The Production of Pure Hydrogen with Simultaneous Capture of Carbon Dioxide

A dissertation submitted for the degree of Doctor of Philosophy

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Preface

This dissertation describes work undertaken in the Department of Chemical Engineering and Biotechnology and the Department of Engineering at the University of Cambridge, between October 2006 and June 2010. It is the original and independent work of the author except where specifically acknowledged in the text. Neither the present thesis, nor any part thereof, has been previously submitted to any other university. This dissertation contains approximately 65,000 words, 20 tables and 80 figures.

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Abstract

The need to stabilise or even reduce the production of anthropogenic CO\(_2\) makes the capture of CO\(_2\) during energy generation from carbonaceous fuels, e.g. coal or biomass, necessary for the future. For hydrogen, an environmentally-benign energy vector whose sole combustion product is water, to become a major energy source, it must be produced in an efficient, CO\(_2\)-neutral manner. A process, which uses a packed bed of iron and its oxides, viz. Fe, Fe\(_{0.947}\)O, Fe\(_3\)O\(_4\) and Fe\(_2\)O\(_3\), has been formulated to produce separate, pure streams of H\(_2\) and CO\(_2\). The process is exothermic and has the following stages:

1. Reduction of Fe\(_2\)O\(_3\) to Fe\(_{0.947}\)O or Fe in syngas (CO + H\(_2\)) from gasifying coal or biomass.
   This stage generates pure CO\(_2\) for sequestration, once the water has been condensed.
2. Subsequent oxidation of Fe or Fe\(_{0.947}\)O to Fe\(_3\)O\(_4\) using steam. This stage generates
   H\(_2\) of sufficient purity for use in polymeric membrane fuel cells.
3. Further oxidation of Fe\(_3\)O\(_4\) to Fe\(_2\)O\(_3\) using air to return the oxide to step (1).

It was shown that reduction to Fe\(_{0.947}\)O in step (1) gave stable yields of H\(_2\) in step (2) after 40 cycles, near those predicted from reaction stoichiometry. By contrast, reduction to Fe, rather than Fe\(_{0.947}\)O, in step (1) gave low levels of H\(_2\) in step (2) after just 10 cycles. This demonstrates that modifying the iron oxide is unnecessary unless reduction to Fe is performed. Wet-impregnation of Fe\(_2\)O\(_3\) was performed with salts of Al, Cr and Mg or with tetraethyl orthosilicate for Si to give loadings of 1-30 mol % of the additive element. The addition of Al stabilised the quantity of H\(_2\) produced when the sample was reduced to Fe. Using a sol-gel method, composite particles with different mass ratios of Fe\(_2\)O\(_3\) and Al\(_2\)O\(_3\) were prepared. For reduction to Fe over 40 cycles, 40 wt. % Al\(_2\)O\(_3\) was required to give stable conversions near 75 % of that expected from reaction stoichiometry. Prior to this research, it had been assumed that the alumina acted as an inert support. However, this was shown to be incorrect since the formation of FeO-Al\(_2\)O\(_3\) was quantitatively confirmed using X-ray diffraction. The presence of the compound, FeO-Al\(_2\)O\(_3\), is significant since it reduces the loss in internal surface area but binds reactive iron, two contradictory effects for the production of H\(_2\).

The production of separate streams of pure H\(_2\) and CO\(_2\) from solid fuels, lignite and sub-bituminous coal, was demonstrated. Pure H\(_2\) with [CO] \(\lesssim\) 50 ppmv and [SO\(_2\)] \(\approx\) 0 ppmv was produced from a low-rank coal, showing that the process is efficacious with an impure fuel. Contaminants found in syngas which are gaseous above 273 K apparently do not adversely affect the iron oxide material or purity of the hydrogen. Subsequent oxidation of the Fe\(_3\)O\(_4\) with air, step (3), removed sulphurous and carbonaceous contaminants deposited during reduction, generated useful heat and did not lead to a decrease in the H\(_2\) yield in step (2). It is therefore recommended that step (3) be included in the process.

Rates of reaction are reported for the reduction of iron oxide particles by a mixture of CO, CO\(_2\) and N\(_2\). Importantly, rates were investigated over multiple cycles. Reduction of either Fe\(_2\)O\(_3\) to Fe\(_3\)O\(_4\) or of Fe\(_2\)O\(_4\) to Fe\(_{0.947}\)O was found to be first-order in CO. With the particle sizes used, the rates of reduction were controlled by intrinsic chemical kinetics. Activation energies and pre-exponential factors are reported. The rates were used to simulate, satisfactorily, the reduction of a packed bed of iron oxide. The rate of reduction was doubled by the addition of 1 mol. % Ce to the granulated iron oxide. The overall rate was shown to be dependent on the active surface area of the iron oxide.

A lattice Boltzmann model, which incorporates hydrodynamics, mass transport and reaction, was developed. The composition of the solid changed with time. Quantitative agreement between the model and experiments for the reduction of a single particle of Fe\(_2\)O\(_3\) to Fe\(_3\)O\(_4\) in CO was achieved. Additionally, the model correctly predicted a sharp front in the CO concentration for reduction of a packed bed of Fe\(_2\)O\(_3\) to Fe\(_3\)O\(_4\).
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Chapter 1

Production of hydrogen

1.1 Global consumption of energy

The shift from fossil fuels to sustainable energy is necessary to mitigate the emission of CO$_2$, a greenhouse gas with positive radiative forcing. Atmospheric levels of CO$_2$ have increased from a pre-industrial value of $\sim 280$ ppmv to $\sim 385$ ppmv currently (NOAA, 2009). The increase of CO$_2$ in the atmosphere has been accompanied by a rise in the global average annual temperature by 0.8°C and a rise in global average sea level by 200 mm since 1870 (IPCC, 2007).

The predominant source of anthropogenic carbon dioxide is the combustion of carbonaceous fuels. Currently, the combustion of oil, natural gas and coal accounts for 88% of the world’s supply of primary energy, as seen in Table 1.1. While combustible renewables, such as wood, peat and animal waste, have not been included in Table 1.1, since they are not traded commercially and therefore difficult to quantify (Hayward, 2009), it is estimated that they would increase the figure for total consumption of energy by an additional 10% (IEA, 2009). Importantly, solar, wind and geothermal renewable sources account for less than 1% of global consumption (IEA, 2009) and are therefore omitted. The total global consumption of energy is $4.74 \times 10^{20}$ J and increased by 1.4% in 2008 (Hayward, 2009). The growth in total energy used between 1998 and 2008 averaged 2.5% (IEA, 2009) per annum.

The estimated reserves of fossil fuels are however limited, as shown in Table 1.1. Oil and natural gas account for less than half of the total reserves of fossil fuels worldwide and are predominantly found in the Middle East. By contrast, coal is more abundant and more widely-distributed with large deposits in the U.S.A., Russia, China and Australia. The ratio of the
Table 1.1: Energy reserves and consumption by fuel in exajoules ($10^{18}$ J) per annum derived from Hayward (2009). Reserves are listed for fossil fuels only, i.e. oil, natural gas and coal. "Per capita" energy consumption is listed in GJ per person, with population information obtained from the CIA (2009).

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<td>0</td>
<td>7185</td>
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<td>114</td>
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</table>

The consumption of primary energy is also shown in Table 1.1: oil is the principal energy vector with global consumption of $1.65 \times 10^{20}$ J/y, whilst nuclear and hydro-electric energy account for less than 12% of overall consumption. From Table 1.1, developed countries consume more energy per capita than the developing ones listed, c.f. China and India with the United States, which consumes over 4 times as much energy as the world average per capita. Given the wide distribution of coal and the limited capacity of renewable energy to substitute, currently, for fossil fuels, it seems likely that for many Western countries a short-term solution to meeting the primary demand for energy in an environmentally-sustainable manner will involve the combustion of coal and subsequent capture and storage of the resulting CO$_2$.

### 1.2 Methods for the production of hydrogen

Hydrogen is an environmentally-benign energy vector since its combustion yields a single product, water. Hydrogen, H$_2$, is a colourless, odourless diatomic gas with molecular weight 2 g/mol. Owing to the Earth having an oxidising atmosphere with 21 vol. % O$_2$, gaseous H$_2$ is scarce and hydrogen is typically found either as H$_2$O or fixed via a C-H bond in organic material. Hydrogen is therefore classified as a secondary energy vector and must be derived
from a primary source such as one of those listed in Table 1.1. It is currently used in industry for, _inter al._, the synthesis of ammonia, the production of methanol, the conversion of hydrocarbon gases to liquid fuel _via_ the Fischer-Tropsch process, hydrodesulphurisation of refined petroleum products such as diesel, hydrocracking and reduction in metallurgy (Isalski, 1989). At present, hydrogen is typically produced in refinery complexes with capacities of ~ 50 kte/y of H₂ (DOE, 2009a); world production in 2008 was 45 Mte/y in total (DOE, 2009b).

The storage and distribution of H₂ remain significant challenges; therefore, methods which enable the production of H₂ at smaller scales are attractive. A summary of methods for the production of hydrogen follows: the first two involve the conversion of a hydrocarbon feedstock into hydrogen. For the production of hydrogen from a carbonaceous fuel to be environmentally benign, however, capture of the resulting CO₂ is necessary. The next three involve supplying energy to split stable molecules of water into H₂ and O₂ using electricity (electrochemical), heat (thermochemical) or sunlight (photochemical). Finally, the production of hydrogen by biological means is discussed.

1. **Steam reforming.** The reforming of a hydrocarbon, such as methane, with steam is currently the predominant route for producing hydrogen (Rostrup-Nielsen, 2005) and accounts for 80 % of the world’s supply of H₂ (Ramage, 2004). Since the reforming reaction (1.1), below, is endothermic, additional O₂ for partial oxidation, reaction (1.2), is introduced. Following reforming, the high and low temperature water-gas shift (WGS) reaction (1.3) is used to reduce the level of CO to ~ 3 vol. % and 0.5 vol. %, respectively (Choudhary and Goodman, 2002; Farrauto _et al._, 2003). The reactions for the reforming of CH₄ with steam, the partial oxidation of methane, and the subsequent shift are given by:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + 3\text{H}_2 & \Delta H^{\circ}_{298K} = +205 \text{ kJ/mol} \quad (1.1) \\
\text{CH}_4 + \text{O}_2 & \rightleftharpoons \text{CO}_2 + 2\text{H}_2 & \Delta H^{\circ}_{298K} = -319 \text{ kJ/mol} \quad (1.2) \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 & \Delta H^{\circ}_{298K} = -41 \text{ kJ/mol} \quad (1.3)
\end{align*}
\]

For steam reforming, reaction (1.1), followed by the WGS reaction (1.3), 4 moles of H₂ _per_ mole of CH₄ can be obtained. Including reaction (1.2) for the adiabatic case such that the overall \(\Delta H^{\circ}_{298K} = 0\), reduces this value to 3.3 moles of H₂ _per_ mole of CH₄. For pure hydrogen, further reduction of the CO contaminant can be obtained by (i) pressure swing
adsorption (Isalski, 1989), (ii) separation using in situ Pd membranes (Grace et al., 2005; Patil et al., 2007) or (iii) preferential oxidation of the CO to CO₂ (PROX) (Pozdnyakov et al., 2006).

2. Decomposition of hydrocarbons. The thermodynamics of the decomposition of methane to solid carbon (Muradov, 1993) gives \( \frac{p_{\text{H}_2}}{p_{\text{CH}_4}} = 1 \) and \( \frac{p_{\text{H}_2}}{p_{\text{CH}_4}} = 55 \) at \( 10^5 \) Pa and at 820 K and 1173 K, respectively. The reaction is endothermic:

\[
\text{CH}_4 \rightleftharpoons \text{C}(s) + 2 \text{H}_2 \quad \Delta H_{298}^o = +75 \text{ kJ/mol} \quad (1.4)
\]

and, overall, two moles of \( \text{H}_2 \) are produced per mole of \( \text{CH}_4 \). The endothermic enthalpy of reaction per mole of hydrocarbon increases with chain length: \( \Delta H_{298}^o = +84 \text{ kJ/mol}, +105 \text{ kJ/mol} \) and \( +209 \text{ kJ/mol} \) for \( \text{C}_2\text{H}_6, \text{C}_3\text{H}_8 \) and \( \text{C}_8\text{H}_{18} \), respectively. In passing, the decomposition of hydrocarbons of length \( \text{C}_2 \) is currently the primary method for the preparation of carbon nanotubes (Awasthi et al., 2005), although this would have little impact on the supply of \( \text{H}_2 \) for energy.

3. Electrolysis. In electrolysis, the energy required for the splitting of water into \( \text{H}_2 \) and \( \text{O}_2 \) is supplied in the form of an electric current. Molecular \( \text{O}_2 \) is produced at the anode and \( \text{H}_2 \) is produced at the cathode:

\[
2 \text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4 \text{H}^+ + 4 e^- \quad E_{\text{an}} = 1.23 - 0.059 \text{ pH} \quad (1.5)
\]
\[
4 \text{H}^+ + 4 e^- \rightleftharpoons 2 \text{H}_2, \quad E_{\text{cat}} = 0.0 - 0.059 \text{ pH} \quad (1.6)
\]

where \( E \) is the Nernstian potential in V vs. the normal hydrogen electrode (NHE). Thus for the production of \( n_{\text{H}_2} = 4100 \text{ mol} \) or \( 100 \text{ m}^3 \) of \( \text{H}_2 \) at 298 K and \( 10^5 \) Pa, the electrical energy requirement is \( n_{\text{H}_2}F(E_{\text{an}} - E_{\text{cat}}) \times (4 \text{ mol } e^-)/(2 \text{ mol } \text{H}_2) \times (1 \text{ h})/(3600 \text{ s}) = 270 \text{ kWh} \), where \( F \) is Faraday’s constant. Recently, a low-temperature, Co-based catalyst for oxygen generation at the anode has been developed which facilitates electrolysis at ambient conditions: pH 7, 298 K and \( 10^5 \) Pa (Kanan and Nocera, 2008).

4. Thermochemical. In thermochemical cycles, energy is supplied as heat to decompose water. For the dissociation of \( \text{H}_2\text{O} \) at a reasonable rate, temperatures in excess of 2500 K are required. Therefore, traditional thermochemical cycles have involved chemical intermediates which permit operating temperatures \( \leq 1123 \) K and include the hydrogen
iodide process and the chlorine process (Ewan and Allan, 2006). Recently, the supply of heat using solar concentrators has been proposed (Steinfeld and Meier, 2004). Here, metal oxides, e.g. ZnO or Fe₃O₄ (Steinfeld, 2005), are thermally dissociated to gaseous oxygen and their reduced form, Zn or FeO, in a highly endothermic reaction. Subsequent reoxidation with steam produces H₂ of high purity.

5. Photochemical. In photochemical cells, photoexcitation is used to generate H₂ directly at the cathode rather than to produce an electric current (Grätzel, 2001). Unlike the case for electricity production where an electrolyte is cycled between reduced and oxidised forms with no net consumption, water is consumed and must be continuously replenished. Photochemical cells for the production of H₂ have primarily focused on nanostructures made of Fe₂O₃ or TiO₂ (Mohapatra et al., 2009) as semiconductor materials for the anode where O₂ is generated.

6. Biological methods. The production of hydrogen by strictly biological means proceeds through pathways such as fermentation. For example, facultative anaerobes, such as Escherichia coli, can produce 2 H₂ per glucose molecule during glycolysis, whilst obligate anaerobes, such as Clostridium pasteurianum, can produce up to 4 H₂ owing to the reduction of 2 NADH to 2 NAD⁺ (Turner et al., 2008).

The above methods of production have various advantages and disadvantages. For example, whilst the reforming of methane with steam is the most developed technology, it involves several reactors and therefore is not suitable for implementation on a smaller, distributed scale. While the decomposition of hydrocarbons obviates the need for CO₂ capture since solid carbon is produced, the energy lost from C + O₂ ⇄ CO₂ means that, compared to conventional combustion, more hydrocarbon must be consumed for the same yield of energy. Renewable strategies currently suffer from low production rates; for example, fermentation is limited by low yields, 2-4 mol H₂/mol glucose, and overall production limits of ~10²-10³ m³ H₂/m³ culture h (Nath and Das, 2004).

1.3 Production of hydrogen with iron

This dissertation focuses on the production of hydrogen with simultaneous capture of CO₂ using the reduction and oxidation of iron oxide. The overall process could be heat-integrated since it is exothermic, could accept either coal or biomass as a primary energy source and could
be implemented on a distributed scale. The oxides of iron are: haematite, Fe$_2$O$_3$, magnetite, Fe$_3$O$_4$, and wuestite, Fe$_{0.947}$O. Here, wuestite is written as Fe$_{0.947}$O; generally, wuestite is written (v. Bogdandy and Engell, 1971) as Fe$_{(1-\delta)}$O, where 0.05 < $\delta$ < 0.17 such that the stoichiometric ratio of Fe/O = 1 is never achieved. The oxygen excess can be construed as iron vacancies in the lattice structure, where the appropriate proportion of iron ions must then be trivalent to maintain electrical neutrality.

The cyclic redox process for producing H$_2$ with simultaneous capture of CO$_2$ uses the following three basic steps, summarised by the chemical reactions listed in Table 1.2. Starting with a packed bed of Fe$_2$O$_3$, maintained at e.g. 1023 K:

1. **Production of CO$_2$ with oxide reduction.** Syngas, a mixture of CO and H$_2$ from e.g. the gasification of coal or biomass with steam or CO$_2$ via reactions (1.7) and (1.8) in Table 1.2, is converted to a stream of CO$_2$ and H$_2$O via reactions (1.9)-(1.14) in Table 1.2 by passing it through a packed bed of particles of Fe$_2$O$_3$. Condensing out the H$_2$O from the off-gas would leave a pure stream of CO$_2$ suitable for sequestration. The concentration gradient along the reactor would enable Fe$_{0.947}$O or even Fe to exist at the gas inlet of the packed bed, while still maintaining Fe$_2$O$_3$ in the packed bed towards the gas outlet.

2. **Production of hydrogen with partial reoxidation of metal oxide.** After the partial reduction of the iron oxide in the bed, passing steam through the reactor would generate

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**Table 1.2: Summary of reaction chemistry for the production of H$_2$ with simultaneous capture of CO$_2$ using the reduction and oxidation reactions of iron and its oxides.** The enthalpy, $\Delta H^o_T$, and Gibbs free energy, $\Delta G^o_T$, are for the reactions as written and were calculated from standard thermodynamic tables (Barin and Knacke, 1973).

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$\Delta H^o_{298\ K}$</th>
<th>$\Delta G^o_{298\ K}$</th>
<th>$\Delta H^o_{1023\ K}$</th>
<th>$\Delta G^o_{1023\ K}$</th>
<th>Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>$C_\text{(s)} + H_2O_\text{(g)} \rightarrow CO + H_2$</td>
<td>+131</td>
<td>+91</td>
<td>+136</td>
<td>-11</td>
<td>Gasification</td>
</tr>
<tr>
<td>1.8</td>
<td>$C_\text{(s)} + CO_\text{(g)} \rightarrow 2\text{CO}$</td>
<td>+172</td>
<td>+120</td>
<td>+170</td>
<td>-9</td>
<td></td>
</tr>
<tr>
<td>1.9</td>
<td>$3\text{Fe}_2\text{O}_3 + CO \rightarrow 2\text{Fe}_3\text{O}_4 + CO_2$</td>
<td>-43</td>
<td>-58</td>
<td>-44</td>
<td>-92</td>
<td>1</td>
</tr>
<tr>
<td>1.10</td>
<td>$1.2\text{Fe}_3\text{O}<em>4 + CO \rightarrow 3.8\text{FeO}</em>\text{0.947}\text{O} + CO_2$</td>
<td>+47</td>
<td>+30</td>
<td>+27</td>
<td>-5</td>
<td>1</td>
</tr>
<tr>
<td>1.11</td>
<td>$\text{FeO}_\text{0.947}\text{O} + CO \rightarrow 0.947\text{Fe} + CO_2$</td>
<td>-17</td>
<td>-12</td>
<td>-20</td>
<td>+6</td>
<td>1</td>
</tr>
<tr>
<td>1.12</td>
<td>$3\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + 2\text{H}<em>2\text{O}</em>\text{0.947}\text{O}$</td>
<td>-3</td>
<td>-30</td>
<td>-10</td>
<td>-90</td>
<td>1</td>
</tr>
<tr>
<td>1.13</td>
<td>$1.2\text{Fe}_3\text{O}_4 + \text{H}<em>2 \rightarrow 3.8\text{FeO}</em>\text{0.947}\text{O} + 2\text{H}<em>2\text{O}</em>\text{0.947}\text{O}$</td>
<td>+88</td>
<td>+58</td>
<td>+61</td>
<td>-4</td>
<td>1</td>
</tr>
<tr>
<td>1.14</td>
<td>$\text{FeO}_\text{0.947}\text{O} + \text{H}_2 \rightarrow 0.947\text{Fe} + 2\text{H}<em>2\text{O}</em>\text{0.947}\text{O}$</td>
<td>+24</td>
<td>+16</td>
<td>+14</td>
<td>+6</td>
<td>1</td>
</tr>
<tr>
<td>1.15</td>
<td>$0.947\text{Fe} + \text{H}<em>2\text{O}</em>\text{0.947}\text{O} \rightarrow \text{FeO}_\text{0.947}\text{O} + \text{H}_2$</td>
<td>-24</td>
<td>-16</td>
<td>-14</td>
<td>-6</td>
<td>2</td>
</tr>
<tr>
<td>1.16</td>
<td>$3.8\text{FeO}_\text{0.947}\text{O} + \text{H}<em>2\text{O}</em>\text{0.947}\text{O} \rightarrow 1.2\text{Fe}_3\text{O}_4 + \text{H}_2$</td>
<td>-88</td>
<td>-58</td>
<td>-61</td>
<td>+4</td>
<td>2</td>
</tr>
<tr>
<td>1.17</td>
<td>$2\text{Fe}_3\text{O}_4 + 1/2\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3$</td>
<td>-240</td>
<td>-200</td>
<td>-238</td>
<td>-102</td>
<td>3</td>
</tr>
<tr>
<td>1.18</td>
<td>$2\text{CO} \rightarrow C_\text{(s)} + \text{CO}_2$</td>
<td>-172</td>
<td>-120</td>
<td>-170</td>
<td>+9</td>
<td>Boudouard</td>
</tr>
<tr>
<td>1.19</td>
<td>$C_\text{(s)} + 1.25\text{H}<em>2\text{O}</em>\text{0.947}\text{O} + 0.375\text{O}_2 \rightarrow \text{CO}_2 + 1.25\text{H}_2$</td>
<td>-90</td>
<td>-108</td>
<td>-84</td>
<td>-156</td>
<td>$\Sigma$</td>
</tr>
</tbody>
</table>
hydrogen and reoxidise the reduced iron oxide to Fe$_3$O$_4$ via reactions (1.15) and (1.16) in Table 1.2.

3. **Complete reoxidation of metal oxide with air.** The reoxidation to Fe$_2$O$_3$ in air produces a stream of N$_2$ with residual O$_2$, reaction (1.17) in Table 1.2. Once the entire packed bed has been regenerated to Fe$_2$O$_3$, the cycle could begin anew at step 1.

Thermodynamic quantities for the relevant reactions, $\Delta H^o_T$ and $\Delta G^o_T$, can be calculated from standard thermodynamic tables (Barin and Knacke, 1973), as outlined in Appendix 1, and are listed in Table 1.2. A phase diagram for the Fe-CO-CO$_2$ and Fe-H$_2$-H$_2$O systems can then be constructed and is shown in Fig. 1.1. The dashed lines are values of the equilibrium constant $K_p = \exp(-\Delta G^o/R T)$, which for reactions (1.9) to (1.11) are equal to the ratio of partial pressures, $p_{CO_2}/p_{CO}$ at equilibrium. The solid lines in Fig. 1.1 show equivalent plots for the Fe-H$_2$-H$_2$O system, *viz.* reactions (1.12) to (1.16). The equilibrium diagrams for both systems, Fe-CO-CO$_2$ and Fe-H$_2$-H$_2$O, are related by the equilibrium constant for the water-gas shift reaction (1.3), $K_W = p_{H_2}/p_{H_2O} \times p_{CO_2}/p_{CO}$; the equilibrium lines intersect one another at 1123 K since at this temperature $K_W = 1$. Figure 1.1 shows that below the triple point at 848 K, magnetite, Fe$_3$O$_4$, is reduced directly to iron, Fe, omitting wuestite, Fe$_{0.947}$O, as the intermediate.

![Figure 1.1: Phase diagram showing $K_p$ versus temperature for the iron system for reactions with CO$_2$ and CO (solid line) and H$_2$O and H$_2$ (dashed line). The two triple points, where Fe$_3$O$_4$, Fe$_{0.947}$O and Fe coexist, is at 848 K for CO$_2$/CO or H$_2$O/H$_2$. The equilibrium for the Boudouard reaction, $K_p = p_{CO_2}/p_{CO}^2$, was converted to the form $K_p = p_{CO_2}/p_{CO}$, by assuming a total pressure of $p_{CO} + p_{CO_2} = 10^5$ Pa and is shown by the grey line which intersects unity at 940 K.](attachment:image.png)
Considering a typical synthesis gas (Cleeton et al., 2009) from the gasification of coal with steam with a composition of 40 vol. % CO, 40 vol. % H₂, 10 vol. % CO₂, 10 vol. % H₂O and the information presented in Fig. 1.1 and Table 1.2, the following thermodynamic conclusions can be drawn for the packed bed:

- At 1023 K in step 1, the syngas would be fully converted to CO₂ and H₂O provided some Fe₂O₃ existed near the outlet and the residence time in this area was sufficiently long to permit near equilibrium conversion since for reactions (1.9) and (1.12) \( \frac{p_{CO_2}}{p_{CO}} = 5 \times 10^4 \) and \( \frac{p_{H_2O}}{p_{H_2}} = 4 \times 10^4 \), respectively, shown by the upper part of Fig. 1.1.

- Reduction to Fe in step 1 would be feasible since the ratios \( \frac{p_{CO_2}}{p_{CO}} \) and \( \frac{p_{H_2O}}{p_{H_2}} \) in the reducing gas are below the respective equilibrium values of \( K_p = 0.6 \) and 0.5 at 1023 K, respectively, as shown in Fig. 1.1.

- The deposition of solid carbon during reduction in pure CO (step 1) will be possible up to \( \sim 1173 \) K, since at this temperature and \( 10^5 \) Pa the equilibrium for the Boudouard reaction (1.18), shown by the grey line in Fig. 1.1, is given by \( K_p = \frac{p_{CO_2}^3}{p_{CO}^2} \approx \frac{p_{CO}}{p_{CO_2}} = 0.03 \). Any deposited carbon could subsequently form carbon oxides, CO and CO₂, upon oxidation of the iron material with steam in step 2 and contaminate the H₂.

- Complete reoxidation of the Fe₃O₄ to Fe₂O₃ using steam in step 2 would be impracticable, since at 1023 K the right hand ordinate of Fig. 1.1 shows that a mole fraction of H₂ as low as 25 ppmv (\( \frac{p_{H_2O}}{p_{H_2}} < 4 \times 10^4 \)) is needed to prevent the transition from Fe₃O₄ to Fe₂O₃. As a result a third step, oxidation with air, would be required to regenerate the original bed of Fe₂O₃.

- At higher temperatures, e.g. 1023 K, reduction reactions and reactions involving oxidation with steam are thermally neutral, whilst the oxidation of Fe₃O₄ to Fe₂O₃ in air is exothermic providing the largest source of heat, as shown in Table 1.2.

For the overall process, there is a tradeoff between the amount of H₂ produced and the amount of usable heat generated. Because the iron species are not consumed in the cyclic process, the overall reaction can be expressed as:

\[
C(s) + yH_2O + (1 - \frac{y}{2})O_2 \rightleftharpoons CO_2 + yH_2, \quad \Delta H_{1023K}^o = 249y - 395kJ/mol \quad (1.20)
\]
where $y$ is the moles of hydrogen produced per mole of $C_{(s)}$ and is limited by the iron transition used:

<table>
<thead>
<tr>
<th>limits</th>
<th>iron transition</th>
<th>reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0 &lt; y &lt; 2$</td>
<td>$\text{Fe}_3\text{O}<em>4 \rightleftharpoons \text{Fe}</em>{0.947}\text{O}$, $\text{Fe}_2\text{O}_3 \rightleftharpoons \text{Fe}$</td>
<td>(1.10,1.16),(1.10,1.11,1.15,1.16)</td>
</tr>
<tr>
<td></td>
<td>$\text{Fe}_{0.947}\text{O} \rightleftharpoons \text{Fe}$</td>
<td>(1.11,1.15)</td>
</tr>
<tr>
<td>$0 &lt; y &lt; \frac{16}{9}$</td>
<td>$\text{Fe}_2\text{O}_3 \rightleftharpoons \text{Fe}$</td>
<td>(1.9-1.11,1.15-1.17)</td>
</tr>
<tr>
<td>$0 &lt; y &lt; 1.25$</td>
<td>$\text{Fe}_2\text{O}<em>3 \rightleftharpoons \text{Fe}</em>{0.947}\text{O}$</td>
<td>(1.9,1.10,1.16,1.17)</td>
</tr>
<tr>
<td>$y = 0$</td>
<td>$\text{Fe}_2\text{O}_3 \rightleftharpoons \text{Fe}_3\text{O}_4$</td>
<td>(1.9,1.17)</td>
</tr>
</tbody>
</table>

For example, the exothermic reaction (1.19) in Table 1.2 is reaction (1.20) with $y = 1.25$, *i.e.* a combination of either reaction (1.7) or (1.8) with reactions (1.9),(1.10) and (1.16),(1.17), and interestingly holds whether CO$_2$ or H$_2$O is used to gasify the carbon. The overall enthalpy can be decreased by decreasing $y$ in reaction (1.20). Figure 1.2 shows the enthalpy against $y$, the moles of H$_2$ produced per mole of C$_{(s)}$, at 1023 K and 10$^5$ Pa. The maximum number of moles of H$_2$ per mole of C$_{(s)}$ that can be obtained while still keeping $\Delta H^o_{1023 \, K} \leq 0$ is 1.59. The end point $y = 0$ corresponds to $\Delta H^o_{1023 \, K} = -395$ kJ/mol, which is simply the enthalpy of reaction for $C_{(s)} + O_2 \rightleftharpoons CO_2$; the end point $y = 2$ corresponds to $\Delta H^o_{1023 \, K} = +102$ kJ/mol, which is the enthalpy of reaction for $C_{(s)} + 2 \, H_2O \rightleftharpoons CO_2 + 2 \, H_2$.

![Figure 1.2: The tradeoff between usable heat and H$_2$ for the overall iron redox reaction, C$_{(s)} + y \, H_2O + (1 - \frac{y}{2}) \, O_2 \rightleftharpoons CO_2 + y \, H_2$, at 1023 K and 10$^5$ Pa.]

Thus, solid carbon from either biomass or coal can be used to produce separate streams of
CO₂ for sequestration and high purity H₂ for energy consumption, as well as heat. Because the process requires neither an input of heat nor complicated separation units, it is suitable for operation on a distributed scale. However, the coupling of enthalpies between the process steps represents a challenge. While the previous description is specific to a packed bed reactor, other schemes capable of producing a concentration gradient, e.g. a counter-current moving bed or a sequence of fluidised beds could be used for the redox reactions (Cleeton et al., 2009).

1.4 Objectives and structure of this dissertation

The principal aim of the work described in this dissertation was to present a fundamental investigation of the production of hydrogen by the reduction and oxidation of iron oxide. In particular, the objectives were as follows:

- to determine the iron oxide species, Fe₂O₃, Fe₃O₄, Fe₀.₉₄7O or Fe, and operating temperature most suitable for the generation of pure hydrogen,
- to investigate the addition of elements Al, Cr, Mg and Si to enhance the yield of H₂ over repeated redox cycles,
- to describe mathematically the intrinsic kinetics of the reactions involved,
- to investigate the improvement of the reaction rates by the addition of promoters, e.g. Ce or Pt,
- to demonstrate the feasibility of producing pure H₂ from representative solid fuels whilst simultaneously capturing CO₂,
- to develop a mathematical model based on kinetic theory, i.e. a lattice Boltzmann model, to provide a fundamental, multi-scale description of the process.

This thesis is structured as follows. Chapter 1 outlines the background and presents an introduction to the production of hydrogen. Chapter 2 demonstrates that the production of hydrogen of high purity with simultaneous capture of CO₂ is possible using the redox reactions of iron oxide. In Chapter 3, an attempt to stabilise iron oxide for repeated reduction to Fe via the back-addition of Al, Cr, Mg or Si is presented. Chapter 4 investigates iron oxide modified with Al prepared using a sol-gel technique. Next, Chapter 5 presents a fundamental study on
the reduction of iron oxide in mixtures of CO, CO$_2$ and N$_2$. Pre-exponential factors and activation energies were derived for the transitions from Fe$_2$O$_3$ to Fe$_3$O$_4$ and Fe$_3$O$_4$ to Fe$_{0.947}$O. The effect of chemical promoters on increasing the rate of reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O is studied in Chapter 6. Chapter 7 demonstrates that the production of pure H$_2$ from solid fuels is feasible. The rate parameters from Chapter 5 are then incorporated into a 3D lattice Boltzmann model of a packed bed in Chapter 8. Finally, conclusions and recommendations for future work are presented in Chapters 9 and 10.

The work presented in this dissertation has been published, or has been accepted for publication, in the following refereed journals (†, corresponding author):


Further work has been published in the following refereed journals:


Chapter 2

Production of hydrogen using the reduction and oxidation of iron oxide

2.1 Introduction

Despite the abundance of literature on the redox reactions of iron and its oxides, it is still unclear as to which temperatures and transitions, \( \text{viz. } \) \( \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}, \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_{0.947}\text{O}, \text{Fe}_3\text{O}_4 \rightarrow \text{Fe} \) or \( \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_{0.947}\text{O} \), are preferable for a cyclic scheme to produce hydrogen. In this Chapter, all four possible transitions are examined at 873, 1023 and 1173 K. The experimental results are then discussed in the light of industrial application, \( \text{e.g. } \) maximising the yield of \( \text{H}_2 \), maximising the heat output and maintaining the purity of the \( \text{H}_2 \).

2.2 Experimental

The particles of iron oxide were prepared from \( \text{Fe}_2\text{O}_3 \) powder (Sigma-Aldrich; purity > 99.9 wt. %; size < 5\( \mu \text{m} \)). Water, which had been purified by reverse osmosis (Millipore Milli-Q; > 18 M\( \Omega \)), was sprayed on to the powder to form agglomerates. The resulting mixture was mechanically stirred both during and after spraying, and then the granules were sieved to the desired sieve size fraction of +425,-600 \( \mu \text{m} \). These particles were then sintered in an oven at 1173 K for 3 h, subsequently cooled in air and then re-sieved to a sieve size of +425,-600 \( \mu \text{m} \).

