_3\text{Na}(\text{NH}_2)_4 + 2\text{LiH} \rightarrow \text{Li}_5\text{Na}(\text{NH})_3 + 2\text{H}_2 + \text{NH}_3 \]

Mixed cation imides are known in the form of $\text{Li}_2\text{Mg}(\text{NH})_2$ and $\text{Li}_2\text{Ca}(\text{NH})_2$. However, these involve lithium and a group 2 metal, and in comparison it does not appear that lithium and
another group 1 metal are able to form a mixed imide by this method. Theoretically, it seems it would not be possible to form the mixed group 1 cation imides without the desorption of NH$_3$ as there would be too much nitrogen present in the amide to charge balance the it within the imide.

10. LiNa$_2$(NH$_2$)$_3$ + 3NaH

LiNa$_2$(NH$_2$)$_3$ was heated with NaH in a 1:3 ratio. This ratio was used in order to ensure a 1:1 amide to hydride ratio as for the LiNH$_2$-LiH system.

1. Temperature Programmed Desorption-Mass Spectrometry

The reaction was originally heated at a rate of 2 °C min$^{-1}$ to 350 °C on TPD-MS apparatus. The gas desorption profile is shown in Figure 3-40. It can be seen that only hydrogen was desorbed. There was no evidence of ammonia desorption. The hydrogen desorption occurred in two main stages, although a slow rate of hydrogen desorption appeared shortly after heating began. The rate of hydrogen desorption increased at 140 °C and rose to 200 °C during which time there were two ‘steps’ in the desorption (157 and 179 °C). At this peak there was an event in the temperature trace. This was confirmed by the furnace power graph (Figure 3-41), which showed an increase in furnace power followed by a drop, before resuming the prescribed heating run. The first desorption ceased at 250 °C. A second desorption started at about 300 °C and rose to a maximum at 350 °C where isothermal heating was reached. The hydrogen desorption dropped very slowly in the stable temperature region. A comparison of this hydrogen release in comparison to that of LiNa$_2$(NH$_2$)$_3$ + 3LiH, LiNa$_2$(NH$_2$)$_3$ + 5LiH and 2LiNa$_2$(NH$_2$)$_3$ + 3MgH$_2$ is shown in Figure 3-34.
The products after heating on TPD-MS were analysed by powder XRD (Figure 3-42). They were found to be NaNH$_2$, Na and Li$_2$O.

Figure 3-40 Thermal decomposition analysis of LiNa$_2$(NH$_2$)$_3$ + 3NaH in a TPD-MS apparatus. The temperature trace is shown in black and the mole percents of H$_2$ and NH$_3$ released are shown in red and green respectively.
2. **Flowing Line Reactions**

The starting materials were heated together up to 140 °C for 12 hours in order to know what products were present when the rate of hydrogen desorption first increased. The phases
present after analysis using powder XRD were starting materials, LiNa$_2$(NH$_2$)$_3$ and NaH, as well as NaNH$_2$ and Li$_3$Na(NH$_2$)$_4$ (Figure 3-43). It was suggested previously, from thermal decomposition data (Figure 3-41), that NaNH$_2$ was present at 200 °C. It can be seen here that it was present from at least 140 °C. For Li$_3$Na(NH$_2$)$_4$ + 4NaH, NaNH$_2$ was also present from a low temperature: 150 °C.

Figure 3-43 Powder XRD pattern of LiNa$_2$(NH$_2$)$_3$ + 3NaH heated to 140 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases LiNa$_2$(NH$_2$)$_3$ (blue tick marks), NaH (black tick marks), NaNH$_2$ (green tick marks), Li$_3$Na(NH$_2$)$_4$ (pink tick marks) and Li$_2$O (purple tick marks). $R_{wp} = 11.645$, $R_{exp} = 7.814$, $\chi^2 = 2.2$.

The products present after heating to 260 °C were investigated in an attempt to establish what phases were present between the two main hydrogen desorptions. These were starting materials again, as well as NaNH$_2$ and Li$_2$O, as before (Figure 3-44). No Li$_3$Na(NH$_2$)$_4$ was present as it had been at 140 °C.
Figure 3-44 Powder XRD pattern of LiNa$_2$(NH$_2$)$_3$ + 3NaH heated to 260 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaNH$_2$ (blue tick marks), NaH (black tick marks), LiNa$_2$(NH$_2$)$_3$ (green tick marks), and Li$_2$O (pink tick marks). $R_{wp} = 11.486$, $R_{exp} = 7.543$, $\chi^2 = 2.3$.

When the reaction was carried out on the flowing line for 20 minutes to 350 °C the products were similar to heating on TPD-MS: NaNH$_2$, but this time LiNa$_2$(NH$_2$)$_3$ was also present along with NaH starting material (Figure 3-45).

Figure 3-45 Powder XRD pattern of LiNa$_2$(NH$_2$)$_3$ + 3NaH heated to 350 °C for 20 minutes on a flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaNH$_2$ (blue tick marks), NaH (black tick marks), LiNa$_2$(NH$_2$)$_3$ (green tick marks) and Li$_2$O (pink tick marks). $R_{wp} = 9.183$, $R_{exp} = 6.262$, $\chi^2 = 2.1$.

The products after heating the starting materials to 350 °C for 12 hours were NaNH$_2$ and Na, as well as a large amount of Li$_2$O and NaH remaining (Figure 3-46). In comparison to heating for 20 minutes, the LiNa$_2$(NH$_2$)$_3$ had disappeared and more Li$_2$O was present. The difference
between products from heating on TPD-MS apparatus (Figure 3-42) and flowing line for 12 hours was the lack of NaH from TPD-MS heating, having formed Na, whereas after 12 hours on the flowing line both NaH and Na were present.

Heating for 12 hours appeared to cause the LiNa$_2$(NH$_2$)$_3$ present (Figure 3-45) to react and not be present (Figure 3-46).

![Figure 3-46 Powder XRD pattern of LiNa$_2$(NH$_2$)$_3$ + 3NaH heated to 350 °C for 12 hours on a flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaNH$_2$ (blue tick marks), NaH (black tick marks), Na (green tick marks) and Li$_2$O (pink tick marks). $R_{wp} = 13.251$, $R_{exp} = 10.684$, $\chi^2 = 1.5$.](image)

Li$_3$Na(NH$_2$)$_4$ was only observed after heating to 140 °C for 12 hours. The first two steps in the hydrogen desorption appeared to occur in the same temperature region as the two endothermic events occurring at about 200 °C, as shown by differential scanning calorimetry (DSC) (Figure 3-47). A sample of LiNa$_2$(NH$_2$)$_3$ + 3NaH was heated at 2 °C min$^{-1}$ up to 350 °C, held there for 20 minutes and then cooled at 2 °C min$^{-1}$ to room temperature. This was carried out under a 3 bar argon atmosphere flowing at 100 ml min$^{-1}$.

The main hydrogen desorption seemed to be exothermic as the DSC power increased. The second main hydrogen desorption occurred alongside an endothermic event in the DSC.
The same endotherm occurred at the end of heating $\text{Li}_3\text{Na(NH}_2\text{)}_4 + 4\text{NaH}$ on DSC to 350 °C (Figure 3-48).

Figure 3-47 Comparison between DSC power and $\text{H}_2$ desorption from the $\text{LiNa}_2\text{(NH}_2\text{)}_3 + 3\text{NaH}$ reaction heated to 350 °C.
Figure 3-48 Comparison of DSC power for the $\text{Li}_3\text{Na}(\text{NH}_2)_4 + 4\text{NaH}$ and $\text{LiNa}_2(\text{NH}_2)_3 + 3\text{NaH}$ reactions.

The comparison of hydrogen desorption from $\text{LiNa}_2(\text{NH}_2)_3 + 3\text{NaH}$ and $\text{Li}_3\text{Na}(\text{NH}_2)_4 + 4\text{NaH}$ is shown in Figure 3-49. It can be seen there was a greater $\text{H}_2$ desorption tail during isothermal heating for $\text{LiNa}_2(\text{NH}_2)_3 + 3\text{NaH}$.
3. Discussion

The NaNH$_2$ and Li$_3$Na(NH$_2$)$_4$ were formed at very low temperatures, possibly from the transformation of LiNa$_2$(NH$_2$)$_3$ to Li$_3$Na(NH$_2$)$_4$ and NaNH$_2$ (Equation 3-6). It had been shown that the mixed cation amides formed an equilibrium (Sections 3.2.1 and 3.2.2).

The melting point temperature of NaNH$_2$ is 210 °C, very close to the endothermic event noticed at 200 °C (Figure 3-41). Melting is endothermic and this could explain the fluctuation in the temperature trace and furnace power at 200 °C. This would suggest NaNH$_2$ was present in the reaction mixture at 200 °C and remained further unreacted up to 350 °C, as it was present in the products then. The endotherm was also present in the DSC trace (Figure 3-47).
The products from \( \text{LiNa}_2(\text{NH}_2)_3 + 3\text{NaH} \) were \( \text{NaNH}_2 \), \( \text{Na} \) and \( \text{Li}_2\text{O} \). These products were the same as those identified for \( \text{Li}_3\text{Na}(\text{NH}_2)_4 + 4\text{NaH} \), but without \( \text{LiNa}_2(\text{NH}_2)_3 \).

From the molar amounts of \( \text{Li} \) and \( \text{Na} \) in the products (Figure 3-46) the sample was deficient in \( \text{Na} \)-containing products. It is possible that sodium was lost through sodium vapour when \( \text{NaH} \) decomposed to \( \text{Na} \) and \( \text{H}_2 \) (Equation 3-7).

These products could be formed by the same mechanism as tentatively suggested in section 3.2.4. That is, oxidation of \( \text{LiNa}_2(\text{NH}_2)_3 \) causes \( \text{Li}^+ \) to diffuse out of \( \text{LiNa}_2(\text{NH}_2)_3 \) and \( \text{Na}^+ \) from \( \text{NaH} \) to diffuse into \( \text{LiNa}_2(\text{NH}_2)_3 \), forming \( \text{Li}_2\text{O} \). This would notionally form \( \text{Na}_3(\text{NH}_2)_3 \), which can be rewritten as \( 3\text{NaNH}_2 \). The \( \text{H}^- \) remaining from \( \text{NaH} \) would form \( \text{H}_2 \). \( \text{NaH} \) remaining would decompose at 350 °C to form \( \text{Na} \) (Equation 3-7).

**Equation 3-19**

\[
2\text{Li}_{1-x}\text{Na}_{2+x}(\text{NH}_2)_3 + (6-2x)\text{NaH} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{Na}_3(\text{NH}_2)_3 + 4\text{NaH} + \text{Li}_2\text{O} + \text{H}_2 \\
6\text{NaNH}_2 + (4-y)\text{NaH} + y\text{Na} + \text{Li}_2\text{O} + (1+\frac{1}{2}y)\text{H}_2
\]

A hydrogen loss of 1.6 wt% was found from the TPD-MS apparatus. This compared favourably to the theoretical mass loss of 1.7 wt% if only the \( \text{NaH} \) were to desorb \( \text{H}_2 \). The long slow \( \text{H}_2 \) desorption during isothermal heating (Figure 3-40) was most likely from the decomposition of \( \text{NaH} \) to \( \text{Na} \) (Equation 3-7).

11. \( 2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2 \)

\( \text{LiNa}_2(\text{NH}_2)_3 \) was heated with \( \text{MgH}_2 \) in a 2:3 ratio. This was in order to maintain a 1:1 ratio between amide and hydride as with the \( \text{LiNH}_2 + \text{LiH} \) system.
1. Temperature Programmed Desorption-Mass Spectrometry

$2\text{LiNa}_2\text{(NH}_2\text{)}_3 + 3\text{MgH}_2$ was initially examined on a TPD-MS apparatus at a heating rate of $2 \degree \text{C min}^{-1}$ up to $350 \degree \text{C}$ (Figure 3-50). The reaction released only hydrogen with no evidence for ammonia desorption. The hydrogen desorption started at $75 \degree \text{C}$ at a slow rate which started to increase at $140 \degree \text{C}$ and was fastest from $170 \degree \text{C}$, up to a peak at $230 \degree \text{C}$. After reaching $230 \degree \text{C}$, the rate of hydrogen desorption decreased to almost background levels by $290 \degree \text{C}$. The mass loss after heating $2\text{LiNa}_2\text{(NH}_2\text{)}_3 + 3\text{MgH}_2$ for 300 minutes was calculated to be 2.2 wt%.

The products after heating this reaction to $350 \degree \text{C}$ were found to be $\alpha$-$\text{Li}_2\text{Mg(NH)}_2$, $\beta$-$\text{Li}_2\text{Mg(NH)}_2$, $\text{Li}_2\text{NH}$ and $\text{Na}$ along with a large amount of oxidation (Figure 3-51). In addition there were also unidentified peaks present. The $\beta$-$\text{Li}_2\text{Mg(NH)}_2$ appeared in the products after TPD-MS here and not in $\text{Li}_3\text{Na(NH}_2\text{)}_4 + 2\text{MgH}_2$ (section 3.2.7) due to the heating in the TPD-MS apparatus being for longer than for $\text{Li}_3\text{Na(NH}_2\text{)}_2 + 2\text{MgH}_2$. The hydrogen desorption here can be compared to that of $\text{LiNa}_2\text{(NH}_2\text{)}_3 + 3\text{LiH}$, $\text{LiNa}_2\text{(NH}_2\text{)}_3 + 5\text{LiH}$ and $\text{LiNa}_2\text{(NH}_2\text{)}_3 + 3\text{NaH}$ is shown in Figure 3-34.
Figure 3-50 TPD-MS analysis of 2LiNa$_2$(NH$_2$)$_3$ + 3MgH$_2$. The temperature trace is shown in black and the mole percentages of H$_2$ and NH$_3$ released are shown in red and green respectively.

Figure 3-51 Powder XRD pattern of 2LiNa$_2$(NH$_2$)$_3$ + 3MgH$_2$, heated to 350 °C on TPD-MS apparatus. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases $\beta$-Li$_2$Mg(NH)$_2$ (blue tick marks), $\alpha$-Li$_2$Mg(NH)$_2$ (black tick marks), Li$_2$NH (green tick marks), NaNH$_2$ (pink tick marks), Mg$_3$N$_2$ (purple tick marks), Na (light green tick marks) and MgO (brown tick marks). $R_{wp} = 15.394$, $R_{exp} = 4.758$, $\chi^2 = 10.5$. 

\begin{itemize}
  \item b Li$_2$Mg(NH)$_2$ 18.04 %
  \item a Li$_2$Mg(NH)$_2$ 16.15 %
  \item Li$_2$NH 10.26 %
  \item NaNH$_2$ 9.21 %
  \item Mg$_3$N$_2$ 6.40 %
  \item Na 2.13 %
  \item MgO 37.79 %
\end{itemize}
2. **Flowing Line Reactions**

After heating the reaction mixture to 300 °C for 12 hours the products were NaNH$_2$, LiNa$_2$(NH$_2$)$_3$, NaH and MgO, as well as lots of unidentified peaks (Figure 3-52).

Figure 3-52 Powder XRD pattern of 2LiNa$_2$(NH$_2$)$_3$ + 3MgH$_2$, heated to 300 °C for 12 hours on a flowing line under argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaNH$_2$ (blue tick marks), LiNa$_2$(NH$_2$)$_3$ (black tick marks), NaH (green tick marks) and MgO (pink tick marks). $R_{wp} = 26.097$, $R_{exp} = 5.825$, $\chi^2 = 20.1$.

The reaction mixture was also heated to 350 °C for 12 hours (Figure 3-53). The products from this were $\beta$-Li$_2$Mg(NH)$_2$, NaNH$_2$ and Na, as well as unidentified peaks. The unidentified peaks were different to those in Figure 3-52.
Figure 3-53 Powder XRD pattern of \(2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2\), heated to \(350 ^\circ \text{C}\) for 12 hours on flowing line under argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases \(\beta-\text{Li}_2\text{Mg(NH)}_2\) (blue tick marks), \(\text{NaNH}_2\) (black tick marks) and \(\text{MgO}\) (green tick marks). \(R_{wp} = 30.545, \ R_{exp} = 7.718, \ \chi^2 = 15.7\).

\(2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2\) was heated together to \(350 ^\circ \text{C}\) for 36 hours. The products were the same as for the 12 hour heating (Figure 3-53). The unidentified peaks were in the same places. The amounts of the known products were similar.

3. Discussion

The furnace power and temperature trace (Figure 3-50) of \(2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2\) showed no fluctuations. This was unlike when \(\text{Li}_3\text{Na(}\text{NH}_2)_4\) was heated with \(\text{MgH}_2\) where an exothermic event was observed at \(180 ^\circ \text{C}\).

The products after heating \(2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2\) to \(350 ^\circ \text{C}\) for 12 hours (Figure 3-53) were similar to those after heating the same reaction on a TPD-MS apparatus (Figure 3-51). The products were \(\beta-\text{Li}_2\text{Mg(NH)}_2\), \(\text{NaNH}_2\), \(\text{MgO}\) and a lot of unidentified peaks. These unidentified peaks were present in both XRD patterns. There were also additional unidentified peaks within the TPD XRD pattern.

\(\text{LiNa}_2(\text{NH}_2)_3\) has a majority of sodium cations within it compared to \(\text{Li}_3\text{Na(}\text{NH}_2)_4\) in which the majority of cations are lithium. The reaction between \(\text{LiNa}_2(\text{NH}_2)_3\) and \(\text{MgH}_2\) can therefore
be compared to that of the sodium-rich NaNH$_2$ and MgH$_2$ reactions (sections 4.2.2 and 4.2.3).

The products after heating $2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2$ to 350 °C on a TPD-MS apparatus were $\alpha$-Li$_2$Mg(NH)$_2$, $\beta$-Li$_2$Mg(NH)$_2$, Li$_2$NH, NaNH$_2$, Mg$_3$N$_2$ and Na along with the release of hydrogen. The Li$_2$Mg(NH)$_2$ appeared to form as if no sodium was present at all. In comparison, the products from the sodium-rich reactions with MgH$_2$ were the mixed Na-Mg imide, NaNH$_2$, Mg$_3$N$_2$ and NaH/Na also with the release of hydrogen (Figure 7-4 and Figure 7-13). It could be seen that the products from both reactions were similar with only the extra Li present forming Li$_2$NH. However, as the composition of the unidentified phases was unknown a full comparison could not be carried out.

$2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2$, heated to 350 °C for 12 hours (Figure 3-53), Li$_3$Na(NH$_2$)$_4 + 2\text{MgH}_2$ heated on TPD-MS (Figure 3-26) and $2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2$ heated to 350 °C on TPD-MS had the same unidentified peaks, but $2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2$ heated on TPD-MS also had additional unidentified peaks present.

Some of the unidentified peaks from $2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2$, heated to 350 °C on TPD-MS (Figure 3-51) were the same as the starting materials heated to 300 °C for 12 hours (Figure 3-52), however many were new. It is interesting to note there was no $\alpha$-Li$_2$Mg(NH)$_2$ formed after heating to 300 °C for 12 hours, as shown in Figure 3-52, whereas in the Li$_3$Na(NH$_2$)$_4 + 2\text{MgH}_2$ mixture under the same conditions, it was present (Figure 3-27).

Attempts were made to characterise the unidentified products from the reactions Li$_3$Na(NH$_2$)$_4 + 2\text{MgH}_2$ and $2\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2$, however all proved unsuccessful. It was unclear in most cases whether the unidentified peaks belonged to one or more phases.
Although under some conditions \(2\text{LiNH}_2 + \text{MgH}_2\) desorbs hydrogen at a lower temperature than \(\text{LiNH}_2 + \text{LiH}\), it could be seen under the conditions here that the release of hydrogen occurred at the same temperature for both reactions. It was possible to compare the hydrogen desorptions for the reactions of mixed cation amides with \(\text{LiH}\) and \(\text{MgH}_2\). It can be seen from Figure 3-54 that both the mixed cation amides, when heated with \(\text{MgH}_2\), desorbed hydrogen at almost 100 °C lower than when heated with \(\text{LiH}\). The reaction of the mixed cation amides with \(\text{LiH}\) occurred at the same temperature as \(\text{LiNH}_2 + \text{LiH}\) and \(2\text{LiNH}_2 + \text{MgH}_2\) under these conditions. The benefit of the addition of \(\text{MgH}_2\) to the mixed cation amides was clear.

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**Figure 3-54** Comparison TPD-MS analysis of \(\text{Li}_3\text{Na(NH}_2)_4 + 4\text{LiH}\), \(\text{LiNa}_2(\text{NH}_2)_3 + 3\text{LiH}\), \(\text{Li}_3\text{Na(NH}_2)_4 + 2\text{MgH}_2\) and \(\text{LiNa}_2(\text{NH}_2)_3 + 3\text{MgH}_2\) with \(2\text{LiNH}_2 + \text{MgH}_2\) and \(\text{LiNH}_2 + \text{LiH}\).
4 Topas, general profile and structure analysis software for powder diffraction data, A. A. Coelho; Bruker AXS, Karlsruhe, Germany, 3.0 ed., 2004
7 D.R. Lide, *CRC Handbook of Chemistry and Physics*, 87th edition
4. \( x\text{NaNH}_2 + y\text{MgH}_2 \)

1. Introduction

The use of LiNH\(_2\) in solid-state hydrogen storage materials has been well researched. LiNH\(_2\) has been combined with LiH,\(^{1,2,3}\) MgH\(_2\),\(^{4,5,6,7}\) CaH\(_2\),\(^{8,9,10,11}\) LiAlH\(_4\)\(^{12}\) as well as forming mixed cation amides \( \text{Li}_3\text{Na(NH}_2)_4 \), \( \text{LiNa}_2\text{(NH}_2)_3 \)\(^{13,14}\) and \( \text{K}_2\text{Li(NH}_2)_3 \)\(^{15}\). However, the use of sodium amide in place of LiNH\(_2\) for hydrogen storage has not been investigated as extensively.

The use of sodium amide over lithium amide would be preferable because of the cost of lithium vs. sodium. Lithium costs 550 €/kg whereas sodium is cheaper by almost a factor of 4. This is largely due to the greater abundance of sodium than lithium. Also, the increase in lithium use in batteries is likely to have the effect of pushing the price up. Unfortunately, sodium weighs more than lithium and so will have a detrimental effect on the mass to hydrogen ratio. Sodium amide itself is less stable than lithium amide. This can be seen in the contrasting enthalpy of formation: LiNH\(_2\) –179.5 kJ mol\(^{-1}\); NaNH\(_2\) –123.8 kJ mol\(^{-1}\). This lower stability should assist in the release of hydrogen from an amide/hydride system containing sodium amide.

The reactions between LiNH\(_2\) and MgH\(_2\) and Mg(NH\(_2\))\(_2\) and LiH have previously been discussed in the introduction (section 1). The electronegativity difference between Li and Mg (Li, 0.98; Mg, 1.31, Pauling scale) in the Li-Mg-N-H system is said to be one driving force in the decreased temperature desorption between Li-Mg-N-H and Li-N-H systems.\(^{16}\) The difference in electronegativity between the cations means there is weaker ionic interaction for sodium with
the $[\text{NH}_2]^-$ anion.\textsuperscript{17} The electronegativity difference between Na and Mg (Na, 0.93) is greater than that between Li and Mg. Therefore, if an intermediate of Na-Mg-N-H can be formed (although not suggested before) it could release hydrogen at a lower temperature than Li$_2$Mg(NH)$_2$. The attraction between the H$^-$ in the ionic NaH and H$^{\delta+}$ in the amide should aid hydrogen desorption, as it has with LiH.\textsuperscript{1,2}

At the time we started research into the Na-Mg-N-H system, no other research had been carried out. In 2010, Dolotko \textit{et al.}\textsuperscript{18} reported investigations into the reaction 2NaNH$_2$ + 3MgH$_2$. Dolotko \textit{et al.}\textsuperscript{18} ball-milled the starting materials for 15 minutes to ensure complete mixing of the reactants. The reactants were pressed into pellets and then placed in an autoclave and evacuated. The sample was heated to the selected temperature and held there until the pressure stabilised and then quenched using forced air (5–10 minutes cooling time). They argued that as the kinetics of the original reaction are slow, the kinetics of the reverse reaction should also be slow.

The reaction was initially carried out to 395 °C and about 5 wt% H$_2$ desorption was observed. The only gas found by the residual gas analyser (RGA) was hydrogen with no evidence of ammonia. The H$_2$ release observed by Dolotko \textit{et al.}\textsuperscript{18} began at 130 °C and appeared to be composed of two parts. The first step occurred between 130 and 270 °C, but was slow up to 210 °C. The second step occurred above 330 °C. Reactions at intermediate temperatures were then carried out in order to establish the desorption mechanism. The final products at 390 °C were Mg$_3$N$_2$ and NaH.
Dolotko et al. tried to rehydride their fully decomposed sample (Mg₃N₂ + NaH). They did this with a pressure of 190 bar hydrogen and 395 °C for 48 hours until the autoclave pressure stabilised. 2.1 wt% hydrogen was taken up; anything lower than this temperature was unsuccessful for hydrogen absorption. After hydrogenation at 395 °C, the products were MgNH along with remaining Mg₃N₂ and NaH.

