Thermodynamics of Nitrogen Carriers for Chemical Looping Ammonia Synthesis



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Declaration

I declare that this thesis is an original work produced by myself, and has not been submitted, in whole or in part, for any other degree or professional qualification.

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Acknowledgements

This thesis is a culmination of my learning environment, past experiences, and attitudes gained before and during my PhD. At the core of these elements are my encounters with people who've knowingly or unknowingly provided invaluable support.

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Published Work

The following publications have resulted from this work, whose content has been adapted from this thesis. Publication (1) is shown in Chapters 3 and 4, and publication (2) in Chapters 5 and 6.

- Lee Pereira, R. J.; Hu, W.; Metcalfe, I. S. (2022) Impact of Gas-Solid Reaction Thermodynamics on the Performance of a Chemical Looping Ammonia Synthesis Process. *Energy and Fuels*, 36(17), 9757-9767. https://doi.org/10.1021/acs.energyfuels.2c01372
- Lee Pereira, R. J.; Metcalfe, I. S.; Hu, W. (2023) High-Throughput Screening of Suitable Nitrogen Carriers for Chemical Looping Ammonia Synthesis. *Applications in Energy and Combustion Sciences*, 16, 100226. <u>https://doi.org/10.1016/j.jaecs.2023.100226</u>

Other Work

Unrelated works have been produced over the course of this program, and material from publication (3) has been referenced in Chapters 3 and 4.

- Lee Pereira, R. J., Argyris, P. A., Spallina, V. (2020) A Comparative Study on Clean Ammonia Production Using Chemical Looping Based Technology. *Appl. Energy*, 280, 115874. <u>https://doi.org/10.1016/j.apenergy.2020.115874</u>
- Lee Pereira, R. J., Yan, Y., Hu, W., Clough, P. T., Mattisson, T., Metcalfe, I. S. (2024) Applying Machine Learning in Screening Perovskite-based Oxygen Carriers for Chemical Looping Applications. *Energy & Environmental Science*. (In preparation for submission)

Abstract

Producing ammonia at lower pressures and temperatures can reduce energy and economic costs of the process. To accomplish this, novel materials and/or synthesis routes with higher ammonia formation rates at lower temperatures are necessary. Chemical looping ammonia synthesis (CL-NH₃) is one such promising route that has shown higher ammonia synthesis rates and at milder temperatures than the current Haber-Bosch process. With CL-NH₃, a solid nitrogen carrying material is used to form ammonia in steps by alternating between pure hydrogen and nitrogen gas feeds. Unlike the Haber-Bosch process, the ammonia yield of the reaction is dependent on the kinetic and thermodynamic properties of the nitrogen carrying material. This introduces additional opportunities for novel designs, though finding suitable materials becomes a challenge.

Thermodynamic properties of solid nitrogen carrying materials are partially available, hence, it is unclear whether these materials produce sufficient or better ammonia yields under relevant operating conditions. Demystifying this question is at the core of this thesis and is fundamental to understanding the potential and feasibility of CL-NH₃. To answer this question, 'sufficient' reaction conversions and material properties were defined through sensitivity studies of a simulated CL-NH₃ process, and ammonia yields greater than 26% were required to achieve parity with the Haber-Bosch process. Thermodynamic models were created to calculate benchmarks for solid thermodynamic properties and equilibrium gas partial pressures (P_{N_2} or P_{H_2}/P_{N_2}) of the chemical looping reactions. With reference to these models, *in silico* screening of nitrogen carriers from literature and the Materials Project show that alkali/alkaline earth metal imides/hydrides though promising from a kinetic perspective, may not meet benchmarks, however, 111 out of 2515 metal nitrides, including Co₃InN, LiZnN, and Zn₂VN₃, show viable equilibrium yields. Further work is required to validate thermodynamic properties of nitrogen carriers and should be paired with kinetic studies to appropriately assess their viability.

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Nomenclature

Abbreviations

BAT	Best Available Technology
CEPCI	Chemical Engineering Plant Cost Index
CIF	Crystallographic Information File
CLC	Chemical Looping combustion
CL-Case	Chemical Looping NH ₃ Process
CL-NH ₃	Chemical Looping Ammonia synthesis
DOE	United States Department of Energy
FTIR	Fourier Transform Infrared analyser
HSC	HSC Thermochemical Database
ICSD	Inorganic Crystal Structure Database
IMO	International Maritime Organisation
KBR	Kellogg Root & Brown
LAC	Linde Ammonia Concept
MP	Materials Project Database
NIST	National Institute of Standard and Technology
PXRD	Powder X-Ray Diffraction
Ref-Case	Reference Haber-Bosch Process
SRK	Soave-Redlich-Kwong Equation of State
SV	Space Velocity
TGA	Thermo-Gravimetric Analyser
TPR	Temperature Programmed Reaction
VLE	Vapour-Liquid Equilibrium

Symbols

Α	Size of equipment
BM	Bare module costs, \$M
b	Quantity of element j, mol
С	Cost of equipment, \$M
c_p	Heat capacity of compound <i>i</i> , J mol ⁻¹ K ⁻¹
$\Delta_r c_p$	Heat capacity change of reaction, J mol ⁻¹ K ⁻¹
F	Equipment cost factor

Symbols	
FOB	Free on bord cost, \$M
f	fugacity of compound <i>i</i> , bar
G	Free energy of compound <i>i</i> , eV atom ⁻¹
G_{total}	Total free energy of system, J
G^{δ}	Free energy descriptor, eV atom ⁻¹
$\Delta_r G$	Free energy change of reaction, kJ mol ⁻¹
ΔG_{gas}	Free energy change of gas species in reaction, kJ mol ⁻¹
ΔG_{solid}	Free energy change of solid species in reaction, kJ mol ⁻¹
Н	Enthalpy of the system, J
$\Delta_{\mathrm{f}} H$	Enthalpy change of formation, kJ mol ⁻¹
$\Delta_{\mathbf{r}}H$	Enthalpy change of reaction, kJ mol ⁻¹
ΔH_{gas}	Enthalpy change of gas species in reaction, kJ mol ⁻¹
ΔH_{solid}	Enthalpy change of solid species in reaction, kJ mol ⁻¹
K	Equilibrium constant of reaction
LM	Labour & Maintenance cost, \$M
LM^*	Labour & Maintenance factor
M_R	Mass of reactor, kg
$M_{r,i}$	Molar mass of compound <i>i</i> , g mol ⁻¹
m	Reduced atomic mass, amu
Na	Avogadro's constant
N_{cap}	Specific nitrogen capacity
N_g	Number of gas compounds
N_s	Number of solid compounds
N_R	Number of reactors
N_{ratio}	Ratio of reactors
n	Quantity of compound <i>i</i> , mol
Р	Pressure of system, bar
P_i	Partial pressure of gas <i>i</i> , bar
$P_{compressors}$	Power consumption of compressors, MW
$P_{turbines}$	Power generation from turbines, MW
PM	Physical module costs, \$M
p	Equipment cost scaling factor
Q	Heat transferred, J
R	Ideal gas constant, J mol ⁻¹ K ⁻¹

Symbols	
r	Rate of reaction k , mmol kg ⁻¹ hr ⁻¹
S	Entropy of compound <i>i</i> , J mol ⁻¹ K ⁻¹
$\Delta_r S$	Entropy change of reaction, J mol ⁻¹ K ⁻¹
ΔS_{gas}	Entropy change of solid species in reaction, J mol ⁻¹ K ⁻¹
ΔS_{solid}	Entropy change of solid species in reaction, J mol ⁻¹ K ⁻¹
Т	Temperature, K
U	Overall heat transfer coefficient, W m ⁻² K ⁻¹
V	Atomic volume, Å ³ atom ⁻¹
V_m	Formula volume, nm ³
V_R	Volume of reactor, m ³
X	Conversion of compound <i>i</i>
Y	Equilibrium yield of compound <i>i</i>
у	mole fraction of compound <i>i</i>

Greek Letters

α	Stoichiometric coefficient of element <i>j</i> in compound <i>i</i>
μ	Chemical potential of compound i , J mol ⁻¹
ν	Reaction stoichiometric coefficient of <i>i</i>
ξ	Extent of reaction, mol
ρ	Density, kg m ⁻³
ϕ	Fugacity coefficient

Subscripts & Superscripts

b	bulk
g	gas
i	i th compound
j	j th element
k	k th reaction
LMTD	Logarithmic Mean Temperature Difference
r	reaction
ref	reference
S	solid
S o	solid standard state

Chapter 1 Introduction

1.1 History & Context

"No nitrogen, no food!" may not be a real quote, but it is a fact which was established by Jean-Baptiste Boussingault in the 19th century (Aulie, 1970). At the time, natural sources of nitrogen fertilisers were limited in supply (See Figure 1.1), therefore, scientists such as Sir William Crookes and Wilhelm Ostwald voiced concerns on how to feed a growing population (Crookes, 1898; Galloway et al., 2013), which also prompted chemists to create synthetic nitrogen fertilisers. Producing ammonia from its elements would satisfy this goal by tapping into the abundancy of nitrogen in air, however, a combination of scientific discoveries was necessary before the creation of this Nobel-prize winning invention.

Early attempts to synthesise ammonia from its elements were unsuccessful (Döbereiner, 1823) because of a lack of understanding of chemical equilibria which was yet to be developed by Le Chatelier (1884). Later, Haber *et al.* determined the equilibrium of the ammonia synthesis reaction to conclude that elevated pressures were required to form practical amounts of ammonia (Haber & Le Rossignol, 1907, 1908; Haber & Oordt, 1905; Jost, 1908; Nernst, 1907). More efficient catalysts were required, and the feasibility of high-pressure chemical synthesis was in question (Topham, 1985). These problems were resolved after partnerships with BASF and Carl Bosch, and in 1914 the first large-scale ammonia production plant was unveiled.

Synthetic nitrogen fertilisers have since been produced at scales orders of magnitude greater than natural sources (See Figure 1.1) and it has been estimated that half of the world's population is supported by this chemical or that half of the nitrogen in human bodies originates from this process (See Figure 1.2)(Erisman et al., 2008). At present, 70% of ammonia is used as fertiliser and the rest for production of plastics, explosives, and synthetic fibres (IEA, 2021a). It is amongst chemicals with the highest production volumes, and in 2021 its global production reached 150 million tonnes per annum and is expected to grow an additional 50 million tonnes per annum by 2050 due to fertiliser and chemicals production. Furthermore, interest outside its present applications has grown

due to its high viability as a low-carbon energy vector and maritime fuel (The Royal Society, 2020), and such applications are estimated to more than double the future demand for ammonia if guided by net-zero policies (IEA, 2021a).



Figure 1.1 Annual consumption of fixed nitrogen from various natural sources (Guano & Chile Saltpetre) and from industrial nitrogen fixation processes (Birkeland-Eyde Process, Frank-Caro Process, Ammonium Sulphate, and Haber-Bosch Process). Figure sourced from (Rouwenhorst et al., 2021) (Copyright © CC BY 3.0).



Figure 1.2 Trend in human population and nitrogen use in the 20th century. Comparison with and without the Haber-Bosch process (i.e., synthetic fertilisers) is shown to demonstrate its impact on the global population. With permission, figure sourced from (Erisman et al., 2008) (Copyright © 2008, Springer Nature Limited)

1.2 Ammonia Production & Applications

Current ammonia production methods utilise natural gas or coal as feed, and consequently this contributes to 2% of the world's energy consumption and 1.3% of global greenhouse gas emissions (IEA, 2021a). Over 70% of ammonia is produced using natural gas as feedstock, and the remainder with coal. In state-of-the-art ammonia plants, conversion of fossil feeds to ammonia is energy and carbon intensive. The best available technologies (BAT) achieve energy consumptions of 28 GJ tonne⁻¹ of NH₃ and emit 1.6 tonnes CO₂ per tonne of NH₃ (Lee Pereira et al., 2020), however the industry average is 46.2 GJ tonne⁻¹ NH₃ and 2.4 tonnes CO₂ per tonne of NH₃, nearly double that of the steel industry and more than thrice the cement industry (IEA, 2021a). Innovation is required to decarbonise the industry, therefore, carbon capture and storage technologies or low-carbon processes based on renewable energy sources are being developed to produce 'blue' and 'green' ammonia respectively.

Majority of ammonia plants produce hydrogen using a two-step reforming process consisting of a steam reformer and autothermal reformer in series (See Figure 1.3 (A) and (C)) (KBR, 2023). Natural gas and steam are converted to syngas using a catalyst at high temperatures. The reaction is endothermic and requires a box furnace to maintain high temperatures. Roughly a third of CO₂ emissions result from fuel use in the furnace (IFA, 2009). The remaining CO₂ emissions from the feedstock are removed by an amine-based absorption unit and/or pressure swing adsorption unit. The latter source of CO₂ is of highpurity and suitable for urea production, enhanced oil recovery, and CO2 storage (DOE/NETL, 2014). The former source requires additional purification via carbon capture technologies, resulting in higher capital and operating costs (Collodi et al., 2017). For existing fossil-based ammonia plants, carbon capture technologies can be a short-term and effective solution if sufficient economic incentive to implement it exists (e.g., carbon taxes). In the long run, finite supplies of fossil fuel and CO₂ storage combined with forecasted increases in demand for ammonia must be considered, which would require scalable ammonia processes based on renewable and abundant feedstocks such as air, water, and electricity (See Figure 1.3 (B) and (C)).





C) Haber-Bosch Process



Figure 1.3 Block diagrams of ammonia synthesis routes using natural gas (A) or electricity (B) to produce hydrogen and nitrogen for the Haber-Bosch process (C).

Renewable energy sources such as wind and solar, although abundant in nature, are intermittent and geographically dispersed (See Figure 1.4). In some cases, the feasibility and costs prohibit its deployment in countries such as Japan (IEA, 2021c), therefore importing low-carbon energy sources has been proposed (IEA, 2021b; METI, 2022a, 2022b). Renewable energy storage and transportation systems are required to accommodate such problems, and green ammonia has been advocated as a potential solution. In comparison to other carbon-free fuels such as liquified hydrogen (-253°C, 1 bar) or compressed hydrogen (25°C, 350 to 700 bar), ammonia can be liquified and stored at room temperature and 10 to 20 bar, however, converting hydrogen to ammonia incurs energy losses (~40% with BAT) (Appl, 2011c). When conversion with storage of these chemicals is compared, ammonia is more efficient (Dias et al., 2020), and an analysis by

(IEA, 2019) has shown that the costs to transport ammonia is cheaper than hydrogen when transported *via* shipping or piped over long distances (>3500 km); these factors suggest that ammonia is a suitable option for exporting energy from countries abundant in renewables such as Australia to countries such as Japan.



Figure 1.4 Geographic distribution of solar (A) and wind (B) power densities. Figures retouched and sourced from (Suri et al., 2020) and (DTU Wind Energy & World Bank Group, 2018) (Copyright © CC BY 4.0).

In addition to applications in energy storage and transportation, green ammonia may be key to decarbonising the maritime industry which contributes to 2.8% of global greenhouse gas emissions (IMO, 2021). Its high volumetric energy density amongst carbon-free fuels (comparable to LPG), developed supply infrastructure near shipping ports, and simple storage conditions make it one of the most viable alternative shipping fuels (Bastardie et al., 2023). Under the IMO's net-zero plans, ammonia for maritime fuel could rival present demands for fertilisers and would require significant scale-ups in green ammonia production capacities. Though preliminary studies have shown it to be the most cost-effective pathway to decarbonising the maritime industry (Smith et al., 2019, 2021), scenarios involving its future adoption assume ammonia prices between 348 to 593 USD per tonne by 2050, whereas current costs for green ammonia are between 750 to 1400 USD per tonne (IRENA and AEA, 2022).

To decarbonise the fertiliser, maritime, and power industries it is necessary to reduce the costs of producing green or low carbon ammonia. Costs of green and blue ammonia are highly correlated with their feedstock prices, as well as capital expenditures related to their hydrogen, nitrogen, and ammonia production processes (Arnaiz del Pozo & Cloete, 2022; Lee Pereira et al., 2020; Zhang et al., 2020). Improving the efficiency, performance, or sizing of these processing units could achieve costs reductions, and research into novel chemical processing technologies show ample room for improvement. Novel ammonia synthesis routes, with potential to reduce the costs of the Haber-Bosch process (See Figure 1.3 (C)) have since become a key research area.

1.3 Novel Materials & Synthesis Routes

Conversion of hydrogen and nitrogen to ammonia *via* the Haber-Bosch process requires high temperatures (350 to 500°C) and pressures (100 to 200 bar), and results in relatively low ammonia yields (15 to 30%) (H. Liu, 2013). Significant costs are associated with the process, primarily due to high pressure operation and separation of ammonia (DOE/NETL, 2011a; H. Liu, 2013). The costs can be greatly reduced if the process can operate at lower pressures, however, due to the equilibrium of the reaction (R1), lower temperatures would be required to achieve acceptable ammonia yields. Over the last century, activities of ammonia catalysts have increased *via* novel formulations, starting with promoted magnetite (K₂O – Fe₃O₄) in 1913 which operated at 350 to 500°C and 300 bar, to wüstite (K₂O – Fe_{1-x}O) in 1986 operating at 350 to 500°C and 120 to 150 bar, and ruthenium (Cs – Ru) in 1992 operating at 325 to 450°C and 90 bar. Next-generation ammonia catalysts are aiming to increase ammonia synthesis rates at milder conditions, and the holy grail is to synthesise ammonia at 25°C and 1 bar which would allow a near-complete reaction conversion at equilibrium and low energy inputs for the process.

$$1.5H_{2(g)} + 0.5N_{2(g)} \rightleftharpoons NH_{3(g)} \quad \Delta_r H^{\circ} = -46.0 \ kJ \ mol^{-1} \tag{R1}$$

The Sabatier principle suggests that interactions between the catalyst and reactant should be neither too strong nor too weak (Che, 2013; Sabatier, 1920). A quantitative approach to this principle has demonstrated that the ammonia synthesis rates of transition metal catalysts are limited by a linear scaling relationship between the adsorption energy and activation energy of nitrogen (Medford et al., 2015). Whilst the current consensus is that the nitrogen dissociation step (See Figure 1.5 (A)) is rate-limiting, effects such as hydrogen inhibition and oxygen poisoning are also important (Figure 1.5 (B)). Therefore, interactions with all three species need to be considered in the design of an active ammonia catalyst.



Figure 1.5 Kinetic mechanism for ammonia synthesis via reaction R1 shown in (A). Inhibition of ammonia synthesis rates can occur via blockage of surface sites due to preferential adsorption of hydrogen or oxygen (B). Oxygen inhibition affect iron and ruthenium catalysts, and include oxygenated compounds such as water, carbon monoxide, and carbon dioxide. Nitrogen, hydrogen, and oxygen atoms are represented by blue, white, and red spheres.

Novel materials and reaction routes have been explored to overcome these rate limitations. Materials such as electrides (Kammert et al., 2020; Wu et al., 2018), hydrides (Gao et al., 2017; P. Wang et al., 2017), nitrides (Daisley & Hargreaves, 2023; Goto et al., 2021; Mckay et al., 2008), and oxides (Ogura et al., 2018; Sato et al., 2020) have been shown to increase synthesis rates of reaction R1 under milder conditions by acting as cocatalysts or promoters for the transition metal catalysts (See Figure 1.6). Alternatively, novel ammonia synthesis routes based on electrocatalytic (Garagounis *et al.*, 2019), photocatalytic (Han et al., 2021), plasma-catalytic (Carreon, 2019), and chemical looping processes (Gao et al., 2023) have the potential to produce ammonia using renewable energy sources or overcome limitations with the conventional route. Despite their potential, current materials for photo, electro, or plasma catalytic ammonia synthesis routes lack sufficient rates of ammonia synthesis or energy efficiencies when compared to benchmarks set by the DOE (Carreon, 2019; Smart, 2022). In contrast, the chemical looping route is similar to the Haber-Bosch process, and studies have shown better kinetics at lower temperatures (<350°C) and ambient pressures than reaction R1 (Gao et al., 2018). Therefore, this work has focused on the chemical looping ammonia synthesis route.



Figure 1.6 Examples of novel materials and routes that have been explored in literature. Images retouched and reprinted with permission from Goto et al. (2021), Kammert et al. (2020), Sato et al. (2020), and P. Wang et al. (2017) for materials (Copyrights © CC BY 4.0, © 2020 American Chemical Society, © 2020 American Chemical Society, © 2016 Springer Nature Limited, respectively), and from Ben Yaala et al. (2019), Burrows & Bollas (2020), Garagounis et al. (2019), and Han et al. (2021) for synthesis routes (Copyrights © CC BY-NC 3.0, © American Institute of Chemical Engineers, © CC BY 4.0, © CC BY 3.0, respectively).

Chapter 2

Background & Literature

2.1 Chemical Looping Ammonia Synthesis

2.1.1 What is Chemical Looping?

Chemical looping was coined in 1987 to describe a reactor for combusting fuel using a solid oxygen carrying material (See Figure 2.1) (Ishida et al., 1987). However, the principle of using an oxygen carrying material for performing gas-solid reactions dates further back to 1903 where iron oxide was used to produce hydrogen from water and town gas (e.g., CO) *via* the 'Lane hydrogen process' (Hurst, 1939). Research on chemical looping resurged due to its inherent ability to produce carbon dioxide and water instead of flue gas (CO₂, N₂, H₂O mixture) when combusting fuel, requiring no additional separation for carbon dioxide and nitrogen gases, making it ideal for carbon capture and storage applications.



Figure 2.1 Basic diagram of metal oxide based chemical looping reactors. A list of some common chemical looping reactions is shown, where step ① corresponds to the reduction of the metal oxide and step ② to the oxidation of the reduced metal.

The technology has evolved towards novel processes for producing hydrogen, syngas (i.e., CO and H₂), oxygen, and bulk chemicals such as alkenes, epoxides, styrenes, and methanol (Zhu et al., 2020). *Via* chemical looping processes, these chemicals have potential to be produced with lower costs and emissions than current catalytic processes, for instance by combining reaction and separation processes (e.g., CLC), improving single-pass equilibrium conversions of reactions (Metcalfe et al., 2019), or improving selectivity's towards reactions (Y.Liu et al., 2019).

2.1.2 Chemical Looping Ammonia Synthesis Reactions

Unlike typical chemical looping reactions which use oxygen carrying materials, or the conventional catalytic process (i.e., Haber-Bosch) which uses a mixture of hydrogen and nitrogen to form ammonia, chemical looping ammonia synthesis (CL-NH₃) uses solid nitrogen carrying materials (or in some cases a hydrogen carrier) to form ammonia through alternating feeds of pure hydrogen and nitrogen (or their precursors). Note further, that nitrogen carriers are not catalysts since they partake in a gas-solid reactions and change state. Several CL-NH₃ processes have been proposed, however, they can be broadly categorised into two groups. The first consist of processes which replace the downstream Haber-Bosch unit (See Figure 2.2), and the second replaces both the upstream hydrogen production process and Haber-Bosch unit to form a single-train process. This work mainly focuses on the former category of CL-NH₃ processes, however, an additional discussion on the latter group is provided in section 2.1.3.



Figure 2.2 Basic diagram of a chemical looping ammonia synthesis reactor where step (1) refers to the nitrogenation of the nitrogen carrier and step (2) refers to the hydrogenation of the nitrogen carrier and formation of ammonia.

Metal Nitride CL-NH₃

$$\frac{1}{y}M_{x}N_{y(s)} + 1.5H_{2(g)} \to \frac{x}{y}M_{(s)} + NH_{3(g)}$$
(R2a)

$$\frac{x}{y}M_{(s)} + 0.5N_{2(g)} \to \frac{1}{y}M_{x}N_{y(s)}$$
(R2b)

Metal Imide/Hydride CL-NH₃

$$\frac{1}{y}M_{x}N_{y}H_{z_{(s)}} + (1.5+w)H_{2(g)} \rightarrow \frac{x}{y}MH_{z/x+2wy/x_{(s)}} + NH_{3(g)}$$
(R3a)

$$\frac{x}{y}MH_{z/x+2wy/x_{(s)}} + 0.5N_{2(g)} \to \frac{1}{y}M_xN_yH_{z_{(s)}} + wH_{2(g)}$$
(R3b)

Thus far, three classes of nitrogen carriers have been proposed for CL-NH₃ processes to replace the downstream Haber-Bosch process: metal nitride, metal imide/hydride, and metal nitride/oxide nitrogen carriers, which follow reactions R2, R3, and either R4 or R5, respectively. Nitrogen carriers which can undergo continuous cycles of reaction R4 or R5 have not been demonstrated experimentally despite being proposed by Michalsky *et al.* (2015, 2011), and the reported conditions for this reaction are far greater than 500°C during the ammonia synthesis step which could imply low equilibrium ammonia yields, therefore this material class was not investigated in this work. Metal nitride and imide/hydride nitrogen carriers which can undergo multiple cycles of reactions R2 and R3 have been investigated in literature, and the latter class of nitrogen carrier has demonstrated high ammonia synthesis rates at low temperatures (<350°C) and ambient pressures (Feng et al., 2021; Gao et al., 2018), which could potentially reduce ammonia production costs. A review of these materials is provided later in section 2.2.

Metal Nitride/Oxide CL-NH₃

$$\frac{1}{y}M_{x}N_{y_{(s)}} + 1.5H_{2}O_{(g)} \to \frac{x}{yz}M_{z}O_{t_{(s)}} + NH_{3(g)}$$
(R4a)

$$\frac{x}{yz}M_zO_{t(s)} + 1.5H_{2(g)} + 0.5N_{2(g)} \to \frac{1}{y}M_xN_{y(s)} + 1.5H_2O_{(g)}$$
(R4b)

3-step Metal Nitride/Oxide CL-NH₃

$$\frac{1}{y}M_{x}N_{y_{(s)}} + 1.5H_{2}O_{(g)} \to \frac{x}{yz}M_{z}O_{t_{(s)}} + NH_{3(g)}$$
(R5a)

$$\frac{x}{yz}M_z O_{t(s)} + 1.5H_{2(g)} \to \frac{x}{y}M_{(s)} + 1.5H_2 O_{(g)}$$
(R5b)

$$\frac{x}{y}M_{(s)} + 0.5N_{2(g)} \to \frac{1}{y}M_{x}N_{y(s)}$$
(R5c)

2.1.3 Alternative Chemical Looping Ammonia Synthesis Reactions

CL-NH₃ processes which replace the hydrogen production (i.e., Steam methane reforming) and Haber-Bosch process use metal nitride/oxide nitrogen carriers to form ammonia from water, nitrogen, and reductants such as carbon (Gálvez, Frei, et al., 2007; Gálvez, Halmann, et al., 2007), methane (Gálvez et al., 2009), electricity (McEnaney et al., 2017), plasma (Sarafraz & Christo, 2021), or light (Swearer et al., 2019). These processes have potential to reduce energy consumptions and costs of producing ammonia either by reducing the number of unit operations required, improving synthesis conditions (e.g., low-pressure ammonia synthesis), or improving reaction yields if suitable kinetics and thermodynamics are available.

Separation requirements for these routes, however, may restrict their process performance. For example, forming ammonia through hydrolysis of metal nitrides *via* reaction R4a requires separation of ammonia–water mixtures, which require at least twice the power consumption for separation (Fernández-Seara & Sieres, 2006) compared to the conventional Haber-Bosch process (H. Liu, 2013; Nielsen, 1995). Additionally, if syngas is produced by carbothermal or methanothermal reduction under nitrogen atmosphere, multiple separation and gas conditioning processes will be required for mixtures of unconverted feed (CH4, N2) and product gases (CO, H2), which is no different and potentially worse than conventional steam reforming plants if reactor conversions are low. Separation of unconverted nitrogen from syngas could be eliminated by performing the nitrogenation of the carrier material and reduction of the oxide separately, however, this has not been investigated in literature. Exploring these alternatives routes can only be justifiable if high single-pass conversions and/or low separation requirements can lead to lower energy or production costs.

Energy and exergy analysis of a CL-NH₃ process using AlN and carbothermal reduction (Reaction R6) found energy consumptions of 6.88 GJ tonne⁻¹ NH₃ and exergy efficiencies of 26% (Fang et al., 2022; X. Wang et al., 2021). Energy consumptions of this CL-NH₃ process vary significantly with the nitrogenation reactor's operating temperature; energy consumptions of 15.96 GJ tonne⁻¹ NH₃ were obtained when a nitrogenation temperature of 1500°C was specified. Although the energy consumption appears lower than state-of-the-art ammonia production plants (28 GJ tonne⁻¹ and 36 GJ tonne⁻¹ for methane and coal, respectively) (IEA, 2021a), the primary energy
consumption of the carbon feed (assumed to be coal) was not accounted for and would be equivalent to ~48 GJ tonne⁻¹ NH₃ if a lower heating value of 29 MJ kg⁻¹ of coal were assumed (ToolBox, 2003), therefore, the process actually requires 55 to 64 GJ tonne⁻¹ NH₃. Back of the envelope calculations indicate that current designs and/or material performances could not compete with conventional processes on the basis of energy consumptions.

Carbothermal Reduction/Hydrolysis of Al₂O₃/AlN

$$Al_2O_{3(s)} + 3C_{(s)} + N_{2(g)} \to 2AlN_{(s)} + 3CO_{(g)}$$
(R6a)

$$2AlN_{(s)} + 3H_2O_{(g)} \to Al_2O_{3(s)} + 2NH_{3(g)}$$
(R6b)

Methanothermal reduction of Al₂O₃ *via* reaction R7 is an alternative to carbothermal reduction, though during this process, Al₂O₃ cracks methane into hydrogen and carbon which forms layers on the oxide surface that inhibit the rate of reduction and solid conversion (Gálvez et al., 2009). Addition of Ni or Fe catalyst increased the solid conversion and could reduce temperatures required for nitrogenation. Similarly, metal catalysts can be used to increase reaction rate of the ammonia synthesis step, however, since the hydrolysis of the metal nitride is performed at temperatures greater than 800°C the decomposition of ammonia *via* the reverse of reaction R1 would also be catalysed (McCabe, 1983), which could result in lower or insignificant yields of ammonia.

Methanothermal Reduction/Hydrolysis of Al₂O₃/AlN

$$Al_2O_{3(s)} + 3CH_{4(s)} + N_{2(g)} \to 2AlN_{(s)} + 3CO_{(g)} + 6H_{2(g)}$$
(R7a)

$$2AlN_{(s)} + 3H_2O_{(g)} \to Al_2O_{3(s)} + 2NH_{3(g)}$$
(R7b)

Reduction of the metal oxide *via* a photochemically driven process has been demonstrated by Swearer et al. (2019). TiN nanoparticles deposited on Mg₃N₂ were exposed to an infrared light source (808 nm) to drive reaction R8a. Ammonia synthesis rates were found to be 1.67 μ mol g⁻¹ hr⁻¹ with ammonia concentrations of ~7 ppm and efficiencies of 0.05%. Literature on light driven chemical looping ammonia synthesis reactions have not appeared since. Simply based on its performance during the ammonia synthesis step and its energy efficiency, the material from this study is far from required standards.