The packed bed reactor was made from 316 stainless steel tubing (I.D. 10.2 mm; total length 430 mm) as shown in Fig. 2.1. A stainless steel plate (1 mm thick) supported the bed: the plate contained 8 evenly-spaced holes on a circular pitch, each with a diameter of
Figure 2.1: Schematic diagram of the reactor containing a packed bed supported on a perforated plate. Resting on the plate was a 4 g plug of sand, supporting the active bed, with another 4 g plug of sand on top. The active bed was either: (i) 20 g Fe$_2$O$_3$ particles, see section 2.3.1, or (ii) 1 g of Fe$_2$O$_3$ particles mixed with 4 g sand, see sections 2.3.2-2.3.6. The thermocouple extends to the centre of the active bed. All measurements are in mm.
The entire assembly was placed in a tubular furnace and the temperature of the bed was controlled by a K-type thermocouple which had been inserted into the bed.

The reduction of the iron oxide particles was performed using mixtures of: (i) 10 vol. % CO with balance N\textsubscript{2} and (ii) pure CO\textsubscript{2} (BOC plc.; laboratory grade). The flowrates of the gases, except CO\textsubscript{2}, were metered into the reactor using mass flow meters (Honeywell AWM5101N) followed by flow control valves. The flowrate of CO\textsubscript{2} was measured with a rotameter. In all cases, the total gas flow was maintained at $\sim 3.3 \times 10^{-5}$ m\textsuperscript{3}/s, as measured at 10\textsuperscript{5} Pa and 298 K. The composition of the reducing gas mixture was chosen, based on Fig. 1.1, to give the desired iron phase at the specified temperature, as seen in Table 2.1. Between each reduction and oxidation stage, the reactor was purged with nitrogen, as shown in Table 2.1.

In order to reoxidise the iron with steam, a syringe pump was used to feed liquid H\textsubscript{2}O through a hypodermic tube (0.8 mm I.D.) into an electrically-heated chamber, which was packed with stainless steel mesh to increase the surface area for heat transfer. The water was vaporised and conveyed into the reactor by means of a N\textsubscript{2} sweep gas. Reoxidation to Fe\textsubscript{2}O\textsubscript{3} was achieved using air from the laboratory compressed air supply, also metered into the reactor using a mass flow meter (Honeywell AWM5101N) and a control valve. Miniature solenoid valves (Burkert) were used to switch gas streams. A summary of cycle times and gases is presented in Table 2.1 for experiments.

The gas leaving the reactor was cooled to condense most of the water, before being passed through a tube filled with CaCl\textsubscript{2} to remove any residual water. The composition of the dried gas was determined by: (1) a non-dispersive infrared (NDIR) analyser measuring [CO\textsubscript{2}] and [CO] (ABB Easyline, both 0-20 vol. %); (2) a more sensitive NDIR for [CO] (ABB Easyline, 0-2000 ppmv); (3) a thermal conductivity meter measuring [H\textsubscript{2}] (ABB Caldos27, 0-30 vol. %). A description of infrared spectroscopy and other experimental techniques used in this dissertation is presented in Appendix 2. Mass balances on CO and CO\textsubscript{2} confirmed that reduction to a specified oxidation state of the metal had occurred for a given temperature with errors in the closure of the balance being less than 10 %.

Depending on the experiment, the bed was loaded in one of two ways. In each case, particles of Fe\textsubscript{2}O\textsubscript{3} were sandwiched between layers of inert quartz sand (David Ball Co.; +425,-500 µm, 4 g), as shown in Fig. 2.1. The upper layer of sand aided in preheating the inlet gas prior to contact with the iron particles; the lower layer prevented iron particles from passing through the holes in the perforated plate. For the experiments described in section 2.3.1, a packed bed of 20.0 g of iron oxide particles (425–600 µm; $d_p = 513$ µm) was used. The active
Table 2.1: Redox cycling: gas mixtures (vol. %), flowrates (m$^3$/s) as measured at 298 K and 10$^5$ Pa and corresponding flow durations (s) for experiments with an initial charge of Fe$_2$O$_3$ of 1 g. Reoxidation to Fe$_2$O$_3$ required air (a).

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Purge</th>
<th>Reduction</th>
<th>Purge</th>
<th>Steam Oxidation</th>
<th>Purge</th>
<th>(a) Air Oxidation</th>
<th>(b) Purge</th>
<th>Figs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-60</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td>60-660</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>3.3 × 10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Figs.</td>
<td>2.5a,2.7,2.9</td>
<td>2.2,2.3,2.5b,2.7</td>
<td>2.4,2.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The bed had a length of $L \sim 200$ mm and an inner diameter of $d_{\text{bed}} \sim 10.2$ mm, giving $L/d_p = 390$ for the bed of iron oxide and $d_{\text{bed}}/d_p = 20$. Here, $L$ = bed length, $d_p$ = particle diameter and $d_{\text{bed}}$ = bed diameter. The bed length of 200 mm was just shorter than the length (250 mm) of the heated section in the furnace. For experiments described in sections 2.3.2 - 2.3.6, the bed was made by carefully mixing 1.0 g of iron oxide particles with 4.0 g of inert sand. The 1 g of active material was mixed with sand to prevent maldistribution of reactant gas and to ensure near isothermal operation during the reduction and oxidation steps. For experiments with only 1 g of particles of Fe$_2$O$_3$, $L/d_p = 137$ and $d_{\text{bed}}/d_p = 20$.

To rule out any reaction of the stainless steel reactor or impurities in the sand, a series of blank experiments were performed with the reactor filled only with sand. The conversion of an equimolar mixture of CO and CO$_2$ in this case was less than 1 % of the conversion seen in a typical experiment when 1 g of Fe$_2$O$_3$ was reduced to Fe$_{0.947}$O by CO.

### 2.3 Results

#### 2.3.1 Capture of CO$_2$ and production of H$_2$

Figure 2.2 shows the composition of the effluent gas as a function of time for an experiment with 20 g of Fe$_2$O$_3$ in a packed bed maintained at 1023 K. The Fe$_2$O$_3$ was not mixed with sand; however, 4 g of sand was placed on either end of the plug of Fe$_2$O$_3$. Initially, N$_2$ was flowing through the reactor. From $t = 90$ s to $t = 810$ s, the reducing gas was passed through the bed. Nearly all the entering CO was converted to CO$_2$ and the mole fraction of CO at the exit remained consistently below 5 ppmv. Once the Fe$_2$O$_3$ was exhausted, i.e. converted to Fe$_{0.947}$O or Fe$_3$O$_4$, CO broke through between $t = 810$ s and $t = 850$ s. The reducing gas
was then turned off, so that minimal CO escaped from the bed. Next, the N₂ purge stream was turned on from $t = 850$ s to $t = 1500$ s. During this time, the trace mole fraction of CO decayed, as shown in Fig. 2.2. Next, from $t = 1500$ s to $t = 2400$ s, steam was supplied and hydrogen of high purity was produced; the concentration of CO did not exceed 5 ppmv during this phase. The purity of this manufactured hydrogen therefore exceeded the constraint required by PEM fuel cells, where CO levels above 50 ppmv are known to poison the Pt anode (Choudhary and Goodman, 2002).

Figure 2.2 demonstrates the feasibility of using the redox reactions (1.9-1.10 and 1.15, respectively, in Table 1.2) of iron oxides to produce both CO₂ suitable for sequestration and H₂ pure enough for use in PEM fuel cells. A mass balance on the effluent stream during reduction ($90 \text{ s} < t < 850 \text{ s}$) shows that more CO₂ is produced than is theoretically obtainable for the transition from Fe₂O₃ to Fe₃O₄ alone. Using the thermodynamically-consistent assumption that the charge of 20 g of Fe₂O₃ reacts sequentially to form Fe₃O₄ and then Fe₀₉₄₇O, the mass balance reveals that $\sim 66$ % of the Fe₃O₄ formed had been reduced to Fe₀₉₄₇O. In the following sections, a sustained CO₂ effluent gas during the reduction phase was not the primary objective. As such, a shorter, differential packed bed with an initial loading of 1.0 g of Fe₂O₃ mixed with sand was used, and reduction was allowed to proceed to completion, i.e. until the composition
of the outlet gas from the reactor was identical to that at the inlet.

### 2.3.2 Reduction and oxidation of oxides of iron

One question regarding the redox reactions of iron oxide in a packed bed is whether the transitions between metal oxides occur at sharp fronts or more gradually. Figure 2.3 shows mole fractions in the effluent gas as a function of time for an experiment in which 1 g of Fe$_2$O$_3$ was reduced to Fe$_{0.947}$O at 1023 K. This experiment is identical to that in Fig. 2.2 except that 1 g of Fe$_2$O$_3$ mixed with sand, not 20 g of Fe$_2$O$_3$ with no sand, was used as the bed and the reducing gas mixture was not switched off at the point of CO slip, i.e. the point at which detectable CO occurs in the effluent. Even in this short bed, complete conversion of the inlet CO occurred for 15 s (such that the CO slip was less than 0.05 vol. %) between $t = 60$ s and $t = 75$ s (point A). A simple mass balance shows that the inflow of CO required for the theoretical conversion of 1g of Fe$_2$O$_3$ to Fe$_3$O$_4$ is nearly identical to the amount entering the bed during this 60-75 s period of time. The kinetics of the transition from Fe$_2$O$_3$ to Fe$_3$O$_4$, therefore, seem fast enough for the gases to reach equilibrium within the residence time of gas in the bed, which, for the given conditions and an assumed voidage of 0.4, was $\sim 0.2$ s.

For the transition from Fe$_3$O$_4$ to Fe$_{0.947}$O, Fig. 1.1 gives $K_p = p_{CO_2}/p_{CO} = 1.87$ at 1023 K. This equilibrium value corresponds to a kink (point C) in the outlet CO and CO$_2$ in Fig. 2.3. The ensuing change in slope (point D) demonstrates that the reaction from Fe$_3$O$_4$ to Fe$_{0.947}$O...
(reaction 1.10 in Table 1.2) is no longer limited by the inlet flow of gas; instead, kinetic or mass transfer effects, or both, come into play. Fig. 2.3 shows that the total time for reaction (1.10) to reach completion is \( t = 250 - 75 = 175 \text{ s} \); significantly longer than the time to reduce \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \). At \( t = 250 \) s, the effluent gas concentration had reached the inlet condition of 9.2 vol. % \( \text{CO}_2 \) and 8.8 vol. % \( \text{CO} \). A mass balance on the CO consumed shows that if reduction occurs in a stagewise process, \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \), 94 mole % of the \( \text{Fe}_3\text{O}_4 \) formed was reduced to \( \text{Fe}_{0.947}\text{O} \). A commensurate mass balance on the \( \text{H}_2 \) produced shows that if all of the \( \text{Fe}_2\text{O}_3 \) is initially reduced to \( \text{Fe}_{0.947}\text{O} \), 92 mole % of the resulting \( \text{Fe}_{0.947}\text{O} \) is subsequently oxidised by steam to \( \text{Fe}_3\text{O}_4 \), demonstrating that acceptable closure between reduction and oxidation can be achieved.

Besides examining the reaction times for the various metal oxide transitions during reduction, the overall reduction time was also compared to the overall oxidation time. Figure 2.4 shows results when the iron oxide was: (a) reduced to \( \text{Fe}_{0.947}\text{O} \) in a mixture of \( \text{CO} \) and \( \text{CO}_2 \) and (b) reoxidised to \( \text{Fe}_3\text{O}_4 \) with steam. In the first cycle, the oxide started as \( \text{Fe}_2\text{O}_3 \); subsequent cycles began with \( \text{Fe}_3\text{O}_4 \). Figure 2.4(a) shows the cumulative amount of \( \text{CO}_2 \) released during the first five cycles of reduction, calculated by integrating the difference between the outlet and inlet mole fractions of \( \text{CO}_2 \) with respect to time. The theoretical amount of \( \text{CO}_2 \) generated in going from \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \) (reaction 1.10, Table 1.2) can be determined from the mass of iron oxide loaded into the reactor, \( \text{viz.} \) 1 g of \( \text{Fe}_2\text{O}_3 \). Figure 2.4(a) shows that the cumulative amount of \( \text{CO}_2 \) generated, given by the solid lines (—), was \( \sim 90 \% \) of the theoretical value, given by the horizontal dashed line (---). Also shown in Fig. 2.4(a) is the amount of \( \text{CO}_2 \) for the case where all the entering \( \text{CO} \) is converted to \( \text{CO}_2 \) (---). Only for the first cycle is the experimental curve a tangent to this line, again demonstrating that the inflow of reactant gas is rate-limiting for the initial reduction of \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \).

Figure 2.4(b) shows the cumulative amount of \( \text{H}_2 \) produced when steam was used to oxidise \( \text{Fe}_{0.947}\text{O} \) back to \( \text{Fe}_3\text{O}_4 \) (reaction 1.16, Table 1.2). The time for the reaction with steam to reach completion is noticeably shorter than that for the reduction in the mixture of \( \text{CO}_2 \) and \( \text{CO} \); this difference becomes increasingly apparent after more cycles. Here, it should be noted that the mole fraction of steam was 25 vol. % (5.2 mol/m\(^3\) at 10\(^5\) Pa, 298 K), whereas that of \( \text{CO} \) had been 9 vol. % (3.7 mol/m\(^3\) at 10\(^5\) Pa, 298 K), so a direct comparison between the rates of reduction and oxidation is not possible.

A comparison between the final molar amounts from the curves in Figs. 2.4(a) and (b) is then given in Fig. 2.4(c). It is clear that the amounts of \( \text{CO}_2 \) released during the reduction
Figure 2.4: Cycles of reduction and oxidation with a 1 g charge of Fe$_2$O$_3$ at 1023 K: reduction by inlet gas containing CO 9 vol. %, CO$_2$ 9 vol. %, N$_2$ 82 vol. %, followed by oxidation using steam 25 vol. %, N$_2$ 75 vol. %. The bed was Fe$_2$O$_3$ at the start of the first cycle; subsequently the oxide cycled between Fe$_3$O$_4$ and Fe$_{0.947}$O. (a) Cumulative integrals of CO$_2$ produced over five cycles. (b) Corresponding cumulative integrals for H$_2$. (c) Comparison between the five final values of each graph. (d) Times to reach 90 % of the final values in (a) and (b). In (a) - (c), the dashed horizontal line (- - -) marks the theoretical limit of H$_2$ or CO$_2$ for conversion of the original charge between Fe$_3$O$_4$ and Fe$_{0.947}$O. The sloped line (- · -) in (a) or (b) marks the integral of the inlet flow for reactant (a) CO or (b) steam.
of $\text{Fe}_3\text{O}_4$ to $\text{Fe}_{0.947}\text{O}$ and the $\text{H}_2$ produced during the oxidation of the reduced oxide back to $\text{Fe}_3\text{O}_4$ are in good agreement. Thus, it seems that all the metal which is reduced to wuestite is subsequently available for reoxidation with steam. Figure 2.4(d) plots the time to reach 90% of the final value for the curves in Figs. 2.4(a) and (b). For hydrogen the final value is assumed to be at $t = 320$ s, while for $\text{CO}_2$ the final value is assumed to be at $t = 580$ s. Figure 2.4(d) suggests that, because the time to 90% conversion increases progressively with increased numbers of cycles, the average rate of reaction falls from one cycle to the next for both reduction and oxidation.

### 2.3.3 Reduction to $\text{Fe}_{0.947}\text{O}$ versus reduction to Fe

If the iron system is to be used for producing hydrogen, one important consideration is how far to reduce the oxide. Reduction to either $\text{Fe}_{0.947}\text{O}$ or Fe depends on the composition of the synthesis gas and the constraint imposed by chemical equilibrium at the chosen reaction temperature, as seen in Fig. 1.1. Reduction to Fe would be advantageous, since the capacity for producing hydrogen over the Fe to $\text{Fe}_3\text{O}_4$ transition is approximately four times greater than that over the transition from $\text{Fe}_{0.947}\text{O}$ to $\text{Fe}_3\text{O}_4$, based on equal masses of $\text{Fe}_3\text{O}_4$.

To examine the difference between reducing $\text{Fe}_2\text{O}_3$ to Fe versus reducing it to $\text{Fe}_{0.947}\text{O}$, redox experiments over both transitions were performed at 873, 1023 and 1173 K. In these experiments, the reducing gas was 10 vol. % CO, 90 vol. % $\text{N}_2$ for reduction from $\text{Fe}_2\text{O}_3$ to Fe and 9 vol. % CO, 9 vol. % $\text{CO}_2$ and 82 vol. % $\text{N}_2$ for reduction from $\text{Fe}_2\text{O}_3$ to $\text{Fe}_{0.947}\text{O}$; oxidation to $\text{Fe}_3\text{O}_4$ used 25 vol. % steam, 75 vol. % $\text{N}_2$; oxidation of the $\text{Fe}_3\text{O}_4$ to $\text{Fe}_2\text{O}_3$ used air (21 vol. % $\text{O}_2$, 79 vol. % $\text{N}_2$), as shown in Table 2.1. Figure 2.5(a) shows that for the $\text{Fe}_2\text{O}_3$ to Fe transition at all three temperatures the amount of $\text{H}_2$ produced decreases rapidly after the first cycle. The most precipitous drops are observed for particles at 1023 K and 1173 K, suggesting that thermal sintering could contribute to the fall in reactivity. At 873 K, the production of $\text{H}_2$ declines less sharply from one cycle to the next; however, after ten cycles, $\text{H}_2$ production at all three temperatures is unsatisfactorily low, having dropped below that achievable with the $\text{Fe}_{0.947}\text{O}$ to $\text{Fe}_2\text{O}_3$ transition. In contrast to Fig. 2.5(a), hydrogen production from $\text{Fe}_{0.947}\text{O}$ remains more consistent from cycle to cycle in Fig. 2.5(b). Here, the average amount of $\text{H}_2$ produced during the tenth cycle is ~80% of that produced during the first cycle. Thus, with the current form of the iron oxide, it is preferable to reduce $\text{Fe}_2\text{O}_3$ to $\text{Fe}_{0.947}\text{O}$ instead of to metallic Fe. It should be noted that the reduction time of 600 s was kept constant.
Figure 2.5: Effect of the number of cycles of reduction/oxidation on the production of hydrogen at different temperatures for alternative transitions: (a) Fe$_2$O$_3$-Fe (b) Fe$_2$O$_3$-Fe$_{0.947}$O; the dashed line gives the theoretical amount of H$_2$ starting with 1 g of Fe$_2$O$_3$. The theoretical amount of H$_2$ starting with a 1 g charge of Fe$_2$O$_3$ in (a) is 16.7 mmol.
for experiments as given in Table 2.1. For the reduction of Fe₂O₃ to Fe the outlet gas had returned to a composition (≥ 9.7 vol. % CO, ≤ 0.3 vol. % CO₂, 90 vol. % N₂) before the valve switch compared to the inlet value (10 vol. % CO, 90 vol. % N₂). Thus, for these experiments some of the iron oxide may still have been reacting or, as discussed in section 2.3.5, carbon was probably being deposited at the end of the reduction cycle.

To determine whether the drop in H₂ produced upon reduction to Fe was a result of incomplete reduction or incomplete oxidation, the quantity of CO consumed during reduction and H₂ produced during oxidation for each cycle at 1023 K was determined and is plotted in Fig. 2.6. The CO consumed in cycle 1 is near that expected from the reduction of a 1 g charge of Fe₂O₃ to Fe, shown by the horizontal solid line, while the H₂ produced upon subsequent oxidation with steam is lower than that expected for the oxidation of Fe to Fe₃O₄, shown by the horizontal dotted line. For reduction in cycle 2, however, the CO consumed is considerably below that expected and also below that expected if only the iron capable of producing H₂ from the previous cycle is considered. Thus, it appears that the loss in reactivity of the solids is a result of both incomplete oxidation in cycle 1 and incomplete reduction in cycle 2. For cycles 3-10, the moles of CO consumed and H₂ produced are very nearly equal and it is difficult to draw firm conclusions. It is noted that while the deposition of solid carbon was possible for experiments in Fig. 2.6, the total moles of CO and CO₂ produced during oxidation with steam and then with air was negligible, < 0.1 mmol in each cycle.

### 2.3.4 Oxidation to Fe₂O₃ versus Fe₃O₄

Besides the issue of how far to reduce the metal oxide, there is also the question of how far to reoxidise it, i.e. back to Fe₃O₄ or to Fe₂O₃. For the proposed process, the presence of Fe₂O₃ near the outlet from the reactor is crucial for minimising CO slip during the reduction of the metal oxide as well as for maintaining ΔH°₀ < 0 overall. Other processes for the production of hydrogen proposed in the literature (Galvita and Sundmacher, 2007), however, only reoxidise to Fe₃O₄. Final oxidation in air has the potential to oxidise any contaminants, e.g. carbon or sulphur, deposited on the particles, but it also causes a large temperature rise in the bed and so could result in thermal sintering.

Experiments were performed with and without additional oxidation of Fe₃O₄ to Fe₂O₃. To ensure that the particles were reacted for the same cycle times, a stream of N₂ replaced the air in experiments without the additional oxidation step. Measurements indicated that the final ox-
Figure 2.6: Starting with 1 g of Fe$_2$O$_3$ mixed with sand at 1023 K, the quantity of CO consumed for Fe$_2$O$_3$ → Fe and subsequent H$_2$ produced for Fe → Fe$_3$O$_4$ is shown; further oxidation of Fe$_3$O$_4$ → Fe$_2$O$_3$ was performed with air. The solid horizontal line gives the theoretical consumption of CO expected; the dotted horizontal line gives the theoretical production of H$_2$ expected.

Figure 2.7: Total amounts of hydrogen produced in cycles using the transitions of iron oxide at 1023 K showing the effect of the number of cycles of reduction/oxidation on producing hydrogen. In each case, the basis was a 1 g charge of Fe$_2$O$_3$. The dashed line gives the theoretical amount of H$_2$ for reduction to Fe$_{0.947}$O, 3.5 mmol; the theoretical amount of H$_2$ for reduction to Fe is 16.7 mmol.
idation in air caused a temperature rise as high as 50 K in a packed bed initially containing 1 g of Fe₂O₃ particles with sand. A simple heat balance confirmed that the theoretical temperature rise when converting Fe₃O₄ to Fe₂O₃ should be just over 50 K, as shown in Appendix 3.

Figure 2.7 shows the total amount of H₂ produced during the transitions from Fe₂O₃ to Fe, Fe₃O₄ to Fe, Fe₂O₃ to Fe₀.₉₄⁷O and Fe₃O₄ to Fe₀.₉₄⁷O at 1023 K. From Fig. 2.7, the drop in hydrogen production for the Fe₂O₃ to Fe transition follows the same course as that for Fe₃O₄ to Fe. Little difference in the capacity for producing hydrogen is observed between the transitions Fe₂O₃ to Fe₀.₉₄⁷O and Fe₃O₄ to Fe₀.₉₄⁷O either. Comparing the results for these transitions, Fig. 2.7 demonstrates that the temperature rise during the additional oxidation in air to give Fe₂O₃ seems to have no adverse effect on the amount of hydrogen generated; a slight improvement can even be observed, for later cycles, when the final oxidation is with air. It should be noted that the reducing gas used in these experiments was of laboratory grade. Consequently, any benefits from the additional oxidation of contaminants other than deposited carbon, such as sulphur, which might be present in industrial synthesis gas, would not have been observed.

### 2.3.5 Deposition of carbon

Thermodynamically it is possible that carbon was deposited on the particles when iron oxide was reduced by CO to Fe at 873 K, 1023 K and 1173 K and also in those experiments involving reduction to Fe₀.₉₄⁷O at 873 K. Once deposited, the carbon could be reoxidised to CO or CO₂ during oxidation in steam or in air.

Figure 2.8 shows the mole fractions of CO₂, CO and H₂ as functions of time for the first cycle, oxidising Fe to Fe₃O₄ in steam at 873 K. Reduction to Fe in 10 vol. % CO, balance N₂ at 873 K was the condition most favourable to the deposition of carbon and represented a worst case for producing H₂ of high purity. The mole fraction of CO reached a maximum of 4600 ppmv and exceeded the benchmark of 50 ppmv for the duration of the oxidation stage, as seen in Fig. 2.8. The mole fraction of CO decreased with increasing T for reduction to Fe.

If the particle was reoxidised to Fe₂O₃, any residual solid carbon, not oxidised during the inflow of steam, reacted with oxygen in the air to form CO₂. Figure 2.9 shows the amounts of CO₂ produced during oxidation with air at 873 K. It is notable that cycles 2 and 3 gave more CO₂ in the off-gas than cycle 4, consistent with the fact that Fe catalyzes (Towhidi and Szekely, 1983) the Boudouard reaction (1.18) and that the amount of reactive Fe diminishes.
Figure 2.8: The first 60 s of the oxidation of Fe to Fe$_3$O$_4$ in steam at 873 K. Prior to the oxidation, 1 g of Fe$_2$O$_3$ had been reduced by a the mixture, CO 10, N$_2$ 90 vol. %, depositing carbon on the particles. Contamination of the H$_2$ by CO and CO$_2$ is apparent.

Figure 2.9: Oxidation in air for the Fe → Fe$_2$O$_3$ and Fe$_{0.947}$O → Fe$_2$O$_3$ transitions at 873 K for cycles 2, 3 and 4. CO$_2$ is produced by oxidation of residual carbon, which was deposited during reduction of the 1 g charge of Fe$_2$O$_3$ in CO and which had not been removed during oxidation with steam. Even though the Boudouard reaction (1.18) is thermodynamically favoured, little CO$_2$ is produced for the case of Fe$_{0.947}$O.
with increasing numbers of redox cycles, as seen by the fall in the amount of H₂ produced in Fig. 2.5(a). Another interesting finding from Fig. 2.9 is that very little CO₂ was produced during oxidation in air, when Fe₀.₉₄₇O was the lowest form of the oxide used at 873 K. This observation suggests that the rate of the Boudouard reaction (1.18) is sufficiently slower than that of the reduction reactions (1.9-1.10) to prevent significant carbon deposition for reduction to Fe₀.₉₄₇O. Here, it should be noted that reduction to Fe occurred in a gas containing 10 vol. % CO, balance N₂ whereas reduction to Fe₀.₉₄₇O occurred in a gas containing 9 vol. % CO, 9 vol. % CO₂, balance N₂ in order to ensure that the Fe₀.₉₄₇O was not reduced further to Fe. The presence of CO₂ in the latter case would also have impeded the kinetics for the deposition of carbon.

2.3.6 Purity of hydrogen

If the hydrogen produced in the packed bed is to be used in low temperature PEM fuel cells, it must contain less than ~ 50 ppmv of CO. It has already been shown for the 20 g bed in Fig. 2.2 that if a sufficiently long period of purging with N₂ is used, H₂ with the necessary purity can be produced. Figure 2.10 shows the mole fraction of CO during the oxidation in steam of Fe₀.₉₄₇O to Fe₃O₄ at 1023 K. Considering this temperature, a pressure of 10⁵ Pa and that reduction occurred with \( p_{\text{CO}}/p_{\text{CO}_2} = 1 \), the Boudouard reaction (1.18) is not thermodynamically feasible since for these conditions \( K_p = p_{\text{CO}_2}/p_{\text{CO}} = 0.3 \), as shown in Fig. 1.1, so carbon should not be deposited during reduction of the metal oxide in a mixture of CO and CO₂. However, some CO was observed during the production of hydrogen and is a result of residual CO from the reduction of Fe₂O₃ to Fe₀.₉₄₇O being swept from the system. In Fig. 2.10, the average mole fraction of CO was determined to be 23 ppmv, demonstrating that a purge of N₂ for 60 s between the reduction cycle and the oxidation with steam is sufficient to produce pure hydrogen. From the decreasing CO curve in Fig. 2.10, it seems that the purity of the hydrogen can be specified to a desired level by adjusting the length of the N₂ purge accordingly, i.e. using a longer purge for higher purity H₂ and shorter purge for lower purity H₂.

2.4 Discussion

If fossil fuels are to be used to produce hydrogen, capture of the byproduct CO₂ is essential. Figure 2.2 showed that a process, which both made H₂ of sufficient purity for use in PEM fuel...
cells and could separate CO₂ for potential sequestration, is feasible using the redox reactions of iron (1.9-1.11,1.15-1.17) in a packed bed. The CO slip was below the detection limit of the analysers used (< 5 ppmv in the CO₂ stream) during the reduction of the iron oxide and the hydrogen produced in the subsequent reoxidation of the iron oxide with steam had a content of CO < 5 ppmv, as seen in Fig. 2.2.

The results in Fig. 2.3 for the first 200 s suggest the following with regard to the reduction of iron oxides in a packed bed: (a) the total conversion of CO to CO₂ during the time 60 – 75 s suggests rapid reaction, giving a sharp front between Fe₂O₃ and Fe₃O₄ (b) the subsequent reduction of Fe₃O₄ to Fe₀.₉₄₇O during the time 75 – 200 s, is slower, so there is an ill-defined ‘front’ where Fe₃O₄ is converted to Fe₀.₉₄₇O. The overall time to reduce the particles is also longer than that to oxidise them for the gas compositions chosen, as seen in Fig. 2.4. A loss in reactivity with increasing cycle number was observed and shown to be more pronounced for reduction than oxidation between Fe₃O₄ and Fe₀.₉₄₇O, as shown in Fig. 2.4(d). Therefore, increasing the rate of reduction to Fe₀.₉₄₇O is critical for improving the overall performance of the process.

The experiments summarised in Fig. 2.7 demonstrate that reducing the metal oxide to Fe resulted in an initial H₂ yield ~ 4× that produced when simply reducing to Fe₀.₉₄₇O. The
additional capacity to produce hydrogen, however, decreased rapidly with increasing cycles. Eliminating such deterioration by using synthetic particles with chemical support will be investigated in Chapters 3 and 4. The drop in H\textsubscript{2} yield for pure Fe\textsubscript{2}O\textsubscript{3} reduced to Fe has subsequently been confirmed by Li \textit{et al.} (2009). The decrease in the H\textsubscript{2} produced following reduction to Fe, seems to be a result of both incomplete reduction and incomplete oxidation, as discussed with Fig. 2.6. In contrast to reducing particles to Fe, Fig. 2.5 shows that reducing iron oxide particles to Fe\textsubscript{0.947}O gave sustained levels of hydrogen for 10 cycles. Again, it should be stressed that the current particles were created from powdered Fe\textsubscript{2}O\textsubscript{3}, free from other metallic additives.

The difference in the production of H\textsubscript{2} between fully oxidising to Fe\textsubscript{2}O\textsubscript{3} versus leaving the particle at Fe\textsubscript{3}O\textsubscript{4} was marginal, as seen in Fig. 2.7. Since additional oxidation in air did not result in particles being sintered, but improved the overall process by: (i) increasing the heat generated, (ii) burning off carbon impurities and (iii) eliminating CO slip during oxide reduction, it seems that fully oxidising the metal oxide to Fe\textsubscript{2}O\textsubscript{3} would be advantageous for producing hydrogen.

One limitation of the above experiments is that a mixture of steam and N\textsubscript{2} was used to reoxidise the metal; this resulted in the produced H\textsubscript{2} being diluted with N\textsubscript{2}. Similarly, the reducing gas used was a mixture of CO, CO\textsubscript{2} and N\textsubscript{2}. For producing pure CO\textsubscript{2} and H\textsubscript{2}, an inlet stream free from any N\textsubscript{2} ballast would be required. For example, synthesis gas from a gasifier operating with inputs of coal and any combination of steam, CO\textsubscript{2} or pure O\textsubscript{2} would suffice. Actual synthesis gas from the gasification of coal or biomass will contain a mixture of CO, CO\textsubscript{2}, H\textsubscript{2} and H\textsubscript{2}O, as well as hydrocarbons, tars, sulphur compounds and other contaminants. Experiments with synthesis gas are presented in Chapter 7; however, in the current Chapter, for the sake of convenience, only mixtures of CO and CO\textsubscript{2} were considered. Addition of H\textsubscript{2}O to the reducing gas has already been shown to improve the purity of the H\textsubscript{2} produced, since the gasification of any solid carbon with H\textsubscript{2}O counteracts its deposition (Gupta \textit{et al.}, 2007).

### 2.5 Conclusions

Starting from synthesis gas, separate streams of very pure hydrogen and carbon dioxide can be produced using cyclical redox reactions with the iron oxides. The preferred cycle for the particles studied here is as follows:

1. Syngas, from coal or biomass, is reacted with Fe\textsubscript{2}O\textsubscript{3} particles; the CO in the synthesis
gas reacts with the iron oxides to give CO$_2$ of sufficient purity for sequestration. The reaction is continued until CO begins to slip from the bed, at which point the iron is in the form of Fe$_{0.947}$O or Fe$_3$O$_4$. Further reduction to metallic iron is not recommended because it gives a loss of reactivity over 10 cycles of reduction and oxidation.

2. The bed of Fe$_{0.947}$O is then purged with nitrogen to remove CO and CO$_2$.

3. Steam is then passed through the bed, giving hydrogen (< 25 ppmv CO) suitable for use in fuel cells; the particles are oxidised to Fe$_3$O$_4$.

4. The bed is further oxidised in air to Fe$_2$O$_3$, giving a usable quantity of heat and burning off any carbon deposited in step (1).

Two critical areas for improving the process involve the iron oxide carrier. Specifically, (i) iron oxide capable of undergoing repeated reduction to Fe and (ii) iron oxide with an increased rate of reduction to Fe$_{0.947}$O, which does not deteriorate with cycling, is desired.
Chapter 3

Stabilising iron oxide used for the production of hydrogen

3.1 Introduction

It is desirable to reduce Fe$_2$O$_3$ to Fe, rather than FeO, because the yield of H$_2$ per unit mass of Fe$_2$O$_3$ is 4$\times$ higher, as shown by comparing the following two reactions:

\[
3 \text{Fe} + 4 \text{H}_2\text{O}(g) \rightleftharpoons \text{Fe}_3\text{O}_4 + 4 \text{H}_2 \quad \Delta H_{1123 \text{K}}^{\circ} = -105.3 \text{ kJ/mol} \quad (3.1)
\]

\[
3 \text{FeO} + \text{H}_2\text{O}(g) \rightleftharpoons \text{Fe}_3\text{O}_4 + \text{H}_2 \quad \Delta H_{1123 \text{K}}^{\circ} = -47.4 \text{ kJ/mol} \quad (3.2)
\]

Here for simplicity, the Fe$^{2+}$ oxide is written as FeO rather than Fe$_{0.947}$O. It has already been shown in Chapter 2, Figs. 2.5-2.7, that reduction to Fe results in a decrease in the quantity of H$_2$ produced by reaction (3.1), below that obtained if FeO had been the most reduced species. In sharp contrast to reduction to Fe, reduction to FeO was shown to generate stable quantities of H$_2$ over repeated cycles, up to 10 in number, as shown in Fig. 2.5(b).