Earlier, Xiong et al.¹⁹ investigated the opposite reaction, that between Mg(NH₂)₂ and NaH in the molar ratios 1:1, 2:3 and 1:2. These sodium rich ratios are analogous to the Li rich reaction between LiNH₂ and MgH₂. The decomposition of Mg(NH₂)₂ alone was initially investigated and then used as a basis for comparison by adding NaH to the reaction. Mg(NH₂)₂ was synthesised in house by the reaction of NH₃ with milled Mg powder at 300 °C overnight. Both Mg(NH₂)₂ alone and the mixtures were all ball-milled (2 days and 1 day respectively). The addition of NaH to Mg(NH₂)₂ greatly changed the temperature programmed desorption (TPD) features of Mg(NH₂)₂ alone.

Mg(NH₂)₂ when decomposed alone desorbed NH₃ preferentially, whereas when mixed with NaH, the release of H₂ was observed, although NH₃ was still desorbed to a lesser amount. This was in contrast to Dolotko et al. who only observed H₂ desorption with their system.

The temperature at which H₂ was desorbed was lower with the Mg(NH₂)₂-NaH mixtures than those of milled Mg(NH₂)₂ or NaH individually.²⁰ Xiong et al. suggested this indicated a lower kinetic barrier in place for these reactions. It was also suggested that an intermediate of Mg(NH₂)₂-NaH may have formed which reduced the activation energy although the nature of this intermediate was not determined. The 1:1 ratio gave a TPD signal that showed a large
amount of NH₃ desorbed (similar to Mg(NH₂)₂ alone). The increased amount of NaH added to
the subsequent reactions suppressed desorption of NH₃ considerably, but not completely. N₂,
which was observed mainly in the 1:1 reaction, was not seen until 400 °C with additional NaH.
Extra NaH significantly improved the suppression of gases other than H₂. Xiong et al. suggested
the Na stabilised the –N or –NH of the units in the reacting mixture, although exactly what they
mean by this is unclear. This stability seems to have been lost at temperatures above 400 °C.
The reversibility of the Mg-Na-N-H system was investigated.¹⁹ The mixtures were pre-desorbed
to 190 °C followed by temperature programmed absorption (TPA) under H₂ at 11 bar. The 1:1
mixture started to absorb H₂ at slightly above room temperature. The mixtures with increased
NaH absorbed H₂ at higher temperatures. Absorption and desorption cycling was carried out for
all mixtures was obtained at 160, 180 and 200 °C. For Mg(NH₂)₂-NaH (1:1), 1.75 wt% H₂ was
reabsorbed. For 2:3 this increased to 2.17 wt% H₂. The 1:2 mixture gave 1.83 wt% H₂ absorption
and showed that the extra 0.5 moles of NaH did not enhance the storage capacity of the
mixture.

Powder X-ray diffraction (XRD) was used to analyse the 2:3 sample when dehydrogenated at
190 °C. The result was that the Mg(NH₂)₂ and NaH had completely disappeared and an
unidentified phase was seen. No attempt was made to characterise this compound. When put
under H₂ pressure at 140 °C, this phase rehydrided back to Mg(NH₂)₂ and NaH. The same phase
was observed under repeated rehydriding/dehydriding cycles.

As this thesis was being written, a third paper was published. Sheppard et al.²¹ ball milled a 1:1
mixture of NaNH₂ and MgH₂ for 3 hours. After ball-milling the starting materials for 3 hours, the
products were NaNH₂ and MgH₂, as well as a small amount of NaH. This showed a metathesis had already started to occur, although no Mg(NH₂)₂ was visible, which was put down to milling-induced amorphisation.

The ball-milled starting materials were then subjected to heating on a TPD-MS apparatus between room temperature and 370 °C.²¹ 3 main hydrogen desorptions were found to occur up to 330 °C. Hydrogen was desorbed almost immediately on heating and a sizable peak occurred at 140 °C. This was concurrent with a small desorption of ammonia. There were hydrogen desorption peaks at 191 and 230 °C and then desorption of hydrogen increased at 280 °C up to 315 °C where ammonia was again desorbed. Above 335 °C, N₂, NH₃ and H₂ production increased. Sheppard et al. were unsure whether N₂ was desorbed directly from the sample or from the decomposition of NH₃.

Sheppard et al.²¹ then examined the phases present at various temperatures after heating on TPD-MS. They repeated the experiment and halted it at 165, 267, 225 and 370 °C. After heating to 165 °C they found the products to be MgH₂, NaH and NaMgH₃. There were also other broad diffraction peaks they were unable to identify. To improve the crystallinity, the sample was placed under 200 bar hydrogen and heated to 300 °C. After heating the 165 °C sample under hydrogen pressure, some of the unidentified peaks were found to be Mg(NH₂)₂. Other unidentified peaks were found to have disappeared and MgNH peaks had emerged. The authors say the lack of discernible hydrogen evolution during this annealing process suggests that the phase associated with the unidentified peaks converted to MgNH without a detectable hydrogen release.
The sample heated to 267 °C was found to have increased amounts of NaH and NaMgH₃, whilst all MgH₂ and Mg(NH₂)₂ had disappeared. The unidentified phase found at 165 °C was seen again, this time with a peak shift. Sheppard et al. identified this phase as the same as formed by Xiong et al. above.

At 335 °C, the peaks of the unidentified phase were sharper and Mg₃N₂ was first observed as a product. There was no NaMgH₃ present. Upon further investigation of the unidentified phase, they indexed it to a trigonal space group, possibly P3c1, with lattice constants \( a = 6.11 \text{ Å} \) and \( c = 17.90 \text{ Å} \).

The XRD pattern of the sample heated to 370 °C was found to contain Na metal, Mg₃N₂ and another unidentified phase. Sheppard et al. reasoned the Na present was due to the decomposition of NaH under residual gas analysis (RGA) conditions. In order to increase the crystallinity of the second unidentified phase, the ball-milled starting materials were first evacuated at 200 °C for 18 hours before being evacuated at 280 °C for 18 hours. The phase was thought to be monoclinic (space group C2) with lattice parameters of \( a = 13.92 \text{ Å} \), \( b = 3.58 \text{ Å} \), \( c = 12.39 \text{ Å} \) and \( \beta = 115.8^\circ \).

Sheppard et al. then used Fourier transform infrared spectroscopy (FTIR) to examine the conversion between amide, imide and nitride. The sample after heating to 165 °C was found to have broad absorption features between 3150 and 3300 cm\(^{-1}\). Although poorly resolved, the position of the peaks were consistent with those of alkali and alkaline-earth amides. After desorption up to 267 °C, the FTIR spectrum of the sample had lost all features present at 165 °C and a single broad absorption at 3171 cm\(^{-1}\) was present. This was indicative of an imide; either a
new unknown structure of MgNH as the peak did not match those of the known structure of MgNH, or alternatively they suggest the presence of a mixed Na-Mg imide. Further heating of the sample to 335 °C found the peak at 3171 cm$^{-1}$ was sharpened as XRD peaks were found to have similarly sharpened. The FTIR spectrum for 370 °C was devoid of discernible features. This was consistent with the conversion of imide phases to their nitrides. As there was so much Mg$_3$N$_2$ present in the XRD pattern it was not possible to define the unknown phase as nitride, but the absence of N-H bonding in the FTIR spectrum ruled out the possibility of amide or imide being formed.

The mass of hydrogen desorbed from the sample at different temperatures was measured. Up to 165 °C 0.5 wt% H$_2$ was desorbed, this was associated with the formation of a small amount of imide-like phase. Between 165–267 °C a yield of 2.0 wt% H$_2$ was attributed to complete decomposition of Mg(NH$_2$)$_2$ to the imide-like unknown phase. Between 267 and 335 °C 0.8 wt% H$_2$ was desorbed. This was assigned to the decomposition of NaMgH$_3$ and the formation of Mg$_3$N$_2$. A total of 3.3 wt% H$_2$ was desorbed; just over half the total hydrogen in the sample.

Sheppard et al. attempted to quantify the Na content of their two unknown phases using XRD by mixing samples with a known amount of an internal standard. This process deteriorated the already poorly crystalline XRD peaks, making quantification impossible.

In the following chapter sodium amide will be used in place of lithium amide in the reaction with magnesium hydride. In order to establish the best possible ratio between reactants, 4 ratios were investigated. 2NaNH$_2$ + 3MgH$_2$ was investigated (without ball-milling). In order to
compare with $2\text{LiNH}_2 + \text{MgH}_2$, $2\text{NaNH}_2 + \text{MgH}_2$ was investigated. In order to compare reaction schemes with Xiong et al.,$^{19}$ $3\text{NaNH}_2 + 2\text{MgH}_2$ and $\text{NaNH}_2 + \text{MgH}_2$ were investigated. These reactions had the same number of each metal ion present in order to compare $\text{Mg(NH}_2)_2 + \text{NaH}$ based reactions with $\text{NaNH}_2 + \text{MgH}_2$ based reactions, but the amide:hydride ratios were different. The full range of ratios were:

$2\text{NaNH}_2 + 3\text{MgH}_2$; $2\text{NaNH}_2 + \text{MgH}_2$; $3\text{NaNH}_2 + 2\text{MgH}_2$ and $\text{NaNH}_2 + \text{MgH}_2$.

In addition to the reactions above, $\text{NaH} + \text{MgH}_2$ and $\text{Mg(NH}_2)_2 + \text{NaNH}_2$ were also investigated in response to findings from the initial $x\text{NaNH}_2 + y\text{MgH}_2$ reactions.

2. Results

1. $2\text{NaNH}_2 + 3\text{MgH}_2$

   1. Temperature Programmed Desorption-Mass Spectrometry

$\text{NaNH}_2$ and $\text{MgH}_2$ were heated together in a 2:3 ratio. The reaction was initially carried out on a TPD-MS apparatus at a heating rate of $2 \, ^\circ\text{C} \, \text{min}^{-1}$ to $350 \, ^\circ\text{C}$. The investigation into this system initially investigated the desorption characteristics in order to see whether there was any similarity with the Li-Mg-N-H system in desorption of hydrogen gas alone, without any accompanying ammonia.

It can be seen from Figure 4-1 that hydrogen was the only gas observed with no evidence of any ammonia desorbed above the detection limit of the mass spectrometer. The hydrogen trace showed the desorption starting from $120 \, ^\circ\text{C}$ with a number of distinct peaks. The first peak at $150 \, ^\circ\text{C}$ was accompanied by a fluctuation in the temperature trace. The rate of hydrogen
desorption decreased between 150 and 180 °C when the rate increased again quite quickly. This peaked at 255 °C before the rate of desorption diminished. The rate again increased for the third and fourth desorptions at 292 °C. The third desorption peaked at 320 °C. The rate decreased, but a shoulder of hydrogen appeared once the temperature had reached 350 °C. The hydrogen desorption then slowly tailed off during isothermal heating. A comparison between this hydrogen desorption and that of the other $x\text{NaNH}_2 + y\text{MgH}_2$ reactions can be seen in Figure 4-30.

Figure 4-1 TPD-MS analysis of the $2\text{NaNH}_2 + 3\text{MgH}_2$ reaction. The temperature trace is shown in black and the MS traces for $\text{H}_2$ and $\text{NH}_3$ are shown in red and green, respectively.
The temperature trace was then compared to that of the furnace power (Figure 4-2). It was seen that the fluctuation in the temperature trace at 150 °C was accompanied by a fluctuation in the furnace power. The temperature trace had a small increase followed by a small drop. The furnace power showed a decrease in power at 150 °C followed by an increase. This indicated this fluctuation was due to an exothermic event.

Figure 4-2 Furnace power during the TPD-MS analysis of 2NaNH₂ + 3MgH₂ reaction to 350 °C. The furnace power and temperature are shown in blue and black respectively.
2. **Flowing Line Reactions**

As the hydrogen trace showed more than one hydrogen desorption, the reaction was carried out to intermediate temperatures in order to find out more about the reaction mechanism occurring in each temperature regime. The first peak in the TPD trace was observed at 150 °C; therefore the reactants were heated together at 150 °C for 12 hours. This temperature also coincided with the exothermic event identified in the furnace power plot of the TPD-MS apparatus (Figure 4-2). The products identifiable from powder XRD were a mixture of Mg(NH$_2$)$_2$ and NaH, as well as some of the starting material MgH$_2$ (Figure 4-7). A very small amount of NaMgH$_3$ was also present in the product mixture.

In order to investigate the origin of the NaMgH$_3$ observed in the reaction products, the formation of NaMgH$_3$ from reaction of the binary hydrides, NaH and MgH$_2$, was studied. NaH and MgH$_2$ were reacted in a 1:1 ratio under argon at various temperatures. After reaction at 150 °C, the temperature at which NaMgH$_3$ was observed in the reaction 2NaNH$_2$ + 3MgH$_2$, only the starting binary hydrides were observed in the powder XRD pattern. Heating to the higher temperature of 250 °C was required in order to produce NaMgH$_3$, although the starting materials and some Mg were also present (Figure 4-3). The presence of Mg is not unexpected as the decomposition of MgH$_2$ to its constituent elements is kinetically slow. The amount of Mg + MgH$_2$ is comparable to NaH.
Figure 4-3 Powder XRD pattern of NaH + MgH$_2$, heated to 250 °C for 24 hours on a flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaMgH$_3$ (blue tick marks), NaH (black tick marks), MgH$_2$ (green tick marks) and Mg (pink tick marks). $R_{wp} = 9.502$, $R_{exp} = 7.880$, $\chi^2 = 1.5$.

Table 4-1 Summary table of weight percents and mole fractions of products of NaH + MgH$_2$ heated to 250 °C for 24 hours.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight Percent in XRD</th>
<th>Mole Fraction/ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaMgH$_3$</td>
<td>57.55</td>
<td>40.28</td>
</tr>
<tr>
<td>NaH</td>
<td>19.78</td>
<td>28.98</td>
</tr>
<tr>
<td>MgH$_2$</td>
<td>18.29</td>
<td>24.38</td>
</tr>
<tr>
<td>Mg</td>
<td>4.38</td>
<td>6.36</td>
</tr>
</tbody>
</table>

On heating the NaH and MgH$_2$ starting materials to 300 °C all MgH$_2$ had converted to Mg and the amount of NaMgH$_3$ present had dropped off, possibly because of the sublimation of Mg. Reducing the reaction temperature to 275 °C and heating for 18 hours gave the highest proportion of NaMgH$_3$, along with Mg and minimal starting materials still present.
Longer heating of the NaMgH$_3$ at this temperature appeared to result in the decomposition of NaMgH$_3$ to NaH and Mg; the temperature was too low to decompose NaH. Overall, NaMgH$_3$ was shown to form by the direct reaction of NaH with MgH$_2$ at temperatures above 250 °C.

The second desorption event of 2NaNH$_2$ + 3MgH$_2$ peaked at 250 °C, with a 1.6 wt% hydrogen loss. The starting materials were heated at 250 °C for 12 hours. The products were then examined by powder XRD and found to be MgH$_2$ and NaH, along with a greater proportion of NaMgH$_3$ than before. There were also many unidentified peaks (unidentified phase A) in the XRD pattern (Figure 4-7). The positions and relative intensities of these peaks were consistent when the reaction was repeated.

The starting materials were heated for longer (18 and 24 hours) and then ground and annealed in order to attempt to form phase A pure. Quenching was also employed, as well as heating the starting materials to slightly higher and lower temperatures (225 and 275 °C). Attempts to form phase A in high purity were unsuccessful, with a certain amount of starting material always present. In order to investigate the internal bonding of phase A Raman spectroscopy was employed.

3. Raman Spectroscopy

Raman spectroscopy of the products of 2NaNH$_2$ + 3MgH$_2$, heated to 250 °C for 12 hours (unidentified phase A, NaH and MgH$_2$) were compared to Mg(NH$_2$)$_2$, NaNH$_2$ and Li$_2$NH. (Unfortunately no Raman spectra could be found for MgNH in the literature.) The Raman spectrum, Figure 4-4 below, showed peaks present in the imide/amide region.
In the Raman spectrum of the products of this reaction there were two major stretches, each with 2 peaks, at 3177 and 3263 cm\(^{-1}\). When compared to Mg(NH\(_2\))\(_2\) and NaNH\(_2\) (Figure 4-5), the new phase stretches had been displaced downfield from the amide region. It can be seen from Figure 4-6 that the stretches from unidentified phase A were in the same region as lithium imide N-H stretches.

Figure 4-4 Raman spectrum of the N-H region of 2NaNH\(_2\) + 3MgH\(_2\) heated at 250 °C for 12 hours. The phases present were MgH\(_2\), NaH and phase A.
Figure 4-5 Comparison of the Raman spectra of the N-H region of $2\text{NaNH}_2 + 3\text{MgH}_2$ heated at 250 °C for 12 hours, $\text{NaNH}_2$ and $\text{Mg(NH}_2)_2$. 

Figure 4-6 Comparison of the Raman spectra of the N-H region of $2\text{NaNH}_2 + 3\text{MgH}_2$ heated at 250 °C for 12 hours and $\text{LiNH}_2$. 
When the $2\text{NaNH}_2 + 3\text{MgH}_2$ starting materials were heated to 300 °C for 12 hours, there was still evidence of unidentified phase A (Figure 4-7). Phase A was fitted with a Pawley fit. The best fit was for a trigonal unit cell with space group $P–3c1$, $P3c1$, $P63cm$, $P–6c2$ or $P63/mcm$ with lattice parameters $a = 6.1077(7)$ Å and $c = 17.881(3)$. There was also a large amount of $\text{Mg}_3\text{N}_2$ and a continued presence of $\text{NaH}$, $\text{NaMgH}_3$ and $\text{MgH}_2$ starting material. The lattice parameters of the other phases are known and were fitted using a Rietveld refinement. This means a weight percentage of the total mixture could be estimated. As the structural model for phase A is unknown, no estimate of the percentage in the mixture can be made. This is referred to as Pawley in the table (Table 4-2) where weight percent and mole fractions should appear. The fitting of phase A with a Pawley fitting does not alter the ratios of the other products to each other.

The $2\text{NaNH}_2 + 3\text{MgH}_2$ reactants were then heated on the flowing gas line at 350 °C for 12 hours. The products were $\text{NaH}$ and $\text{Mg}_3\text{N}_2$ (Figure 4-7). There was also a large amount of Na present. There was no evidence of phase A at this temperature.

$\text{Mg}_3\text{N}_2$ and Na were the fully dehydrided products of this reaction of $2\text{NaNH}_2 + 3\text{MgH}_2$. The overall reaction could be expressed as:

\[
\text{Equation 4-1} \quad 2\text{NaNH}_2 + 3\text{MgH}_2 \rightarrow \text{Mg}_3\text{N}_2 + 2\text{Na} + 5\text{H}_2
\]
Figure 4-7 Stack plot of powder XRD patterns of $2\text{NaNH}_2 + 3\text{MgH}_2$ heated to 150 °C (black), 250 °C (blue), 300 °C (green) and 350 °C (red). The individual XRD patterns can be found in the appendix.
Table 4-2: Summary table of weight percents and mole fractions of products of 2NaNH\(_2\) + 3MgH\(_2\) from powder XRD shown in Figure 4-7.

<table>
<thead>
<tr>
<th>Phase</th>
<th>150</th>
<th>250</th>
<th>300</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight %</td>
<td>Mole Fraction</td>
<td>Weight %</td>
<td>Mole Fraction</td>
</tr>
<tr>
<td>MgH(_2)</td>
<td>44.34</td>
<td>49.58</td>
<td>34.95</td>
<td>37.57</td>
</tr>
<tr>
<td>NaH</td>
<td>32.27</td>
<td>38.70</td>
<td>42.31</td>
<td>49.72</td>
</tr>
<tr>
<td>Mg(NH(_2))(_2)</td>
<td>18.82</td>
<td>9.54</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>NaNH(_2)</td>
<td>3.40</td>
<td>2.60</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>NaMgH(_3)</td>
<td>1.17</td>
<td>0.58</td>
<td>22.74</td>
<td>12.71</td>
</tr>
<tr>
<td>Mg(_3)N(_2)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Phase A</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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</tr>
</tbody>
</table>
| Na         | NA     | NA      | NA     | NA     | NA       | NA       | 13.51    | 34.21         

2NaNH\(_2\) + 3MgH\(_2\)
4. Rehydriding Studies

$2\text{NaNH}_2 + 3\text{MgH}_2$ were heated together at 250 °C for 12 hours in an attempt to maximise the amount of new phase A present. This sample was then tested on an intelligent gravimetric analyser (IGA) in order to assess its ability to rehydride. The sample was heated to 200 °C under 18 bar hydrogen for 100 hours. Upon heating, the sample immediately started to take up hydrogen. After rehydriding it was found to have absorbed 1.82 wt% H$_2$ (Figure 4-8). This was in comparison to a theoretical uptake of 2.6 wt%. The uptake was not quite complete when the reaction was stopped. Although the hydrogen uptake was not complete, substantial rehydriding had occurred; full rehydriding may only have been possible after a significantly longer time, higher hydrogen pressure or different temperature.

![Graph showing mass gain over time](image)

Figure 4-8 Mass gain of the products of $2\text{NaNH}_2 + 3\text{MgH}_2$ when heated to 250 °C for 2 hours, rehydried under 18 bar hydrogen at 200 °C for 100 hours.
5. Discussion

The first stage of this multi-step reaction appeared to be an exothermic metathesis reaction, although it was slow and incomplete under the conditions examined here. The products from heating to 150 °C (Figure 4-7) were a mixture of MgH₂ and a small amount of NaNH₂ starting materials as well as Mg(NH₂)₂ and NaH products. These are products that would be present had a salt metathesis reaction occurred. MgH₂ starting material would also be expected to be present, as it was in excess for the metathesis (Equation 4-2).

\[
\text{Equation 4-2} \quad 2\text{NaNH}_2 + 3\text{MgH}_2 \rightarrow \text{Mg(NH}_2\text{)}_2 + 2\text{NaH} + 2\text{MgH}_2
\]

A salt methathesis reaction between a group one amide LiNH₂ and MgH₂ has been shown to occur previously,²² before going on to react further. A mixture of 2LiNH₂ + MgH₂ was heated to 220 °C under 100 bar H₂ for 2 hours in order to establish the reaction mechanism. The powder XRD after this experiment showed the presence of Mg(NH₂)₂ and LiH, as well as the starting materials LiNH₂ and MgH₂. This is analogous to our metathesis observed. Thermodynamics suggests the enthalpy of formation of Mg(NH₂)₂ plus NaH is more exothermic than that of NaNH₂ and MgH₂ (Table 4–3). The addition of heat to this reaction was enough to surmount the activation energy and cause the metathesis to take place.
Table 4-3 Enthalpy of formation values for NaNH$_2$, MgH$_2$, Mg(NH$_2$)$_2$ and NaH.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta_f H^\circ$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNH$_2$</td>
<td>-123.8$^{23}$</td>
</tr>
<tr>
<td>MgH$_2$</td>
<td>-75.3</td>
</tr>
<tr>
<td>Mg(NH$_2$)$_2$</td>
<td>-325.0$^{26}$</td>
</tr>
<tr>
<td>NaH</td>
<td>-56.3</td>
</tr>
</tbody>
</table>

\[
\Delta H^\circ = \left( \Delta_f H^\circ(\text{Mg(NH}_2)_2) + 2\Delta_f H^\circ(\text{NaH}) \right) - \left( 2\Delta_f H^\circ(\text{NaNH}_2) + \Delta_f H^\circ(\text{MgH}_2) \right)
\]

\[
\Delta H^\circ = (-325.0 + (2 \times -56.3)) - ((2 \times -123.8) - 75.3)
\]

\[
\Delta H^\circ = -114.7 \text{ kJ mol}^{-1}
\]

Sheppard et al.$^{21}$ ball-milled NaNH$_2$ + MgH$_2$ and found a metathesis reaction occurred. They found NaH appeared in their XRD pattern, however Mg(NH$_2$)$_2$ was not observed due to amorphisation.

The salt metathesis reaction can be identified as the exothermic event that was observed in the furnace power (Figure 4-2). The metathesis involved the exchange of [NH$_2$]$^-$ and H$^-$ between NaNH$_2$ and MgH$_2$. Theoretically there should not be any hydrogen desorption associated with the metathesis. The relatively small hydrogen desorption (0.11 wt%) that was observed in the TPD-MS trace was possibly due to the increase in temperature caused by the exothermic nature of the metathesis. This could have raised the temperature enough locally in the sample to promote hydrogen release. The hydrogen desorption was unlikely to have occurred from the starting materials. The decomposition temperature of sodium amide is 210 °C and this would not release only hydrogen; magnesium hydride is well documented to decompose at 280–
300 °C very slowly, with the release of hydrogen. The newly formed magnesium amide decomposes with the release of ammonia at 350 °C and sodium hydride decomposes with the release of hydrogen at above 400 °C. The hydrogen release at 150 °C was likely to have been from the reaction of some of these materials together.

Sheppard et al. also observed hydrogen release from their 2NaNH$_2$ + 3MgH$_2$ reaction below 165 °C. This was accounted for by the formation of the imide-like phase.