Photochemical CL-NH₃

$$\frac{3}{2}MgO_{(s)} + \frac{3}{2}CH_{4(g)} + \frac{1}{N} \rightarrow \frac{3}{2}Mg_{(s)} + \frac{3}{2}CO_{(g)} + 3H_{2(g)}$$
(R8a)

$$\frac{3}{2}Mg_{(s)} + 0.5N_{2(g)} \to 0.5Mg_3N_{2(s)}$$
(R8b)

$$0.5Mg_3N_{2(s)} + \frac{3}{2}H_2O_{(g)} \to \frac{3}{2}MgO_{(s)} + NH_{3(g)}$$
(R8c)

An electrochemical CL-NH₃ process studied in McEnaney *et al.* (2017) showed promising faradaic efficiencies (88.5%) which satisfied DOE targets for electrochemical ammonia synthesis (Smart, 2022). Ammonia is synthesised in three consecutive steps wherein air, water, and electricity are used to form a chemical looping reaction with Li₃N (Reaction R9). The process is promising but has high energy consumptions of ~86 GJ/tonne of NH₃ produced (McEnaney *et al.*, 2019), and this value could be higher due to the energy requirements for separating ammonia from water.

Electrochemical CL-NH₃

$$Electrochemical Cell: 3LiOH \rightarrow 3Li + 1.5H_2O_{(g)} + \frac{3}{4}O_{2(g)}$$
(R9a)

$$3Li_{(s)} + 0.5N_{2(g)} \rightarrow Li_3N_{(s)} \tag{R9b}$$

$$Li_3N_{(s)} + 3H_2O_{(g)} \to 3LiOH_{(s)} + NH_{3(g)}$$
 (R9c)

In summary, alternative ammonia synthesis may be promising from a sustainability or cost reduction point of view but are currently constrained by reaction yields, total energy consumptions, and lack of appropriate process designs, which impact the feasibility of CL-NH₃. It also is unclear what the maximum benefit would be provided in terms of energy efficiency or costs with these processes if better materials were found. Addressing this question could justify further research for these synthesis routes.

2.2 Materials for Chemical Looping Ammonia Synthesis

2.2.1 Metal Nitride Carrier Materials

The earliest known attempt to form ammonia from its elements using solid nitrogen carriers was made by (Haber & Oordt, 1905) using calcium and manganese nitrides, however, high temperatures (>800°C) were required, and ammonia yields were unsatisfactory at those conditions. When a suitable catalyst was found for the process, research on solid-mediated ammonia synthesis routes ceased for nearly a century. At the end of this hiatus, research into metal nitrides as catalysts for ammonia synthesis resurged, though mainly on their reactivity under pure hydrogen atmospheres (i.e., the hydrogenation step or reaction R2a). A summary of these nitrides and their ammonia synthesis rates is provided in Table 2.1 and shown on Figure 2.3. In Figure 2.3, 'carriers' refer to solid nitrogen carrying materials which undergo a gas-solid reaction (e.g., R2 or R3) whereas catalysts refer to materials which catalyse reaction R1.



Figure 2.3 Experimental values for ammonia synthesis rates of metal nitride and imide/hydride nitrogen carriers compared to metal amide/imide and commercial catalysts. Plotted rates are at 300 to 500°C and 1 to 10 bar, conditions for each point can be found in Table 2.1 and Table 2.2.

Synthesis of these nitrides was performed *via* ammonolysis of their metal oxide precursors, and under exposure to hydrogen gas at high temperatures and ambient pressures, nitrides listed in Table 2.1 as well as other nitrides such as $ZrFe_2N_x$, NbFe₂N_x, MoFe₂N_x, VFeN_x (Itoh et al., 1999), CeFe₇N_x, NdFe₇N_x, SmFe₇N_x (Itoh et al., 2004), Fe₃Mo₃N (Mckay et al., 2008), γ -Mo₂N (Mckay et al., 2008), and Co₄N (Alexander et al., 2013) form ammonia.

Over the last decades, ammonia synthesis rates of metal nitrides *via* reaction R2a have increased (See Figure 2.3), and Ni₃ZnN has shown the highest rate among this class of nitrogen carriers for CL-NH₃ (Goto *et al.*, 2021). Nitrides such as Cu₃N and Ni₃N show relatively high rates of ammonia synthesis at temperatures as low as 250°C, however these nitrides are unstable and release nitrogen gas under pure hydrogen atmospheres (Alexander *et al.*, 2012); this is common with other metal nitrides though to a lesser extent. Although rates of ammonia synthesis with nitrides are lower than industrial iron catalysts, rates at higher pressures have not been observed yet and the materials could be optimised further.

Regeneration of metal nitrides with nitrogen gas is a pre-requisite with CL-NH₃, however, none of the nitrides in Table 2.1 have had their nitrogenation rates quantified, though it has been attempted with nitrides such as TiFe₂N_x, Ce₂Fe₇N_x, Mn₆N_{2.58}, Ca₃N₂, and Sr₂N. With TiFe₂N_x and Ce₂Fe₇N_x; note that regeneration of TiFe₂N_x with nitrogen gas was only feasible when a ruthenium catalyst was added to the material, this also allowed formation of ammonia over five cycles (Machida et al., 1998). Regeneration and synthesis of metal nitrides is facile with ammonia, whereas higher temperatures are usually required to achieve sufficient nitrogenation rates with nitrogen gas; this is likely due to the higher activation energy required to dissociate the nitrogen triple bond. Overall, metal nitride carriers from literature do not appear to be viable candidates for CL-NH₃ due to their slow rates of reactions R2a and R2b, and if they cannot be regenerated with nitrogen gas these materials are not suitable for CL-NH₃.

Materials	r _{NH3} (mmol g ⁻¹ h ⁻ ¹)	NH3 yield ^a (%)	Reaction Conditions	SV ^c (L g ⁻¹ h ⁻¹)	Reference		
Benchmark Catalysts							
Wustite Catalyst	5.4	0.74	300°C, 10 bar	36	(Kitano et al., 2018)		
Fe-K ₂ O-Al ₂ O ₃	2.0	0.16	300°C, 9 bar	9	(Kojima & Aika, 2001a)		
Ru(10%)- Cs/MgO	0.6	0.08	300°C, 9 bar	36	(Kitano et al., 2018)		
Metal Nitride Chemical Looping							
TiFe ₂ N _x	8.6 × 10 ⁻⁶	1.2 × 10 ⁻⁵	450°C, 1 bar	1.8	(Itoh et al., 1999)		
$Ce_2Fe_7N_x$	2.1×10^{-6}	2.9 × 10 ⁻⁶	300°C, 1 bar	1.8	(Itoh et al., 2004)		
Co ₃ Mo ₃ N ^b	0.098	2.7 × 10 ⁻²	400°C, 1 bar	9	(Hargreaves & Mckay, 2009)		
Ni2Mo3N ^b	0.011	3.0 × 10 ⁻³	400°C, 1 bar	9	(Hargreaves & Mckay, 2009)		
Cu ₃ N ^b	~0.89	0.18	250°C, 1 bar	12	(Alexander et al., 2012)		
Ni ₃ N ^b	~0.43	8.9 × 10 ⁻²	250°C, 1 bar	12	(Alexander et al., 2012)		
$Zn_3N_2 \ ^b$	~0.85	0.18	400°C, 1 bar	12	(Alexander et al., 2012)		
Ta ₃ N ₂ ^b	~0.080	1.7×10^{-2}	400°C, 1 bar	12	(Alexander et al., 2012)		
Fe ₂ N ^b	< 0.050	1.0×10^{-2}	400°C, 1 bar	12	(Alexander et al., 2013)		
Re ₃ N ^b	< 0.13	2.7 × 10 ⁻²	350°C, 1 bar	12	(Alexander et al., 2013)		
Mn ₆ N _{2.58}	0.053	2.3 × 10 ⁻³	850°C, 1 bar	58	(Michalsky, Avram, et al., 2015)		
Ca_3N_2	0.095	4.1 × 10 ⁻³	850°C, 1 bar	58	(Michalsky, Avram, et al., 2015)		
Sr ₂ N	0.080	3.4 × 10 ⁻³	850°C, 1 bar	58	(Michalsky, Avram, et al., 2015)		
$Ta_{2.5}Co_{0.5}N_y{}^b$	~0.4	8.3 × 10 ⁻²	500°C, 1 bar	12	(Laassiri et al., 2017)		
$Ta_{2.5}Fe_{0.5}N_y \ ^b$	~0.033	6.8 × 10 ⁻³	500°C, 1 bar	12	(Laassiri et al., 2017)		
$Ta_{2.5}Re_{0.5}N_y{}^b$	~0.067	1.4×10^{-2}	500°C, 1 bar	12	(Laassiri et al., 2017)		
Li-Mn-N ^b	0.35	7.2 × 10 ⁻²	400°C, 1 bar	12	(Laassiri et al., 2018)		
Ni ₃ ZnN ^b	2.1	0.29	400°C, 1 bar	18	(Goto et al., 2021)		
Co ₃ ZnN ^b	0.75	0.1	400°C, 1 bar	18	(Goto et al., 2021)		
Co ₃ InN ^b	0.061	8.4 × 10 ⁻³	400°C, 1 bar	18	(Goto et al., 2021)		
Ni3InN ^b	0.22	3.0 × 10 ⁻²	400°C, 1 bar	18	(Goto et al., 2021)		

Table 2.1 Comparison of experimentally determined ammonia synthesis rates of metal nitrides to industrial catalysts.

^a y_{NH_3} values calculated from r_{NH_3} and SV. ^b Rates obtained under 3:1 H₂/Ar atmosphere whereas other materials were studied under pure hydrogen. ^c Space velocity (SV) defined as the volumetric flowrate of gas feed divided by the mass of material used.

2.2.2 Alkali & Alkaline Earth Metal Imide/Hydride Carrier Materials

When paired with transition metal catalysts, alkali and alkaline earth metal hydrides have been shown to overcome rate limitations as a result of scaling relations between the adsorption energy and activation energy of nitrogen (P. Wang *et al.*, 2017) and can act as nitrogen carriers when employed in a chemical looping scheme. Ball-milling hydrides with transition metal catalysts (Ni, Co, Fe, Mn, Pd, and Cr) can promote otherwise inactive catalyst with the conventional (Gao *et al.*, 2017; P. Wang *et al.*, 2017) and chemical looping routes (Feng *et al.*, 2021; Gao *et al.*, 2018; Guan *et al.*, 2021; R. Wang *et al.*, 2023; Yan *et al.*, 2021). More importantly, the materials significantly increased rates of ammonia synthesis and nitrogenation at temperatures lower than 350°C and 1 bar when used as nitrogen carriers for CL-NH₃ (See Table 2.2).

When nickel and barium hydride mixtures are supported on alumina, the ammonia synthesis rate at 300°C and 1 bar is roughly 3 times higher than industrial iron (wüstite) catalyst at 300°C and 10 bar (See Table 2.2) and a half higher than the average rate of a two-bed reactor loaded with wüstite catalyst at 350–480°C and 110 bar (H. Liu, 2013). Furthermore, the carrier material can be nitrogenated under the same conditions, thereby allowing the material to produce ammonia over multiple cycles. Due to its high ammonia synthesis rate at lower temperatures, there is potential to increase the single-pass ammonia yield, thereby reducing the required operating pressure and costs of the process.

Compared to metal nitride carriers, metal imide/hydride carriers show feasible rates of ammonia synthesis and regeneration with nitrogen gas. Of note, is that mixtures of manganese catalyst with lithium hydride form Mn₄N during reaction R3b, allowing manganese to act as either catalyst or nitrogen carrier (Feng et al., 2021). Ammonia synthesis rates with Mn₄N-LiH are four times higher than wüstite catalyst at the same conditions (See Table 2.2). Alkali/Alkaline earth metal hydride mixtures with Fe, Ni, Co, and Pd have not presented evidence suggesting formation of metal nitrides postnitrogenation, however, mixtures of Zn with LiH form intermetallic LiZn as well as LiZnN post-nitrogenation (R. Wang *et al.,* 2023). It may be possible that combinations of these materials may allow metal nitride carriers to achieve higher ammonia synthesis rates *via* chemical looping.

Materials ^c	r _{NH3} (mmol g ⁻¹ h ⁻ 1)	NH3 yield ^a (%)	Reaction Conditions	SV e (L g ⁻¹ h ⁻¹)	Reference		
Benchmark Catalysts	e e						
Wustite Catalyst	5.4	0.74	300°C, 10 bar	36	(Kitano et al., 2018)		
Fe-K ₂ O-Al ₂ O ₃	2.0	0.16	300°C, 9 bar	9	(Kojima & Aika, 2001a)		
Ru(10%)-Cs/MgO	0.6	0.08	300°C, 9 bar	36	(Kitano et al., 2018)		
Metal Imide/Hydride Chemical Looping							
Ni-BaH ₂ /Al ₂ O ₃	17.6 ^b	1.44	300°C, 1 bar	60	(Gao et al., 2018)		
Ni(50%)-BaH ₂	9.4 ^b	0.77	300°C, 1 bar	60	(Gao et al., 2018)		
Fe(20%)-BaH ₂	5.2 ^b	0.43	300°C, 1 bar	60	(Gao et al., 2018)		
Co(20%)-BaH ₂	5.6 ^b	0.41	300°C, 1 bar	60	(Gao et al., 2018)		
Ni(50%)-LiH	4.6 ^b	0.38	350°C, 1 bar	60	(Gao et al., 2018)		
Mn4N(30%)-BaH2	13.1 ^b	1.08	300°C, 1 bar	60	(Feng et al., 2021)		
Mn4N(42%)-LiH	23.7 ^b	1.94	300°C, 10 bar	60	(Feng et al., 2021)		
Mn ₄ N(42%)-LiH	15.8 ^b	1.30	300°C, 1 bar	60	(Feng et al., 2021)		
Pd(40%)-Li2NH	N/A ^d	N/A	300°C, 1 bar	60	(Yan et al., 2021)		
Zn(50%)-LiH	N/A ^d	N/A	350°C, 1 bar	80	(R. Wang et al., 2023)		
Metal Amide/Hydride Catalysts							
Fe(58%)-LiH	~4.7	0.39	300°C, 10 bar	60	(P. Wang et al., 2017)		
Co(58%)-LiH	~5.0	0.41	300°C, 10 bar	60	(P. Wang et al., 2017)		
Ni(58%)-LiH	<0.1	0.01	300°C, 10 bar	60	(P. Wang et al., 2017)		
V(58%)-LiH	~0.25	0.02	300°C, 10 bar	60	(P. Wang et al., 2017)		
Cr(58%)-LiH	~4.0	0.33	300°C, 10 bar	60	(P. Wang et al., 2017)		
Mn(58%)-LiH	~3.0	0.25	300°C, 10 bar	60	(P. Wang et al., 2017)		
Co(5%)-BaH ₂ /CNTs	4.8	0.40	300°C, 10 bar	60	(Gao et al., 2017)		
Co(8%)/Ba-Ca(NH2)2	6.6	0.90	300°C, 9 bar	36	(Kitano et al., 2018)		
Ru(10%)/Ba-Ca(NH ₂) ₂	23.3	3.16	300°C, 9 bar	36	(Kitano et al., 2018)		

Table 2.2 Comparison of ammonia synthesis rates of alkali & alkaline earth metal imide/hydride nitrogen carriers to industrial catalyst and alkali & alkaline earth metal amide/hydride catalysts.

^a y_{NH_3} values calculated from r_{NH_3} and SV. ^b Reaction rates converted from amounts per cycle to amounts during the ammonia synthesis step.

^c Percentages in compound name corresponding to weight percent compositions.

^d Duration of reaction step not provided therefore the rate of the ammonia synthesis step is not known.

^e Space velocity (SV) defined as the volumetric flowrate of gas feed divided by the mass of material used.

2.3 Thermodynamics of Chemical Looping Ammonia Synthesis

Alkali/alkaline earth metal imide/hydride nitrogen carriers are promising due to their high ammonia synthesis rates under milder conditions, however, the thermodynamics of CL-NH₃ differ from the conventional reaction, which can impact the cost of producing ammonia. For a given reaction scheme, such as reaction R2 or R3, the gas species, the reaction stoichiometry, and the gas phase thermodynamic properties are well-defined, whereas the solid phase can be varied. If suitable solid phase thermodynamic properties are present, the equilibrium conversions of ammonia synthesis or nitrogenation reactions can be increased. However, the solid properties of many metal imide/hydride and nitride carriers are unknown; hence, it is unclear whether a more favourable or sufficient equilibrium conversion can be achieved with nitrogen carriers investigated in literature, despite high reaction rates seen with metal imide/hydride nitrogen carriers.

Previous studies have calculated the Gibbs free energy change of chemical looping reactions to select thermodynamically feasible metal nitride (Michalsky *et al.*, 2015) or metal imide/hydride (Gao *et al.*, 2018) nitrogen carriers for experimental studies. *In silico* screening of nitrogen carriers based on the Gibbs free energy change of pre-defined reaction sets has found 14 suitable material pairings from the HSC database (Experimental data) (Burrows *et al.*, 2021) and 4795 potential material pairings from the Materials Project database (Theoretical data) (Fan *et al.*, 2022). The discrepancy between the number of screened outputs from experimental *versus* theoretical databases provides a wide scope for discovering suitable material pairings for CL-NH₃, and to some extent, it highlights the lack of experimental data on nitrogen carrying materials.

Although a negative Gibbs free energy change of reaction is useful for evaluating the thermodynamic feasibility of CL-NH₃, it does not indicate whether the reaction can achieve sufficiently high equilibrium conversions. This also raises the question of what a 'sufficient' conversion would be for CL-NH₃. Furthermore, the equilibrium of the system is complicated further when side reactions such as the reverse of reaction R1, the decomposition of the nitrogen carrier, or the reverse of the nitrogenation reaction are considered. These issues need to be addressed to understand the thermodynamic limitations or opportunities with CL-NH₃.

2.4 Summary & Thesis Aim

Ammonia synthesis at lower temperatures can decrease the operating pressure of the reaction, thereby reducing ammonia production costs. Alternative ammonia synthesis routes have been explored to address this challenge, and chemical looping has demonstrated potential as a viable synthesis route. Low-temperature and ambient pressure ammonia synthesis appears to be feasible with CL-NH₃, specifically with metal imide/hydride nitrogen carriers. Research on the topic is nascent and has mostly focused on the material kinetics, yet the feasibility of CL-NH₃ also depends on its thermodynamics. Material screenings suggest that CL-NH₃ is thermodynamically feasible, however, it is unclear whether these nitrogen carriers possess appropriate gas-solid thermodynamic properties to achieve satisfactory or better equilibrium conversions under these conditions. Therefore, this work has aimed to investigate the value proposition of CL-NH₃ from a thermodynamic perspective.

2.5 Thesis Content & Objectives

Chapter 3. *Design and Evaluation of a Chemical Looping Ammonia Synthesis Process:* A novel design for a chemical looping ammonia synthesis process was considered. The design requirements were compared to the Haber-Bosch process. The effects of reactor conditions such as single-pass conversions, temperature, and pressure on the operating conditions of the chemical looping reactors and ancillaries of the process were also evaluated. Based on this study, reactor conditions were selected to perform a sensitivity analysis in Chapter 4.

Chapter 4. Sensitivity Analysis of a Chemical Looping Ammonia Synthesis Process: Benchmarks such as the energy and economic costs of the simulated CL-NH₃ process were calculated for the processes simulated in Chapter 3, and their sensitivity towards the reactor's operating conditions was determined. The results were compared to a reference Haber-Bosch process to determine the required operating conditions for a viable CL-NH₃ process. In Chapter 5, the operating conditions of the reactor were used as a proxy for the gas-solid thermodynamic properties of the nitrogen carrying material. In this manner, benchmarks for the thermodynamic properties of nitrogen carriers could be defined.

Chapter 5. *Gas-Solid Thermodynamics of Chemical Looping Ammonia Synthesis:* Thermodynamic models were generated to evaluate the equilibrium of the gas-solid reaction. One of the models was used to calculate the required solid thermodynamic properties to achieve a specified equilibrium gas conversion, which were defined in Chapter 4. A second model uses the equilibrium nitrogen partial pressure or conversion of the nitrogenation reaction to benchmark the performance of the CL-NH₃ reaction. The latter model can account for side reactions during the ammonia synthesis step such as the decomposition of ammonia or the reverse of the nitrogenation reaction. These models are used to screen nitrogen carriers in Chapter 6.

Chapter 6. *Thermodynamic Screening of Nitrogen Carriers for Chemical Looping Ammonia Synthesis:* High-throughput *in silico* screening of nitrogen carriers from the Materials Project database was used to identify potential nitrogen carriers for CL-NH₃. Screened materials were compared to thermodynamic models in Chapter 5 to benchmark their performance. Candidates were compared to performances estimated from literature to identify discrepancies with the screening methodology.

Chapter 7. *Thermodynamic Characterisation of Metal Imide/Hydride Nitrogen Carriers:* Feasibility of nitrogenating and forming ammonia from hydrides was determined in a custom-built reactor rig. The gas phase equilibrium composition of lithium hydride under nitrogen gas was determined, and this result was compared to values obtained in Chapter 6. Thermogravimetric analysis of the same reaction was performed for further comparison. Challenges with evaluating the materials thermodynamic properties have been identified in this chapter.

Chapter 3

Design & Evaluation of a Chemical Looping Ammonia Synthesis Process

3.1 Introduction

Chemical looping ammonia synthesis processes described in literature boast superior process conditions due to high reaction rates at lower temperatures and pressures, and generally this is thought to reduce the energy consumption and thus costs of ammonia production. However, without considering the entirety of the process and the impact of reaction conditions on the ancillary components of the process (e.g., separation systems, heat exchangers), such conditions may not be justifiable. In this chapter, a design for a novel CL-NH₃ process is proposed and simulated in Aspen Plus, and the impact of the chemical looping reactor's operating conditions on the overall process was evaluated and compared to a reference ammonia synthesis unit. The design and base case simulations in this chapter are used in Chapter 4 to perform a sensitivity analysis on key performance metrics towards the chemical looping reactors operating conditions.

The objectives of Chapter 3 are as follows:

- Simulate a reference ammonia synthesis unit (Ref-Case)
- Design & simulate a novel CL-NH₃ process (CL-Case).
- Evaluate the impact of reactor conditions such as gas conversion, temperature, and pressure on the operating conditions of ancillaries.

3.2 General Methodology

Simulations of a conventional ammonia synthesis unit (Ref-Case) and chemical looping ammonia synthesis unit (CL-Case) were generated in Aspen Plus for a 500 000 tonne of NH₃ per annum capacity. The design for the Ref-Case (described in section 3.3) was based on state-of the-art commercial processes whose conditions and performances are well documented in literature (Appl, 2011a, 2011c, 2011b; DOE/NETL, 2011b; H. Liu, 2013; Nielsen, 1995). Design considerations for the CL-Case are discussed in section 3.4, and since similar reactions and chemical species to the Ref-Case are involved, similar process equipment are re-considered for the CL-Case. Simulation of the chemical looping reactors, and more specifically reaction conditions such as temperature, pressure and reaction conversions are discussed in section 3.5. To evaluate the impact of reactor conditions on the process, the reaction conversion of the base CL-Case was varied, and its impact on the reactor temperature and separators performance was evaluated.

3.3 Reference Haber-Bosch Process & Simulation

The reference Haber-Bosch process is shown in Figure 3.1, and its design is based off the Haldor Topsøe ammonia process from (DOE/NETL, 2011b). The Haber-Bosch process can be described by the following steps which consists of feed gas compression, feed preheating, the ammonia synthesis reactor, steam generation and cooling of the product gas, condensation of ammonia *via* water and/or refrigeration followed by vapour liquid separation, recycling and re-compression of unconverted feed gases, and gas purging with purification of the purge gas. Altogether, these components are essential to achieving appropriate thermodynamic and kinetic conditions to form ammonia with high conversions, to obtain a high-purity ammonia product, and to maximise the process's conversion of feed gas and heat recovery.



Figure 3.1 Reference Haber-Bosch process based off (DOE/NETL, 2011b)

3.3.1 Feed Gas Preparation

Feed gas with a 3:1 ratio of H₂/N₂ is specified in the simulation, this ratio allows the highest equilibrium conversion and reaction rates to be achieved with iron-based catalysts. In a commercial process, ammonia synthesis gas contains inert gases such as CH₄ and Ar and is conditioned to achieve less than 10 ppm of oxygenated compounds such as oxygen, water, and carbon dioxide (Appl, 2011b; Nielsen, 1995). These compounds were not accounted for in the simulation since they have negligible impacts on the energy consumption and costs of the process; the gas purging and purification unit was also ignored for similar reasons. The feed gas is compressed to 150 bar in a multi-stage compressor, and after mixing with the recycled feed gas, it is pre-heated to 350°C using the product gas from the reactor.

3.3.2 Commercial Ammonia Synthesis Reactor

In the ammonia synthesis reactor, an iron-based catalyst is used to convert nitrogen and hydrogen feed gases to ammonia. Heat generated from the reaction increases temperatures across the catalyst bed which lower equilibrium conversions. Hence, to achieve and maintain high conversions pre reactor pass, heat must be removed from the reaction. Heat removal can be achieved in three different ways, such as through heat exchangers or quench cooling between multiple catalyst beds, or through an internal heat exchanger which continuously cools the reactor. The impact of these schemes on the reactor conversion is shown in Figure 3.2. In the Haldor Topsøe ammonia process, a radial reactor with internal heat exchanger is used, the exit temperature of the product gas is 495°C and the gas mixture is assumed to be at equilibrium with an ammonia concentration of 16% (DOE/NETL, 2011b); these conditions are assumed for the simulated reactor in the reference case.



Figure 3.2 Optimum operating temperature lines for ammonia synthesis reactors with (a) heat removal between beds (ca. 4), (b) heat removal via quench cooling, (c) heat removal with an internal heat exchanger. Figure redrawn from (H. Liu, 2013) (Copyright © 2023 World Scientific Publishing Co Pte Ltd).

3.3.3 Heat Recovery, Ammonia Separation, Gas Recycling

Heat contained in the product gas is used to generate high-pressure steam and preheat the feed gas to the reactor. The remaining heat from the product gas is removed with cooling water to achieve a temperature of 30°C and condensed ammonia is removed with a separator. Ammonia is condensed further by cooling the separated gas to -30°C with refrigeration, the liquid product is separated and mixed from that of the previous separator to obtain a final product with purity greater than 99.5% for commercial use (Dyno Nobel Inc., 2023). Unconverted gases leaving the final separator are re-compressed to 150 bar and recycled to the ammonia synthesis reactor.

3.4 Chemical Looping NH₃ Process Design

The CL-Case was designed for metal imide/hydride nitrogen carriers since the materials have demonstrated high reaction rates at lower temperatures than the commercial process, can form ammonia over multiple cycles, and data on the reaction rates of R10a and R10b are provided in literature. The material considered is a nickel catalyst deposited on barium hydride, wherein the later component serves as the nitrogen carrier.

$$BaNH_{(s)} + 2H_{2(g)} \rightarrow BaH_{2(s)} + NH_{3(g)} \quad \Delta_r H^\circ = +0.3 \ kJ \ mol^{-1} \ NH_3$$
 (R10a)

 $BaH_{2(s)} + 0.5N_{2(g)} \rightarrow BaNH_{(s)} + 0.5H_{2(g)} \quad \Delta_r H^{\circ} = -46.3 \ kJ \ mol^{-1} \ NH_3$ (R9b)



Figure 3.3 Process flow diagram of the proposed chemical looping ammonia synthesis process.

Two separate gas products (H_2/NH_3 mixture and N_2/H_2 mixture) are formed from reactions R10a and R10b, therefore, the CL-NH₃ process requires two distinct loops (See Figure 3.3) to separate and purify the gas products (Described in section 3.4.2). The ammonia synthesis loop hydrogenates the nitrogen carrier to form ammonia and is identical to the Haber-Bosch process (Figure 3.1), however, the nitrogenation loop is a novel addition and requires additional considerations for its design and operation. The design and simulation of the chemical looping reactor is discussed in section 3.5, whereas for ancillaries such as the feed conditioning, separation, and recycling processes, it is discussed in this section. The base CL-Case was simulated with the same production capacities (500 000 tonnes per annum), synthesis loop pressures (150 bar), and ammonia yields (y_{NH_3} = 16%) as the Ref-Case.

3.4.1 Feed Gas Preparation

The CL-NH₃ process is assumed to require separate and pure feeds of hydrogen and nitrogen. Most ammonia plants today are based on KBR's ammonia process (See Figure 1.3 (A)) which introduces nitrogen *via* an autothermal reformer to produce a mixture of hydrogen and nitrogen as ammonia synthesis gas, however, with the Linde ammonia concept (LAC) (Appl, 2011c) or a green hydrogen process it is possible to produce two separate feeds of nitrogen and hydrogen gas. Like the Ref-Case, oxygenated compounds should be eliminated to prevent the reaction from being inhibited. Although the impact of trace quantities of oxygenated compounds on reaction rates are not known for nitrogen carrying materials, alkali and alkaline earth metal imides and hydroides are known to react readily with these compounds and irreversibly form hydroxides or oxides which consequently reduces the nitrogen capacity of the material. In addition, the latter class of compounds are reactive towards methane, however, hydrogen produced from an LAC or water electrolysis process would contain negligible or zero amounts of methane, respectively. For similar reasons mentioned in section 3.3, these compounds are assumed to be zero in the simulation.

Pure nitrogen and hydrogen feeds are specified in the simulation, and like the Ref-Case, the feeds are compressed to 150 bar and pre-heated using hot gases produced from the chemical looping reactors. The pre-heating temperature is defined by the kinetics of the chemical looping reaction, with metal imide/hydride carriers the material is active at temperatures greater than 250°C at 1 bar (Gao et al., 2018); this value was taken as the minimum feed gas temperature of the reactor. Note that the sum of the stoichiometry of feed gases in reaction R10 is 1.25 times greater per mol of NH₃ than the conventional reaction R1, solely because a higher amount of hydrogen feed is required (2 vs 1.5 mol H₂ per mol NH₃) which should imply higher amounts of hydrogen feed compression and preheating to the reference case. Hydrogen produced during reaction R10b can be purified and recycled for reaction R10a, which could negate some of the energy and cost penalties associated with the increased hydrogen feed. If a 100% conversion was assumed for R10b, and a pure hydrogen stream at the same pressure was produced, this penalty would be negated and an equal feed compression duty to the Ref-Case would be achieved. However, this is unlikely therefore additional energy and costs are expected with the CL-Case for its feed preparation (Discussed further in Chapter 4).

3.4.2 Separation of Gas Products

In addition to requiring two separate feeds, two separate products are produced from the chemical looping reactors: a partially condensable mixture of ammonia and hydrogen gases from the ammonia synthesis step (R10b) and a non-condensable mixture of nitrogen and hydrogen gases from the nitrogenation step (R10a). Generally, there is economic incentive to recover and recycle hydrogen due to its high heating value and cost of production. Separation of non-condensable gases such as hydrogen from nitrogen is mature and common in ammonia plants seeking to recover hydrogen from purge gases containing hydrogen, nitrogen, methane, and argon. This separation is typically achieved with membranes, adsorbents, or cryogenic distillation (Appl, 2011c; Linde, 2019). The separation cost for N_2/H_2 produced from reaction R10b relative to conventional purge gas separation processes is dependent on the conversion of the reaction; low conversions or low hydrogen partial pressures increase such costs, and vice versa.

With CL-NH₃ accumulation of hydrogen in the nitrogenation loop should also be avoided, and hydrogen recycled to the ammonia synthesis loop should not contain mixtures of hydrogen and nitrogen since it can reduce the rate of ammonia synthesis with these materials (Feng et al., 2021; Gao et al., 2018), therefore, it was assumed that a nitrogen-free hydrogen stream should be produced from the nitrogenation loops separation system. Ideally, the separation process should minimise re-compression requirements for the purified nitrogen and hydrogen. Furthermore, the nitrogenation step is generally exothermic for CL-NH₃ reactions and may require cooling before and preheating after separation, therefore a separation process which operates at high temperatures would be preferable to avoid additional heat exchangers.