In the present Chapter, to circumvent the limitation posed by reduction to Fe, the addition of a metal oxide support to particles of iron oxide was investigated. Since iron forms chemical intermediates with most supports, e.g. FeO-Al$_2$O$_3$ with Al$_2$O$_3$, the hypothesis proposed is that choosing an additive which forms an intermediate with a higher melting temperature than that of the iron species could improve the capacity of the oxide carrier to react fully to produce a stoichiometric quantity of H$_2$ in each cycle. Table 3.1 lists the melting temperature, $T_m$, for intermediates with Si, Mg, Cr and Al, where Si was specifically chosen to give low-melting silicates for comparison. To reiterate, the iron species are defined as Fe, FeO, Fe$_3$O$_4$ and
Table 3.1: Melting points, $T_m$, in kelvin for iron species and intermediates in ascending order from left to right (Barin and Knacke, 1973). Silicates have lower melting points than iron and its oxides. The decomposition point of Fe$_2$O$_3$ at $P_{O_2} = 0.21$ is given.

<table>
<thead>
<tr>
<th>silicates</th>
<th>iron species</th>
<th>other intermediates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m$ (K)</td>
<td>FeO·SiO$_2$</td>
<td>2FeO·SiO$_2$</td>
</tr>
<tr>
<td>1413</td>
<td>1493</td>
<td>1650</td>
</tr>
<tr>
<td>2143</td>
<td>2143</td>
<td>2143</td>
</tr>
<tr>
<td></td>
<td>2143</td>
<td>2143</td>
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<td></td>
<td>2143</td>
<td>2143</td>
</tr>
</tbody>
</table>

Fe$_2$O$_3$. The proposed process outlined in Chapter 1, section 1.3 can be summarised by the following three steps:

1. Reduction of Fe$_2$O$_3$ or Fe$_3$O$_4$ in CO to generate Fe and CO$_2$.
2. Oxidation of Fe to Fe$_3$O$_4$ in steam to produce pure H$_2$.
3. Oxidation of Fe$_3$O$_4$ to Fe$_2$O$_3$ in air.

Addition of additives to iron oxide to improve their redox stability is not new. Otsuka et al. (2003) investigated the effects of 26 different additives on the redox behaviour of iron oxide prepared by co-precipitation over the temperature interval 523-823 K. The quantity of doped metal was 3 mol. % throughout their study, and cycling between Fe$_3$O$_4$ and Fe was performed with 50 vol. % H$_2$, balance Ar as the reducing gas. They found that oxides of Al, Mo and Ce stabilised the amount of hydrogen produced in each cycle. In similar experiments, Wang et al. (2008) confirmed the positive effects of 5 mol. % Mo on the reduction of impregnated Fe$_2$O$_3$ powder. Galvita et al. (2008a) developed co-precipitated iron oxide particles with a base composition of 80 wt. % Fe$_2$O$_3$, 20 wt. % Ce$_{0.5}$Zr$_{0.5}$O, which when impregnated with 2 wt. % Mo, resisted sintering and gave stable H$_2$ yields over 100 cycles at a temperature of 873 K.

This work is distinct from previous investigations in three respects. First, previous research has focused on reaction temperatures below 1000 K, while the chosen reaction temperature in this study was 1123 K to accommodate the effluent gas from a typical gasifier. Second, if the redox process is to be used to convert a carbonaceous fuel, such as coal or biomass, into hydrogen, reducing gases with significant CO content must be considered and previous investigations have performed reduction in H$_2$ only (Otsuka et al., 2003; Wang et al., 2008) or mixtures with ([CO]/[H$_2$]) $\leq$ 1/2 (Galvita et al., 2008a). Third, this work investigates the influence that oxidation in air, step 3 in the process, has on the yield of H$_2$. 
In this work, activity is defined as the number of times an overall reaction takes place per active site per unit time. If the effect of adding a second chemical species, which itself lacks significant activity, to the catalyst has a positive effect on activity, it is termed a promoter. If it has a negative effect, it is termed an inhibitor. Promoters can be distinguished based on their effect, either physical or chemical (Satterfield, 1980). Physical promoters, often termed textural promoters, typically maintain active sites by preventing the sintering of crystals. They are effectively chemically inert and so do not alter adsorption isotherms or apparent activation energies; but they can influence the pre-exponential factor. A special case of physical promotion involves using large quantities of inert with a high surface area on which an expensive catalyst is dispersed. The physical promoter is then termed a support, examples of which include alumina, silica, activated carbon or zirconia. In contrast to physical promoters, chemical promoters alter the chemical properties of the catalyst by e.g. introducing lattice defects or modifying electronic structure. Chemical promoters will change adsorption isotherms and alter apparent activation energies. Because of the complex nature of interactions between the catalyst and the promoter, it is often difficult to distinguish whether a species has a strictly physical or a chemical effect. In the following Chapter, an additive is defined as a foreign element, e.g. Si, Mg, Al or Cr. Since the quantity of additive mixed with the Fe$_2$O$_3$ was kept < 30 mol. % and since the measurements were concerned with overall conversion, rather than kinetics, the additive is referred to as a support rather than a promoter. Finally, stability is defined as the ability of a particle to produce a constant quantity of H$_2$ in each redox cycle.

The objective of this Chapter is to find a support which, with minimal loading, will enable stable quantities of H$_2$ close to those expected from the stoichiometry of reaction (3.1), to be produced over repeated cycles.

### 3.2 Thermodynamics

The high process temperature, 1123 K, and the switching between reducing and oxidising environments means that the additive, Al, Cr, Mg or Si, is not necessarily inert. The formation of intermediates, e.g. aluminates, chromates and silicates, at various partial pressures of CO and CO$_2$ was investigated using thermodynamic data published by Barin and Knacke (1973) and considering the following groups of compounds: [Al, Al$_2$O$_3$, FeO·Al$_2$O$_3$], [Cr, Cr$_2$O$_3$, FeO·Cr$_2$O$_3$], [Mg, MgO, MgO·Fe$_2$O$_3$], or [Si, SiO$_2$, FeO·SiO$_2$ and 2FeO·SiO$_2$]. Minimisation of the Gibbs free energy subject to the constraints of conservation of atomic
and molecular species was used to generate a phase diagram, Fig. 3.1(c). Here species CO, CO₂, Fe, FeO, Fe₃O₄ and Fe₂O₃ were considered separately with each group of support compounds. A detailed description of the minimisation of the Gibbs free energy is given in Appendix 1. At 1123 K, the intermediates which thermodynamically occur over the largest range of \( y_{CO_2} = (1 - y_{CO}) \), are FeO·Al₂O₃ > FeO·Cr₂O₃ > 2FeO·SiO₂, as shown in Fig. 3.1(c). The compound MgO·Fe₂O₃ is only stable in pure CO₂ and readily decomposes to MgO and Fe₃O₄ in the presence of trace amounts of CO at 1123 K. The dashed line in Fig. 3.1(a) and (c) denotes the equilibrium of the Boudouard reaction (1.18), 2CO ⇌ C(s) + CO₂, and shows that deposition of solid carbon at 1123 K and 10⁵ Pa does not occur if \( y_{CO_2} > 0.05 \). From the minimisation of Gibbs free energy, it was found that at 1123 K, carbides, e.g. Al₄C₃, Fe₃C, and Cr₄C, did not form. The compound 2FeO·SiO₂ was found to exist over a wider range of \( y_{CO_2} \) than FeO·SiO₂; therefore, only 2FeO·SiO₂ is plotted in Fig. 3.1(b) and (c). Based on thermodynamic considerations (McBride et al., 2002), the formation of CrO, CrO₂ and CrO₃, which are gaseous from 800-1400 K, will not occur. A diagram similar to Fig. 3.1, which is based on mixtures of CO₂ and CO, can be produced for the system containing H₂ and steam.

From thermodynamics, oxides of the support elements Al, Cr, Mg and Si each have distinctive characteristics at 1123 K and 10⁵ Pa which can be summarised as follows:

**FeO·Al₂O₃** During reduction, FeO·Al₂O₃ is thermodynamically stable for \( 1 \geq y_{CO_2} > 0.01 \). The FeO·Al₂O₃ will only reoxidise to Fe₂O₃ and Al₂O₃ in air, not in CO₂ or H₂O. The FeO·Al₂O₃ can be reduced to Fe and Al₂O₃ in CO or H₂. The melting temperatures of FeO·Al₂O₃ and Al₂O₃ are higher than those of the iron species.

**FeO·Cr₂O₃** During reduction, FeO·Cr₂O₃ is thermodynamically stable for \( 0.98 > y_{CO_2} > 0.14 \). The FeO·Cr₂O₃ can be reoxidised to Fe₃O₄ and Cr₂O₃ by CO₂ or H₂O and to Fe₂O₃ and Cr₂O₃ by air. The FeO·Cr₂O₃ can be reduced to Fe and Cr₂O₃ in CO or H₂. The melting temperatures of FeO·Cr₂O₃ and Cr₂O₃ are higher than those of the iron species.

**MgO·Fe₂O₃** During reduction, MgO·Fe₂O₃ is not stable, but decomposes to MgO and Fe₃O₄ in trace amounts of CO; it cannot be decomposed to Fe₂O₃ and MgO by pure CO₂ or H₂O or air. The melting temperatures of MgO·Fe₂O₃ and MgO are higher than those of the iron species.

**2FeO·SiO₂** During reduction, 2FeO·SiO₂ is thermodynamically stable for \( 0.96 > y_{CO_2} > 0.17 \);
Figure 3.1: (a) The equilibrium for the Boudouard reaction is shown as a dashed line passing through \( y_{\text{CO}_2} = 0.5 \) at 940 K. Below the line, in the shaded region, solid carbon will deposit. Above the line, in the white region, no carbon will form. (b) Thermodynamic stability of 2FeO-SiO\(_2\) in mixtures of CO and CO\(_2\) between 800 and 1400 K at 10\(^5\) Pa. The top line corresponds to the reaction: \( 3 (2\text{FeO-SiO}_2) + 2 \text{CO}_2 \rightleftharpoons 2 \text{Fe}_3\text{O}_4 + 3 \text{SiO}_2 + 2 \text{CO} \). The bottom line corresponds to the reaction: \( 2\text{FeO-SiO}_2 + 2 \text{CO} \rightleftharpoons 2 \text{Fe} + \text{SiO}_2 + 2 \text{CO}_2 \). (c) Thermodynamic stability of FeO-Al\(_2\)O\(_3\), FeO-Cr\(_2\)O\(_3\), MgO-Fe\(_2\)O\(_3\) and 2FeO-SiO\(_2\), in mixtures of CO and CO\(_2\) between 800 and 1400 K at 10\(^5\) Pa. At the experimental temperature of 1123 K, FeO-Al\(_2\)O\(_3\) is stable for \( 1 \geq y_{\text{CO}_2} > 0.01 \), FeO-Cr\(_2\)O\(_3\) for \( 0.98 > y_{\text{CO}_2} > 0.14 \) and 2FeO-SiO\(_2\) for \( 0.96 > y_{\text{CO}_2} > 0.17 \). MgO-Fe\(_2\)O\(_3\) is only stable in pure CO\(_2\), and decomposes to MgO and Fe\(_3\)O\(_4\) in trace quantities of CO.
FeO·SiO$_2$ is stable within a subset of this range. The 2FeO·SiO$_2$ can be reoxidised to Fe$_3$O$_4$ and SiO$_2$ by CO$_2$ or H$_2$O and to Fe$_2$O$_3$ and SiO$_2$ by air. The 2FeO·SiO$_2$ and FeO·SiO$_2$ can be reduced to Fe and SiO$_2$ in CO or H$_2$. Both 2FeO·SiO$_2$ and FeO·SiO$_2$ have lower melting temperatures than the iron species.

Thus, only samples with Al should be affected by oxidation with air, which will oxidise any FeO·Al$_2$O$_3$ to Fe$_2$O$_3$ and Al$_2$O$_3$. The samples with Mg will not form an intermediate species with iron of oxidation state $+2$, Fe$^{2+}$, c.f. FeO·Al$_2$O$_3$, FeO·Cr$_2$O$_3$ and 2FeO·SiO$_2$. Only samples with Si should form intermediates (2FeO·SiO$_2$ or FeO·SiO$_2$) with lower melting points than those of the iron species.

### 3.3 Experimental

The particles of iron oxide were prepared as in Chapter 2 by spraying water (Millipore Milli-Q; $> 18$ MΩ) on to Fe$_2$O$_3$ powder (Sigma-Aldrich; purity $> 99.9$ wt. %; size < 5µm) and mechanically mixing. The resulting agglomerates were heated at 1173 K for 3 h and then sieved to $d_p = +300, -425$ µm. Unlike in traditional catalysis in which an active species is deposited on an inert support, here the support was back-added to the iron oxide by wet impregnation. For the back-addition of Al, Cr, and Mg, the corresponding nitrate, Al(NO$_3$)$_3$·9H$_2$O (Fisher; $> 98$ wt. %), Mg(NO$_3$)$_2$·6H$_2$O (Acros; $> 99$ wt. %) or Cr(NO$_3$)$_3$·9H$_2$O (Acros; $> 99$ wt. %), was dissolved in 300 mL water, purified by reverse osmosis, to give a 0.05 M solution based on the moles of metal, $M$. The mole fraction of the additive was defined as:

\[
x_m = \frac{\text{mol } M}{\text{mol } M + \text{mol Fe}}.
\]  

For molar loadings of $x_m = 0.01, 0.1$ and 0.3, 2 g of Fe$_2$O$_3$ particles were placed in beakers with 5 mL, 55 mL or 115 mL of the respective 0.05 M solution. The liquid was then evaporated at 353 K (below the boiling point) until dry. All of the nitrate was deposited on the particles for $x_m = 0.01$ and 0.1; minimal nitrate residue was observed on the beakers for $x_m = 0.3$. For the addition of Si, 47 mL of ethanol (Fisher; $> 98$ wt. %) was mixed with 3.3 mL of tetraethyl orthosilicate (TEOS; Acros; $> 98$ wt. %). This solution was added dropwise over 0.5 h to 250 mL 0.2 M HCl; the resulting mixture was then stirred at 298 K for 5 h to permit the acid-catalysed hydrolysis of the TEOS. Then 2 g of Fe$_2$O$_3$ particles were added to beakers of 5 mL, 55 mL and 115 mL of this transparent solution before drying at 333 K, a lower temperature.
Table 3.2: Experimental molar loading of support, $x_m = (\text{mol } M)/(\text{mol } M + \text{mol Fe})$, determined gravimetrically. The BET surface area prior to, and after (in parentheses), 10 redox cycles (reactions 1.9, 1.10, 1.11 and 1.15, 1.16 for cycle 1; reactions 1.10, 1.11 and 1.15, 1.16 for cycles 2-10) is listed for selected samples, denoted by *. The surface area for unmodified Fe$_2$O$_3$ after 10 redox cycles was below the measurement tolerance of the instrument. The figure number corresponding to the experiment in which each sample was used is listed.

<table>
<thead>
<tr>
<th>Experimental Loading</th>
<th>Target Values</th>
<th>BET (m$^2$/g)</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_m = 0.01$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$x_m = 0.1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$x_m = 0.3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unmodified Fe$_2$O$_3 \rightleftharpoons Fe$</td>
<td>1.50 (2)</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Unmodified Fe$_2$O$_3 \rightleftharpoons FeO$</td>
<td>1.50 (0.76)</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.009</td>
<td>0.043</td>
<td>0.083*</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0125</td>
<td>0.100*</td>
<td>0.288</td>
</tr>
<tr>
<td>Cr</td>
<td>0.010</td>
<td>0.093*</td>
<td>0.272</td>
</tr>
<tr>
<td>Al</td>
<td>0.013</td>
<td>0.097*</td>
<td>0.293</td>
</tr>
</tbody>
</table>

than before to prevent boiling the ethanol. No residue of SiO$_2$ was observed on the beaker for $x_m = 0.01$ and 0.1; some residue was observed on the beaker for $x_m = 0.3$. After evaporation of the solutions to dryness, the impregnated particles were poured into crucibles and converted to a fully oxidised state by sintering in air at 1173 K for 3 h. This step decomposed any nitrate and converted chlorides to gaseous form for removal.

The experimentally-achieved loading of the support metal oxide was then determined on a mass basis by weighing the resulting particles using a balance (OHaus) with a precision of 10$^{-4}$ g and assuming that the support was present as, Al$_2$O$_3$, Cr$_2$O$_3$, MgO or SiO$_2$. Experimental loadings are listed in Table 3.2 and agree with the expected values. The Si sample loadings were below the expected values, demonstrating that not all of the Si added as TEOS was deposited and suggesting that not all of the TEOS underwent hydrolysis.

The reduction and oxidation of the modified iron oxides was performed in a packed bed reactor made from a tube (I.D. = 10 mm) of recrystallised Al$_2$O$_3$ (Multi-Lab Ltd.; > 99 wt.% purity), similar to that of stainless steel shown in Fig. 2.1. A frit made from Al$_2$O$_3$ containing 4 holes, each 1.5 mm dia., was used to support the bed. The bed was loaded by placing (i) 2 g of +1.4,-1.7 mm Al$_2$O$_3$ (Boud Mineral; > 99 wt.% purity), (ii) 2 g of +300,-425 µm Al$_2$O$_3$, (iii) modified Fe$_2$O$_3$ particles with a mass equivalent of 0.3 g Fe$_2$O$_3$ resieved to +300,-425 µm with no sand or Al$_2$O$_3$ mixed in (iv) 8 g of +1.4,-1.7 mm Al$_2$O$_3$ into the reactor. Thus for unmodified Fe$_2$O$_3$, 0.3 g of sample was introduced; for samples with additives, the total mass was greater than 0.3 g because of the presence of the additive metal oxides. A tubular furnace maintained the temperature at 1123 K in all experiments, as measured by a type K thermocouple (O.D. 36
Table 3.3: Redox cycling: gas mixtures (vol. %), flowrates (m$^3$/s) as measured at 298 K and 10$^5$ Pa and corresponding flow durations (s) for experiments with an initial charge of 0.3 g equivalent of Fe$_2$O$_3$. Reoxidation to Fe$_2$O$_3$ required air which was diluted in N$_2$. The total cycle time was 1200 s and 960 s for experiments with and without oxidation in air, respectively.

<table>
<thead>
<tr>
<th>time (s)</th>
<th>T</th>
<th>symbol</th>
<th>purge</th>
<th>reduction</th>
<th>purge</th>
<th>steam oxidation</th>
<th>purge</th>
<th>air oxidation</th>
<th>figs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-120</td>
<td>1123 K</td>
<td>▲.■.■</td>
<td>N$_2$</td>
<td>10% CO/90% N$_2$</td>
<td>N$_2$</td>
<td>75% N$_2$/25% steam</td>
<td></td>
<td></td>
<td>3.2-3.6, 3.7</td>
</tr>
<tr>
<td>120-720</td>
<td>1123 K</td>
<td>×</td>
<td>N$_2$</td>
<td>10% CO/10% CO$_2$/80% N$_2$</td>
<td>N$_2$</td>
<td>75% N$_2$/25% steam</td>
<td></td>
<td></td>
<td>3.2</td>
</tr>
<tr>
<td>720-780</td>
<td>773 K, 1123 K</td>
<td>□,○</td>
<td>N$_2$</td>
<td>10% H$_2$/90% N$_2$</td>
<td>N$_2$</td>
<td>75% N$_2$/25% steam</td>
<td></td>
<td></td>
<td>3.2-3.6</td>
</tr>
<tr>
<td>780-960</td>
<td>773 K, 1123 K</td>
<td>*</td>
<td>N$_2$</td>
<td>10% CO/90% N$_2$</td>
<td>N$_2$</td>
<td>75% N$_2$/25% steam</td>
<td>N$_2$</td>
<td>95% N$_2$/5% O$_2$</td>
<td>3.2-3.6, 3.7</td>
</tr>
<tr>
<td>960-1020</td>
<td>773 K, 1123 K</td>
<td>×</td>
<td>N$_2$</td>
<td>10% CO/90% N$_2$</td>
<td>N$_2$</td>
<td>75% N$_2$/25% steam</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1020-1200</td>
<td>773 K, 1123 K</td>
<td>×</td>
<td>N$_2$</td>
<td>10% CO/90% N$_2$</td>
<td>N$_2$</td>
<td>75% N$_2$/25% steam</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.5 mm) placed within the layer of iron oxide. Gas was supplied to the reactor as in Chapter 2; the flowrates, temperatures and compositions of inlet streams are shown in Table 3.3.

Scanning electron microscopy (SEM, a JSM-5800LV operated at 15 kV with an energy dispersive X-ray spectrometer (EDS), Oxford INCAPentaFET-×3) and X-ray diffraction (XRD, Philips model PW1830/00, Cu K$_{α}$, 40 kV and 40 mA, 0.05° per 5 s, in air at 298 K) were used to examine the morphology and composition of the particles. The specific surface area of the samples was calculated from N$_2$ adsorption isotherms (Micromeritics, Tristar 3000) using the BET model (Brunauer et al., 1938) as outlined in Appendix 2.

3.4 Results

3.4.1 Stability of unmodified Fe$_2$O$_3$

Figure 3.2 shows the total quantity of hydrogen produced during cyclic reduction and oxidation of different oxides with unmodified Fe$_2$O$_3$ as a control. The quantity of hydrogen produced was determined by integrating the mole fraction of hydrogen in the effluent gas over time and multiplying by the total molar flowrate of the gas. The theoretical quantity of hydrogen from 0.3 g of Fe$_2$O$_3$ reduced to Fe can be determined from reaction (3.1) as:

$$\frac{0.3 \text{ g}}{M_{\text{Fe}_2\text{O}_3}} \times \frac{8}{3} = 5 \text{ mmol H}_2,$$

where $M_{\text{Fe}_2\text{O}_3}$ is the molecular weight of Fe$_2$O$_3$. This value is indicated by the upper horizontal dashed line in Fig. 3.2.

From Fig. 3.2, the quantity of H$_2$ produced in each cycle by the unmodified iron oxide, pre-
Figure 3.2: Hydrogen produced per cycle over 10 cycles by Fe or FeO from the reduction of 0.3 g of 100 mol. % Fe₂O₃ at 1123 K or 773 K. The upper dashed horizontal line gives the theoretical quantity of H₂ expected, 5.0 mmol, from Fe oxidised to Fe₃O₄. The lower dashed horizontal line gives the theoretical quantity of H₂ expected, 1.25 mmol, from FeO oxidised to Fe₃O₄.

Previously reduced by 10 vol. % CO, balance N₂, decreased substantially with increasing cycles. The quantity of hydrogen produced in cycle 10 is less than 5 % of that expected. Figure 3.2 also shows the total quantity of hydrogen produced in each cycle over 10 cycles when reduction proceeds only to FeO and not to Fe. Here, reduction was performed in 10 vol. % CO, 10 vol. % CO₂, balance N₂. The H₂ produced per cycle in the experiment is stable over 10 cycles and is near the expected quantity of 1.25 mmol, predicted from stoichiometry assuming FeO was produced from the reduction of a batch of 0.3 g of Fe₂O₃. This limit of 1.25 mmol is shown by the lower horizontal dashed line in Fig. 3.2.

The yield of H₂ for unmodified iron oxide reduced to Fe in 10 vol. % H₂, balance N₂ exhibited a similar decrease to that observed for reduction to Fe in 10 vol. % CO, balance N₂, suggesting that the choice of reducing gas, either H₂ or CO, does not influence the behaviour of the unmodified Fe₂O₃. Decreasing the temperature of reduction from 1123 K to 773 K,
however, resulted in a more gradual decrease in the quantity of H₂ produced for the unmodified Fe₂O₃ sample, as seen in Fig. 3.2. The results for reduction in H₂ suggest that a thermal process, e.g. sintering, might be one cause of the loss in activity of the metal oxide. Lower temperatures could not be used for reduction in CO owing to the deposition of solid carbon via the Boudouard reaction (1.18).

The effect of including oxidation with air on the subsequent yield of hydrogen over 10 cycles is also shown in Fig. 3.2. For these experiments, samples of unmodified Fe₂O₃ were reduced to Fe in 10 vol. % CO, balance N₂ at 1123 K. Next, oxidation in steam and N₂ to produce H₂ and return the Fe to Fe₃O₄ was performed. Finally, the Fe₃O₄ was converted to its initial state, Fe₂O₃, by oxidation in air. The amount of H₂ produced by unmodified Fe₂O₃ decreases less rapidly with number of cycles than before, but is only 15 % of the expected quantity by cycle 10, below that achievable if reduction had only proceeded to FeO.

Thus, the transitions from Fe₂O₃ to Fe₃O₄ and from Fe₃O₄ to FeO do not appear to affect the repeated redox performance of the carrier; rather, the transition from FeO to Fe appears to be the critical step requiring stabilisation. The initial surface area of the unmodified Fe₂O₃, given in Table 3.2 line 1, is 1.5 m²/g. Table 3.2 line 2 demonstrates that repeated reduction to FeO results in a decrease in surface area of 50 % after 10 cycles; comparatively, all of the active surface area is destroyed, line 1, after repeated reduction to Fe in CO+N₂. It is noted that for the surface area measurements the state of the reacted iron oxide was Fe₃O₄ since reoxidation occurred in steam only, while the state of the fresh samples had been Fe₂O₃.

### 3.4.2 Stability of Fe₂O₃ supported with SiO₂, MgO, Cr₂O₃ and Al₂O₃

Next, modification of the iron oxide through the addition of $x_m = 0.01, 0.04$ or 0.08 Si was investigated. Figure 3.3 shows conversion, $X_{H_2}$, against cycle number. No correlation between the loading of Si and yield of H₂ is observed and in all cases, the quantity of H₂ produced in each cycle decreased to less 10 % of the expected value by cycle 10. Changing the reducing gas from CO to H₂ did not affect the yield of H₂, nor did oxidation in air. Thus, the addition of Si to Fe₂O₃ did not increase the yield of H₂ over the unmodified Fe₂O₃.

Figure 3.4 shows the quantity of H₂ produced against cycle number for samples of Fe₂O₃ with $x_m = 0.01, 0.1$ or 0.3 Mg. For cycle 1, quantities of H₂ near the theoretical limit are obtained in all cases. At the low loading of $x_m = 0.01$ Mg, the yield of H₂ decreased to less than 4 % of that expected by cycle 10 and offered no improvement over unmodified Fe₂O₃,
Figure 3.3: Hydrogen produced per cycle over 10 cycles by Fe from the reduction of Fe$_2$O$_3$ modified with $x_m = 0.01, 0.04$ or 0.08 Si at 1123 K. The dashed horizontal line gives the theoretical quantity of H$_2$ expected, 5.0 mmol, from Fe oxidised to Fe$_3$O$_4$.

c.f. Fig. 3.2. The quantity of H$_2$ produced increased with the molar loading, however, giving 0.2 mmol, 0.8 mmol and 3.3 mmol H$_2$ in cycle 10 for $x_m = 0.01, 0.1$ and 0.3, respectively. No difference in yield of H$_2$ was observed for reduction in CO versus H$_2$. Including oxidation in air, step 3, resulted in a slower decrease in the quantity of H$_2$ obtained, but by cycle 10 the yield of H$_2$ was similar to experiments without oxidation in air. The sample containing $x_m = 0.3$ Mg showed the most improvement in yield of H$_2$ over unmodified Fe$_2$O$_3$ and gave an average value of 3.0 mmol H$_2$ or 60 % of the expected quantity over cycles 5-10.

The quantity of H$_2$ produced against cycle number is shown in Fig. 3.5 for samples of Fe$_2$O$_3$ modified with $x_m = 0.01, 0.1$ or 0.3 Cr. In all cases, values near the theoretical limit were achieved in cycle 1. Increasing the molar loading led to increased quantities of H$_2$ in subsequent cycles. For a loading of $x_m = 0.01$, 1.7 mmol or 35 % of the expected yield, was obtained over cycles 5-10 and offered no improvement over unmodified Fe$_2$O$_3$, c.f. Fig. 3.2. The quantity of H$_2$ produced for the sample with $x_m = 0.1$ Cr decreased over cycles 1-4, but remained stable over cycles 5-10 giving ~ 35 % of the theoretical yield. For reduction in H$_2$,
Figure 3.4: Hydrogen produced per cycle over 10 cycles by Fe from the reduction of Fe$_2$O$_3$ modified with $x_m = 0.01, 0.1$ or 0.3 Mg at 1123 K. The dashed horizontal line gives the theoretical quantity of H$_2$ expected, 5.0 mmol, from Fe oxidised to Fe$_3$O$_4$. 
this kink at cycle 5 was reproduced and nearly identical yields of H₂ were obtained compared to experiments with reduction in CO, which demonstrates that the choice of reducing gas, either H₂ or CO, has little effect on the performance of the sample. Additional oxidation of the $x_m = 0.1$ Cr sample in air, step 3, slowed the decrease in the yield of H₂ observed for an identical sample oxidised in steam only; however, a prolonged improvement in the yield of H₂ was not maintained. For a loading of $x_m = 0.3$ Cr, however, stable yields of H₂ were obtained over 10 cycles, maintaining 82% of the expected quantity. Overall, the sample with $x_m = 0.3$ Cr provided the best improvement in the quantity of H₂ produced giving an average of 4.1 mmol over cycles 1-10.

Figure 3.6 shows the quantity of H₂ produced against cycle number for samples of Fe₂O₃ with $x_m = 0.01, 0.1$ or 0.3 Al. Here, the quantity of H₂ produced no longer increases with increased loading of support as was observed for Mg and Cr. Rather, the sample with $x_m = 0.3$ Al generated less H₂ than the sample with $x_m = 0.1$. Similar to previous results, however, a loading of $x_m = 0.01$ Al did not improve the yield of H₂ over that observed with unmodified
Fe$_2$O$_3$, and gave 0.2 mmol in cycle 10. For 100 mol. % Fe$_2$O$_3$ and the samples modified with Si, Mg and Cr investigated previously, the choice of the reducing gas, either CO or H$_2$, did not influence the quantity of H$_2$ produced during subsequent oxidation. Figure 3.6, however, demonstrates that reduction of samples with $x_m = 0.1$ Al in H$_2$ resulted in noticeably larger quantities of H$_2$ produced in cycle 10 compared to an identical sample reduced in CO. Also, additional oxidation in air, step 3, improved the yield of H$_2$ and permitted on average 4.7 mmol or 94 % of the theoretical value to be produced over 10 cycles. Using samples with $x_m = 0.1$ Al and including additional oxidation in air thus provided, in total, the most H$_2$ over 10 cycles of any sample tested.

![Graph](image-url)

Figure 3.6: Hydrogen produced per cycle over 10 cycles by Fe from the reduction of Fe$_2$O$_3$ modified with $x_m = 0.01, 0.1$ or 0.3 Al at 1123 K. The dashed horizontal line gives the theoretical quantity of H$_2$ expected, 5.0 mmol, from Fe oxidised to Fe$_3$O$_4$.

To confirm the effect of oxidation with air on the sample with $x_m = 0.1$ Al, Fig. 3.7 shows the quantity of H$_2$ produced over twelve cycles based on a single experiment. For cycles 1-8, oxidation was performed only in steam to return the Fe to Fe$_3$O$_4$ via step 2; for cycles 9-12 oxidation was performed in steam to return the Fe to Fe$_3$O$_4$ via step 2, followed by oxidation in a mixture of N$_2$ and air to return the Fe$_3$O$_4$ to Fe$_2$O$_3$ via step 3. An increase in the H$_2$
produced by 0.7 mmol is observed following the oxidation with air between cycles 8 and 9. This corresponds to an increase in H$_2$ of 3× that expected from the release of reactive iron previously bound as FeO-Al$_2$O$_3$ assuming that all of the Al$_2$O$_3$ had formed FeO-Al$_2$O$_3$. Further investigation of the formation of FeO-Al$_2$O$_3$ is deferred until Chapter 4.

![Graph](image)

Figure 3.7: Hydrogen produced per cycle over 12 cycles by Fe from the reduction of Fe$_2$O$_3$ modified with $x_m = 0.1$ Al at 1123 K. The sample was reduced in 10 vol. % CO, balance N$_2$ and (●) oxidised in 25 vol. % steam, balance N$_2$ only for cycles 1-8 and (○) oxidised in 25 vol. % steam, balance N$_2$, followed by 95 vol. % N$_2$, 5 vol. % O$_2$ for cycles 9-12. The dashed horizontal line gives the theoretical quantity of H$_2$ expected, 5.0 mmol, from Fe oxidised to Fe$_3$O$_4$.

The deposition of solid carbon during reduction in 10 vol. % CO, balance N$_2$ was observed. The Si samples or samples with molar loadings of 0.01 did not produce enough hydrogen to merit a study of CO contamination. For the Fe$_2$O$_3$ modified with $x_m = 0.1$ and 0.3 Al and Mg over cycles 2-10, the average quantity of CO in the effluent stream, obtained by dividing the moles of CO by the sum of the moles of CO and H$_2$ obtained during oxidation in steam, was 5000 vol. ppm. A higher CO contamination was observed in cycle 1. The average total molar quantity of CO in the effluent stream during oxidation with steam was 25000 vol. ppm for reoxidation of the samples with $x_m = 0.1$ and 0.3 Cr for cycles 2-10.

Previous work by Otsuka et al. (2003) and Wang et al. (2008) on the redox reactions of modified iron oxide has focused on iron as a storage medium for hydrogen generation in vehicles. For this application, the US Department of Energy (DOE, 2007) and International Energy Agency (IEA, 2004) list target gravimetric hydrogen storage capacities (g H$_2$/g storage
Table 3.4: Gravimetric hydrogen storage capacity, (g H\textsubscript{2})/(g Fe + g oxide support)×100 %, for the modified iron oxide samples in this work averaged over cycles 5-10. The figure number from which the H\textsubscript{2} yields were taken is listed.\textsuperscript{a}x\textsubscript{m} = 0.04 for Si, \textsuperscript{b}x\textsubscript{m} = 0.08 for Si.