Both Mg(NH$_2$)$_2$ and MgH$_2$ were present after the metathesis. It might be expected they would react together with further heating, cf. LiNH$_2$-LiH, to form MgNH.

Nakamori et al., having successfully formed Mg(NH$_2$)$_2$, investigated the reaction between Mg(NH$_2$)$_2$ and MgH$_2$ in 1:1 and 1:2 ratios.

They expected the reactions to proceed as follows:

\[
\text{Equation 4-3} \quad \text{Mg(NH}_2\text{)}_2 + \text{MgH}_2 \rightarrow 2\text{MgNH} + 2\text{H}_2 \\
\]

\[
\text{Equation 4-4} \quad \text{Mg(NH}_2\text{)}_2 + 2\text{MgH}_2 \rightarrow \text{Mg}_3\text{N}_2 + 4\text{H}_2
\]

These reactions are analogous to the LiNH$_2$-LiH system. However, from TG data it could be seen that weight loss reactions occurred at 357 °C and 447–477 °C. The weight losses were approximately 24 wt% and 16 wt% for Mg(NH$_2$)$_2$ + MgH$_2$ and Mg(NH$_2$)$_2$ + 2MgH$_2$, respectively. These mass losses were much greater than expected for the reactions above (Equation 4-3 and

---

* Mg(NH$_2$)$_2$ was formed by exposing MgH$_2$ (and Mg present in starting material) to 5 bar of ammonia. This was heated to 330-380 °C for 1 week. Mg(NH$_2$)$_2$ was optimally formed at 340 °C.
Equation 4-4). (4.9 wt% and 7.4 wt%, respectively.) It was suggested that the release of ammonia along with hydrogen would give rise to these increased mass losses. As the temperature at which the mass losses were observed were the same as for the Mg(NH$_2$)$_2$ NH$_3$ releasing decomposition to form MgNH, it can be seen that the addition of MgH$_2$ to Mg(NH$_2$)$_2$ did not result in any reaction between the amide and hydride. Nakamori et al. reasoned the slow kinetics between MgH$_2$ and ammonia in order to form Mg(NH$_2$)$_2$ was the cause of the lack of interaction. This indicated the reaction of MgH$_2$ and ammonia was in the order of days, unlike LiH and ammonia which is ultra fast (25ms), and therefore unlikely to result in the same kinetic products.

Leng et al.$^{24}$ ball-milled Mg(NH$_2$)$_2$† with 2MgH$_2$ for two hours. The reaction mixture was then heated up to 500 °C. Hydrogen was observed being desorbed from 80 °C, but there was no peak in the desorption until 415 °C. The low desorption temperature was said to be due to the low decomposition temperature of the Mg(NH$_2$)$_2$ starting material. Leng et al. said this was probably due to the ball-milling. The wide temperature range for the hydrogen desorption was said to be due to the slow reaction between MgH$_2$ and NH$_3$. This was regarded as disappointing by Leng et al. as a major desorption of hydrogen gas was not observed until a higher temperature then the LiNH$_2$ + LiH system to which Mg(NH$_2$)$_2$ + 2MgH$_2$ was compared.

In order to build upon the failed attempts at a reaction between Mg(NH$_2$)$_2$ and MgH$_2$ by Nakamori et al.,$^7$ Hu et al.$^{25}$ ball-milled Mg(NH$_2$)$_2$‡ in a 1:1 ratio with MgH$_2$. Hydrogen was found

---

† Mg(NH$_2$)$_2$ was formed by heating ball-milled MgH$_2$ under an ammonia atmosphere of 4 bar.
‡ Hu et al. formed Mg(NH$_2$)$_2$ by reacting Mg powder with 8.3 bar ammonia at 300 °C.
to be the only gaseous product generated during ball-milling. The reactants were ball-milled for up to 72 h. Up to 5 h of ball-milling no gas was detected. Only with further milling, and therefore a greater decrease in particle size, did any detectable solid state reaction occur.

The reactants, ball-milled for different lengths of time, were then exposed to heating on a TPD-MS apparatus. The sample milled for 5 h released hydrogen above 200 °C whereas after milling for 11 h or longer, the hydrogen started to desorb as low as 65 °C.

Hu et al.\textsuperscript{26} found their ball-milling of Mg(NH\textsubscript{2})\textsubscript{2} + MgH\textsubscript{2} in a 1:1 ratio was successful in releasing only hydrogen. Hu et al.\textsuperscript{25} continued their work on this system by mixing equimolar amounts of H\textsuperscript{δ+} in amide and H\textsuperscript{−} in hydride in a 1:1 ratio i.e. Mg(NH\textsubscript{2})\textsubscript{2} + 2MgH\textsubscript{2}. The mixture of starting materials was initially milled for 72 h at room temperature. The pressure inside the ball mill increased with time. The gas responsible for the pressure build-up was found to be pure hydrogen. Hydrogen release started after 2 h and accelerated after 5 h. The rate of release slowed after 20 h. As neither starting material released hydrogen when ball-milled alone, the hydrogen release must have been from the reaction between the Mg(NH\textsubscript{2})\textsubscript{2} and MgH\textsubscript{2}. The delayed time before release was due to the particle sizes of the reactants being too large. After 72 h ball-milling all the hydrogen was released from the starting materials. From FTIR and XRD the phases present throughout ball-milling where found first to be Mg(NH\textsubscript{2})\textsubscript{2}, followed by MgNH and finally Mg\textsubscript{3}N\textsubscript{2}. The enthalpy of formation of Mg(NH\textsubscript{2})\textsubscript{2} was found to be \(-325\) kJmol\textsuperscript{−1}. In comparison to work carried out previously by Hu et al.,\textsuperscript{26} it can be seen the additional MgH\textsubscript{2} caused the reaction mixture to dehydride fully and form Mg\textsubscript{3}N\textsubscript{2}. 
NaMgH$_3$ was also found to be present, although in a very small amount (as shown in Figure 7-1). The formation of NaMgH$_3$ has been reported to occur at 480 °C when NaH was heated with Mg metal in equimolar amounts for 24 hours under 10 bar H$_2$ (Equation 4-5).$^{27}$ Clearly the conditions described here were beneficial for the formation of NaMgH$_3$ at a radically lower temperature than previously reported. NaMgH$_3$ was also observed by Sheppard et al.$^{21}$ after ball-milling NaNH$_2$ + MgH$_2$ and heating to 160 °C. The unit cell published by Bouamrane et al.$^{27}$ is shown in Figure 4-9. It is orthorhombic, space group $Pnma$ and lattice parameters of $a = 5.4634$ Å, $b = 7.703$ Å and $c = 5.4108$ Å.

Equation 4-5

\[ \text{NaH} + \text{Mg} + \text{H}_2 \rightarrow \text{NaMgH}_3 \]

Figure 4-9 Crystal structure of NaMgH$_3$. Sodium is shown in blue, magnesium sites in green and hydrogen in grey. The unit cell is shown in black.$^{27}$
Shortly after this work, Ronnebro et al.\textsuperscript{28} formed NaMgH\textsubscript{3} by heating different ratios of ground NaH and MgH\textsubscript{2} in a pressed tablet up to 380 °C under 70 bar H\textsubscript{2} for 1 week. NaMgH\textsubscript{3} only formed when a 1:1 ratio of starting materials was heated to 350 °C under 70 bar H\textsubscript{2} for a few hours.

Several years later Ikeda et al.\textsuperscript{29} were the first group to synthesise NaMgH\textsubscript{3} by ball-milling NaH and MgH\textsubscript{2}. This occurred at 300 °C under H\textsubscript{2} for 20 h at room temperature. The crystal structure was found to be thermally stable to 300 °C. They also attempted to form LiMgH\textsubscript{3}, however under these conditions, it was not possible.

Ikeda et al.\textsuperscript{30,31} continued their work on NaMgH\textsubscript{3} by investigating the reversibility of hydriding and dehydriding the material. The sample was formed as above by ball-milling, and was then heat-treated at 300 and 500 °C, under 10 bar H\textsubscript{2} for 3 hours. The structure here was stable to 500 °C under 10 bar H\textsubscript{2}. Upon heating to 400 °C under 10 bar He, the mass loss was found to be 5.8 ± 0.2 wt% within 8 minutes. This mass coincided with the hydrogen content of NaMgH\textsubscript{3}.

Using powder XRD the dehydriding process was found to proceed along the following steps:

\begin{align*}
\text{Equation 4-6} & \quad \text{NaMgH}_3 \rightarrow \text{NaH} + \text{Mg} + \text{H}_2 \\
\text{Equation 4-7} & \quad \text{NaH} + \text{Mg} + \text{H}_2 \rightarrow \text{Na} + \text{Mg} + \frac{3}{2}\text{H}_2
\end{align*}

Rehydriding was possible by heating up the elemental Na and Mg to 400 °C for 3 hours under 10 bar of hydrogen.
The same group continued their work\textsuperscript{32} and found the charge density distributions\textsuperscript{5} indicated that NaMgH\textsubscript{3} contained two hydrogen anions on different crystallographic sites.

Wu et al.\textsuperscript{33} found the hydriding/dehydriding of NaMgH\textsubscript{3} could occur at temperatures as low as 350 °C, an improvement of 50 °C compared to Ikeda et al.\textsuperscript{30}

It is possible that NaMgH\textsubscript{3} could be formed under the conditions used in $x$NaNH\textsubscript{2} + $y$MgH\textsubscript{2} reactions from the decomposition of a mixed Na-Mg amide formed. Alternatively, NaMgH\textsubscript{3} may be formed from the diffusing of Na\textsuperscript{+} from NaNH\textsubscript{2} into MgH\textsubscript{2}, therefore forming NaMgH\textsubscript{3} as an intermediate, or from a direct reaction between NaH, formed from the metathesis, and MgH\textsubscript{2}, starting material.

The peaks from phase A present after heating to 250 °C, in Figure 4-7, were found to be similar to those previously reported by Xiong et al.,\textsuperscript{4} after heating a ball-milled 2Mg(NH\textsubscript{2})\textsubscript{2} + 3NaH mixture to 190 °C and recently indexed by Sheppard et al.\textsuperscript{21} This phase identified by Xiong et al.\textsuperscript{4} rehydrided to Mg(NH\textsubscript{2})\textsubscript{2} and NaH.

Xiong et al.\textsuperscript{4} did not attempt to index their XRD pattern and therefore identify the material involved. Our attempts to index the peaks have so far suggested a trigonal unit cell with space group $P\overline{3}c1$, $P3c1$, $P63cm$, $P\overline{6}c2$ or $P63/mcm$ with lattice parameters $a = 6.1077(7)$ Å and $c = 17.881(3)$ Å. Since our indexing of the phase, Sheppard et al.\textsuperscript{21} published their lattice parameters of the same phase. They also indexed it to a trigonal unit cell with possible space group $P3c1$ and lattice constants $a = 6.11$ Å and $c = 17.90$ Å. These parameters matched very closely with ours.

\textsuperscript{5} Charge density distributions found from maximum entropy method (MEM)/Rietveld method from synchrotron XRD.
It might be expected that an amide minus hydrogen would result in an imide, as is the case with LiNH₂ + LiH or 2LiNH₂ + MgH₂. In this case, with 2NaNH₂ + 3MgH₂, a mixed Na-Mg imide could be formed. There was also a lack of nitrogen present in crystalline form in the identified products, along with the lack of ammonia, NH₃, detected. However, in the literature there are no known mixed Na-Mg-cation imides or amides, sodium imide or indeed any sodium containing imides. There was no Na₃N formed at any point during any of these reactions. Na₃N has only been formed with great difficulty by passing electrical discharges through sodium under low nitrogen pressure or more recently by plasma-assisted synthesis. Moldenhauer and Mottig disagreed with Wattenberg et al. and suggested that evaporating a mixture of sodium azide (NaN₃) and Na could form sodium nitride. Its formation has not been observed under conventional synthesis conditions.

The Raman spectroscopy undertaken (Figure 4-4) showed clear evidence of nitrogen present in the products, due to the presence of peaks in the N-H region of the spectrum. This must have been present in phase A and any amorphous products present, as neither of the known products (NaH and MgH₂) contained nitrogen.

The release of hydrogen from the system, as well as the position of the N-H stretches in the N-H region of the Raman spectrum, point to the formation of an imide rather than a mixed Na-Mg amide. The imide could be either an unknown polymorph of MgNH or a new mixed Na-Mg imide; these suggestions concur with the conclusions of Sheppard et al. Sodium imide is unlikely to be formed, as it is unknown in the literature. The two peaks for each of the main stretches were most likely due to two different N-H environments within the phase. If a mixed Na-Mg
imide was formed, and both cations were bonded to N-H groups, the twin peaks in the Raman spectrum could be accounted for.

By charge balancing the possible imide along with the excess hydrides, it was possible to suggest the following idealised reaction (Equation 4-8):

Equation 4-8  \[ \text{Mg(NH}_2\text{)}_2 + 2\text{NaH} + 2\text{MgH}_2 \rightarrow 2\text{Mg}_{(1-x)}\text{Na}_{2x}\text{(NH)} + (1+2x)\text{MgH}_2 + (2-4x)\text{NaH} + 2\text{H}_2 \]

The ratio of moles of MgH\textsubscript{2} to NaH observed was 7:9. This could be used to suggest a value for \( x \).

For \( (1+2x)/(2-4x) = 7/9 \), \( x = 0.11 \). The mixed imide would have the possible formula Mg\textsubscript{0.89}Na\textsubscript{0.22}(NH\textsubscript{2}), this approximately equates to Mg\textsubscript{9}Na\textsubscript{2}(NH\textsubscript{10}.

Dolotko et al.\textsuperscript{18} heated their 2NaNH\textsubscript{2} + 3MgH\textsubscript{2} mixture to 250 °C and found decreased amounts of NaH, MgH\textsubscript{2} and Mg(NH\textsubscript{2})\textsubscript{2} (as we did); however, Dolotko et al. had an increase in the intensities of the XRD peaks for NaMgH\textsubscript{3} and Mg\textsubscript{3}N\textsubscript{2}. 250 °C is a lower temperature than we found the formation of Mg\textsubscript{3}N\textsubscript{2} to occur. They made no mention of finding a new phase at this temperature.

Dolotko et al.\textsuperscript{18} also investigated the analogous reaction 2LiNH\textsubscript{2} + 3MgH\textsubscript{2}. After heating to 250 °C, LiH (a metathesis product) was present along with Li\textsubscript{2}Mg(NH\textsubscript{2})\textsubscript{2}, Mg\textsubscript{3}N\textsubscript{2} and unreacted starting material MgH\textsubscript{2}. These products are equivalent to those found by our 2NaNH\textsubscript{2} + 3MgH\textsubscript{2} reaction heated to 250 °C.

Mg\textsubscript{3}N\textsubscript{2} first appeared as a product of our reaction after heating to 300 °C (Figure 4-7). There was no longer MgH\textsubscript{2} starting material present. As mentioned above, nitrides can result from the
reaction of an appropriate imide and a hydride. The Mg$_3$N$_2$ was thought to be present due to decomposition of the mixed imide upon reaction with excess MgH$_2$. This was backed up by the observation of continued hydrogen desorption (Equation 4-9).

Equation 4-9   \[
2\text{Mg}_{(1-x)}\text{Na}_{2x}(\text{NH}) + (1+2x)\text{MgH}_2 + (2-4x)\text{NaH} \rightarrow \text{Mg}_3\text{N}_2 + 2\text{NaH} + 2\text{H}_2
\]

On further heating their sample, Dolotko et al. found a decreased amount of MgH$_2$ and an increased proportion of LiH and Mg$_3$N$_2$.

Sheppard et al.\textsuperscript{21} found the products after heating 2NaNH$_2$ + 3MgH$_2$ to 335 °C to be Mg$_3$N$_2$, NaH and the possible mixed imide. No MgH$_2$ or NaMgH$_3$ was present.

In Figure 4-7, the products from our reaction at 350 °C were Mg$_3$N$_2$ and Na. The Na present was thought to be due to the decomposition of NaH (Equation 4-10). The long tail off of hydrogen at 350 °C in Figure 4-1 is consistent with this. The decomposition of NaH to its elemental form has been reported to occur at temperatures around 425 °C.\textsuperscript{20} It is possible the conditions that were present during this reaction may be conducive to lowering this temperature, to just below 350 °C. Further investigations by us showed NaH alone to decompose to Na and hydrogen under flowing argon gas (zero hydrogen partial pressure) at 350 °C (Equation 4-10).

Equation 4-10   \[
2\text{NaH} \rightarrow 2\text{Na} + \text{H}_2
\]
Sheppard et al.\textsuperscript{21} also found Na present after heating their sample to 370 °C and also put it down to the decomposition of NaH to Na.

Dolotko et al.\textsuperscript{18} heated a sample of 2NaNH\textsubscript{2} + 3MgH\textsubscript{2} to 395 °C. They found the final products were Mg\textsubscript{3}N\textsubscript{2} and NaH along with desorbed H\textsubscript{2}. After ball-milling, they heated their starting materials to 147 °C, and found products similar to ours: no NaNH\textsubscript{2}, decreased MgH\textsubscript{2} and newly formed Mg(NH\textsubscript{2})\textsubscript{2}, NaH and NaMgH\textsubscript{3}. They also observed the metathesis reaction. Their mixture was then heated to 320 °C and the products were found to be an increased amount of Mg\textsubscript{3}N\textsubscript{2} and decreased amounts of MgH\textsubscript{2} and NaMgH\textsubscript{3}.

The overall reaction scheme for our 2NaNH\textsubscript{2} + 3MgH\textsubscript{2} heated on a flowing line is shown below, in Table 4-4.

Table 4-4 Overall reaction scheme of 2NaNH\textsubscript{2} + 3MgH\textsubscript{2} heated to various temperatures. The products from each temperature are shown, the temperature at which new phases form and the lattice parameters of the new phases.

<table>
<thead>
<tr>
<th>Temp/°C</th>
<th>Reaction Scheme</th>
<th>Products</th>
<th>New Phase(s)</th>
<th>Lattice Parameters/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>2NaNH\textsubscript{2} + 3MgH\textsubscript{2} → Mg(NH\textsubscript{2})\textsubscript{2}, NaH, NaMgH\textsubscript{3}, MgH\textsubscript{2}</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>Mg(NH\textsubscript{2})\textsubscript{2} + 2NaH + 2MgH\textsubscript{2} → MgH\textsubscript{2}, NaH, H\textsubscript{2}</td>
<td>Mg\textsubscript{3}N\textsubscript{2}, Mg\textsubscript{3}N\textsubscript{2}(NH)</td>
<td>a = 6.1382(4), c = 17.945(19)</td>
<td></td>
</tr>
<tr>
<td>275</td>
<td>NaH + MgH\textsubscript{2}</td>
<td>NaMgH\textsubscript{3}</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>300</td>
<td>2Mg\textsubscript{2}(1-x)Na\textsubscript{2x}(NH) + (1+2x)MgH\textsubscript{2} + (2–2x)NaH → Mg\textsubscript{3}N\textsubscript{2}, NaH, H\textsubscript{2}</td>
<td>Mg\textsubscript{3}N\textsubscript{2}, Mg\textsubscript{3}N\textsubscript{2}(NH)</td>
<td>a = 6.1077(7), c = 17.881(3)</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>NaH → Na, H\textsubscript{2}</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

Dolotko et al.\textsuperscript{18} also investigated the reversibility of this reaction and found an uptake of 2.1 wt% on heating Mg\textsubscript{3}N\textsubscript{2} and NaH to 395 °C for 48 hours. This was carried out under 190 bar
hydrogen, in contrast to our reaction at 18 bar. The products of Dolotko et al. were MgNH, Mg$_3$N$_2$ and NaH. 2.1 wt% hydrogen uptake was consistent with the products found, as the theoretical mass gain for Equation 4-11 is 2.7 wt%.

\begin{equation}
\text{Equation 4-11} \hspace{1cm} \text{Mg}_3\text{N}_2 + 2\text{NaH} + 2\text{H}_2 \rightarrow 2\text{MgNH} + 2\text{NaH} + \text{MgH}_2
\end{equation}

The continued presence of Mg$_3$N$_2$ showed the reaction had not managed to complete the first stage of rehydrogenation. The ideal equation for the first step of rehydrogenation is shown in Equation 4-12.

\begin{equation}
\text{Equation 4-12} \hspace{1cm} \text{Mg}_3\text{N}_2 + 2\text{H}_2 \leftrightarrow 2\text{MgNH} + \text{MgH}_2
\end{equation}

Our hydrogen uptake value was similar to Dolotko et al. although Dolotko et al. were rehydriding from Mg$_3$N$_2$, whereas we attempted the rehydriding of the Mg$_{(1-x)}$Na$_{2x}$(NH) intermediate. It was thought longer heating and greater pressure would be required in order to complete our rehydrogenation forming Mg(NH$_2$)$_2$ from MgNH. Dolotko et al. may have further problems as Kojima et al.\textsuperscript{38} investigated the hydriding of Mg$_3$N$_2$ by ball-milling under 10 bar H$_2$ at room temperature. Mg$_3$N$_2$ only had a 0.5 wt% uptake under these conditions. This was put down to small heats of formation.\textsuperscript{39} These were $-2$ and $-43$ kJ mol$^{-1}$ H$_2$, respectively from first principle calculations (Equation 4-12 and Equation 4-13). It can be suggested that if Kojima et al.
increased the pressure of the hydrogen gas, a more successful hydrogen uptake may have been achieved.

Equation 4-13 \[ 2\text{MgNH} + 2\text{H}_2 \leftrightarrow \text{Mg(NH}_2\text{)}_2 + \text{MgH}_2 \]

It was seen in the case of Dolotko et al. that additional pressure did not force the rehydrogenation any further than ours. Their problem appeared to be reforming an intermediate that could promote further hydrogenation. If the reaction was fully reversible back to \( \text{Mg(NH}_2\text{)}_2 \), the theoretical hydrogen uptake value would be 5.1 wt% (Equation 4-14).

Equation 4-14 \[ \text{Mg}_3\text{N}_2 + 4\text{H}_2 + 2\text{NaH} \rightarrow \text{Mg(NH}_2\text{)}_2 + 2\text{MgH}_2 + 2\text{NaH} \]

It is interesting to note that attempts by Dolotko et al. to rehydride the \( \text{Mg}_3\text{N}_2 \) and LiH products from the analogous \( 2\text{LiNH}_2-3\text{MgH}_2 \) system were not successful. They suggested the presence of NaH is important to the rehydriding of \( \text{Mg}_3\text{N}_2 \) as no NaH was present when rehydriding failed with LiH.

Xiong et al.\textsuperscript{19} rehydrided their unidentified phase under \( \text{H}_2 \). The products were \( \text{Mg(NH}_2\text{)}_2 \) and NaH, which were their original starting materials. Evidence (Table 4–3) suggests \( \text{Mg(NH}_2\text{)}_2 \) and NaH represent a lower energy state than NaNH\textsubscript{2} and MgH\textsubscript{2}. It is well documented that \( \text{Li}_2\text{Mg(NH)}_2 \) rehydrides to \( \text{Mg(NH}_2\text{)}_2 \) and LiH, whether formed from \( 2\text{LiNH}_2 + \text{MgH}_2 \) or \( \text{Mg(NH}_2\text{)}_2 + 2\text{LiH} \).\textsuperscript{4,5,6}
It was published by Juza et al.\textsuperscript{40} that Mg(NH\textsubscript{2})\textsubscript{2} could be formed directly from the reaction of Mg\textsubscript{3}N\textsubscript{2} under 10 bar NH\textsubscript{3} at 350 °C for 4–6 weeks.\textsuperscript{41} If this reaction could be speeded up, it would ensure the full reaction could be reversed and make an excellent fully reversible hydrogen storage solution.

Cycling of the sample would be beneficial in order to clarify whether the sample maintains its level of dehydriding/rehydriding.

2. 2NaNH\textsubscript{2} + MgH\textsubscript{2}

1. Temperature Programmed Desorption-Mass Spectrometry

Having investigated the magnesium rich reaction 2NaNH\textsubscript{2} + 3MgH\textsubscript{2}, our interest turned to a direct comparison of 2NaNH\textsubscript{2} + MgH\textsubscript{2} with 2LiNH\textsubscript{2} + MgH\textsubscript{2}, therefore, 2NaNH\textsubscript{2} + MgH\textsubscript{2} was heated in order to establish whether a mixed sodium-magnesium imide could again be formed. NaNH\textsubscript{2} and MgH\textsubscript{2} were heated together in a 2:1 ratio. The reaction was initially carried out on a TPD-MS apparatus, at a heating rate of 2 °C min\textsuperscript{−1} to 350 °C.

It can be seen from Figure 4-10 that hydrogen was the majority gas desorbed from the reaction of 2NaNH\textsubscript{2} and MgH\textsubscript{2}. There appeared to be a very small amount of ammonia desorbed at the peak of the hydrogen desorption. The hydrogen desorption peaked at three different temperatures; 155, 234 and 316 °C. The desorption started at about 115 °C when a small amount of hydrogen release occurred. This peaked at 155 °C and was accompanied by a fluctuation in the temperature trace. The rate of hydrogen desorption then decreased until 180 °C when the rate of release increased again up to a peak at 234 °C. This peak was the major
desorption event. Again, the rate of desorption decreased, until 316 °C when a small increase occurred, followed by a long slow tail off as the isothermal heating region commenced. A comparison between this hydrogen desorption and that of the other $x\text{NaNH}_2 + y\text{MgH}_2$ reactions can be seen in Figure 4-30.