Production of nitrogen-free hydrogen *via* cryogenic, adsorption, or polymer-based membrane separation processes for CL-NH₃ may require additional costs compared to conventional ammonia purge gas recovery which does not require pure hydrogen to be recycled. Purified gases exit at low temperatures with these processes and require

additional costs for pre-heating recycled gases. However, cryogenic process can retain high pressures for the nitrogen and hydrogen products, whether this advantage compensates for additional pre-heating is beyond the scope of this work. Alternatively, inorganic membranes are known to be highly selective processes and likely to be more cost-effective for producing high purity hydrogen (Al-Mufachi *et al.*, 2015; Appl, 2011b; Burkhanov *et al.*, 2011; Pall Corporation *et al.*, 2012). Membranes made with palladium can operate at temperatures close to or equal to the chemical looping reactor (Burkhanov *et al.*, 2011), thereby circumventing the need for nitrogen feed preheating. The potential downside with this technology is the loss in hydrogen pressure in the permeate stream relative to the partial pressure in the feed, thereby requiring additional energy and costs for re-compression. The downstream impact of this pressure loss could be alleviated with higher nitrogen conversions per reactor pass. Since a palladium-based membrane system can achieve the purification requirements, the technology was selected for the simulation.

Palladium membranes can produce hydrogen with purities greater than 99.999%, in addition the membrane is suited to operating temperatures ranging from 300 to 600°C, where higher temperatures yield higher permeation rates and therefore smaller equipment sizes (Burkhanov *et al.*, 2011; IEA, 2012). Emerson *et al.* (2012) have shown that hydrogen recoveries of 95% are achievable in a pilot-scale system, therefore this value was specified in the simulation. The outlet pressure of the hydrogen product is assumed to be equal to its partial pressure in the membranes feed. For the ammonia synthesis loops separation, this can be performed like the Ref-Case (Figure 3.1) wherein the gas mixture is cooled to -25°C and the condensed ammonia is removed in a vapour liquid separator.

3.4.3 Heat Recovery

Ammonia synthesis from its elemental constituents is exothermic and provides opportunities for generating steam and pre-heating gas feeds. With a chemical looping reaction, the sum of the hydrogenation and nitrogenation reactions (R2a and R2b, or R3a and R3b) are exothermic however the heat generating step is dependent on the formation enthalpies of the solids, therefore both or a single reaction step can be exothermic. The heat exchange network for the base CL-Case is shown in Figure 3.4. With barium imide/hydride, the enthalpy change of the nitrogenation reaction is exothermic and the hydrogenation loop. Pre-heating of gas feeds is only required for the hydrogenation loop since the recycled nitrogen is produced at high temperatures; this can be achieved with hot gas from the hydrogenation and/or nitrogenation loop, and for the base CL-Case, pre-heating with the hydrogenation loops hot gas was sufficient.



Figure 3.4 Heat exchange network diagram showing the reactor heat recovery system that was simulated in Aspen Plus.

3.5 Simulation of Chemical Looping Reactors

Operating conditions of the chemical looping reactor such as temperature, pressure, and gas conversions are defined by the thermodynamics and kinetics of the nitrogen carrying material, and the type of chemical looping reactor employed. In this section, the range of feasible operating conditions and designs for the chemical looping reactor is discussed along with its implementation in the simulation.

3.5.1 Reactor Operating Conditions

Since the subject is still in its infancy, kinetic and thermodynamic data are limited for metal nitride and imide/hydride nitrogen carriers, however the range of operating conditions and possible outputs can be constrained within reasonable limits. For example, the lower temperature limit of the reactor can be defined by the chemical looping materials activity. With alkali and alkaline earth metal imide carriers (e.g., BaNH, Li₂NH) mixed with catalysts (e.g., nickel, iron, cobalt), the material is active to hydrogen or nitrogen gases at temperatures greater than 250°C (Feng *et al.*, 2021; Gao *et al.*, 2018). The overall reaction is exothermic and reactor temperatures can be maintained above the lower temperature limit. Ammonia formation *via* R10a releases negligible amounts of heat compared to the conventional reaction (R1), therefore changes in reaction temperature may be negligible. On the other hand, the nitrogenation step (R10b) is highly exothermic and could produce temperatures which decompose BaH₂ or BaNH. Barium hydride decomposes into barium metal at temperatures above 600°C (Schumb *et al.*, 1947; Verbraeken *et al.*, 2015). Therefore, the maximum operating temperature of the bed was limited to this value.

$$BaNH_{(s)} + 2H_{2(g)} \rightarrow BaH_{2(s)} + NH_{3(g)} \quad \Delta_r H^\circ = +0.3 \ kJ \ mol^{-1} \ NH_3$$
 (R10a)

$$BaH_{2(s)} + 0.5N_{2(g)} \rightarrow BaNH_{(s)} + 0.5H_{2(g)} \quad \Delta_r H^{\circ} = -46.3 \ kJ \ mol^{-1} \ NH_3 \qquad (R10b)$$

Assuming the difference in solid entropies are zero in R10b, the equilibrium constant was determined from the free energy change of reaction at ambient conditions, and the constant yields a >99.999% equilibrium conversion of nitrogen gas. This exceeds nitrogen conversions *via* R1, and since the enthalpy change of reaction is similar, an adiabatically operated reactor would exceed the specified maximum temperature if the nitrogen conversion per reactor pass was allowed to reach equilibrium. Like the conventional

process, heat management strategies are required to prevent the reactor from exceeding temperatures that would decompose the nitrogen carrier or limit equilibrium conversion of reaction R10a. In the simulation, an excess amount of nitrogen is fed to limit the nitrogen conversion per reactor pass such that the reaction temperature is no greater than 600°C. Higher nitrogen conversions per reactor pass could be achieved with a more effective heat removal strategy, however, this aspect is outside the scope of this work. The reactor has no known constraints for pressure, and the hydrogen conversion per pass was not constrained.

3.5.2 Reactor Design & Configuration

Various designs and operation for chemical looping reactors exist as shown in Figure 3.5, and each variant has their respective advantages and disadvantages. Circulating fluidised bed reactors can produce continuous outputs with near isothermal operation in each reaction step, however, solid circulation is required and can lead to entrainment of fine particles. Solid circulation can be eliminated by operating multiple moving bed reactors, which are essentially dynamically operated fluidised bed reactors. Alternatively, multiple dynamically operated packed bed reactors can be employed to eliminate solid circulation and reduce particle entrainment.



Figure 3.5 Designs and mode of operations for chemical looping reactors. Reactors can produce a steady-state output with a) circulating fluidised bed reactors or be operated dynamically without circulating solids using b) multiple fluidised bed reactors or c) multiple packed bed reactors. Depleted nitrogen carriers are represented in blue whereas filled carrier material is represented in yellow.

Each reactor configuration has different impacts on the temperature profile of the reactor and consequently the equilibrium gas conversion and rate of reaction. With circulating fluidised bed reactors, the solid temperature is uniform, and gases can be assumed to thermally equilibrate with the solid, therefore, the temperature difference between the nitrogenation and hydrogenation steps is large. With multiple fluidised bed or packed bed reactors, more heat would be retained by the solid between reaction steps since gases and solids may not reach thermal equilibrium, thus a lower difference in operating temperature between the two steps could be obtained compared to a circulating fluidised bed reactor. In the simulation, gases and solids in the chemical looping reactor are assumed to be thermally equilibrated. This closely matches how a circulating fluidised bed reactor operates.

3.5.3 Reactor Mass & Energy Balance

To simulate the outputs of the chemical looping reactor, a custom model was implemented in Aspen Plus such that it satisfies the assumptions provided in this section along with the energy and mass balance of the unit. Aspen Plus is generally unsuitable for modelling dynamic unit operations. Although this can be compensated for by integrating a dynamic model from MATLAB or Python or with the software's custom model tool, a simpler approach is to model steady-state outputs of the reactor under the assumption that a steady-state or cyclic steady-state is achieved with circulating fluidised bed reactors or dynamically operated reactors, respectively.

Unlike a mixed reaction, the solid products of the nitrogenation and ammonia synthesis steps are coupled, therefore heat released from the nitrogen conversion step is transferred to the ammonia synthesis step *via* the solid and vice versa. Furthermore, the gas conversions per reactor pass and operating pressures are manually specified, however the outlet temperatures of reactions R9a and R9b are unknown and required to solve the energy balance of the reactors. To approach this problem, the enthalpy changes of the process described in Figure 3.6 were evaluated and implemented in Aspen Plus to solve an energy balance and obtain these outlet temperatures.



Figure 3.6 For an adiabatic reactor (Q = 0), the enthalpy change of the system (Going from state (1) directly to (4)) can be calculated based on the enthalpy changes required to go in sequence from states (1), (2), (3), and (4). Subscripted numbers denote the state whereas the subscripted letters a and b denote the nitrogenation and hydrogenation reactions, respectively.

Each number in Figure 3.6 represents a different state of enthalpy (denoted by the number in the subscript) for the nitrogenation and hydrogenation reaction (denoted by subscripts *a* and *b*, respectively). States number one and two represent the reactants at their inlet and ambient conditions (T = 25°C, P = 1 atm), respectively, whereas states number four and three represent the products at their outlet and ambient conditions, respectively. The reactors are assumed to operate adiabatically and under isobaric conditions, therefore, the change in internal energy (U) and enthalpy between states one and four is zero (See Eq. (3.1)).

$$\Delta U_{1\to 4} = 0 \quad \text{and} \quad \Delta H_{1\to 4} = \Delta U_{1\to 4} + \Delta (PV)_{1\to 4} = 0 \tag{3.1}$$

The goal is to obtain values for the outlet temperatures of the products by calculating the enthalpy changes from states one to two $(\Delta H_{1\rightarrow 2})$, two to three $(\Delta H_{2\rightarrow 3})$, and three to four $(\Delta H_{3\rightarrow 4})$, which are equal to the change from state one directly to state four $(\Delta H_{1\rightarrow 4})$ (Eq. (3.2)). Equation (3.2) can be re-arranged and each term can be separated into a gas and solid phase component denoted by the subscripts *g* and *s* (Eq. (3.4)).

$$\Delta H_{1 \to 4,a} = \Delta H_{1 \to 2,a} + \Delta H_{2 \to 3,a} + \Delta H_{3 \to 4,a} = 0$$
(3.2)

$$\Delta H_{3 \to 4,a} = -(\Delta H_{1 \to 2,a} + \Delta H_{2 \to 3,a})$$
(3.3)

$$\Delta H_{3 \to 4, a, g} + \Delta H_{3 \to 4, a, s} = -(\Delta H_{1 \to 2, a, g} + \Delta H_{2 \to 3, a, s} + \Delta H_{1 \to 2, a, g} + \Delta H_{2 \to 3, a, s})$$
(3.4)

Enthalpy changes from states one to two (Eq. (3.5)) and three to four (Eq. (3.6)) correspond to the heat gained or lost by the reactants and products respectively. Enthalpy changes from states three to four (Eq. (3.7)) are equal to the standard enthalpy of the reaction.

$$\Delta H_{1 \to 2} = H_2 - H_1 = \sum_i n_i \int_{T_1}^{T_2} c_p(T) dT$$
(3.5)

$$\Delta H_{3\to 4} = H_4 - H_3 = \sum_i n_i \int_{T_3}^{T_4} c_p(T) dT$$
(3.6)

$$\Delta H_{23} = \mathrm{H}_3 - \mathrm{H}_2 = \Delta_r H^{\circ} \tag{3.7}$$

Substituting these terms into equation (3.4) gives equation (3.8). In addition, the following assumptions were made and applied to equations (3.2) to (3.9) to obtain equation (3.10):

- Reactor is under adiabatic conditions therefore Q = 0.
- Gases and solids are thermally equilibrated therefore $T_g = T_s$.
- Solid temperature is uniform across the reactor bed.
- Initial temperature of solids is equal to the final temperature from previous steps.
- Heat capacity of solids estimated using Dulong-Petit's rule.
- Solid reactants and products heat capacities are equal.

$$\sum_{g_{out}} \int_{T_3}^{T_{4,a}} n_{g,a} c_{p_{g,a}}(T) dT + \sum_{s_{out}} \int_{T_3}^{T_{4,a}} n_{s,a} c_{p_{s,a}} dT$$

$$= -\left[\sum_{g_{in}} \int_{T_{1,a,g}}^{T_2} n_{g,a} c_{p_{g,a}}(T) dT + \sum_{s_{in}} \int_{T_{1,a,s}}^{T_2} n_{s,a} c_{p_{s,a}} dT + \xi_a \Delta_r H_a^\circ \right]$$
(3.8)

$$\sum_{g_{out}} \int_{T_3}^{T_{4,a}} n_{g,a} c_{p_{g,a}}(T) dT + n_{s,a} c_{p_{s,a}} (T_{4,a} - T_3) + n_{s,a} c_{p_{s,a}} (T_2 - T_{1,a,s})$$

$$= -\sum_{g_{in}} \int_{T_{1,a,g}}^{T_2} n_{g,a} c_{p_{g,a}}(T) dT - \xi_a \Delta_r H_a^\circ$$
(3.9)

$$\sum_{g_{out}} \int_{T_3}^{T_{4,a}} n_{g,a} c_{p_{g,a}}(T) dT + n_{s,a} c_{p_{s,a}} (T_{4,a} - T_{1,a,s}) = -\sum_{g_{in}} \int_{T_{1,a,g}}^{T_2} n_{g,a} c_{p_{g,a}}(T) dT - \xi_a \Delta_r H_a^\circ$$
(3.10)

Each term in equation (3.10) is represented in Aspen Plus using appropriate unit operation blocks. However, the target of the simulation is to obtain the outlet temperature of gases ($T_{4,a}$ and $T_{4,b}$), therefore equations (3.11) and (3.12), which represent the energy balances of reactions R9a and R9b respectively, were solved in the simulation.

$$\sum_{g_{out}} \int_{T_3}^{T_{4,a}} n_{g,a} c_{p_{g,a}}(T) dT = -\sum_{g_{in}} \int_{T_{1,a,g}}^{T_2} n_{g,a} c_{p_{g,a}}(T) dT - \xi_a \Delta_r H_a^\circ - n_{s,a} c_{p_{s,a}} (T_{4,a} - T_{1,a,s})$$
(3.11)

$$\sum_{g_{out}} \int_{T_3}^{T_{4,b}} n_{g,b} c_{p_{g,b}}(T) dT = -\sum_{g_{in}} \int_{T_{1,b,g}}^{T_2} n_{g,b} c_{p_{g,b}}(T) dT - \xi_b \Delta_r H_b^{\circ} - n_{s,b} c_{p_{s,b}} (T_{4,b} - T_{1,b,s})$$
(3.12)

The flowsheet in Aspen Plus used to simulate the chemical looping reactors is shown in Figure 3.7. The exact unit operations and their corresponding mathematical descriptions are shown in Table 3.1. Properties of gases and their quantities are calculated in Aspen Plus, however, a linked excel sheet was used to specify solid properties and calculate values for the enthalpy change of reaction and enthalpy change of solid (See Table 3.1). The heat capacity of the solid was calculated using Dulong-Petit's rule (i.e., $c_{p_s} = 3R \ atom^{-1}$) and the standard heat of reaction was calculated from enthalpies of formations obtained from (Churney *et al.*, 1982; Gao *et al.*, 2018). The specified inputs for this system are thus the extents of reactions (ξ), enthalpy of reaction ($\Delta_r H^\circ$), and solid heat capacity (c_{p_s}).



Figure 3.7 Aspen Plus implementation of the chemical looping reactor. Heat exchangers and streams were used to calculate the mass and energy balance of the reactor under steady-state conditions.

Table 3.1 Nomenclature and equations of the streams and unit operations shown in Figure 3.7.

Definition	Symbol or Equation	Unit Operation	Identity
Enthalpy of state 1	$H_{1,b}$	Stream	R2-H1
Enthalpy of state 2	$H_{2,b}$	Stream	R2-H2
Enthalpy of state 3	$H_{3,b}$	Stream	R2-H3
Enthalpy of state 4	$H_{4,b}$	Stream	R2-H4
Enthalpy change of gas products $(3 \rightarrow 4)$:	$\sum_{g_{out}} \int_{T_3}^{T_{4,b}} \mathbf{n}_{g,b} c_{p_{g,b}}(T) dT$	Heat exchanger block	R2-H34
Enthalpy change of gas reactants $(1 \rightarrow 2)$:	$-\sum_{g_{in}}\int_{\mathrm{T}_{1,b,g}}^{T_2}\mathrm{n}_{\mathrm{g},\mathrm{b}}c_{p_{g,b}}(T)dT$	Heat exchanger block	R2-H12
Enthalpy change of reaction $(2 \rightarrow 3)$:	$-\xi_b\Delta_r H_b^\circ$	Excel sheet/Stream	R2-H23
Enthalpy change of solid $(1 \rightarrow 4)$:	$-n_{s,b}c_{p_{s,b}}(T_{4,b}-T_{1,b,s})$	Excel sheet/Stream	S

3.6 Impact of Reactor Conditions on the Process

The outlet composition and condition (T & P) of the chemical looping reactor is defined by the reactor conversions per pass and reaction enthalpies. These parameters have been specified for the BaH₂/BaNH pair, and the impact of equilibrium gas conversions on the operating conditions of the reactor (section 3.6.1 and 3.6.2) and outputs of ancillary systems in the process (section 3.6.3 and 3.6.5) are evaluated in this section. Ammonia yields, nitrogen conversions, and reactor pressures for the base CL-Case were varied to evaluate its impact on the chemical looping reactor's outlet conditions. Mainly the outlet temperature, pressure, and gas composition of the chemical looping reactors have an impact on ancillaries such as the ammonia separation and hydrogen separation units. Outputs of other ancillaries like compressors and heat exchangers are not dependent on the chemical looping reactor, however their energy and economic performance is affected and discussed further in Chapter 4.

3.6.1 Equilibrium Ammonia Yield

The impact of the reactor's operating pressure and ammonia yield per reactor pass is shown in Figure 3.8. Compared to the ammonia yield, operating pressures have little effect on the outlet temperature and conversion of reaction R10. Although reaction pressures do impact rates of ammonia synthesis (Feng *et al.*, 2021), the latter is unaccounted for in the current reactor model since it assumes that the gas and solid achieve thermal and chemical equilibrium. With dynamically operated reactors, the nonuniform temperature of the bed would affect the outlet temperature and conversion of the reaction. Furthermore, operating pressures could have a greater impact on the reactor's performance since the kinetics would also affect the temperature profile of the bed and resulting outlet ammonia yields over time. Note though that the current data on the materials thermodynamics and kinetics is partially available or constrained to a narrow range of operating conditions, which would not permit a dynamic model to be constructed with sufficient detail.

Ammonia yields higher than the base CL-Case (>27.5%) reduce the total flowrate of hydrogen to the chemical looping reactors resulting in higher outlet temperatures during the hydrogenation step (See Figure 3.8 (B)) since less gas is available to remove heat from the reactor. With increasing ammonia yields, a smaller fraction of the total heat produced from the reaction is removed during the hydrogenation reaction, and the nitrogen

conversion per reactor pass would decrease since the initial temperature of the bed would be higher during this step (See Figure 3.8 (A)). Although it is assumed that specified ammonia yields are close to the reaction's equilibrium, higher temperatures can limit equilibrium yields and result in lower ammonia yields than those specified in this simulation. Hence, heat removal from the reactor may be a pre-requisite to maintain reasonable operating temperatures during the nitrogenation step, but also for maintaining high ammonia yields per reactor pass during the hydrogenation step. Heat removal strategies are necessary in the Haber-Bosch process (described in section 3.3.2) and similar techniques could be employed for CL-NH₃.



Figure 3.8 Impact of ammonia yields on the nitrogen conversion per reactor pass of R10b (A) and hydrogenation outlet temperature of R10a (B). In these simulations, the outlet temperature of the nitrogenation step is specified to be 600° C by varying the nitrogen conversion.

3.6.2 Equilibrium Nitrogen Conversion

Nitrogen conversions per reactor pass affect downstream separation and recycling processes in the nitrogenation loop (See Figure 3.3), and operating conditions of the chemical looping reactor. It's impact on the palladium membrane unit is discussed separately in section 3.6.5, whereas in this section its impact on the chemical looping reactors operating conditions will be discussed. The nitrogen conversion per reactor pass is limited by the maximum operating temperature of the nitrogen carrier (600°C for BaH₂), however, the equilibrium of reaction R10b was estimated to be higher (>99.999%, see section 3.5.1). If the constraint was not present, higher nitrogen conversions per pass could be obtained which would lower separation and recycling requirements downstream of the reactor. However, for a fixed ammonia yield ($Y_{NH_3} = 27.5\%$),

increasing the nitrogen conversion per pass (beyond the current constraint) reduces the amount of nitrogen recycled back to the reactor, resulting in less gas to remove heat during this reaction step and higher outlet temperatures for reactions R10a and R10b (See Figure 3.9). Similar conclusions to section 3.6.1 apply here, meaning that heat removal strategies would benefit the nitrogen gas conversion per reactor pass.



Figure 3.9 Impact of nitrogen conversions on the chemical looping reactors outlet temperatures. Reaction temperatures are representative of a circulating fluidised bed reactor. For dynamically operated reactors, the outlet temperatures would approach the mean temperature shown above.

3.6.4 Ammonia Separation Unit

Separation of ammonia from non-condensable gases (e.g., hydrogen, nitrogen) is performed by condensation followed with vapour-liquid separation. The feasibility of this process is dependent on the vapour-liquid equilibrium (VLE) of the gas mixture. Operating pressures and ammonia concentrations must be above the dew point pressure of the mixture (See Figure 3.10) to be able to condense and separate ammonia. The differences between the VLE of gas mixtures produced from a chemical looping reactor or catalytic reactor is insignificant, therefore the criteria to achieve a feasible separation is equal in either case.



Figure 3.10 Dew point pressures of NH_3 - H_2 - N_2 and NH_3 - H_2 mixtures at T = 30°C (A) and T = -30°C (B), obtained in Aspen Plus. To achieve a feasible ammonia separation, the operating pressure of the system should be greater than the dew point pressure at T = -30°C for a given ammonia concentration.

Operating pressures of the ammonia synthesis unit should be sufficiently high to recover enough ammonia from the reactor product, otherwise, unrecovered ammonia fed to the reactor would inhibit the reaction thereby requiring larger reactor sizes. The amount of ammonia recovered from the ammonia separation unit is dependent on the operating pressure and ammonia concentration of the chemical looping reactor; pressures and concentrations required to achieve specified recoveries are shown in Figure 3.11. Although low-pressure ammonia synthesis could lower feed compression duties and costs, the VLE of the ammonia separation unit is favoured by high pressures. Additionally, higher ammonia concentrations would be necessary to maintain high ammonia recoveries in the separation system and avoid excessive energy consumptions.



Figure 3.11 Required synthesis loop pressures to achieve the specified recoveries in the ammonia separation unit. Dew point pressures at $T = 30^{\circ}C$ and $T = -30^{\circ}C$ are shown to determine whether the conditions allow for separation via cooling water and refrigeration, respectively. Data obtained in Aspen Plus.

3.6.5 Hydrogen Separation Unit

The hydrogen partial pressure in the palladium membranes feed is determined by the operating pressure of the chemical looping reactor and its nitrogen conversion per reactor pass (See Figure 3.12). Larger hydrogen partial pressure differences between the feed and permeate streams and higher operating temperatures can increase permeation rates and recovery fractions in the palladium membrane (Burkhanov et al., 2011). Note however that the current assumption for the difference in hydrogen partial pressure between the feed and permeate represents a best-case value and that a lower permeate pressure would be more realistic. However, it may be desirable to minimise the partial pressure difference to reduce energy consumptions associated with the hydrogen's recompression. Further study, outside the scope of this work, is necessary to determine optimal operating conditions and size requirements to apply palladium membranes for CL-NH₃.

Alternatively, improving nitrogen conversions in the chemical looping reactor can increase the hydrogen partial pressure in the membrane feed, thereby improving hydrogen permeation rates and recoveries of the membrane, and reducing recompression costs. Based on initial estimates for the equilibrium conversion of nitrogen gas *via* R4b (Mentioned in section 3.5.1), a near-complete conversion of nitrogen to hydrogen is possible which could eliminate the need for this process. Though, as

discussed in sections 3.6.1 and 3.6.2 additional heat removal is required to achieve a higher nitrogen conversion per reactor pass without exceeding the operating temperature limits of the material or without reducing the equilibrium ammonia yield of the hydrogenation reaction.



Figure 3.12 Impact of nitrogen conversions on the partial pressure of hydrogen in the palladium membrane separator's feed (A) and on the operating temperature of the membrane (B).

3.7 Summary

Design requirements for a CL-NH₃ process are similar to the Haber-Bosch process. However, the CL-NH₃ process is more complex because of the dynamic operation of reactors, increased number of process equipment (i.e., heat exchangers and compressors), and H₂/N₂ separation. Additional complexities are acceptable if compensated by better performances, and this is contingent on the chemical looping reactor's operating conditions and performance. Of note, is that the gas conversions per reactor pass determine the feasibility and performance of the gas separation processes, therefore, improving gas conversions in the chemical looping reactor can lead to better performances with the process. Nitrogen carriers with suitable thermodynamic and kinetic properties are necessary to achieve high gas conversions, but like the Haber-Bosch process, heat removal strategies may be necessary to control reaction conditions and maintain high single-pass equilibrium gas conversions. Based on literature, kinetics of metal imide/hydride carriers appear favourable; however, the thermodynamic properties of these materials are not fully available and can dictate the feasibility of the process. Therefore, in Chapter 4 the impact of the nitrogen carrier's thermodynamic properties on the process will be evaluated by using the reactor conditions as a proxy.
Chapter 4

Sensitivity Analysis of a Chemical Looping Ammonia Process

4.1 Introduction

The gas-solid thermodynamics of reaction R3 are inextricably linked to the energy consumption and economics of the CL-NH₃ process proposed in Chapter 3. Although the thermodynamic properties of gas phase reactants and products are known, those of the solid nitrogen carrying materials are only partially available, such as with LiH/Li₂NH or BaH₂/BaNH. Hence, it is unclear whether nitrogen carriers such as alkali/alkaline earth metal imides possess suitable properties for CL-NH₃ processes. In this chapter, the chemical looping reactors operating conditions and outputs will be used as a proxy for the nitrogen carriers' thermodynamic properties, and their impact on the process performance will be evaluated and compared to a reference case. In doing so, the required solid thermodynamic properties for CL-NH₃ (See Chapter 5). Typically, an ammonia synthesis process is benchmarked based on its energy consumption and cost of production per tonne of ammonia, therefore, this chapter aims to determine the required reactor operating conditions to achieve comparable or better performances to the reference case.

The objectives of Chapter 4 are as follows:

- Calculate energy consumptions and costs of the simulated base cases in Chapter
 3.
- ◆ Compare performances of the CL-NH₃ and Haber-Bosch processes.
- Evaluate the sensitivity of the CL-NH₃ process towards the reactor conditions.

4.2 Energy Analysis & Costing Methodology

Production costs are a key factor when selecting appropriate ammonia process designs. Commercial processes have not changed significantly since their inception but have aimed towards more energy-efficient designs due to the scale of ammonia production and strong correlation with natural gas prices (Figure 4.1). Therefore, the performance of an ammonia plant is generally evaluated based on their energy consumption per unit tonne of ammonia produced. Historically this value has decreased over time (Figure 4.2) and best available technologies today for methane-based ammonia production achieve energy consumptions of 28 GJ tonne⁻¹ NH₃ (Appl, 2011a; IEA, 2021a).



Figure 4.1 Ammonia and natural gas prices in Europe. The price of fertilizer (i.e., ammonia) is correlated to natural gas prices. Figure sourced and re-touched from (IEF, 2021) (Copyright © IEF 2020).



Figure 4.2 Energy consumption of ammonia processes over time with comparison to the best available technologies (BAT) and theoretical minimum energy consumptions. Figure obtained with permission from (C. Smith et al., 2020) (Copyright © CC BY 3.0).

A breakdown of the energy inputs and outputs of a conventional methane-based ammonia production process was obtained from Lee Pereira *et al.* (2020) and is shown in Figure 4.3 (A). Natural gas is the main energy input to the process (29.1 GJ tonne⁻¹ NH₃), and only a small fraction of the input is imported as electricity (0.4 GJ tonne⁻¹ NH₃) to drive compressors in the process (Lee Pereira *et al.*, 2020). Natural gas feed is also the predominant operating costs of the system (~70%) and consists of 29% of the ammonia price, as shown by the ammonia production costs breakdown in Figure 4.3 (B).



Figure 4.3 Sankey diagram showing percentage energy consumptions relative to the total energy input of a conventional ammonia plant (A), and ammonia production costs breakdown (B). Costing method was taken from the United States Department of Energy (DOE) (DOE/NETL, 2011b). Figures sourced and re-touched from Lee Pereira et al. (2020).

The downstream ammonia synthesis unit can be treated as an isolated process from the hydrogen production process since a negligible amount of purge gas is returned upstream and other forms of energy consumption or generation in either process are not dependent on each other (See Figure 4.4). The ammonia synthesis unit's energy inputs and outputs consist of electricity or steam for compressors and steam generated from the heat of reaction, respectively. The unit is a net electricity consumer in the ammonia production process and accounts for 83% of the net electricity consumption of the process (Lee Pereira *et al.*, 2020), despite this, its energy consumption is negligible compared to natural gas requirements in the overall process. Although operating costs associated with the ammonia synthesis unit are relatively small compared to other sources, the unit contributes significantly to the capital costs of the system, which makes up 25% of the ammonia production costs (See Figure 4.3 (B)). Since the capital costs of the unit plays a significant role in the ammonia price, it is likely to be an important indicator for the performance of the process and can be used to benchmark the economic costs of the unit.



Figure 4.4 System boundaries around the ammonia synthesis unit in a conventional ammonia production plant. Only purge gas is returned to the hydrogen production unit and is used to generate heat in the steam methane reformer's furnace.

4.2.1 Energy Consumption Analysis

In the CL-NH₃ and Haber-Bosch processes, the main energy consumers in the designs shown in Figure 3.1 and Figure 3.3 are the feed compressors, ammonia refrigeration compressor, and recycled gas compressors. Electricity is generated from high-pressure steam which was produced by recovering heat released from the ammonia synthesis reactions (R10a or R1). The total and net power consumption of the processes were calculated using Eqs. (4.1) and (4.2), respectively. Compressors and turbine efficiencies were assumed and are provided in appendix A.3. The energy consumption of the ammonia refrigeration compressor was determined based on the coefficient of performance for ammonia refrigerants. For an evaporator temperature of -30° C, a coefficient of performance of 2 was specified in the simulation (see appendix A.3). Steam produced from the process is used to generate electricity in a multi-stage steam turbine as shown by in Figure 4.5.

Total Power Consumption (MW) =
$$P_{compressors}$$
 (4.1)

Net Power Consumption (MW) =
$$P_{compressors} - P_{turbines}$$
 (4.2)



Figure 4.5 Multi-stage steam turbine modelled in Aspen Plus. See appendix A.3 for assumptions used.