<table>
<thead>
<tr>
<th></th>
<th>x\textsubscript{m} = 0.01</th>
<th>x\textsubscript{m} = 0.1\textsuperscript{a}</th>
<th>x\textsubscript{m} = 0.3\textsuperscript{b}</th>
<th>x\textsubscript{m} = 0.1\textsuperscript{a} in H\textsubscript{2}</th>
<th>x\textsubscript{m} = 0.1\textsuperscript{a} in air</th>
<th>Figure</th>
</tr>
</thead>
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<td>0.5</td>
<td>0.5</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
<td>3.3</td>
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<tr>
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<td>0.9</td>
<td>0.8</td>
<td>0.6</td>
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<td>3.4</td>
</tr>
<tr>
<td>Cr</td>
<td>0.5</td>
<td>1.6</td>
<td>3.4</td>
<td>1.8</td>
<td>2.3</td>
<td>3.5</td>
</tr>
<tr>
<td>Al</td>
<td>0.2</td>
<td>2.7</td>
<td>1.3</td>
<td>3.4</td>
<td>3.7</td>
<td>3.6</td>
</tr>
</tbody>
</table>

medium) of 6.5 wt. % and 5.0 wt. %, respectively. The theoretical production capacity of H\textsubscript{2} for Fe can be calculated from reaction stoichiometry (3.1) and is 4.8 wt. %, below both targets. Stabilising reaction (3.1) was the objective of the current study, so for comparison with previous work Table 3.4 lists the average hydrogen storage capacity for the modified samples investigated here. The storage capacity was calculated by averaging the quantity of H\textsubscript{2} produced in cycles 6-10 and considering the sample as a composite of Fe together with either Al\textsubscript{2}O\textsubscript{3}, Cr\textsubscript{2}O\textsubscript{3}, MgO or SiO\textsubscript{2}. The x\textsubscript{m} = 0.3 Cr and x\textsubscript{m} = 0.1 Al modified samples provide the best storage capacities of 3.4 wt. % and 3.7 wt. %, respectively, as seen in Table 3.4. These values are smaller than those in other work, \textit{e.g.} Wang et al. (2008), which were \textasciitilde 4.5 wt. %; however, in the present work, a significantly higher temperature was used, 1123 K vs. 873 K, and longer cycling was performed, 10 cycles vs. 5 cycles.

### 3.4.3 SEM-EDS characterisation

The distribution of the additives within the iron oxide matrix will influence the yields of H\textsubscript{2} observed. The introduction of a support should have the most beneficial effect if it can be uniformly distributed throughout the iron oxide matrix. Figure 3.8 (a) shows a SEM cross-section of a particle with x\textsubscript{m} = 0.1 of Al. The particle has a diameter of 400 \(\mu\)m, within the sieve range of +300,-425 \(\mu\)m. EDS spectra at the eight points shown by black circles give elemental mole fractions of Al = 0.03 ± 0.01, Fe = 0.36 ± 0.07 and O = 0.61 ± 0.06, in good agreement with predicted values for a sample with x\textsubscript{m} = 0.1 Al, \textit{viz.} Al = 0.04, Fe = 0.36 and O = 0.6, respectively. The EDS linescan in Fig. 3.8 (b) across the portion of the particle shown by the white horizontal line in Fig. 3.8 (a), confirms that the Al is uniformly distributed. In contrast to samples prepared from nitrate solutions, the samples with Si, prepared by the hydrolysis of tetraethyl orthosilicate in HCl solution, displayed an uneven distribution of support. Figures 3.8 (c) and (d) show SEM-EDS results for a particle with x\textsubscript{m} = 0.08 Si and a diameter
of 420 µm after calcination in air at 1173 K. A larger mole fraction of Si near the exterior is observed.

Figure 3.8: (a) Cross-section of a particle of Fe₂O₃ modified with xₘ = 0.1 Al prior to reaction. Elemental analysis (EDS) at eight points corresponding to the black circles gave mole fractions of Al, Fe and O of 0.03 ± 0.01, 0.36 ± 0.07 and 0.61 ± 0.06; in agreement with predicted values for xₘ = 0.1 Al of 0.04, 0.36 and 0.6 respectively. (b) EDS scans corresponding to the white cross-sectional line in (a) confirming the uniform distribution of Al throughout the sample. (c) SEM cross-section of Fe₂O₃ modified with xₘ = 0.08 Si prior to reaction. (d) EDS analysis of points 1-3 in (c) showing decreasing Si loading towards the interior.

### 3.4.4 X-ray diffraction

Figure 3.9 shows X-ray diffraction patterns for the Fe₂O₃ modified with Al, Cr, Mg and Si at different stages of the reduction cycle: (a) after reduction in 10 vol. % CO, balance N₂, (b) after reduction in 10 vol. % CO, 10 vol. % CO₂ balance N₂, (c) after reoxidation in 25 vol. % steam, balance N₂, and (d) prior to any reduction or reoxidation. The predicted phase of the iron for each image, (a) Fe, (b) FeO, (c) Fe₃O₄ or (d) Fe₂O₃, is also given and was taken from
Figure 3.9: X-ray diffraction spectra of samples of Fe$_2$O$_3$ modified with $x_m = 0.1$ Al, Cr and Mg and with $x_m = 0.08$ Si (a) after reduction with 10 vol. % CO, balance N$_2$ with Fe as reference; (b) after reduction with 10 vol. % CO, 10 vol. % CO$_2$, balance N$_2$ with FeO as reference; (c) after reoxidation with steam with Fe$_3$O$_4$ as reference; (d) prior to experiments after sintering in air at 1173 K with Fe$_2$O$_3$ as reference. Peaks corresponding to 2FeO-SiO$_2$ ($\Delta$), MgO (■), FeO-Cr$_2$O$_3$ (◇) and MgO-Fe$_2$O$_3$ (□) are identified.

In Fig. 3.9 (a), the expected state of the Si is SiO$_2$; however experimentally, 2FeO-SiO$_2$ was detected. If the time of reaction is not sufficiently long, species other than those predicted from equilibrium might arise and could be the reason for the observation of 2FeO-SiO$_2$. Neverthe-
less, the formation of $2\text{FeO} \cdot \text{SiO}_2$ is confirmed. The intermediate $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ in Fig. 3.9(b) is also in agreement with the thermodynamic predictions of section 3.2. Peak broadening is observed and is most pronounced for Figs. 3.9 (b) and (c). A decrease in the crystallite size below approximately 1 $\mu$m or strain in the crystal lattice could cause broadening of the X-ray diffraction peaks. Overall, the XRD analysis confirms that the support additive cannot be considered inert.

### 3.5 Discussion

Studies of the production of hydrogen using the redox reactions of iron oxide (Otsuka et al., 2003; Wang et al., 2008; Galvita et al., 2008a) have demonstrated that the stability of the iron carrier when reduced fully to Fe, even at temperatures below 1000 K, is an obstacle. Figure 3.2 showed that the capacity of the unmodified $\text{Fe}_2\text{O}_3$ to produce $\text{H}_2$ was specifically impaired by the transition from FeO to Fe, since: if FeO was the most reduced form of the oxide, stable yields of $\text{H}_2$ over 10 cycles were obtained; while if Fe was the most reduced form, decreasing yields of $\text{H}_2$ were observed over successive cycles.

The effect of reduction to Fe on decreasing the yield of $\text{H}_2$ can partially be explained by considering molar volumes. The molar density, $M_V$, for each iron species can be calculated using its mass density (kg/m$^3$) and molecular weight (kg/kmol) $^1$, giving 32.6, 22.2, 84.2 and 136.1 kmol/m$^3$ for $\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$, FeO and Fe, respectively. Considering molecular formulae, reduction from $\text{Fe}_2\text{O}_3$ to $\text{Fe}_3\text{O}_4$ will result in no change of the Fe molar density since 1 kmol $\text{Fe}_2\text{O}_3$ (1/32.6 = 0.031 m$^3$) gives 2/3 kmol $\text{Fe}_3\text{O}_4$ occupying 2/(3 × 22.2) = 0.030 m$^3$; reduction from $\text{Fe}_3\text{O}_4$ to FeO will result in a 20 % increase in the Fe molar density; reduction from FeO to Fe will result in a 70 % increase in the molar density. Thus, while the actual particle may not vary in diameter, contraction of the iron lattice as oxygen is removed during reduction will be most severe for the transition between FeO and Fe. The addition of additives would alleviate changes in molar volume. Assuming $\text{FeO} \cdot \text{Al}_2\text{O}_3$, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, MgO and $2\text{FeO} \cdot \text{SiO}_2$ form and do not decompose (this assumption only holds over specific $\gamma\text{CO}_2$ values and is thermodynamically reasonable), reduction from FeO to Fe with of $x_m = 0.1$ Al, Cr, Mg or Si, will result in a 52, 51, 60 and 43 % increase in the molar density of Fe, respectively, compared to 70 % in the unmodified sample.

$^1$The specific gravities used are $\text{Fe}_2\text{O}_3$, 5.2; $\text{Fe}_3\text{O}_4$, 5.15; FeO, 5.8; Fe, 7.6; $\text{Al}_2\text{O}_3$, 4.0; $\text{Cr}_2\text{O}_3$, 5.21; MgO, 3.58; SiO$_2$, 2.63; $\text{FeO} \cdot \text{Al}_2\text{O}_3$, 3.95; $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, 4.79; $2\text{FeO} \cdot \text{SiO}_2$, 4.39.
Considering each additive separately, the samples with Si did not improve the yields of H\(_2\) compared to unmodified Fe\(_2\)O\(_3\), as seen from comparing Figs. 3.2 and 3.3. The rapid decrease in the yield of H\(_2\) produced after cycle 1 might be attributable to the formation of the silicates, FeO-SiO\(_2\) and 2FeO-SiO\(_2\), which have melting temperatures \(~\)200 K below that of the iron species or to the uneven coverage of the Si support, which was shown in Fig. 3.8(c)-(d). The presence of 2FeO-SiO\(_2\) was confirmed by X-ray diffraction, as shown in Fig. 3.9. Low melting silicates would increase lattice mobility (3D) and surface atom mobility (2D), since they have lower Tammann and H"uttig temperatures, given by 0.3\(\,T_m\) and 0.5\(\,T_m\), respectively (Satterfield, 1980; Ertl et al., 1999). Hence, the rate of morphological changes would be increased in the Fe\(_2\)O\(_3\) modified with Si, compared to the unmodified Fe\(_2\)O\(_3\), and could lead to a reduction in active surface area. The formation of 2FeO-SiO\(_2\) is known to occur during reduction and oxidation of mixtures of Fe\(_2\)O\(_3\) and SiO\(_2\) (Lund and Dumesic, 1981; Zhang et al., 2006). Additionally, in iron-silicon alloys with loadings between 0.09 < \(x_m\) < 0.33 Si, oxidation can result in the formation of an external SiO\(_2\) film which considerably inhibits observed rates of reaction (Adachi and Meier, 1986). Overall, experiments demonstrate that Si is not suitable as support for iron oxide undergoing repeated redox cycling.

Figure 3.4 showed that as the MgO content in the sample increased, the amount of H\(_2\) produced increased towards the theoretically expected quantity. However, in the best case shown in Fig. 3.4 with \(x_m\) = 0.3 Mg, yields of H\(_2\) equivalent to only 60 % of the theoretical quantity over cycles 5-10 were obtained; Mg is not a suitable support for the proposed process.

Figure 3.5 demonstrated that as the quantity of Cr added to the sample increased, yields of H\(_2\) also increased towards the theoretical limit. If the assumption is made that only the Fe capable of forming the intermediate FeO-Cr\(_2\)O\(_3\) is stabilised and all the remaining Fe is inactive due to \(e.g.\) sintering, stoichiometry dictates that for loadings of \(x_m\) = 0.1 and 0.3, the expected stable quantity of H\(_2\) produced would be 0.25 and 0.75 mmol H\(_2\), respectively. Instead, from Fig. 3.5, averaging the H\(_2\) produced in cycles 5-10 gives 1.7 mmol and 4.0 mmol, a factor 5 – 7\(\times\) higher. Hence, the Cr has a much larger effect than simply stabilising the iron sample through the formation of FeO-Cr\(_2\)O\(_3\). Additional production of H\(_2\) through the reaction of Cr, which itself has several oxides, \(e.g.\) CrO, CrO\(_2\) and CrO\(_3\), was not found to be possible at 1123 K and 10\(^5\) Pa owing to thermodynamic constraints. Fe\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) are known to form continuous solid solutions at high temperature (Birks et al., 2006). Also, FeO-Cr\(_2\)O\(_3\) spinel forms solid solutions with Fe\(_3\)O\(_4\). Thus, some mixing of lattice Cr and Fe will occur during the redox cycling and could help prevent sintering. While the addition of Cr increased
the yield of H₂, it was not able to offer as significant an improvement as Al.

Results from the samples supported with Al showed that, unlike for those with Mg and Cr, increasing the content of Al did not always improve the yield of H₂. The sample with \( x_m = 0.3 \) Al gave lower yields of H₂ than that with \( x_m = 0.1 \) Al, as shown in Fig. 3.6. Since the aluminate, FeO-Al₂O₃, is stable for \( y_{CO_2} > 0.01 \) (Fig. 3.1), any Al in the sample will bind Fe as FeO-Al₂O₃ and prevent it from undergoing repeated redox cycles. Increased Al loadings would therefore mean that more iron is bound as aluminate and unavailable for the generation of H₂. The optimum Al loading will therefore be a tradeoff between having enough Al for support and maintaining free Fe for reaction. The current experiments suggest that this value lies in the range 0.01 < \( x_m < 0.3 \) for particles prepared by the back-addition of Al using wet impregnation. The positive effect of Al addition on the yield of H₂ can be explained by considering the Fe-Al-O system. Fe₂O₃ and Al₂O₃ are known to form solid solutions of up to 27 mol % Al₂O₃ in Fe₂O₃ and of up to 9 mol % Fe₂O₃ in Al₂O₃ (Popović et al., 1995). Additionally, at high temperature FeO-Al₂O₃ spinel readily forms solid solutions with Fe₃O₄. Therefore, some diffusion, i.e. mixing, of lattice Al and Fe will occur during redox cycling and could help prevent sintering. From the literature, the addition of Al appears to stabilise iron by the formation of dispersed islands of FeO-Al₂O₃ (Topsøe et al., 1973); the formation of FeO-Al₂O₃ will be investigated further in Chapter 4.

Overall, Figs. 3.3-3.6 demonstrated that the choice of reducing gas, either CO or H₂, had little influence on the quantity of H₂ produced for samples of \( x_m = 0.1 \) Si, Mg or Cr. Only the sample with \( x_m = 0.1 \) Al produced higher yields of H₂ when the reducing gas was H₂. The ratio of measured BET surface area after, and prior to, 10 redox cycles was largest for \( x_m = 0.1 \) Al and equal to 0.43/3.96 = 0.11, as calculated from Table 3.2. Thus, Al maintains active surface area. Comparing results from the tenth cycle in Figs. 3.3-3.6, the additional oxidation in air had the most noticeable effect on the yield of H₂ for the sample containing Al. From thermodynamics, oxidation in air will decompose any FeO-Al₂O₃ to Fe₂O₃ and Al₂O₃. This release of reactive iron, which has the potential to participate in the subsequent redox cycle, could explain the increased yields of H₂ observed.

### 3.6 Conclusions

The effect of the addition of Al, Cr, Mg and Si to iron oxide undergoing repeated redox reactions for the generation of H₂ was investigated in a packed bed reactor at 1123 K. Metal
additives, which (i) formed an intermediate with a higher melting temperature than the iron species involved and (ii) formed an intermediate which decomposed either during reduction or oxidation to release reactive iron, improved the yield of H₂. Si did not improve yields of H₂ at any loading between 1 and 8 mol %, probably owing to the formation of low melting point silicates and also because SiO₂ was difficult to evenly distribute throughout the particle via the hydrolysis of tetraethyl orthosilicate. For Mg, the H₂ yields increased as the loading increased from 1 to 30 mol % Mg. Addition of Cr also increased the amount of H₂ produced, with quantities of H₂ near the theoretical limit for 30 mol % Cr. The presence of Cr facilitated the formation of FeO-Cr₂O₃, an intermediate with a high melting temperature. Addition of Al up to 10 mol % increased the quantity of H₂ produced; a sample with 30 mol % Al, however, showed lower yields of H₂ compared to one with 10 mol % Al. Unlike for samples with Cr, Mg and Si, oxidation in a mixture of air and N₂ had a marked effect on samples impregnated with Al, presumably owing to the release of reactive iron during decomposition of FeO-Al₂O₃ to Fe₂O₃ and Al₂O₃. The Fe₂O₃ modified with \( x_m = 0.1 \) Al and \( x_m = 0.3 \) Cr investigated in this study can maintain stable yields of H₂ over 10 cycles at a temperature of 1123 K, and are the most promising candidates for H₂ production using the redox reactions of modified iron oxide. Overall, Al provided the best improvement in H₂ yields over unmodified Fe₂O₃ for reduction to Fe at 1123 K. Surprisingly, the back-addition of a small quantity of Al support, 10 mol %, permitted stable quantities of H₂, near the theoretical limit, to be generated over 10 redox cycles.
Chapter 4

Development of iron oxide carriers using the sol-gel process

4.1 Introduction

Conventional methods for preparing mixed metal oxides do not always produce materials with both (i) a high, internal surface area and (ii) homogeneously-mixed components on the molecular scale. For example, co-precipitation does not always favour homogeneity because hydroxides of different metallic cations generally do not precipitate at the same pH. Mechanically-mixed oxides usually do not have high surface areas and suffer from inhomogeneities of the mixed materials (Ward and Ko, 1995). The sol-gel method has received much attention in catalysis (Ertl et al., 1999; Brinker and Scherer, 1989) because it allows the homogenous mixing of components almost at the molecular level as well as the control of pore structure and surface area using a low temperature synthesis. While limited research on Ni-based (Ishida and Jin, 1996; Zhao et al., 2008) oxygen carriers prepared using a sol-gel technique exists, only recently have similar Fe-based (Li et al., 2009) oxygen carriers been investigated for chemical looping combustion.

A complete introduction to sol-gel theory is given in Brinker and Scherer (1989). Briefly, a colloid is defined as a suspension where the dispersed phase is so small (~ 1 – 1000 nm) that gravitational forces are negligible. A sol is defined as a colloidal suspension of solid particles. Sol-gel chemistry relies on two reactions: hydrolysis and condensation.

Starting with a molecule containing a trivalent metal and using M to denote the metal, R
an alkyl group, OR an alkoxy group and ROH an alcohol, hydrolysis proceeds according to

\[ \text{M(OR)}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HO} - \text{M(OR)}_2 + \text{ROH}. \tag{4.1} \]

Metal alkoxides are preferred precursors for sol-gel chemistry because they readily react with water. If all of the OR groups in the M(OR)_3 reacted to form M(OH)_3, the metal would be fully hydrolysed. Fully or partially hydrolysed molecules can bond via condensation:

\[ (\text{OR})_2\text{M} - \text{OH} + \text{HO} - \text{M(OR)}_2 \rightleftharpoons (\text{OR})_2\text{M} - \text{O} - \text{M(OR)}_2 + \text{H}_2\text{O} \tag{4.2} \]

\[ (\text{OR})_2\text{M} - (\text{OR}) + \text{HO} - \text{M(OR)}_2 \rightleftharpoons (\text{OR})_2\text{M} - \text{O} - \text{M(OR)}_2 + \text{ROH}. \tag{4.3} \]

The metallic species on the right hand side of reactions (4.2) and (4.3) are polymers. A gel is defined (Brinker and Scherer, 1989) as a continuous solid chain of polymers encapsulating a continuous liquid phase and is formed when a polymer grows to the dimensions of the solution, e.g. the size of the containing beaker. Drying a gel in air will produce a xerogel; supercritical drying, which eliminates capillary pressure and gel shrinkage, will produce an aerogel (Brinker and Scherer, 1989).

The most common support for Fe_2O_3 for chemical looping applications is Al_2O_3 and Chapter 3 has already shown that the addition of Al_2O_3 to iron oxide permits stable quantities of H_2 to be produced over 10 cycles even when the iron oxide is reduced fully to Fe. Table 4.1 gives a summary of some composite particles of Fe_2O_3 and Al_2O_3 used in the literature and the corresponding preparation method and reference. While methods of preparation range from the mechanical mixing of oxide powders (Ishida et al., 2005) to drying aqueous solutions of Fe and Al nitrate precursors (Jin et al., 1999; Ishida et al., 1998), a single weight ratio of 60 wt. % Fe_2O_3 and 40 wt. % Al_2O_3 is typically used. Other supports for Fe_2O_3 include ZrO_2 (Mattisson et al., 2004; Adánez et al., 2004; Galvita et al., 2008b), TiO_2 (Mattisson et al., 2004; Ishida et al., 1998; Jin et al., 1999; Adánez et al., 2004), MgO (Jin et al., 1999), MgAl_2O_4 (Mattisson et al., 2004) and yttria-stabilised zirconia (YSZ) (Ishida et al., 1998). Notably, SiO_2 is unsuitable, owing to the formation of unreactive silicates with low melting points, shown in Chapter 3.

The objective of this study is to compare the performance of pure Fe_2O_3 carriers made by mechanical mixing with composite xerogels of Fe_2O_3 and Al_2O_3 made using a sol-gel method, especially with respect to the ability to be reduced completely to Fe over ~ 40 cycles.
Table 4.1: Table summarising Fe$_2$O$_3$ and Al$_2$O$_3$ composite carriers used in chemical looping combustion. Preparation methods include: mechanical mixing of powders of Fe$_2$O$_3$ and Al$_2$O$_3$, freeze granulation of mechanically-mixed oxide powders, mixing aqueous solutions of iron and aluminum nitrates, and wet-impregnation of γ-Al$_2$O$_3$ support. The final composition of the oxygen carrier is listed as the weight percent of Fe$_2$O$_3$ after calcination; the remaining mass fraction is Al$_2$O$_3$. The crushing stress is given for the fresh oxygen carrier.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Preparation</th>
<th>Composition (wt. % Fe$_2$O$_3$)</th>
<th>Calcining Temp</th>
<th>Time</th>
<th>Crushing Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li et al. (2009)</td>
<td>sol-gel</td>
<td>60 %</td>
<td>1173 K</td>
<td>12 h</td>
<td>10</td>
</tr>
<tr>
<td>Ishida et al. (2005)</td>
<td>mech. mix</td>
<td>25 %</td>
<td>1073 K</td>
<td>10 h</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Fe$_2$O$_3$, Al$_2$O$_3$</td>
<td></td>
<td>1643 K</td>
<td>10 h</td>
<td>54</td>
</tr>
<tr>
<td>Jin et al. (1999)</td>
<td>dissolution Fe(NO$_3$)$_3$·9H$_2$O, Al(NO$_3$)$_3$·6H$_2$O</td>
<td>60 %</td>
<td>1573 K</td>
<td>6 h</td>
<td>44.3</td>
</tr>
<tr>
<td>Ishida et al. (1998)</td>
<td>mech. mix &amp; freeze granulation</td>
<td></td>
<td>1573 K</td>
<td>6 h</td>
<td>44.3</td>
</tr>
<tr>
<td>Mattsson et al. (2004)</td>
<td>mech. mix &amp; freeze granulation</td>
<td></td>
<td>1373 K</td>
<td>6 h</td>
<td>18</td>
</tr>
<tr>
<td>Mattsson et al. (2004)</td>
<td>Fe(NO$_3$)$_3$·9H$_2$O impregnated γ-Al$_2$O$_3$</td>
<td>22 %</td>
<td>1373 K</td>
<td>6 h</td>
<td>167</td>
</tr>
<tr>
<td>Adánez et al. (2004)</td>
<td>mech. mix &amp; 10 wt. % graphite for pores</td>
<td></td>
<td>80 %</td>
<td>1373/1573 K</td>
<td>6 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 %</td>
<td>1373/1573 K</td>
<td>6 h</td>
<td>5/25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40 %</td>
<td>1373/1573 K</td>
<td>6 h</td>
<td>5/29</td>
</tr>
</tbody>
</table>

4.2 Experimental

Oxygen carriers with different mass ratios of Fe$_2$O$_3$ and Al$_2$O$_3$ (60:40, 80:20, 90:10 wt./wt.) were prepared using the Yoldas sol-gel process (Yoldas, 1975). In a typical synthesis, aluminium isopropoxide (Acros Organics; > 98 wt. % purity) was added to water which had been purified by reverse osmosis and heated to 348 K; the mixture was allowed to hydrolyse slowly for 2 h with constant stirring. The resulting slurry was peptised with nitric acid (Fisher; 70 wt. %, diluted). In all syntheses, the molar ratio between Al$^3+$, water and H$^+$ was constant and equal to 0.5:50:0.07. The temperature was then raised to 363 K and the sol was refluxed for 12 h. Subsequently, the appropriate amount of Fe(NO$_3$)$_3$·9H$_2$O (Acros Organics, > 98 wt. % purity) dissolved in water at 363 K to obtain a ~ 1 M aqueous solution was added. The resulting slurry was refluxed for another 12 h at 363 K, followed by cooling to room temperature. The encapsulated solvents were removed by drying the gel in an oven at 373 K overnight. The resulting xerogel was calcined for 3 h at 1173 K and then sieved to +300,-425 µm.

For comparison, particles of unmodified iron oxide were prepared as in Chapter 2 by spraying water on to Fe$_2$O$_3$ powder (Sigma-Aldrich, purity > 99.9 wt. %, size < 5 µm) and mechanically mixing. The resulting agglomerates were sintered for 3 h at 1173 K and then sieved to $d_p = +300,-425$ µm. Table 4.2 shows results of the BET surface area and mean pore diameter, $\bar{d}_{pore}$, for mechanically-mixed Fe$_2$O$_3$ particles and particles prepared by the sol-gel
Table 4.2: Measured BET surface area, BJH pore volume, mean pore diameter and crushing stress after calcination and prior to reaction for the 60, 80 and 90 wt. % Fe$_2$O$_3$ oxygen carriers prepared using the sol-gel process; 100 wt. % Al$_2$O$_3$ prepared using the sol-gel process; and unmodified Fe$_2$O$_3$ prepared by mechanical mixing. Determination of the crushing stress involved particles of diameter +1700,-2060 µm; all other characterisations involved particles of diameter +300,-425 µm.

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Composition</th>
<th>BET (m$^2$/g)</th>
<th>BJH (cm$^3$/g)</th>
<th>$d_{pore}$ (nm)</th>
<th>Calcining Temp</th>
<th>Time (h)</th>
<th>Crushing Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sol-gel</td>
<td>60 wt. % Fe$_2$O$_3$, 40 wt. % Al$_2$O$_3$</td>
<td>15.5</td>
<td>0.09</td>
<td>24</td>
<td>1173 K</td>
<td>3</td>
<td>0.2</td>
</tr>
<tr>
<td>sol-gel</td>
<td>80 wt. % Fe$_2$O$_3$, 20 wt. % Al$_2$O$_3$</td>
<td>8.5</td>
<td>0.06</td>
<td>27</td>
<td>1173 K</td>
<td>3</td>
<td>0.6</td>
</tr>
<tr>
<td>sol-gel</td>
<td>90 wt. % Fe$_2$O$_3$, 10 wt. % Al$_2$O$_3$</td>
<td>10.5</td>
<td>0.06</td>
<td>22</td>
<td>1173 K</td>
<td>3</td>
<td>0.3</td>
</tr>
<tr>
<td>sol-gel</td>
<td>100 wt. % Al$_2$O$_3$</td>
<td>168</td>
<td>0.35</td>
<td>6</td>
<td>1173 K</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>sol-gel</td>
<td>100 wt. % Al$_2$O$_3$</td>
<td>299</td>
<td>0.40</td>
<td>4</td>
<td>773 K</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>mech. mix</td>
<td>100 wt. % Fe$_2$O$_3$</td>
<td>1.5</td>
<td>0.00</td>
<td>7</td>
<td>1173 K</td>
<td>3</td>
<td>3.3</td>
</tr>
</tbody>
</table>

process, both dried in an oven at 373 K, followed by calcination at typically 1173 K.

The reduction and oxidation of the oxygen carrier was performed in the apparatus described in Chapter 3. The temperature of the packed bed was maintained at 1123 K in all experiments, as measured by a type K thermocouple inside the bed. The total mass of particles added to the bed was 0.3 g in all cases. The composition of the effluent gas was measured using identical analysers in the same arrangement as in Chapter 2, section 2.2. The flowrates, compositions of the inlet gases and cycle times for each experiment are listed in Table 4.3.

For a sphere subjected to a force, $F_z$, on opposite sides of a diameter, the crushing stress was calculated from the empirical relation:

$$\sigma_T = k_F \frac{F_z}{R^2},$$  \hspace{1cm} (4.4)

where $\sigma_T$ is the crushing stress (Pa), $F_z$ is the applied force (N), $R$ is the sphere’s external radius (m), and $k_F$ is a dimensionless constant with a typical value of $k_F = 0.22$ (Jaeger, 1967; Ishida et al., 2005). The average value of the crushing stress, $\sigma_T$, was determined (Stable Micro Systems, TA-XT2 Texture Analyser with a 5 kg load cell) using 20 separate particles with $R = 950$ µm, omitting the maximum and minimum value, and is reported in Table 4.2. Since many authors report crushing force (N) rather than stress (N/m$^2$), some calculations were necessary. For example, the crushing stress for oxygen carriers from Mattisson et al. (2004) was calculated using Eq. (4.4) with a particle radius of 112 µm and using their reported breakage forces for particles calcined at 1373 K and 1573 K of 1 N and 9.5 N, respectively, given in Fig. 5 of Mattisson et al. (2004). Abad et al. (2007) used an identical oxygen carrier.
Table 4.3: Redox cycling: gas mixtures (vol. %), flowrates as measured at 298 K and 10^5 Pa, and corresponding flow durations for experiments with an initial charge of 0.3 g of oxygen carrier. Reoxidation to Fe₂O₃ required air. The total cycle time was 20 min and 16 min for experiments with and without oxidation in air.

<table>
<thead>
<tr>
<th>time (s)</th>
<th>purge</th>
<th>reduction</th>
<th>purge</th>
<th>oxidation</th>
<th>purge</th>
<th>oxidation</th>
<th>Figs.</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-120</td>
<td>3.3 × 10⁻⁵</td>
<td>3.3 × 10⁻⁵</td>
<td>3.3 × 10⁻⁵</td>
<td>3.3 × 10⁻⁵</td>
<td>3.3 × 10⁻⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120-720</td>
<td>3.3 × 10⁻⁵</td>
<td>3.3 × 10⁻⁵</td>
<td>3.3 × 10⁻⁵</td>
<td>3.3 × 10⁻⁵</td>
<td>3.3 × 10⁻⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>720-780</td>
<td>8.33 × 10⁻⁵</td>
<td>H₂O(l)</td>
<td>N₂</td>
<td>10% CO/10% CO₂/80% N₂</td>
<td>N₂</td>
<td>75% N₂/25% steam</td>
<td>4.2, 4.3, 4.4</td>
<td>▲, ▪, □, ♦</td>
</tr>
<tr>
<td>780-960</td>
<td>960-1020</td>
<td>N₂</td>
<td>75% N₂/25% steam</td>
<td>N₂</td>
<td>75% N₂/25% steam</td>
<td>4.2, 4.3, 4.4</td>
<td>▲, ▪, □, ♦</td>
<td></td>
</tr>
<tr>
<td>1020-1200</td>
<td>N₂</td>
<td>air</td>
<td>N₂</td>
<td>air</td>
<td>4.2, 4.3, 4.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A field emission scanning electron microscope (FESEM, JSM-6340F) operated at 5 kV was used to obtain high resolution images of the morphology of the oxygen carriers prior to the redox experiments. X-ray diffraction (XRD, Philips model PW1830/00, Cu Kα, 40 kV and 40 mA, 0.01° s⁻¹, receiving and anti-scatter slits 1°, divergence slit 0.3 mm, in air at 298 K) was used to detect the presence of FeO·Al₂O₃. The specific surface area of the samples was calculated from N₂ adsorption isotherms (Micromeritics, Tristar 3000) using the BET model (Brunauer et al., 1938); the cumulative pore volume for pores between 1.7 and 200 nm in diameter was estimated using the BJH model (Barrett et al., 1951), as described in Appendix 2.

4.3 Results

4.3.1 SEM characterisation

Prior to any redox experiments, the morphology of the oxygen carriers was investigated using scanning electron microscopy for (a) the unmodified Fe₂O₃ particles prepared by mechanical
Figure 4.1: Field emission scanning electron microscope (FESEM) images of (a) the unmodified Fe$_2$O$_3$ prepared by mechanically mixing and (b) a 60 wt. % Fe$_2$O$_3$, 40 wt. % Al$_2$O$_3$ carrier prepared using the sol-gel process. The particles are shown in their fully oxidised state after calcining at 1123 K for 3 h and prior to any reaction. A difference in grain size is noticeable; the scale bars in each figure are of equal length, 100 nm.

mixing and (b) the 60 wt. % Fe$_2$O$_3$, 40 wt. % Al$_2$O$_3$ particles prepared using the sol-gel method, as shown in Figure 4.1. The important difference between these images is the disparity in the size of the individual grains. Unmodified Fe$_2$O$_3$ has grains with an average diameter of 500 nm, while the sol-gel carrier has grains with an average diameter of 80 nm, nearly one order of magnitude smaller. This difference in grain size translates into a similar order of magnitude difference in specific surface areas, as shown in Table 4.2. The morphological difference between these two samples could contribute towards the difference in conversion discussed later.

### 4.3.2 Stability of unmodified Fe$_2$O$_3$

To quantify the ability of the oxygen carrier to produce H$_2$ over repeated redox cycles, a conversion was defined as:

$$X_{H_2} = \frac{m_{H_2}}{x_w m_{ox}} \cdot \left( \frac{M_{Fe_2O_3}}{M_{H_2}} \cdot \frac{3}{8} \right) \approx \frac{m_{H_2}}{x_w m_{ox}} \cdot 30,$$

where $m_{H_2}$ is the mass of the H$_2$ produced, $m_{ox}$ is the mass of the fully oxidised carrier as Fe$_2$O$_3$ and Al$_2$O$_3$, $x_w$ is the mass fraction of Fe$_2$O$_3$ in the fully oxidised carrier and $M_{Fe_2O_3}$ and $M_{H_2}$ are the molecular weights of Fe$_2$O$_3$ and H$_2$, respectively. Here it is noted that the loading of Al$_2$O$_3$ is reported as a mass % rather than a mole % as done in Chapter 3; also the quantity of H$_2$ produced is reported as a conversion, rather than an absolute molar quantity.
Figure 4.2: (a) Measured conversion, $X_{H_2}$, as a function of cycle number for the mechanically-mixed oxygen carrier reacted at 1123 K. (b) Measured conversion, $X_{H_2}$, as a function of cycle number for the oxygen carriers produced by the sol-gel method, reacted at 1123 K. A conversion of $X_{H_2} = 1$ represents the theoretical quantity of $H_2$ expected from oxidation of Fe to Fe$_3$O$_4$ in steam, as shown by the right hand ordinate; the theoretical conversion, $X_{H_2}$, for oxidation of FeO to Fe$_3$O$_4$ is also indicated.