![Figure 4-10 TPD-MS analysis of the 2$\text{NaNH}_2 + \text{MgH}_2$ reaction. The temperature trace is shown in black and the MS traces for $\text{H}_2$ and $\text{NH}_3$ are shown in red and green, respectively.](image)

The temperature trace was then compared to that of the furnace power. It could be seen that the fluctuation in the temperature trace at 155 °C was echoed in the furnace power at the same temperature (Figure 4-10). The temperature trace showed an increase followed by a small drop.
The power of the furnace dropped first and was followed by a rise. This was indicative of an exothermic event occurring within the sample. This occurred at the same temperature as for $2\text{NaNH}_2 + 3\text{MgH}_2$.

![Graph showing furnace power and temperature over time](image)

Figure 4-11 Furnace power during the TPD-MS analysis of $2\text{NaNH}_2 + \text{MgH}_2$ reaction. The furnace power and temperature are shown in blue and black respectively.

After heating in the TPD-MS apparatus the products were analysed by powder XRD and found to be Na, NaH, a little MgNH and NaNH$_2$ remaining starting material. The majority of the peaks were due the phase designated the Na-Mg imide.
In order to quantify the amount of hydrogen released at each desorption event, thermogravimetric analysis (TGA) was performed.

2. Thermogravimetric Analysis

The $2\text{NaNH}_2 + \text{MgH}_2$ starting materials were heated on a TGA-MS apparatus, at a rate of 2 °C min$^{-1}$ to 350 °C where heating ceased. It was found that only hydrogen gas was desorbed (Figure 4-12). No ammonia was seen above the detection limit of the mass spectrometer. The hydrogen desorption occurred in 3 peaks as in the TPD-MS experiment (Figure 4-10). The peaks of hydrogen desorption occurred at 182, 246 and 328 °C. The initial hydrogen desorption occurred roughly 30 °C later on the TGA-MS apparatus than on the TPD-MS apparatus. The reaction was again exothermic and the accompanying hydrogen release was large and sharp. What had been the main desorption on TPD-MS was comparatively small on TGA-MS, although it did occur at the same temperature.

The overall mass loss from this experiment was 3.7 wt %, very close to the theoretical mass loss value of 3.9 wt % for the imide product (Equation 4-15).

\[
\text{Equation 4-15} \hspace{1cm} 2\text{NaNH}_2 + \text{MgH}_2 \rightarrow \text{MgNa}_{2y} (\text{NH})_{1+y} + (2-y)\text{NaH} + 0.5y\text{MgH}_2 + 1.5\text{H}_2
\]

**In this case the mixed cation imide formula has been recast as $\text{Mg}_{[1-y]}\text{Na}_{2y} (\text{NH})_{1+y}$ as it is the only magnesium containing product.**
The desorption of $2\text{NaNH}_2 + \text{MgH}_2$ makes an interesting comparison with that of $\text{Mg(NH}_2\text{)}_2 + 2\text{NaH}$ as they have equivalent amounts of each ion in the reaction. (Background and formation of $\text{Mg(NH}_2\text{)}_2$ is in section 4.2.1.5.) The reaction $\text{Mg(NH}_2\text{)}_2 + 2\text{NaH}$ was carried out on a TGA-MS apparatus (Figure 4-13). The reaction was heated up to 350 °C. There was hydrogen desorbed along with a small rise in ammonia from 315 °C. It was seen that hydrogen was desorbed in two steps. The initial desorption started slowly at 145 °C. The rate of hydrogen desorption increased at 170 °C up to a peak at 234 °C. The rate of desorption decreased to 261 °C before increasing up to about 306 °C. The rate of desorption then dropped off rapidly.
3. Flowing Line Reactions

In order to investigate the first step in the observed reaction, a flowing line reaction was carried out by heating 2NaNH$_2$ + MgH$_2$ to 150 °C for 12 hours. This was at the same temperature as the first, small hydrogen desorption in the TPD-MS data and the major desorption even in the TGA data. The products from this reaction were found to be starting materials, NaNH$_2$ and MgH$_2$, as well as NaH and Mg(NH$_2$)$_2$ (Figure 4-14). There were also a few new unidentified peaks (phase B) which did not match NaMgH$_3$, NaOH, MgO, Na$_2$O, MgNH, Na, Mg or the trigonal phase assigned as a sodium-magnesium imide (phase A).
Figure 4-14 Stack plot of powder XRD patterns of $2\text{NaNH}_2 + \text{MgH}_2$ heated to 150 °C (black), 200 °C (blue), 250 °C (green), 300 °C (orange) and 350 °C (red). The individual XRD patterns can be found in the appendix.
Table 4-5 Summary table of weight percents and mole fractions of products of $2\text{NaNH}_2 + \text{MgH}_2$ from powder XRD shown in Figure 4-14.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>MγH₂</td>
<td>Mγ(NH₂)₃</td>
<td>NaH</td>
<td>Mγ(NH₂)₃</td>
<td>NaH</td>
</tr>
<tr>
<td>Weight % in XRD</td>
<td>79.26</td>
<td>52.95</td>
<td>52.95</td>
<td>52.95</td>
<td>52.95</td>
</tr>
<tr>
<td>Mole Fraction</td>
<td>71.95</td>
<td>47.05</td>
<td>47.05</td>
<td>47.05</td>
<td>47.05</td>
</tr>
<tr>
<td>Phase C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It was plausible that the new phase observed could be due to the formation of a mixed Na-Mg amide, as is observed for LiNa$_2$(NH$_2$)$_3$, Li$_3$Na(NH$_2$)$_4$, K$_2$Li(NH$_2$)$_3$ and K$_2$Li(NH$_2$)$_3$. In order to investigate whether the formation of a mixed sodium-magnesium amide was favourable NaNH$_2$ was heated with Mg(NH$_2$)$_2$ in a 1:1 ratio to 220 °C for 12 hours (Figure 4-15).

Figure 4-15 Powder XRD pattern of NaNH$_2$ + Mg(NH$_2$)$_2$, heated at 220 °C for 12 hours under flowing argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Mg(NH$_2$)$_2$ (blue tick marks), NaNH$_2$ (black tick marks) and MgO (green tick marks). $R_{wp} = 16.124$, $R_{exp} = 4.755$, $\chi^2 = 11.5$. 
Table 4-6 Summary table of weight percents and mole fractions of products of NaNH$_2$ + Mg(NH$_2$)$_2$ heated to 220 °C for 12 hours.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight Percent in XRD</th>
<th>Mole Fraction/ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(NH$_2$)$_2$</td>
<td>40.81</td>
<td>32.79</td>
</tr>
<tr>
<td>NaNH$_2$</td>
<td>19.16</td>
<td>22.24</td>
</tr>
<tr>
<td>MgO</td>
<td>40.02</td>
<td>44.97</td>
</tr>
</tbody>
</table>

The result of this reaction was a powder XRD pattern that showed the presence of both starting materials, but also a range of unidentified peaks (Figure 4-15). The positions and relative intensities of the 4 largest unidentified Bragg peaks closely match those of the unidentified peaks present in the sample of 2NaNH$_2$ + MgH$_2$ heated to 150 °C for 12 hours (Figure 4-14). This is consistent with the partial formation of a sodium-magnesium amide which did not go to completion under the reaction conditions investigated.

The known products Mg(NH$_2$)$_2$ and NaH from the reaction 2NaNH$_2$ + MgH$_2$ heated to 150 °C for 12 hours indicated the same metathesis as for 2NaNH$_2$ + 3MgH$_2$ occurred (Equation 4-16).

Equation 4-16  
2NaNH$_2$ + MgH$_2$ → Mg(NH$_2$)$_2$ + 2NaH

The salt metathesis again was the cause of the exothermic event at 155 °C.

The 2NaNH$_2$ + MgH$_2$ starting materials were then heated to 200 °C for 12 hours. This was just above the temperature at which the main hydrogen desorption started when heated on TPD-
MS apparatus (Figure 4-10). The products from this reaction were found to be NaH and MgNa$_{2y}$(NH)$_{1+y}$ (Figure 4-14) along with remaining NaNH$_2$ starting material.

The 2NaNH$_2$ + MgH$_2$ mixture was then heated to 250 °C for 12 hours. This temperature was after the main peak of hydrogen. Again, the crystalline products were identified as NaNH$_2$, NaH and MgNa$_{2y}$(NH)$_{1+y}$ (Figure 4-14, Figure 7-7).

The 2NaNH$_2$ + MgH$_2$ mixture was also heated to 300 °C for 12 hours. 300 °C was between the second and third hydrogen desorptions. As before, the products found by powder XRD were NaH, MgNa$_{2y}$(NH)$_{1+y}$ and remaining NaNH$_2$ starting material (Figure 4–16). There was also the appearance of another set of 8 major peaks which had not been observed previously (phase C).

The $hkl$ values, peak positions, $d$-spacings and intensities of the Bragg peaks are shown in Table 4-7. The table includes the peaks less easy to distinguish from the XRD pattern, but of great enough intensity to be in the phase C pattern (below).

![Figure 4-16 Powder XRD pattern of 2NaNH$_2$ + MgH$_2$, heated at 300 °C for 12 hours under flowing argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaNH$_2$ (blue tick marks) and NaH (black tick marks). Phase A (green tick marks) and phase C (pink tick marks) were fitted using a Pawley fit (red line). $R_{wp} = 17.251$, $R_{exp} = 10.587$, $X^2 = 2.7.$](image)
4. Rehydriding

The products from the starting materials that had been heated to 300 °C for 12 hours were subjected to high pressure hydrogen at a range of temperatures in order to assess whether the products would readily reform the reactants. The products of the reaction $2\text{NaNH}_2 + \text{MgH}_2$ ($\text{NaH}$ and $\text{MgNa}_{2y}(\text{NH})_{3+y}$, with NaNH$_2$ starting material) were heated under a hydrogen atmosphere.
for 24 hours at a pressure of 75 bar $\text{H}_2$. After the rehydrogenation attempt, the observed products were $\text{Mg(NH}_2\text{)}_2$ and $\text{MgNH}$ along with NaH present at the start (Figure 4-17). $\text{Mg(NH}_2\text{)}_2$ and NaH are the expected products from the initial metathesis of the starting materials NaNH$_2$ and MgH$_2$, indicating that similarly to the Li-Mg system, the alkaline earth metal amide is the rehydrogenation product of the mixed imide in preference to the alkali metal amide.

Figure 4-17 Powder XRD pattern of 2NaNH$_2$ + MgH$_2$ heated at 300 °C and rehydrated at 300 °C for 24 hours under 75 bar $\text{H}_2$. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases $\text{Mg(NH}_2\text{)}_2$ (blue tick marks), NaH (black tick marks), MgNH (green tick marks) and MgO (pink tick marks). $R_{wp} = 12.041$, $R_{exp} = 9.625$, $\chi^2 = 1.6$. 

<table>
<thead>
<tr>
<th>Component</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(NH$_2$)$_2$</td>
<td>40.24 %</td>
</tr>
<tr>
<td>NaH</td>
<td>38.55 %</td>
</tr>
<tr>
<td>MgNH</td>
<td>8.74 %</td>
</tr>
<tr>
<td>MgO</td>
<td>12.47 %</td>
</tr>
</tbody>
</table>
Table 4-8 Summary table of weight percents and mole fractions of products of \(2\text{NaNH}_2 + \text{MgH}_2\) heated to 300 °C and rehydrided at 300 °C for 24 hours under 75 bar \(\text{H}_2\).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight Percent in XRD</th>
<th>Mole Fraction/ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Mg(NH}_2\text{)}_2)</td>
<td>40.24</td>
<td>25.04</td>
</tr>
<tr>
<td>(\text{NaH})</td>
<td>38.55</td>
<td>56.32</td>
</tr>
<tr>
<td>(\text{MgNH})</td>
<td>8.74</td>
<td>7.79</td>
</tr>
<tr>
<td>(\text{MgO})</td>
<td>12.47</td>
<td>10.85</td>
</tr>
</tbody>
</table>

5. Discussion

A small amount of ammonia was desorbed at the peak of the hydrogen desorption shown in Figure 4-10. After heating the sample to 350 °C on the TPD-MS apparatus, \(\text{MgNH}\) was present. The \(\text{MgNH}\) could have resulted from the decomposition of \(\text{Mg(NH}_2\text{)}_2\) (Equation 4-17). The formation of \(\text{MgNH}\) from \(\text{Mg(NH}_2\text{)}_2\) would cause the small ammonia desorption. The \(\text{Mg(NH}_2\text{)}_2\) could be present from not being used in forming \(\text{MgNa}_{2y}(\text{NH})_{1+y}\), and would not yet have formed \(\text{Mg}_3\text{N}_2\) as the sample was not heated long enough.

Equation 4-17 \[\text{Mg(NH}_2\text{)}_2 \rightarrow \text{MgNH} + \text{NH}_3\]

The peaks present after heating the starting materials to 150 °C were \(\text{NaNH}_2\), \(\text{Mg(NH}_2\text{)}_2\), \(\text{NaH}\) and \(\text{MgH}_2\) as well as unidentified phase B (comparatively in Figure 4‒14 and Figure 7-5). These Bragg peaks did not match any known Na-N-H or Mg-N-H phase, or mixed cation imide as found in the \(2\text{NaNH}_2 + 3\text{MgH}_2\) reaction. A brief investigation into the identity of phase B peaks was
carried out (Figure 4-15). As there are known compounds of both sodium and magnesium amides ($\text{NaNH}_2$, $\text{Mg(NH}_2)_2$) and hydrides ($\text{NaH}$, $\text{MgH}_2$) as well as a mixed sodium-magnesium hyride ($\text{NaMgH}_3$) it was possible a mixed sodium-magnesium amide may have been formed. Reactions of $\text{Mg(NH}_2)_2$ with $\text{NaNH}_2$ indicated that phase B was most likely a mixed Na-Mg amide.

Mixed group 1 and 2 amides have been formed before. Jacobs \textit{et al.} \textsuperscript{42} formed $\text{NaCa(NH}_2)_3$ in 1979 using ammonothermal synthesis between 297–397 °C. It was found to have an orthorhombic unit cell with lattice parameters given as $a = 21.78$ Å, $b = 10.44$ Å and $c = 7.37$ Å with an $\text{Fddd}$ space group. On decomposition the mixed Na-Ca amide formed $\text{NaNH}_2$ and $\text{MgNH}$ with the release of $\text{NH}_3$ (Equation 4-18).

\text{Equation 4-18} \quad \text{NaCa(NH}_2)_3 \rightarrow \text{NaNH}_2 + \text{CaNH} + \text{NH}_3

Jacobs \textit{et al.} \textsuperscript{43} further investigated the formation of $\text{NaCa(NH}_2)_3$ and compared it to the amides of heavier group 1 and 2 cations. Jacobs \textit{et al.} formed their mixed amides by reacting the metals (in this case sodium and calcium) with supercritical ammonia at about 5 kbar in autoclaves at temperatures in the range 200 to 500 °C. They found well-crystallised amides were produced under these conditions.

In investigating the caesium-magnesium system Birkenbeul \textit{et al.} \textsuperscript{44} found one ternary amide $\text{Cs}_2[\text{Mg(NH}_2)_4]$. It was formed in an autoclave at 142 °C and with an ammonia pressure of 2 kbar.
for 2 days. It was monoclinic with the space group $P12_1/c1$ and with lattice parameters of $a = 9.447 \, \text{Å}$, $b = 7.027 \, \text{Å}$, $c = 12.372 \, \text{Å}$ and $\beta = 94.80^\circ$.

It appeared that our new phase (Figure 4–14) could only form in very small amounts at low temperatures during the $2\text{NaNH}_2 + \text{MgH}_2$ reaction, because at temperatures a little higher, the hydrogen desorption became more prevalent and overwhelmed the formation of this new compound. It is unknown what stoichiometry this new phase took and further investigations would be necessary to form it pure and characterise it. Reactions under supercritical ammonia similar to those mentioned previously may be necessary for the formation of the mixed amide in order to suppress the decomposition reaction.

The decomposition of the mixed Na-Ca amide formed by Jacobs et al.$^{43}$ produced a group 2 imide as well as ammonia. It is possible following the small investigation above into a possible Na-Mg amide that a similar decomposition of Na-Mg amide had occurred. This is another possibility for the MgNH and ammonia present after heating to 350 °C (Equation 4-19). This could also account for some of the large amount of NaNH$_2$ present on heating the $2\text{NaNH}_2 + \text{MgH}_2$ starting materials to various temperatures. The apparent deficiency of MgNH present could be due to it existing as a poorly crystalline phase.$^{45}$

\begin{equation}
\text{NaMg(NH}_2)_3 \rightarrow \text{NaNH}_2 + \text{MgNH} + \text{NH}_3
\end{equation}

Equation 4-19

In the temperature range investigated the $2\text{NaNH}_2 + \text{MgH}_2$ reaction appeared to have gone to completion by forming $\text{MgNa}_{2y}(\text{NH})_{2+2y}$. This phase had lattice parameters of $a = 6.1249(3) \, \text{Å}$ and
$c = 17.916(11)$ Å after being formed at 250 °C. This was in comparison to those from our investigations into $2\text{NaNH}_2 + 3\text{MgH}_2$ which found lattice parameters of $a = 6.1077(7)$ Å and $c = 17.881(3)$ Å. Sheppard et al.\textsuperscript{21} found lattice parameters of $a = 6.11$ Å and $c = 17.90$ Å. This product was an imide, and therefore was not fully dehydried. This is in comparison to $2\text{NaNH}_2 + 3\text{MgH}_2$ which saw fully dehydrided products, Na and $\text{Mg}_3\text{N}_2$. It could be suggested that the additional MgH$_2$ present in $2\text{NaNH}_2 + 3\text{MgH}_2$ could react with the mixed imide to form $\text{Mg}_3\text{N}_2$, as the mixture is stoichiometric with regard to magnesium and nitrogen (Equation 4-9). The lack of magnesium in $2\text{NaNH}_2 + \text{MgH}_2$ could inhibit $\text{Mg}_3\text{N}_2$ formation.

This is analogous to work carried out on $2\text{LiNH}_2 + (3)\text{MgH}_2$. It has been shown by Dolotko et al.\textsuperscript{12} that $3\text{MgH}_2$ reacted with $2\text{LiNH}_2$ forms LiH and $\text{Mg}_3\text{N}_2$ as products, whereas other work by Rijssenbeek et al.\textsuperscript{49} showed the reaction between $2\text{LiNH}_2$ and MgH$_2$ can only go as far as $\text{Li}_2\text{Mg(NH)}_2$. Up to 530 °C only $\text{Li}_2\text{Mg(NH)}_2$ and no $\text{Mg}_3\text{N}_2$ was found.

Because of relatively small amounts of phase B observed in the powder XRD patterns of the reaction products, so far it has not been possible to confirm the identity of phase B. The few peaks present in Figure 4–16 that were unidentified (phase C) matched another previously unidentified phase published by Sheppard et al.\textsuperscript{21} Figure 4–18 below shows the unidentified peaks fitted with the lattice parameters suggested by Sheppard et al. Their lattice parameters were $a = 13.92$ Å, $b = 3.58$ Å, $c = 12.39$ Å and $\beta = 115.8$ °. Using the lattice parameters of Sheppard et al., we indexed phase C and refined it to be $a = 13.945(1)$ Å, $b = 3.5847(18)$ Å, $c = 12.405(1)$ Å and $\beta = 115.78(6)$ °. As our parameters were fitted to a minority phase, they
compare well to those of Sheppard et al., who made a case for this new phase to be a mixed Na-Mg nitride as they found no FTIR peaks for an amide or imide.

Figure 4-18 Powder XRD pattern of $2\text{NaNH}_2 + \text{MgH}_2$, heated at 300 °C for 12 hours under flowing argon, with peaks due to Phase C as determined for a Pawley refinement highlighted. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases $\text{NaNH}_2$ (blue tick marks), $\text{NaH}$ (black tick marks) and $\text{MgNa}_2y(\text{NH})_{1+y}$ (green tick marks) and phase C (pink tick marks) fitted using a Pawley fit (red line). $R_{wp} = 17.252$, $R_{exp} = 10.587$, $\chi^2 = 2.7$.

The overall reaction scheme for $2\text{NaNH}_2 + \text{MgH}_2$ heated to various temperatures is shown in Table 4–9.
Table 4-9 Overall reaction scheme $2\text{NaNH}_2 + \text{MgH}_2$ of heated to various temperatures. The products from each temperature are shown, the temperature at which new phases form and the lattice parameters of the new phases.

<table>
<thead>
<tr>
<th>Temp/°C</th>
<th>Reaction Scheme</th>
<th>Products</th>
<th>New Phase(s)</th>
<th>Lattice Parameters/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>$2\text{NaNH}_2 + \text{MgH}_2 \rightarrow$</td>
<td>Mg(NH$_2$)$_2$, 2NaH</td>
<td>Na-Mg amide (Phase B)</td>
<td>–</td>
</tr>
<tr>
<td>200</td>
<td>Mg(NH$_2$)$_2 + 2\text{NaH} \rightarrow$</td>
<td>NaNH$_2$, NaH, H$_2$</td>
<td>MgNa$<em>{2y}$(NH)$</em>{1+y}$ (Phase A)</td>
<td>$a = 6.1372(4)$, $c = 17.935(2)$</td>
</tr>
<tr>
<td>220</td>
<td>Mg(NH$_2$)$_2 + \text{NaNH}_2 \rightarrow$</td>
<td>NaNH$_2$, NaH, H$_2$</td>
<td>NaNH$_2$, NaH, H$_2$</td>
<td>MgNa$<em>{2y}$(NH)$</em>{1+y}$ (Phase A)</td>
</tr>
<tr>
<td>250</td>
<td>Mg(NH$_2$)$_2 + 2\text{NaH} \rightarrow$</td>
<td>NaNH$_2$, NaH, H$_2$</td>
<td>MgNa$<em>{2y}$(NH)$</em>{1+y}$ (Phase A)</td>
<td>$a = 6.1230(3)$, $c = 17.913(16)$</td>
</tr>
<tr>
<td>300</td>
<td>NaNH$_2$, NaH, H$_2$</td>
<td></td>
<td>Na-Mg nitride Phase C</td>
<td>$a = 13.945(10)$, $b = 3.5847(18)$, $c = 12.405(10)$, $\beta = 115.777(6)$</td>
</tr>
</tbody>
</table>

The comparison between the TGA-MS graphs of $2\text{NaNH}_2 + \text{MgH}_2$ (Figure 4-12) and Mg(NH$_2$)$_2 + 2\text{NaH}$ (Figure 4-13) shows only slight differences. The TGA-MS graph of $2\text{NaNH}_2 + \text{MgH}_2$ has three peaks, whereas Mg(NH$_2$)$_2 + 2\text{NaH}$ only had the latter two. This was due to there being no metathesis reaction present in Mg(NH$_2$)$_2 + 2\text{NaH}$. The latter temperature two peaks from the TGA-MS graph of $2\text{NaNH}_2 + \text{MgH}_2$ match reasonably well to the peaks present in Mg(NH$_2$)$_2 + 2\text{NaH}$. The amount of hydrogen desorbed in the latter two peaks in Figure 4-12 was much less than that shown in Figure 4-13 from Mg(NH$_2$)$_2 + 2\text{NaH}$. This was due to the initial reaction in Figure 4-12 being very exothermic. This raised the heat locally enough to desorb the majority of hydrogen at the lower peak temperature. The later peaks were therefore smaller. Overall this would cause the same amount of hydrogen to be desorbed, but the relative amount of
hydrogen released at different peak temperatures to differ. The total mass loss after heating the reactions to 350 °C was the same for both 2NaNH₂ + MgH₂ and Mg(NH₂)₂ + 2NaH, 3.7 wt% H₂. The TPD-MS hydrogen desorption peaks from Figure 4-10 match the temperatures well in comparison to TGA-MS 2NaNH₂ + MgH₂ (Figure 4-12), but slightly better to Mg(NH₂)₂ + 2NaH (Figure 4-13) as there was no large exothermic event to disrupt to rest of the hydrogen desorption.