4.2.2 Capital Costing Methodology

Equipment costs were determined using scaling correlations from (Woods, 2007). Equipment sizes (*A*) and their calculation methods are described in section 4.2.3. Cost correlation parameters are listed in Table 4.1 and were used with equation (4.3) to calculate free on-board costs (FOB), which represents the costs of the equipment and its shipment. Using the methodology in Table 4.2, the bare module costs (BM) was calculated; this value represents the cost to fully install a functional piece of equipment. Costs obtained from (Woods, 2007) are for the year 2003 (CEPCI = 1000), therefore, to account for changes in equipment costs over time the Chemical Engineering Plant Cost Index (CEPCI) was used to adjust costings to the year 2020 (CEPCI = 596.2). The equipment costs methodology has an accuracy of $\pm 30\%$ which is typical for parametric cost estimation models (Christensen et al., 2011; Woods, 2007).

$$FOB(\$M) = FC_{ref} \left(\frac{A}{A_{ref}}\right)^p \tag{4.3}$$

Equipment	Size (A)	Unit	Size range	Aref	Cref (\$M)	р	F	LM*
Radial Flow Reactor	Volume	m ³	10 - 180	100	1.3	0.4	а	1.54
Packed Bed Reactors	Volume	m ³	1 - 500	20	0.11	0.52	а	1.54
Fluidised Bed Reactors	Volume	m ³	1 - 500	12	5	0.67	-	1.54
Compressor (Low Duty)	Power	MW	0.15 – 3	1	2.85	0.65	b	1.505
Compressor (High Duty)	Power	MW	3 - 13	10	26	0.7	b	1.50
Refrigeration Unit	Capacity	MW	0.02 – 5	1	0.8	0.77	3c	1.3
Membrane Unit	Flowrate	m³/s	-	1	2	0.93	-	0.8
Heat Exchanger	Area	m ²	20 - 2000	100	0.07	0.71	d	1.96

Table 4.1 Cost correlation parameters for equation (4.3) obtained from (Woods, 2007).

^a Material and pressure factor applied. Stainless steel. Pressure factor calculated as follows $f_P = 0.1778 * P(bar) \div 10 + 0.7179$. ^b Material factor applied. ^c Evaporator temperature factor applied. ^d Material and heat exchanger configuration factor applied.

Table 4.2 Capital costing methodology from (Woods, 2007).

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Equipment costs	
Free on-Board Cost [FOB]	See Eq. (4.3)
Labour and Maintenance Factor [LM*]	Values obtained from (Woods, 2007)
Labour and Maintenance Cost [LM]	$LM = FOB \times LM^*$
Physical Module Cost [PM]	PM = LM + 20% FOB
Bare Module Cost [BM]	BM = PM + 20% LM

4.2.3 Equipment Sizing

Compressor sizes are based on their net power consumption or generation, and for the refrigeration unit, the net cooling duty in the heat exchanger was used. Sizing and costing of the steam turbine were ignored since in theory the amount of heat recovered in the CL-Case and Ref-Case should be similar, furthermore, the turbines are an off-site cost. Heat exchangers are sized based on the heat exchange area (See Eq.(4.7)) whose values are calculated in Aspen Plus based on the logarithmic mean temperature difference of the heat exchanger (See Eq.(4.6)) and a specified overall heat transfer coefficient. For gas to gas, gas to liquid, and liquid to liquid heat exchangers, the overall heat transfer coefficient (U) was specified to be 300, 400, and 1000 W m⁻² K⁻¹, respectively (Sinnott & Towler, 2013). The palladium membrane separator is sized based on its inlet gas flowrate.

$$\Delta T_{LMTD} = \frac{\Delta T_1 - \Delta T_2}{\ln \frac{\Delta T_1}{\Delta T_2}}$$
(4.4)

$$Area = \frac{Q}{U\Delta T_{LMTD}} \tag{4.5}$$

For the reactor sizing, ammonia reactor volumes for the Ref- Case were obtained from (H. Liu, 2013) and was linearly scaled according to the plant capacity. To size and cost the chemical looping reactors, the volume of a single fixed-bed reactor (V_R) and number of reactor beds (N_R) was determined. These parameters are dependent on the reaction rates of the chemical looping steps (r_{R10a} and r_{R10b}), which have been extrapolated from (Gao *et al.*, 2018) and used to obtain equations (4.6) and (4.7) for R10a and R10b respectively (See Figure 4.6). For the fixed-bed reactor configuration, the reaction temperature (T, K) for both R10a and R10b was taken as the mean temperature of the outlets. For the fluidised bed configuration, the reaction temperatures corresponded to the values found in the simulation since a uniform solid temperature was assumed in the reactor model.

$$BaNH_{(s)} + 2H_{2(g)} \rightarrow BaH_{2(s)} + NH_{3(g)} \quad \Delta_r H^{\circ} = +0.3 \ kJ \ mol^{-1} \ NH_3$$
 (R10a)

$$BaH_{2(s)} + 0.5N_{2(g)} \rightarrow BaNH_{(s)} + 0.5H_{2(g)} \quad \Delta_r H^{\circ} = -46.3 \ kJ \ mol^{-1} \ NH_3 \tag{R10b}$$

$$r_{R10b}\left(\frac{mmol\,NH_3}{kg.hr}\right) = \exp(-4005.05 \times T^{-1} + 10.12) \tag{4.6}$$

$$r_{R10a}\left(\frac{mmol \, H_2}{kg. hr}\right) = \exp(-5486.71 \times T^{-1} + 11.11) \tag{4.7}$$



Figure 4.6 Rates of ammonia production (R10a) and nitrogen consumption (R10b) versus temperature for Ni-BaH₂. Data obtained from (Gao et al., 2018) was used to fit Eqs. (4.6) and (4.7).

The required single reactor masses for the hydrogenation and nitrogenation reactors $(m_{R10a} \text{ and } m_{R10b})$ were calculated from the reaction rates $(r_{R10a} \text{ and } r_{R10b})$ and product flowrates $(n_{H_2} \text{ and } n_{NH_3})$ of the simulated reactor (Eq. (4.8)). This mass was used to size for a circulating fluidised bed reactor configuration. With multiple fixed-bed reactors, the ratio of required reactor masses is equal to the ratio of fixed-bed reactors (N_{ratio}) required to operate in parallel at any given time (Eq. (4.9)). Assuming the fastest reaction step only requires a single bed at any time, the ratio was used to obtain the number of fixed-bed reactors for each reaction step $(N_{R10a} \text{ and } N_{R10b})$ and the total number of fixed-bed reactors (N) (Eq. (4.10)). The mass of a single fixed-bed reactor (M_R) is calculated using equation (4.11), and assuming a bulk density (ρ_b) of 2859 kg m⁻³ for nickel (50 wt.%), the volume of a single fixed-bed reactor or

circulating fluidised bed reactor (V_R) can be found (Eq. (4.12)). The more conservative cost between the fluidised or fixed-bed reactor systems was selected.

$$m_{R10a} = \frac{n_{H_2}}{r_{R10a}} \qquad m_{R10b} = \frac{n_{NH_3}}{r_{R10b}} \tag{4.8}$$

$$N_{ratio} = \frac{m_{R10a}}{m_{R10b}} = \frac{N_{R10a}}{N_{R10b}}$$
(4.9)

$$N_R = 1 + N_{ratio} \tag{4.10}$$

$$M_R = \frac{m_{R10a}}{N_{R10a}} = \frac{m_{R10b}}{N_{R10b}}$$
(4.11)

$$V_R = \frac{M_R}{\rho_b} \tag{4.12}$$

4.3 Sensitivity Study Methodology

As a result of their impact on the reaction conversions and the overall energy and economic costs of the system, the sensitivity of the CL-NH₃ process toward the gas–solid reaction thermodynamics was evaluated. Thermodynamic properties, such as the reaction enthalpy and entropy, influence the chemical equilibrium of reactions R3a and R3b. The values of these properties vary with the composition of the material and are partially available for metal nitride and imide/hydride carriers, including BaH₂/BaNH. The chemical equilibrium is described by the equilibrium temperature, pressure, and yield of the reactions. These parameters are used to simulate the equilibrium of the chemical looping reactors and can be used as a proxy to represent the enthalpy and entropy of the gas–solid reactions.

With metal imide/hydride nitrogen carriers, the nitrogenation reactions conversion per reactor pass is not limited by equilibrium (Mentioned in section 3.5.1) but instead by the maximum operating temperature of the material. Although the nitrogen conversion is not dependent on the thermodynamic properties of the metal imide/hydride, its impact on the process's performance will be evaluated, nonetheless. Reaction temperatures are dependent on the conversions per reactor pass of reactions R10a and R10b, therefore it was excluded from the study. The ammonia yield and reactor pressure have noticeable effects on the performance of ancillary systems such as the feed compressors, recycle compressors, and separators, which are the main energy and economic costs within the system. The sensitivity study will therefore focus on the effects of reaction pressures and ammonia yields, since they are constrained by the nitrogen carriers' thermodynamic properties and have a clear impact on the operating conditions, energy consumptions, and costs of the CL-NH₃ process.

4.4 Base-Case Performances

4.4.1 Power Consumption

A comparison between the reference (Ref-Case) and chemical looping (CL-Case) cases (described in Chapter 3) is shown in Table 4.3, and the power consumptions of the nitrogenation (CL-Case (N₂)) and hydrogenation (CL-Case (H₂)) loops of the CL-Case are included. The CL-Case has a higher net (+9.7%) and total (+18%) power consumption than the Ref-Case due the increased feed and recycle compression duties. Majority of the power consumption (85%) originates from the hydrogenation loop which alone has an equal power consumption to the Ref-Case.

Plant Performance Results		Ref-Case	CL-Case	CL-Case (H ₂)	CL-Case (N ₂)
Reactor Conversion	%	26.2	-	26.1	15.7
Feed Compressors	MW	12.0	11.8	8.9	2.9
Recycle Compressors	MW	1.9	6.3	5.2	1.1
Refrigeration Compressor	MW	8.6	8.4	8.4	-
Steam Turbines	MW	-8.0	-10.7	-	-10.7
Total Power Consumption	MW	22.5	26.5	22.5	4.0
Net Power Consumption	MW	14.5	15.9	-	-

Table 4.3 Performance comparison between the reference ammonia synthesis unit (Ref-Case) and the chemical looping ammonia synthesis unit (CL-Case). The energy consumptions and reaction conversions per-pass associated with the hydrogenation loop (CL-Case(H_2)) and nitrogenation loop (CL-Case(N_2)) are shown.

In comparison to the Ref-Case, the hydrogen conversion per pass is equal, while the nitrogen conversion per pass is lower because it is limited by the maximum operating temperature of the material. Consequently, compared to the Ref-Case, additional energy (4.0 MW) is required for nitrogen recompression and for recycling hydrogen produced from the membrane separator to the hydrogenation loop. The nitrogenation reaction is non-equilibrium limited and high equilibrium conversions (>90%) should be attainable (see section 3.5.1). Achieving a complete nitrogen conversion per reactor pass could

significantly reduce the power consumption of the nitrogenation loop. Whilst unlikely, this would decrease the power consumption of the CL-Case by 4.3 MW and provide a slight reduction in energy consumption to the Ref-Case. The impact of the nitrogen conversion on the energy consumption of the process is evaluated further in section 4.5.1.

It was assumed that ammonia yields specified for the chemical looping reactors are close to or at equilibrium, however it is possible for this value to be higher. In theory a near-complete hydrogen conversion per reactor pass would eliminate the need for ammonia separation and hydrogen recycling. Although idealistic, doing so would decrease the total power consumption of the CL-Case by 12.2 MW. The impact of the specified equilibrium ammonia yield on the process performance is evaluated further in section 4.6.

The total power consumption of the Ref-Case (22.5 MW) are underestimated by 30% compared to (Nielsen, 1995) and (DOE/NETL, 2011b). This could be due to uncertainties associated with the omission of inert compounds, compressor efficiencies, and the coefficient of performance of the refrigeration unit. However, the error associated with these assumptions should impact both the Ref-Case and CL-Case similarly; therefore, the difference between the two would not change significantly.

4.4.2 Capital Costs

A summary of equipment costs is given in Table 4.4, and a detailed list is given in appendix A.4. Initial comparisons suggest that the CL-Case has a marginally lower (~2%) capital cost than the Ref-Case. The largest costs in both the Ref-Case and CL-Case were from the compressors and ammonia separator; note that the latter includes a compressor. Capital costs of compressors were 21% higher for the CL-Case and are due to the lower conversion per pass of reaction R10b and higher feed compressor duties. The majority of capital costs in the CL-Case are in the hydrogenation loop, which constitutes 84.5% of the capital costs. Hence, from both an energy and economic perspective, there is incentive to reduce compression duties and more so with the CL-Case. In addition, reducing energy consumptions in the hydrogenation loop can achieve the greatest cost savings.

Table 4.4 Capital costs comparison between the Ref-Case and CL-Case. The capital costs associated with the hydrogenation loop (CL-Case(H_2)) and nitrogenation loop (CL-Case(N_2)) are shown.

Capital Costs	Ref-Case	CL-Case	CL-Case (H ₂)	CL-Case (N ₂)
---------------	-----------------	----------------	---------------------------	---------------------------

Compressors	\$M	36.0	43.6	39.6	4.0
Reactors	\$M	15.0	5.6 ^a	-	-
Separators	\$M	22.5	23.8	22.2	1.6
Heat Exchangers	\$M	10.5	9.1	7.6	1.5
Total	\$M	84.0	82.1	-	-

^a Value corresponds to multiple fixed bed reactors. With circulating fluidised bed reactors, it is estimated to be 14.8
 \$M

Even though the uncertainties associated with the costing methodology can be up to 30%, the relative deviation of the Ref-Case and CL-Case from the true values should be similar because most unit operations involved are comparable and of similar costs. However, the reactor configuration and cost correlation are different, which can introduce error in the difference observed between the Ref-Case and CL-Case. The correlation used to estimate reactor costs in the Ref-Case accounts for the complexities in its design, such as the radial flow, multi-bed support, and interbed cooling. A multi-bed system with intercooling is necessary to achieve high yields; otherwise, the exothermic nature of the reaction lowers the equilibrium ammonia yield of the reaction (H. Liu, 2013; Nielsen, 1995), whereas in the CL-Case, the nitrogenation reaction is exothermic, nonequilibrium-limited, and separate from the ammonia synthesis step; hence, no intercooling was assumed to be required. Integrating a heat exchange component in the chemical looping reactors design could increase the nitrogen conversion per pass and result in lower process costs (see section 4.5.2). However, a more detailed reactor model may be necessary to appropriately quantify the cost-benefit of various heat removal strategies for CL-NH₃ processes.

Uncertainties associated with the reaction rates used for the reactor sizing are large because it was extrapolated from lab-scale experiments performed at 1 bar, 200 to 350°C, and with high space velocities (Gao *et al.*, 2018). Although pressures above ambient conditions can help to increase the rate of the hydrogenation reaction (Feng *et al.*, 2021), the apparent reaction rate will also be reduced by resistances as a result of mass transport phenomena, operation close to chemical equilibria, and degradation of hydrides and imides (e.g., irreversible oxidation by oxygenated species). On balance, the reaction rates used here are likely optimistic and, therefore, lead to a conservative estimate of the reactor size.

4.5 Sensitivity to the equilibrium nitrogen conversion

4.5.1 Power Consumption

Nitrogen conversions per pass are lower with the base CL- Case than the Ref-Case (15.7 vs 26.2%) therefore more energy is required to re-compress recycled nitrogen and hydrogen from the palladium membrane separator. The nitrogenation loop for the base CL-Case consumes 4.0 MW (See Table 4.3), however since the reaction is not limited by equilibrium, increasing the conversion per reactor pass would reduce the energy consumption of compressors associated with the loop's performance. As shown in Figure 4.7(A), increasing the nitrogen conversion per reactor pass decreases the power consumption in the nitrogenation and hydrogenation loops, and more specifically, the recompression of unconverted nitrogen and compression of separated hydrogen from the nitrogenation loop are reduced in each loop, respectively (See Figure 4.7(B)). If a 100% conversion were achieved, the power consumption of the process could be reduced by up to 4.3 MW compared to the base CL-Case since no power consumption would be required for nitrogen recycling, and hydrogen produced from the nitrogenation loop would require minimal re-compression. However, as discussed in section 3.6.1, heat must be removed from the nitrogenation step to reach higher nitrogen conversions and to avoid excessively high temperatures during the ammonia synthesis step.



Figure 4.7 Total power consumption of the CL-Case, CL-Case (N_2), and CL-Case (H_2) versus the nitrogen conversion per reactor pass (A), and compressor duties associated with the nitrogen conversion per reactor pass (B).

4.5.2 Capital Costs

The nitrogenation loop contributes to 8.6% of capitals costs (See Table 4.4) and increasing the nitrogen conversion per reactor pass can reduce or eliminate this expenditure, as shown in Figure 4.8(A). Although all categories of equipment would reduce in costs, the compressors for recycling nitrogen and hydrogen produced from the membrane separator account for 10.2% of the total costs, and these components experience the largest reduction in costs when the nitrogen conversion is increased (See Figure 4.8(B)). If a 100% nitrogen conversion per pass were achieved, the capital cost of the base CL-Case can be reduced by up to 12.2% due to negligible requirements for compression of recycled gases and separation of hydrogen from the nitrogenation loop.



Figure 4.8 Variation in equipment cost of the CL-Case (A) and compressor costs associated with the nitrogenation loop (B) versus the nitrogen conversion per reactor pass.

In this process model, the pressure of the recovered hydrogen is assumed to be 95% of the feed's hydrogen partial pressure. In reality, the permeation rate and recovery of the membrane would vary with the nitrogen conversion per reactor pass. Sieverts' Law suggests that the hydrogen flux is proportional to the root of the difference in feed and permeate hydrogen pressures of the membrane separator (Alraeesi & Gardner, 2021). Current pressure differences in the model appear to be within ranges that allow for high recoveries, purities, and hydrogen partial pressures (IEA, 2012). It is likely that the performance of the membrane is overestimated, and that cost may be underestimated for the hydrogen re-compressor and separator.

4.6 Sensitivity to the equilibrium ammonia yield & operating pressure

4.6.1 Power Consumption

Although the base CL-Case was less favourable in terms of energy consumption and capital costs than the Ref-Case, the comparison of the base cases (section 4.4) suggest that higher ammonia yields can decrease ammonia production costs via CL-NH₃. The variation in power consumption with ammonia yield for the CL-Case at 150 bar is shown in Figure 4.9(A). The trend in power consumption for a given pressure can be described by three defining features and is near-equal in both the Ref-Case and CL-Case. The beginning of the trend is marked by a vertical asymptote, which represents the vapor pressure of ammonia in the refrigeration unit (-30°C). At sufficiently high ammonia vapor pressures or an ammonia yield of at least 20% at a total pressure of 150 bar, the ammonia gas is partially condensable by cooling water (30°C) and larger decreases in power consumption can be obtained than with refrigeration alone. At a 100% yield, a horizontal asymptote is formed, which equals the power consumption of feed compressors and recycle compressors in the nitrogenation loop. Decreases in synthesis loop pressures cause the equilibrium vapor pressures of ammonia (at $T = 30^{\circ}C$ and $-30^{\circ}C$) to increase and feed compressor duties to decrease. This causes a positive horizontal shift in the trend and some stretching because the change in vapor pressure is not linear with pressure (See Figure 4.9(B)).



Figure 4.9 (A) Variations in total power consumption with ammonia yield for the CL-Case at 150 bar. The lines describing the trend are determined by the ammonia vapour pressure at -30° C (1), the ammonia vapour pressure at 30° C (2), and the minimum power consumption at an ammonia yield of 100% (3). The arrows indicate how these lines shift with decreasing pressure, and the dotted lines correspond to lines for the CL-Case at 100 bar. (B) Sensitivity of the CL-NH₃ processes' total power consumption towards the synthesis loop pressure and ammonia yield. The results are compared to the Ref-Case's power consumption denoted by a dashed line.

In comparison to the Ref-Case (Dashed line in Figure 4.9(B)), yields of at least 36% are required to achieve a power consumption with the CL-Case. When variations in the synthesis loop pressure are considered (Figure 4.9(B)), it is found that power consumptions at yields between 22 – 58% do not vary as significantly with pressure and an optimal synthesis loop pressure exists at a given yield. This invariance is largely due to the trade-off between the energy required for feed compression and that required for separation and recycling (see Figure 4.10). To synthesise ammonia at low pressures and

temperatures is a widely promoted goal in the literature; however, the results indicate that the maximum ammonia yield achievable is a key parameter when developing new materials and processes for ammonia synthesis. This constraint has not been generally recognized until now.



Figure 4.10 Effect of synthesis loop pressures on the separation and recycling compressors (Coloured) and feed compressors (black) for varying ammonia yields.

4.6.2 Capital Costs

The capital cost variation with the yield for the base CL-Case (Figure 4.11) appears to be correlated with the power consumption of the unit. Although the relative decreases in both benchmarks are similar, the capital costs predominate the ammonia price and are therefore more significant. As the synthesis loop pressure decreases, the results remain invariant at 50–150 bar; this invariance is due to the trade-off between the feed compression duty and the separation and recycling duties. This would suggest that the ammonia yield is a stronger predictor of capital costs than the operating pressure. According to Figure 4.11, a similar or better capital cost to the reference case would require an ammonia yield equal to or greater than 26% at pressures between 50 to 150 bar. If uncertainties in capital costs are considered for the CL-Case (±30%), the required ammonia yield would be between 16 to 45% at pressures between 50 to 150 bar.



Figure 4.11 Sensitivity of the CL-NH₃ processes' capital costs towards the synthesis loop pressure and ammonia yield. The results are compared to the Ref-Cases' power consumption.

A significant difference in capital costs is observed at 25 bar, which decreases with the ammonia yield. The increase is due to larger hydrogen recycling duties and lower outlet temperatures for the hydrogenation reaction, which increased capital costs of the recycled hydrogen compressor and hydrogen preheater (see Figure 4.12). The latter cost is a result of the given design and could be reduced by preheating the feed of the hydrogenation reactor with heat from the nitrogenation loop. However, the recycle compression costs are dependent on the ammonia yield and synthesis loop pressure; operation at lower pressure would require higher ammonia yields to maintain low capital costs.



Figure 4.12 Capital of the recycled hydrogen compressor (A) and hydrogen pre-heater (B) versus the ammonia yield and operating pressure of the CL-NH₃ process. Note that there is a significant increase in these costs at P = 25 bar.

4.7 Summary

Sensitivities of the energy consumption and capital costs of a CL-NH₃ process towards the reaction yield, pressure, and temperature of a chemical looping ammonia synthesis reactor were evaluated. The performance of the process was most sensitive towards the reactor's ammonia yield, and to a lesser extent the nitrogen conversion per reactor pass. For the ranges of ammonia yields and nitrogen conversions specified in the simulation, the process performance was not sensitive towards the reaction temperature of pressure. Amongst these parameters, the ammonia yield is the strongest predictor of capital costs, a key performance indicator, and can be used as a benchmark for the chemical looping reactor's performance. In comparison to the reference case, ammonia yields greater than 26% were required to compete on a cost basis. Note that, this criterion is a conservative value because reactor costs are likely underestimated for the chemical looping case. Whether this minimum ammonia yield can be achieved will depend on the thermodynamic and kinetic properties of the nitrogen carrying material, and the potential of the former property will be investigated further in following chapters.

Chapter 5

Gas-Solid Thermodynamics of Chemical Looping Ammonia Synthesis

5.1 Introduction

The desired operating conditions and reaction yields of a chemical looping ammonia synthesis reactor are dependent on the thermodynamic properties of the gas and solid species in the reaction. Although properties of gases are known, those of solid nitrogen carrying materials are partially available. This information is essential to determine the thermodynamic feasibility and suitability of nitrogen carriers for CL-NH₃. In this chapter, thermodynamic models which describe the gas-solid equilibrium of CL-NH₃ have been developed to evaluate relations between equilibrium gas conversions and solid thermodynamic properties. In addition, the thermodynamic relation between the hydrogenation (R2a or R3a), nitrogenation (R2b or R3b), and conventional (R1) reactions was used to account for side reactions such as the reverse of the nitrogenation and conventional reactions which may occur during the hydrogenation reaction. Relations between the equilibrium gas conversions of the hydrogenation and nitrogenation reactions were established and used to identify potential thermodynamic limitations with CL-NH₃ and identify ranges of suitable properties for nitrogen carriers. These models are used in Chapter 6 to screen for viable nitrogen carriers based on their solid properties or gas phase equilibrium conversion.

The objectives of Chapter 5 are as follows:

- Generate models for the gas-solid thermodynamics of nitrogen carriers.
- Evaluate these models with reference to required operating conditions (Chapter 4).
- Discuss limitations and opportunities with the gas-solid equilibrium of CL-NH₃.

5.2 Gas-Solid Thermodynamics of Chemical Looping Ammonia

Synthesis

For a specified set of thermodynamic conditions such as the temperature, pressure, equilibrium nitrogen conversion (Eq. (5.1)), and equilibrium ammonia yield (Eq. (5.2)), the equilibrium constant (K) of reactions R1, R2, or R3 can be determined using Eqs. (5.3) to (5.7).

$$X_{N_2}(R3b) = y_{H_2} \tag{5.1}$$

$$Y_{NH_3}(R2a) = \frac{y_{NH_3}}{1 + y_{NH_3}} \qquad Y_{NH_3}(R3a) = \frac{2y_{NH_3}}{1 + y_{NH_3}}$$
(5.2)

Haber-Bosch Equilibrium Constant

$$1.5H_{2(g)} + 0.5N_{2(g)} \rightleftharpoons NH_{3(g)}$$
 (R1)

$$K_{R1} = \frac{f_{NH_3}}{f_{N_2}^{0.5} f_{H_2}^{1.5}} = \frac{y_{NH_3}}{y_{N_2}^{0.5} y_{H_2}^{1.5}} \frac{\phi_{NH_3}}{\phi_{N_2}^{0.5} \phi_{H_2}^{1.5}} \frac{P^{\circ}}{P_{R1}}$$
(5.3)

Nitride Carrier Equilibrium Constants

$$\frac{1}{y}M_{x}N_{y_{(s)}} + 1.5H_{2(g)} \to \frac{x}{y}M_{(s)} + NH_{3(g)}$$
(R2a)

$$\frac{x}{y}M_{(s)} + 0.5N_{2(g)} \to \frac{1}{y}M_xN_{y(s)}$$
 (R2b)

$$K_{R2a} = \frac{f_{NH_3}}{f_{H_2}^{1.5}} = \frac{y_{NH_3}}{\left(1 - y_{NH_3}\right)^{1.5}} \frac{\phi_{NH_3}}{\phi_{H_2}^{1.5}} \frac{P^{\circ 0.5}}{P_{R2a}^{0.5}}$$
(5.4)

$$K_{R2b} = \frac{1}{f_{N_2}^{0.5}} = \frac{1}{P_{N_2}^{0.5} \phi_{H_2}^{0.5}}$$
(5.5)

Imide/Hydride Carrier Equilibrium Constants

$$\frac{1}{y}M_xN_yH_{z_{(s)}} + (1.5+w)H_{2(g)} \to \frac{x}{y}MH_{\frac{z}{x}+\frac{2wy}{x_{(s)}}} + NH_{3(g)} \quad w = 0.5$$
(R3a)

$$\frac{x}{y}MH_{z/x+2wy/x_{(s)}} + 0.5N_{2(g)} \to \frac{1}{y}M_xN_yH_{z_{(s)}} + wH_{2(g)} \qquad w = 0.5$$
(R3b)

$$K_{R3a} = \frac{f_{NH_3}}{f_{H_2}^2} = \frac{y_{NH_3}}{\left(1 - y_{NH_2}\right)^2} \frac{\phi_{NH_3}}{\phi_{H_2}^2} \frac{P^{\circ}}{P_{R3a}}$$
(5.6)

$$K_{R3b} = \frac{f_{H_2}^{0.5}}{f_{N_2}^{0.5}} = \frac{y_{H_2}^{0.5}}{\left(1 - y_{H_2}\right)^{0.5}} \frac{\phi_{H_2}^{0.5}}{\phi_{N_2}^{0.5}}$$
(5.7)

Where f_i and ϕ_i represent the fugacity and fugacity coefficient of compound *i*, and the latter is calculated using the Soave-Redlich-Kwong equation of state (SRK); y_i represents the gas phase mole fraction of species *i*; P_k represents the total pressure of the system under which reaction *k* is taking place and P° is the reference pressure, taken to be 1 bar. Solids are assumed to have an activity of 1. Through the equilibrium constant of the reaction, the properties of the gases and solids (e.g., Gibbs free energy, enthalpy of formation, entropy) can be associated to the equilibrium conversions of the reactions and operating conditions of the reactor (assuming it is operated under equilibrium conditions).

5.3 Thermodynamic Models

5.3.1 Nitrogen Carrier Thermodynamic Properties

The equilibrium constants of reactions R2 and R3 are used to calculate their standard Gibbs free energy change of the reaction ($\Delta_r G^{\circ}$) using Eq. (5.8), and in turn the required enthalpy ($\Delta_r H^{\circ}$) and entropy ($\Delta_r S^{\circ}$) changes of the reaction are determined using Eq. (5.9).

$$\Delta_r G^{\circ}(T) = -RT \ln K_{eq} \tag{5.8}$$

$$\Delta_r G^{\circ}(T) = \Delta_r H^{\circ}(T) - T \Delta_r S^{\circ}(T)$$
(5.9)

The enthalpy and entropy of reactions (Eq. (5.12) and (5.13)) are defined by the differences in formation enthalpies ($\Delta_f H_i^\circ$) and entropies (S_i°) of the products and reactants (Eq. (5.10) and (5.11)), where ν_i represents the reactions stoichiometric coefficient for compound *i*.

$$\Delta_f H_i^{\circ}(T) = \Delta_f H_i^{\circ}(298K) + \int_{298K}^T c_{p,i}(T) dT$$
(5.10)

$$S_{i}^{\circ}(T) = S_{i}^{\circ}(298K) + \int_{298K}^{T} \frac{c_{p,i}(T)}{T} dT$$
(5.11)

$$\Delta_r H^{\circ}(T) = \sum_i \nu_i \Delta_f H_i^{\circ}(T)$$
(5.12)

$$\Delta_r S^{\circ}(T) = \sum_i \nu_i S_i^{\circ}(T)$$
(5.13)

These properties are well known for gases such as ammonia, hydrogen, and nitrogen, and are available on the National Institute of Standard and Technology (NIST) database. However, for metal nitrides (e.g., Mn₄N), hydrides (e.g., BaH₂), and imides (Li₂NH), these properties are only partially available. Hence, whether the chemical looping reaction achieves sufficient equilibrium conversion at a given temperature and pressure depends on the solid thermodynamics' properties, and the required equilibrium conditions can be defined by the solid's thermodynamic properties.

The enthalpy and entropy of reaction can be re-defined by Eq. (5.14) and (5.15) which separates the terms into the enthalpy and entropy change of gas (Eq. (5.17) and (5.19)) and solid species (Eq. (5.16) and (5.18)) in a reaction. Reaction R10a is used as an example here:

$$\Delta_r H^{\circ}(T) = \Delta H^{\circ}_{solid}(T) + \Delta H^{\circ}_{gas}(T)$$
(5.14)

$$\Delta_r S^{\circ}(T) = \Delta S^{\circ}_{solid}(T) + \Delta S^{\circ}_{gas}(T)$$
(5.15)

$$\Delta H_{solid}^{\circ}(T) = \Delta_f H_{BaH_2}^{\circ}(T) - \Delta_f H_{BaNH}^{\circ}(T)$$
(5.16)

$$\Delta H_{gas}^{\circ}(T) = \Delta_f H_{NH_3}^{\circ}(T) - 2\Delta_f H_{H_2}^{\circ}(T)$$
(5.17)

$$\Delta S_{solid}^{\circ}(T) = S_{BaH_2}^{\circ}(T) - S_{BaNH}^{\circ}(T)$$
(5.18)

$$\Delta S_{gas}^{\circ}(T) = S_{NH_3}^{\circ}(T) - 2S_{H_2}^{\circ}(T)$$
(5.19)

The enthalpy and entropy changes of solids required to achieve a specified conversion at a given temperature and pressure are determined using equation (5.20) and can be used to determine whether a compound achieves benchmarks defined in Chapter 4.

$$\Delta H^{\circ}_{solid}(T) = \left(\Delta_r G^{\circ}(T) - \Delta G^{\circ}_{gas}(T)\right) + T\Delta S^{\circ}_{solid}(T)$$
(5.20)

Shown in Figure 5.1 are the changes in enthalpy and entropy of the gas phase species for reactions R2 and R3. The contribution to the enthalpy of reaction from gas phase species in reaction R2 is lower than reaction R3; although minor, it may cause the required ΔH_{solid}° with nitrides to be lower than with imides/hydrides. More notably, the contribution to the entropy change of reaction from the gas species is significantly different with reactions R2 and R3. With nitrides, the entropy change of the nitrogenation reaction is dominated by the gas phase species, however with the imides it is dominated by the solid phase species. With the hydrogenation reaction, the entropy change of the gas phase species is dominant with imides/hydrides, and negligible for nitrides. These differences are reflected in the models discussed later in section 5.5.