Initially, 10 redox cycles with 0.3 g of the unmodified Fe$_2$O$_3$ oxygen carrier were performed at 1123 K. Figure 4.2(a) shows $X_{H_2}$ versus cycle number. Reduction to FeO in a mixture of 10 vol. % CO, 10 vol. % CO$_2$, balance N$_2$ resulted in stable quantities of $H_2$, near that predicted from stoichiometry (reaction 1.16), being produced during subsequent oxidation with steam, regardless of whether samples were oxidised in steam or a sequence of steam and air. In contrast to reduction to FeO, for unmodified Fe$_2$O$_3$ reduced to Fe, $X_{H_2}$ drops to 0.1 by cycle 2 and 0.03 by cycle 10. If additional oxidation in air, reaction (1.17), is performed to return the oxide to Fe$_2$O$_3$, this drop is less precipitous; however, Fig. 4.2 shows that even in this case a low conversion of $X_{H_2} = 0.1$ is obtained by cycle 10. Thus, for repeated produc-
tion of H\textsubscript{2} it seems preferable to reduce unmodified Fe\textsubscript{2}O\textsubscript{3} only to FeO, since by cycle 10, experiments involving reduction to FeO generated higher quantities of H\textsubscript{2} than experiments involving reduction to Fe.

4.3.3 Stability of composites of Fe\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} prepared using the sol-gel process

Next, reduction of the sol-gel oxygen carriers with $x_{w} = 0.6, 0.8$ and 0.9 Fe\textsubscript{2}O\textsubscript{3}, balance Al\textsubscript{2}O\textsubscript{3} was performed at 1123 K; the Fe\textsubscript{2}O\textsubscript{3} was reduced completely to Fe. Figure 4.2(b) demonstrates that the production of H\textsubscript{2} using the redox of iron oxides is promising for sol-gel derived carriers with 80 and 90 wt. % Fe\textsubscript{2}O\textsubscript{3} over 10 cycles, with conversions of $X_{H_2} \approx 0.9$. Open symbols represent experiments where oxidation was performed with 25 vol. % steam, balance N\textsubscript{2} only, i.e., reaction (3.1); filled symbols represent experiments where oxidation was performed in 25 vol. % steam, balance N\textsubscript{2}, reaction (3.1), followed by oxidation in air, reaction (1.17), to Fe\textsubscript{2}O\textsubscript{3}. In Fig. 4.2(b) for particles with 60 wt. % Fe\textsubscript{2}O\textsubscript{3}, the observed conversion is lower than the value predicted from stoichiometry in reaction (3.1). Here, an average over 10 cycles gives $X_{H_2} = 0.78$ and $X_{H_2} = 0.56$ for experiments with and without additional oxidation in air, respectively. Notably, the filled symbols in Fig. 4.2 consistently give higher values of $X_{H_2}$ than their open symbol counterparts, corroborating the finding in Chapter 3 that oxidation of the Al carrier with air, via reaction (1.17), after oxidation in steam, reaction (3.1), has a beneficial effect. An explanation for this observation is provided later, based on the formation of FeO·Al\textsubscript{2}O\textsubscript{3}. The volume fraction of CO in the effluent at the end of each reduction cycle in Fig. 4.2 was $\geq 9.7$ vol. %; the inlet concentration of CO was 10 vol. %. Therefore, no large discrepancy between the inlet and outlet concentration of CO existed prior to switching off the reducing gas.

Figure 4.2 demonstrated a marked increase in $X_{H_2}$ for composite particles of Fe\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} prepared using the sol-gel process compared to that for unmodified Fe\textsubscript{2}O\textsubscript{3} over 10 cycles. However, for chemical looping combustion on an industrial scale, the oxygen carrier must withstand hundreds or even thousands of redox cycles. The sol-gel carriers with $x_{w} = 0.6, 0.8$ and 0.9 Fe\textsubscript{2}O\textsubscript{3} were therefore tested at 1123 K over 30-40 cycles for reduction on each cycle to Fe. Figure 4.3 shows the conversion of the oxygen carrier, $X_{H_2}$, calculated using Eq. (4.5), versus cycle number. The fraction of CO in the effluent at the end of each reduction cycle in Fig. 4.3 was $\geq 9.7$ vol. %; the inlet concentration of CO was 10 vol. %. Therefore, no large
discrepancy between the inlet and outlet concentration of CO existed prior to switching off the reducing gas. In all cases, air was introduced after the steam to oxidise the Fe₃O₄ to Fe₂O₃ via reaction (1.17). For the 80 and 90 wt. % Fe₂O₃ oxygen carriers, $X_{H_2} > 0.9$ for the initial 7 cycles. From cycle 8 to 25, shown between the dashed vertical lines, however, the conversion decreased to $X_{H_2} = 0.43$ and $X_{H_2} = 0.34$ for the 80 and 90 wt. % Fe₂O₃ carriers, respectively. From cycle 25 to 36 a further reduction of the conversion is observed. In Fig. 4.3, conversions for the 90 wt. % Fe₂O₃ carrier are consistently lower than those for the 80 wt. % Fe₂O₃ carrier. Surprisingly, the 60 wt. % Fe₂O₃ oxygen carrier displayed a nearly constant conversion with an average value of $X_{H_2} = 0.75$ over 40 cycles, as shown in Fig. 4.3. The total moles of H₂ produced per unit mass of carrier with 60 wt. % Fe₂O₃, gave 7.5 mmol H₂/ g carrier compared to ~ 4.5 mmol H₂/ g carrier in cycle 35 for the samples with 80 and 90 wt. % Fe₂O₃. Figure 4.3 also shows $X_{H_2}$ for unmodified Fe₂O₃, reduced to FeO only in a mixture of 10 vol. % CO, 10 vol. % CO₂, balance N₂. The conversion is again stable with $X_{H_2} = 0.15$ or 3.0 mmol H₂/ g carrier over 40 cycles. All of the sol-gel carriers, i.e. $x_w = 0.6, 0.8$ and 0.9, outperform, for 40 the cycles, the unmodified, mechanically-mixed Fe₂O₃ reduced to FeO.

The point inside the dashed circle at cycle 42 in Fig. 4.3, represents an experiment where the reduction time was increased from 10 min to 20 min for the 90 wt. % Fe₂O₃ carrier. The reducing gas composition was still 10 vol. % CO, balance N₂. Doubling the reduction time increased the conversion from $X_{H_2} = 0.25$ to 0.35, indicating that reduction had not reached completion after the 10 min interval used here. The remaining values in Fig. 4.3, labelled with temperatures of 1013 K and 873 K, were taken from other studies and will be discussed later.

For use in polymeric electrolyte membrane (PEM) fuel cells, the hydrogen must have a contamination of CO < 50 ppmv so as not to poison the Pt on the anode. Other processes, e.g. ammonia synthesis or hydrocracking (Isalski, 1989), have less stringent [CO] requirements. The H₂ in this study had an average contamination, calculated from the results in Figs. 4.2 and 4.3 for the 80 and 90 wt. % Fe₂O₃ oxygen carriers, of [CO]/([H₂]+[CO]) = 1 vol. % = 10000 ppmv, much in excess of the 50 ppmv limit for PEM fuel cells. For the 60 wt. % Fe₂O₃ oxygen carriers, experiments in Figs. 4.2 and 4.3 gave 0.1 vol. % = 1000 ppmv CO. By contrast, reduction of unmodified, mechanically-mixed oxygen carriers to FeO only at 1123 K, $10^5$ Pa and a partial pressure of $p_{CO}/p_{CO} = 1$ were shown to give [CO]< 0.005 vol. % = 50 ppmv in Chapter 2, section 2.3.6.

From the experiments shown in Fig. 4.3, the conversion as a function of time for 0.3 g of the (a) 60, (b) 80 and (c) 90 wt. % Fe₂O₃ oxygen carriers reduced in 10 vol. % CO, balance
Figure 4.3: Measured conversion, $X_{\text{H}_2}$, for 0.3 g of oxygen carrier over 30 to 40 cycles at 1123 K. Results for carriers with 60 (▲), 80 (●) and 90 (■) wt. % Fe$_2$O$_3$ prepared using the sol-gel process and reduced to Fe, as well as for unmodified Fe$_3$O$_4$ prepared by mechanically mixing and reduced only to FeO (×) are shown. Increasing the reduction time from 1200 to 2400 s with a gas composition of 10 vol. % CO, balance N$_2$ resulted in a higher conversion for the 90 wt. % Fe$_2$O$_3$ particles (■), shown by the point within the dashed circle. Final conversions for modified particles from the literature reacted (Galvita and Sundmacher, 2007) at 1013 K (+) and (Galvita et al., 2008a) at 873 K (-,◊,* ) are shown for comparison. A conversion of $X_{\text{H}_2} = 1$ represents the theoretical quantity of H$_2$ expected from oxidation of Fe to Fe$_3$O$_4$ in steam, as shown by the right hand ordinate; the theoretical conversion, $X_{\text{H}_2}$, for oxidation of FeO to Fe$_3$O$_4$ is also indicated.
Figure 4.4: Measured conversion, $X_{\text{CO}}$, versus time for 0.3 g of (a) 60, (b) 80 and (c) 90 wt. % Fe$_2$O$_3$ carrier prepared using the sol-gel process for cycles $n = 1, 5, 10$ and 30 at 1123 K corresponding to experiments in Fig. 4.3. In all cases, reduction was performed in 10 vol. % CO, balance N$_2$ for 600 s. Black dots represent the time to reach 50 %, 80 % and 100 % of the final conversion at $t = 600$ s.

N$_2$ at 1123 K was derived and is displayed in Fig. 4.4. Each line consists of 600 points and corresponds to a specific cycle from Fig. 4.3. The conversion, $X_{\text{CO}}$, was calculated from the amount of CO consumed by:

$$X_{\text{CO}} = \frac{m_{\text{CO}}}{x_w m_{\text{ox}}} \cdot \left( \frac{M_{\text{Fe}_2\text{O}_3}}{M_{\text{CO}}} \cdot \frac{1}{3} \right) \approx \frac{m_{\text{CO}}}{x_w m_{\text{ox}}} \cdot 1.9,$$

(4.6)

where $m_{\text{CO}}$ is the mass of the CO consumed, $m_{\text{ox}}$ is the mass of the fully oxidised carrier, $x_w$ is the mass fraction of Fe$_2$O$_3$ in the fully oxidised carrier and $M_{\text{Fe}_2\text{O}_3}$ and $M_{\text{CO}}$ are the molecular weights of Fe$_2$O$_3$ and CO, respectively. Since the CO reacts to form a commensurate quantity of CO$_2$, the conversion based on the CO$_2$ signal, $X_{\text{CO}_2}$, provided a useful check; typically, $X_{\text{CO}} = X_{\text{CO}_2} \pm 0.05$ where $X_{\text{CO}}$ and $X_{\text{CO}_2}$ vary between 0 and 1. In Fig. 4.4(a) the final conversion for the 60 wt. % Fe$_2$O$_3$ carrier shown by the black dots at $t = 600$ s decreased from $X_{\text{CO}} = 0.87$ in cycle 1 to $X_{\text{CO}} = 0.68$ in cycle 30. In Fig. 4.4(b), the final conversion of the 80 wt. % Fe$_2$O$_3$ oxygen carrier decreased with cycle number and was $X_{\text{CO}} = 1.0$ and 0.27 for cycles 1 and 30, respectively. In Fig. 4.4(c), the final conversion for the 90 wt. % Fe$_2$O$_3$ oxygen carrier decreases with cycle number and is given by $X_{\text{CO}} = 0.95$ and 0.22 for cycles 1 and 30, respectively. Black dots and dashed arrows indicate that the time to reach 50 % and 80 % of the final conversion, increased with cycle number for oxygen carriers with 80 and 90 wt. % Fe$_2$O$_3$, but remained approximately constant for that with 60 wt % Fe$_2$O$_3$. 

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4.3.4 Formation of FeO·Al₂O₃

A thermodynamic analysis of the stability of FeO·Al₂O₃ at 1123 K and 10⁵ Pa was presented in Chapter 3. The formation of FeO·Al₂O₃ was found to be favourable for 0.01 < \( p\text{CO}_2/p\text{CO} < 1.0 \) and 0.01 < \( p\text{H}_2\text{O}/p\text{H}_2 < 1.0 \). Thus, FeO·Al₂O₃ should be stable over the entire redox cycle for the case without oxidation in air, since during reduction incoming CO is readily oxidised to CO₂ giving \( p\text{CO}_2/p\text{CO} > 0.01 \) and during oxidation even trace amounts of H₂ will cause \( p\text{H}_2\text{O}/p\text{H}_2 < 1.0 \). The FeO·Al₂O₃ will be oxidised to Fe₂O₃ and Al₂O₃ only if oxidation in air is performed. Considering equilibrium, the preceding experimental observations suggest that (i) increasing the amount of labile Al₂O₃ in the oxygen carrier will result in more atomic Fe being bound as FeO·Al₂O₃ and unavailable for reaction and therefore lead to lower initial conversions in oxygen carriers with a higher mass fraction of Al₂O₃, as shown in Fig. 4.2(b); (ii) since FeO·Al₂O₃ decomposes to Fe₂O₃ and Al₂O₃ in air, oxidation in air will release reactive iron oxide once per cycle and could lead to higher values for \( X_{\text{H}_2} \), also shown in Fig. 4.2(b).

To verify the formation of FeO·Al₂O₃ experimentally, X-ray diffraction (XRD) was used. Figure 4.5 shows the diffraction pattern for the 60 wt. % Fe₂O₃, 40 wt. % Al₂O₃ carrier which had been reduced in 10 vol. % CO, balance N₂ and oxidised in 25 vol. % steam, balance

![Figure 4.5: Experimental X-ray diffraction pattern (•) and Rietveld fit (—) for a 60 wt. % Fe₂O₃, 40 wt. % Al₂O₃ oxygen carrier which had been reduced in 10 vol. % CO, balance N₂ and oxidised in 25 vol. % H₂O, balance N₂ for 10 cycles. The difference is plotted below the diffraction patterns and is nearly zero. Pairs of vertical lines show diffraction peaks for identical Bragg reflection planes of pure Fe₃O₄ (red, left line in each pair) and FeO·Al₂O₃ (grey, right line in each pair). The experimental diffraction peak consistently lies between each line pair indicating a mixture of Fe₃O₄ and FeO·Al₂O₃.](image-url)
Figure 4.6: Illustration of the cubic Fd-3m structure of (a) Fe$_3$O$_4$ and (b) FeO·Al$_2$O$_3$ (ICSD, 2010). Blue, grey and red spheres represent Fe, Al and O atoms, respectively.

N$_2$ over 10 cycles. The full peak widths at half of the maximum intensity (FWHM) were typically 0.3 – 0.5° and suggested peak broadening for 20° < 2θ < 80°. For comparison, the instrument broadening estimated from a pure sample of Fe$_3$O$_4$ of known crystallite size gave ~ 0.17° (FWHM) at 2θ = 34.8°. Peak broadening is common in samples with either small crystallites below 1 µm or those where there is significant lattice stress. In the present case, lattice stress owing to chemical heterogeneity is likely, since the lattice dimensions vary from $a = b = c = 8.39$ Å to 8.16 Å for Fe$_3$O$_4$ and FeO-Al$_2$O$_3$, respectively (ICSD, 2010). Figure 4.6 shows a schematic illustration of the structure of Fe$_3$O$_4$ and FeO·Al$_2$O$_3$, where it is noted that both compounds are cubic. The diffraction pattern for the sample in Fig. 4.5 also suggested a mixture of crystallites of Fe$_3$O$_4$ and FeO·Al$_2$O$_3$ (JCPDS, 2005c). The maximum peak for the sample consistently lies within the bounds of 2θ given by pairs of vertical lines corresponding to the peaks for identical Bragg reflection (hkl) planes of Fe$_3$O$_4$ (left, red) and FeO·Al$_2$O$_3$ (right, black). Phase identification, using published information (JCPDS, 2005c), revealed the presence of Fe$_3$O$_4$ and FeO·Al$_2$O$_3$; the peak at 41.90° was attributed to FeO which is also cubic and has a listed primary peak at 41.93°. The lack of intensity at 25.58° was used to rule out the presence of corundum, Al$_2$O$_3$. A multi-phase Rietveld refinement using standards from the ICSD database (ICSD, 2010) was performed to quantify each phase. Figure 4.5 shows the experimental diffraction pattern for the oxygen carrier given by points, the predicted diffraction pattern shown by the fitted line from the quantitative Rietveld analysis and the difference between the two. Good reproduction of peaks and peak shoulders was obtained. The quantitative estimate of each phase gave 76 mol % FeO·Al$_2$O$_3$, 20 mol % Fe$_3$O$_4$ and 4 mol %
FeO. The actual mole fraction of FeO·Al₂O₃ in the sample assuming it is composed entirely of Fe₃O₄ and FeO-Al₂O₃ consistent with thermodynamics, was 75 mol %, in good agreement. The formation of FeO-Al₂O₃ has therefore been quantitatively confirmed and is consistent with Topsøe et al. (1973) who suggested the formation of FeO-Al₂O₃ during reduction of an iron based ammonia catalyst.

4.4 Discussion

The redox reactions of iron oxide enable synthesis gas derived from either coal or biomass to be upgraded to H₂ with the simultaneous capture of CO₂. Figure 4.2 showed that oxygen carriers prepared using a sol-gel method with 60, 80 and 90 wt. % Fe₂O₃ could successfully produce H₂ over 10 cycles at 1123 K. For increased numbers of cycles of operation, a noticeable drop in X₉₉ with cycle number was observed for oxygen carriers with 80 and 90 wt. % Fe₂O₃, giving X₉₉ < 0.35 after 35 cycles, as shown in Fig. 4.3. By contrast, carriers with 60 wt. % Fe₂O₃, 40 wt. % Al₂O₃ gave stable quantities of H₂ over 40 cycles with an average conversion of X₉₉ = 0.75. In general, for experiments involving additional oxidation in air, Fig. 4.3 demonstrates that higher conversions, X₉₉, are obtained with sol-gel carriers with higher initial surface areas, viz (X₉₉ for xₜ = 0.6 > X₉₉ for xₜ = 0.8 > X₉₉ for xₜ = 0.9). Higher surface area composite particles might be obtainable by using iron alkoxide as the iron precursor rather than the iron nitrate used here. The measured BET surface area for the 90 wt. % Fe₂O₃ particles used for Fig. 4.3 after 42 cycles was 0.1 m²/g; the surface area for the 60 wt. % Fe₂O₃ particles used for experiments in Fig. 4.3 after 40 cycles was 0.4 m²/g.

It has already been shown in Figs.4.2(a) and (b) that without support, Fe will not produce H₂ over repeated cycles. One question remaining though is how much Al₂O₃ support is required per mole of Fe to achieve stable conversions over repeated cycles. Specifically, whether the amount of Al₂O₃ required is equal to that found in FeO-Al₂O₃. If two moles of Al were able to stabilise one mole of Fe, the expected conversions for carriers with xₜ = 0.9, 0.8 and 0.6 would be X₉₉ = 0.09, 0.20 and 0.52, respectively. The observed conversions after 40 cycles are slightly higher than these values and are X₉₉ = 0.25, 0.35 and 0.75. Thus it seems that only considering the Fe capable of forming FeO-Al₂O₃ at some point during the reduction or oxidation cycle is nearly, but not totally, sufficient to account for all of the H₂ produced. The molar ratio of Al to Fe necessary to achieve stable conversions over repeated cycles therefore appears to be slightly less than 2. Agglomeration between the Al₂O₃ packing material and
the oxygen carrier was not observed in any experiment on emptying the tube containing the packed bed. The stable conversions observed for the reduction of a 60 wt. % \( \text{Fe}_2\text{O}_3 \), 40 wt. % \( \text{Al}_2\text{O}_3 \) oxygen carrier prepared using the sol-gel process are consistent with Li et al. (2009).

Composite particles of iron oxide from other research groups often contain a variety of different additives. From Fig. 8 of Galvita and Sundmacher (2007), the quantity of hydrogen produced per unit mass of oxygen carrier with a composition of 5 wt. % \( \text{Cr}_2\text{O}_3 \), 38 wt. % \( \text{Fe}_2\text{O}_3 \) and 57 wt. % of equimolar \( \text{CeO}_2 \) and \( \text{ZrO}_2 \) was calculated to be, on average, 1.7 mmol/g carrier. The equivalent conversion, \( X_{\text{H}_2} \), was then determined by multiplying the quantity of hydrogen produced per unit mass of oxygen carrier by \( M_{\text{Fe}_2\text{O}_3} \times 3/8 \) and dividing by the mass fraction of \( \text{Fe}_2\text{O}_3 \), \( x_w = 0.38 \), as in Eq. (4.5). The average conversion over the first 40 cycles was therefore \( X_{\text{H}_2} = 0.27 \), as shown in Fig. 4.3. Assuming that the iron oxide reduces sequentially according to \( \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe} \), this conversion suggests that the reduced state of the oxygen carrier was a mixture of \( \text{FeO} \) and \( \text{Fe} \), shown by the reported values lying between the ticks for these phases on the right hand ordinate of Fig. 4.3. An identical procedure was applied to Fig. 10(a)-(c) of Galvita et al. (2008a) for samples with (a) 2 wt. % \( \text{Mo} \), 78 wt. % \( \text{Fe}_2\text{O}_3 \), 20 wt. % \( \text{CeO}_2 \) and \( \text{ZrO}_2 \), (b) 5 wt. % \( \text{Mg} \), 76 wt. % \( \text{Fe}_2\text{O}_3 \), 19 wt. % \( \text{CeO}_2 \) and \( \text{ZrO}_2 \) and (c) 5 wt. % \( \text{Cu} \), 78 wt. % \( \text{Fe}_2\text{O}_3 \), 19 wt. % \( \text{CeO}_2 \) and \( \text{ZrO}_2 \). Assuming sequential conversion, the most reduced state of the oxygen carrier in Galvita et al. (2008a) was a mixture of \( \text{Fe}_3\text{O}_4 \) and \( \text{FeO} \). The current research has shown however that if \( \text{FeO} \) is the lowest oxide, no support is necessary since from Fig. 4.3 for reduction to \( \text{FeO} \) over 40 cycles, unmodified \( \text{Fe}_2\text{O}_3 \) gave a stable yield of \( \text{H}_2 \) of 3.0 mmol \( \text{H}_2/g \) carrier with low CO contamination, confirmed in Chapter 2, Fig. 2.10. Overall, Fig. 4.3 demonstrated that in terms of conversion, \( X_{\text{H}_2} \), the oxygen carriers prepared by the sol-gel process compare favourably to those from the literature.

4.5 Conclusions

Oxygen carriers with different ratios of \( \text{Fe}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) by mass (60:40, 80:20 and 90:10 wt./wt.) were prepared using a sol-gel technique and tested for use in the production of hydrogen. Samples were characterised using scanning electron microscopy and by measuring crushing stress, BET surface area and BJH pore volume. A packed bed reactor at 1123 K was used to reduce 0.3 g of the oxygen carrier in a mixture of CO and \( \text{N}_2 \); oxidation was performed in a mixture of steam and \( \text{N}_2 \), followed by oxidation in air in some cases. It was found that:
1. For reduction to the FeO phase, no Al\textsubscript{2}O\textsubscript{3} support is required for stable conversions over 40 cycles.

2. For reduction to the Fe phase, 10 wt. % Al\textsubscript{2}O\textsubscript{3} is required to give stable conversions of $X_{\text{H}_2} > 0.9$ over 10 cycles. This conversion dropped to $< 0.35$ after 30-40 cycles.

3. For reduction to the Fe phase over 40 cycles, 40 wt. % Al\textsubscript{2}O\textsubscript{3} is required and gave stable conversions of $X_{\text{H}_2} = 0.75$. No loss in conversion with cycle number was observed, suggesting that the 40 wt. % Al\textsubscript{2}O\textsubscript{3} could endure longer cycling. The stability of the 40 wt. % Al\textsubscript{2}O\textsubscript{3} was definitively linked to the formation of FeO-Al\textsubscript{2}O\textsubscript{3}, which was confirmed quantitatively with X-ray diffraction.

4. Steam followed by air is the recommended sequence for oxidising carrier particles.

The 60 wt. % Fe\textsubscript{2}O\textsubscript{3}, 40 wt. % Al\textsubscript{2}O\textsubscript{3} oxygen carrier produced using the sol-gel process gave conversions competitive with those in other studies and seems the most promising of the sol-gel carriers for use in chemical looping applications for the production of H\textsubscript{2}. 
Chapter 5

Kinetics of the reduction of iron oxide by mixtures containing CO and CO$_2$

5.1 Introduction

For the production of hydrogen using the redox reactions of iron oxide, understanding the kinetics of reduction is necessary for a fundamental understanding of the process. The reduction of Fe$_2$O$_3$ by CO occurs by reactions (1.9)-(1.11) in Table 1.2, repeated here for convenience:

\[
3 \text{Fe}_2\text{O}_3 + \text{CO} \rightleftharpoons 2 \text{Fe}_3\text{O}_4 + \text{CO}_2 \quad \Delta H_{1023}^\circ = -44.3 \text{ kJ/mol} \quad (5.1)
\]

\[
1.2 \text{Fe}_3\text{O}_4 + \text{CO} \rightleftharpoons 3.8 \text{Fe}_{0.947}\text{O} + \text{CO}_2 \quad \Delta H_{1023}^\circ = +27.1 \text{ kJ/mol} \quad (5.2)
\]

\[
\text{Fe}_{0.947}\text{O} + \text{CO} \rightleftharpoons 0.947 \text{Fe} + \text{CO}_2. \quad \Delta H_{1023}^\circ = -20.3 \text{ kJ/mol} \quad (5.3)
\]

While the equilibrium constants for reactions (5.1)-(5.3) are well-established and derivable from standard thermodynamic data (Barin and Knacke, 1973; McBride et al., 2002), their intrinsic kinetics are less easily obtained. Historically, research on the kinetics of the reduction of iron oxide has stemmed from the steel industry and has been characterised by a progression towards increasingly-complicated rate models. Initial investigations used a single-step reduction mechanism, whereby Fe$_2$O$_3$ was reduced to Fe without the intermediates Fe$_3$O$_4$ and Fe$_{0.947}$O (Omori, 1987) being explicitly considered. McKewan (1958, 1962) studied single-step reduction using H$_2$. Later, two-step models including wuestite, Fe$_{0.947}$O, were developed (Omori, 1987). A model involving all four species of iron and its oxides was then proposed by Spitzer et al. (1966) for porous pellets, the reduction of which in H$_2$ was controlled.
by internal transport and reaction resistances at three, sharply-defined shrinking cores corresponding to the boundaries, at successively decreasing radii, between Fe, Fe$_{0.947}$O, Fe$_3$O$_4$ and Fe$_2$O$_3$. Murayama et al. (1977) applied this shrinking core approach to the reduction of iron oxide with mixtures of CO and CO$_2$. Implicit in these models is the assumption that reactions occur at sharp interfaces.

To address reduction with diffuse interfaces, Szekely and Evans (1970) proposed a grain model where the overall pellet is comprised of dense spherical subparticles which themselves are chemically reduced at sharp interfaces. This model has been applied to the reduction of iron oxide, e.g. Valipour and Saboohi (2007). Alternatively, Trushenski et al. (1974) proposed a model for reaction occurring over a specific volume of the pellet, rather than over the surface area of an interface. Both the model from Szekely and Evans (1970) and that from Trushenski et al. (1974) have been successfully employed to describe experimental results over broad ranges of temperature and gas composition.

The motivation for further research into the kinetics of the reduction of iron oxide is twofold. First, the rate parameters in the previous models were obtained by fitting theoretical predictions to experimental results influenced by intra-particle gaseous diffusion, e.g. Trushenski et al. (1974); Szekely et al. (1976). As such, the rate constants did not have as significant an effect on the models’ predictions as would be the case in a purely kinetically-controlled regime. Second, for gas-solid looping cycles, the kinetics of the reduction of iron oxide need to be studied over repeated cycles of reduction and oxidation, instead of just during an initial cycle. It has already been shown in Chapter 2 that repeated reduction to Fe by reaction (5.3) for particles made purely of Fe$_2$O$_3$ is not possible, since yields of H$_2$ far below those predicted from the stoichiometry of reactions (1.15)-(1.16) are obtained. Therefore here, only the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$, reaction (5.1), and the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O, reaction (5.2), are investigated for pure iron oxide. The objectives were therefore:

1. to determine pre-exponential factors and activation energies for the reduction of the iron oxides by mixtures of CO and CO$_2$ in the kinetically-controlled regime at industrially-relevant temperatures and pressures;

2. to investigate any changes in the kinetics with increasing numbers of cycles and;

3. to compare theoretical predictions with measurements obtained in experiments different from those used to derive the kinetic parameters, e.g. by using the rate parameters obtained in a fluidised bed to predict the reduction of a fixed bed of iron oxide.
Mechanically-mixed particles of iron oxide were prepared, as described in Chapter 2, section 2.2, by spraying water from reverse osmosis on to Fe$_2$O$_3$ powder (Sigma-Aldrich; purity > 99.9 wt. %) while mechanically mixing. The resulting agglomerates were heated at 1173 K for 3 h and then sieved to the desired size ranges. The BET surface area of the sintered Fe$_2$O$_3$ particles with $d_p = +300, -425 \, \mu m$ was $1.0 \pm 0.5 \, m^2/g$ (Micromeritics, Tristar 3000); the porosity, measured by Hg porosimetry (Micromeritics, Autopore IV) was $0.60 \pm 0.06$. The surface area of particles of Fe$_3$O$_4$ with $d_p = +300, -425 \, \mu m$, prepared by reducing the particles of Fe$_2$O$_3$ at 1173 K in 3 vol. % CO, 15 vol. % CO$_2$, 82 vol. % N$_2$, was $1.0 \pm 0.5 \, m^2/g$ with a porosity of $0.58 \pm 0.06$.

The fluidised bed reactor is shown in Fig. 5.1 and consisted of a tube of recrystallised Al$_2$O$_3$ (I.D. 20 mm) with a perforated plate distributor, also of Al$_2$O$_3$; both had purities > 99.9 wt. %. The plate had 5 holes, each 1 mm dia., four aligned in a square array of side 8 mm, with one central hole. The tube and disc were joined using ceramic cement (ALCS, Multilab). Approximately 10 g of Al$_2$O$_3$ ($d_p = +1400, -1700 \, \mu m; \rho_{Al_2O_3} = 3770 \, kg/m^3$; Boud Mineral) formed a packed bed beneath the distributor, held in place with quartz wool; this packing preheated the gas entering the reactor, as shown in Fig. 5.1. The depth of the unfluidised bed, $H_0$, was 30 mm, giving an aspect ratio, $H_0/d_{bed} = 1.5$. At typical operating conditions of 1023 K, the pressure drop across the distributor was 0.02 bar, considerably in excess of the pressure drop across the material fluidised (typically 15 g of Al$_2$O$_3$ (purity > 99.9 wt. %) sieved to $d_p = +300, -425 \, \mu m$) given by the weight of the bed divided by the nominal cross-sectional area, viz. amounting to 0.003 bar, hence ensuring uniform fluidisation. The reactor was placed in a tubular furnace, and its temperature was measured by a type K thermocouple, positioned 5 mm above the distributor, inside the bed. In all experiments, the particles were added to the reactor as Fe$_2$O$_3$ and the mass of the batch was measured using a balance with a precision of $10^{-4} \, g$ (OHaus). A packed bed reactor made of 316 stainless steel (I.D. 10.2 mm), described in 2.2, replaced the fluidised bed in the experiments in section 5.4.3.

Gas was supplied to the reactor from cylinders (BOC plc.) and steam was supplied using a syringe pump, as described in Chapter 2, section 2.2. The total flowrate of gas was adjusted in all experiments to give $U/U_{mf} \sim 7$ determined, for the mixture of reducing gas and Al$_2$O$_3$ bed particles, from the correlation of Wen and Yu (1966). The effluent gas was monitored by continuously withdrawing a sample at a flowrate of $1.67 \times 10^{-5} \, m^3/s$, as measured at 298 K and
Figure 5.1: Schematic diagram of the fluidised bed reactor. The inert bed material was 15 g of Al\(_2\)O\(_3\) with \(d_p = +300,-425 \mu m\); active iron oxide, Fe\(_2\)O\(_3\), in various size ranges was added to the top of the bed. All dimensions are in mm.
$10^5$ Pa, through a quartz probe (5 mm I.D.) and measuring its composition by nondispersive infrared and thermal conductivity analysers as described in Chapter 2.

Since steam was used to convert the Fe$_{0.947}$O to Fe$_3$O$_4$, three impinger tubes immersed in an ice bath (273 K), followed by a tube filled with CaCl$_2$, were used to dry the sampled gas prior to analysis. Experiments involving cycling between Fe$_2$O$_3$ and Fe$_3$O$_4$ did not require the sampled gas to be dried. The response time of the sampling line in series with the analysers was determined by placing the quartz probe in a flow of calibration gas, either 10 vol. % CO, balance N$_2$ (BOC plc.) or 10 vol. % CO$_2$, balance N$_2$ (BOC plc.) for CO or CO$_2$, respectively, and rapidly removing the probe manually in order to approximate a step change. The response times with and without the drying tubes, respectively, were then determined for the infrared analysers to be $\tau_{\text{mix CO}} = 2.0$ s, $\tau_{\text{mix CO}_2} = 3.5$ s and $\tau_{\text{mix CO}} = 1.0$ s, $\tau_{\text{mix CO}_2} = 2.5$ s. Deconvolution of the CO and CO$_2$ signals was performed, but did not significantly alter the results, since in all cases the total time for reaction was at least one order of magnitude greater than the reported time constants and the rate was determined over a large range of conversion, $0.1 < X < 0.7$, as discussed later.