Mg(NH₂)₂ + 2NaH (Figure 4-13) was heated for an hour at 350 °C, whereas 2NaNH₂ + MgH₂ (Figure 4-12) had heating stopped as soon as the thermocouple reached 350 °C. A comparison of the products showed the Mg(NH₂)₂ + 2NaH products to be NaNH₂, Na and phase C, whereas 2NaNH₂ + MgH₂ had Na, MgNa₂y(NH)₁⁺y, phase C and NaNH₂ starting material. This fitted in well with the suggestion that phase C was a nitride because it would indicate the more prolonged heating of Mg(NH₂)₂ + 2NaH caused the products to be more hydrogen deficient compared to the products of 2NaNH₂ + MgH₂. The final mass losses of the two TGA reactions back this up. Although after heating to 350 °C both had lost 3.7 wt% H₂, after the additional isothermal heating of Mg(NH₂)₂ + 2NaH, 4.9 wt% H₂ had been lost in total. This was in agreement with the observed products being a mixture of hydrogen deficient (phase C-possible nitride) and those not [Na, MgNa₂y(NH)₁⁺y]. If a pure Na-Mg nitride were formed cf. LiMgN,⁴⁶ then there would be a theoretical mass loss of 5.8 wt% H₂ from these reactions (Equation 4-20). It can be seen from Equation 4-20 that NaNH₂ appeared as a starting material and as a product.
Xiong et al.\textsuperscript{19} heated \( \text{Mg(NH}_2\text{)}_2 + 2\text{NaH} \) to 390 °C after ball-milling. The desorption characteristics of the reaction included the release of hydrogen at 180 °C, as well as the release of ammonia and nitrogen above 300 °C. They suggested the nitrogen released was probably due to the decomposition of \( \text{NH}_3 \) desorbed. In contrast, we observed no evidence of \( \text{N}_2 \) desorption. The reaction by Xiong et al. releasing hydrogen at a slightly lower temperature was probably due to the initial ball-milling carried out on the reactants. The smaller particle size means shorter diffusion lengths for desorbed gases from the bulk phase, as well as the possible addition of catalytic metal during milling as steel pots and balls were used.

\( 2\text{NaNH}_2 + \text{MgH}_2 \) after dehydrogenation at 300 °C for 12 hours was subjected to 75 bar hydrogen for 12 hours at 300 °C. It could be seen from the XRD pattern (Figure 4-17), that the products were more hydrogen rich than before rehydrogenation. \( \text{Mg(NH}_2\text{)}_2 \) as well as a small amount of \( \text{MgNH} \) was present, along with \( \text{NaH} \). This is consistent with the argument that phase A, from \( 2\text{NaNH}_2 + 3\text{MgH}_2 \), was an imide, as it was possible to rehydride it back to the lowest energy starting materials, namely the \( \text{Mg(NH}_2\text{)}_2 \) and \( \text{NaH} \) (post metathesis products).

\( 2\text{NaNH}_2 + \text{MgH}_2 \) was originally investigated to provide a comparison to \( 2\text{LiNH}_2 + \text{MgH}_2 \). When \( 2\text{LiNH}_2 + \text{MgH}_2 \) is heated up it forms \( \text{Li}_2\text{Mg(NH}_2\text{)}_2 \). On rehydriding, this reaction also was also found to revert to \( \text{Mg(NH}_2\text{)}_2 + \text{group 1 hydride} \) (Equation 4-22).\textsuperscript{4,5,6,7} It would therefore not be surprising with sodium amide and magnesium hydride that after heating and then rehydriding, magnesium amide was formed along with \( \text{NaH} \). The \( \text{MgNH} \) present would presumably...
rehydrogenate to Mg(NH$_2$)$_2$ and MgH$_2$ if exposed to the rehydriding conditions for a longer time or at a higher temperature pressure than 75 bar.

Equation 4-21

\[ 2\text{NaNH}_2 + \text{MgH}_2 \rightarrow \text{Mg(NH}_2\text{)$_2$} + 2\text{NaH} \leftrightarrow \text{MgNa}_{2y}(\text{NH})_{1+y} + (1-x)\text{NaNH}_2 + (1-x)\text{NaH} + (1+x)\text{H}_2 \]

Equation 4-22

\[ 2\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{Mg(NH}_2\text{)$_2$} + 2\text{LiH} \leftrightarrow \text{Li}_2\text{Mg(NH)} + 2\text{H}_2 \]

It can be seen in Equation 4-21 that NaH along with NaNH$_2$ starting material were both present from the reaction in a 1:1 ratio. Converting the wt% calculated by quantitative phase analysis using Topas into mole% produces NaNH$_2$:NaH as approximately a 1:1 ratio as predicted.

From Figure 4-18, 63.27 wt% / 39.01235 = 1.62 mol% for NaNH$_2$; 36.73 wt% / 23.99771 = 1.53 mol%. As the mol% for NaNH$_2$ and NaH were consistent throughout heating, the ratio of NaNH$_2$:NaH as products also remained at approximately 1:1.

3. $3\text{NaNH}_2 + 2\text{MgH}_2$

When the sodium rich reaction $2\text{NaNH}_2 + \text{MgH}_2$ was carried out the products were NaNH$_2$, NaH and MgNa$_{2y}$(NH)$_{1+y}$. As NaNH$_2$ was consistently the major product of $2\text{NaNH}_2 + \text{MgH}_2$, we therefore reduced the amount of Na in the ratio of Na:Mg by investigating the reaction of NaNH$_2$ and MgH$_2$ in a 3:2 ratio.
1. *Temperature Programmed Desorption-Mass Spectrometry*

NaNH$_2$ and MgH$_2$ were heated together in a 3:2 ratio. The reaction was carried out on a TPD-MS apparatus in order to establish whether this system desorbed hydrogen like the other NaNH$_2$–MgH$_2$ systems. It was heated at 2 °C min$^{-1}$ to 350 °C and held there for approximately 1 hour. It can be seen from Figure 4-19 that, like other $x$NaNH$_2$ + $y$MgH$_2$ reactions (Figure 4-30), hydrogen was desorbed from this reaction also. There was only a very small amount of ammonia desorbed at the peak of the second major hydrogen desorption. The hydrogen desorption started at 126 °C and increased to a peak at 154 °C. The rate of desorption quickly slowed. A second increase in the rate of hydrogen desorption started at 182 °C and peaked twice at 243 and 265 °C before the hydrogen desorption dropped away. At 325 °C there was a small additional hydrogen desorption which tailed off slowly.

There was a very small fluctuation in the temperature trace that occurred at the same temperature as the first hydrogen desorption. This was same as temperature fluctuations for the other $x$NaNH$_2$ + $y$MgH$_2$ reactions (Figure 4-2 and Figure 4-11). The fluctuation was mirrored in the furnace power indicating an exothermic event as described previously. This indicated an exothermic event.
Figure 4-19 TPD–MS analysis of the $3\text{NaNH}_2 + 2\text{MgH}_2$ reaction. The temperature trace is shown in black and the MS traces for $\text{H}_2$ and $\text{NH}_3$ released are shown in red and green, respectively.

The products after TPD–MS analysis of the $3\text{NaNH}_2 + 2\text{MgH}_2$ reaction were $\text{NaH}$ and $\text{MgNa}_{2y}(\text{NH})_{1+y}$ along with $\text{NaNH}_2$ starting material (Figure 4-20). These are the same products as from the reaction $2\text{NaNH}_2 + \text{MgH}_2$. 
Figure 4-20 Powder XRD pattern of $3\text{NaNH}_2 + 2\text{MgH}_2$, after TPD-MS analysis to 350 °C. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaH (blue tick marks), NaNH$_2$ (black tick marks), Na (green tick marks) and MgNa$_{2y}$(NH)$_{1+y}$ (pink tick marks) fitted using a Pawley fit (red line). $R_{wp} = 10.767$, $R_{exp} = 9.032$, $\chi^2 = 1.4$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight Percent in XRD</th>
<th>Mole Fraction/ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaH</td>
<td>59.91</td>
<td>69.72</td>
</tr>
<tr>
<td>NaNH$_2$</td>
<td>36.98</td>
<td>26.49</td>
</tr>
<tr>
<td>Na</td>
<td>3.11</td>
<td>3.79</td>
</tr>
<tr>
<td>MgNa$<em>{2y}$(NH)$</em>{1+y}$</td>
<td>Pawley</td>
<td>NA</td>
</tr>
</tbody>
</table>

2. Thermogravimetric Analysis

It can be seen from the TGA–MS trace that a similar hydrogen desorption to that in the TPD-MS was observed. The 3 main hydrogen desorptions were visible (Figure 4-21). The first, sharp peak occurred at 181 °C, 30 °C after the initial peak on TPD-MS. No ammonia was detected in TGA, although the sample size was smaller than in the TPD-MS therefore releasing a smaller amount...
of ammonia which may not be detectable above the detection limit of the mass spectrometer. Heating was stopped at 350 °C. The products after TGA were Na and phase C along with remaining NaNH$_2$ (Figure 4-22). There was no MgNa$_{2y}$(NH)$_{1+y}$ present here. This was the first time the presence of phase C was observed in the absence of MgNa$_{2y}$(NH)$_{1+y}$.

Figure 4-21 TGA–MS of the 3NaNH$_2$ + 2MgH$_2$ reaction. The H$_2$ release is shown in red and the percentage mass loss is shown in black.
Figure 4-22 Powder XRD of $3\text{NaNH}_2 + 2\text{MgH}_2$ heated to 350 °C on a TGA-MS apparatus. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Na (blue tick marks), NaNH$_2$ (black tick marks), NaOH (green tick marks) and phase C (pink tick marks) fitted using a Pawley fit (red line). $R_{wp} = 6.903$, $R_{exp} = 4.745$, $\chi^2 = 2.1$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight Percent in XRD</th>
<th>Mole Fraction/ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>31.47</td>
<td>44.28</td>
</tr>
<tr>
<td>NaNH$_2$</td>
<td>14.73</td>
<td>12.21</td>
</tr>
<tr>
<td>NaOH</td>
<td>53.80</td>
<td>43.51</td>
</tr>
<tr>
<td>Phase C</td>
<td>Pawley</td>
<td>NA</td>
</tr>
</tbody>
</table>

3. **Flowing Line Reactions**

As in previous sections, (section 4.2.1 and 4.2.2) the reaction was carried out at intermediate temperatures in order to establish the desorption mechanism. The starting materials were first heated to 150 °C for 12 hours. This was shortly before the exothermic event and the start of the hydrogen desorption. The products after heating under these conditions were starting
materials, NaNH$_2$ and MgH$_2$, as well as NaH and Mg(NH$_2$)$_2$, which have previously been shown to be metathesis products (Figure 4–24, Equation 4-2). The few unidentified peaks present are the same as those labelled ‘phase B’ in section 4.2.2 from the reaction of NaNH$_2$ with Mg(NH$_2$)$_2$ – the possible Na-Mg amide.

The starting materials were then heated to 200 °C for 12 hours. This was the approximate temperature at which the second desorption started. The known product was NaH along with NaNH$_2$ starting material. The peaks from MgNa$_{2y}$(NH)$_{1+y}$ were also present (Figure 4-24).

The 3NaNH$_2$ + 2MgH$_2$ reaction mixture was also heated to 250 °C for 12 hours. This temperature was between the two peaks of the second desorption. The products were the same as those after heating to 200 °C, NaH and MgNa$_{2y}$(NH)$_{1+y}$ as well as NaNH$_2$ (Figure 4–24).

After the temperature in the TPD-MS experiment reached 300 °C the major hydrogen desorption was over. The products from heating the starting materials to 300 °C on a flowing line experiment were as identified after heating to 250 °C, NaH and MgNa$_{2y}$(NH)$_{1+y}$ and remaining NaNH$_2$ (Figure 4-24) as well as the higher temperature phase C found earlier in section 4.2.2 (Figure 4–18).

The same reaction was carried out at 350 °C and held there for 4 hours. The observed products were more crystalline than observed after reaction at 300 °C, as evidenced by sharper Bragg peaks in the powder XRD pattern. There was no evidence of phase C that had been present at 300 °C. The products were NaH and MgNa$_{2y}$(NH)$_{1+y}$ in addition to NaNH$_2$ (Figure 4-23).
Figure 4-23 Powder XRD pattern of $3\text{NaNH}_2 + 2\text{MgH}_2$, heated to $350 \, ^\circ\text{C}$ for 4 hours under flowing argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaH (blue tick marks), NaNH$_2$ (black tick marks) and MgNa$_{2y}$(NH)$_{1+y}$ (green tick marks) fitted using a Pawley fit (red line). $R_{wp} = 9.865$, $R_{exp} = 6.803$, $\chi^2 = 2.1$.

Table 4-12 Summary table of weight percents and mole fractions of products of $3\text{NaNH}_2 + 2\text{MgH}_2$ heated to $350 \, ^\circ\text{C}$ for 4 hours.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight Percent in XRD</th>
<th>Mole Fraction/ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaH</td>
<td>61.38</td>
<td>72.10</td>
</tr>
<tr>
<td>NaNH$_2$</td>
<td>38.62</td>
<td>27.90</td>
</tr>
<tr>
<td>MgNa$<em>{2y}$(NH)$</em>{1+y}$</td>
<td>Pawley</td>
<td>NA</td>
</tr>
</tbody>
</table>

The starting materials were heated together to $350 \, ^\circ\text{C}$ and held there for 12 hours. Again, NaNH$_2$ was present along with the products, but this time Na was present with no NaH. The MgNa$_{2y}$(NH)$_{1+y}$ phase was again present (Figure 4-24). $350 \, ^\circ\text{C}$ was above the final hydrogen desorption temperature and this final desorption can be put down to the decomposition of NaH to Na and hydrogen (Equation 4-10).
Figure 4-24 Stack plot of powder XRD patterns of 3NaNH₂ + 2MgH₂ heated to 150, 200, 250, 300 and 350 °C. The individual XRD patterns can be found in the appendix.
Table 4-13 Summary table of weight percents and mole fractions of products of $3\text{NaNH}_2 + 2\text{MgH}_2$ from powder XRD shown in Figure 4–24.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Phase</th>
<th>Weight % in XRD</th>
<th>Mole Fraction of $\text{NaNH}_2$</th>
<th>Mole Fraction of $\text{NaH}$</th>
<th>Mole Fraction of $\text{MgH}_2$</th>
<th>Mole Fraction of $\text{Mg(NH}_2)$</th>
<th>Mole Fraction of $\text{Na}<em>2\text{(NH)}</em>{1+y}$</th>
<th>Pawley</th>
<th>Phase C</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>3NaH</td>
<td>NA</td>
<td>3.66 NA</td>
<td>21.95 NA</td>
<td>NA</td>
<td>74.14 NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>300</td>
<td>3NaH</td>
<td>60.33 NA</td>
<td>71.20 NA</td>
<td>28.80 NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>42.80</td>
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<td>NA</td>
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<tr>
<td>250</td>
<td>3NaH</td>
<td>68.58 NA</td>
<td>57.31 NA</td>
<td>42.69 NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>200</td>
<td>3NaH</td>
<td>72.22 NA</td>
<td>72.81 NA</td>
<td>27.19 NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>32.20</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>150</td>
<td>3NaH</td>
<td>63.22 NA</td>
<td>68.58 NA</td>
<td>32.80 NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>39.67</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

For the phase $\text{Na}_2\text{(NH)}_{1+y}$, the mole fraction is not reported.
4. Rehydriding

The products after heating $3\text{NaNH}_2 + 2\text{MgH}_2$ to $300 \, ^\circ\text{C}$ for 12 hours were then exposed to a hydrogen atmosphere in order to rehydride the sample. The phases present before hydrogenation were $\text{NaNH}_2$, $\text{NaH}$, $\text{MgNa}_2\text{y(NH)}_{1+y}$ and phase C, and they were heated under hydrogen to $300 \, ^\circ\text{C}$ for 24 hours at 75 bar $\text{H}_2$. The products after this attempted rehydriding were $\text{MgO}$, $\text{NaH}$, $\text{Mg(NH}_2)_2$ and a very small amount of $\text{MgNH}$ (Figure 4-25). The oxidation was most probably due to poor cycling of the high pressure system to remove the air.

Figure 4-25 Powder XRD pattern of $3\text{NaNH}_2 + 2\text{MgH}_2$ heated to $300 \, ^\circ\text{C}$ and then rehydrided at $350 \, ^\circ\text{C}$ for 24 hours under 75 bar $\text{H}_2$. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases $\text{NaH}$ (blue tick marks), $\text{Mg(NH}_2)_2$ (black tick marks), $\text{MgNH}$ (green tick marks) and $\text{MgO}$ (pink tick marks) fitted using a Pawley fit (red line). $R_{wp} = 18.706$, $R_{exp} = 9.866$, $\chi^2 = 3.6$. 

### Table

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
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<td>NaH</td>
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</tr>
<tr>
<td>Mg(NH$_2$)$_2$</td>
<td>4.45 %</td>
</tr>
<tr>
<td>MgNH</td>
<td>0.15 %</td>
</tr>
<tr>
<td>MgO</td>
<td>63.12 %</td>
</tr>
</tbody>
</table>
Table 4-14 Summary table of weight percents and mole fractions of products of $3\text{NaNH}_2 + 2\text{MgH}_2$ heated to 300 °C and then rehydrided at 350 °C for 24 hours under 75 bar $\text{H}_2$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight Percent in XRD</th>
<th>Mole Fraction/ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaH</td>
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<td>$\text{Mg(NH}_2\text{)}_2$</td>
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<td>MgNH</td>
<td>0.15</td>
<td>0.27</td>
</tr>
<tr>
<td>MgO</td>
<td>63.12</td>
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</tr>
</tbody>
</table>

5. Discussion

The fluctuation in the furnace power and its appearance in the temperature trace of the TPD-MS trace (Figure 4-19) showed less of an exothermic reaction than had been evidenced before (Figure 4-2, Figure 4-11). This was as expected as the reaction was not stoichiometric with respect to the metathesis.

After heating the starting materials, the products from the salt metathesis were seen to occur. The metathesis had nearly gone to completion; only a little NaNH$_2$ was still present (Figure 4-13). The idealised metathesis reaction for $3\text{NaNH}_2 + 2\text{MgH}_2$ is shown in Equation 4-23.

Equation 4-23

$$6\text{NaNH}_2 + 4\text{MgH}_2 \rightarrow 3\text{Mg(NH}_2\text{)}_2 + 6\text{NaH} + \text{MgH}_2$$

By 200 °C all the $\text{Mg(NH}_2\text{)}_2$ and MgH$_2$ had either become amorphous ($\text{Mg(NH}_2\text{)}_2$) or been used up (MgH$_2$). Only NaNH$_2$, NaH and MgNa$_{2y}$(NH)$_{1+y}$ could be seen from the powder XRD pattern.
The lattice parameters of MgNa$_{2y}$(NH)$_{1+y}$ were a little larger than published – $a = 6.1431(4)$ Å and $c = 17.941(19)$ Å in comparison to $a = 6.11$ Å and $c = 17.90$ Å.$^{21}$

Equation 4-24

$$3\text{Mg(NH}_2\text{)}_2 + 6\text{NaH} + \text{MgH}_2 \rightarrow \text{MgNa}_{2y}(\text{NH})_{1+y} + (2-4x)\text{NaNH}_2 + (4-4x)\text{NaH} + (4+4x)\text{H}_2$$

Using the starting materials heated to 350 °C (Figure 4-24) which shows Na product, if we assume that all the Na comes from NaH, $\frac{2-4y}{4-4y} = 2/7$ (ratio of NaNH$_2$:NaH), this gives $y = 0.3$ and the imide has the possible formula MgNa$_{0.6}$(NH)$_{1.3}$.

Some very small peaks belonging to phase C were visible in the XRD pattern for the starting materials heated to 250 °C. These occurred along with the same products seen at 200 °C. This was the lowest temperature at which phase C had been observed. The lattice parameters for MgNa$_{2y}$(NH)$_{1+y}$ formed at this temperature were as published.$^{21}$

By 300 °C, the lattice parameters had shrunk to $a = 6.1242(3)$ Å and $c = 17.9253(8)$ Å, and by 350 °C the lattice parameters were $a = 6.1158(19)$ Å and $c = 17.8967(7)$ Å for 4 hours and $a = 6.1199(4)$ Å and $c = 17.909(12)$ Å for 12 hours of heating.

Throughout all of the temperatures investigated, the lattice parameters of NaNH$_2$ were larger than those published by Nagib.$^{47}$ This may mean that some Mg was present within the NaNH$_2$ although there has previously been no suggestion of NaNH$_2$ of having a mixed stoichiometry. However, the formula unit size of Mg(NH$_2$)$_2$ compared to NaNH$_2$ is smaller, 33.86 Å$^3$ versus 47.14 Å$^3$, not larger, meaning it would be unlikely the inclusion of Mg within the NaNH$_2$ unit cell
would increase its lattice parameters. The lattice parameters of NaH were consistent with those published, throughout.

It appeared the proportion of MgNa$_{2y}$(NH)$_{1+y}$ had increased with increasing temperature, but there were no additional Mg containing phases seen. It was possible that amorphous Mg phases were still present.

The products of the 3NaNH$_2$ + 2MgH$_2$ reactions were the same as 2NaNH$_2$ + MgH$_2$. However, the percentages of NaH and NaNH$_2$ refined by powder XRD using quantitative phase analysis were different (although no account is taken of MgNa$_{2y}$(NH)$_{1+y}$ – the ratios of NaNH$_2$ to NaH were comparable). It is possible the MgNa$_{2y}$(NH)$_{1+y}$ phase had a variable stoichiometry. Here there was more NaH present, however in 2NaNH$_2$ + MgH$_2$ there was more NaNH$_2$. This suggests that there was too much amide present in 2NaNH$_2$ + MgH$_2$. For both sodium rich reactions, 2NaNH$_2$ + MgH$_2$ and 3NaNH$_2$ + 2MgH$_2$, sodium phases were dominant in the XRD patterns. Therefore, suggesting that there must have been too much sodium present in the starting materials. It is therefore proposed that using xMg(NH$_2$)$_2$ + yNaH as the starting reaction would give better control over the number of starting material units (Mg$^{2+}$, Na$^+$, NH$_2^-$ and H$^-$). For example:

2NaNH$_2$ + MgH$_2$ gave 2Na, 2[(NH$_2$)$_2$$\text{^-}$], 1Mg and 2H, the reaction products gave excess NaNH$_2$. We then reduced the amount of sodium amide present to react 3NaNH$_2$ + 2MgH$_2$ which gave 3Na, 3[(NH$_2$)$_2$$\text{^-}$], 2Mg and 4H. This reaction gave excess NaH. Therefore, by having xMg(NH$_2$)$_2$ + yNaH starting materials, the reactants can have less sodium hydride added to them, whilst
maintaining the [(NH$_2$)$^\text{-}$]:H$^\text{-}$ ratio. This ratio is important as it defines how far the reaction can proceed.

The peaks of phase C seen after heating to 300 °C were fitted using the parameters found by Sheppard et al.$^{21}$ for a phase suggested to be a nitride. The fitted peaks can be seen in Figure 4–26. Our lattice parameters were $a = 13.950(14)$ Å, $b = 3.5849(5)$ Å, $c = 12.403(15)$ Å and $\beta = 115.753(8)$ °. These compare well to those published by Sheppard et al. of $a = 13.92$ Å, $b = 3.58$ Å, $c = 12.39$ Å and $\beta = 115.8$ °.

Figure 4-26 Powder XRD pattern of 3NaNH$_2$ + 2MgH$_2$, heated to 300 °C for 12 hours under flowing argon with phase C fitted. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaH (blue tick marks), NaNH$_2$ (black tick marks) and MgNa$_{2y}$(NH)$_{1+y}$ (green tick marks) and phase C (pink tick marks) fitted using a Pawley fit (red line). $R_{wp} = 13.469$, $R_{exp} = 10.482$, $\chi^2 = 1.7$.

The full set of reactions for 3NaNH$_2$ + 2MgH$_2$ heated on a flowing line is shown in Table 4-15.
Table 4-15 Overall reaction scheme $3\text{NaNH}_2 + 2\text{MgH}_2$ of heated to various temperatures. The products from each temperature are shown, the temperature at which new phases form and the lattice parameters of the new phases.

<table>
<thead>
<tr>
<th>Temp/$^\circ\text{C}$</th>
<th>Reaction Scheme</th>
<th>Products</th>
<th>New Phase(s)</th>
<th>Lattice Parameters/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>$3\text{NaNH}_2 + 2\text{MgH}_2 \rightarrow$</td>
<td>$\text{Mg(NH}_2)_2$, NaH, MgH$_2$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>200</td>
<td>$3\text{Mg(NH}_2)_2 + 6\text{NaH} + \text{MgH}_2 \rightarrow$</td>
<td>NaH, $\text{NaNH}_2$, H$_2$</td>
<td>$\text{MgNa}<em>{2y}(\text{NH})</em>{1+y}$ (Phase A)</td>
<td>$a = 6.1431(4)$, $c = 17.941(19)$</td>
</tr>
<tr>
<td>250</td>
<td>NaH, $\text{NaNH}_2$, H$_2$</td>
<td>$\text{MgNa}<em>{2y}(\text{NH})</em>{1+y}$ (Phase A)</td>
<td>$a = 6.1195(2)$, $c = 17.8966(9)$</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>NaH, $\text{NaNH}_2$, H$_2$</td>
<td>$\text{MgNa}<em>{2y}(\text{NH})</em>{1+y}$ (Phase A)</td>
<td>$a = 6.1243(3)$, $c = 17.9254(8)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na-Mg nitride Phase C</td>
<td>$a = 13.950(14)$, $b = 3.5849(5)$, $c = 12.403(15)$, $\beta = 115.753(8)$</td>
</tr>
<tr>
<td>350</td>
<td>Na, $\text{NaNH}_2$, NaH, H$_2$</td>
<td>$\text{MgNa}<em>{2y}(\text{NH})</em>{1+y}$ (Phase A)</td>
<td>$a = 6.1199(4)$, $c = 17.909(12)$</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>NaH $\rightarrow$</td>
<td>Na, H$_2$</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

The reaction heated on the TGA apparatus gave the first appearance of phase C without any $\text{MgNa}_{2y}(\text{NH})_{1+y}$ (Figure 4-22). We fitted the Sheppard et al.$^{21}$ phase to our XRD pattern (Figure 4-27). This gave lattice parameters of $a = 13.918(10)$ Å, $b = 3.5891(19)$ Å, $c = 12.356(15)$ Å and $\beta = 115.460(5)$°, slightly smaller than those of Sheppard et al. The oxidation as evidenced by the presence of NaOH may have been due to poor sample preparation for XRD.
Figure 4-27 Powder XRD of 3NaNH₂ + 2MgH₂ heated to 350 °C on a TGA-MS apparatus with Phase C fitted. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Na (blue tick marks), NaNH₂ (black tick marks), NaOH (green tick marks) and phase C (pink line) fitted using a Pawley fit (red line) $R_{wp} = 6.903$, $R_{exp} = 4.745$, $\chi^2 = 2.1$.