Figure 5.1 Enthalpy (A) and entropy (B) changes of the gas phase species versus temperature of metal nitride and imide/hydride nitrogen carriers following reactions R2 and R3, respectively.

5.3.2 Equilibrium of the Gas Phase

The equilibrium nitrogen partial pressure (P_{N_2} , bar) of a nitride impacts the nitrogenation reaction (R2b) directly. Equivalently, with alkali and alkaline earth metal imide/hydride carriers, the ratio of the equilibrium nitrogen to hydrogen partial pressures (P_{N_2}/P_{H_2}) impacts the nitrogenation reaction (R3b). Assuming R2b or R3b has reasonable kinetics, then if the P_{N_2} or P_{N_2}/P_{H_2} in the system is low during hydrogenation (R2a or R3a), the reverse of the nitrogenation reaction (R2b or R3b) would also take place until equilibrium of R2b or R3b is achieved or all the $M_x N_y$ or $M_x N_y H_z$ is consumed. Therefore, in practice a mixture of hydrogen, nitrogen, and ammonia gases would be present in the hydrogenation step. Assuming further that the gas phase achieves equilibrium according to Reaction R1 as well (e.g., *via* decomposition of ammonia in the gas phase), the equilibria of R1, R2a, and R2b or R1, R3a and R3b need to be considered simultaneously during the hydrogenation reaction, as shown by Eqs. (5.3) to (5.7). Furthermore, at any given temperature it is also necessary that

$$K_{R1} = K_{R2a} K_{R2b} \quad or \quad K_{R1} = K_{R3a} K_{R3b}$$
(5.21)

for metal nitrides or metal imides, respectively. Using Eqs. (5.3) to (5.7) and (5.21), y_{NH_3} achieved through reaction R2a or R3a at equilibrium can be uniquely determined given a reaction temperature, K_1 , and K_{R2b} (or equivalently the decomposition pressure of $M_x N_y$) for metal nitrides or K_{R3b} (or equivalently the ratio $P_{H_2}^{0.5}/P_{N_2}^{0.5}$) for metal imides. While K_{R1} is readily available, K_{R2b} and K_{R3b} are specific to the $M_x N_y/M$ and $M_x H_{z+2w}/M_x N_y H_z$ (w = 0.5) pairs, respectively, and experimental values are largely unavailable and needs to be estimated in many cases.

5.4 Material Property Benchmarks

In Chapter 4, the sensitivity of the CL-NH₃ process towards the chemical looping reactors ammonia yield, nitrogen conversion, temperature, and pressure was evaluated. These parameters can be used as a proxy for the chemical looping reactions gas-solid thermodynamic properties, and to define requirements for the properties of the nitrogen carrying material. Amongst these variables, the ammonia yield was found to have the most influence on the performance of the process. Compared to the Haber-Bosch process (Ref-Case), ammonia yields equal to or greater than 26% at 150 bar were found to be necessary for the CL-NH₃ process to compete on a cost-basis (see section 4.6.2). Few ammonia synthesis catalysts are sufficiently active below 200°C temperature (Fu et al., 2023), and operating temperatures of the ammonia synthesis step (R3a) ranged between 250 – 400°C over the range of ammonia yields (Y_{NH_3}) evaluated in Chapter 3 (10 to 60%, see Figure 3.8). In addition, the material should achieve similar nitrogen conversions (X_{N_2}) to those found in the sensitivity study (14 – 18%), however, a more conservative value of 10% could be used instead. These conditions $(Y_{NH_3}, X_{N_2}, T, P)$ can be used to calculate the required equilibrium constant of reaction R3a using Eqs. (5.2) and (5.6), and that of reaction R3b using Eqs. (5.1) and (5.7). The equilibrium constant can then be used to calculate the required $\Delta_r G^{\circ}$ using Eq. (5.8) and the required ΔH°_{solid} and ΔS°_{solid} as described in section 5.3.1.

Note that these requirements were obtained for simulations of a metal imide/hydride based CL-NH₃ process and these requirements would be different for metal nitrides. The reaction and separation requirements for the ammonia synthesis step (R2a and R3a, respectively) should be identical and imply that the ammonia yield is also a strong predictor of costs with the nitride based process. On the other hand, there are differences in their separation and purification requirements for gas species in the nitrogenation reaction (R2b and R3b, respectively), and depending on the operating conditions of the nitrogenation loop this could incur lower or greater costs than with metal imides/hydrides.

Metal imide/hydrides require separation of H₂/N₂ mixtures followed by recompression of the purified gases, whereas metal nitrides may only require the latter. Although theoretical estimates for the equilibrium nitrogen conversion of metal imide/hydride carriers show near-complete conversions (see appendix B.6), the nitrogen pressure required to regenerate the metal nitride carriers can vary between 10⁻⁶ to 10⁴¹ bar (see supplementary data in Lee Pereira et al. (2023) due to the large number of possible compositions and resulting properties (see Figure 6.1). Metal nitrides carriers which require nitrogen pressures above 150 bar (highest pressure specified in simulations) for reaction R2b would require additional energy for the nitrogen feed compression and lead to additional costs compared to the metal imide/hydride process evaluated in Chapter 4. Metal nitrides also do not require hydrogen separation or recompression of the hydrogen permeate which could reduce costs. Note however that the latter costs is negligible compared to the costs associated with the hydrogenation loop (see Chapter 4). Therefore, if additional costs were to be incurred compared to the metal imide/hydride processes, it would be due to high nitrogenation pressures. This has not been evaluated in detail in this work, therefore, nitrogen conversions greater than or equal to 10% at 150 bar were assumed to be a requirement for metal nitrides, which should lead to a more conservative benchmark.

5.5 Thermodynamic Property Requirements for Nitrogen Carriers

5.5.1 Metal Nitride Carriers

Based on the benchmarks described in the previous section (5.4), the required ΔH_{solid}° and ΔS_{solid}° for nitride pairs which can undergo reaction R2's scheme were calculated using the method described in section 5.3.1. For temperatures between 200 to 500°C, viable values of ΔH_{solid}° and ΔS_{solid}° have been plotted on Figure 5.2. Note that the viable regions overlap at some temperatures hence why it has been displayed over a temperature 'span'. Nitride pairs with ΔH_{solid}° and ΔS_{solid}° situated within the highlighted region can achieve the benchmarks defined for reaction R2a and R2b in Chapter 4. Furthermore, values situated below this region achieve higher equilibrium y_{NH_3} values than the benchmark, whereas values above the region achieve lower equilibrium P_{N_2} values than the benchmark.



Figure 5.2 ΔH_{solid}° and ΔS_{solid}° for reaction R2a to achieve an equilibrium $y_{NH_3} > 0.16$ via R2a and $P_{N_2} < (0.9 \times 150 \text{ bar})$ via R2b at a total operating pressure of 150 bar. The coloured region shows the temperature span (within a range of 200 to 500°C) that allows viable equilibrium conversions via R2a and R2b. Above the midsection of the region, the temperature span is located at the upper temperature range (closer to 500°C), and the contrary below the midsection (closer to 200°C).

The midsection of the plot (dark red region) marks the region for the ΔH°_{solid} and ΔS°_{solid} to be viable at all temperatures between 200 to 500°C. Note that above the midsection of the highlighted region, ΔH°_{solid} and ΔS°_{solid} values are viable at a higher temperature range, and conversely below. Because the ΔH°_{solid} and ΔS°_{solid} of a nitride pair

is dependent on temperature, a viable nitride does not have to be constrained within the dark red region. Therefore, at low temperatures (e.g., 200°C) it can meet requirements by having ΔH_{solid}° and ΔS_{solid}° values below the midsection, whereas at high temperatures (e.g., 500°C) it would meet requirements by having values above the midsection.

If additivity rules for the entropy of solids were considered then the entropy of the solid products should be lower than the solid reactants (Glasser, 2022a) since the number of atoms in the solid phase for R2a decreases by one nitrogen atom, therefore a negative change in ΔS_{solid}° is likely and metal nitrides with ΔH_{solid}° values located in the widest temperature span can be found. Entropy contributions from a nitrogen atom have been estimated to be 23.37 J K⁻¹ mol⁻¹ (Glasser, 2022a); using this value for ΔS_{solid}° (-23.37 J K⁻¹ mol⁻¹), according to Figure 5.2 the required ΔH_{solid}° would be between 25 to 50 kJ mol⁻¹. Considering the ΔH_{gas}° of reaction R2a (see Figure 5.1 (A)), the heat release from the reaction ($\Delta_r H^{\circ}(R2a)$) with a suitable metal nitride would be mildly exothermic at low temperatures or close to zero at high temperatures. As discussed in Chapter 3, large increases in temperatures should be avoided during the ammonia synthesis step to maintain high equilibrium ammonia yields, though this should be balanced with the materials kinetics which are favoured by high temperatures, therefore a slightly exothermic reaction may be preferred to control the reaction temperature and metal nitride with viable ΔH_{solid}° values would be capable of this.

5.5.2 Imide/Hydride Carriers

In a similar fashion, the benchmarks in section 5.4 were used to calculated the required ΔH_{solid}° and ΔS_{solid}° for metal imide/hydride pairs. The resulting values at temperatures between 200 to 500°C are shown in Figure 5.3, and unlike the metal nitrides there is no overlap at different temperatures over the range of ΔH_{solid}° and ΔS_{solid}° observed on Figure 5.3. Metal imide/hydride pairs situated within the coloured regions can achieve viable equilibrium gas conversions *via* reaction R3. Values situated above the band representing the benchmark for R3a, and those situated below the band for R3b do not meet the benchmarks for one of the two reaction's requirements.



Figure 5.3 ΔH_{solid}° and ΔS_{solid}° for reaction R3a to achieve equilibrium $y_{NH_3} = 0.16$ via R3a and $X_{N_2} = 10\%$ via R3b at a total operating pressure of 150 bar. The plotted lines show the requirements versus temperature, and suitable materials are situated between the two regions plotted for reaction R3a and R3b.

Metal imide/hydride pairs with ΔH_{solid}° and ΔS_{solid}° values of roughly 0 to 60 kJ mol⁻¹ and -40 to 50 J mol⁻¹ K⁻¹, respectively, achieve the benchmarks at all temperatures between 200 to 500 °C (marked as the 'most viable region'). Compared to requirements for metal nitrides, the range of viable solid properties appears to be wider with metal imides/hydrides. This is mainly due to the differences in gas stoichiometries between the two reaction schemes (see Figure 5.1), which play a role in the requirements for the solid thermodynamic properties. These differences cause a horizontal translation in the

requirements for the ΔS_{solid}° in Figure 5.3, and more positive ΔS_{solid}° are necessary with metal imide/hydride carriers following reaction R3.

If additivity rules from (Glasser, 2022a; Glasser & Jenkins, 2009) were considered for the entropy of imides/hydrides, the entropy contribution from nitrogen is larger than hydrogen (23.37 vs 10.64 J mol⁻¹ K⁻¹, respectively) therefore the ΔS_{solid}° is expected to be equal to -12.73 J mol⁻¹ K⁻¹ for reaction R3a compared to -23.37 J mol⁻¹ K⁻¹ for reaction R2a. However, entropy contributions from an element in a solid are largely dependent on its volume (Glasser, 2022b; Glasser & Jenkins, 2009; Jenkins & Glasser, 2003), and since the ionic radii of hydride ions (H⁻, 134 pm) (Hayashi et al., 2014) is far greater than hydrogen atoms (H⁺) and similar to nitrogen ions (N³⁻, 146 pm) (Shannon, 1976), ΔS_{solid}° could be positive or close to zero with metal imide/hydride nitrogen carriers. Therefore, larger values for ΔH_{solid}° are required to achieve viable conversions *via* reaction R3. When the ΔH_{gas}° is considered (-50 kJ mol⁻¹, see Figure 5.1 (A)), the ammonia synthesis step (R3a) with viable metal imide/hydrides carriers should be exothermic though to a lesser degree than with R2a.

5.6 Gas Phase Equilibrium Property Requirements

5.6.1 Equilibrium Nitrogen Pressures of Metal Nitride Carriers

The gas phase composition at equilibrium of reaction R2a can be described using the equilibrium P_{N_2} as outlined in section 5.3.2. The range of operating temperatures and equilibrium P_{N_2} values achieving a viable y_{NH_3} is shown by the enclosed region in Figure 5.4; values outside this region may not achieve economic parity to the Haber-Bosch process. This region is defined by benchmarks described in section 5.4. The first limitation is due to the chosen minimum operating temperature of 200°C, below which materials are unlikely to be sufficiently reactive – of course, in practice this lower temperature limit would vary depending on the nitrogen carrier used. The second limit is defined by the minimum value of y_{NH_3} required (equal to 16% at 150 bar) to avoid excessive ammonia separation cost (Lee Pereira et al., 2022). At lower operating pressures, the minimum y_{NH_3} needed to achieve economic parity increases (see appendix B.6). As a result, the enclosure shrinks and the range of feasible P_{N_2} and operating temperatures is smaller.

Similar with reaction R1, the equilibrium y_{NH_3} of reaction R2a is favoured by high pressures, though to a lesser extent due to the lower ratio of gas phase reactants to products. Unlike reaction R1, the ammonia synthesis step (R2a) can be either exothermic or endothermic. If R2a is endothermic, the equilibrium y_{NH_3} increases with temperature, which can be desirable. However, R2b would be more exothermic than R1 as a consequence; and the nitrogenation step may require cooling like in the Haber-Bosch process. If both R2a and R2b are mildly exothermic, the temperature controls of the reactors would be more straightforward. This may be preferable even though the equilibrium y_{NH_3} decreases with temperature as is in R1, albeit less strongly so.



Figure 5.4. Equilibrium ammonia mole fraction as a function of equilibrium P_{N_2} and temperature of reaction R2a at 150 bar. Nitrides with equilibrium P_{N_2} values situated within the enclosure are potentially viable nitrogen carriers. Nitrides with equilibrium P_{N_2} values outside of the enclosure face kinetic limitations or process limitations. Ideally the equilibrium P_{N_2} of the nitride would be equal to the maximum $y_{N_{H_3}}$ curve.

A high ammonia mole fraction is desirable and the maximum equilibrium y_{NH_3} via R2a is shown on Figure 5.4. Although P_{N_2} values above the line of maximum y_{NH_3} still achieve viable ammonia mole fractions, it requires higher operating pressures to regenerate the nitride, and would result in higher nitrogen losses between reaction steps (R2a and R2b) and increased separation requirements for recycled hydrogen. Therefore, the most suitable nitrides should have equilibrium P_{N_2} values close to or below the line of maximum y_{NH_3} according to Figure 5.4.

Due to the assumption that the gas phase reaches equilibrium (shown by Eq. (5.21) in section 5.3.2), the maximum y_{NH_3} of R2a is equal to the equilibrium y_{NH_3} of reaction R1. However, under a non-equilibrium state, it may be possible to exceed this maximum and reduce separation costs by forming ammonia which is kinetically stable (See Figure 5.5). The equilibrium y_{NH_3} from R2a would have to be higher than R1; in terms of kinetics, a high reaction rate of R2a, slow ammonia decomposition *via* R1, and slow nitride decomposition *via* R2b are required simultaneously. In practice, a slow nitride decomposition also implies a slow nitrogenation of the nitride, which may need to be

compensated for by operating at higher temperatures during the nitrogenation step. In addition, it is unlikely that a nitrogen carrier would be active towards R2a and not catalyse ammonia decomposition *via* R1 at the same time (Rasaki et al., 2018).



Figure 5.5 Equilibrium ammonia mole fraction as a function of the equilibrium P_{N_2} and temperature of reaction R2a at 150 bar. Decomposition of the nitrogen carrier and decomposition of ammonia were ignored in this calculation to obtain equilibrium y_{NH_3} values for kinetically stable ammonia produced via R2a. To increase the equilibrium y_{NH_3} the material should have higher equilibrium P_{N_2} values and the reaction should be operated at lower temperatures.

Values shown in Figure 5.4 are based on a model which accounts for the equilibrium of reactions R2a, R2b, and R1, whereas those in Figure 5.5 account for reaction R2a alone. Overlaying these values shows the region where the equilibrium ammonia yield of reaction R2a can be greater than that of the mixed reaction model (see Figure 5.6). In this region, the mixed reaction model represents a lower bound and the single reaction model shows an upper bound for the equilibrium ammonia concentration. However, below this region the equilibrium ammonia concentration can be no greater than via reaction R2a alone and is lower than the Haber-Bosch reaction (R1). In reality, the ammonia yield would be situated between values shown on Figure 5.4 and Figure 5.5 for a given metal nitride pair.



Figure 5.6 Highlighted region shows the area where the equilibrium ammonia mole fraction of reaction R2a (See Figure 5.5) is greater than when a mixed reaction model is assumed (See Figure 5.4).

5.6.2 Equilibrium Nitrogen Conversion of Metal Imide/Hydride Carriers

With metal imide/hydride nitrogen carriers, the gas phase composition at equilibrium of reaction R3a can be described using the equilibrium X_{N_2} as outlined in section 5.3.2. Equilibrium X_{N_2} values situated outside the enclosed region do not achieve satisfactory equilibrium y_{NH_3} values or have insufficient temperatures (<200°C) to achieve feasible rates of ammonia synthesis using present catalysts. With imides following reaction R3, the equilibrium yield of the ammonia synthesis step is favoured by high pressures, and its dependence on temperature can change with ΔH_{solid}° . The dependence on pressure is similar to reaction R1 and greater than R2a when the stoichiometry of gas species is considered.



Figure 5.7 Equilibrium ammonia mole fraction as a function of the equilibrium nitrogen conversion of reaction R3b and temperature of reaction R3a at 150 bar. Values situated within the enclosure achieve equilibrium y_{NH_3} values greater than 0.16 at temperatures greater than 200°C. Metal imide/hydride nitrogen carriers with equilibrium X_{N_2} values equal to 75% attain the maximum equilibrium y_{NH_3} at a given temperature.

Under the assumptions provided in section 5.3.2, the maximum equilibrium y_{NH_3} is achieved at an equilibrium X_{N_2} equal to 75% *via* reaction R3b, and this maximum is equal to the equilibrium y_{NH_3} *via* reaction R1. However, when the equilibrium y_{NH_3} *via* reaction R3a is considered without reactions R1 and R3b (shown in Figure 5.8), the equilibrium X_{N_2} required to achieve high equilibrium y_{NH_3} values are significantly lower compared to Figure 5.7. The maximum equilibrium ammonia concentration shown on Figure 5.7 is
mostly a result of the Haber-Bosch reaction (R1), and would only be accurate if the reaction rate of R1 is fast under chemical looping conditions for metal imides/hydrides, which is not the case according to literature (Feng et al., 2021; Gao et al., 2018). Since R1 is not easily catalysed by imide/hydride materials under chemical looping conditions, the equilibrium ammonia yield is likelier to follow the model shown in Figure 5.8.



Figure 5.8 Equilibrium ammonia mole fraction as a function of the equilibrium X_{N_2} of reaction R3b and temperature of reaction R3a at 150 bar. Only the equilibrium constant of reaction R3a is considered here.

Overlaying Figure 5.7 and Figure 5.8 shows a highlighted region wherein the equilibrium y_{NH_3} via the mixed reaction model (Figure 5.7) is lower than via reaction R3a alone (see Figure 5.9). In the highlighted region, ammonia formed via reaction R3a can decompose via reaction R1 or be diluted with nitrogen formed from the reverse of reaction R3b. Whether the gas phase equilibrium would follow Figure 5.7 or Figure 5.8 in this region depends on the kinetics of reactions R1 and R3b and also on whether ammonia is formed with y_{NH_3} values prone to the reverse of reaction R1. However, in the shaded region above it would mostly be constrained by reaction R3a and the reverse of R3b, and equilibrium ammonia yields in this region would not be greater than the Haber-Bosch reaction (R1).



Figure 5.9 Highlighted enclosure shows the region with equilibrium y_{NH_3} values via reaction R3a greater than the equilibrium y_{NH_3} when reactions R3a, R3b, and R1 are considered.

Based on Figure 5.8, equilibrium ammonia yields close to reaction R1 require equilibrium X_{N_2} values of 6 to 9% at temperatures between 300 to 473°C. Lower X_{N_2} values can yield greater ammonia yields than reaction R1, but like the metal nitrides (discussed in section 5.6.1), there are similar pre-requisites for the kinetics of reaction R3b and R1. These X_{N_2} values are lower than in the simulations shown in Chapters 3 and 4 (12 to 50%) and would increase costs associated with the nitrogenating the carrier material. It is possible for the process to be more sensitive to the nitrogen conversion if it were at lower values, however, there is a potential trade-off with higher equilibrium ammonia yields which has not been fully established yet.

5.7 Summary

The gas-solid thermodynamics of CL-NH₃ vary according to the selected nitrogen carrier and its thermodynamic properties. With chemical looping reactions, properties of a nitrogen carrier can favour a half-reaction (e.g., R2a) at the expense of the other (e.g., R2b). A range of suitable values for the ΔH_{solid}° and ΔS_{solid}° of metal nitrides and imides/hydrides was thus identified with respect to benchmarks for reactions R2 and R3. In addition, an alternate model was created to evaluate the gas-solid thermodynamics of nitrogen carriers based on the equilibrium P_{N_2} or X_{N_2} of metal nitrides and imides/hydrides, respectively. The equilibrium y_{NH_3} of the hydrogenation reaction (R2a or R3a) was determined from this model, and side reactions such as the nitrogenation reaction (R2b or R3b) and reaction R1 were accounted for. The latter model suggests that the equilibrium y_{NH_3} of CL-NH₃ can be no greater than that of reaction R1, provided that all reactions are allowed to reach equilibrium. However, if suitable kinetics are present a kinetically stable form of ammonia with an equilibrium y_{NH_3} greater than that of reaction R1 could be obtained. Values identified in these models are used in Chapter 6 to screen for viable nitrogen carriers.

Chapter 6

Thermodynamic Screening of Nitrogen Carriers for Chemical Looping Ammonia Synthesis

6.1 Introduction

Nitrogen carriers studied in literature have reported high rates of ammonia synthesis at ambient pressures and low temperatures (Feng et al., 2021; Gao et al., 2018; Goto et al., 2021), however, these studies do not examine the maximum ammonia yield achievable, a key factor for the viability of a CL-NH₃ process (See Chapter 4). Other studies in literature have performed systematic in silico screening of potential nitrides and identified nitrides that would yield a negative Gibbs energy of reaction for a pre-defined reaction set. Nevertheless, a negative Gibbs energy of reaction does not always guarantee sufficiently high yield of ammonia to be achieved at equilibrium, and the pre-defined reaction set does not allow the possibility of side reactions such as decomposition of nitrogen carrier forming undesired solid phases. In this chapter, Nitrogen carriers from materials databases were screened with high-throughput computation methods to determine the gas and solid products at equilibrium. From these calculations, the equilibrium partial pressure of nitrogen or nitrogen conversion for metal nitrides and nitride and imide/hydrides were determined, respectively, and were compared to thermodynamic models from Chapter 5 to identify suitable nitrogen carriers for CL-NH₃ on a thermodynamic basis.

The objectives of Chapter 6 are as follows:

- Identify stable solid species and reactions *via* equilibrium calculations.
- Benchmark nitrogen carriers according to thermodynamic models from Chapter 5.
- Compare performances of screened materials with literature.

6.2 Estimation of Solid Thermodynamic Properties

Experimental data on thermodynamic properties of nitrides, hydrides, and imides under relevant conditions for CL-NH₃ are partially available in the case of nitrides and alkali or alkali earth metal hydrides/imide, and since these properties cannot be readily computed they must be estimated. Where available, the Gibbs free energy of formation of solid materials are taken from the FactSage database (see appendix B.3 for list of materials)(Bale et al., 2016), otherwise, one of two methods described in the following sections are employed to estimate the Gibbs free energies of solids, which are referred to as method 1 and 2, respectively.

6.2.1 Empirical Equation for Estimating Solid Properties (Method 1)

Standard formation enthalpies of solid compounds are available on the Materials Project database, and standard entropies of solids were estimated using volume-based thermodynamic methods, shown by Eq. (6.1),

$$S_i^{\circ}(298K) (J \ mol^{-1} \ K^{-1}) = 1360 \ V_{m,i}(nm^3) + 15$$
 (6.1)

$$V_{m,i} = \frac{MMR_i}{\rho_{s,i}N_A} \tag{6.2}$$

where V_m is the formula unit volume of the compound (Eq. (6.2)), ρ_s is the solid density obtained from the MP database, *MMR* is the relative molecular mass, and N_A is Avogadro's number (Jenkins & Glasser, 2003). Formation enthalpies and entropies obtained in this manner are applicable at ambient conditions and require additional assumptions to obtain values under relevant conditions. Assuming Dulong-Petit's rule for the heat capacity of solids ($c_{p_s} = 3R \ atom^{-1}$), the formation enthalpy and entropy of a compound were estimated at higher temperatures using Eqs. (5.10) and (5.11), respectively.

$$\Delta_f H_i^{\circ}(T) = \Delta_f H_i^{\circ}(298K) + \int_{298K}^T c_{p,i}(T) dT$$
(5.10)

$$S_{i}^{\circ}(T) = S_{i}^{\circ}(298K) + \int_{298K}^{T} \frac{c_{p,i}(T)}{T} dT$$
(5.11)

6.2.2 Physical Descriptor for Estimating Solid Properties (Method 2)

Alternatively, the correlation proposed by (Bartel *et al.*, 2018) can be used to determine the Gibbs free energy of solids:

$$G^{\delta}(T) = (-2.48 \times 10^{-4} \times \ln(V) - 8.94 \times 10^{-5} m/V) \times T + 0.181 \times \ln(T) - 0.882$$
(6.3)

$$G^{\circ}(T) = \Delta_{f} H^{\circ}(298K) + G^{\delta}(T)$$
(6.4)

The free energy of the solid is estimated by calculating the free energy descriptor $(G^{\delta}(T), \text{ eV atom}^{-1})$ in addition to its standard enthalpy of formation $(\Delta_f H(298K))$ as a function of the atomic volumes $(V, \text{Å}^3 \text{ atom}^{-1})$ and reduced atomic masses (m, amu) of the compound. V and $\Delta_f H(298K)$ are all obtained from the MP database and m is calculated according to Bartel *et al.* (2018) using Eq. (6.5) (here N is the total number of elements in the compound, i and j refer to elements within the compound). Entropies of solids are obtained using Eq. (5.9), and Dulong-Petit's rule ($c_{p_s} = 3R \text{ atom}^{-1}$) is used to estimate the formation enthalpy of the solid at higher temperatures using Eq. (5.10).

$$m = \frac{1}{(N-1)\sum_{i=1}^{N} \alpha_i} \sum_{i \neq j}^{N} (\alpha_i + \alpha_j) \frac{M_{r,i} M_{r,j}}{M_{r,i} + M_{r,j}}$$
(6.5)

$$\Delta_r G^{\circ}(T) = \Delta_r H^{\circ}(T) - T \Delta_r S^{\circ}(T)$$
(5.9)

6.3 Determination of Equilibrium via Gibbs Free Energy Minimisation

Gas-solid equilibria of nitrogen carriers screened from the MP database are determined using a non-stoichiometric approach (Binous & Bellagi, 2022). With this method, equilibrium quantities of specified compounds (n_i , mol) are determined by minimising the total free energy of the system (G_{total} , J mol⁻¹) at a given *T* and *P* as shown by Eq. (6.6). A constrained minimisation algorithm was employed (i.e. interior-point algorithm in the 'fmincon' function on MATLAB) to solve the optimisation problem (The MathWorks Inc., 2022), subject to molar conservation (Eq. (6.7)) and non-negative quantities (Eq. (6.8)) as constraints.

$$G_{total} = \sum_{i}^{N_s} n_i \mu_i^{\circ} + \sum_{i}^{N_g} n_i (\mu_i^{\circ} + RT \ln \phi_i P_i)$$
(6.6)

$$\sum_{i}^{N_s + N_g} \alpha_{ij} n_i = b_j \tag{6.7}$$

$$n_i \ge 0 \tag{6.8}$$

Here, α_{ij} is the stoichiometric coefficient of element *j* in compound *i*, and b_j (mol) represents the total amount of element *j* present in the system. Solid compounds are treated as pure phases (i.e., activities equal to 1), hence only their standard chemical potentials (μ_i° , J mol⁻¹ where $\mu_i^{\circ} = G_i^{\circ} \sum_j \alpha_{ij}$) are considered in Eq. (6.6). Gases are treated as mixtures and their non-idealities are accounted for by calculating their fugacity coefficients (ϕ_i) using the Soave-Redlich-Kwong (SRK) equation of state, described in *Perry's Handbook of Chemical Engineering* (Robert & Green, 2008). The total numbers of solid and gaseous compounds are denoted by N_s and N_g , respectively.

6.3.1 Equilibrium Nitrogen Partial Pressure (Metal Nitrides)

The equilibrium of reaction R2b was considered to determine the reaction stoichiometry (ν) and equilibrium P_{N_2} of the metal nitrides. The minimisation is performed over a range of temperatures (150 to 500°C) and pressures (10^{-4.5} to 100 bar). Phase changes at each temperature and pressure step were used to identify the corresponding reaction as follows. Based on the stoichiometric coefficients (α) of the identified compounds (i) before and after the phase change, the reaction stoichiometry (ν) can be determined by solving Eq. (6.9). The identified reaction stoichiometry is then used to calculate the free energy change of the reaction ($\Delta_r G^\circ$) (Eq. (6.10)) and equilibrium P_{N_2} (Eq. (6.11)). Nitrogen capacities (N_{cap} , $g_{N_2} g_{solid}^{-1}$) of materials are calculated using Eq. (6.12) where $M_{r,i}$ is the molar mass of compound i.

$$\alpha_{ji}\nu_i = 0 \tag{6.9}$$

$$\Delta_r G^{\circ} = \sum_i^{N_s + N_g} \nu_i \, \mu_i^{\circ} \tag{6.10}$$

$$P_{N_2} = e^{\left(\frac{-2\Delta_r G^\circ}{RT}\right)} \tag{6.11}$$

$$N_{cap} = \nu_{N_2} M_{r,N_2} \div \sum_{i}^{N_{s,reactants}} \nu_i M_{r,i}$$
(6.12)

6.3.2 Equilibrium Nitrogen Conversion (Metal Imides/Hydrides)

Metal imide/hydride pairs are assumed to follow reaction R3. The equilibrium nitrogen gas conversion (X_{N_2}) of reaction R3b was determined by calculating the equilibrium constant of the reaction using Eq. (5.7), from its Gibbs free energy change of reaction (Eq. (5.9)). Nitrogen capacities of the metal imide/hydride pairs were calculated using Eq. (6.12). Based on estimated X_{N_2} values for metal imide/hydride pairings in this work (see appendix B.6), metal imide/hydrides screened in this work have X_{N_2} values close to unity and would not meet the minimum equilibrium y_{NH_3} shown in appendix B.6.