The transition from Fe$_2$O$_3$ to Fe$_3$O$_4$ was studied between 723 and 973 K, using mixtures of N$_2$+CO+CO$_2$ (respectively, 82, 3 and 15 vol. %) during the reduction of Fe$_2$O$_3$ and mixtures of N$_2$+air+CO$_2$ (respectively, 82, 3 and 15 vol. %) during the oxidation of Fe$_3$O$_4$. For the transition from Fe$_3$O$_4$ to Fe$_{0.947}$O, mixtures of N$_2$+CO+CO$_2$ (respectively, 82, 9 and 9 vol. %) were used to reduce Fe$_3$O$_4$ and mixtures of N$_2$+steam (respectively, 82 and 18 vol. %) were used to oxidise Fe$_{0.947}$O over 923 - 1173 K. These values of CO and CO$_2$ were chosen from Fig. 1.1 in order to give the desired phase of iron oxide, assuming that thermodynamic equilibrium was established. A purge of N$_2$ for 60-120 s was employed between reduction and oxidation stages to prevent mixing, and therefore reaction, of the reducing and oxidising gases. Prior to any iron oxide being introduced into the reactor, one reduction and one oxidation, together constituting one cycle, were performed and satisfactorily verified the inertness of the reactor, its contents, and the thermocouple in each experiment. The iron oxide particles were then poured into the reactor during a period of N$_2$ flow, enabling equilibration to the bed's temperature and the displacement of any air inside the iron oxide particles prior to reduction. The requisite reduction and oxidation cycling was then performed.
5.3 Theory

In a single particle, the reduction reactions (5.1) and (5.2) could, in principle, be controlled by one or more of the following: (i) mass transport of gaseous reactant to the exterior of the particle, (ii) diffusion of the reactant through the particle matrix, (iii) chemical reaction, (iv) diffusion of the gaseous product through the particle matrix and (v) mass transport of gaseous product into the bulk gas. Assuming (a) pseudo-steady state and (b) first order kinetics of the form $r' \propto (c_{CO} - c_{CO_2}/K_p)$, a material balance over a differential volume of a single spherical particle gives:

$$D_{e,CO} \left[ \frac{2}{r} \frac{dc_{CO}}{dr} + \frac{d^2c_{CO}}{dr^2} \right] = k_i \left( c_{CO} - \frac{c_{CO_2}}{K_p} \right),$$

(5.4)

where $c_{CO}$ is the concentration of CO, $D_{e,CO}$ is the effective diffusivity of CO, $k_i$ is the intrinsic rate constant for the forward step of reaction (5.1) or (5.2) and $r$ is the radial position within the particle. Substituting (Smith and Amundson, 1951) $u_{CO} = c_{CO} r$ and employing boundary conditions of $c_{CO} = \text{constant} = c_{CO,s}$ at $r = R$ and finiteness of $c_{CO}$ at $r = 0$ gives:

$$c_{CO}(r) = b_1 + \frac{2c_1}{r} \sinh(r \sqrt{P}),$$

(5.5)

where $b_1$, $c_1$ and $P$ are constants given in Appendix 4 and $c_{CO,s}$ and $c_{CO_2,s}$ are the concentrations at the external surface of the particle. A similar procedure can be used to solve for $c_{CO_2}(r)$.

The effectiveness factor and Thiele modulus are then given, respectively, by:

$$\eta = \frac{3}{\phi^2} (\phi \coth \phi - 1), \quad \phi = R \sqrt{\frac{k_i}{D_{e,CO}}} + \frac{k_i}{K_p D_{e,CO_2}}.$$  

(5.6)

This definition is similar to that of Levenspiel (1999), except that $\phi$ includes the reverse reaction represented by the term containing $K_p$. Incorporating the resistance to external mass transfer through the film layer, the specific rate of reaction, $r'$, in mol/(s g) for the particle can be written as:

$$r' = \frac{k}{\rho_{Fe_2O_3}} \left( c_{CO,p} - \frac{c_{CO_2,p}}{K_p} \right),$$

$$\frac{1}{k} = \frac{R}{3k_{g,CO}} + \frac{1}{k_i \eta} + \frac{R}{3k_{g,CO_2} K_p}.$$  

(5.7)

Here, $c_{CO,p}$ and $c_{CO_2,p}$ are the concentrations in the particulate or bulk phase of the reactor, $\rho_{Fe_2O_3}$ is the density of the particle, $k_{g,CO}$ and $k_{g,CO_2}$ are the mass transfer coefficients, $k_i$ is the intrinsic rate constant for reaction (5.1) or (5.2) and $R$ is the external radius of the parti-
cle. Unless otherwise specified, the equilibrium constant, $K_p$, was determined from published thermodynamic data (Barin and Knacke, 1973).

![Figure 5.2](image)

Figure 5.2: The measured ratio, $c_{\text{CO, out}}/c_{\text{CO, in}}$, as increasing masses of Fe$_2$O$_3$, $W$, were added to the fluidised bed at (•) 823 K, (○) 923 K, (■) 1023 K and (□) 1123 K. The grey lines indicate least squares fits using Eq. (5.8) and were used to determine $X_f$.

The bubble to particulate phase resistance of the fluidised bed was considered using the two-phase model of Davidson and Harrison (1963) with crossflow factor, $X_f$. In poorly-mixed fluidised beds, some of the entering reactant will bypass the particulate phase as bubbles and thus never react. Experimentally, the crossflow factor, which quantifies bypassing, was evaluated by measuring the ratio of $c_{\text{CO, out}}/c_{\text{CO, in}}$ when increasing masses of Fe$_2$O$_3$ were added to the bed and reduced to Fe$_3$O$_4$ in 3 vol. % CO, 15 vol. % CO$_2$, balance N$_2$ at the operating condition $U/U_{mf} \sim 7$. Results were then fitted using Eq. (6.9) from (Davidson and Harrison, 1963):

$$c_{\text{CO, out}}/c_{\text{CO, in}} = \beta e^{-X_f} + \frac{(1 - \beta e^{-X_f})^2}{(kW/q_{\text{Fe}_2\text{O}_3}) + 1 - \beta e^{-X_f}}, \tag{5.8}$$

where $eta = (1 - U/U_{mf}) = 6/7$, $k$ is the rate constant including mass transfer effects, $W$ is the mass of particles added to the bed, $q$ is the superficial volumetric flowrate through the bed, $\rho_{\text{Fe}_2\text{O}_3}$ is the initial particle density and any back reaction was ignored owing to the large equilibrium constant, $K_p = 1.47 \times 10^5$. In deriving the term in brackets in the denominator of Eq. (5.8), it was assumed the volume of particles per unit volume of the particulate phase was constant and equal to $W/(\rho_{\text{Fe}_2\text{O}_3} H_0 A_s)$. Fig. 5.2 shows $c_{\text{CO, out}}/c_{\text{CO, in}}$ versus $W$ at temperatures...
of 823, 923, 1023 and 1123 K. Here, \( c_{\text{CO, out}} \) corresponds to the maximum initial rate of consumption of CO. The terms \( (kW/q\rho_{\text{Fe}_2\text{O}_3}) \) and \( X_{\text{fl}} \) were then determined by performing a least squares fit to the experimental values in Fig. 5.2 using Eq. (5.8). For all experiments, \( X_{\text{fl}} > 2.5 \), suggesting complete mixing within the whole bed. The particles of \( \text{Al}_2\text{O}_3 \) and iron oxide were also of similar size and density such that no segregation was observed upon emptying the bed after it was rapidly defluidised and cooled to room temperature. The absence of segregation and the high crossflow factor imply that the bed behaves like a CSTR with respect to both the gas and solids. Values of \( k \) are presented later with the discussion of Fig. 5.7.

In this study, the final rate expression used to analyze the reduction of \( \text{Fe}_2\text{O}_3 \) particles with particle density, \( \rho_{\text{Fe}_2\text{O}_3} \), is expressed in units of mol/(s g) as:

\[
r' = \frac{k}{\rho_{\text{Fe}_2\text{O}_3}} \left( c_{\text{CO, out}} - \frac{c_{\text{CO}_2, \text{out}}}{K_p} \right).
\]  

(5.9)

Here, the mass transfer coefficients, \( k_{g, \text{CO}} \) and \( k_{g, \text{CO}_2} \), in the expression for \( k \) in Eq. (5.7) for one particle were estimated from \( Sh = 2\epsilon_{mf} + 0.69Re_p^{1/2}S c^{1/3} \), similar to LaNauze (1985), where \( Sh = k_g d_p / D_{\text{mix}} \) with \( \epsilon_{mf} = 0.45; Re_p \) is based on the size of the bed material, viz. \( d_p = +300, -425 \mu \text{m} \). The effective diffusivity of CO or \( \text{CO}_2 \) in Eqs. 5.4-5.6 was calculated from \( D_e = \epsilon_p (1/D_k + 1/D_{\text{mix}})^{-1}/\tau_p \) using either values for CO or for \( \text{CO}_2 \). Values for the diffusion coefficients, \( D_{\text{mix}} \), were taken from Hirschfelder et al. (1954). The Knudsen diffusivity was calculated (Satterfield, 1980) using \( D_k = 2r_e (8RT/\pi M_w)^{1/2}/3 = 2.13 \epsilon_p (RT/M_w)^{1/2}/(S_g \rho_{\text{Fe}_2\text{O}_3}) \), where \( r_e \) is the effective radius of a cylindrical pore, \( \epsilon_p = 0.6 \) is the porosity for \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \); \( \tau_p \) was a fitted tortuosity, found to be 2.4 and 2.5 for \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \), respectively; \( \rho_{\text{Fe}_2\text{O}_3} = 2060 \text{ kg/m}^3 \) and \( \rho_{\text{Fe}_3\text{O}_4} = 2180 \text{ kg/m}^3 \); \( T \) is the absolute temperature; \( S_g = 1.0 \text{ m}^2/\text{g} \) is the specific surface area for \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) and \( M_w \) is the molecular mass of the gaseous species. The influence of Knudsen diffusion on the overall effective diffusivity, \( D_e \), was found to be minimal for both CO and \( \text{CO}_2 \). Table 5.1 lists typical values of parameters used. Values of \( k_i \) are reported in section 5.4.1 for the reduction of \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \) and in section 5.4.2 for the reduction of \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \).
Table 5.1: Parameters used in the determination of the intrinsic rate constant, $k_p$, for particles with $d_p = +300, -425 \mu m$. The superficial flow of gas through the reactor in (m$^3$/s) is $q = 7U_{mf}A_s$, where the cross-sectional area is $A_s = \pi(0.02 \, m)^2/4$. Here, $1/D_{e,CO} = \tau_p/(1/D_{k,CO} + 1/D_{mix,CO})/\varepsilon_p$. A value of $Nu = h d_p/\lambda_{mix} = 2$ was used to estimate $h$; $Bi = h d_p/6 \lambda_c$.

<table>
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<tr>
<th>Reduciton of Fe$_3$O$_4$ to FeO$_2$</th>
<th>$T$ (K)</th>
<th>$W$ (g)</th>
<th>$U_{mf}$ (m/s)</th>
<th>$\varepsilon_p$</th>
<th>$\rho_{Fe_3O_4}$ (kg/m$^3$)</th>
<th>$S_\theta$ (m$^2$/kg)</th>
<th>$k_{g,CO}$ (m/s)</th>
<th>$k_{g,CO_2}$ (m/s)</th>
<th>$D_{mix,CO}$ (m$^2$/s)</th>
<th>$D_{mix,CO_2}$ (m$^2$/s)</th>
<th>$D_{h,CO}$ (m$^2$/s)</th>
<th>$D_{h,CO_2}$ (m$^2$/s)</th>
<th>$\lambda_e$ (W/(m K))</th>
<th>$\lambda_{max}$ (W/(m K))</th>
<th>$h$ (W/(m K))</th>
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<td>1$^3$</td>
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</table>

| Reduction of FeO$_2$ to Fe$_3$O$_4$ | $T$ (K) | $W$ (g) | $U_{mf}$ (m/s) | $\varepsilon_p$ | $\rho_{FeO_2}$ (kg/m$^3$) | $S_\theta$ (m$^2$/kg) | $k_{g,CO}$ (m/s) | $k_{g,CO_2}$ (m/s) | $D_{mix,CO}$ (m$^2$/s) | $D_{mix,CO_2}$ (m$^2$/s) | $D_{h,CO}$ (m$^2$/s) | $D_{h,CO_2}$ (m$^2$/s) | $\lambda_e$ (W/(m K)) | $\lambda_{max}$ (W/(m K)) | $h$ (W/(m K)) | $Bi$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 923 | 2.18 | 0.077 | 0.58 | 2.5 | 2180 | 1$^3$ | 0.53 | 0.43 | 1.37$\times$10$^{-4}$ | 1.08$\times$10$^{-4}$ | 2.96$\times$10$^{-4}$ | 2.36$\times$10$^{-4}$ | 2.18$\times$10$^{-5}$ | 1.72$\times$10$^{-5}$ | 0.5 | 0.063 | 345 | 0.04 |
| 973 | 1.52 | 0.073 | 0.58 | 2.5 | 2180 | 1$^3$ | 0.57 | 0.46 | 1.50$\times$10$^{-4}$ | 1.18$\times$10$^{-4}$ | 3.04$\times$10$^{-4}$ | 2.42$\times$10$^{-4}$ | 2.33$\times$10$^{-5}$ | 1.84$\times$10$^{-5}$ | 0.5 | 0.065 | 359 | 0.04 |
| 1023 | 0.80 | 0.072 | 0.58 | 2.5 | 2180 | 1$^3$ | 0.61 | 0.49 | 1.63$\times$10$^{-4}$ | 1.28$\times$10$^{-4}$ | 3.11$\times$10$^{-4}$ | 2.48$\times$10$^{-4}$ | 2.48$\times$10$^{-5}$ | 1.96$\times$10$^{-5}$ | 0.5 | 0.068 | 374 | 0.05 |
| 1073 | 0.77 | 0.070 | 0.58 | 2.5 | 2180 | 1$^3$ | 0.65 | 0.52 | 1.77$\times$10$^{-4}$ | 1.39$\times$10$^{-4}$ | 3.19$\times$10$^{-4}$ | 2.54$\times$10$^{-4}$ | 2.54$\times$10$^{-5}$ | 2.08$\times$10$^{-5}$ | 0.5 | 0.070 | 388 | 0.05 |
| 1123 | 0.52 | 0.067 | 0.58 | 2.5 | 2180 | 1$^3$ | 0.68 | 0.55 | 1.91$\times$10$^{-4}$ | 1.49$\times$10$^{-4}$ | 3.26$\times$10$^{-4}$ | 2.60$\times$10$^{-4}$ | 2.79$\times$10$^{-5}$ | 2.20$\times$10$^{-5}$ | 0.5 | 0.073 | 402 | 0.05 |
| 1173 | 0.39 | 0.066 | 0.58 | 2.5 | 2180 | 1$^3$ | 0.73 | 0.58 | 2.05$\times$10$^{-4}$ | 1.61$\times$10$^{-4}$ | 3.33$\times$10$^{-4}$ | 2.66$\times$10$^{-4}$ | 2.94$\times$10$^{-5}$ | 2.32$\times$10$^{-5}$ | 0.5 | 0.075 | 416 | 0.05 |
5.4 Results

5.4.1 Transition from Fe$_2$O$_3$ to Fe$_3$O$_4$

The reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ was studied between 723 and 973 K with inlet mole fractions of CO and CO$_2$ from 1.5 to 3.5 vol. % and 14 to 16 vol. %, respectively. Figure 5.3(a) shows the effluent mole fractions of CO and CO$_2$ for a typical experiment at 823 K. Here, 0.5 g of Fe$_2$O$_3$ particles with $R \sim 180 \mu$m were introduced into the hot bed when fluidised by N$_2$. After the first reduction and oxidation, the fluidising gas was suddenly switched from N$_2$ to the mixture of CO, CO$_2$ and N$_2$ at $t = 30$ s. A fraction of the entering CO reacted with the Fe$_2$O$_3$ to form Fe$_3$O$_4$ and was thereby converted to CO$_2$. From stoichiometry, the production of CO$_2$ must be commensurate with the consumption of CO, and Fig. 5.3(a) shows that the CO and CO$_2$ curves are indeed complementary.

Upon completion of the reaction at $t = 100$ s, the CO and CO$_2$ mole fractions returned to their inlet values of 2.2 vol.% and 14.8 vol.% respectively. Following a period of purging with N$_2$, the particles were then reoxidised with a mixture of N$_2$+air before undergoing subsequent reduction cycles.

The conversion of the solid at a specific time can be calculated by integrating a plot (against time) of the decrease in CO, and, or, increase in CO$_2$. The grey area in Fig. 5.3(a), for example, corresponds to a conversion of 0.4 for the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$. The rate at this specific conversion was then obtained by taking the instantaneous difference between the inlet and outlet mole fractions of CO or CO$_2$, depicted by the grey circles in Fig. 5.3(a), multiplying by the molar flowrate, and dividing by the mass of particles added: this gave the rate of reaction, $r'$, moles/(s g). Thus, from the graph in Fig. 5.3(a) a plot of rate versus conversion can be constructed and is shown in Fig. 5.3(b). The point corresponding to the rate at $X = 0.4$ is shown by the grey circle in Fig. 5.3(b). Good agreement between the rates calculated using the CO and CO$_2$ signals is observed, although the reduced noise in the CO signal makes it preferable for determining the rate.

The initial rate, or rate at $X = 0$, can be derived from either Fig. 5.3(a) or (b). In Fig. 5.3(a), the effluent mole fraction of CO can be approximated by a linear fit shown by the grey line and extrapolated back to the point of the gas switch. This method gives $r' = 5.3 \times 10^{-5}$ mol/(s g). In Fig. 5.3(b), the initial rate can be calculated by a linear fit of $r'$ versus $X$ in the interval $0.1 < X < 0.7$. The intercept of the best fit line then gives the rate at $X = 0$, shown by point
Figure 5.3: (a) Mole fraction of CO (♦) and CO$_2$ (◊) in the effluent gas *versus* time for the reduction of 0.5 g of Fe$_2$O$_3$ to Fe$_3$O$_4$ at 823 K. Grey circles show the difference between the inlet and outlet CO and CO$_2$ at $X = 0.4$. (b) Rate *versus* conversion calculated from the CO (♦) and CO$_2$ (◊) analyser signals in (a). The initial rate is given by the intersection of the fitted line with the ordinate at $X = 0$, shown by point A. The grey circle indicates the rate at $X = 0.4$. 


A. This method gives, $r' = 4.8 \times 10^{-5}$ mol/(s g), which is in agreement to within 10 % of that found from Fig. 5.3(a). For consistency, the rates reported hereinafter were determined from the plots of $r'$ versus $X$. Rates for the first reduction cycle are not reported, as it was found that the plots of [CO] and [CO$_2$] in the effluent were markedly different from those for cycles 2 to 10, perhaps owing to a morphological change or the presence of adsorbed gaseous species in cycle one. The anomalous behaviour during the first cycle remains puzzling and highlights the importance of investigating the rate over repeated cycles. To prevent all the inlet CO from being consumed at higher temperatures, the mass of Fe$_2$O$_3$ added to the bed was decreased progressively with temperature from 2.0 g at 623 K to 0.1 g at 973 K, so that the maximum deviation over the inlet [CO] was 30 %.

![Figure 5.4: (a) Relative intensity (cps) against 2θ for the reduced iron oxide as Fe$_3$O$_4$; a simulated scan from a standard reference (JCPDS, 2005b) is shown with a vertical offset and demonstrates good agreement.](image)

X-ray diffraction (Philips model PW1830/00, Cu Kα, 40 kV and 40 mA, scanning rate 0.01 degrees s$^{-1}$, in air at 298K) confirmed the presence of Fe$_3$O$_4$ after reduction of 5 g of Fe$_2$O$_3$ of sieve size $d_p = +300$, $-425$ µm only in CO, CO$_2$ and N$_2$ at 973 K, i.e. without any Al$_2$O$_3$ in the bed, and is shown in Fig. 5.4. The experimental diffraction pattern is shown below that of a simulated scan from a standard reference for Fe$_3$O$_4$ (JCPDS, 2005b) and definitively demonstrates the presence of Fe$_3$O$_4$ with no unexplained contaminants. In Chapter 3, no Al$_2$O$_3$ contamination had been detected from X-ray diffraction patterns of modified Fe$_2$O$_3$ reacted in a packed bed between layers of inert Al$_2$O$_3$, suggesting that the Al$_2$O$_3$ was indeed inert.

The previous analysis assumed that the rate was first order in the outlet concentrations of
Figure 5.5: Initial measured rate, $r'$, at $X = 0$ versus inlet fraction of CO for reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ at 823 K. The straight line through the origin is a best fit, exhibiting a first order dependence on [CO]. The inlet fraction of CO$_2$ was fixed at 15 vol.%.

CO and CO$_2$, i.e. $r' \propto (c_{CO,out} - c_{CO_2,out}/K_p)$ in Eq. (5.9). Envisaging the reactor as a well-mixed CSTR operating at constant temperature and pressure enables one to replace $c_{CO,out}$ and $c_{CO_2,out}$ with expressions of $c_{CO,in}, c_{CO_2,in}$ using the material balances:

$$ r' = \left( \frac{q}{W} \right) (c_{CO,in} - c_{CO,out}) = \left( \frac{q}{W} \right) (c_{CO_2,out} - c_{CO_2,in}), \quad (5.10) $$

where $q$ is the total volumetric flowrate of gas through the reactor and $W$ is the total mass of Fe$_2$O$_3$ initially introduced. Using Eq. (5.10) and substituting for $c_{CO,out}$ and $c_{CO_2,out}$ in $r' \propto (c_{CO,out} - c_{CO_2,out}/K_p)$ gives $r' \propto [1/(1+W/q+W/qK_p)](c_{CO,in} - c_{CO_2,in}/K_p) \propto (c_{CO,in} - c_{CO_2,in}/K_p)$ for constant $q$, $W$ and $K_p$, which is a useful expression since the inlet concentrations were easily measurable and controllable. By fixing the inlet mole fraction of CO$_2$ at 15 vol. % and varying the inlet mole fraction of CO between 0 and 10 vol. %, the dependence of the rate on the inlet CO was investigated. Figure 5.5 shows a plot of $r'$ versus the mole fraction of CO in the inlet gas; the mass of Fe$_2$O$_3$ added ranged from 0.3 to 0.8 g, with smaller masses used for higher mole fractions of CO. From Fig. 5.5, the rate can be satisfactorily described by a first order fit. The dependence on CO$_2$ could not be measured, since the large equilibrium constant, $K_p = 1.47 \times 10^5$, overwhelms any effect of CO$_2$. The back reaction is therefore negligible.

The effect of external mass transfer was found to be negligible and is examined quantitatively in the discussion. Next, to determine whether the reduction of particles of Fe$_2$O$_3$ to Fe$_3$O$_4$ was limited by intrinsic kinetics or intraparticle diffusion, the rate was investigated for particles of varying radii at 823 K, fixed inlet mole fractions of CO and CO$_2$ of 2.5 vol.% and
Figure 5.6: Reduction of 0.5 g of Fe$_2$O$_3$ to Fe$_3$O$_4$ at 823 K.

(a) Plot of initial rate constant $k$ at $X = 0$ versus average radius, $R$, of the iron oxide particles for cycles 2 (▲), 3 (○) and 4 (♦). The corrected intrinsic rate constant at zero conversion, $k_0$, which accounts for $\eta < 1$ is also shown for cycle 2 (♦) and has an average value given by the dashed line of 490 s$^{-1}$.

(b) Effectiveness factor, $\eta = k/490$ s$^{-1}$, versus calculated $\phi$ from Eq. (5.6) for cycles 2 (▲), 3 (○) and 4 (♦), corresponding to the points in (a). For smaller particles $\eta = 1.0$; as particle size increases $\eta$ approaches $3/\phi$. 

81
15 vol.%, respectively, and a fixed batch mass of 0.5 g of Fe$_2$O$_3$. The observed rate constant, $k$, was found by dividing the rate, $r'$, by the concentration driving force of the outlet gas and multiplying by the bulk density, i.e. rearranging Eq. (5.9). The initial intrinsic rate constant, $k_0$, which is simply $k_i$ at $X = 0$, was obtained by iteratively solving for $\eta$ using Eqs. (5.6) and (5.9). For example, starting with Eq. (5.9) and assuming $\eta = 1$, an initial estimate of $k_0$ was determined. This $k_0$ was then used in Eq. (5.6) to obtain an estimate for $\phi$, which was subsequently used in Eq. (5.6) to find a new value for $\eta$. This new value for $\eta$ was then inserted into Eq. (5.9) to generate a new estimate of $k_0$. The procedure was repeated until $\eta$ converged to a single value. Here, the value of the tortuosity used in the determination of the effective diffusivities was a fitting parameter and was determined based on the ability to recover a constant $k_i$ from the values of $k$ obtained from reacting particles of various sizes. Here, $\tau_p = 2.4$ was chosen. This value is typical of commercial pellets of catalyst (Satterfield, 1980). Figure 5.6 (a) shows the observed initial rate constant, $k$, plotted versus particle radius, $R$. For $R < 300 \mu$m, $k$ remains approximately constant at $490 \text{ s}^{-1}$. As $R$ increases, $k$ decreases; this pattern holds for the three reduction cycles investigated. Figure 5.6 (a) also shows the initial intrinsic rate constant, $k_0$, for cycle 2. Applying the effectiveness factor correction has little effect on the rate constant for particles with $R < 300 \mu$m, since here $k = k_0$, implying $\eta = 1$. For larger particles, however, the correct value of $k_0 = 490 \text{ s}^{-1}$ can be recovered from the values of $k$. Plotting $\eta = k/490 \text{ s}^{-1}$ versus the calculated $\phi$ from Eq. (5.6) for each point, Fig. 5.6(b) confirms that $\eta \approx 1$ for $R < 300 \mu$m. Also, it can be seen that for the largest particles $\eta$ approaches $3/\phi$. This region corresponds to where intraparticle diffusion dominates the observed reaction rate. The size range of the particles which can be used for a kinetic study was therefore bounded by the transition to internal diffusion control at $R$ greater than about $300 \mu$m and the experimental observation of elutriation for $R$ less than about $100 \mu$m. Therefore, particles with $150 \mu$m < $R$ < $210 \mu$m were used to determine the rate constants in subsequent experiments.

To determine whether heat transfer to the particle was limiting, an order of magnitude estimate of the Biot number, $(hd_p/6\lambda_e)$, for a single particle with $R \sim 180 \mu$m was performed and gave $Bi << 1$ and typically, $Bi \approx 0.04$ as shown in Table 5.1, indicating that the temperature across a single particle was uniform. Here, $\lambda_e = 0.5 \text{ W/(m K)}$ was used (Takegoshi et al., 1984), and $h$ was estimated conservatively using the thermal conductivity of the gas with $Nu = hd_p/\lambda_{mix} = 2$ as listed in Table 5.1. Next, a simple heat balance was used to estimate the maximum temperature difference between a single particle and the bed during reduction,
given by:
\[
r' \Delta H^o_{T_{\infty}, \rho_{Fe_2O_3}} \left( \frac{4\pi R^3}{3} \right) = h \left( 4\pi R^2 \right) (T - T_{\infty}),
\]
(5.11)
in which it has been assumed that the radiative component of heat transfer is small. The temperature in the particle, \( T \), was assumed uniform since \( Bi \ll 1 \); the rate was assumed equal to the initial rate at \( X = 0 \); \( h \) listed in Table 5.1 was used; \( (T - T_{\infty}) \) was the temperature difference between the particle, \( T \), and the bed, \( T_{\infty} \). The maximum temperature difference between the reacting particle and the surrounding bed was found to be < 10 K for all cases. Thus, it is reasonable to conclude that the temperature within a particle was the same as that of the bed.

![Figure 5.7: Initial rate constant, \( k_0 \), at zero conversion over multiple cycles of reduction and temperatures of 723 K (\( \Delta \)), 773 K (\( \blacktriangle \)), 823 K (\( \Diamond \)), 873 K (\( \bullet \)), 923 K (\( \lozenge \)) and 973 K (\( \lozenge \)) for the reduction of \( Fe_2O_3 \) to \( Fe_3O_4 \). Here, \( k_0 \) increases with temperature and remains approximately constant over multiple cycles.](image)

From Fig. 5.7, it can be observed that the rate constant at zero conversion increases monotonically with temperature and remains approximately constant from cycle 2 to cycle 10 for a fixed temperature. The rate constant initially increases with cycle number in experiments above 873 K.

The initial rate constant was assumed to be of Arrhenius form with \( k_0 = A \exp(-E/RT) \), where \( A \) is the pre-exponential factor, \( E \) the activation energy, \( R \) the gas constant and \( T \) the
Figure 5.8: Arrhenius plot showing the activation energy, $E$, based on the initial rate constant, $k_0$, for the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ for cycles 2, 6 and 10 for particles with $R \sim 180 \mu$m. The average value was $E = 75$ kJ/mol. The $E$ calculated from $k$ for particles with $R \sim 940 \mu$m, where intraparticle diffusion is rate-limiting, was slightly greater than 1/2 that of particles with $R \sim 180 \mu$m, where intrinsic kinetics were rate-limiting.

The plot of ln($k_0$) versus $10^3/(RT)$ is shown in Fig. 5.8 and was used to determine the activation energy for particles with $R \sim 180 \mu$m. The activation energy was found to be $E = 72 \pm 12$ kJ/mol, $76 \pm 9$ kJ/mol and $78 \pm 11$ kJ/mol for cycles 2, 6 and 10, respectively. The activation energy was approximately constant over nine cycles with an average of $E = 75 \pm 11$ kJ/mol. The pre-exponential factor from the intercept of the best fit line with the ordinate at $10^3/RT = 0$, was determined as ln($A$) = 17.0±1.6, giving $A = 2.4\times10^7$ s$^{-1}$.

The experimental error is reported as an error in both the activation energy and pre-exponential factor using the standard error for the line’s slope and intercept, respectively, multiplied by the $t$-statistic for a 90% confidence interval with $(m−2)$ degrees of freedom, where $m$ is the number of experimental points. The errors in the activation energy and pre-exponential factor should not be combined, since they were derived from a single error in $k_0$ and such a combination would lead to inflated error estimates for $k_0$. Also shown in Fig. 5.8 is the activation energy obtained from $k$ for particles with $R \sim 940 \mu$m. For all particles in Fig. 5.7, external mass transfer was negligible, so $k = \eta k_i$. It has already been shown in Fig. 5.6 that for the 940 µm particles, $\eta = 3/\phi$; combining this with $k = \eta k_i$ gives $k = 3k_i/\phi$ and using the relation $\phi \propto k_i^{1/2}$.
from Eq. (5.6) gives \( k \propto k_i^{1/2} \). This relation demonstrates that the activation energy of the larger particles should be approximately one half that for the particles controlled by intrinsic kinetics, assuming the effective diffusivity does not change appreciably with temperature. Figure 5.8 shows that the activation energy for the particles with \( R \sim 940 \mu m \) is \( 48 \pm 12 \) kJ/mol, which overlaps with half the value of \( E = 75 \pm 11 \) kJ/mol for particles with \( R \sim 180 \mu m \).

![Figure 5.9: Plot of rate constant, \( k_i \), against conversion, \( X \), for cycle 2 at various temperatures. For \( X > 0.54 \), depicted by the shaded region, \( k_i \) begins to descend to zero and the monotonic increase of \( k_i \) with temperature is lost. The solid lines represent the fit, \( k_0(1 - X/0.8)^{0.4} \). The maximum conversion of \( X = 0.8 \) indicates that some of the weighed Fe\(_2\)O\(_3\) never reacts.](image)

To model chemical reactions, predicting the variation of \( r' \) with the conversion of Fe\(_2\)O\(_3\) is important. Figure 5.9 is a plot of \( k_i \) versus \( X \) for cycle 2 at six different temperatures. Higher values of \( k_i \) were found for higher temperatures when \( X < 0.5 \), as shown by the shaded region in Fig. 5.9. For all temperatures, \( k_i \) reaches zero at \( X \approx 0.8 \). Since conversion does not reach unity, some of the material never reacts. The variation of \( k_i \) can be quantified by fitting \( k_0f(X) = k_0(1 - X/0.8)^a \) to the experimental points in Fig. 5.9. This choice of \( f(X) \) is the simplest function which satisfies the constraints \( f(X)_{X=0} = 1 \) and \( f(X)_{X=0.8} = 0 \). A least squares analysis gave \( a = 0.4 \) and the resulting fits are shown by the solid lines in Fig. 5.9. The rate of reduction of Fe\(_2\)O\(_3\) to Fe\(_3\)O\(_4\) as a function of temperature and conversion over repeated
cycles of reduction can finally be summarised as

\[ r' = \frac{2.4 \times 10^7 \exp(-\frac{75000}{R T})}{\rho_{Fe_2O_3}} \left( c_{CO} - \frac{c_{CO_2}}{K_p} \right) \left( 1 - \frac{X}{0.8} \right)^{0.4}, \]  

(5.12)

where the pre-exponential factor has units (1/s), R has units J/(mol K), T is the absolute temperature in kelvin, \( \rho_{Fe_2O_3} \) is the bulk density of the \( Fe_2O_3 \) starting material in (g/m^3), \( c_{CO} \) and \( c_{CO_2} \) are concentrations in (mol/m^3), \( K_p \) is the dimensionless equilibrium constant, and \( X \) is the dimensionless conversion.

### 5.4.2 Transition from \( Fe_3O_4 \) to \( Fe_{0.947}O \)

The reduction of \( Fe_3O_4 \) to \( Fe_{0.947}O \) was studied between 923 K and 1173 K with inlet mole fractions of CO and CO\(_2\) both set between 8.5 and 9.5 vol.%. The rate at various conversions was determined from the corresponding plots of \( r' \) versus \( X \). X-ray diffraction confirmed the presence of \( Fe_{0.947}O \) after reduction of 5 g of \( Fe_2O_3 \) of sieve size \( d_p = +300, -425 \) µm in 9 vol.% CO, 9 vol.% CO\(_2\), balance N\(_2\) at 1173 K without any Al\(_2\)O\(_3\) in the bed and is shown in Fig. 5.10. The experimental diffraction pattern is shown below that of a simulated scan from a standard reference (JCPDS, 2005b) and clearly demonstrates the presence of \( Fe_{0.947}O \).