NaH was present in a large amount in the phases that were to be rehydrided. NaH was a rehydrided product and therefore would not be expected to change upon being exposed to a hydrogen atmosphere.

The products from the rehydrogenation included a large amount of MgO, unfortunately. There was, however, a small amount of Mg(NH₂)₂ present which showed that at least part of the sample was able to be rehydrided, as 2NaNH₂ + MgH₂ was (Figure 4-18).

Having concluded that there was too much sodium amide present in the starting materials of the sodium rich reactions, 2NaNH₂ + MgH₂ and 3NaNH₂ + 2MgH₂, in the next section we investigate starting materials with less sodium amide present i.e., the reaction of NaNH₂ and MgH₂ in a 1:1 ratio.
4. NaNH$_2$ + MgH$_2$

1. Temperature Programmed Desorption-Mass Spectrometry

NaNH$_2$ and MgH$_2$ were heated together in a 1:1 ratio. The reactants were first heated together on a TPD–MS apparatus at a heating rate of 2 °C min$^{-1}$ to 350 °C and held at 350 °C for approximately 2 hours. From Figure 4-28, it can be seen that hydrogen was the major gas desorbed, with a very small amount of ammonia desorbed at the peak of hydrogen release. The hydrogen desorption started very slowly around 72 °C, significantly lower temperature then observed for other compositions, with the rate increasing around 120 °C. This desorption peaked at 155 °C before dropping off. The rate increased again at around 183 °C. The second desorption was the major hydrogen release that peaked at 245 °C. As the rate decreased there were 2 shoulders: one at 260 °C, the other at 320 °C. The hydrogen desorption then tailed off. The TPD-MS trace for hydrogen desorbed from NaNH$_2$ + MgH$_2$ can be compared to gas release from other $x$NaNH$_2$ + $y$MgH$_2$ reactions (Figure 4-30).
Figure 4-28 TPD–MS analysis of the NaNH$_2$ + MgH$_2$ reaction. The temperature trace is shown in black and MS traces of H$_2$ and NH$_3$ released are shown in red and green respectively.

The temperature trace was then compared to the furnace power in order to see whether there was any thermal event in the furnace power that had not been translated onto the temperature trace. As seen in Figure 4-29 there was no obvious alteration the furnace power in comparison to other furnace power traces. There may be a small fluctuation at 150 °C, which would match with fluctuations seen in other compositions, but this event was significantly smaller.
Figure 4-29 Furnace power during the TPD-MS analysis of NaNH₂ + MgH₂ reaction. The furnace power and temperature are shown in blue and black respectively.
Figure 4-30 Comparison of TPD–MS analysis of the $x\text{NaNH}_2 + y\text{MgH}_2$ reactions. The temperature trace is shown in black and MS traces of H$_2$ released are shown in green, (2:3), red, (2:1), purple (3:2) and blue (1:1).

The products after TPD-MS were analysed using powder XRD. They were found to be NaH, Na, Mg$_3$N$_2$ and MgNa$_{2y}$(NH)$_{1+y}$ (Figure 4-31).
Figure 4-31 Powder XRD pattern of NaNH$_2$ + MgH$_2$, after TPD–MS analysis to 350 °C. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaH (blue tick marks), Mg$_3$N$_2$ (black tick marks), Na (green tick marks) and MgNa$_2y$(NH)$_{1+y}$ (pink tick marks) fitted using a Pawley fit (red line). $R_{wp} = 11.625$, $R_{exp} = 9.413$, $\chi^2 = 1.5$.

Table 4-16 Summary table of weight percents and mole fractions of products of NaNH$_2$ + MgH$_2$ heated to 350 °C on TPD-MS apparatus.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight Percent in XRD</th>
<th>Mole Fraction/ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaH</td>
<td>54.32</td>
<td>65.71</td>
</tr>
<tr>
<td>Mg$_3$N$_2$</td>
<td>24.09</td>
<td>6.98</td>
</tr>
<tr>
<td>Na</td>
<td>21.58</td>
<td>27.33</td>
</tr>
<tr>
<td>MgNa$<em>2y$(NH)$</em>{1+y}$</td>
<td>Pawley</td>
<td>NA</td>
</tr>
</tbody>
</table>

2. Thermogravimetric Analysis

The NaNH$_2$ + MgH$_2$ reaction mixture was heated at 2 °C min$^{-1}$ to 350 °C where heating ceased. The sample desorbed only H$_2$ (Figure 4-32). Again there was a large, sharp initial desorption. This occurred at 170 °C, before rapidly dropping off. There were two other desorptions which peaked at 222 and 350 °C. The mass loss after heating to 350 °C was 5.3 wt%. This agreed well
with the theoretical mass loss of 5.4 wt% for this reaction if all NaH is converted to Na (Equation 4-10).

Figure 4-32 TGA–MS of the NaNH$_2$ + MgH$_2$ reaction. The H$_2$ release is shown in red and the percentage mass loss is shown in black.

3. **Flowing Line Reactions**

The starting materials were again heated at intermediate temperatures in order to investigate the chemical processes involved during dehydrogenation. NaNH$_2$ + MgH$_2$ were heated to 150 °C for 12 hours. This was after the first, small hydrogen desorption observed in the TPD-MS experiment. The products after heating under these conditions were NaH, Mg(NH$_2$)$_2$, NaMgH$_3$
and remaining MgH$_2$ (Figure 4-33), as well as some small phase B peaks, previously suggested to be a mixed Mg-Na amide.

The starting materials, NaNH$_2$ and MgH$_2$, were then heated together for 12 hours to 200 °C. At this temperature, the rate of hydrogen desorption was increasing towards its peak. The products from heating were NaH, Mg(NH$_2$)$_2$, NaMgH$_3$ and MgNa$_{2y}$(NH)$_{1+y}$ and remaining MgH$_2$ (Figure 4-33).
Figure 4-33 Stack plot of powder XRD patterns of NaNH$_2$ + MgH$_2$ heated to 150 °C (black), 200 °C (blue), 250 °C (green), 300 °C (orange) and 350 °C (red).
Table 4-17 Summary table of weight percents and mole fractions of products of NaNH$_2$ + MgH$_2$ from powder XRD shown in Figure 4–33.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>NhMgH$_2$</th>
<th>Phase</th>
<th>Mole Fraction</th>
<th>% in XRD</th>
<th>Weight % in XRD</th>
<th>Mole Fraction</th>
<th>% in XRD</th>
<th>Weight % in XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>300</td>
<td>250</td>
<td>200</td>
<td>150</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>350</td>
<td>300</td>
<td>250</td>
<td>200</td>
<td>150</td>
<td>MgH$_2$</td>
<td>80.30</td>
<td>NA</td>
<td>63.58</td>
</tr>
<tr>
<td>350</td>
<td>300</td>
<td>250</td>
<td>200</td>
<td>150</td>
<td>NaH</td>
<td>11.52</td>
<td>NA</td>
<td>8.71</td>
</tr>
<tr>
<td>350</td>
<td>300</td>
<td>250</td>
<td>200</td>
<td>150</td>
<td>Mg(NH$_2$)$_2$</td>
<td>7.03</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>350</td>
<td>300</td>
<td>250</td>
<td>200</td>
<td>150</td>
<td>NaMgH$_3$</td>
<td>7.19</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>350</td>
<td>300</td>
<td>250</td>
<td>200</td>
<td>150</td>
<td>Mg$_3$N$_2$</td>
<td>8.18</td>
<td>NA</td>
<td>8.71</td>
</tr>
<tr>
<td>350</td>
<td>300</td>
<td>250</td>
<td>200</td>
<td>150</td>
<td>Na</td>
<td>8.18</td>
<td>NA</td>
<td>8.71</td>
</tr>
</tbody>
</table>
The starting materials were also heated to 250 °C. At this temperature the hydrogen desorption had peaked. The products after analysis with powder XRD were NaH, NaMgH$_3$, and MgNa$_{2y}$(NH)$_{1+y}$ as well as remaining MgH$_2$ starting material (Figure 4-33).

The reaction was carried out to 300 °C for 12 hours. The only products were NaH and MgNa$_{2y}$(NH)$_{1+y}$ (Figure 4-33).

When the reaction was carried out at 350 °C for 4 hours, the final products were the same as those after heating on the TPD–MS apparatus: NaH, Mg$_3$N$_2$ and MgNa$_{2y}$(NH)$_{1+y}$ along with some Na (Figure 4-33). Phase C, the suggested mixed Mg-Na nitride, was not seen in the XRD products for this series of reactions.

The full reaction scheme can be written as:

\[
\text{Equation 4-25} \quad 4\text{NaNH}_2 + 4\text{MgH}_2 \rightarrow 2\text{MgNa}_{2y}(\text{NH})_{1+y} + (1-y)\text{Mg}_3\text{N}_2 + (4-4y)\text{NaH} + (3y-1)\text{MgH}_2 + (6-2y)\text{H}_2
\]

No excess MgH$_2$ was observed in the reaction products. For $y = \frac{1}{2}$, MgH$_2$ would be 0. This would give a formula for the imide as Mg$_3$Na$_2$(NH)$_4$. This was close to the possible value for $y$ calculated for 3NaNH$_2$ + 2MgH$_2$, $y = 0.3$.

We found a hydrogen desorption of 3.6 wt% from the TPD-MS apparatus data. This is less than the theoretical mass loss of 4.6 wt% for this reaction.
4. Rehydriding

The products after heating NaNH$_2$ + MgH$_2$ to 300 °C for 12 hours were then subjected to rehydriding conditions. The phases observed by powder XRD prior to rehydrogenation were NaH and MgNa$_{2y}$(NH)$_{1+y}$. These materials were then heated to 350 °C for 24 hours under 75 bar H$_2$ in order to assess whether it was possible to rehydride this system. The products after rehydriding were NaH, MgNH and Mg(NH$_2$)$_2$ (Figure 4-34). Unfortunately, there was also a large amount of MgO present.

Figure 4-34 Powder XRD pattern of NaNH$_2$ + MgH$_2$ heated to 300 °C and then rehydrided at 350 °C for 24 hours under 75 bar H$_2$. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaH (blue tick marks), MgNH (black tick marks), Mg(NH$_2$)$_2$ (green tick marks) and MgO (pink tick marks). $R_{wp} = 15.101$, $R_{exp} = 9.964$, $\chi^2 = 2.3$. 

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaH</td>
<td>35.00 %</td>
</tr>
<tr>
<td>MgNH</td>
<td>26.50 %</td>
</tr>
<tr>
<td>Mg(NH$_2$)$_2$</td>
<td>8.29 %</td>
</tr>
<tr>
<td>MgO</td>
<td>30.21 %</td>
</tr>
</tbody>
</table>
Table 4-18 Summary table of weight percents and mole fractions of products of NaNH₂ + MgH₂ heated to 300 °C and then rehydrided at 350 °C for 24 hours under 75 bar H₂.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight Percent in XRD</th>
<th>Mole Fraction/ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNH</td>
<td>35.00</td>
<td>48.15</td>
</tr>
<tr>
<td>MgNH</td>
<td>26.50</td>
<td>22.25</td>
</tr>
<tr>
<td>Mg(NH₂)₂</td>
<td>8.29</td>
<td>4.85</td>
</tr>
<tr>
<td>MgO</td>
<td>30.21</td>
<td>24.75</td>
</tr>
</tbody>
</table>

5. Discussion

The initial hydrogen desorption peaked at the same temperature as for 3NaNH₂ + 2MgH₂. This was also at the same temperature as the salt metathesis in the other NaNH₂ and MgH₂ reactions, about 150 °C. The furnace power had only a little fluctuation at the metathesis temperature. This indicated minimal metathesis had occurred. This was as expected as less of a metathesis in comparison to 2NaNH₂ + MgH₂ could occur, due to less NaNH₂ being present.

The products after heating NaNH₂ + MgH₂ to 350 °C on TPD-MS (Figure 4–31) were MgNa₂y(NH)₁+y which was a major product from the sodium rich reactions, 2NaNH₂ + MgH₂ and 3NaNH₂ + 2NaH (sections 4.2.2, 4.2.3) and Mg₃N₂ which was the majority product from 2NaNH₂ + 3MgH₂ without any MgNa₂y(NH)₁+y present (section 4.2.1).

After heating for 12 hours at 150 °C the full salt metathesis had occurred (Equation 4-26).

Equation 4-26  
2NaNH₂ + 2MgH₂ → Mg(NH₂)₂ + NaH + MgH₂
The reaction of NaNH$_2$ with MgH$_2$ in a 1:1 molar ratio can be compared to that of LiNH$_2$ + MgH$_2$ (1:1). The starting materials (LiNH$_2$ + MgH$_2$) in the work of Liu et al.$^{48}$ were ball-milled together, and after 12 hours of milling at room temperature, the products were: Mg(NH$_2$)$_2$, LiH and MgH$_2$ (Equation 4-27). These are the equivalent metathesis products to our reaction.

$$\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{Mg(NH}_2)_2 + \text{LiH} + \text{MgH}_2$$

From the reaction to 350 °C there was no amide phase present (Figure 4-33). This indicated a complete desorption reaction had occurred at this temperature.

The products from this reaction concur with the analogous 2LiNH$_2$ + (3)MgH$_2$ reactions. As mentioned above, the 2LiNH$_2$ + MgH$_2$ reaction$^{49}$ only goes as far as Li$_2$Mg(NH)$_2$, whereas 2LiNH$_2$ + 3MgH$_2$ went to completion, giving Mg$_3$N$_2$ and LiH as products. A ratio of starting materials between 2LiNH$_2$ + MgH$_2$ and 2LiNH$_2$ + 3MgH$_2$ would be expected to have mixed products. The Na observed was due to the thermal decomposition of NaH (Equation 4-10).

The final products from NaNH$_2$ + MgH$_2$ also agree with LiNH$_2$ + MgH$_2$ from Liu et al.$^{48}$ Their final products were Mg$_3$N$_2$, LiH and Li$_2$Mg(NH)$_2$ (Equation 4-28). We have the equivalents for our system, Mg$_3$N$_2$, NaH and MgNa$_{2y}$(NH)$_{1+y}$ (Equation 4-25).

$$4\text{LiNH}_2 + 4\text{MgH}_2 \rightarrow \text{Mg}_3\text{N}_2 + 2\text{LiH} + \text{Li}_2\text{Mg(NH}_2)_2 + 6\text{H}_2$$
The lack of Mg\(\text{Na}_{2y}(\text{NH})_{1+y}\) and the presence of Mg\(\text{NH}_2\) in the XRD pattern after rehydriding showed that the rehydriding attempt was partially successful (Figure 4-34). Usually, it would be suggested that longer heating or increased hydrogen pressure would force the MgNH to convert fully to Mg\(\text{NH}_2\) and MgH\(\text{H}_2\). However, as there was not enough nitrogen present, MgNH could not go directly to Mg\(\text{NH}_2\). There was much more MgNH present after this rehydriding in comparison to other rehydrogenation reactions of \(x\text{NaNH}_2 + y\text{MgH}_2\) reactions shown above. This may be related to the large amount of MgO present.

Liu et al.\(^{52}\) attempted to rehydride the products of heating Li\(\text{NH}_2\) + MgH\(\text{H}_2\) to 390 °C (Mg\(\text{N}_3\), Li\(\text{H}_2\)Mg\(\text{NH}_2\) and LiH). After rehydriding, the products were Mg\(\text{N}_3\), LiH and Mg\(\text{NH}_2\). This result was similar to Dolotko et al. who rehydrided the products from 2Li\(\text{NH}_2\) + 3MgH\(\text{H}_2\) [Mg\(\text{N}_3\) and LiH]. It can be seen the mixed imide could be rehydrided, whereas the Mg\(\text{N}_3\) could not. The Mg\(\text{N}_3\) remaining from both these rehydrogenation attempts showed that by stopping the forward reaction before Mg\(\text{N}_3\) was formed a complete rehydrogenation was much more likely to go fully under moderate temperatures and pressures.

Xiong et al.\(^{19}\) investigated the reaction between Mg\(\text{NH}_2\) and NaH in a 1:1 ratio. However, rehydrogenation was only attempted for Mg\(\text{NH}_2\) + NaH in a 2:3 ratio. This reaction, when heated, formed the same Mg\(\text{Na}_{2y}(\text{NH})_{1+y}\) phase as formed by Sheppard et al.\(^{21}\) When rehydrided the products were Mg\(\text{NH}_2\) and NaH.

The full reaction scheme for \(\text{NaNH}_2 + \text{MgH}_2\) heated in a flowing line is shown in Table 4-19.
Table 4-19 Overall reaction scheme of NaNH$_2$ + MgH$_2$ heated to various temperatures. The products from each temperature are shown, the temperature at which new phases form and the lattice parameters of the new phases.

<table>
<thead>
<tr>
<th>Temp/ °C</th>
<th>Reaction Scheme</th>
<th>Products</th>
<th>New Phase(s)</th>
<th>Lattice Parameters/ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>NaNH$_2$ + MgH$_2$ → NaH, Mg(NH$_2$)$_2$, MgH$_2$</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>200</td>
<td>Mg(NH$_2$)$_2$ + 2NaH + MgH$_2$ → NaH, MgH$_2$, Mg(NH$_2$)$_2$, NaMgH$_3$, H$_2$</td>
<td>MgNa$<em>{2y}$(NH)$</em>{1+y}$ (Phase A)</td>
<td>$a = 6.1677(8)$, $c = 17.997(5)$</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>NaH, NaMgH$_3$, MgH$_2$</td>
<td>MgNa$<em>{2y}$(NH)$</em>{1+y}$ (Phase A)</td>
<td>$a = 6.1299(4)$, $c = 17.928(14)$</td>
<td></td>
</tr>
<tr>
<td>275</td>
<td>NaH + MgH$_2$ → NaMgH$_3$</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>350</td>
<td>Mg(NH$_2$)$_2$ + 2NaH + MgH$_2$ → NaH, Mg$_3$N$_2$, Na, H$_2$</td>
<td>MgNa$<em>{2y}$(NH)$</em>{1+y}$ (Phase A)</td>
<td>$a = 6.1182(3)$, $c = 17.9117(9)$</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>NaH → Na, H$_2$</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

In this study, it was found over the course of the investigation that excess MgH$_2$ after metathesis was always present when Mg$_3$N$_2$ was formed. Therefore, we conclude that excess MgH$_2$ is the reason that Mg$_3$N$_2$ is formed in some $\alpha$NaNH$_2$ + $\gamma$MgH$_2$ reactions and not others.

One possibility is that the MgH$_2$ still present after heating the reaction to 250 °C reacted with MgNa$_{2y}$(NH)$_{1+y}$ in order to form Mg$_3$N$_2$. Where there was a limited amount of MgH$_2$, only some of the MgNa$_{2y}$(NH)$_{1+y}$ could be converted into Mg$_3$N$_2$ (NaNH$_2$ + MgH$_2$). It was found that heating magnesium metal with NaNH$_2$ formed Mg$_3$N$_2$ along with sodium metal with the release of hydrogen (Equation 4-29). It might therefore be possible for the remaining MgH$_2$ after forming MgNa$_{2y}$(NH)$_{1+y}$, to decompose to Mg metal which could have gone on to displace Na from MgNa$_{2y}$(NH)$_{1+y}$ to form Mg$_3$N$_2$. The continued hydrogen release suggests this was a possible mechanism for the formation of Mg$_3$N$_2$. It may be unlikely however, due to electrode potentials.
The formation of the Mg$_3$N$_2$ was the driving factor for the decomposition of Mg$_{(1-0.5x)}$Na$_x$(NH) as sodium does not form a stable nitride.

Equation 4-29

\[ 2\text{NaNH}_2 + 3\text{Mg} \rightarrow \text{Mg}_3\text{N}_2 + 2\text{Na} + 2\text{H}_2 \]

Mg$_3$N$_2$ was present with NaNH$_2$ + MgH$_2$ as with 2NaNH$_2$ + 3MgH$_2$, therefore enough MgH$_2$ was present. In order to make MgNa$_{2y}$(NH)$_{1+y}$ pure, less MgH$_2$ is needed. 4NaNH$_2$ + 3MgH$_2$ may help in the formation of a pure MgNa$_{2y}$(NH)$_{1+y}$, although it would be difficult to make it pure without knowing the exact stoichiometry. The results from 3NaNH$_2$ + 2MgH$_2$ and NaNH$_2$ + MgH$_2$ suggest $x = 0.3 – 0.333$, this would help in defining the optimum starting materials to form the mixed imide pure.

The overall reaction schemes of each of the $x\text{NaNH}_2 + y\text{MgH}_2$ reactions have been detailed by Table 4-4, Table 4-9, Table 4-15 and Table 4-19. It can be seen at what temperatures the new phases (A, B and C) form at and how their lattice parameters vary with temperatures at which they were formed. It can also be seen at what temperatures the side reactions form at when independent of the other starting materials.

Throughout this work it could be seen that Mg$_{(1-0.5x)}$Na$_x$(NH)/MgNa$_{2y}$(NH)$_{1+y}$ could be rehydrided back to Mg(NH)$_2$ and NaH. Sometimes a longer heating time, greater pressure or ball-milling may have been needed to complete the rehydrogenation. As the rehydriding was carried out on hand ground mixtures was shown to be partially successful, the increased surface area that comes with ball-milling could significantly improve rehydrogenation kinetics. The only reaction
to attempt to rehydride Mg$_3$N$_2$ and Na was from 2NaNH$_2$ + 3MgH$_2$ reacted at 250 °C. This rehydrogenation could only form NaH and a little MgNH. A higher pressure of 190 bar H$_2$ was found not to assist in the rehydrogenation of this reaction.$^{12}$ In order to allow for a completely reversible reaction pathway, the products from heating must go no further than Mg$_{6(1-0.5x)}$Na$_x$(NH)/MgNa$_2y$(NH)$_{1+y}$. Rehydrogenation of Mg$_3$N$_2$ was not possible under the conditions investigated in this study or in the literature (Kojima$^{38}$) although Leng et al. and Nakamori et al. found it possible.$^{6,51}$

Liu et al.$^{52}$ investigated the effect of Na compounds upon the Li-Mg-N-H system with partial substitution of Mg(NH$_2$)$_2$ for NaNH$_2$ and LiH for NaH. It was found that the hydrogen desorption kinetics of the Na containing reactions were markedly improved. NH$_3$ desorption was also lessened. As the activation energies were less, the Na containing reactions desorbed their hydrogen quicker and at lower temperatures. Due to the higher mass of Na compared to Li, the gravimetric hydrogen capacity of the system is less than in the Li-Mg system. The dehydrogenation products were different depending on the molar ratios between Li, Mg and Na.