6.4 Screening of Nitrogen Carriers from Materials Databases

Binary and ternary metal nitrides $(M_x N_y \text{ and } M'_x M''_u N_y, \text{ respectively})$ were identified through an API query from the Materials Project (MP) database (Jain *et al.*, 2013), which contains 154718 materials (as of April 2023). Non-metals, noble gases, and radioactive elements (i.e., Tc, Pm, Po, At, and period 7 elements) were excluded from the search, and 2515 nitrides with unique formulae were identified as potential nitrogen carriers. In addition to these nitrides, their respective metal and bimetallic alloys were queried to account for the various possible side reactions which could occur in the system; but hydride, amide and imide solid phases are not included to keep the scope of this work manageable. The impact of the latter compounds is discussed further in appendix B.1. The list of nitrogen carriers and their related compounds are shown in the supplementary data in Lee Pereira *et al.* (2023).

Ternary nitrides, forming the majority of candidates, are composed of alkali or alkaline earth metals mixed with transitions metals (ca. 873), as can be seen from Figure 6.1. The properties of most of these nitrides have been computed from (Sun et al., 2019), and their contributions to the database include both stable and metastable nitrides. It is worth noting that more recently, (Fan *et al.*, 2022) have generated a substantial number of ternary nitrides (> 500 million) amongst which 4698 were found to at least exhibit metastability but they are yet to be included in the Materials Project database. Thus, the scope of materials observed in this work does not represent the full range of possible nitrides, and there are continuous efforts to expand the number of potential nitride compounds. However, the methodology and conclusions described here can be readily applied to newly identified nitrides for CL-NH₃ once available.



Figure 6.1 Distribution of elements present in screened metal nitride carriers (excl. polymorphs) from the MP database. Elements situated on the terraced diagonal are binary nitrides whereas those below are ternary nitrides.

6.5 Identified Reactions for Metal Nitride Carriers

The corresponding decomposition reactions of the screened metal nitrides do not all follow R2b, where the specified nitride is the source of nitrogen gas. Several nitrides are unstable under the range of conditions specified in section 6.3.1 and decompose into secondary nitride phases without releasing nitrogen gas, *via* R11 for binary and R12 or R13 for ternary nitrides. Nitrides formed from R11, R12, or R13 can subsequently release nitrogen gas *via* R2b. These secondary nitrides are considered in separate calculations, and the parent nitride is deemed unviable and is excluded from further examination.

$$M'N_y \to M'_u N_v + M'_{(x-u)} N_{(y-v)}$$
 (R11)

$$M'_{x}M''_{u}N_{y} \to M'_{x}N_{y} + uM'' \tag{R12}$$

$$M'_{x}M''_{u}N_{y} \to M'_{x}N_{y} + M''_{u}N_{v} \tag{R13}$$

However, for some ternary nitrides, the products from R12 or R13 can subsequently react and release nitrogen *via* R14 or R15, and these are not excluded from the viable set. The complete list of identified reactions and assigned category of each nitride is shown in the supplementary data in Lee Pereira *et al.* (2023).

$$M'_x N_y + u M'' \to M'_x M''_u + 0.5 y N_2$$
 (R14)

$$M'_{x}N_{y} + M''_{u}N_{v} \to M'_{x}M''_{u} + 0.5(y+v)N_{2}$$
 (R15)

6.6 Solid Thermodynamic Properties of Screened Nitrogen Carriers

6.6.1 Imide/Hydride Carriers

Estimated ΔH_{solid}° and ΔS_{solid}° of metal imide/hydride pairs compared to benchmarks from Figure 5.3 are shown in Figure 6.2. Material pairings situated within the highlighted band achieve the criteria imposed in section 5.4, and those situated above or below have insufficient equilibrium ammonia yields ($y_{NH_3} < 0.16$) or low equilibrium nitrogen conversions ($X_{N_2} < 10\%$), respectively. Only the Li₂NH/LiH pair at 250°C with values estimated using estimation method 2 appear to meet the criteria. Note however, that there are significant uncertainties with estimation methods 1 and 2 (see appendix B.5) and that other imide/hydride pairings such as BaNH/BaH₂, SrNH/SrH₂ could be viable. Overall, theoretical estimates suggests that alkaline/alkaline earth metal imide/hydride nitrogen carriers are unlikely to be suitable for CL-NH₃ or yield better equilibrium ammonia yields than the Haber-Bosch process.

A comparison of the estimation methods shows that the ΔS_{solid}° of metal imide/hydride pairs using method 2 is ~50 J mol⁻¹ K⁻¹ greater than method 1, and more variation with each pairing is present with method 2. This difference contributes to a negative free energy change of reaction R3a resulting in greater equilibrium ammonia yields *via* method 2 than method 1. Additivity rules (Glasser, 2022b) suggest ΔS_{solid}° values around -13 or near 0 J mol⁻¹ K⁻¹ at 298K (see discussion in section 5.5.2), and this appears to support method 2. Regardless, it is not clear where this difference arises from, and either estimation method may not be applicable to solid imides or hydrides since Eqs. (6.1) and (6.3) are based on empirical or statistical correlations of data obtained from materials databases who possess a limited number of metal hydride or imide compounds. To affirm these results, the thermodynamic properties of these materials under relevant conditions would need to be determined experimentally.



Figure 6.2 The minimum ΔH_{solid}° and ΔS_{solid}° to achieve equilibrium $y_{NH_3} \ge 0.16$ and $X_{N_2} \ge 10\%$ via R3 is highlighted by the parallel bands. Metal imide/hydride pairings situated within the highlighted region have properties enabling them to have comparable or better performance than the Haber-Bosch process. Three temperatures are considered for the benchmark, at 150 bar.

6.6.2 Nitride Carriers

The ΔH_{solid}° and ΔS_{solid}° of the identified metal nitride pairs were compared to benchmarks from Figure 5.2, as shown in Figure 6.3. A total of 89 and 111 metal nitrides were found to be viable within temperatures of 200 to 500°C and 150 bar, using methods 1 and 2 respectively. These materials meet the benchmarks described in section 5.4, and can be regenerated using nitrogen partial pressures less than or equal to 150 bar. In addition, 26 of these viable nitrides, calculated using either estimation method, could achieve greater equilibrium y_{NH_3} values with reaction R2a than R1 at 400°C according to Figure 6.3. Viable metal nitride candidates and their comparison with literature are discussed further in section 6.8.

Generally, theoretical estimates for metal nitrides show that they have low equilibrium P_{N_2} values and therefore more materials meet the benchmark imposed on reaction R2b than those for reaction R2a; this is the case with either solid property estimation method. Most metal nitrides have ΔH_{solid}° and ΔS_{solid}° values which places these pairings either above or within the viable region on Figure 6.3. Method 2 does produce more positive values for ΔS_{solid}° than method 1, thereby yielding more negative values of $\Delta_r G^{\circ}$ and a greater number of viable candidates. Compared to additivity rules which suggests a ΔS_{solid}° of -23.37 J mol⁻¹ K⁻¹ at 298K (Glasser, 2022b), methods 1 and 2 have average ΔS_{solid}° values between -22 to -33 and -12 to -25 J mol⁻¹ K⁻¹ at 200 up to 500°C, respectively, for the screened metal nitrides. These average values for the ΔS_{solid}° of metal nitrides agree with Glasser (2022b), however, it does not match the discrepancy found with metal imides/hydrides which would suggests that there is a group contribution effect from the imide or hydride ion which cannot be accounted for with these solid property estimation methods.



Figure 6.3 The minimum ΔH_{solid}° and ΔS_{solid}° to achieve an equilibrium $y_{NH_3} \ge 0.16$ and $P_{N_2} \le 150$ bar via R2 is highlighted by the parallel bands. Metal Nitride pairings situated within the highlighted region have properties enabling them to have comparable or better performance than the Haber-Bosch process. The red dashed line shows the requirements to achieve ammonia concentrations greater than reaction R1 under the same reaction pressures and temperatures; pairings siturated below this line satisfy this condition. Three temperatures are considered for the benchmark, at 150 bar.

6.7 Equilibrium Nitrogen Partial Pressure of Metal Nitride Carriers

Amongst the 2515 nitrides screened in this work, 111 were found to have viable equilibrium P_{N_2} values identified in Figure 5.4. Ideally, the equilibrium P_{N_2} values of these nitrides would match the line of maximum y_{NH_3} over a wider range of temperatures. However, this usually happens at a single temperature for a given material (See Figure 6.4). Therefore, each nitride has an optimal temperature located near the intersection between the nitride's equilibrium P_{N_2} curve and line of maximum y_{NH_3} . When selecting materials, the nitrogen capacity and reaction rate around the optimal temperature should be considered together. Figure 6.4 shows selected candidates (No. 1 to 6) from the supplementary data, that can achieve high nitrogen capacities (> 0.1 $g_{N_2} g_{solid}^{-1}$, see appendix B.2).



Figure 6.4. Comparison of nitrides with the highest capacities (No. 1 to 6) or equilibrium y_{NH_3} values (No. 7) to Figure 5.4.

Fe₂NiN₂ (No.7, Figure 4) has an equilibrium P_{N_2} curve which closely resembles the line of maximum y_{NH_3} , and would exhibit a wider range of viable operating temperatures than candidates shown on Figure 6.4. The variation with temperature of $\Delta_r G^\circ$ for R2b, and

by proxy the equilibrium P_{N_2} , is dependent on the heat capacity change of the reaction $(\Delta_r c_p)$ (Eq. (6.13)) and standard enthalpy $(\Delta_r H^{\circ})$ and entropy $(\Delta_r S^{\circ})$ changes of reaction at 298K, as shown by Eq. (6.14).

$$\Delta_r c_p(T) = \sum_i v_i c_{p,i}(T) \tag{6.13}$$

$$\Delta_r G^{\circ}(T) = \Delta_r H^{\circ}(298K) - T\Delta_r S^{\circ}(298K) + \int_{298K}^{T} \Delta_r c_p(T) dT - T \int_{298K}^{T} \frac{\Delta_r c_p(T)}{T} dT$$
(6.14)

Assuming Dulong-Petit's law and ideal gases, the $\Delta_r c_p$ of R2b is approximately 10 J mol⁻¹ K⁻¹ at room temperature or higher. With this assumption together with Eq.(6.14), the required $\Delta_r H^{\circ}(298 K)$ and $\Delta_r S^{\circ}(298 K)$ to achieve the maximum equilibrium y_{NH_3} at each temperature was determined (See Figure 6.5). It appears that if $\Delta_r H^{\circ}(298 \text{ K})$ of R2b is around -15 kJ mol⁻¹ and $\Delta_r S^{\circ}(298 \text{ K})$ around -35 J mol⁻¹ K⁻¹, then equilibrium y_{NH_3} values close to the theoretical maximum, as shown in Figure 5.4, can be achieved over the full range of temperatures investigated. Interestingly, the $\Delta_r H^{\circ}(298 K)$ and $\Delta_r S^{\circ}(298 \text{ K})$ of the identified nitrogenation reaction for Fe₂NiN₂ (See Figure 6.4) estimated using Eq. (6.4) are -26 kJ mol⁻¹ and -67 J mol⁻¹ K⁻¹ respectively, which suggests that the implied $\Delta_r c_p$ from Eq. (6.4) is far from that predicted by Dulong-Petit's law. This is perhaps not surprising given the different terms present between Eq. (6.4) and Eq. (6.14) (for example, Eq. (6.14) has a $T \ln T$ term associated with $\Delta_r c_p$ whereas Eq. (6.4) has a $\ln T$ term). It is clear from inconsistencies between different semi-empirical approaches such as this that potential materials identified from large scale in silico screening are still not sufficiently accurate and experimental validation is still needed at present to confirm their thermodynamic properties.



Figure 6.5. Required standard enthalpy and entropy changes for reaction R2b at 298K to achieve the maximum equilibrium y_{NH_3} via R2a at a given reaction temperature, assuming a constant heat capacity change of reaction of -10 J mol⁻¹ K⁻¹.

6.8 Comparison of Screened Metal Nitrides with Literature

The most common type of viable nitrides are ternary nitrides composed of alkali or alkaline earth metals mixed with transition, post-transition metals or metalloids (ca. 47) (See Figure 6.6). Ternary nitrides such as MgSnN₂, Zn₃MoN₄ (Zakutayev et al., 2022), Zn₂VN₃ (Zhuk et al., 2021), Fe₃RhN (Houben et al., 2005), Co₃InN (Cao et al., 2009; Goto et al., 2021), LiZnN (Juza & Hund, 1946), and Na₃BN₂ (Evers et al., 1990) have been synthesised experimentally and the ammonia synthesis rate associated with the hydrogenation (R2a) of Co₃InN has been determined. Candidates deemed unviable from this screening have also been investigated in literature for their ammonia synthesis rates, and include ternary nitrides (e.g., TiFe2Nx (Machida et al., 1998), Co3Mo3N (Kojima & Aika, 2001), Ni₂Mo₃N (Hargreaves & Mckay, 2009), Ni₃InN, Ni₃ZnN (Goto et al., 2021), Ni₃CuN (Daisley *et al.*, 2022)), binary alkali and alkaline earth metal nitrides (e.g., Ca₃N₂, Sr₂N (Michalsky et al., 2015), Li₃N (Goshome et al., 2015; Ravi & Makepeace, 2022; Shinzato et al., 2022; Yamaguchi et al., 2020)), and binary transition metal nitrides (e.g., Ni₃N, Re₃N, Cu₃N, Ta₃N₅ (Alexander *et al.*, 2012; Daisley & Hargreaves, 2023), Mn_xN (Aframehr *et al.*, 2020; Feng *et al.*, 2021; Laassiri *et al.*, 2018; Michalsky *et al.*, 2015; Mohammadi Aframehr & Pfromm, 2021)). Among these, ammonia synthesis rates of Ni₃ZnN, Ni₃InN, Co₃Mo₃N, and Ni₂Mo₃N have been determined (Goto et al., 2021; Hargreaves & Mckay, 2009). X-ray diffraction analysis of solid products from these nitrides post-hydrogenation was used to identify reactions listed in Table 6.1. Note that the reaction products reported differ from those identified in this work and this is likely due to errors with the screening methodology; this point is discussed later in this section.



Figure 6.6. Ternary and binary nitride map of viable nitrides. The elemental compositions of the materials and the number of materials with those compositions are shown. Viable candidates have P_{N_2} values situated within the enclosure shown in Figure 5.4.

Table 6.1 Comparison of identified nitrogen release reaction in literature and from this work.

Nitride (Ref)	Reaction in literature	Reaction in this work		
Ni₃ZnN (Goto et al., 2021)	$Ni_3ZnN + 1.5H_2 \rightarrow Ni_3Zn + NH_3$	$Ni_3ZnN + 1.5H_2 \rightarrow 2Ni + NiZn + NH_3$		
Co3InN (Goto et al., 2021)	$Co_3InN + 1.5H_2 \rightarrow 2.5Co + 0.5CoIn_2 + NH_3$	$Co_3InN+1.5H_2 \rightarrow 2.5Co+0.5CoIn_2+NH_3$		
Ni₃InN (Goto et al., 2021)	$Ni_3InN + 1.5H_2 \rightarrow Ni_3InN_{1-x} + xNH_3$	N/A		
Co ₃ Mo ₃ N (Hargreaves & Mckay, 2009)	$2Co_3Mo_3N+1.5H_2 \rightarrow Co_6Mo_6N+NH_3$	N/A		
Ni ₂ Mo ₃ N (Hargreaves & Mckay, 2009)	$Ni_2Mo_3N + 1.5H_2 \rightarrow Ni_2Mo_3N_{1-x} + xNH_3$	N/A		

Reported maximum ammonia synthesis rates of these nitrides at 400°C and 1 bar are listed in Table 6.2 and they have been used to estimate the corresponding equilibrium y_{NH_3} (see footnotes of Table 6.2). Amongst these nitrides, Ni₃ZnN achieves the highest equilibrium y_{NH_3} (at least 3.7 × 10⁻³) and is close to that of reaction R1 at 1 bar (4.3 × 10⁻³, Haber-Bosch process). At higher pressures (P = 150 bar), there is a significant difference

between the equilibrium y_{NH_3} obtained with Ni₃ZnN (0.043) *via* R2a compared to reaction R1 (0.31) since the equilibrium constant of reaction R2a is less dependent on pressure than reaction R1. Previous analysis on chemical looping NH₃ synthesis with metal hydrides have shown that y_{NH_3} of at least 0.16 is needed for the chemical looping process to be competitive (Lee Pereira *et al.*, 2022). This is still higher than the estimated y_{NH_3} based on existing experimental evidence, although, it should be noted that the estimated y_{NH_3} values from literature in Table 6.2 represent a lower limit only.

Furthermore, estimated equilibrium y_{NH_3} values for Ni₃ZnN and Co₃InN based on experimental evidence were compared to theoretical equilibrium y_{NH_3} values determined using the thermodynamic models described in section 5.6.1 at 1 bar and 150 bar in Table 6.2. The mixed reaction model (considering the equilibria of R2a, R2b and R1 simultaneously, as presented in Figure 5.4), provides a lower bound of the theoretical equilibrium y_{NH_3} . On the other hand, the single reaction model (considering the equilibrium of R2a Only, as presented in Figure 5.5) yields the upper bound of the theoretical equilibrium y_{NH_3} via CL-NH₃. According to literature, Ni₃ZnN and Co₃InN form minimal amounts of nitrogen gas, therefore, equilibrium y_{NH_3} values for these materials may be more comparable to the single reaction model (considering R2a Only)(Goto *et al.*, 2021). However, estimated equilibrium y_{NH_3} values of Ni₃ZnN and Co₃InN based on maximum rate observed are approximately two orders of magnitude lower, and not yet reached a viable level of $y_{NH_3} \ge 0.16$ at 400°C and 150 bar.

Although the equilibrium y_{NH_3} cannot be calculated for the hydrogenation of Ni₃InN, Co₃Mn₃N and Ni₂Mo₃N, due to missing solid products from the MP database, the estimated equilibrium y_{NH_3} based on maximum observed reactions rates are also too low. This could be attributed to either the kinetics of ammonia synthesis being rate limiting at the reported experimental conditions, or there being significant errors associated with the thermodynamic data obtained through DFT calculations. In any case, it is yet to be demonstrated experimentally that these metal nitrides possess suitable thermodynamic properties to produce NH₃ through the chemical looping route that can potentially outperform the Haber-Bosch process economically. This missing information is also important from a theoretical perspective as it serves to validate the theoretical calculations from the MP database and from (Bartel *et al.*, 2018).

Nitride (Ref)	Marine NII	y _{NH3} ^{b,c} (Literature)		y _{NH3} (This Work)			
	synthesis rate ^a			Mixed Reaction ^d		R2a Only	
		P = 1 bar	P = 150 bar	P = 1 bar	P = 150 bar	P = 1 bar	P = 150 bar
	(µmol g ⁻¹ h ⁻¹)	(fraction)	(fraction)	(fraction)	(fraction)	(fraction)	(fraction)
Ni3ZnN (Goto et al., 20	2082	$\geq 3.7\times 10^{.3}$	$\geq 4.3 \times 10^{-2}$	7.2 × 10 ⁻⁴	2.5×10^{-1}	1.6 × 10-1	6.4 × 10 ⁻¹
Co₃InN (Goto et al., 20	61	$\geq 1.1 \times 10^{-4}$	$\geq 1.3\times 10^{-3}$	2.6 × 10 ⁻⁶	3.8×10^{-4}	1	1
Ni3InN (Goto et al., 20	220	$\geq 3.9\times 10^{-4}$	≥ 4.8 × 10 ⁻³	N/A ^e	N/A ^e	N/A ^e	N/A ^e
Co3Mo3 (Hargreaves & Mcka	N 98 ay, 2009)	$\geq 3.5\times 10^{-4}$	≥ 4.3 × 10 ⁻³	N/A ^e	N/A ^e	N/A ^e	N/A ^e
Ni2MO3N (Hargreaves & Mcka	V av. 2009) 11	≥ 3.9 × 10 ⁻⁵	$\geq 4.8\times 10^{-4}$	N/A ^e	N/A ^e	N/A ^e	N/A ^e

Table 6.2. Experimentally determined ammonia synthesis rates of nitrides via R2a, and their equilibrium y_{NH_3} and P_{N_2} . The estimations assume that the rates provided reflect the equilibrium of the reaction.

^a Ammonia synthesis rates measured at 400°C and 1 bar under 60 ml min⁻¹ flowrate of hydrogen (75%) in argon (25%) gas. Initial rates of reaction were obtained from literature and were assumed to be the maximum achievable rate. ^b y_{NH2} calculated from the maximum ammonia synthesis rate under pure hydrogen atmospheres.

 ${}^{c}y_{NH_{3}}$ scaled from 1 bar to 150 bar pressures using the pressure dependence of the equilibrium constant of reaction R2a. d Total pressure is not constant for these nitrides since the equilibrium $P_{N_{2}}$ is greater than the starting total pressure. e Solids are missing from the materials project database to calculate values for these materials.

On the other hand, the equilibrium P_{N_2} values estimated in this work appear to be high compared to estimates from experimental work $(2.2 \times 10^2 \text{ vs } 9.4 \times 10^{-2} \text{ bar for})$ Ni₃ZnN, respectively). If accurate, this implies that the materials are unstable and potentially difficult to nitrogenate. Experimental evidence suggests that synthesis of metal nitrides with nitrogen gas is only feasible with few metals (e.g., Mn_xN) and high temperatures (>500°C) are required to achieve sufficient nitrogenation rates (Michalsky et al., 2015). Many nitrides studied in literature, including those in Table 6.2, are synthesized using ammonia as the source of nitrogen instead. Nitrogenation of other nitrides in nitrogen gas such as TiFe₂N_x (Machida et al., 1998), Li₃N (Goshome *et al.*, 2015; Shinzato et al., 2022), Ca₃N₂, Sr₂N (Michalsky et al., 2015), Co₃CuN, Ni₃CuN (Daisley et al., 2022), and Mn_xN (Feng et al., 2021; Michalsky et al., 2015; Mohammadi Aframehr & Pfromm, 2021) has been attempted, however, these nitrides are found to be either unreactive towards nitrogen gas or have slow nitrogenation rates. This poses a significant challenge to achieving a feasible CL-NH3 process based on metal nitrides, however some work has shown that combinations of metal nitrides with hydrides can facilitate the nitrogen triple bond dissociation and increase nitrogenation rates (Feng et al., 2021; Gao et al., 2018; Yan et al., 2021). Additionally, the nitrogenation step can be operated at a higher temperature to increase reaction rates, however, this is at the expense of lower equilibrium conversions of nitrogen gas.

If metal nitrides can only be synthesised in ammonia, it can be speculated that these materials are more suitable for ammonia decomposition rather than ammonia synthesis. Ammonia decomposition *via* chemical looping could be a viable application for metal nitrides, and the methodology shown in this work can be used to identify the required equilibrium P_{N_2} for the reaction along with potential materials. Unlike CL-NH₃, the reaction would not compete with *R*1, and a low equilibrium P_{N_2} could increase the ammonia conversion to hydrogen gas beyond the decomposition reactions equilibrium.

In terms of the accuracy in the estimation of Gibbs free energy and therefore the equilibrium P_{N_2} obtained in this work, it has been reported that standard enthalpy of formation MP database has a mean absolute error of 0.12 eV atom⁻¹ for a given compound (see appendix B.5) and the temperature correction term introduced by (Bartel et al., 2018) has a mean absolute error of 0.046 eV atom⁻¹, this typically represents a -50 to +20% error in estimated Gibbs free energies (see appendix B.5). More importantly, this error translates to an uncertainty in equilibrium P_{N_2} of several orders of magnitude. In the case of Co₃InN, the equilibrium P_{N_2} could vary between 1.56 × 10⁻⁸ to 9.98 × 10¹⁸ bar. Therefore, it is uncertain whether this material and by extension others identified here, are actually within the envelope in Figure 5.4. Better theoretical estimates are needed to identify suitable compounds for CL-NH₃ with confidence. Required accuracies for the equilibrium P_{N_2} have been calculated using the method described in appendix B.4 and are shown in appendix B.5. To determine whether a material is situated within the envelope at T = 400°C, the error of the reaction should be 62 meV atom⁻¹ of N which is 19 times smaller than the average error of identified reactions (1.15 eV atom⁻¹ of N, see appendix B.5).

6.9 Summary

The equilibrium P_{N_2} or X_{N_2} of nitrogen carriers was used as a proxy for the equilibrium y_{NH_2} , a key performance indicator for CL-NH₃. Thermodynamic models from Chapter 5 have identified requirements for the equilibrium P_{N_2} or X_{N_2} of metal nitrides or imides, respectively. To maximise the equilibrium y_{NH_3} , the equilibrium gas partial pressures during the nitrogenation reaction should be such that equilibrium y_{NH_3} values close to or equal to that of R1 over a wide range of temperatures can be achieved. Although improbable, nitrides with very high equilibrium P_{N_2} values or imides with very low equilibrium X_{N_2} values could in theory lead to greater y_{NH_3} values than that possible through the Haber-Bosch route, provided that the decomposition of NH₃ is kinetically limited. A screening of materials from the Materials Project database shows that 111 nitrides achieve sufficient equilibrium P_{N_2} values and are thus considered viable whereas no metal imides/hydrides appear viable. However, uncertainties associated with theoretical estimation of thermodynamic properties of materials are an order of magnitude too large thereby lending insufficient confidence in material screening results. It has been identified that while the reactivity towards nitrogen and hydrogen gases has been evaluated for some metal nitrides, their thermodynamic equilibria need to be determined experimentally to ascertain whether the materials are suitable for CL-NH₃. Advances in experimental and/or theoretical work are needed to identify suitable nitrogen carriers for CL-NH₃ with more certainty.

Chapter 7

Thermodynamic Characterisation of Metal Imide Nitrogen Carriers

7.1 Introduction

Experimental studies on metal imide/hydride nitrogen carriers for CL-NH₃ demonstrated high rates under milder conditions (Feng et al., 2021; Gao et al., 2018), sparking interests in this material for ammonia synthesis. Although kinetics are important, for CL-NH₃ the thermodynamics of the gas-solid reaction plays an equally important role in determining the feasibility and performance of the process. In previous chapters (Chapters 3 to 6), it has been demonstrated that the thermodynamic properties of nitrogen carrying materials affect key performance indicators for CL-NH₃ processes. Based on estimates for the thermodynamic properties of imide/hydride carriers (see section 6.6.1), these materials may not be viable and should produce low ammonia yields at equilibrium. However, experimental work is necessary to ascertain these results since theoretical estimates have large uncertainties. In this chapter, a preliminary investigation on the feasibility of nitrogenating and hydrogenation metal imide/hydride nitrogen carriers was made since these materials can form ammonia via multiple cycles of chemical looping reactions. Additionally, the equilibrium of the hydrogenation and nitrogenation reactions using lithium imide/hydride was determined for a limited range of conditions (*T*, *P*, solid composition).

Objectives:

- Determine the feasibility of storing nitrogen and forming ammonia from hydrides.
- Obtain preliminary estimates for the thermodynamic properties of imide/hydride nitrogen carriers and compare to results in Chapter 6.
- Evaluate the gas-solid equilibrium of imide/hydride nitrogen carriers.

7.2 Experimental Methodology

7.2.1 Materials & Synthesis

Alkali and alkaline earth metal hydrides such as LiH (Sigma Aldrich Lithium hydride powder, -30 mesh, >95% purity) and BaH₂ (Strem, Barium hydride powder, -60 mesh, >99% purity) were purchased and handled in a glove box filled with argon gas. Argon, nitrogen, and 5% hydrogen (in argon) with less than 10 ppm of impurities were used during experiments. Metal imides such as Li₂NH and BaNH were synthesised by reacting hydrides with nitrogen gas (R16b and R10b, respectively) at high temperatures (500°C) and ambient pressures using the equipment described in section 7.2.2.

$$Li_2NH_{(s)} + 2H_{2(g)} \rightarrow 2LiH_{(s)} + NH_{3(g)}$$
 (R16a)

$$2LiH_{(s)} + 0.5N_{2(g)} \to Li_2NH_{(s)} + 0.5H_{2(g)}$$
(R16b)

$$BaNH_{(s)} + 2H_{2(g)} \rightarrow BaH_{2(s)} + NH_{3(g)}$$
(R10a)

$$BaH_{2(s)} + 0.5N_{2(g)} \to BaNH_{(s)} + 0.5H_{2(g)}$$
 (R10b)

7.2.2 Chemical Looping Ammonia Synthesis Rig

To study reactions with alkali and alkaline earth metal imides/hydride, their contact with oxygenated compounds (O₂, H₂O, CO₂) should be minimised throughout the process, therefore, an experimental rig was built to handle their air-sensitive nature (Shown in Figure 7.1 & appendix C.1). Contaminants can originate from gas cylinders, from air present in the flow system, and from air introduced *via* leaks in the flow system. To address these three problems, oxygen and moisture traps were installed to remove contaminants from the gas stream (Agilent, OT3-2 Combination Trap), inert gas (Argon) was used to purge the system of air, metal gasket fittings (Swagelok, VCR fittings) were used to reduce leaks around detachable components, and a pressure decay test was used to quantify the leak rate of the system.



Figure 7.1 Experimental rig for reacting metal hydrides/imides with reactive gases (H_2 or N_2). Two different flow systems can be used to continuously flow gas over the sample or perform the reaction under batch conditions. The design for the utube reactor is shown in appendix C.1.

Samples loaded into the reactor rig (Figure 7.1) can be exposed to nitrogen or hydrogen gases at temperatures between 200 to 600°C. Two flow system configurations have been installed involving continuous gas flows or batch reaction conditions. The former configuration is used to synthesise metal imides from their hydrides or perform chemical looping reactions (R2 or R3). The latter configuration is used to equilibrate the gas-solid reactions and measure the equilibrium composition of the reaction (See section 7.2.3). Analysis of gas products is performed with a mass spectrometer (Hiden Analytical, QGA analyser) when measuring hydrogen or nitrogen gases or FTIR gas analyser (MKS Instruments, MultiGas 2000 FTIR Gas analyser) when measuring ammonia.

7.2.3 Gas-Solid Equilibration Experiments

Using the batch flow system in Figure 7.1, samples of lithium hydride were exposed to a fixed amount of reactive gases at ambient conditions. The temperature of the batch system was ramped at a rate of 10°C/min and held at 500°C. After equilibrating the gas and solid reactants, the contents of the batch system were fed to gas analysers to quantify the amounts of products and reactants present in the reactor. In this work, the equilibrium of reaction R16b was observed, however, its results can be used to infer the equilibrium of reaction R16a (see Chapter 5). Furthermore, reaction R16a has poor kinetics and would be more challenging to measure. Estimates from preliminary experiments indicate that the equilibrium y_{H_2} is within detectable limits of the mass spectrometer (discussed further in section 7.5).