![Figure 5.10: Relative intensity (cps) against 2\( \theta \) for the reduced iron oxide as \( Fe_{0.947}O \); a simulated scan from a standard reference (JCPDS, 2005b) is shown with a vertical offset and demonstrates good agreement](image)

Prior to attempting to determine the activation energy and pre-exponential factor, the assumption that the reaction is first order with respect to CO was investigated at a fixed tem-
perature of 1023 K with a fixed batch mass of 0.8 g of Fe$_2$O$_3$. Using material balances and assuming the bed behaves as a CSTR, the rate given by Eq. (5.9) as $r' \propto (c_{CO,\text{out}} - c_{CO,\text{out}}/K_p)$ can be expressed in terms of the inlet concentrations so that $r' \propto (c_{CO,\text{in}} - c_{CO,\text{in}}/K_p)$, as was explained previously in the text following Eq. (5.10). Figure 5.11 (a) shows the observed initial rate at $X = 0$ obtained by holding the inlet CO$_2$ constant at 9 vol. % and varying the inlet CO. The rate can be described satisfactorily by a linear fit, indicating that the reaction is indeed first order with respect to [CO]. The circles on the abscissa in Fig. 5.11 (a) indicate the thermodynamic equilibrium points at the boundary between phases Fe$_3$O$_4$ and Fe$_{0.947}$O (i) and Fe$_{0.947}$O and Fe (ii), calculated from thermodynamic tables (Barin and Knacke, 1973). The intersection of the linear fit in Figure 5.11 (a) with the abscissa gives an experimental value of $K_p = 1.7$ for the transition from Fe$_3$O$_4$ to Fe$_{0.947}$O, found by dividing the inlet CO$_2$ value of 9 vol.% by the CO intercept value of 5.2 vol.%. Figure 5.11 (b) shows the observed initial rate at $X = 0$ obtained by holding the inlet CO constant at 9 vol. %, but varying the inlet CO$_2$. The rate varies linearly with the inlet concentration of CO$_2$. The circles in Fig. 5.11(b) represent the thermodynamic boundaries between phases Fe$_3$O$_4$ and Fe$_{0.947}$O (i) and Fe$_{0.947}$O and Fe (ii) calculated from thermodynamic tables (Barin and Knacke, 1973). Here, the intersection of the solid fit line with the abscissa gave CO$_2$ = 18 vol% and $K_p = 2.1$ for the equilibrium between phases Fe$_3$O$_4$ and Fe$_{0.947}$O. The theoretical calculated equilibrium value (Barin and Knacke, 1973) of 1.87, therefore lies between the two experimentally-determined values from Fig. 5.11(a) and (b) of 1.7 and 2.1, respectively, for the transition from Fe$_3$O$_4$ and Fe$_{0.947}$O at 1023 K.

The effect of external mass transfer was also found to be negligible and is examined quantitatively in the discussion. Next, to determine the regime where intrinsic kinetics solely control the observed rate, the initial rate at $X = 0$ was measured at a fixed temperature of 1023 K and fixed batch mass of 0.8 g of Fe$_2$O$_3$, whilst varying the size of the particles. The observed initial rate constant, $k$, is related to the true initial rate constant, $k_0$, by $k = k_0 \eta$ in the absence of external mass transfer. Figure 5.12(a) plots $k$ as a function of particle radius, $R$, over three cycles. As the particle size increases, $k$ falls roughly proportionally to $3/\phi$. For particles with $R < 300 \mu m$, $k$ is approximately constant at 640 s$^{-1}$. The true initial rate constant at zero conversion, $k_0 = 640$ s$^{-1}$, was found by iteratively solving for $k_0$ and $\eta$ using Eqs. 5.6 and 5.9 as previously outlined. The resulting values for $k_0$ are shown in Fig. 5.12 for cycle 2. Applying the iterative effectiveness factor correction has little effect on the rate constant for particles with $R < 300 \mu m$, since $k = k_0$. Here, the tortuosity, $\tau_p$, was a fitting parameter.
Figure 5.11: (a) The order of reaction for [CO] for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O at 1023 K. The inlet mole fraction of CO$_2$ was held constant at ~ 9 vol. %, and a first order fit is satisfactory. The circles on the abscissa show thermodynamic equilibrium (Barin and Knacke, 1973) of (i) 9 vol% CO$_2$ and 4.8 vol% CO with a mixture of Fe$_3$O$_4$ and Fe$_{0.947}$O and (ii) 9 vol.% CO$_2$ and 15.4 vol% CO with Fe$_{0.947}$O and Fe.

(b) Relation between reaction rate and [CO$_2$] for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O at 1023 K. Here, the inlet mole fraction of CO was maintained at ~ 9 vol. %. The rate varies linearly with inlet [CO$_2$]. The circles on the abscissa show thermodynamic equilibrium of (i) 16.8 vol.% CO$_2$ and 9 vol% CO with a mixture of Fe$_3$O$_4$ and Fe$_{0.947}$O and (ii) 5.3 vol% CO$_2$ and 9 vol% CO with a mixture of Fe$_{0.947}$O and Fe.
as was determined based on the ability to recover a constant \( k_i \) from the values of \( k \) obtained from reacting particles of various sizes. The value of \( \tau_p \) was set to 2.5, typical of porous pellets (Satterfield, 1980). Figure 5.12(b) shows an approximation for the effectiveness factor, \( \eta = k/640 \text{ s}^{-1} \), versus the calculated value of \( \phi \) from Eq. (5.6) over three cycles. For particles with \( R < 300 \mu m \), \( \eta \sim 1 \) indicating that the observed rate is limited by intrinsic kinetics. For larger particles, \( \eta \) approaches \( 3/\phi \), indicating that the rate is governed by intraparticle diffusion. Therefore, to avoid elutriation whilst still capturing the intrinsic kinetics, particles with \( 150 \mu m < R < 210 \mu m \) were used in all subsequent experiments.

To determine whether heat transfer was limiting, an order of magnitude estimate of the Biot number, \((h d_p/6 \lambda_e)\), for a single particle with \( R \sim 180 \mu m \) was performed and gave \( Bi << 1 \) and typically, \( Bi \approx 0.05 \), as shown in Table 5.1, indicating that the temperature across a single particle was uniform. Next, a simple heat balance using Eq. (5.11) was used to estimate the maximum temperature difference between the particle and the bed during reduction. The temperature in the particle was assumed uniform since \( Bi << 1 \), and the rate was assumed equal to the initial rate at \( X = 0 \); a conservative estimate of the heat transfer coefficient was obtained using \( Nu = 2 \) and the thermal conductivity of the reactant gas. The maximum temperature difference between the reacting particle and the surrounding bed was found to be \(< 6 \text{ K} \) for all cases. Thus, it is reasonable to conclude that the temperature within a particle was the same as that of the bed.

Previously, to determine the order of reaction and the regime where intrinsic kinetics dominate the reduction of \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \), the initial rate at \( X = 0 \) was used. To determine the pre-exponential factor and activation energy for the reduction of \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \), however, better precision in the value of the rate constant, \( k_i \), was achieved by using rates evaluated at \( X > 0 \). The reason derives from Eq. (5.9) for \( k_i \), which gives \( k_i \propto r^\prime/(c_{\text{CO},\text{out}} - c_{\text{CO}_2,\text{out}}/K_p) \) for negligible mass transfer resistance and \( \eta = 1 \). For large rates, fast kinetics permit nearly complete conversion of \( \text{CO} \) to the equilibrium limit. The evaluation of the rate constant, \( k_i \), therefore relies on division by a concentration term of small magnitude. Using smaller rates, \( i.e. \) at \( X > 0 \), reduces the uncertainty in \( k_i \) introduced by this term. Figure 5.13(a) shows the concentration of \( \text{CO} \) and \( \text{CO}_2 \) in the effluent gas as a function of time for the reduction of \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \) at 1023 K. Figure 5.13(b) then shows the corresponding concentration term, \((c_{\text{CO},\text{out}} - c_{\text{CO}_2,\text{out}}/K_p)\), calculated from the results in Fig. 5.13(a), where only every fifth point is plotted. The tradeoff between (i) a large enough batch mass to give measurable changes in the outlet concentrations during reaction as well as reduction times significantly greater than the
Figure 5.12: Reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O at 1023 K.

(a) Plot of initial rate constant $k$ at $X = 0$ versus average radius, $R$, of the iron oxide particles for cycles 2 (♦), 3 (○) and 4 (▲). The corrected intrinsic rate constant at zero conversion, $k_0$, is also shown for cycle 2 (♦) and has an average value of 640 s$^{-1}$.

(b) Effectiveness factor, $\eta = k/640$ s$^{-1}$, versus $\phi$ for particles of various radii for cycles 2 (♦), 3 (○) and 4 (▲), corresponding to the points in (a). For smaller particles, $\eta = 1.0$; as particle size increases $\eta$ approaches $3/\phi$. 
Figure 5.13: (a) Concentration of CO and CO$_2$ in the effluent gas as a function of time for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O in a fluidised bed for cycle 2 at 1023 K. The initial charge was either 0.3 g or 0.8 g as Fe$_2$O$_3$ and had been reduced to Fe$_{0.947}$O in a mixture of CO, CO$_2$ and N$_2$ and then oxidised to Fe$_3$O$_4$ in a mixture of steam and N$_2$ prior to $t = 0$.

(b) Concentration term, $(c_{\text{CO,out}} - c_{\text{CO}_2,\text{out}}/K_p)$, against time corresponding to the experiments in (a).

Figure 5.14 shows $k_i$ evaluated at $X = 0.3$ over nine cycles and temperatures from 923 K to 1173 K. The inlet CO and CO$_2$ were both fixed at 9 vol.% for all cases. Unlike the rate constant for the transition from Fe$_2$O$_3$ to Fe$_3$O$_4$, which remained approximately constant with cycle number, $k_i$ decreases with cycle number. The drop in $k_i$ is more pronounced at higher temperatures.

The rate constant was assumed to be of Arrhenius form with $k_i = A \exp(-E/RT)$. A plot
Intrinsic rate constant, $k_i$, at $X = 0.3$ for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O. Here, $k_i$ increases with temperature, but decreases with the number of cycles.

Figure 5.14: Intrinsic rate constant, $k_i$, at $X = 0.3$ for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O. Here, $k_i$ increases with temperature, but decreases with the number of cycles.

The variation of the rate, $r'$, with conversion, $X$, must be determined. Figure 5.16 is a plot of $k_i$ against $X$. As shown by the shaded regions, for values of $X > 0.6$ the monotonic increase in $k_i$ with temperature is lost; for values of
Figure 5.15: Activation energy diagram for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O. A slight decrease in $E$ with cycle number is observed. The $E$ calculated from $k$ for particles with $R \sim 940 \mu$m is half that observed for particles with $R \sim 180 \mu$m.

$X < 0.2$ above 1023 K, $k_i$ increases rapidly: the rate of reaction was too fast to obtain results for $X < 0.2$. The range of conversions where values of $k_i$ could reasonably be obtained was $0.2 < X < 0.6$. In this range, values for $E$ agreed well with those determined earlier for $X = 0.3$. A least-squares fit with the functional form $k_i = k_0(1 - X/0.8)^a$ gave $a = 1.2$. The fit was performed such that the correct value of $k_i$ at $X = 0.3$ was recovered. The pre-exponential factor, $A$, for the initial rate constant, $k_0$, could then be obtained from the previously reported values of $A$ for $k_i$ at $X = 0.3$ by adding $-1.2 \ln(1 - 0.3/0.8) \sim 0.55$ to $\ln(A)$. Hence, the pre-exponential factors for $k_0$ are $\ln(A) = 17.6 \pm 2.1, 17.1 \pm 1.9$ and $16.3 \pm 1.8$ for cycles 2, 6 and 10 respectively, corresponding to $A = 4.3 \times 10^7$, $2.5 \times 10^7$ and $1.2 \times 10^7$ s$^{-1}$. Thus, the rate constants as a function of temperature and conversion for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O for cycles 2, 6 and 10 can be summarised by:

$$r' = \frac{4.3 \times 10^7 \exp\left(-\frac{94000}{RT}\right)}{\rho_{Fe_3O_4}} \left( \frac{c_{CO} - c_{CO_2}}{K_p} \right) \left(1 - \frac{X}{0.8}\right)^{1.2}$$

$$r' = \frac{2.5 \times 10^7 \exp\left(-\frac{94000}{RT}\right)}{\rho_{Fe_3O_4}} \left( \frac{c_{CO} - c_{CO_2}}{K_p} \right) \left(1 - \frac{X}{0.8}\right)^{1.2}$$

$$r' = \frac{1.2 \times 10^7 \exp\left(-\frac{94000}{RT}\right)}{\rho_{Fe_3O_4}} \left( \frac{c_{CO} - c_{CO_2}}{K_p} \right) \left(1 - \frac{X}{0.8}\right)^{1.2}.$$  (5.13)
where \( r' \) again has units of mol/(s g of original particle as Fe\(_2\)O\(_3\)).

![Figure 5.16: Plot of the rate term, \( k_i \), versus conversion, \( X \), for cycle 2 at various temperatures. The rapid rise of \( k_i \) for \( X < 0.2 \) and the decrease of \( k_i \) towards zero with \( X > 0.6 \) is evident, as shown by the shaded regions. Rates within the interval \( 0.2 < X < 0.6 \) gave a best fit of \( k_i = k_0(1 - X/0.8)^{1.2}; \) this fit is indicated by the solid lines.]

### 5.4.3 Packed Bed

To verify the kinetic parameters obtained from the fluidised bed experiments, the reduction of iron oxide was investigated in a packed bed at 1023 K. A simplified 1D model of a packed bed, which used the rate constants determined from the fluidised bed experiments given in Eqs. (5.12) and (5.13), was constructed to compare experimental results with theory. To formulate a mathematical description of the system, it was assumed that (i) the bed was isothermal, (ii) only axial concentration gradients were significant, i.e. the problem was treated as one-dimensional, (iii) the reaction rate was limited only by intrinsic kinetics and external mass transfer, not by intraparticle diffusion, (iv) the dispersion coefficient was constant for both CO and CO\(_2\) along the bed, (v) gas flowed through the interstices only, not through the porous particles, and (vi) frictional losses were insignificant so that pressure did not vary along the bed. The assumption of isothermal operation was based on the experimental observation that the maximum measured change in temperature during reduction was small, < 30 K, compared
to the operating temperature 1023 K. The evolution of the gaseous and metal oxide species in the pseudohomogeneous bed as a function of time, \( t \), and position, \( x \), are then given for CO and Fe\(_2\)O\(_3\) by:

\[
\left( \frac{\partial c_{CO}}{\partial t} \right)_{x} = -v \left( \frac{\partial c_{CO}}{\partial x} \right)_{t} + D \left( \frac{\partial^{2} c_{CO}}{\partial x^{2}} \right)_{t}, \tag{5.14}
\]

\[
- \frac{(1 - \varepsilon_{\text{bed}})}{\varepsilon_{\text{bed}}} \left[ k \left( c_{CO} - \frac{c_{CO_{2}}}{K_{p}} \right) \left( 1 - \frac{X}{0.8} \right)^{0.4} + k \left( c_{CO} - \frac{c_{CO_{2}}}{K_{p}} \right) \left( 1 - \frac{X}{0.8} \right)^{1.2} \right] \text{reaction 5.1}
\]

\[
\left( \frac{\partial n_{Fe_{2}O_{3}}}{\partial t} \right)_{x} = -3 \left[ K \left( c_{CO} - \frac{c_{CO_{2}}}{K_{p}} \right) \left( 1 - \frac{X}{0.8} \right)^{0.4} \right] \text{reaction 5.1}, \tag{5.15}
\]

where the parameters, \( k \), \( K_{p} \) and \( X \), are defined as appropriate for whether reaction (5.1) or (5.2) is being considered, consistent with Eqs. (5.12) and (5.13) in the previous discussion. Here, \( \varepsilon_{\text{bed}} = 0.36 \) is the mean measured interstitial porosity of the bed, \( v = 3.88 \) m/s is the interstitial velocity, \( K_{p} \) are the equilibrium constants, \( n_{Fe_{2}O_{3}} \) is the number of moles of Fe\(_2\)O\(_3\) per unit volume particle, \(-3\) is the stoichiometric coefficient from reaction (5.1), and \( D = 8 \times 10^{-4} \) m\(^2\)/s is the dispersion coefficient, calculated using Eq. (12) from Gunn (1968) and verified with Levenspiel’s Fig. 13.17 (Levenspiel, 1999). The mass transfer coefficients, \( k_{g,CO} \) and \( k_{g,CO_{2}} \), from the bulk gas to the surface of the particles, which appear in the rate constant, \( k \), were calculated using the correlation of Wakao and Funazkri (1978), \( S h = 2.0 + 1.1Re^{0.6}Sc^{1/3} \) and gave \( k_{g,CO} = 1.96 \) m/s and \( k_{g,CO_{2}} = 1.61 \) m/s. Hence, the values of \( k \) for reactions (5.1) and (5.2) are

\[
\begin{align*}
\text{Fe}_{2}\text{O}_{3} \rightarrow \text{Fe}_{3}\text{O}_{4} & : \quad \frac{1}{k} = \frac{R}{3k_{g,CO}} + \frac{1}{2.4 \times 10^{7} \exp(-75000/R_{T})} + \frac{R}{3k_{g,CO_{2}}K_{p}} = \frac{1}{3200} \text{s}^{-1}, \\
\text{Fe}_{3}\text{O}_{4} \rightarrow \text{Fe}_{0.947}\text{O} & : \quad \frac{1}{k} = \frac{R}{3k_{g,CO}} + \frac{1}{4.3 \times 10^{7} \exp(-94000/R_{T})} + \frac{R}{3k_{g,CO_{2}}K_{p}} = \frac{1}{660} \text{s}^{-1},
\end{align*}
\tag{5.16}
\]

respectively, for the second cycle of reduction. It is noted that the effect of the mass transfer is minimal: eliminating terms with \( k_{g,CO} \) and \( k_{g,CO_{2}} \) in Eq. (5.16) results in values of \( k \) of 3580 s\(^{-1}\) and 680 s\(^{-1}\) for reactions (5.1) and (5.2), respectively, less than 12 % change in \( k \) for reaction (5.1) and less than 3 % change in \( k \) for reaction (5.2). Thus, all the parameters were determined experimentally with the exception of the mass transfer and dispersion coefficients.
Furthermore, the effect of the dispersion coefficient was small due to the large Péclet number, $Pe = vL/D = 160$. The equations were discretised using an upwind finite difference scheme. The length of the bed was $L = 33$ mm and the number of grid points used was 100. Boundary conditions were chosen to be of the Danckwerts form and were expressed for the case of CO as: $v[c_{CO}(0) - c_{CO,in}] - D(∂c_{CO}/∂x)_{x=0} = 0$ and $(∂c_{CO}/∂x)_{x=L} = 0$ at the inlet and outlet, respectively (Beers, 2007). Here, $c_{CO}(0)$ is the concentration of CO at the grid point at the inlet to the bed, whereas $c_{CO,in}$ is the specified inlet concentration, which for an approximately 9 vol. % fraction at 1023 K and $10^5$ Pa gives $c_{CO,in} = 1$ mol/m$^3$. The inlet $[CO_2]$ was also 1 mol/m$^3$. To prevent the model from producing negative amounts of Fe$_{0.947}$O, an additional thermodynamic constraint was added: the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O, reaction (5.2), in a differential element was not permitted unless locally $p_{CO_2}/p_{CO} < 2.1$, which represents the experimental equilibrium constant. Finally, once a conversion $X = 0.8$ had been reached for a reaction in a differential cell, the corresponding $k_i$ was set to 0.

![Figure 5.17: Comparison between the effluent concentration of CO and CO$_2$ as a function of time for experimental results (•, •) and model predictions (—), respectively, with $D = 8 \times 10^{-4}$ m$^2$/s for the reduction of 5 g of Fe$_2$O$_3$ to Fe$_{0.947}$O at 1023 K. Results with an increased dispersion of $D = 8 \times 10^{-3}$ m$^2$/s are shown by the dashed lines (- - -); results for a decreased dispersion of $D = 8 \times 10^{-5}$ m$^2$/s are similar to the original result (—).](image)

The packed bed, containing 5 g of Fe$_2$O$_3$ particles with $R \sim 180 \mu$m, was heated to 1023 K in a stream of air. The reactor was subsequently purged with $N_2$ for 500 s. At $t = 0$, the
gas was suddenly changed from \( \text{N}_2 \) to a mixture of \( \text{N}_2 + \text{CO} + \text{CO}_2 \) (respectively, 82, 9 and 9 vol. %), which from thermodynamics will reduce the \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \), forming \( \text{Fe}_3\text{O}_4 \) as an intermediate. Reoxidation was performed with \( \text{N}_2 + \text{steam} \) (respectively, 82 and 18 vol. %) and \( \text{N}_2 + \text{air} \) (respectively, 82 and 18 vol. %). Figure 5.17 shows the concentrations of CO and \( \text{CO}_2 \) at the reactor outlet, \( x = L \), as a function of time for the second reduction cycle. Initially, for \( 0 \text{ s} < t < 90 \text{ s} \), Figure 5.17 shows that the entering CO is fully converted to \( \text{CO}_2 \). In this interval, a front corresponding to the reduction of \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \) in reaction (5.1), propagates down the bed. The intrinsic kinetics are sufficiently fast to permit equilibrium to be reached, so that the ratio \( c_{\text{CO, out}} / c_{\text{CO}_2, \text{out}} = 1/K_p \approx 0 \). The relation between the residence time of the gas and the characteristic kinetic time constant also demonstrates that reactant gases have sufficient time to react fully, since \( 1/k < L/v \). The breakthrough of the front after \( t \approx 95 \text{ s} \) is characterised by a rapid rise and fall in the concentrations of CO and \( \text{CO}_2 \), respectively. At this stage the \( \text{Fe}_2\text{O}_3 \) along the bed has been fully converted to \( \text{Fe}_3\text{O}_4 \); also \( \text{Fe}_{0.947}\text{O} \) has appeared at the reactor inlet. The conversion of \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \), which has already commenced at the beginning of the bed for \( t < 95 \text{ s} \), continues until \( t \approx 410 \text{ s} \). For \( t > 200 \text{ s} \), the curvature of the outlet concentrations is primarily governed by kinetics and the accuracy of the value of \( k \) for reaction (5.2) is demonstrated by the good agreement between the experimental and modelled concentration curves. For \( t > 410 \text{ s} \) no more reaction occurs and the concentrations of CO and \( \text{CO}_2 \) in the outlet are equal to those at the inlet, \( i.e. \) 1 mol/m\(^3\). The arrows in Fig. 5.17 indicate the times when various metal oxide species eligible of undergoing reaction were present above 5 mol % at the reactor outlet, \( i.e. \) in the final computational cell. The narrow overlap between the \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) lines indicates a sharp front, compared to the more gradual transition between \( \text{Fe}_3\text{O}_4 \) and \( \text{Fe}_{0.947}\text{O} \).

The influence of the dispersion coefficient was also investigated by increasing and decreasing \( D \) in the range \( D = 8 \times 10^{-3} \text{ m}^2/\text{s} \) to \( D = 8 \times 10^{-5} \text{ m}^2/\text{s} \). Figure 5.17 shows that altering \( D \) by two orders of magnitude does not influence the results, as expected given the large \( Pe \) number, \( Pe = 160 \).

Figure 5.18 shows how changes in \( k_i \) for the reduction of \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \) affect \( c_{\text{CO, out}} \) and \( c_{\text{CO}_2, \text{out}} \) predicted by the model. Values of \( 1/2k_i, k_i, 2k_i \) and \( 10k_i \), giving \( k = 340, 660, 1280 \) and 5060 s\(^{-1} \) were used. Figure 5.18 shows that the front corresponding to the transition from \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \) does not change appreciably; this is expected since the rate parameter for this transition was not altered and since reduction of \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \) was limited by the inflow of reactant CO. In contrast, the front corresponding to the transition from \( \text{Fe}_3\text{O}_4 \) to
Figure 5.18: Effluent concentration of CO and CO$_2$ against time for the reduction of 5 g of Fe$_2$O$_3$ to Fe$_{0.947}$O at 1023 K. The effect of changing $k_i$ for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O, reaction (5.2) on the effluent concentrations, front thickness and front speed is shown.

Fe$_{0.947}$O grows sharper with increasing $k_i$, depicted by the decreasing overlap between species of Fe$_3$O$_4$ to Fe$_{0.947}$O, shown by grey regions above the graph in Fig. 5.18. Here, the CO and CO$_2$ effluent curves approximate step functions when $k_i$ is raised 10×. Interestingly, the CO and CO$_2$ effluent curves for each simulation intersect at $t = 320$ s, suggesting that for the given inlet flowrate and inlet concentrations, an infinitely large $k_i$ would cause an infinitely thin front to emerge at this time. Also interesting to note is how the total quantity of Fe$_{0.947}$O in the bed changes at a fixed time, say $t = 90$ s or just before CO$_2$ breakthrough, in order to understand how the theoretical yield of H$_2$ could change with increased kinetics. Summing the quantity of Fe$_{0.947}$O in each node along the reactor at $t = 90$ s, shows that for $1/2k_i$, $2k_i$ and $10k_i$, 0.91×, 1.05× and 1.10× as much Fe$_{0.947}$O is present compared to the case with $k_i$. More Fe$_{0.947}$O in the bed will result in more H$_2$ upon subsequent oxidation in steam. Therefore, an experimental investigation into increasing the rate of reaction of the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O is presented in the next Chapter.
5.5 Discussion

For the design of equipment to reduce Fe$_2$O$_3$ using CO with subsequent reoxidation in steam to produce H$_2$, the long-term stability of the rate of reduction over many cycles is important. Figure 5.7 shows that the initial rate constant, $k_0$, for the reduction from Fe$_2$O$_3$ to Fe$_3$O$_4$ did not decrease, but remained constant over nine cycles.

For the rate constants in Fig. 5.8 for particles with $R \sim 180$ µm, the ratios of the resistance of external mass transfer of CO to the resistance of intrinsic kinetics, i.e. the ratio of the sum of the first and third terms in Eq. (5.7) divided by the second term, was $\sim 0.01$ and $\sim 0.15$ at 723 K and 923 K, respectively, thus ensuring that the experimental rates were dominated by intrinsic kinetics. Figure 5.6(b) confirmed that the effectiveness factor was near unity at 823 K for particles with $R \approx 150 – 210$ µm. It was observed that the deduced activation energy was approximately halved when the particle size was increased, as seen in Fig. 5.8, suggesting that the effectiveness factor was unity for small particles and that the rate of reduction for the larger particles was controlled by intraparticle diffusion. For the initial rate constant, $k_0$, a pre-exponential factor of $2.4 \times 10^7$ s$^{-1}$ and an activation energy of $75 \pm 11$ kJ/mol was obtained; both values were constant and reproducible over repeated cycles. By comparison, Trushenski et al. (1974) give $69.0$ kJ/mol $< E < 100.0$ kJ/mol and Szekely et al. (1976) report $E = 114$ kJ/mol. These authors’ values were extracted from experiments with significant mass-transfer resistance. Figure 5.9 showed that the effect of conversion, $X$, can be represented by the function $(1 – X/0.8)^{0.4}$. Interpreting the exponent, $a = 0.4$, we find that terms of $(1 – X)^{1/3}$ and $(1 – X)^{1/2}$ are typical for theoretical rate expressions involving shrinking cores in spherical and cylindrical geometries, respectively, where the reaction is limited by intrinsic kinetics. However, in the current study, shrinking cores could not exist on the length scale of an individual particle, since the highly porous matrix allowed gas to diffuse across the entire cross-section and effectiveness factors near unity were calculated. A shrinking core interpretation might, however, be applicable at the subparticle, e.g. grain, length scale.

For the transition from Fe$_3$O$_4$ to Fe$_{0.947}$O, $K_p$ is of order unity and the influence of the back reaction, because it reduced the overall rate, permitted higher temperatures and reactant concentrations to be used in the determination of the rate constant, $k_i$. At a conversion of $X = 0.3$, the ratio of the resistance due to external mass transfer of CO and CO$_2$ to that of the chemical reaction, i.e. the central term in the second equation of Eq. (5.7) divided by the sum of the two mass transfer terms in the second equation of Eq. (5.7), was given as $\sim 0.02$ and
0.17 at 923 K and 1173 K, respectively, for particles with \( R \sim 180 \mu m \). The primary control of intrinsic kinetics was thus ensured and confirmed by effectiveness factors near unity for particles with \( R \sim 180 \mu m \), see Fig. 5.12. Unlike the transition from \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \), Fig. 5.14 showed that the rate constant decreased with cycle number. Efforts to produce particles for the repeated generation of \( \text{H}_2 \) should therefore focus on reaction (5.2) and investigate how promoters or stabilising agents could be used to prevent the decrease in rate over a number of cycles.

That the observed decrease in rate with cycle number (Fig. 5.14) was a result of a decrease in the pre-exponential factor is demonstrated by the fact that the activation energy in Fig. 5.15 showed only a slight decrease with cycle number: the average value of \( E \) was 94 ± 25 kJ/mol. Interpreting the activation energy and pre-exponential factor as a chemical barrier and a probability of a reactive collision occurring at a surface, respectively, these observations imply that the probability of reaction decreases with cycle number whilst the intrinsic chemical barrier remains constant. Physically, this interpretation suggests a decrease in active surface area with cycle number, which was observed for the reduction of \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \) in a packed bed and shown in Table 3.2, line 2. Figure 5.15 showed that \( E \), found using the observed rate constant for particles which were one order of magnitude larger than those in the kinetic study, resulted in an apparent \( E \) half as large as that found in the kinetic study. Comparing \( E = 94 \pm 25 \) kJ/mol obtained here, Trushenski et al. (1974) gives 64.4 kJ/mol < \( E < 78.2 \) kJ/mol and Szekely et al. (1976) report \( E = 73.6 \) kJ/mol. These authors’ values were obtained from experiments with significant mass-transfer resistance, but fidelity to within the error estimate is obtained. Figure 5.16 showed that the effect of conversion for the transition from \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \) was best represented by \((1 - X/0.8)^2\). The term \((1 - X)^a\) with \( a = 1 \) is typical for a uniform reaction over a porous sphere.

One question regarding the reduction of iron oxide in mixtures of CO and CO\(_2\) which requires attention is that of the mechanism of reduction and of the corresponding rate-limiting step. While there is no consensus in the literature on the mechanism, the most accepted theory is that proposed by Birks et al. (2006) who studied oxidation in the context of corrosion, i.e. the reverse reactions of those here. They suggested that the interaction of CO and CO\(_2\) with the surface of the metal was rate limiting when the external \( \text{Fe}_{0.947}\text{O} \) layer was < 18 \( \mu m \). In other words, the limiting reaction is

\[
\text{CO}_\text{g} + \text{O}_{\text{ad}} \rightleftharpoons \text{CO}_2\text{g},
\]

(5.17)
which immediately lends itself to interpretation by the rate expression:

\[
\frac{\text{mol}}{\text{m}^2 \text{s}} = \frac{k_i}{S_0} \left( c_{\text{CO}} - \frac{c_{\text{CO}_2}}{K_p} \right),
\]

where \( S_0 \) is the surface area of the particle per unit volume in \( \text{m}^2/\text{m}^3 \). Rate Eqs. (5.12) and (5.13) multiplied by \( S_g \), the specific surface area in \( \text{m}^2/\text{g} \), are of the form of Eq. (5.18) when \( X = 0 \). Here it should be noted that individual grains had diameters of 0.5 \( \mu \text{m} \) as shown in Fig. 4.1, considerably less than the < 18 \( \mu \text{m} \) limit for the validity of Eq. (5.18). In the current study a decrease in the reaction with \( X \) was observed. The dependence on \( X \) could be explained by a decrease in the surface area of the particle with conversion or due to the diffusion of cations or cation vacancies within the lattice becoming rate limiting (Birks et al., 2006).

The rate constants were verified by investigating the consecutive reduction of \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_{0.947}\text{O} \) in a packed bed. Figure 5.17 showed good agreement between observed and predicted values of \([\text{CO}]\) and \([\text{CO}_2]\) in the effluent for the reduction of \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \), for \( t > 94 \text{ s} \). The model showed that the reduction of \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \) occurred at a sharper front than the more gradual reduction of \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \), see Fig. 5.17. This observation is a direct result of the value of the rates, since \( r' \) for reaction (5.1) is much greater than \( r' \) for reaction (5.2) at a given temperature.

### 5.6 Conclusions

Results were obtained for the repeated reduction of iron oxide particles, 300-425 \( \mu \text{m} \) dia., by mixtures of CO, \( \text{CO}_2 \) and \( \text{N}_2 \) in a fluidised bed. The transitions from \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \) and from \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_{0.947}\text{O} \) were studied at \( 10^5 \text{ Pa} \) and at temperatures of 723-973 K and 923-1173 K, respectively. The following conclusions were reached:

- The order of reaction for CO was found to be unity in both reduction reactions.
- With the particle sizes used the rates of the reduction reactions are controlled by intrinsic chemical kinetics. The variation of the rate with solids’ conversion and temperature was
expressed as:

\[
\begin{align*}
\text{Fe}_2\text{O}_3 & \rightarrow \text{Fe}_3\text{O}_4 \\
: r' &= \frac{2.4 \times 10^7 \exp(\frac{-75000}{RT})}{\rho_{\text{Fe}_2\text{O}_3}} \left( c_{\text{CO}} - \frac{c_{\text{CO}_2}}{K_p} \right) \left( 1 - \frac{X}{0.8} \right)^{0.4} \tag{5.19} \\
\text{Fe}_3\text{O}_4 & \rightarrow \text{Fe}_{0.947}\text{O} \\
: r' &= \frac{4.3 \times 10^7 \exp(\frac{-94000}{RT})}{\rho_{\text{Fe}_2\text{O}_3}} \left( c_{\text{CO}} - \frac{c_{\text{CO}_2}}{K_p} \right) \left( 1 - \frac{X}{0.8} \right)^{1.2} , \tag{5.20}
\end{align*}
\]

where the pre-exponential factor in Eq. (5.20) is reported for cycle 2. The activation energies were verified by showing that for larger particles where intraparticle diffusion limits the rate, the observed activation energy approximately halves.

- The first cycle gave anomalous results, but (a) the rate of reduction of Fe\(_2\)O\(_3\) to Fe\(_3\)O\(_4\) remained constant over cycles 2-10; (b) the rate of reduction of Fe\(_3\)O\(_4\) to Fe\(_{0.947}\)O declined by 60-85 % over cycles 2-10.

- The rate constants, determined in a fluidised bed, were used to predict successfully the reduction of iron oxide in a packed bed.
Chapter 6

Increasing the rate of reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O

6.1 Introduction

The objective of the preliminary work presented in this Chapter is to survey a variety of chemical species to find a promoter, either physical or chemical, which increases the rate of reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O by increasing the rate constant, $k_i$. Since $k_i$ is of Arrhenius form with $k_i = A \exp(-E/RT)$, an increase in $k_i$ can be obtained by either increasing the pre-exponential factor, $A$ (physical promotion), or by decreasing the activation energy, $E$ (chemical promotion).

6.2 Experimental

For the preparation of particles of iron oxide, three methods were used:

1. As a control, the technique given in Chapter 2, section 2.2 was followed. Water was sprayed on to Fe$_2$O$_3$ powder ($< 5 \ \mu$m, Sigma-Aldrich) with a purity $> 99+$ wt. % to form agglomerates. The resulting mixture was mechanically stirred both during and after spraying, and then the granules were sieved to the desired size fraction of +300,-425$\mu$m. These particles were then sintered in an oven at 1173 K for 3 h, cooled in air and then re-sieved to +300,-425$\mu$m.