A comparison of the lattice parameters of Mg$_{6(1-0.5x)}$Na$_x$(NH)/MgNa$_2y$(NH)$_{1+y}$ (phase A) throughout the reactions at different temperatures was carried out. The Mg$_{6(1-0.5x)}$Na$_x$(NH)/MgNa$_2y$(NH)$_{1+y}$ phase occurring at 200 °C for all reactions had significantly larger lattice parameters than the phase appearing at higher temperatures. The phases at 200 °C had much broader peaks in their respective XRD patterns than at higher temperatures. This may be due to higher temperatures being necessary to form a more crystalline form of
Mg\(_{(1-0.5x)}\)Na\(_{x}\)(NH)/MgNa\(_{2y}\)(NH)\(_{1+y}\). The most crystalline peaks were those formed at 300 °C. The variation in the lattice parameters may also be due to the variability in stoichiometry of the imide or a solid solution being formed. There are already known stoichiometric and non-stoichiometric phases associated with group 1/2 phases. For example, a non-stoichiometric amide like Li\(_x\)Mg\(_{2-x}\)(NH\(_2\))\(_{2+x}\) for 0 < x < 1,\(^4^0\) a stoichiometric imide Li\(_2\)Mg(NH)\(_2\),\(^4^6\) or non-stoichiometric nitrides—(Li\(_x\)Mg\(_{1-x}\))\(_3\)N\(_{2-x}\), 0 < x < 0.2 and (Li\(_x\)Mg\(_{1-x}\))\(_2\)N\(_{2/3}\), 0.5 < x < 0.6.\(^5^3\) Mixed amide/imides were also formed by Aoki et al.\(^5^4\) when reacting 3Mg(NH\(_2\))\(_2\) with 12LiH. They found new tetragonal and orthorhombic phases. These corresponded to Li\(_4\)Mg\(_3\)(NH\(_2\))\(_2\)(NH)\(_4\) and Li\(_{4+\epsilon}\)Mg\(_3\)(NH\(_2\))\(_2\)(NH)\(_{4+\epsilon}\) (\(x = 0.4, 1, 2\)) respectively. Of course, LiNH\(_2\) and Li\(_2\)NH can also be non-stoichiometric as described in Equation 4-30.

\[
\text{Equation 4-30} \quad \text{Li}_{2-x}\text{NH}_{1+x} + \epsilon \text{H}_2 \rightarrow \text{Li}_{2-x}\text{NH}_{1+x} \epsilon \text{H} + \epsilon \text{LiH}
\]

where non-stoichiometric lithium imide has a lithium deficient/proton excess composition. \(x\) denotes the number of lithium vacancies which must equal the number of excess protons.\(^5^5\)

Lithium is also known to form both stoichiometric and non-stoichiometric amides with sodium (LiNa\(_2\)(NH\(_2\))\(_3\)) and Li\(_{6-x}\)Na\(_x\)(NH\(_2\))\(_4\) for 0 ≤ x ≤ 1.\(^5^5\) Sheppard et al. suggested the MgNa\(_{2y}\)(NH)\(_{1+y}\) phase was a solid solution due to the peak shift occurring at different temperatures. This was thought to occur due to compositional changes in the imide structure due to Na or Mg migration to or from the phase as a function of reaction and/or temperature.
Luo and Sickafoue et al.\textsuperscript{22} also found another Li-Mg-N-H phase on rehydriding Li$_2$Mg(NH)$_2$, Li$_2$MgN$_2$H$_{3.2}$ (Equation 4-31).

\textbf{Equation 4-31} \hspace{1cm} \text{Li}_2\text{MgN}_2\text{H}_2 + 0.6\text{H}_2 \rightarrow \text{Li}_2\text{MgN}_2\text{H}_{3.2}

The reactions of $x\text{NaNH}_2 + y\text{MgH}_2$ and $x\text{LiNH}_2 + y\text{MgH}_2$ appear to be very similar in mechanism. The stoichiometric and non-stoichiometric phases above show the possible phases that may be formed by a mixed Na-Mg-N-H system. Further work would need to be carried out in order to establish how many Li-Mg-N-H phases have analogous Na-Mg-N-H counterparts.

\begin{itemize}
\end{itemize}


F. Ephraim, Zeitschrift für Anorganische Chemie, 44 (1905) 185–199


5. NaNH₂ + NaH

1. Introduction

1. NaNH₂

Although interesting products and reaction schemes have been discovered in the process of reacting light metal amides and hydrides together, it is important to understand as fully as possible what reaction pathways the starting materials take when they are heated alone. Most of the starting materials used in this research have been fully investigated outside of this work; however, NaNH₂ has been relatively neglected and therefore further experiments were required in order to confirm the decomposition products of NaNH₂. Also of interest was whether there are any similarities between the reactions of NaNH₂ + NaH and LiNH₂ + LiH. In the Li-based system, it is well known that LiNH₂ decomposes, both alone and when heated with LiH, to Li₂NH.¹ ² There is, however, no known analogous sodium imide phase. Titherley et al.³ originally investigated the decomposition of NaNH₂ heated under vacuum. They found there was no change until 200 °C when the sodium amide started to distil as an almost colourless liquid with a green tinge. 210 °C is the known melting point of NaNH₂. At 300–400 °C the liquid appeared dark green and apparently unchanged, but at 500–600 °C gas was evolved owing to the decomposition of the amide. The sample was kept at that temperature for 1 hour. Sodium metal was the only observed product, but there was no evidence of sodium nitride.

When Titherley et al.³ investigated the decomposition of sodium amide, they found it decomposed down to its elements and not sodium nitride as suggested by Gay Lussac et al.⁴
Titherley et al. did find, however, that the ratio of $N_2$ to $H_2$ release was not 1:2 as expected. The deficiency of hydrogen was put down to its reducing action on the glass of the reacting vessel and some absorption by the metallic sodium. There was only slight decomposition on approaching 600 °C and none at all at 300–400 °C.

Further experiments done on heating sodium amide at 300–350 °C for 1 h under hydrogen found a scarcely appreciable amount of gas desorbed and the sodium amide remained unchanged. When repeated at 450 °C the decomposition was again scarcely appreciable with gas evolved very slowly. The gas comprised chiefly of ammonia, with a little hydrogen and nitrogen. At higher temperatures the same result as under vacuum occurred. However, on heating sodium amide under flowing ammonia at “dull-redness” temperature (500–600 °C) the ammonia is continuously decomposed to its elements. Titherley et al. concluded that the sodium amide split into its constituent elements, nitrogen, hydrogen and sodium, with sodium going to reform sodium amide under the ammonia atmosphere and decomposing again, therefore forming endless amounts of nitrogen and hydrogen at a lower temperature than normal, in other words sodium amide was a catalyst for the decomposition of ammonia. They concluded that neither Na$_2$NH nor Na$_3$N could be formed by heating NaNH$_2$.

The authors$^3$ then investigated whether the action of sodium on sodium amide could form either of the above products. Excess sodium was heated with sodium amide under hydrogen. If Na$_2$NH were formed hydrogen would be released (Equation 5-1). If the sodium merely remained in solution with the sodium amide, no gas release would be observed.

$$\text{Equation 5-1} \quad 2\text{NaNH}_2 + 2\text{Na} \rightarrow 2\text{Na}_2\text{NH} + \text{H}_2$$
The reaction was carried out under vacuum, hydrogen and nitrogen but no gas release was observed. It was suggested that compounds of formula \((\text{NaNH}_3)_2\) (sodammonium) or \((\text{Na} \cdot \text{NaNH}_2)_2\) (disodammonium, alternatively written as \(\text{Na}_2\text{H}_2\text{N} \cdot \text{NH}_2\text{Na}_2\)) was formed but no experiments were carried out to ascertain exactly what had been formed.

McGee \textit{et al.}\textsuperscript{6} found the rate of decomposition of \(\text{NaNH}_2\) at 210 °C (the melting temperature) was slow, but increased with increasing temperature. The evolved gas at 300 °C was collected and tested. It was found to be ammonia, with no evidence of nitrogen or hydrogen. Further testing was carried out on the residue left in the cell. When decomposed with absolute alcohol and distilled water, only ammonia was desorbed, with no hydrogen, as would have been expected had sodium metal been present. The conclusion of McGee \textit{et al.} was that the residue was either sodium imide (Equation 5-2) or nitride (Equation 5-3), and not sodium metal, along with undecomposed amide.

\begin{align*}
\text{Equation 5-2} & \quad 2\text{NaNH}_2 \rightarrow \text{Na}_2\text{NH} + \text{NH}_3 \\
\text{Equation 5-3} & \quad 3\text{NaNH}_2 \rightarrow \text{Na}_3\text{N} + 2\text{NH}_3
\end{align*}

Although a little unclear, the conclusions of Titherley \textit{et al.}\textsuperscript{3} result from \(\text{NaNH}_2\) being heated to between 500 and 600 °C, and therefore not comparable with the work of McGee \textit{et al.}\textsuperscript{6} carried out at 300 °C. Bergstrom \textit{et al.}\textsuperscript{7} commented directly on the work of McGee \textit{et al.} to suggest the decomposition of the amide into imide had its origin in the reaction of the amide with the glass container and, possibly, also in the reaction with platinum present.
In 1933, Bergstrom et al.\textsuperscript{7} carried out further work. They commented on NaNH\textsubscript{2} heated at 300–400 °C only to say it was unchanged, except for a little darkening of the liquid. At 400 °C they commented that the substance started to volatilize and then rapidly evolved gas between 500 and 600 °C. Bergstrom et al. found this gas to be hydrogen and nitrogen evolved in a 2:1 ratio with metallic sodium remaining. This suggests the reaction:

\begin{equation}
2\text{NaNH}_2 \rightarrow 2\text{Na} + 2\text{H}_2 + \text{N}_2
\end{equation}

However, it depends on how well the volumes of each could be measured, as it is possible NH\textsubscript{3} was decomposing to give the H\textsubscript{2} and N\textsubscript{2} evolved. It may be possible that although the ultimate decomposition is to the elements, that a nitrogen containing intermediate product could be formed (Equation 5-2 or Equation 5-3) along with the release of ammonia. The intermediate may then decompose to sodium metal with the release of nitrogen, along with the decomposition of ammonia gas.

Further investigations into the decomposition of NaNH\textsubscript{2} were carried out by Sakurazawa et al.\textsuperscript{8} referenced by Juza et al.\textsuperscript{9} This work suggested that between 335 and 400 °C two possible modes of thermal decomposition of sodium amide can occur depending on the overall pressure of the system. If the pressure of the system is greater than the dissociation pressure of NaH, then NaH is the solid product accompanied by N\textsubscript{2} and H\textsubscript{2} (Equation 5-5).

\begin{equation}
2\text{NaNH}_2 \rightarrow 2\text{NaH} + \text{N}_2 + \text{H}_2
\end{equation}
However, if the total pressure is below the dissociation pressure of NaH, then the NaH decomposes to Na giving a greater desorption of H₂, along with N₂, (Equation 5–4). Ammonia was also produced along with the nitrogen and hydrogen, but they gave no indication of how much.

The crystal structure of NaNH₂ was first solved in 1956 concurrently by Juza et al.¹⁰ and Zalkin et al.¹¹ The conclusion of both groups found it to be an orthorhombic structure of space group Fddd. Zalkin et al. found the lattice parameters were $a = 8.964(3) \, \text{Å}$, $b = 10.456(3) \, \text{Å}$ (Figure 5-1) and $c = 8.073(3) \, \text{Å}$, in comparison to $a = 8.06 \, \text{Å}$, $b = 8.929 \, \text{Å}$ and $c = 10.427 \, \text{Å}$ published by Juza et al.

![Figure 5-1 Crystal structure of NaNH₂. Sodium sites are shown in dark blue, nitrogen sites in light blue and hydrogen sites in white. The unit cell is shown in black.¹¹](image)

2. Na₃N

Research has also been carried out into the viability of the formation of Na₃N. Gay-Lussac et al.⁴ first suggested the formation of Na₃N on the decomposition of NaNH₂. They identified a dark, infusible mass, when NaNH₂ was heated in a glass tube, as Na₃N (Equation 5-3). This
was dismissed by Titherley et al.\textsuperscript{3} because sodium amide behaves differently when not heated in contact with glass. The dark colour quoted by Gay-Lussac et al.\textsuperscript{4} was not present when NaNH\textsubscript{2} was heated in a different vessel. The liquid NaNH\textsubscript{2} was observed to have a pale green colour that became colourless on cooling. As it is now known that sodium and other alkali metals react with glass turning it dark brown, the differences in reactions observed can be explained by the reaction of sodium amide with the vessel the experiment was carried out in. Titherley et al.\textsuperscript{3} tried to form Na\textsubscript{3}N by heating NaNH\textsubscript{2} with Na\textsubscript{2}O unsuccessfully. The reactants only fused and mixed together and were possible to separate again by heating strongly and distilling off the amide from the oxide.

Moldenhauer and Mottig suggested that evaporating a mixture of sodium azide (NaN\textsubscript{3}) and Na could go to form sodium nitride (Equation 5-6).\textsuperscript{12} However, no further work has been investigated in order to confirm the results of Moldenhauer and Mottig.

\textbf{Equation 5-6} \hspace{1cm} NaN\textsubscript{3} + 8Na \rightarrow 3Na\textsubscript{3}N

Na\textsubscript{3}N was formed by passing electrical discharges through sodium under low nitrogen pressure.\textsuperscript{13,14} Na\textsubscript{3}N was also prepared by reacting metallic Na or liquid Na-K alloy with plasma activated nitrogen at low pressure. Its formation seems not to be possible under more conventional chemical conditions.

The crystal structure of Na\textsubscript{3}N, as formed by Vajenine et al. is shown below (Figure 5-2). It was found to be cubic, space group \textit{Pm\textendash}3\textit{m}, with a lattice parameter of \(a = 4.7250(16)\) Å.
In stark contrast to Na$_3$N, Li$_3$N forms spontaneously from the elements at room temperature. Na$_3$N does not form spontaneously and evidence so far seems to be that Na$_3$N is only formed under unusual conditions. Fischer and Jansen formed Na$_3$N from generating Na and N$_2$ in a vacuum chamber and co-depositing them on a cooled substrate. This resulted in a statistical mixture of the atoms. This was then heated to room temperature. Their XRD pattern showed a pattern that could be refined to Na$_3$N.

The difficulty in making Na$_3$N highlights a difference from the Li-system. It is unlikely that if Na$_2$NH did form, that Na$_3$N would result from the decomposition of it. This effectively excludes Equation 5-3 as a possibility. Na$_3$NH has been discounted as forming (Equation 5-2) therefore other than that, it seems the solid product expected from the decomposition of NaNH$_2$ can only be Na or NaH.
2. Results

1. NaNH$_2$

1. Temperature Programmed Desorption-Mass Spectrometry

NaNH$_2$ starting material was heated at 2 °C min$^{-1}$ to 350 °C for 4 hours on a flowing gas line. The powder XRD pattern taken after heating gave a set of peaks that did not match any known phase in the JCPDS database (Figure 5-3). There was no evidence of NaH or Na. A small amount of NaNH$_2$ was present. NaNH$_2$ is labelled in Figure 5-3 as 100% as it was the only Rietveld refined phase present.

![Figure 5-3 Powder XRD pattern (from ID31, ESRF) of NaNH$_2$ heated to 350 °C for 4 hours. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phase NaNH$_2$ (blue tick marks). $R_{wp} = 34.699$, $R_{exp} = 3.403$, $\chi^2 = 104.0$.](image)

The same reaction was carried out on a TPD-MS apparatus in order to establish whether any gas had been desorbed. From the desorption profile of NaNH$_2$ (Figure 5-4), it was seen that ammonia, NH$_3$, was the major gas desorbed. It can be seen that N$_2$ was also desorbed at the peak of NH$_3$ desorption. It was possible that an equilibrium between NH$_3$ and N$_2$/H$_2$ was present here. The H$_2$ desorption level also increased slightly at the same point (0.3 wt%
total). Unfortunately we were unable to quantify accurately the amount of $N_2$ released as the TPD-MS apparatus used was not calibrated for $N_2$.

There was a fluctuation in the temperature trace at around 200 °C. This is close to the melting point of NaNH$_2$ (210 °C). The onset of ammonia release was shortly after the sample had melted, at 220 °C. A comparison of the temperature fluctuation in Figure 5-4 with the furnace power (Figure 5-5) at the same temperature can see the power input into the sample increases before decreasing. This was a sign of an endothermic event occurring which was consistent with a melting event. The peak of desorption was at 330 °C, just before the isotherm at 350 °C. The total ammonia desorbed was 17.5 wt%.

![Figure 5-4 TPD-MS analysis of the heating of NaNH$_2$. The temperature trace is shown in black and the MS traces for H$_2$, NH$_3$ and N$_2$ are shown in red, green and orange, respectively.](image-url)
2. **Flowing Line Reactions**

The same reaction was carried out at 20 °C intervals between 230 and 350 °C for 4 hours. From the powder XRD patterns shown in Figure 5-6, it can be seen in comparison to NaNH$_2$ heated to 230 °C (no change to starting material) that the unidentified peaks were first visible after heating NaNH$_2$ to 270 °C. By 350 °C, the majority of NaNH$_2$ had disappeared although a small amount still remained. The starting material peaks were very distinctive until 330 °C. At no point was NaH or Na visible. Indexing was unsuccessful when attempted on the product from heating to 350 °C for 4 hours.

![Figure 5-5 Furnace power during the TPD-MS analysis of NaNH$_2$ reaction. The furnace power and temperature are shown in blue and black respectively.](image)
Figure 5-6: Powder XRD patterns of NaNH$_2$ heated to 230 °C (red), 250 °C (dark green), 310 °C (light green), 290 °C (dark blue), 330 °C (light blue), 310 °C (dark blue) and 350 °C (purple). The spectra are offset on the vertical scale for clarity.

NaNH$_2$, 2°C/min to 230°C, 4 hours, 2°C/min to 20°C, fg Ar
Operations: Import
NaNH$_2$, 2°C/min to 350°C, 4 hours, 2°C/min to 20°C, fg Ar
Operations: Add Y Scale 200 | Add Y Scale 1 | Add Y Scale 142 | Add Y Scale 400 | Add Y Scale 1 | Add Y Scale 2000 | Import
NaNH$_2$, 2°C/min to 330°C, 4 hours, 2°C/min to 20°C, fg Ar
Operations: Add Y Scale 142 | Add Y Scale 400 | Add Y Scale 1 | Add Y Scale 2000 | Import
NaNH$_2$, 2°C/min to 310°C, 4 hours, 2°C/min to 20°C, fg Ar
Operations: Add Y Scale 1000 | Add Y Scale 3000 | Import
NaNH$_2$, 2°C/min to 290°C, 4 hours, 2°C/min to 20°C, fg Ar
Operations: Add Y Scale 142 | Add Y Scale 400 | Add Y Scale 1 | Add Y Scale 2000 | Import
NaNH$_2$, 2°C/min to 270°C, 4 hours, 2°C/min to 20°C, fg Ar
Operations: Add Y Scale 1000 | Add Y Scale 3000 | Import
NaNH$_2$, 2°C/min to 250°C, 4 hours, 2°C/min to 20°C, fg Ar
Operations: Add Y Scale 2000 | Add Y Scale 6000 | Import
NaNH$_2$, 2°C/min to 230°C, 4 hours, 2°C/min to 20°C, fg Ar
Operations: Add Y Scale 200 | Add Y Scale 1 | Add Y Scale 1000 | Add Y Scale 3000 | Import
There was little change to the lattice parameters of NaNH$_2$ throughout the heating of these reactions (Table 5-1). The possible variation of NaNH$_2$ lattice parameters were compared in order to establish whether a Na$_{2-x}$NH$_{1+x}$ type solid solution would be formed. This would be similar to the solid solution observed for LiNH$_2$-Li$_2$NH. The unit cell volume reduced upon heating in comparison to the lattice parameters found for the NaNH$_2$ starting material. The greatest difference in volume of NaNH$_2$ unit cell was noticed for samples heated to 230 °C and 250 °C.

Table 5-1 Lattice parameters of NaNH$_2$ heated to between 230 and 350 °C.

<table>
<thead>
<tr>
<th>Temp/ °C</th>
<th>$a$/ Å</th>
<th>$b$/ Å</th>
<th>$c$/ Å</th>
<th>Volume/ Å$^3$</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td>R. T.</td>
<td>8.968</td>
<td>10.458</td>
<td>8.076</td>
<td>757.427</td>
<td>-</td>
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<td>230</td>
<td>8.96097(4)</td>
<td>10.45227(5)</td>
<td>8.07276(4)</td>
<td>756.115(6)</td>
<td>-0.172</td>
</tr>
<tr>
<td>250</td>
<td>8.96046(4)</td>
<td>10.45341(5)</td>
<td>8.07316(4)</td>
<td>756.192(7)</td>
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<tr>
<td>270</td>
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<td>10.4477(12)</td>
<td>8.07462(9)</td>
<td>756.13(14)</td>
<td>-0.164</td>
</tr>
<tr>
<td>290</td>
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<td>8.0757(2)</td>
<td>756.20(4)</td>
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</tr>
<tr>
<td>310</td>
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<td>8.0767(2)</td>
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</tr>
<tr>
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<td>8.0772(5)</td>
<td>756.29(7)</td>
<td>-0.152</td>
</tr>
<tr>
<td>350</td>
<td>8.9663(3)</td>
<td>10.435(3)</td>
<td>8.085(2)</td>
<td>756.4(4)</td>
<td>-0.131</td>
</tr>
</tbody>
</table>

Although there was a small amount of NaNH$_2$ still present at 350 °C, this was greatly reduced in comparison to the sample heated to 330 °C. NaNH$_2$ was heated to 350 °C for 12 hours in order to see if the transformation to the new phase would complete over a longer time. No NaNH$_2$ was present after the longer heating time (Figure 5-7).
3. Rehydriding

A sample of NaNH$_2$ heated to 350 °C was put under 100 bar H$_2$ pressure at 300 °C for 48 hours in order to see if it would take up hydrogen. These experiments were unsuccessful and the only peaks present in the XRD pattern afterwards were the previously unidentified peaks (Figure 5-8).

Figure 5-7 Powder XRD pattern of NaNH$_2$ heated to 350 °C for 12 hours.

Figure 5-8 Powder XRD pattern comparison of NaNH$_2$ heated to 350 °C (purple pattern) put under 100 bar H$_2$ at 300 °C for 48 hours (black pattern).
2. NaNH$_2$ + NaH

1. Temperature Programmed Desorption-Mass Spectrometry

No previous work has been reported on the reaction of NaNH$_2$ with NaH. This reaction was of interest to investigate as it could then be compared to the reaction of lithium amide with lithium hydride (Equation 5-7). In the latter reaction, lithium imide was formed with the release of hydrogen (Equation 5-7). Of interest was whether the reaction of NaNH$_2$ with NaH would release ammonia, like NaNH$_2$ alone (Figure 5-4), or hydrogen, like LiNH$_2$ + LiH.

\[
\text{Equation 5-7} \quad \text{LiNH}_2 + \text{LiH} \rightarrow \text{Li}_2\text{NH} + \text{H}_2
\]

NaNH$_2$ and NaH were heated together in a 1:1 ratio at 2 °C min$^{-1}$ to 350 °C and held for 4 hours. The XRD pattern from this reaction (Figure 5-9) gave the same set of unidentified peaks as NaNH$_2$ heated alone to 350 °C (Figure 5-3) alongside some NaNH$_2$ remaining.

Figure 5-9 Powder XRD pattern (from ID31, ESRF) of NaNH$_2$ + NaH heated to 350 °C for 4 hours. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaNH$_2$ (blue tick marks). $R_{wp} = 33.107$, $R_{exp} = 2.546$, $\chi^2 = 169.1$. 

[Diagram of XRD pattern]
Figure 5-10 Powder XRD patterns (from ID31, ESRF) comparing NaNH$_2$ (black) heated to 350 °C for 4 hours and NaNH$_2$ + NaH (green) heated to 350 °C for 4 hours. The powder XRD patterns with the observed phase of NaNH$_2$ (blue tick marks) beneath are shown.

As before, the reaction was then carried out on a TPD-MS apparatus in order to establish what gas(es), if any, were desorbed. As can be seen in Figure 5-11, only hydrogen gas was released. The desorption started slowly as soon as heating was commenced. The rate of desorption increased at about 200 °C and peaked at about 318 °C. As the rate of desorption decreased, a second amount of hydrogen was desorbed as the isothermal heating started and slowly tailed off.
Figure 5-11 TPD-MS analysis of the reaction of NaNH$_2$ + NaH. The temperature trace is shown in black and the MS traces for H$_2$, NH$_3$ and N$_2$ are shown in red, green and orange, respectively.

2. **Flowing Line Reactions**

As with heating NaNH$_2$ alone, we heated the NaNH$_2$ + NaH mixture to intermediate temperatures between 230 and 350 °C for 4 hours. Heating to below 350 °C for the same length of time gave starting materials as well as the unidentified new peaks present in the XRD pattern. The new peaks first appeared at 290 °C. At 350 °C there was still NaNH$_2$ present. No NaH or Na was found at any temperature (Figure 5-12).
Figure 5-12 Powder XRD patterns of NaNH$_2$ + NaH heated to 230 °C (red), 250 °C (orange), 270 °C (light green), 290 °C (dark green), 310 °C (light blue), 330 °C (dark blue) and 350 °C (purple). The spectra are offset on the vertical scale for clarity.