7.2.4 Thermogravimetric Analysis

A thermogravimetric analyser (TGA) (Rubotherm dyntwo THERM unit) was used to measure weight changes of lithium hydride versus time when exposed to nitrogen gas at high temperatures (up to 500°C) and high flowrates (200 ml min⁻¹). The temperature was ramped at a rate of 2.5°C/min and the onset temperature of the reaction and quantity of nitrogen stored by the hydride was determined. Hydride materials were briefly (<5 min) exposed to ambient air when loaded into the TGA. Sample weights were obtained in the glovebox before loading samples into the TGA, and the oxidation during the loading was determined from the initial weight recorded on the TGA (~2 to 3 mg). A blank run (crucible with no solid sample) was performed to correct for buoyancy effects in the TGA. Additionally, a run with sample under argon gas was performed to correct for the weight

gained by the sample due to trace amounts of oxygenated compounds in the TGA flow system.

7.2.5 Powder X-Ray Diffraction Analysis

Compositions of metal hydrides/imides pre- and post-reaction were determined using powder x-ray diffraction analysis (PXRD). Sample handling was performed in the glovebox, and to mitigate contact with air, samples were sealed with cellophane tape when a flat plate holder was used (Figure 7.2 (A)), or flame-sealed for glass capillary tubes (Figure 7.2 (B)). Samples loaded on the flat plate holder were scanned with a Bruker D2 Phaser, whereas capillaries were scanned with a Philips X'Pert Pro MPD diffractometer. Both instruments emit Copper K- α ($\lambda = 1.54$ Å) radiation from the X-ray source. Samples were collected over angles of $2\theta = 10 - 120$ °. Samples on the flat-plate require minimal time to obtain diffraction patterns (ca. 1 hour), however, the tape introduces a background signal which can mask smaller peaks or phases present in small amounts. Samples loaded in flame-sealed glass capillaries have little to no background from the glass capillary (borosilicate) and can provide higher peak resolution, however, the collection times are greater (12 – 24 hours) (see appendix C.3 for comparison). In this work, materials were scanned using the flat plate holder.

(A) Reflection

(B) Transmission



Figure 7.2 Diffractometer schematics for reflection (A) and transmission (B) geometries. Flat plate sample holders are used with the reflection geometry whereas cylindrical capillaries are used with the transmission geometry.

Rietveld refinement was performed using TOPAS (Evans, 2010), to quantify solid phases with reference to crystallographic information files (CIFs) obtained from the ICSD database (Bergerhoff *et al.*, 1987; Zagorac *et al.*, 2019). Diffraction patterns of barium and lithium compounds from the ICSD database are shown in appendix C.2. Based on the diffraction patterns of barium and lithium compounds, it is possible to distinguish each phase based on the set of peak positions and relative intensity of each peak for each compound.

7.3 Imide Synthesis & Characterisation

Imides of barium and lithium were synthesised at 500°C under a continuous flow of nitrogen gas for 5.5 hours. Post-reaction samples were analysed *via* PXRD and purities of 95 wt.% and 93 wt.% for lithium and barium imide were determined *via* Rietveld analysis, respectively (See Figure 7.3). Nitrogenating lithium hydride forms a cubic non-stoichiometric imide. When the lattice parameter and nitrogen occupancy in the original CIF for lithium imide (Li₂NH, ICSD 28683) were refined in TOPAS, an imide with formula Li_{3.15}NH was obtained.



Figure 7.3 Diffraction patterns of synthesised lithium and barium imide (B) compared to fresh hydride samples (A).

Studies on nitrogen- and hydrogen-based lithium compounds have demonstrated structural similarities (See Figure 7.4) between the nitride-hydride (Li₄NH), imide (Li₂NH), and amide (LiNH₂) phases of lithium, which may explain the presence of non-

stoichiometric lithium imides (Makepeace *et al.*, 2021). Lattice parameters of lithium imides with varying stoichiometric compositions were measured in (Makepeace *et al.*, 2021) (See Figure 7.4), based on their results, the composition of lithium imide synthesised in this work can be estimated as Li_{2.5}NH (5.021 Å).



Figure 7.4 Lattice parameter versus the stoichiometric composition of lithium imides. The structure of the amide, imide, and nitride-hydride (left to right) is shown below. Figures sourced and re-touched from Makepeace et al. (2021) (Copyright © CC BY 3.0).

7.4 Ammonia Synthesis from Lithium Imide

The continuous flow system (See Figure 7.1) was used to perform a temperature programmed reaction (TPR) and measure ammonia formed *via* reaction R16a. Lithium imide samples (described in section 7.3) were exposed to 5% hydrogen (in argon) flowing at 20 ml min⁻¹, and the sample temperature was increased by 5°C min⁻¹ from ambient temperatures and held at 500°C for one hour. As shown in Figure 7.5, the reaction initiates at 100°C and ppm levels of ammonia are observed. Compared to literature, Gao et. al (2018) found a higher onset temperature of 250°C when hydrogenating lithium imide under pure hydrogen. Ammonia was measured using a mass spectrometer in their work, which may not be sensitive to trace (ppm) quantities of ammonia and could explain why the onset temperature was higher in their study.



Figure 7.5 Temperature programmed reaction of $Li_{2+x}NH$ with 5% H_2 in Ar. Ammonia formation measured via FTIR.

At 500°C, a maximum ammonia formation rate of 6.5 μ mol g⁻¹ h⁻¹ is obtained, however the reaction rate peaks at this temperature. Based on the total amount of ammonia evolved during, 1.6% of the solid was converted, therefore it is likely that the material lost activity due to the solid composition, however, further analysis of the material post hydrogenation is required to verify this. Visual inspection of the solid post-reaction shows sintering of the powder and formation of a rigid plug in the quartz tube sample holder. The reduced porosity of the sample would cause the system to be limited by mass transfer through the packed bed and could be another explanation for the reduction in ammonia formation rates. Conversion of LiH to Li₂NH causes the volume of the sample to shrink (1.28 cm³ to 1.22 cm³ when 1g of LiH is converted) and this change in morphology can decrease the porosity of the material during the reaction and cause mass transfer limitations in the system.

In Gao *et. al* (2018), an ammonia formation rate of 315 µmol g⁻¹ h⁻¹ at 350°C and 1 bar under pure hydrogen atmosphere was measured. Several factors could have contributed to the low rates of reaction observed in this work such as mass transfer limitations, gas bypassing the quartz tube in the stainless-steel sheath (see appendix C.1), and the lower hydrogen partial pressure employed in this work (5% H₂ in Ar). Gas fed to the U-tube reactor can flow inside the quartz tube or bypass it through gaps in the stainless-steel tube. Based on the tubing dimensions (see appendix C.1) 18.4% of the cross-sectional area of the flow is outside the quartz tube; back-of-the-envelope calculations would suggest that the reaction rate is 8.4 µmol g⁻¹ h⁻¹ at 500°C under 1 bar of 5% H₂ in Ar. Gas bypassing the quartz tube may affect the observed rate of ammonia formation however it is unlikely to be causing this discrepancy with literature. If ammonia formation rates are assumed to be proportional to $P_{H_2}^2$, a reaction rate up to 2600 µmol g⁻¹ h⁻¹ (400 times 6.5 µmol g⁻¹ h⁻¹) could be obtained at 500°C under 1 bar of pure hydrogen gas. In comparison to other presumed kinetic limitations, the hydrogen partial pressure is the most plausible explanation for the low ammonia formation rates in this work.

7.5 Gas Phase Equilibrium Composition of Lithium Hydride

Equilibrium properties such as the free energy change of reaction R16 were estimated using the maximum rate of ammonia formation obtained from Figure 7.5. Although this value is not an accurate representation of the equilibrium properties of reaction R16a, it can be used to estimate a lower bound value for the equilibrium ammonia concentration and by proxy the free energy change of reaction R16a and R16b, as shown in Figure 7.6. It may also be used to estimate the equilibrium y_{H_2} of reaction R16b at 500°C and 1 bar, which can be less than or equal to 36.6%. Estimates obtained for $\Delta_r G^\circ$ of reaction R16a from Chapter 6 were found to underestimate the equilibrium y_{NH_3} when compared to experimental results.



Figure 7.6 (A) Free energy change of reaction R16a versus the equilibrium y_{NH_3} in a diluted mixture of 5% hydrogen in argon. (B) Free energy change of reaction R16b versus the equilibrium y_{H_2} in nitrogen gas. Values are shown for T=500°C. Maximum y_{NH_3} values from the TPR experiment (Figure 7.5) were used to estimate the equilibrium y_{NH_3} and y_{H_2} of reactions R16a and R16b, respectively. Theoretical estimates described in Chapter 6 (green and yellow markers) are shown for comparison.

Multiple attempts to obtain the equilibrium gas composition of reaction R16b at 500°C were made with lithium hydride. Initial attempts were inconsistent due to the method for pulsing gas (manual) and potential oxidation of material in the reactor (leaks). The last three attempts (marked in green on Figure 7.7) were found to be consistent after resolving leakages in the system and maintaining a consistent procedure for gas pulsing. Attempts lasting 18 hours were found to be consistent with an attempt lasting 4 hours, therefore the system could have equilibrated in less than 4 hours. Reaction of lithium hydride with the quartz tube releases hydrogen, however, under argon gas the y_{H_2} was found to be lower than under nitrogen gas (see Figure 7.7), therefore this side-reaction

does not prevent reaction R16b from reaching its equilibrium y_{H_2} at 500°C and 1 bar. This side-reaction would be more problematic if the equilibrium y_{H_2} were lower than that obtained under argon which may be the case at higher operating temperatures.



Figure 7.7 Equilibrium y_{H_2} of reaction R16b when LiH is exposed to pure nitrogen gas at 500°C and ~1.05 bar. Multiple attempts with varying holding times at 500°C were made. Inconsistencies between attempts occurred such as the valve switching method or lack of maintenance, therefore the last three attempts were considered for equilibrium value of y_{H_2} . Hydrogen evolved from LiH reacting with the quartz tube under argon gas is shown by the blue line.



Figure 7.8 PXRD analysis of lithium imide/hydride formed after equilibration under nitrogen gas for 17.5 (A), 18 (B), and 4 hours (C). Equilibrium gas concentrations for these attempts are highlighted by the green points on Figure 7.7. The lattice parameter of $Li_{2+x}NH$ for all three attempts were found to be 4.96 Å.
The obtained value for the equilibrium y_{H_2} via reaction R3b ($y_{H_2} = 0.097$), compared to benchmarks shown in Figure 5.8, are higher than the required value at 500°C ($y_{H_2} = 0.047$ or $P_{H_2}/P_{N_2} = 4.9 \times 10^{-2}$). An equilibrium $y_{NH_3} = 0.12$ could be obtained at 500°C and 150 bar based on Figure 5.8, which would not satisfy the benchmark imposed in section 5.4 ($y_{NH_3} = 0.16$), therefore under these conditions the material is unviable. In comparison to previous experimental estimates, the y_{H_2} obtained in Figure 7.7 is nearly an order of magnitude larger than that shown on Figure 7.6 (0.047 vs 0.366) since the reaction was far from its equilibrium state. Furthermore, theoretical estimates for the y_{H_2} are largely inaccurate when compared to the value on Figure 7.7 (0.047 vs ~1) (see appendix B.6 for theoretical estimate). In its current state, theoretical estimates using the solid property estimation methods in this work cannot predict the equilibrium of reaction R3 with sufficient accuracy.

Although the LiH/Li_{2+x}NH pair does not satisfy the benchmark at 500°C according to Figure 7.7, this may not be the case at lower temperatures. Furthermore, the equilibrium gas composition is not only dependent on temperature and pressure but also the stoichiometry of Li_{2+x}NH (Metcalfe *et al.*, 2019). Shown on Figure 7.8 are the imide compositions of the material post-reaction. The three attempts lasting 4, 17.7, and 18 hours at 500 °C all yield the same lattice constant for the imide sample which indicates they have the same imide composition (according to Figure 7.4. If imide synthesis under pure nitrogen gas (see section 7.3) yields Li_{2.51}NH, it would indicate that the imide rich composition (*x* close to 2) has a lower equilibrium y_{H_2} than imides with low concentrations of nitrogen, such as that obtained on Figure 7.8. Therefore, the relation between the composition of Li_{2+x}NH and P_{H_2}/P_{N_2} appears to increase with increasing values of P_{H_2}/P_{N_2} , as shown in Figure 7.9.



Figure 7.9 Relation between the equilibrium partial pressure of gas during reaction R16b and the stoichiometric composition of $Li_{2+x}NH$. The arrow presented on the figure is there for illustrative purposes and indicates the trend for the imide composition vs the equilibrium gas partial pressures of the reaction.

At high nitrogen compositions (e.g., Li_{2.51}NH), a lower equilibrium P_{H_2}/P_{N_2} can be obtained at 500°C and would imply that the nitrogen rich imide could yield viable equilibrium y_{NH_3} values *via* reaction R16a. It is not clear how this trend would behave in between the two points displayed on Figure 7.9, and these results require further validation and investigation over a wider range of conditions (*T* and solid composition). Additionally, the solid imide composition has not fully equilibrated under pure nitrogen gas therefore the starting point on Figure 7.9 is not representative of the equilibrium of reaction R16b. Similar studies have been performed on non-stoichiometric perovskite oxides for other chemical looping reactions (de Leeuwe *et al.,* 2021), however imide/hydride materials will introduce further challenges such as their air-sensitivity, slow rates of rates of reaction (without catalyst), and reactivity with most oxide materials (e.g., quartz).

7.6 Thermogravimetric Analysis of Lithium Hydride

Temperature programmed nitrogenation of lithium hydride in the TGA shows that the nitrogenation reaction initiates at ~460°C (See Figure 7.10 (A)). After ~13 hours, lithium hydride approaches its maximum nitrogen uptake under pure nitrogen gases. Based on the weight gained, a composition of Li_{2.45}NH was calculated. Under a mixture of 5% H₂ in argon with nitrogen ($P_{H_2}/P_{N_2} = 5.5 \times 10^{-3}$), the weight gained by the material is closer to completion than under pure nitrogen gas, and a composition of Li_{2.40}NH was found (See Figure 7.10 (B)). Compared to the imide synthesis described in section 7.3, a richer imide is obtained since longer nitrogenation times were permitted at 500°C (13.3 vs 5.5 hours). In both cases the solid composition has not fully equilibrated.



Figure 7.10 Nitrogen weight gain relative to the initial amount of lithium hydride is shown on (A); the maximum corresponds to the composition for Li₂NH. Nitrogenation under pure nitrogen (green line) and under mixtures of hydrogen with nitrogen $(0.5\%/9.5\%/90\% H_2/Ar/N_2)$ (purple line) are shown. Based on the nitrogen uptake of the material, the composition of Li_{2+x}NH was found (B). Note that at x > 2, the hydride is partially converted therefore the stoichiometry corresponds to a mixture of LiH and Li_{2+x}NH, therefore x for the imide phase is truly known at these values. Rates of nitrogenation are shown in (C), however due to noise in the data, the peak nitrogenation rate is lower than what is shown by the data.

Formation of pure imides with nitrogen gas appears feasible and was found to initiate at 460°C (see Figure 7.10 (A)). This temperature is higher than cited values of 400°C in literature (Feng *et al.*, 2021; *Gao et al.*, 2018; Ravi & Makepeace, 2022). In terms of kinetics, the nitrogenation rates of lithium hydride in literature (Feng *et al.*, 2021) are within similar ranges of values than those found on Figure 7.10 (C).

7.7 Summary

In previous Chapters, lithium imide/hydride was deemed unviable based on theoretical estimates. Herein, the thermodynamic properties of the gas-solid reaction were investigated in a custom-built rig to verify these predictions and to determine whether the material would produce viable ammonia yields. Equilibrium compositions of gases produced from the nitrogenation reaction (R16b) were determined and compared to thermodynamic models in Chapter 5 to determine the viability of the material. Nitrogenation of lithium hydride produces a non-stoichiometric imide, therefore, the equilibrium conversion of gas is not only dependent on temperature, but also the composition of the solid phase. Under a continuously flow of pure nitrogen gas Li_{2.54}NH was formed, whereas under batch conditions Li_{3.5}NH was produced and the equilibrium y_{H_2} = 0.097 was found. Theoretical estimates suggest near-complete conversions for reaction R3b (see appendix B.6) and are highly inaccurate compared to experimental results (125% error for $\Delta_r G^{\circ}(R3b)$). In terms of the viability of the material, an equilibrium y_{H_2} of 0.047 is required to obtain sufficiently high ammonia yields, and although low solid conversions (e.g. Li_{3.5}NH, $y_{H_2} = 0.097$) do not meet this requirement, high solid conversions can achieve lower equilibrium y_{H_2} values (e.g. Li_{2.54}NH, $y_{H_2} \approx 0$). A wider range of conditions (*T*, imide composition) would need to be evaluated to validate these results. In addition, thermodynamic models in Chapter 5 only consider stoichiometric materials with a single-phase change and may not be suitable for comparison for non-stoichiometric materials. Although these results are not conclusive evidence on the thermodynamic feasibility of the material, it should be highlighted that there may be opportunities to increase equilibrium ammonia yields of CL-NH₃ reactions via appropriate material selection and design.

Chapter 8 Conclusions & Future Work

8.1 Conclusion

This thesis highlights requirements for the gas-solid thermodynamics of chemical looping ammonia synthesis reactions, from a process and materials point of view. CL-NH₃ has demonstrated high ammonia synthesis rates at lower temperatures and pressures than the conventional Haber-Bosch process (Feng *et al.*, 2021; Gao *et al.*, 2018). Although the conventional reactions thermodynamics would suggest that higher ammonia yields would be obtained *via* CL-NH₃, the introduction of a solid nitrogen carrier adds an additional degree of freedom to the system and can dictate the thermodynamic feasibility of the reaction under the same reaction conditions.

In Chapters 3 and 4, the impact of the gas-solid thermodynamics on the design and performance of a CL-NH₃ process was investigated. Gas conversions per reactor pass determine the feasibility and performance of downstream gas separation processes, therefore, improving gas conversions in the chemical looping reactor can lead to better performances with the process. Based on costs comparisons, the ammonia yield was found to be the key factor affecting the CL-NH₃ process. Ammonia yields greater than 26% are required to compete with the reference case, and this value was used as a benchmark for screening nitrogen carrying materials.

In Chapter 5, thermodynamic models were created to identify suitable values of ΔH_{solid}° and ΔS_{solid}° for nitrogen carriers based on the required gas phase conversion at equilibrium for the nitrogenation and hydrogenation reactions. Additionally, since the equilibrium conversion of the nitrogenation and hydrogenation reactions are interconnected, an additional model was created to relate the gas phase equilibrium conversions of the two half reactions (R2a and R2b, or R3a and R3b). This model can be used to assess the performance of the CL-NH₃ reactions based on the gas-solid equilibrium of the nitrogenation step. Furthermore, the latter model has suggested that the equilibrium y_{NH_3} of CL-NH₃ can be no greater than that of the conventional reaction (Haber-Bosch), provided that all reactions are allowed to reach equilibrium. However, if

suitable kinetics are present a kinetically stable form of ammonia with an equilibrium y_{NH_3} greater than that of reaction R1 could be obtained *via* CL-NH₃.

In Chapter 6, nitrogen carriers were screened against thermodynamic models from Chapter 5 and process requirements were defined in Chapters 3 & 4. Thermodynamic properties of nitrogen carriers are not fully available, therefore, theoretical material databases with estimation methods for thermodynamic properties were employed. Although 111 nitrides were found to be viable whereas no imide/hydride pairs were viable, these results are accompanied with large uncertainties resulting mostly from the materials database and in part from property estimation methods. Therefore, these results are unreliable and would require further experimental work or better theoretical estimates to identify appropriate nitrogen carriers with enough certainty.

Chapter 7 attempts to measure such properties for imide/hydride nitrogen carriers using in-house experimental equipment. Equilibrium compositions of gases produced from the nitrogenation reaction (R3b) were determined and compared to thermodynamic models in Chapter 5 to determine the viability of the material. However, nitrogenation of lithium hydride produces a non-stoichiometric imide, therefore, the equilibrium conversion of gas is not only dependent on temperature, but also the composition of the solid phase. At 500 °C, the equilibrium of partial pressure of gases was found to be unviable at low nitrogen contents whereas at high nitrogen contents it may be viable. A wider range of conditions (Temperature, Solid Composition) should be evaluated to validate these results, however if thermodynamic models from Chapter 5 are applicable, the material could achieve comparable or better performances than the Haber-Bosch reaction.

This research provides a thermodynamic framework for evaluating CL-NH₃ processes and materials, establishing critical benchmarks for nitrogen carrier performance, and demonstrating the importance of accurate thermodynamic data in material screening. The findings mainly highlight challenges in identifying suitable nitrogen carriers, as well as conditions in which CL-NH₃ could form ammonia more efficiently than the Haber-Bosch process. Future work should focus on improving the accuracy of theoretical estimates for material properties, expanding experimental investigations of promising nitrogen carriers across broader temperature and composition ranges. Additionally, for cases involving non-stoichiometric materials such as lithium hydride/imide, further research is needed to develop more comprehensive models that account for the complex relationship between solid composition and gas-phase equilibrium. Ultimately, this work lays foundations for future research efforts in developing novel ammonia synthesis processes.

8.2 Future Work

Although this work has emphasised the role of thermodynamics in CL-NH₃, this does not mean that other areas have been explored sufficiently since research on the kinetics, for example, have yet to be replicated and validated by a significant large number of research groups. Furthermore, few combinations of catalysts and nitrogen carrying materials have been explored. Not all transition metals have been attempted, such as early transition metals and precious metals, and the former are known to form nitrides which may alter the thermodynamics of the reaction (Feng *et al.*, 2021; Mohammadi Aframehr & Pfromm, 2021), whereas the latter are known to be highly active towards ammonia synthesis (e.g., Ru) (H. Liu, 2013). Many of these materials may be inactive for the conventional reaction but can be active under chemical looping conditions (e.g., Ni) (Gao *et al.*, 2018). Future work in this area would aim to compare rates of ammonia formation and nitrogenation for different material formulations. In addition, the synthesis method can play a crucial role in the reaction rates of the material such as with Li₂NH (Ravi & Makepeace, 2022).

For the Haber-Bosch and CL-NH₃ process, the materials interaction with hydrogen, nitrogen, and oxygenated species must be considered (Lee Pereira *et al.*, 2022). With metal imide/hydride nitrogen carriers, although the material can react with nitrogen gas at low temperatures and does not appear affected by surface hydrogen poisoning (Gao *et al.*, 2018; P. Wang *et al.*, 2017), it is also highly reactive with moisture, oxygen, and carbon dioxide. Contact with these impurities normally leads to temporary poisoning of the catalysts with the Haber-Bosch process (Nielsen, 1995) but leads to permanent loss of nitrogen capacity and activity with CL-NH₃. Some could argue that the Haber-Bosch process has sufficiently strict requirements for the oxygen content of the ammonia synthesis gas (<2 ppm), however, with metal imides/hydrides this may become infeasible to maintain at larger ammonia production capacities. Given that this area of research requires better material selection and understanding of its kinetic and thermodynamic properties, this particular topic may not be the foremost problem to address.

With regard to the work in Chapters 3 & 4, the benchmarks obtained are highly conservative since the performance of the reactor model is likely overestimated, therefore true benchmarks are likely to be higher than in this work. Kinetic data over a wider range of process conditions (Temperature & Pressure) are required to

appropriately size the reactor, likewise, thermodynamic data over the same operating conditions are required for the reactor model. Obtaining such data is necessary to simulate the reactor's operation and to determine the impact of temperature or pressure swings on the system. Currently, the models in this work do not evaluate a sufficiently wide range of conditions and the data shown is discontinuous for some conditions. In the case of metal imide/hydride carriers, data at lower nitrogen conversions than in process simulations may be necessary since thermodynamic models indicate that high ammonia yields would be obtained. Further work in this area could aim to run process simulations for multiple reaction conditions (Temperature, pressure, nitrogen conversion, ammonia yield), this would be a computationally intensive tasks therefore one idea to alleviate this problem would be to train surrogate models using machine-learning methods.

Thermodynamic models presented in Chapter 5 are explicitly limited to reactions R2 and R3. Similar principles can be applied to obtain thermodynamic models for other CL-NH₃ reaction schemes shown in Chapter 2, which would be useful for screening nitride/oxide pairings or other nitride pairings for those schemes. Furthermore, the applicability of the model for non-stoichiometric materials such as Li_{2+x}NH has not been validated and is necessary to evaluate the performance of non-stoichiometric nitrogen carriers for CL-NH₃.

Screening of nitrogen carriers from materials databases in Chapter 6 have highlighted significant uncertainties with thermodynamic properties. Furthermore, in Chapter 7 a significant discrepancy was found between theoretical estimates and experimental values for the lithium imide/hydride pair. At present, this method does not provide sufficient certainty for identifying nitrogen carriers, however, if it were to reach accuracies shown in Figure B.4 it may be used to screen a larger numbers of materials than through more laborious experimental methods. Alternatively, DFT models with high-fidelity could be used, and in combination with machine-learning algorithms, more accurate screenings of a wide number of nitrogen carriers (Fan *et al.*, 2022), however, the accuracy and applicability of this method has not been investigated in enough detail to warrant further experimental investigation.

Chapters 3 to 6 have laid groundwork for the thermodynamic requirements of CL-NH₃, however, further experimental work is required to identify suitable nitrogen carriers for a competitive CL-NH₃ process. Few studies have characterised the thermodynamic properties of nitrogen carriers for CL-NH₃, and although it has been attempted in this work, the results are preliminary in nature and thus inconclusive. The experimental methodology described in Chapter 7 does not allow for continuous measurements of either the gas or solid composition when at equilibrium; ideally, both would be measured in future experimental works and over a wide range of conditions.

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Appendices

Appendix A: Process Design & Simulation

A.1 Mass & Energy Balances of the Base Ref-Case



Figure A.1 Process flow diagram of the reference ammonia synthesis unit.

	Р	P T		m	MW	Composition (% mol)		
#ID	bar	°C	kmol/s	kg/s	kg/kmol	NH ₃	N_2	H_2
1	25.0	25.0	2.00	17.0	8.52		25.0	75.0
2	149.7	338.3	7.62	65.6	8.61	1.1	24.7	74.2
3	145.2	510.0	6.62	65.6	9.90	16.3	20.9	62.8
4	139.5	13.3	6.32	60.5	9.57	12.3	21.9	
5	200.0	-8.6	0.99	16.9	17.02	99.9		0.01
6	135.1	24.5	5.62	48.6	8.64	1.5	4.6	73.9

Table A.1 Mass balance of the reference ammonia synthesis unit.



A.2 Mass & Energy Balances of the Base CL-Case

Figure A.2 Process flow diagram for the chemical looping ammonia synthesis unit.

	Р	Т	Ν	m	MW	Comp	osition (%	6 mol)
#ID	bar	°C	kmol/s	kg/s	kg/kmol	NH ₃	N_2	H ₂
1	25.0	25.0	1.50	3.02	2.02			100.0
2	149.7	250.0	7.72	16.7	2.17	1.1		99.0
3	145.2	327.6	6.72	29.7	4.42	16.0		84.0
4	140.0	13.7	6.40	24.2	3.79	11.8		88.2
5	20.0	-7.3	1.00	17.0	17.02	99.9		0.01
6	135.1	24.5	5.72	12.7	2.22	1.4		98.6
7	25.0	25.0	0.50	13.96	28.01		100	
8	150.0	250.0	3.35	93.1	27.81		99.2	0.8
9	145.5	598.7	3.35	80.2	23.94		84.3	15.7
10	140.6	281.9	2.85	79.1	27.77		99.1	0.9
11	22.6	50.0	0.50	1.00	2.02			100.0

Table A.2 Mass balance for the chemical looping ammonia synthesis unit.



A.3 Process Simulation Assumptions

Figure A.3 Coefficient of performance for ammonia refrigeration based on its condensation temperature for a fixed evaporator temperature of -30°C. Figure taken from (Ouadha et al., 2005)(Copyright © 2023 Inderscience Enterprises Ltd.).

Table A.3 Specified compressor and turbine efficiencies in the Aspen Plus simulations.

Compressor & Turbine Efficiencies	Value			
Compressor isentropic efficiency (%)	85			
Compressor mechanical efficiency (%)	99			
Turbine isentropic efficiency (%)	HP (40 bar) = 80 MP (15 bar) = 75 LP (6 bar) = 70 Cond (0.05 bar) = 60			
Turbine mechanical efficiency (%)	99			
Coefficient of performance for NH_3 refrigeration	2			

A.4 Equipment Costing of Base Cases

Table A.4 Detailed equipment costs for the reference and chemical looping base cases.

Equipment	Costs (\$M) Ref-Case	Equipment	Costs (\$M) CL-Case
Ammonia Synthesis Reactor	15.0	Chemical Looping Reactors	5.6
Feed Compressor	31.4	H ₂ Feed Compressor	27.5
Recycle Compressor	4.6	H ₂ Recycle Compressor	5.0
Refrigeration Unit	22.5	H ₂ Tail Gas Compressor	7.0
Feed Pre-Heater	5.3	N ₂ Feed Compressor	2.6
Steam Super-Heater	0.4	N ₂ Recycle Compressor	1.4
Steam Evaporator	0.4	Refrigeration Unit	22.2
Gas Cooler (Water)	1.7	Membrane Unit	1.6
Gas Cooler (Cold Gas)	1.6	H ₂ Pre-Heater	2.6
Gas Cooler (Refrigeration)	1.1	Steam Super-Heater	0.8
		Steam Evaporator 1	0.4
		Steam Evaporator 2	0.2
		Gas Cooler (Water)	1.4
		Gas Cooler (Cold Gas)	2.2
		Gas Cooler (Refrigeration)	1.4
Total	84.0	Total	82.1

Appendix B: Material Screening

B.1 Additional Considerations for Hydride/Imide/Amide Phases

Of the 2515 screened nitrides, 1229 ternary nitrides and 39 binary nitrides contain alkali or alkali earth metals (see Figure 6.1). Of the 111 viable nitrides found in this work, 77 ternary nitrides and 5 binary nitrides contain these elements. Alkali and alkali earth metals can form nitrides, hydrides, nitride-hydrides, imides, or amides depending on the reaction conditions. Under conditions for CL-NH₃, lithium & alkali earth metals are known to form metal hydride and imide compounds (Gao et al., 2018). For example, barium and lithium imide undergo the following reactions to synthesise ammonia via CL-NH₃:

 $BaNH + 2H_2 \rightleftharpoons BaH_2 + NH_3$ $BaH_2 + 0.5N_2 \rightleftharpoons BaNH + 0.5H_2$ $Li_2NH + 2H_2 \rightleftharpoons 2LiH + NH_3$ $2LiH + 0.5N_2 \rightleftharpoons Li_2NH + 0.5H_2$

The different stoichiometric coefficients of gas species for the hydrogenation and nitrogenation reactions would need to be considered and can vary from the provided example. For lithium and alkaline earth metals, such as in the above examples, their required thermodynamic properties have been benchmarked in Lee Pereira et al. (2022). Nitrides of other alkali metals such as Na, K, Rb, Cs are not known to form metal imides but can form hydrides or amides under appropriate conditions (Gao et al., 2018), ammonia synthesis via CL-NH₃ with these compounds has not yet been demonstrated. Overall, for these various cases, a different methodology and analysis of their reaction equilibrium is necessary.



B.2 Nitrogen Capacities of Screened Materials

Figure B.1 Histogram of nitrogen capacities for viable metal nitrides.