NaNH$_2$ + NaH, 2C/min to 230°C, 4 hours, 2C/min to 20°C, fg Ar
Operations: Import
NaNH$_2$ + NaH, 2C/min to 350°C, 4 hours, 2C/min to 20°C, fg Ar - File: AK98.RAW - Type: PSD fast-scan - Operations: Y Scale Add -1275 | Y Scale Add 1500 | Y Scale Add -1000 | Y Scale Add 2000 | Import
NaNH$_2$ + NaH, 2C/min to 330°C, 4 hours, 2C/min to 20°C, fg Ar - File: AK99.RAW - Type: PSD fast-scan - Operations: Y Scale Add -1825 | Y Scale Add 2401 | Y Scale Add -1000 | Y Scale Add 3000 | Import
NaNH$_2$ + NaH, 2C/min to 310°C, 4 hours, 2C/min to 20°C, fg Ar - File: AK100.RAW - Type: PSD fast-scan - Operations: Y Scale Add -3475 | Y Scale Add 4500 | Y Scale Add -1000 | Y Scale Add 4000 | Import
NaNH$_2$ + NaH, 2C/min to 290°C, 4 hours, 2C/min to 20°C, fg Ar - File: AK101.RAW - Type: PSD fast-scan - Operations: Y Scale Add -4575 | Y Scale Add 6000 | Y Scale Add -1000 | Y Scale Add 5000 | Import
NaNH$_2$ + NaH, 2C/min to 270°C, 4 hours, 2C/min to 20°C, fg Ar - File: AK102.RAW - Type: PSD fast-scan - Operations: Y Scale Add 100 | Y Scale Add 375 | Y Scale Add 1200 | Y Scale Add -1000 | Import
NaNH$_2$ + NaH, 2C/min to 250°C, 4 hours, 2C/min to 20°C, fg Ar - File: AK103.RAW - Type: PSD fast-scan - Operations: Y Scale Add 5 | Y Scale Add 925 | Y Scale Add 1200 | Y Scale Add -1000 | Import
NaNH$_2$ + NaH, 2C/min to 230°C, 4 hours, 2C/min to 20°C, fg Ar - File: AK104.RAW - Type: PSD fast-scan - Operations: Y Scale Add -167 | Y Scale Add 925 | Y Scale Add 1200 | Y Scale Add -1000 | Import

Lin (Counts)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
2-Theta - Scale
5 10 20 30 40 50 60 70
The lattice parameters for the NaNH$_2$ and NaH starting materials after heating were compared to the lattice parameters established from the starting materials at room temperature (Table 5-2). For NaNH$_2$, the greatest difference was for the samples heated to 230, 250 and 270 °C. The unit cell volume had decreased by approximately 0.3 %. This was a greater decrease than observed on heating NaNH$_2$ alone, where the unit cell volume decreased only slightly. After heating at 290 °C the decrease in the unit cell volume had decreased to approximately 0.1 %. This temperature was the first for which the unidentified phase was first seen.

The lattice parameters of NaH were consistent after heating at different temperatures (Table 5-3), although they were all smaller than the unheated sample. There is no literature referring to hydrogen deficient NaH. The percentage difference was greater than that for NaNH$_2$.

### Table 5-2 Lattice parameters of NaNH$_2$ after heating to between 230 and 350 °C with NaH. The errors for each parameter are included. The percentage difference between the volume of the starting material and those heated was included for comparison.

<table>
<thead>
<tr>
<th>Temp/ °C</th>
<th>$a$/ Å</th>
<th>$b$/ Å</th>
<th>$c$/ Å</th>
<th>Volume/ Å$^3$</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. T.</td>
<td>8.968</td>
<td>10.458</td>
<td>8.076</td>
<td>757.427</td>
<td>0.000</td>
</tr>
<tr>
<td>230</td>
<td>8.96357(7)</td>
<td>10.438(10)</td>
<td>8.06982(7)</td>
<td>755.03(12)</td>
<td>-0.310</td>
</tr>
<tr>
<td>250</td>
<td>8.96349(9)</td>
<td>10.4341(12)</td>
<td>8.07003(9)</td>
<td>754.75(14)</td>
<td>-0.359</td>
</tr>
<tr>
<td>270</td>
<td>8.96283(8)</td>
<td>10.4344(11)</td>
<td>8.07134(8)</td>
<td>754.84(13)</td>
<td>-0.347</td>
</tr>
<tr>
<td>290</td>
<td>8.9643(5)</td>
<td>10.4320(6)</td>
<td>8.0897(4)</td>
<td>756.51(7)</td>
<td>-0.120</td>
</tr>
<tr>
<td>310</td>
<td>8.9654(7)</td>
<td>10.4300(8)</td>
<td>8.0897(7)</td>
<td>756.5(10)</td>
<td>-0.138</td>
</tr>
<tr>
<td>330</td>
<td>8.9683(8)</td>
<td>10.429(10)</td>
<td>8.0902(8)</td>
<td>756.7(13)</td>
<td>-0.104</td>
</tr>
<tr>
<td>350</td>
<td>8.972(18)</td>
<td>10.434(2)</td>
<td>8.085(18)</td>
<td>756.9(3)</td>
<td>-0.074</td>
</tr>
</tbody>
</table>
Table 5-3 Lattice parameters of NaH after heating to between 230 and 350 °C with NaNH₂. The errors for the parameter are included. The percentage difference between the volume of the starting material and those heated was included for comparison.

<table>
<thead>
<tr>
<th>Temp/ °C</th>
<th>(a/ \text{Å})</th>
<th>Volume/ Å(^3)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. T.</td>
<td>4.89858(6)</td>
<td>117.547(5)</td>
<td>0.000</td>
</tr>
<tr>
<td>230</td>
<td>4.88483(2)</td>
<td>116.560(13)</td>
<td>-0.855</td>
</tr>
<tr>
<td>250</td>
<td>4.88527(3)</td>
<td>116.591(3)</td>
<td>-0.855</td>
</tr>
<tr>
<td>270</td>
<td>4.88475(3)</td>
<td>116.554(2)</td>
<td>-0.855</td>
</tr>
<tr>
<td>290</td>
<td>4.8841(15)</td>
<td>116.51(10)</td>
<td>-0.916</td>
</tr>
<tr>
<td>310</td>
<td>4.8840(2)</td>
<td>116.50(16)</td>
<td>-0.916</td>
</tr>
<tr>
<td>330</td>
<td>4.8845(5)</td>
<td>116.54(3)</td>
<td>-0.855</td>
</tr>
<tr>
<td>350</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The starting materials were then heated to 350 °C for 24 hours. It was found that there was no change in the unidentified phase after this longer period of time. The starting materials were also heated to 400 °C for 24 hours. Again, the product was the same as before.

NaNH₂ and NaH were then heated together to 350 °C for 7 days (168 hours). The products, although similar, were not identical to the others observed after heating for a shorter time. The peak positions in the powder XRD were similar but some peaks had diminished in relative size and other new peaks had appeared (Figure 5-13). This was an indication that either the relative amount of difference phases change over time, or that there is a change in the crystal structure of the phase responsible for the Bragg reflections.

The phase could be compared after heating for 4 hours and 168 hours (Figure 5-14). It could be seen the peaks were similar in position, but some peak intensities had varied. The longer heating had resulted in a more crystalline XRD pattern, as evidenced by the sharpness of the Bragg reflections. The comparison of NaNH₂ heated to 350 °C for 168 hours and NaNH₂ + NaH for 168 hours showed the same level of crystallinity, but the peak ratios varied and peaks had shifted to both higher and lower \(d\)-spacings (Figure 5-15).
Figure 5-13 Powder XRD pattern of NaNH$_2$ + NaH heated to 350 °C for 168 hours.

Figure 5-14 Powder XRD patterns of comparison of NaNH$_2$ + NaH (black) (from ID31, ESRF) heated to 350 °C for 168 hours and NaNH$_2$ + NaH (green) heated to 350 °C for 4 hours.

Figure 5-15 Powder XRD patterns of comparison of NaNH$_2$ (black) heated to 350 °C for 168 hours and NaNH$_2$ + NaH (green) heated to 350 °C for 168 hours.
3. Raman

The Raman spectrum of NaNH$_2$ + NaH heated to 350 °C for 12 hours is shown in Figure 5-16. It can be seen that peaks were present in the N-H stretching region. NaNH$_2$ + NaH heated to 350 °C can be compared to the spectrum of NaNH$_2$ starting material (Figure 5-16). The sodium phases can also be compared with Li$^+$/[-NH$_2$]$^-$ with Li$^+$/2[-NH]$^{2-}$, as shown in Figure 5-17. The N-H stretches of NaNH$_2$ were observed at 3211.48 and 3252.14 cm$^{-1}$; whereas the main peak from the reaction product of NaNH$_2$ + NaH occurred at 3192.10 cm$^{-1}$.

Figure 5-16 Raman spectra of NaNH$_2$ at room temperature and NaNH$_2$ + NaH, heated to 350 °C: amide stretching region.
4. Rehydriding

The unidentified products after heating NaNH$_2$ + NaH to 350 °C were exposed to 100 bar hydrogen at 200 °C for 48 hours. Attempts to rehydride the unidentified phase failed as they did for NaNH$_2$ heated alone. There was no evidence of any additional phase, other than the unidentified peaks present before hydriding, although the peak positions and intensities had altered from NaNH$_2$ + NaH heated to 350 °C before rehydriding was attempted.
3. Discussion

It could be seen that when NaNH$_2$ alone was heated it formed a previously unidentified diffraction pattern with the release of ammonia. This could be analogous to LiNH$_2$. When LiNH$_2$ is heated alone it releases ammonia and forms Li$_2$NH$^\dagger$ (Equation 5-8), raising the possibility that a previously dismissed sodium imide phase may have been formed through these reactions.

\[
\text{Equation 5-8} \quad 2\text{LiNH}_2 \rightarrow \text{Li}_2\text{NH} + \text{NH}_3
\]

If Na$_2$NH was formed from the heating of NaNH$_2$ (Equation 5-2), there would be a theoretical mass loss of 21.8 wt% NH$_3$ (1 mole NH$_3$), which can be compared to the 17.5 wt% loss inferred from the MS data, although the 17.5 wt% loss does not include the nitrogen and hydrogen released. This is the equivalent of 0.8 NH$_3$ moles released.

In the temperature trace (Figure 5-5) it could be seen that there was a fluctuation at 210 °C. This was accompanied by a large variation in the furnace power. This started with an
increase in power, swiftly followed by a drop in power and was indicative of an endothermic event. As 210 °C is the melting point of NaNH₂, it can be assumed that the fluctuation was due to the melting of NaNH₂.

NaNH₂ has a significant vapour pressure below its 210 °C melting point. This could lead to sodium loss from the system. It is possible that the unknown phase is a hydrogen rich non-stoichiometric version of Na₂NH (Na₂₋ₓNH₁₊ₓ) (analogous to that observed in the lithium system Li₂₋ₓ(NH₁₊ₓ))

When NaNH₂ was heated with NaH the only gas released was hydrogen. The XRD gave the same pattern as for NaNH₂ heated alone (Figure 5-10). Again, this is similar to the LiNH₂-LiH system. When LiNH₂ and LiH are heated together, they form Li₂NH along with the release of hydrogen (Equation 5-7).

The amount of hydrogen desorbed after heating NaNH₂ + NaH together was 2.1 wt%. This was in comparison to a theoretical release of 3.2 wt% if the reaction proceeded as the analogous LiNH₂-LiH reaction, forming Na₂NH

An often proposed mechanism for the release of hydrogen desorption from the reaction of LiNH₂ + LiH is an ammonia mediated one. The LiNH₂ decomposes to Li₂NH with the release of NH₃. The NH₃ then reacts “ultrafast”¹⁷ with the LiH present to form further LiNH₂ with the release of hydrogen and the cycle begins again.

Equation 5-9

\[ \text{LiH} + \text{NH}_3 \rightarrow \text{LiNH}_2 + \text{H}_2 \]

As seen above, NaNH₂ decomposed to an unknown phase with the release of ammonia. It has been reported that NaH, when ball-milled with ammonia gas, can form NaNH₂ after
1 hour whereas the formation of LiNH$_2$ (Equation 5-9) took 2 hours. This suggests that there could also be a fast reaction between NaH and ammonia equivalent to lithium hydride. The NaH and NH$_3$ react to form further NaNH$_2$ and release the hydrogen observed in the reaction NaNH$_2$ + NaH (Figure 5-11).

In the TPD-MS trace (Figure 5-11), the above mechanism could account for the first hydrogen desorption peak and the second, slower higher temperature peak may result from any NaH, left over, decomposing to Na and H$_2$ (Equation 5-10). Although no Na was detected in the products of the reaction heated to 350 °C, it is possible the Na came off the reaction as a vapour and was therefore not detectable. A small amount of NaNH$_2$ was still present in the products after heating by TPD-MS. There was a small rise in ammonia at the end of the heating on TPD-MS. This may have come from the remaining NaNH$_2$ continuing to release ammonia, but with no NaH to react with due to NaH decomposing to Na.

Equation 5-10 \[ 2\text{NaH} \rightarrow 2\text{Na} + \text{H}_2 \]

The longer heating time for NaNH$_2$ + NaH appeared to give a more crystalline XRD pattern and a pattern that indicated different content (Figure 5-14). There was no change in the XRD pattern between heating NaNH$_2$ at 350 °C for 4 hours and 168 hours.

Evidence from the Raman spectra showed nitrogen was still present in the product (Figure 5-16), due to the peaks present in the N-H stretching region of the Raman spectra. This suggested either [NH$_2$]$^-$ or [NH]$^{2-}$ units were present in the unidentified phase after heating NaNH$_2$ with NaH.
The \([\text{NH}_2]^-\) units from NaNH\(_2\) were shown in Figure 5-16 to exhibit peaks at higher wavenumbers than the N-H stretches in the unknown phase. Interestingly, the N-H stretching peaks of LiNH\(_2\) are known to occur at a higher wavenumber than those of Li\(_2\)NH (Figure 5-17). This was also found by Kojima et al.\(^{19}\), and Bohger et al.\(^{20}\) confirmed the position of the LiNH\(_2\) peaks. Mg(NH\(_2\))\(_2\) peaks occur at 3274 and 3333 cm\(^{-1}\),\(^{21,22}\) whereas the peaks of MgNH occur at lower wavenumbers: 3251 and 3199 cm\(^{-1}\).\(^{21,23}\) It would therefore be expected that the peaks of Na\(_2\)NH would be shifted from the higher wavenumber of NaNH\(_2\) to a lower wavenumber, like MgNH and Li\(_2\)NH.

The published positions for the IR N-H stretching bands of LiNH\(_2\) are 3260 and 3315 cm\(^{-1}\). LiNH\(_2\) has two stretches- the symmetric and the asymmetric bands. The symmetric band appears alone at approximately 3260 cm\(^{-1}\), whereas there can be evidence of 2 asymmetric bands occurring at slightly higher wavenumbers, 3310 and 3315 cm\(^{-1}\).\(^{20}\) However the numbers of stretches within Li\(_2\)NH has not been confirmed. It has been noted by Ichikawa et al.\(^{24,25}\) that Li\(_2\)NH has one IR band, by Kojima et al. and Bogher et al.\(^{19,20,26}\) that it has 2 bands (3180 and 3250 cm\(^{-1}\)) and by Varin et al.\(^{27}\) that it has 3 bands in the N-H region. The variation in number of bands observed within Li\(_2\)NH IR/Raman, may be due to the non-stoichiometry possible within Li\(_2\)NH.\(^{28}\)

The Li\(_2\)NH [N-H]\(^{2-}\) peaks were found to be broader than those for LiNH\(_2\) and NaNH\(_2\). Kojima et al. also showed the same broadening in their Li\(_2\)NH Raman peaks produced from the thermal decomposition of LiNH\(_2\). They put the broadening down to small crystallite size and/or disorder in the crystallites. Chen et al.\(^{25}\) suggested the broadening of the IR band of Li\(_2\)NH was due to some unknown chemical/structural environments within the Li-N-H crystal.
The bands of the unknown phase were also found to be broader than LiNH$_2$ and NaNH$_2$, in the same way as Li$_2$NH.

The Raman evidence is consistent with the suggestion that the N-H bands in the unknown phase could be from [NH]$^{2-}$ as these peaks are known to appear at a lower wavenumber to amide units as well as having a broader peak width.

Another possibility was that a mixed sodium amide-imide was formed (Na$_{2-x}$(NH)$_x$(NH)$_{1-x}$, 0 ≤ x ≤ 1). LiNH$_2$-Li$_2$NH is known to be non-stoichiometric with respect to the Li$^+$/H$^+$ ions. The mixed stoichiometry possible from a mixed amide-imide could account for the similarities in the XRD patterns from heating NaNH$_2$ and NaNH$_2$ + NaH, and forming similar, but obviously not the same, products.

Further investigation is needed in order to confirm the structure of the possible Na$_{2-x}$NH$_{1+x}$.

The NaNH$_2$-NaH system did not appear to be successful for hydrogen storage as although hydrogen was released, it was not at a lower temperature than hydrogen desorption in the LiNH$_2$-LiH and LiNH$_2$-MgH$_2$ systems. However, the information garnered from this research and from further investigations into NaNH$_2$ may well assist in the understanding of the mechanism of hydrogen desorption for other amide-imide systems.

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6. Conclusions

From this work it could be seen that the mixed cation amides, Li$_3$Na(NH$_2$)$_4$ and LiNa$_2$(NH$_2$)$_3$, desorbed substantial amounts of hydrogen when heated with lithium hydride and magnesium hydride. When heated with sodium hydride only the decomposition of NaH was observed. This indicates that, in contrast to simple amides like LiNH$_2$ and consistent with TPD results on the mixed amides, the production of hydrogen did not occur via reaction of the hydrides with NH$_3$, but through direct reaction between amide and hydride. Sodium hydride was found to be unreactive in this respect, but was observed as a product of the reactions of the amides with both LiH and MgH$_2$. As NaH decomposes at relatively low temperatures, this is more likely to reflect the lack of stable alternative sodium-containing products (imide or nitride) than any special thermodynamic stability of the hydride itself. It was also found that minimal ammonia was desorbed which is consistent with the conclusions above and potentially of considerable benefit for a hydrogen storage material. When the mixed cation amides were heated with MgH$_2$ the hydrogen was desorbed at a temperature almost 100 °C lower than when heated with LiH. Unlike when lithium amide is heated with LiH and desorbs hydrogen with the formation of lithium imide, when the mixed cation amides were heated with LiH, no mixed imide was formed; instead lithium imide and NaH were formed. The products after heating the mixed cation amides with MgH$_2$ contained one or more unidentified phases, along with the known products.

Future work is needed to differentiate between the unidentified phases formed from the mixed cation amide reactions with MgH$_2$ and characterise them. Improvements to the
kinetics of the mixed cation amide + MgH₂ reactions could be made by ball-milling the starting materials and/or seeding with decomposition products [Li₂NH or Li₂Mg(NH)].

All the reactions of xNaNH₂ + yMgH₂ were found to react together to desorb hydrogen, without any ammonia detected. The stoichiometry of the magnesium with respect to Mg₃N₂ was important as it was an indication as to how far the reaction would go to full dehydrogenation.

The ratio of the starting materials was also important in the reversibility of the system. The heating of the 2NaNH₂ + 3MgH₂ system gave fully dehydrogenated products of Na and Mg₃N₂. These products were very difficult to rehydride under the conditions investigated here. By the addition of less MgH₂ (2NaNH₂ + MgH₂) the final product on heating to 350 °C was a mixed Na-Mg imide. This was possible to rehydride to Mg(NH₂)₂ and NaH at 300 °C, under 75 bar H₂ for 24 hours. On heating 2NaNH₂ + 3MgH₂, Na-Mg imide was formed at a lower temperature than Mg₃N₂, however the temperature at which to stop heating in order to only form the mixed imide was difficult to determine.

The unknown products of these reactions were thought to be a mixed Na-Mg amide, Na-Mg imide and Na-Mg nitride. Further work is required to characterise these phases.

From the work on NaNH₂ it was found that when heated to 350 °C NaNH₂ decomposed to an unknown phase and ammonia. When NaNH₂ was heated with NaH to 350 °C, an unknown phase, similar to that produced on heating NaNH₂ alone, was formed along with the release of hydrogen. This is analogous to the products of LiNH₂ when heated alone (Equation 5-8) and with LiH (Equation 5-7), indicating it is possible a sodium imide was formed. This had previously been dismissed in the literature.
The powder XRD patterns of the two phases (after heating NaNH$_2$ alone and with NaH) were similar, but not the same. This indicated possible non-stoichiometry, which is also present in the LiNH$_2$-Li$_2$NH system.

Attempts to rehydrogenate both unknown phase(s) did not reform the original reactant(s), although both XRD patterns were different to those before rehydrogenation.

Further work on this system would involve characterisation of the new phase(s). Continued work on the rehydrogenation of the possible imide should also be carried out.

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7. Appendix

1. $2\text{NaNH}_2 + 3\text{MgH}_2$

![XRD pattern of $2\text{NaNH}_2 + 3\text{MgH}_2$ after heating to 150 °C for 12 hours on a flowing line.](image1)

Figure 7-1 Powder XRD pattern of $2\text{NaNH}_2 + 3\text{MgH}_2$ after heating to 150 °C for 12 hours on a flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases $\text{MgH}_2$ (blue tick marks), $\text{NaH}$ (black tick marks), $\text{Mg(NH}_2)_2$ (green tick marks), $\text{NaNH}_2$ (pink tick marks) and $\text{NaMgH}_3$ (purple tick marks). $R_{wp} = 14.980$, $R_{exp} = 9.842$, $\chi^2 = 2.3$.

![XRD pattern of $2\text{NaNH}_2 + 3\text{MgH}_2$, heated to 250 °C for 12 hours on a flowing line.](image2)

Figure 7-2 Powder XRD pattern of $2\text{NaNH}_2 + 3\text{MgH}_2$, heated to 250 °C for 12 hours on a flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases $\text{NaH}$ (blue tick marks), $\text{MgH}_2$ (black tick marks) and $\text{NaMgH}_3$ (green tick marks). $R_{wp} = 22.184$, $R_{exp} = 8.665$, $\chi^2 = 6.6$. 

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Figure 7-3 Powder XRD pattern of $2\text{NaNH}_2 + 3\text{MgH}_2$, heated at 300 °C for 12 hours on flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaH (blue tick marks), Mg$_3$N$_2$ (black tick marks), NaMgH$_3$ (green tick marks), MgH$_2$ (pink tick marks) and phase A (blue arrows) fitted using a Pawley fit (red line). $R_{wp} = 7.681$, $R_{exp} = 4.905$, $\chi^2 = 2.5$.

Figure 7-4 Powder XRD pattern of $2\text{NaNH}_2 + 3\text{MgH}_2$, heated at 350 °C for 12 hours on a flowing line. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases Mg$_3$N$_2$ (blue tick marks), Na (black tick marks) and NaH (green tick marks). $R_{wp} = 15.975$, $R_{exp} = 11.615$, $\chi^2 = 1.9$.

*Phase A is marked as 0% on the XRD pattern, because it was fitted to the pattern using a Pawley fit.
2. $2\text{NaNH}_2 + \text{MgH}_2$

Figure 7-5 Powder XRD pattern of $2\text{NaNH}_2 + \text{MgH}_2$, heated at 150 °C for 12 hours under flowing argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaH (blue tick marks), Mg(NH$_2$)$_2$ (black tick marks), NaNH$_2$ (green tick marks) and MgH$_2$ (pink tick marks). $R_{wp} = 14.906$, $R_{exp} = 9.139$, $\chi^2 = 2.7$.

Figure 7-6 Powder XRD pattern of $2\text{NaNH}_2 + \text{MgH}_2$, heated at 200 °C for 12 hours under flowing argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaNH$_2$ (blue tick marks), NaH (black tick marks) and MgNa$_{2y}$(NH)$_{1+y}$ (green tick marks) fitted using a Pawley fit (red line). $R_{wp} = 12.454$, $R_{exp} = 10.39$, $\chi^2 = 1.4$. 
Figure 7-7 Powder XRD pattern of $2\text{NaNH}_2 + \text{MgH}_2$, heated at 250 °C for 12 hours under flowing argon. The observed powder XRD pattern (black line) was fitted using a Pawley fit (red line) to the observed phases $\text{NaNH}_2$ (blue tick marks), $\text{NaH}$ (black tick marks) and $\text{MgNa}_{2y}(\text{NH})_{1+y}$ (green tick marks) fitted using a Pawley fit (red line). $R_{wp} = 13.643$, $R_{exp} = 10.475$, $\chi^2 = 1.7$.

Figure 7-8 Powder XRD pattern of $2\text{NaNH}_2 + \text{MgH}_2$, heated at 350 °C for 12 hours under flowing argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases $\text{NaNH}_2$ (blue tick marks) and $\text{MgO}$ (black tick marks). $\text{MgNa}_{2y}(\text{NH})_{1+y}$ (green tick marks) and phase C (pink tick marks) were fitted using a Pawley fit (red line). $R_{wp} = 17.511$, $R_{exp} = 10.828$, $\chi^2 = 2.6$. 
3. $3\text{NaNH}_2 + 2\text{MgH}_2$

Figure 7-9 Powder XRD pattern of $3\text{NaNH}_2 + 2\text{MgH}_2$, heated to 150 °C for 12 hours under flowing argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaH (blue tick marks), Mg(NH$_2$)$_2$ (black tick marks), MgH$_2$ (green tick marks) and NaNH$_2$ (pink tick marks). $R_{wp} = 14.232$, $R_{exp} = 8.904$, $\chi^2 = 2.6$.

Figure 7-10 Powder XRD pattern of $3\text{NaNH}_2 + 2\text{MgH}_2$, heated to 200 °C for 12 hours under flowing argon. The observed powder XRD pattern (black line) was fitted using a Rietveld fit (red line) to the observed phases NaH (blue tick marks), NaNH$_2$ (black tick marks) and MgNa$_{2y}$(NH)$_{1+y}$ (green tick marks) fitted using a Pawley fit (red line). $R_{wp} = 13.406$, $R_{exp} = 10.986$, $\chi^2 = 1.5$. 
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4. NaNH$_2$ + MgH$_2$

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NaH 100.00 %
MgNa$_{2y}$(NH)$_{1+y}$ 0.00 %

NaH 63.62 %
Mg$_3$N$_2$ 27.70 %
Na 8.67 %
MgNa$_{2y}$(NH)$_{1+y}$ 0.00 %
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