Tuble D.1 Mill ogen cupucilies of metal innue/nyunue puns.	Table B	.1 Nitrogen	capacities	of metal	imide/	/hydride po	airs.
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Metal Imide/Hydride Pair	Nitrogen Capacity (g _{N2} g _{solid} ⁻¹)
Li ₂ NH/LiH	0.88
MgNH/MgH ₂	0.53
CaNH/CaH ₂	0.33
SrNH/SrH ₂	0.16
BaNH/BaH ₂	0.10

B.3 FactSage Materials List

Ag18Te11	B2V3	Co1Zr3	Fe18Sc10	Li13Si4	Nd2Sb1	Re2Te5	Tb3Sn7
Ag1Ba1	B3V2	Co23Hf6	Fe1Al3	Li1B3	Nd2Si3	Re3As7	Tb3Zn11
Ag1Ca1	B4Nd1	Co23Zr6	Fe1B1	Li1Pb1	Nd2Sn5	Re5Si3	Tb3Zn22
Ag1Ca3	B5Nd2	Co2Al9	Fe1Be12	Li1Zn1	Nd2Te3	Rh1Te1	Tb5Mg24
Ag1Mg3	B66Nd1	Co2B1	Fe1Be2	Li1Zn4	Nd2Zn17	Rh1Te2	Tb5Si3
Ag1Mg4	B6Nd1	Co2Ce1	Fe1Be5	Li22Si5	Nd3Al1	Ru1Te2	Tb5Si4
Ag1Sc1	Ba1B6	Co2Gd1	Fe1Sb1	Li23Sr6	Nd3Al11	Sb1Fe2	Tb5Sn3
Ag1Sr1	Ba1Be13	Co2Hf1	Fe1Sb2	Li2Sr3	Nd3Si4	Sb1Ni2	Tb5Sn4
Ag1Ti2	Ba1Cu1	Co2Nb1	Fe1Si1	Li2Te1	Nd3Sn5	Sb2Sn3	Tb6Fe23
Ag1Zr1	Ba1Cu13	Co2Nd1	Fe1Si2	Li3Bi1	Nd3Sn7	Sb2Te3	Tb6Mn23
Ag1Zr2	Ba1Pb3	Co2Nd5	Fe1Sn1	Li4Ba1	Nd3Zn11	Sc1Si1	Th1Al3
Ag2Ba1	Ba1Si1	Co2Pr1	Fe1Sn2	Li7Si3	Nd3Zn22	Sc1Te1	Th1Mg2
Ag2Ba3	Ba1Si2	Co2Pr5	Fe1Te2	Mg12Zn13	Nd4Sb3	Sc2Si3	Th1Re2
Ag2Ca1	Ba1Sn3	Co2Sc1	Fe1Ti1	Mg17Ba2	Nd5Fe17	Sc2Te3	Th1Si1
Ag2Ga1	Ba1Te1	Co2Si1	Fe23Zr6	Mg17Sr2	Nd5Mg41	Sc5Si3	Th1Si2
Ag2Sc1	Ba1Zn1	Co2Sm1	Fe2B1	Mg1B2	Nd5Sb3	Sc5Si4	Th1Te1
Ag2Sr1	Ba1Zn13	Co2Sm5	Fe2Mo1	Mg1B20	Nd5Si3	Si1As1	Th1Te2
Ag2Sr3	Ba1Zn2	Co2Ta1	Fe2Nb1	Mg1B4	Nd5Si4	Si1As2	Th3Si2
Ag2Te1	Ba1Zn5	Co2Tb1	Fe2Sc1	Mg1B7	Nd5Si9	Si1B14	Th3Si5
Ag3Ca5	Ba2Pb1	Co2Ti1	Fe2Si1	Mg1Be13	Nd5Sn3	Si1B3	Ti1B1
Ag3Ga2	Ba2Si1	Co2Y1	Fe2Ti1	Mg1Cd1	Nd5Sn4	Si1B6	Ti1B2
Ag3Mg1	Ba2Sn1	Co2Zr1	Fe2W1	Mg1Cd3	Nd6Mn23	Si1Ta3	Ti1Si1
Ag3Sb1	Ba2Zn1	Co3B1	Fe3B1	Mg1Ce1	Ni11As8	Si1Ti1	Ti1Si2
Ag4Sc1	Ba3Si4	Co3Ce1	Fe3Mo2	Mg1Co2	Ni1Al1	Si1Ti3	Ti1Te1
Ag4Sr1	Ba5Si3	Co3Gd1	Fe3Si1	Mg1Ga1	Ni1As1	Si1Zr1	Ti1Te2
Ag5Ba1	Be1Te1	Co3Gd4	Fe3Si7	Mg1Ga2	Ni1As2	Si1Zr2	Ti1Zn1
Ag5Sr1	Bi1In1	Co3La2	Fe3Sn2	Mg1Ni2	Ni1B1	Si2Te3	Ti1Zn10
Ag5Sr3	Bi1In2	Co3Mo1	Fe3W2	Mg1Si1	Ni1Bi1	Si2Ti1	Ti1Zn15
Ag7Ca2	Bi1Li1	Co3Nb1	Fe5Si3	Mg1Te1	Ni1In1	Si2V1	Ti1Zn2
Ag9Ca2	Bi1Na1	Co3Nd1	Fe5Sn3	Mg1Zn2	Ni1Sb1	Si2W1	Ti1Zn3
Al10V1	Bi1Te1	Co3Nd2	Fe6Sc29	Mg23Ba6	Ni1Sb2	Si2Zr1	Ti1Zn5
Al11Cr2	Bi2K1	Co3Nd4	Fe7W6	Mg23Sr6	Ni1Sc1	Si2Zr3	Ti2Cr1
Al11Mn4	Bi2K3	Co3Pr1	Fe9Sc5	Mg2Ba1	Ni1Si1	Si3Ta5	Ti2Mn1
Al12Mn1	Bi2Te1	Co3Pr4	Ga1As1	Mg2Ca1	Ni1Si2	Si3Ti1	Ti2Te1
Al12Mo1	Bi2Te3	Co3Si1	Ga1Sb1	Mg2Cu1	Ni1Sn1	Si3V5	Ti2Te3
Al12W1	Bi3In5	Co3Sm1	Ga1Te1	Mg2Ga1	Ni1Sr1	Si3W5	Ti2Zn1
Al13Co4	Bi3Ni1	Co3Sn2	Ga2Cu1	Mg2Ga5	Ni1Te1	Si3Zr5	Ti3Al1
Al14Ca13	Bi4K5	Co3Tb1	Ga2Te3	Mg2Ge1	Ni1Te2	Si4Ti5	Ti3B4
Al17Mo4	Ca14Si19	Co3Tb4	Ga2Ti1	Mg2Ni1	Ni1Ti1	Si4Zr5	Ti3Si1
Al17Ti8	Ca1B6	Co3Ti1	Ga39Na22	Mg2Pb1	Ni1Ti2	Si5V6	Ti3Sn1
Al1As1	Ca1Be13	Co3V1	Ga3Ti1	Mg2Si1	Ni1V3	Si6Al5	Ti4Te7
Al1Au1	Ca1Cu1	Co3W1	Ga3Ti2	Mg2Sn1	Ni1W1	Sm11Sn10	Ti5Si3
Al1Au2	Ca1Cu5	Co3Y1	Ga3Ti5	Mg2Sr1	Ni1W2	Sm13Zn58	Ti5Si4
Al1Au4	Ca1Li2	Co3Y2	Ga4Cu9	Mg2Zn1	Ni1Y1	Sm1Al1	Ti5Sn3
Al1B12	Ca1Ni2	Co3Y4	Ga4Na1	Mg2Zn11	Ni1Y3	Sm1Al2	Ti5Te4
Al1B2	Ca1Ni3	Co4Zn9	Gd11Sn10	Mg2Zn3	Ni1Zn8	Sm1Al3	Tl1Te1
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Al1Ce3	Ca1Ni5	Co5Ce1	Gd12Co7	Mg38Sr9	Ni1Zr1	Sm1Fe2	Tl2Te1
Al1Co1	Ca1Pb1	Co5Gd1	Gd13Zn58	Mg3Bi2	Ni1Zr2	Sm1Fe3	Tl2Te3
Al1Cr2	Ca1Pb3	Co5La1	Gd1Al1	Mg3Cd1	Ni2Al3	Sm1Mg1	U1Al2
Al1Cu1	Ca1Si1	Co5Nd1	Gd1Al2	Mg3Sb2	Ni2B1	Sm1Mg2	U1Al3
Al1Cu2	Ca1Si2	Co5Pr1	Gd1Al3	Mg4Si7	Ni2Cr1	Sm1Mg3	U1Al4
Al1Hf1	Ca1Te1	Co5Sm1	Gd1Fe2	Mg4Si8	Ni2Ge1	Sm1Mg5	U1B12
Al1Hf2	Ca1Zn1	Co5Tb1	Gd1Fe3	Mg51Zn20	Ni2In1	Sm1Mn2	U1B2
Al1Mg1	Ca1Zn11	Co5Y1	Gd1Mg1	Mg5Ga2	Ni2In3	Sm1Sb1	U1B4
Al1Mo3	Ca1Zn13	Co5Y8	Gd1Mg2	Mg5In2	Ni2Mo1	Sm1Sb2	U1Bi1
Al1Sb1	Ca1Zn2	Co7Ce2	Gd1Mg3	Mg5Si6	Ni2Si1	Sm1Si1	U1Bi2
Al1Sc1	Ca1Zn3	Co7Gd2	Gd1Mg5	Mg6Si3	Ni2Ta1	Sm1Si2	U1Cd11
Al1Sc2	Ca1Zn5	Co7La2	Gd1Mn12	Mg6Si4	Ni2Te3	Sm1Sn2	U1Fe2
Al1Ta1	Ca2Cu1	Co7Nb2	Gd1Mn2	Mg9Si5	Ni2V1	Sm1Sn3	U1Ge1
Al1Ti1	Ca2Ni7	Co7Nd2	Gd1Si1	Mn10Si17	Ni2Y1	Sm1Te1	U1Ge2
Al1Y1	Ca2Pb1	Co7Pr2	Gd1Si2	Mn11Si19	Ni2Y3	Sm1Zn1	U1Ge3
Al1Y2	Ca2Si1	Co7Sm2	Gd1Sn2	Mn19Sn6	Ni3Al1	Sm1Zn11	U1Pd3
Al1Zr1	Ca2Sn1	Co7Ta2	Gd1Sn3	Mn1As1	Ni3B1	Sm1Zn12	U1Rh3
Al1Zr2	Ca3Bi2	Co7Tb12	Gd1Te1	Mn1B1	Ni3In1	Sm1Zn2	U1Ru3
Al1Zr3	Ca3Sb2	Co7Tb2	Gd1Zn1	Mn1B2	Ni3In7	Sm1Zn3	U1Si1
Al22Mo5	Ca3Si4	Co7Y2	Gd1Zn11	Mn1B4	Ni3Mo1	Sm1Zn5	U1Si2
Al23V4	Ca3Zn1	Co7Y6	Gd1Zn12	Mn1Be12	Ni3Sb1	Sm2Al1	U1Si3
Al2Au1	Ca5Pb3	Cr1B1	Gd1Zn2	Mn1Be2	Ni3Si1	Sm2Fe17	U1Te1
Al2Ba1	Ca5Si3	Cr1B2	Gd1Zn3	Mn1Be5	Ni3Si2	Sm2Sb1	U1Te2
Al2Ca1	Ca5Zn3	Cr1B4	Gd1Zn5	Mn1Bi1	Ni3Sn1	Sm2Sn3	U1Te3
Al2Ce1	Cd1Sb1	Cr1Si1	Gd2Al1	Mn1Ni1	Ni3Sn2	Sm2Sn5	U2Te3
Al2Cu1	Cd1Te1	Cr1Si2	Gd2Fe17	Mn1Ni2	Ni3Sn4	Sm2Te3	U3Bi4
Al2Cu3	Cd3As2	Cr1Zn13	Gd2Te3	Mn1Ni3	Ni3Ta1	Sm2Zn17	U3Ge5
Al2Fe1	Cd3In1	Cr1Zn17	Gd2Zn17	Mn1Sb1	Ni3Ti1	Sm3Al11	U3Si1
Al2Hf1	Ce11Sn10	Cr2B1	Gd3Al2	Mn1Sc4	Ni3V1	Sm3Si5	U3Si2
Al2Hf3	Ce13Zn58	Cr2Hf1	Gd3Si5	Mn1Si1	Ni3Y1	Sm3Sn7	U3Si5
Al2Li1	Ce1Al1	Cr2Ta1	Gd3Sn7	Mn1Sn2	Ni4B3	Sm3Zn11	U3Te4
Al2Li3	Ce1Al3	Cr2Ti1	Gd3Zn11	Mn1Te1	Ni4W1	Sm3Zn22	U3Te5
Al2Sc1	Ce1B6	Cr2Zr1	Gd3Zn22	Mn1Te2	Ni4Y1	Sm4Sb3	U3Te7
Al2Sr1	Ce1Cu1	Cr3B4	Gd4Sn11	Mn23Sc6	Ni5As2	Sm4Sn3	U5Ge3
Al2Te3	Ce1Cu2	Cr3Mn5	Gd5Si3	Mn2B1	Ni5Sb2	Sm5Mg41	V1B1
Al2Ti1	Ce1Cu4	Cr3Si1	Gd5Si4	Mn2Ni1	Ni5Si2	Sm5Sb3	V1B2
Al2W1	Ce1Cu5	Cr5B3	Gd5Sn3	Mn2Sb1	Ni7Sc2	Sm5Si3	V1Sn2
Al2Y3	Ce1Cu6	Cr5Si3	Gd5Sn4	Mn2Sc1	Ni7Si13	Sm5Si4	V1Te1
Al2Zr1	Ce1Fe2	Cs1Na2	Gd6Fe23	Mn2Sn1	Ni7Y2	Sm5Sn3	V1Zn16
Al2Zr3	Ce1In2	Cs2Te1	Gd6Mn23	Mn2Ti1	Ni8Ta1	Sm5Sn4	V1Zn3
Al30Mg23	Ce1In3	Cu10Zr7	Ge1As1	Mn2Ti2	Ni9Te10	Sm6Mn23	V2B3
Al3Ca8	Ce1Mg1	Cu15Si4	Ge1As2	Mn2Zr1	Os1Te2	Sn1Ag3	V2Hf1
Al3Co1	Ce1Mg12	Cu19Si6	Ge1Te1	Mn3B4	Pb10Nd11	Sn1As1	V2Ta1
Al3Cr1	Ce1Mg2	Cu1Be2	Ge49Te51	Mn3Ni1	Pb10Pr11	Sn1Ca1	V2Zr1
Al3Cu1	Ce1Mg3	Cu1Eu1	Hf1B1	Mn3Si1	Pb1Nd3	Sn1Fe2	V3B2
	-						

Al3Cu2	Ce1Sb1	Cu1Eu2	Hf1B2	Mn3Ti1	Pb1Pr3	Sn1Li1	V3B4
Al3Hf1	Ce1Sb2	Cu1La1	Hf1Si1	Mn5Si3	Pb1Sr1	Sn1Na1	V3Si1
Al3Hf2	Ce1Si1	Cu1Mg2	Hf1Si2	Mn5Sn3	Pb1Sr2	Sn1Na3	V4Zn5
Al3Hf4	Ce1Si2	Cu1Nd1	Hf1Sn2	Mn6Si1	Pb1Tb1	Sn1Ni2	V5Si3
Al3Li1	Ce1Sn3	Cu1Pr1	Hf2Cr1	Mn7Mo6	Pb1Te1	Sn1Sr1	V7Al45
Al3Mg1	Ce1Te1	Cu1Sc1	Hf2Si1	Mn9Si2	Pb1Zr4	Sn1Sr2	W1B1
Al3Mo1	Ce1Zn1	Cu1Sm1	Hf3Si2	Mo1B1	Pb2Au1	Sn1Te1	W1Si2
Al3Nb1	Ce1Zn11	Cu1Sr1	Hf5Si3	Mo1B4	Pb2Nd1	Sn1Ti2	W1Te2
Al3Ni1	Ce1Zn12	Cu1Te1	Hf5Si4	Mo1Ni3	Pb2Pr1	Sn1Zr4	W2B1
Al3Ni5	Ce1Zn2	Cu1Ti2	Hf5Sn3	Mo1Ni4	Pb2Tb1	Sn20Ca31	W2B9
Al3Sc1	Ce1Zn5	Cu1Y1	Hf5Sn4	Mo1Si2	Pb2Zr1	Sn23Ca36	W2Zr1
Al3Ta1	Ce2Al1	Cu1Zr1	Hg1Te1	Mo1Te2	Pb3Au1	Sn2Li5	W5Si3
Al3Ta2	Ce2Fe17	Cu1Zr2	In1Ag3	Mo1Zn22	Pb3Nd1	Sn2Na1	Y11Sn10
Al3V1	Ce2In1	Cu2Eu1	In1As1	Mo1Zn7	Pb3Nd5	Sn2Zr1	Y13Zn58
Al3Y1	Ce2Mg17	Cu2La1	In1Ca3	Mo2B1	Pb3Pr1	Sn3Ca1	Y1Al2
Al3Zr1	Ce2Sb1	Cu2Mg1	In1Li2	Mo2B5	Pb3Pr5	Sn3Ca5	Y1Fe2
Al3Zr2	Ce2Sn5	Cu2Nd1	In1Li6	Mo2Hf1	Pb3Sr1	Sn3Li7	Y1Fe3
Al3Zr5	Ce2Te3	Cu2Pr1	In1Mg2	Mo2Zr1	Pb3Sr2	Sn3Li8	Y1Mn12
Al4Ba1	Ce2Zn17	Cu2Sb1	In1Na1	Mo3B5	Pb3Sr5	Sn3Na1	Y1Mn2
Al4Ca1	Ce3Al11	Cu2Sm1	In1Na2	Mo3Ni11	Pb3Tb1	Sn3Na4	Y1Ni5
Al4Ce1	Ce3In1	Cu2Te1	In1Sb1	Mo3Si1	Pb3Tb5	Sn3Sr1	Y1Re2
Al4Cr1	Ce3In5	Cu2Ti1	In1Te1	Mo4Ni3	Pb3Zr5	Sn3Sr5	Y1Si1
Al4Fe1	Ce3Si2	Cu2Y1	In2Ag1	Mo5Ru3	Pb4Nd3	Sn3Zr5	Y1Si2
Al4Li9	Ce3Si5	Cu2Zr1	In2Ca1	Mo5Si3	Pb4Nd5	Sn4As3	Y1Sn2
Al4Mn1	Ce3Sn1	Cu33Si7	In2Li3	Mo5Sn3	Pb4Pr3	Sn4Li17	Y1Sn3
Al4Mo1	Ce3Sn5	Cu37La3	In2Te1	Mo9Pd11	Pb4Pr5	Sn4Na1	Y1Te1
Al4Sr1	Ce3Sn7	Cu3As1	In2Te3	Na1B15	Pb4Sr5	Sn4Na15	Y1Zn1
Al4W1	Ce3Zn11	Cu3Ge1	In3Li13	Na1B6	Pb4Tb5	Sn4Na9	Y1Zn11
Al4Zr5	Ce3Zn22	Cu3Sb1	In5Na3	Na1Ba1	Pb5Li22	Sn4Sr1	Y1Zn12
Al5Ba4	Ce4Sb3	Cu3Sn1	In9Na5	Na1Cd2	Pb5Sr3	Sn5Li13	Y1Zn2
Al5Co2	Ce5In4	Cu3Ti2	Ir1Te2	Na1Si1	Pd1Te1	Sn5Li2	Y1Zn3
Al5Li1	Ce5Mg41	Cu4In1	Ir3Te8	Na1Te1	Pd1Te2	Sn5Sr3	Y1Zn4
Al5Mo1	Ce5Si3	Cu4La1	K1B6	Na1Te3	Pm1Te1	Sn5Ti6	Y1Zn5
Al5W1	Ce5Si4	Cu4Nd1	K1Si1	Na1Zn13	Pm2Te3	Sn6Ca7	Y2Fe17
Al63Mo37	Ce5Sn3	Cu4Pr1	K1Zn13	Na2K1	Pr11Sn10	Sn6Na1	Y2Sn5
Al69Ta39	Ce5Sn4	Cu4Sb1	K2Te1	Na2Te1	Pr13Zn58	Sr1B6	Y2Te3
Al6Fe1	Ce9In11	Cu4Sc1	K3Bi1	Na3As1	Pr1Al1	Sr1Be13	Y2Zn17
Al6Mn1	Co11Ce24	Cu4Sm1	La11Sn10	Na3Bi1	Pr1Al2	Sr1Mg2	Y3Si5
Al77W23	Co11Hf2	Cu4Ti3	La13Zn58	Na3Sb1	Pr1Al3	Sr1Si1	Y3Zn11
Al7Cr1	Co11Zr2	Cu4Y1	La1Al1	Na4Ba1	Pr1Mg1	Sr1Si2	Y3Zn22
Al7Sr8	Co13La1	Cu51Zr14	La1Al2	Nb1B1	Pr1Mg12	Sr1Te1	Y5Si3
Al7Ta5	Co16Nb9	Cu5Eu1	La1Al3	Nb1B2	Pr1Mg2	Sr1Zn1	Y5Si4
Al7W3	Co17Ce2	Cu5La1	La1Mg1	Nb1Co2	Pr1Mg3	Sr1Zn13	Y5Sn3
Al8Cr5	Co17Gd2	Cu5Nd1	La1Mg12	Nb1Cr2	Pr1Sh1	Sr1Zn2	Y5Sn4
Al8Mo3	Co17La20	Cu5Pr1	La1Mg?	Nb1Fe2	Pr1Sh2	Sr17n5	Y6Fe23
AlgV5	Co17Nd2	Cu5Sm1	La1Mo2	Nh1Ni8	Pr1Si1	Sr2Mg17	Y6Mn22
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Al99Mn23	Co17Pr2	Cu5Sr1	La1Ni1	Nb1Si2	Pr1Sn1	Sr2Si1	Zn12Sc1
Al9Co2	Co17Pr20	Cu5Zr8	La1Ni3	Nb1Sn2	Pr1Sn2	Sr5Si3	Zn17Sc2
Al9Cr4	Co17Sm2	Cu6La1	La1Ni5	Nb1Zn1	Pr1Sn3	Sr6Mg23	Zn17Sc3
Al9Cu11	Co17Tb2	Cu6Nd1	La1Si1	Nb1Zn15	Pr1Te1	Sr9Mg38	Zn1As2
As1Co1	Co17Y2	Cu6Pr1	La1Si2	Nb1Zn2	Pr1Zn1	Ta1B2	Zn1Sb1
As1Cu8	Co19Ce5	Cu6Sm1	La1Sn1	Nb1Zn3	Pr1Zn11	Ta1Fe2	Zn1Sc1
As1Fe1	Co19La5	Cu7Ga2	La1Sn3	Nb1Zn7	Pr1Zn12	Ta1Si2	Zn1Te1
As1Ge1	Co19Nd5	Cu7In3	La1Te1	Nb2B3	Pr1Zn2	Ta2Co1	Zn1Zr1
As1In1	Co19Pr5	Cu7Y2	La1Zn1	Nb2Zn3	Pr1Zn3	Ta2Si1	Zn1Zr2
As1Na1	Co19Sm5	Cu8Zr3	La1Zn11	Nb3B2	Pr1Zn5	Ta5Si3	Zn22Zr1
As2Co1	Co1B1	Cu9Si2	La1Zn12	Nb3B4	Pr2Al1	Tb11Sn10	Zn2Li1
As2Na1	Co1Gd3	Cu9Zr2	La1Zn13	Nb5B6	Pr2Fe17	Tb13Zn58	Zn2Sc1
As2Te3	Co1Hf1	Eu13Zn58	La1Zn2	Nb5Si3	Pr2Sb1	Tb1Al1	Zn2Zr1
Au1Cd1	Co1Hf2	Eu1Al1	La1Zn3	Nb5Sn3	Pr2Sn3	Tb1Al2	Zn2Zr3
Au1Cu1	Co1In2	Eu1Al2	La1Zn4	Nb6Fe7	Pr2Sn5	Tb1Al3	Zn39Zr5
Au1Cu3	Co1In3	Eu1Al4	La1Zn5	Nd11Sn10	Pr2Te3	Tb1Fe2	Zn3As2
Au1In1	Co1La3	Eu1Mg1	La22Al53	Nd13Zn58	Pr2Zn17	Tb1Fe3	Zn3Li2
Au1In2	Co1Nd3	Eu1Mg2	La2Mg17	Nd1Al1	Pr3Al1	Tb1Mg1	Zn3Sb2
Au1Pb2	Co1Pr3	Eu1Mg4	La2Ni3	Nd1Al2	Pr3Al11	Tb1Mg2	Zn3Zr1
Au1Sb2	Co1Sb1	Eu1Mg5	La2Ni7	Nd1Al3	Pr3Si4	Tb1Mg3	Zn4Sb3
Au1Sn1	Co1Sb2	Eu1Si1	La2Sn3	Nd1Mg1	Pr3Sn1	Tb1Mn12	Zn58Sc13
Au1Sn2	Co1Sb3	Eu1Sn3	La2Te3	Nd1Mg2	Pr3Sn5	Tb1Mn2	Zn5Li2
Au1Sn4	Co1Sc1	Eu1Zn1	La2Zn17	Nd1Mg3	Pr3Sn7	Tb1Si1	Zn5Sb3
Au1Te2	Co1Sc2	Eu1Zn11	La3Al1	Nd1Mn2	Pr3Zn11	Tb1Si2	Zn7Li3
Au1Ti3	Co1Sc3	Eu1Zn12	La3Al11	Nd1Sb1	Pr3Zn22	Tb1Sn2	Zn9Mn1
Au1Zn3	Co1Si1	Eu1Zn13	La3Ni1	Nd1Sb2	Pr4Sb3	Tb1Sn3	Zr1B1
Au2Pb1	Co1Si2	Eu1Zn2	La3Si2	Nd1Si1	Pr5Mg41	Tb1Te1	Zr1B12
Au2Ti1	Co1Sm3	Eu1Zn3	La3Si5	Nd1Sn1	Pr5Sb3	Tb1Zn1	Zr1B2
Au3In1	Co1Sn1	Eu1Zn5	La3Sn5	Nd1Sn2	Pr5Si3	Tb1Zn11	Zr1Si2
Au5Zn3	Co1Sn2	Eu2Mg17	La3Zn11	Nd1Sn3	Pr5Si4	Tb1Zn12	Zr1Te2
Au7In3	Co1Tb3	Eu2Zn17	La3Zn22	Nd1Te1	Pr5Si9	Tb1Zn2	Zr1Te3
B1Cr1	Co1Ti1	Eu3Si5	La5Mg41	Nd1Zn1	Pr5Sn3	Tb1Zn3	Zr3Si1
B1Fe1	Co1Ti2	Eu3Zn11	La5Si3	Nd1Zn11	Pr5Sn4	Tb1Zn5	Zr5Sn3
B1Fe2	Co1V3	Eu3Zn22	La5Si4	Nd1Zn12	Pr6Mn23	Tb2Al1	
B1Ni1	Co1Y1	Eu50Si87	La5Sn3	Nd1Zn2	Pt1Te1	Tb2Fe17	
B1Ni3	Co1Y3	Eu5Si3	La5Sn4	Nd1Zn3	Pt1Te2	Tb2Te3	
B1Ti1	Co1Zn7	Eu5Si4	La7Ni16	Nd1Zn5	Re1Si1	Tb2Zn17	
B1V1	Co1Zr1	Eu8Si11	La7Ni3	Nd2Al1	Re1Si2	Tb3Al2	
B2Mn1	Co1Zr2	Fe10Te9	Li12Si7	Nd2Fe17	Re1Te2	Tb3Si5	

B.4 Error Analysis Calculations

The Gibbs free energy of materials calculated using Eq. (6.4) (method 2) have errors resulting from Eq. (6.3) (Kirklin et al., 2015) and DFT calculated formation energies, and entropies calculated using Eq. (6.1) (method 1) have errors ranging from the correlation's fitting procedure (Glasser, 2022a). A comparison of Gibbs free energies calculated using method 1 and 2 (see section 6.2.1 and 6.2.2, respectively) show mean absolute errors of 0.13 and 0.131 eV atom⁻¹, respectively, when compared to experimental values from the FactSage database (see appendix B.5). Based on the error of the compounds Gibbs free energy (G_{error}) and its reaction stoichiometry, the error of $\Delta_r G^\circ$ ($\pm \Delta G_{error}$) (Eq. (B.1)) and its impact on the equilibrium P_{N_2} can be determined (Eq. (B.2)).

$$\pm \Delta G_{error} = \sqrt{\sum_{i=1}^{N_s} G_{error,i}^2 |v_i|}$$
(B.1)

$$P_{N_2,error} = P_{N_2} \times e^{\left(\frac{\pm 2\Delta G_{error}}{RT}\right)}$$
(B.2)

In addition to this source of error, there may be phases missing from calculations which can lead to results which misrepresent the most stable reaction for metal nitrides. This source of error cannot be quantified and should be verified with experimental results.



B.5 Estimation Method Errors

Figure B.2 Comparison of calculated Gibbs free energies, enthalpies, and entropies to experimental values from the FactSage database at T = 400 °C. Binary compounds are shown in these plots such as bimetallics, oxides, hydrides, and nitrides.



Figure B.3 Distribution of relative errors for estimated Gibbs free energies, Entropies, and Enthalpies in comparison to experimental values from the FactSage database. Distribution plots for both estimation methods are shown, and on each plot the distribution curve, mean, standard deviation, and double of the standard deviation are shown.



Figure B.4 Relation between the relative error of the equilibrium P_{N_2} versus the error in the free energy change of reaction R2b per unit of nitrogen. This relation is described at three different temperatures, and for each temperature the relative error in P_{N_2} required to remain within the envelope shown on Figure 5.4 is shown. Based on these points, the error for $\Delta_r G^\circ$ should be within the shaded regions shown at each temperature.



Figure B.5 Distribution of errors of $\Delta_r G^{\circ}$ of reaction R2b for viable nitrides screened in this work. The mean, standard deviation, and 2x standard deviation are shown. Errors range from 0.3 to 2 eV atom⁻¹ of N within one standard deviation, and the mean error is 1.15 eV atom⁻¹ of N.



B.6 Effect of Pressure on Equilibrium P_{N_2}

Figure B.6 Relation between the equilibrium P_{N_2} and y_{NH_3} of metal nitrides following reaction R2 at various temperatures and at total pressures of 50 and 25 bar (top and bottom chart, respectively). The viable region shrinks as the systems pressure decreases.



B.7 Equilibrium Nitrogen Conversion of Metal Imides/Hydrides

Figure B.7 Comparison of X_{N_2} values for metal imide/hydride carriers with values from Figure 5.8. Note that SrNH is outside the limits of the y-axis and has $X_{N_2} < 10^{-15}$. The dashed line corresponds to the required X_{N_2} to achieve an equilibrium $y_{NH_3} = 0.16$.

Appendix C: Experimental Work

C.1 U-tube Reactor Design & Dimensions



Figure C.1 Dimensions of U-tube reactor used in the chemical looping ammonia synthesis rig (see Figure 7.1). Dimensions of the quartz tube used to hold the sample is shown below. Quartz tube is sheathed in the U-tube reactor during operation. Drawing is to scale.



C.2 Diffraction Patterns of Reference CIFs

Figure C.2 Diffraction patterns obtained from the ICSD database for barium compounds containing hydrogen (A), oxygen (B), and nitrogen (C).



Figure C.3 Diffraction patterns obtained from the ICSD database for lithium compounds containing hydrogen (A), oxygen (B), and nitrogen (C).



C.3 Flat Plate Versus Capillary Holder XRD Pattern

Figure C.4 Comparison of XRD geometries (Reflection (A) vs Transmission (B) for fresh lithium (top) and barium (bottom) hydride samples. Transmission produces lower peak intensities, however, less of the sample is oxidised by moisture.