2. For the addition of promoter, 5 ml of a 0.05 M solution based on the promoter cation was added to 2 g of Fe$_2$O$_3$ powder in a beaker, stirred vigorously and placed in an oven
Table 6.1: Method of preparation, promoter, molar loading \((x_m)\), \(\text{Fe}_2\text{O}_3\) precursor, total calcining time and measured BET surface area for select samples with diameter \(+300,-425\ \mu\text{m}\) prior to experiments. The figure number corresponding to the experiment in which each sample was used is listed.

<table>
<thead>
<tr>
<th>Experimental Method</th>
<th>Particle Preparation</th>
<th>Cation (x_m)</th>
<th>(\text{Fe}_2\text{O}_3) Precursor</th>
<th>Calcining Time (h)</th>
<th>BET (m(^2)/g)</th>
<th>Figs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) unmodified</td>
<td>0.0</td>
<td>particle</td>
<td>3 h</td>
<td>1.2</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>(ii) unmodified</td>
<td>0.0</td>
<td>powder</td>
<td>3 h</td>
<td>1.2</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>(ii) with Ce</td>
<td>0.01</td>
<td>powder</td>
<td>3 h</td>
<td>2.8</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>(iii) with Ce</td>
<td>0.01</td>
<td>particle</td>
<td>6 h</td>
<td>1.3</td>
<td>6.3</td>
<td></td>
</tr>
</tbody>
</table>

at 353 K until dry. The powder was then sintered at 1173 K for 3 h, cooled in air and sieved to \(+300,-425\ \mu\text{m}\).

3. To simulate the addition of promoter to a naturally-occurring ore, appropriate volumes of a 0.05 M solution based on the promoter cation were added to a beaker containing 2 g of sintered \(\text{Fe}_2\text{O}_3\) particles prepared following method (1) above. After drying in an oven at 353 K, the resulting particles were sintered at 1173 K for 3 h, cooled in air and sieved to \(+300,-425\ \mu\text{m}\).

The precursors for the promoter were \(\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}\) (Acros Organics; > 99.5 wt. %), \(\text{PtCl}_2\) (Acros Organics; 73 wt. % Pt), \(\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}\) (Fisher; > 98 wt. %), \(\text{Cu(NO}_3)_2 \cdot 2.5\text{H}_2\text{O}\) (Acros Organics; > 98 wt. %) and \(\text{ZrO(NO}_3)_2 \cdot n\text{H}_2\text{O}\) (Fisher; 99.5 wt. % up to 4 wt. % Hf).

While the use of Pt might be uneconomical in industrial applications, the focus of the study was to determine effective promoters and Pt has therefore been included. Dissolution of Pt was aided by the addition of 1 drop of 1 M of HCl. The loading of promoter using methods (2) and (3) is reported on a molar basis, and is defined identically to Chapter 3:

\[
x_m = \frac{\text{mol } M}{\text{mol } M + \text{mol Fe}^+}
\]

where \(M\) is the promoter, \(e.g.\) Ce. No deposition of the precursor was observed on the beakers after drying indicating complete uptake by the iron oxide. As in Chapter 3 the molar loading was confirmed gravimetrically for particles prepared using method (3) with \(x_m = 0.1\) and typically gave \(x_m = 0.1 \pm 0.01\). Table 6.1 lists the method of preparation, promoter, molar loading, \(\text{Fe}_2\text{O}_3\) precursor, total calcining time and BET surface area (Brunauer et al., 1938) for selected particles, as well as the figure number corresponding to the experiment in which each was used.
Table 6.2: Redox cycling: gas mixtures (vol. %), flowrates (m$^3$/s) as measured at 298 K and 10$^5$ Pa, and corresponding flow durations (s) for experiments. The total cycle time was 600 s.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Purge</th>
<th>Reduction</th>
<th>Purge</th>
<th>Steam Oxidation</th>
<th>Figs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-120</td>
<td>0.33 $\times 10^{-5}$</td>
<td>0.33 $\times 10^{-5}$</td>
<td>0.33 $\times 10^{-5}$</td>
<td>0.33 $\times 10^{-5}$</td>
<td>N$_2$, 8.9% CO/8.9% CO$_2$/82.2% N$_2$, N$_2$, 25% steam/75% N$_2$</td>
</tr>
</tbody>
</table>

The experimental apparatus used to measure rates of reaction was identical to that described in Chapter 5. The temperature of the fluidised bed was maintained at 1023 K in all experiments, as measured by a type K thermocouple inside the bed. The mass of unmodified Fe$_2$O$_3$ and promoted Fe$_2$O$_3$ added to the bed was fixed at 0.3 g in all cases. The compositions and flowrates of the inlet gas are listed in Table 6.2. The composition of the effluent gas was measured using identical analysers in the same arrangement as in Chapter 5, section 5.2.

6.3 Results

The measured rate at $X = 0.3$ was used with Eq. (5.9) from Chapter 5:

$$r' = \frac{k}{\rho_{Fe_2O_3}} \left( c_{CO, out} - \frac{c_{CO_2, out}}{K_p} \right)$$

$$\frac{1}{k} = \frac{R}{3k_{g,CO}} + \frac{1}{k_i} + \frac{R}{3k_{g,CO_2}K_p}$$

(6.2)

to determine $k_i$ as follows. For an effectiveness factor $\eta = 1$ an initial estimate for $k_i$ was obtained. This value of $k_i$ was then used in Eq. (5.6) to calculate a new value of $\eta$. Equations (6.2) and (5.6) were then used iteratively until $k_i$ and $\eta$ converged. Typically, $\eta = 0.95$, $k_i = O(10^5)$ s$^{-1}$ and since $R = 181$ $\mu$m, $k_{g,CO} = 0.6$ m/s and $k_{g,CO_2} = 0.5$ m/s, Eq. (6.2) could be simplified to

$$k_i \approx \frac{r' \rho_{Fe_2O_3}}{c_{CO, out} - \frac{c_{CO_2, out}}{K_p}}. \quad (6.3)$$

For the results reported here, the iterative method involving the effectiveness factor was always applied to obtain values for $k_i$, which typically agreed with those from Eq. (6.3) to within 20%. The final conversion for all of the experiments presented in this Chapter was $X \approx 0.8$.

Figure 6.1 shows $k_i$ for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O in a mixture of 8.9 vol. % CO, 8.9 vol. % CO$_2$, balance N$_2$ using an initial charge of 0.3 g of unmodified Fe$_2$O$_3$ at 1023 K and served as a control. Particles were prepared using either experimental method (1) or method
Figure 6.1: Intrinsic rate constant, $k_i$, against cycle number for the reduction of unmodified Fe$_3$O$_4$ to Fe$_{0.947}$O in a mixture of 8.9 vol. % CO, 8.9 vol. % CO$_2$, balance N$_2$ at 1023 K. The initial charge was 0.3 g of unmodified Fe$_3$O$_3$ particles of diameter $+300$,-$425$ μm. Values of $k_i$ for individual experiments ($\times$) are shown. The lower line represents a least squares fit to the mean values ($\bullet$), with error bars representing the error calculated from a two-sided $t$-test with a confidence interval of 95 %. The upper line represents values of $k_i$ from Eq. (5.13) and shows good agreement.

(2), with water substituted for the aqueous solution of promoter, and gave reproducible results. Mean values from at least 5 experiments are shown by the black dots and the corresponding error is given by the error bars comprising the shaded region; the values of $k_i$ are listed in Table 6.3. The error was determined by multiplying the $t$-statistic for a two-tailed $t$-test, with the number of degrees of freedom, equal to the sample size minus one, for a 95 % confidence interval by the standard deviation of the sample and dividing by the square root of the sample size. The lower black line in Fig. 6.1 indicates a least-squares fit to the mean values; the upper black line indicates the values of $k_i$ reported for cycles 2 and 6 from Eq. (5.13) in Chapter 5 and is in good agreement.

Next, iron oxide powder which had been promoted with $x_m = 0.01$ of Ce or Pt using method (2) was examined at identical conditions to those used for the experiments in Fig. 6.1. Figure 6.2 shows $k_i$ as a function of cycle number. An improvement in $k_i$ by a factor of at least 1.5× is evident for particles promoted with Pt. An even larger improvement of $k_i$ by at least 2.1× is evident for promotion with Ce. To make a meaningful statistical comparison with unmodified iron oxide, two assumptions were made. First, it was assumed that the true mean of $k_i$ for unmodified iron oxide could be approximated by the sample mean calculated from
Figure 6.2: Intrinsic rate constant, $k_i$, against cycle number for the reduction of promoted Fe$_3$O$_4$ to Fe$_{0.947}$O in a mixture of 8.9 vol. % CO, 8.9 vol. % CO$_2$, balance N$_2$ at 1023 K. The initial charge was 0.3 g of particles of diameter +300,-425 µm prepared by promoting Fe$_2$O$_3$ powder with $x_m = 0.01$ Ce (△) or $x_m = 0.01$ Pt (■). The black line represents the mean $k_i$ for unmodified iron oxide and was taken from Fig. 6.1; promotion clearly increases $k_i$.

Fig. 6.1. Second, it was assumed that the $k_i$ from a sample of iron oxide without an effective promoter has an equal probability, 1/2, of lying above and below the mean $k_i$ for unmodified iron oxide. Statistical significance was then determined using a Bernoulli or binomial probability, calculated by

$$P_b = \binom{n_t}{n_s} \left( \frac{1}{2} \right)^{n_t},$$

(6.4)

where $n_t$ is the number of trials and $n_s$ is the number of successes, i.e. the number of times $k_i$ for the sample was greater than $k_i$ for the unmodified iron oxide. Table 6.3 lists $k_i$ for various samples over 5 cycles and the corresponding probability. Thus from Table 6.3 the addition of a small quantity, $x_m = 0.01$, of Ce or Pt promoter to the iron oxide powder prior to sintering can lead to a statistically significant increase in $k_i$.

For the proposed process involving the production of H$_2$ with simultaneous capture of CO$_2$ to be implemented on an industrial scale, naturally-occurring sponge iron would most likely be chosen as the starting iron oxide. It would therefore be invaluable to be able to increase the rate of reaction of a bulk particle of iron oxide by the addition of promoter. To simulate the addition of a promoter to porous sponge iron, sintered particles of Fe$_2$O$_3$ identical to those used for experiments in Fig. 6.1 were impregnated with aqueous solutions of various promoters, as outlined under method (3) in the experimental section. Figure 6.3 shows $k_i$ as a function of
Figure 6.3: Intrinsic rate constant, $k_i$, against cycle number for the reduction of promoted Fe$_3$O$_4$ to Fe$_{0.947}$O in a mixture of 8.9 vol. % CO, 8.9 vol. % CO$_2$, balance N$_2$ at 1023 K. The initial charge was 0.3 g of particles of diameter +300,-425 µm prepared by promoting calcined Fe$_2$O$_3$ particles with $x_m = 0.01, 0.05$ and 0.1 Ce, Cu, Ni and Zr. The black line represents the mean $k_i$ for unmodified iron oxide was taken from Fig. 6.1.

cycle number for particles prepared with $x_m = 0.01, 0.05$ and 0.1 of Ce, Ni, Cu and Zr. The dashed line indicates $k_i$ for particles of pure iron oxide mixed with water and was used as a control. The solid black line is identical to that in Fig. 6.1 for unmodified particles which had been sintered at 1173 K for 3 h and is in good agreement with the unmodified control particles which had been sintered for a total of 6 h. Most metal additives, with the exception of Cu, seem to increase $k_i$ at some loading. However, from Fig. 6.1, no clear correlation between metal loading, $x_m$, and $k_i$ exists. Interestingly, particles with $x_m = 0.01$ Ce do not display values of $k_i$ near those obtained for impregnated Fe$_2$O$_3$ powder, c.f. Figs. 6.2 and 6.3. It appears therefore that while Ce can promote reduction by increasing $k_i$, the method by which it is added is critical and merits further investigation.

### 6.4 Discussion

Overall, the results in Figs. 6.1 and 6.2 showed that the addition of a small quantity, $x_m = 0.01$, of Ce could increase the intrinsic rate constant, $k_i$, by $2.1 \times$. Comparing the surface area of the iron oxide particles with Ce added to that for unmodified iron from Table 6.1 gave 2.8 m$^2$/g compared to 1.2 m$^2$/g, respectively. Thus the increase in $k_i$ is most likely a result of the increase in surface area, since $(2.8 \text{ m}^2/\text{g})/(1.2 \text{ m}^2/\text{g}) = 2.3$. That the rate increases proportionally to
Table 6.3: Measured intrinsic rate constant, $k_i$, for various samples over cycles 2-6. The figure number for the corresponding $k_i$ is listed.

<table>
<thead>
<tr>
<th>Fe / promoter loading</th>
<th>cycle 2</th>
<th>cycle 3</th>
<th>cycle 4</th>
<th>cycle 5</th>
<th>cycle 6</th>
<th>Bernoulli probability, $P_b$</th>
<th>Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>mean</td>
<td>355</td>
<td>327</td>
<td>267</td>
<td>261</td>
<td>216</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>error</td>
<td>±51</td>
<td>±60</td>
<td>±41</td>
<td>±40</td>
<td>±37</td>
<td>6.1</td>
</tr>
<tr>
<td>Ce</td>
<td>0.01</td>
<td>723</td>
<td>720</td>
<td>719</td>
<td>635</td>
<td>528</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>723</td>
<td>720</td>
<td>719</td>
<td>635</td>
<td>528</td>
<td>6.2</td>
</tr>
<tr>
<td>Pt</td>
<td>0.01</td>
<td>699</td>
<td>481</td>
<td>445</td>
<td>397</td>
<td>593</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>699</td>
<td>481</td>
<td>445</td>
<td>397</td>
<td>593</td>
<td>6.2</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01</td>
<td>289</td>
<td>252</td>
<td>299</td>
<td>238</td>
<td>250</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>337</td>
<td>255</td>
<td>268</td>
<td>255</td>
<td>192</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>257</td>
<td>210</td>
<td>264</td>
<td>173</td>
<td>0.063</td>
<td>6.3</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
<td>386</td>
<td>300</td>
<td>277</td>
<td>218</td>
<td>0.375</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>509</td>
<td>290</td>
<td>233</td>
<td>204</td>
<td>0.250</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>566</td>
<td>377</td>
<td>458</td>
<td>0.125</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0.01</td>
<td>398</td>
<td>429</td>
<td>303</td>
<td>339</td>
<td>0.063</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>500</td>
<td>510</td>
<td>295</td>
<td>235</td>
<td>0.125</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>522</td>
<td>392</td>
<td>338</td>
<td>493</td>
<td>0.063</td>
<td>6.3</td>
</tr>
<tr>
<td>Ce</td>
<td>0.01</td>
<td>425</td>
<td>366</td>
<td>373</td>
<td>290</td>
<td>0.063</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>337</td>
<td>311</td>
<td>439</td>
<td>354</td>
<td>0.375</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>516</td>
<td>329</td>
<td>308</td>
<td>379</td>
<td>0.063</td>
<td>6.3</td>
</tr>
</tbody>
</table>

The surface area lends further credence to the rate-limiting mechanism proposed in Chapter 5, viz.:

$$\text{CO}_{(g)} + \text{O}_{\text{ad}} \rightleftharpoons \text{CO}_{2(g)}, \quad (6.5)$$

Thus, expressing $k_i = k_s S_0$, where $k_i$ is the rate calculated in Chapters 5 and 6, $k_s$ is the intrinsic rate for the surface reaction (6.5) in (m/s), and $S_0$ is the surface area per unit volume (m$^2$/m$^3$), would give a single intrinsic rate constant $k_s$ independent of surface area. The ability of Ce to maintain surface area in mixed oxides of Fe and Ce, is well established in catalysis literature (Perez-Alonso et al., 2006). Since $k_i$ was only increased in particles where Ce was added prior to sintering, c.f. Figs. 6.2 and 6.3, the effect of Ce as a physical promoter seems certain.

The objective of the current preliminary experiments was to identify a promoter which could increase the rate of reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O by increasing the rate constant, $k_i$. This objective was achieved for the addition of Ce. It appears that Ce acts as a physical promoter by maintaining the surface area, rather than as a chemical promoter. Further experiments which study reduction at different temperatures, e.g. using temperature programmed reduction (TPR) or fluidised bed experiments at two different temperatures, could be used to determine activation energies and clarify whether Ce promotes chemically. For reduction of a packed bed of Fe$_2$O$_3$, an increase in the intrinsic rate constant for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O
by ~ 2x would result in a front between Fe$_{0.947}$O and Fe$_3$O$_4$ that is 1.7x as sharp, as shown in Chapter 5, Fig. 5.18.

6.5 Conclusions

The addition of a promoter to iron oxide was shown to increase the rate of reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O in a mixture of CO, CO$_2$ and N$_2$ over 6 cycles at 1023 K. The conclusions were as follows:

- Addition of a promoter, $x_{in} = 0.01$ of Ce, to iron oxide powder which was subsequently sintered to form particles with $d_p = +300$, $-425$ $\mu$m, led to an increase in the rate constant, $k_i$, for the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O by 2.1x.

- This increase in $k_i$ seems to be a result of the ability of Ce to maintain the active surface area of the particle, i.e. Ce acts as a physical promoter.
Chapter 7

Production of hydrogen from solid fuels

7.1 Introduction

The previous Chapters have demonstrated that the production of hydrogen from mixtures of gases from cylinders is feasible. However, for the production of hydrogen using the redox reactions of iron oxide to be implemented on an industrial scale, it must be demonstrated that separate streams of hydrogen and carbon dioxide of high purity can be produced from a solid fuel. A proof-of-concept for the steam-iron process is not new. The steam-iron process has long been known to produce high purity hydrogen from a carbon feedstock, with 99 vol. % H₂ achieved in 1920 (Taylor, 1921). Current circumstances - the increasing need to incorporate carbon capture technologies and the requirement of low temperature polymeric membrane fuel cells for H₂ uncontaminated with CO - provide a setting which merits a more fundamental analysis of the process. Particularly, the purity of the H₂ at a ppmv level and the capture of CO₂ provide new perspectives on the technology overlooked in past literature.

In Chapter 1 it was shown that large reserves of coal are well distributed amongst Western countries. The composition of coal is generally presented as a proximate analysis, which parallels carbonisation, and an ultimate analysis, which gives the elemental composition of the coal. Carbonisation is the extent to which the original plant mass has been converted by geological action to pure carbon, and is used to determine the rank of a coal according to the following categories on an air dried, mineral matter free basis (Laurendeau, 1978): lignite (65-72% C) < sub-bituminous (72-80% C) < bituminous (75-90% C) < anthracite (90-95% C).

The objectives of this study are (i) to demonstrate that hydrogen can be produced from three representative coals - a German lignite, a UK sub-bituminous coal, and a Russian sub-
bituminous coal, (ii) to demonstrate that high conversions of the iron oxide over multiple cycles can be achieved, (iii) to determine whether other constituents, not present in cylinder gases, \( \text{e.g.} \) \( \text{SO}_2 \) and \( \text{CH}_4 \), affect the production of hydrogen, (iv) to demonstrate that the \( \text{H}_2 \) is of high purity and (v) to discuss the process in the light of industrial application.

### 7.2 Experimental

The experimental apparatus consisted of a gasifier in series with a packed bed of iron oxide and gas analysers, as shown in Fig. 7.1. The gasifier was an externally-heated fluidised bed reactor of 316 stainless steel with an internal diameter of 76 mm, provided with a perforated plate as the distributor containing 37 holes, each 0.4 mm in diameter. At maximum heating power, the furnace supplied a total power output of \( \sim 13 \text{ kW} \); to heat the bed from 298 K to 1123 K took approximately 1.5 h. At typical fluidising conditions (1 m\(^3\)/h of \( \text{N}_2 \) and 0.07 m\(^3\)/h of \( \text{CO}_2 \) as measured at 293 K and 10\(^5\) Pa) with the bed maintained at 1123 K, the pressure drop across the distributor was at least 0.3 bar, considerably in excess of the pressure drop across the material fluidised (typically \( \sim 1.2 \text{ kg carrier solids} \) given by the mass multiplied by the acceleration due to gravity and divided by the nominal cross-sectional area, \( \text{viz.} \) amounting to 0.025 bar, hence ensuring uniform fluidisation. The temperature of the bed was measured by a K-type thermocouple inserted from the top of the bed so that the tip was about 100 mm above the distributor. All flowrates to the fluidised bed were measured using calibrated rotameters.

The stainless steel packed bed reactor was independent of the gasifier and identical to that in Chapter 2, shown in Fig. 2.1. The particles of iron oxide were prepared, as in Chapter 2, and had a sieve size of \(+425, \sim 600 \mu\text{m} \). The packed bed was loaded by placing 3 g of \( \text{Fe}_2\text{O}_3 \) particles between two layers of inert \( \text{Al}_2\text{O}_3 \) each \( \sim 7 \text{ g} \) with a sieve size of \(+1.4, \sim 1.7 \text{ mm} \). The reactor was operated in a downflow arrangement; the temperature was monitored by a type K thermocouple (O.D. 1.5 mm) placed within the layer of iron oxide.

The proximate and ultimate analysis for the three representative coals - a lignite from Ham-bach, Germany (GER-lig), a sub-bituminous coal from Littleton Colliery, UK (UK-sub) and a Russian sub-bituminous coal from Talkdinskaya Fuel and Energy Company (RUS-sub) - are listed in Table 7.1. The German lignite and Russian sub-bituminous coal were supplied by RWE npower Swindon, UK; the UK sub-bituminous coal was supplied by the former Coal Research Establishment Stoke Orchard, UK. The fuels were crushed and sieved to \(+1.0, \sim 2.4 \text{ mm} \) and kept in sealed containers prior to experiments.
Table 7.1: Proximate (air dried basis) and ultimate (air dried, mineral matter free basis) analyses for the three coals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture</th>
<th>Volatile Matter</th>
<th>Fixed Carbon</th>
<th>Ash</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>GER-lig</td>
<td>18.0</td>
<td>41.0</td>
<td>37.5</td>
<td>3.5</td>
<td>69.6</td>
<td>5.5</td>
<td>23.4</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>UK-sub</td>
<td>7.1</td>
<td>33.7</td>
<td>54.9</td>
<td>4.3</td>
<td>80.7</td>
<td>5.1</td>
<td>8.9</td>
<td>1.7</td>
<td>1.1</td>
</tr>
<tr>
<td>RUS-sub</td>
<td>9.2</td>
<td>32.7</td>
<td>44.7</td>
<td>13.4</td>
<td>82.4</td>
<td>6.1</td>
<td>8.2</td>
<td>2.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Fuel was added to the top of the gasifier using a screwfeeder. The feeder consisted of an aluminium screw (O.D. 9 mm, pitch 35 mm, width of thread 2 mm, length 250 mm) protruding into the bottom of the hopper and was connected via a drive shaft and ball bearings to an aluminium block. A stepper motor (McLennan, 34HSX-208) controlled the speed of feeding by altering the rotation of the screw in the range 0-25 rot/s. Finding a satisfactory feeder design was not trivial: a motor with sufficient torque to prevent jamming of the screw was necessary; vibrations from the large motor also prevented bridging of the coal particles in the neck of the hopper.

The sampling line was arranged as in Fig. 7.1. Moisture and substances which were not gaseous at 273 K (e.g. tars) were removed from the effluent gas by two impinger tubes im-
mersed in an ice bath, followed by a tube with granulated CaCl₂ prior to entering the packed bed. Using solenoid valves (Burkert), the effluent gas from the gasifier could either be (i) fed into the packed bed reactor (ii) bypassed to the extraction vent or (iii) fed into the sampling line following the packed bed for analysis in the gas analysers. Owing to the collection of ash, the blower required cleaning after most experiments.

The composition of the effluent gas from either the gasifier or the packed bed was determined using (i) nondispersive infrared analysers measuring [CO] and [CO₂] in the range 0-20 vol. % (ABB, EasyLine), (ii) a nondispersive infrared analyser measuring [CH₄] in the range 0-30 vol. % (ABB, EasyLine), (iii) a nondispersive infrared analyser measuring [SO₂] in the range 0-10000 ppmv (ABB, EL3020), (iv) a nondispersive infrared analyser measuring [CO] in the range 0-2000 ppmv (ABB, EasyLine), (v) a thermal conductivity analyser measuring [H₂] in the range 0-30 vol. % (ABB, Caldos27) and (vi) a paramagnetic analyser measuring O₂ in the range 0-100 vol. % (ABB, EL3020) giving a total of four analysers. Cylinders of pure gases (BOC) with compositions of (i) 10 vol. % CO, balance N₂ and 10 vol. % CO₂, balance N₂, (ii) 20 vol. % CH₄, balance N₂, (iii) 1000 ppmv SO₂, balance N₂, (iv) 1 vol. % CO, balance N₂, (v) 10 vol. % H₂, balance N₂ and (vi) laboratory air were used for calibration. The total flow through the packed bed was 0.06 – 0.12 m³/h as measured at 298 K and 10⁵ Pa.

Cycling of the iron oxide proceeded in three stages, summarised by the following reactions:

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + \text{CO} & \rightleftharpoons 2\text{FeO} + \text{CO}_2 & \Delta H_{1123}^{\circ} &= 0.3 \text{kJ/mol} \quad (7.1) \\
3\text{FeO} + \text{H}_2\text{O}(g) & \rightleftharpoons \text{Fe}_3\text{O}_4 + \text{H}_2 & \Delta H_{1123}^{\circ} &= -61 \text{kJ/mol} \quad (7.2) \\
2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 & \rightleftharpoons 3\text{Fe}_2\text{O}_3. & \Delta H_{1123}^{\circ} &= -238 \text{kJ/mol} \quad (7.3)
\end{align*}
\]

In reaction (7.1), CO from the gasification of coal with steam was used to reduce Fe₂O₃. After the partial reduction of the iron oxide in the bed, passing steam through the reactor generated hydrogen and reoxidised the reduced iron oxide to Fe₃O₄ in reaction (7.2). Complete reoxidation to Fe₂O₃ in air produced a stream of N₂ with residual O₂ via reaction (7.3). Once the entire packed bed had been regenerated to Fe₂O₃, the cycle could begin anew at step 1.

In a typical experiment, the gasifier and packed bed containing the iron oxide were initially treated as independent units and heated to operating temperatures of 1123 K and 1073 K, respectively, under the flow of air. Next, feeding of the coal into the gasifier was commenced for ~ 40 min until a stable effluent composition - a mixture of CO, CO₂, H₂, CH₄ and N₂ after drying - was achieved. For sufficiently high partial pressures of CO, H₂ and CH₄, this mixture
was capable of reducing the Fe$_2$O$_3$ to Fe; generally, reduction of the Fe$_2$O$_3$ only proceeded to FeO by limiting the reduction time. Oxidation occurred in a mixture of 30 vol. % steam, balance N$_2$, followed by air mixed with N$_2$ to give $\sim$ 4 vol. % O$_2$, balance N$_2$. The reactor was purged with N$_2$ for 120 s between each reduction and oxidation step.

### 7.3 Results

Figure 7.2 shows the mole fractions of CO, CO$_2$, H$_2$, CH$_4$ and O$_2$ in the effluent gas from the packed bed as a function of time over three cycles for experiments involving (a) the German lignite, (b) the UK sub-bituminous coal and (c) the Russian sub-bituminous coal. All of the entering CO and H$_2$ is converted to CO$_2$ and H$_2$O, respectively, at the start of each reduction cycle. For carbon capture this period is paramount and could be extended by increasing the residence time in the bed, through e.g. decreasing the flowrate of the gas or increasing the amount of iron oxide in the bed, as was demonstrated in Fig. 2.2 of Chapter 2. The high flowrates used in the current study of 0.06-0.12 m$^3$/h as measured at 298 K and 10$^5$ Pa gave a residence time within the iron oxide of $\sim$ 0.03 s and were chosen to increase the number of cycles achievable in a given time. As reduction of the iron oxide progresses, the mole fractions in the effluent gas approach those at the exit of the gasifier, which can be approximated for Fig. 7.2(a) to be [5.4, 5.5, 1.4, 0.2] mol. % for CO, CO$_2$, H$_2$ and CH$_4$, respectively. Since oxidation of 1 mole of CO in the presence of iron oxide produces 1 mole of CO$_2$, the CO and CO$_2$ mole fractions should be complementary and Fig. 7.2 confirms that this is indeed the case. Next, oxidation in steam generated hydrogen of high purity. Finally, air was used to oxidise the Fe$_3$O$_4$ to Fe$_2$O$_3$ before beginning a new cycle.

Figure 7.2(a) shows that gasification of the German lignite produced no CH$_4$ and a lower fraction of H$_2$ compared to that of either the Russian or the UK sub-bituminous coals. Thus, longer cycles of reduction were required. For reduction using the gasification of the UK sub-bituminous coal, steam was inadvertently added to the reduction gas, giving approximately 20 mol. % of the total mixture with flowrate of 0.08 m$^3$/h as measured at 298 K and 10$^5$ Pa, prior to its passing through the packed bed. The approximate mixture fractions from the gasifier on a dry basis were [5.2, 4.8, 2.6, 0.7] mol. % for CO, CO$_2$, H$_2$ and CH$_4$, respectively, as shown in Fig. 7.2(b). For reduction using the gasification of the Russian sub-bituminous coal, the average mixture fractions from the gasifier were [4.7, 5.3, 3.0, 1.2] mol. % for CO, CO$_2$, H$_2$ and CH$_4$, respectively. The higher values of H$_2$ in Fig. 7.2(c) compared to those in Figs. 7.2(a)
Figure 7.2: Mole fractions of CO, CO$_2$, H$_2$, CH$_4$ and O$_2$ in the effluent gas from the packed bed operated at 1123 K with an initial charge of 3 g of Fe$_2$O$_3$ for cycle 2. The reducing gas was produced from the gasification of (a) a German lignite, (b) a UK sub-bituminous coal, and (c) a Russian sub-bituminous coal. Oxidation occurred in a mixture of steam and N$_2$, followed by a mixture of air and N$_2$. 

(a) GER-lig
(b) UK-sub
(c) RUS-sub
or (b) at the very start of oxidation are not indicative of higher quantities of total H\(_2\) produced, but rather were caused by the sudden inflow of steam at the switch of the solenoid valve. In Fig. 7.2(c), the portion of the line above 10 mol. % consist of fewer than 10 points comprising only 10 s since sampling occurred at 1 Hz. A mass balance for the H\(_2\) produced was calculated and is deferred until the discussion of Fig. 7.4. Reduction times varied from 500 s for cycle 1 in Fig. 7.2(c) to 1800 s for cycle 3 in Fig. 7.2(b); the time for oxidation with steam was constant at \(\sim 500\) s; the time for oxidation with air varied between 300 s in (a) and (c) to a maximum of 500 s for cycles 2 and 3 in (b). The objective in all cases was to reach steady state in each stage for each cycle prior to switching the inlet gas.

Figure 7.3 shows the mole fractions of H\(_2\) and O\(_2\) (mol %) and CO and SO\(_2\) (ppmv) in the effluent against time for the oxidation period corresponding to Fig. 7.2. During oxidation with air, it is clear from Fig. 7.3(c) that CO and SO\(_2\) are released. Comparing the rise in CO and O\(_2\) in Fig. 7.3(c) at \(t = 2650\) s shows that all of the incoming O\(_2\) is consumed for a period at the start of oxidation giving a stream of pure N\(_2\) with [CO] < 10 ppmv. Also, the rise in SO\(_2\) is concurrent with the rise in O\(_2\), indicating that deposited sulphurous species are released as SO\(_2\) in a strongly oxidising environment. Comparing SO\(_2\) traces across experiments demonstrates that SO\(_2\) is only found during oxidation with air for experiments with the Russian and UK sub-bituminous fuels. The maximum SO\(_2\) value was 22 and 15 ppmv in each case, respectively. No SO\(_2\) was observed for experiments with the German lignite coal. From Table 7.1, the UK and Russian sub-bituminous fuels have the highest sulphur contents of 1.1 and 0.9 wt. %, respectively. Noticeably, no SO\(_2\) was detected during oxidation with steam indicating that the H\(_2\) was without SO\(_2\) contamination. Calculations based on the feed rate of coal and the flowrates of gas to the gasifier and packed bed indicated that the SO\(_2\) released during oxidation with air is < 0.5 mol. % of the total sulphur fed during reduction, \textit{i.e.} the adsorption of sulphurous species or the formation of FeS during reduction is negligible. In Fig. 7.3, comparing the CO traces during oxidation with steam shows that [CO] \(\lesssim 50\) ppmv for all experiments except those with the Russian sub-bituminous fuel, where [CO] reached a maximum of 215 ppmv before dropping below 50 ppmv. The CO trace is most likely a result of residual carbon, deposited during reduction, being oxidised with steam.

Figure 7.4 shows the total quantity of H\(_2\) produced in each of the 5 cycles performed. The dashed horizontal line at 12.5 mmol equals the quantity of H\(_2\) expected from an initial charge of 3 g of Fe\(_2\)O\(_3\), which had been reduced to FeO. For reduction to Fe, the expected quantity of H\(_2\) is 4 times the previous value, \textit{i.e.} 50.0 mmol. It can be seen from Fig. 7.4 that in some cases
Figure 7.3: Mole fractions of $\text{H}_2$ and $\text{O}_2$ (mol. %) and of $\text{CO}$ and $\text{SO}_2$ (ppmv) in the effluent gas from the packed bed operated at 1123 K with an initial charge of 3 g of $\text{Fe}_2\text{O}_3$ for cycle 2. The reducing gas was produced from the gasification of (a) a German lignite, (b) a UK sub-bituminous coal and (c) a Russian sub-bituminous coal. The $\text{H}_2$ is not contaminated by $\text{SO}_2$; except for (c) the $\text{H}_2$ has $\text{CO} \lesssim 50$ ppmv.
reduction beyond FeO to a mixture of Fe and FeO occurred, as indicated by points lying above the dashed line. Nevertheless, stable quantities of H₂ were achieved over 5 cycles in all cases.

![Graph showing H₂ production over 5 cycles](image)

**Figure 7.4:** Total quantity of H₂ produced over 5 cycles using an initial charge of 3 g of Fe₂O₃ reduced with gas from the gasification of a German lignite, a UK sub-bituminous coal or a Russian sub-bituminous coal and oxidised in a mixture of steam and N₂, followed by a mixture of air and N₂ at 1123 K.

### 7.4 Discussion

The effluent profile per unit mass carrier for the reduction of a 3 g charge of Fe₂O₃ with synthesis gas is similar to that obtained for the reduction of a 1 g charge of Fe₂O₃ in a mixture of N₂, CO and CO₂ from cylinder gases, *c.f.* Figs. 7.2 and 2.3. The constancy of yields of H₂, *c.f.* Figs. 7.4 and 2.5(b), also suggest that simulated syngas, produced by mixing pure gases from cylinders, provides a good approximation for true syngas produced from the gasification of coal.

If the deposition of solid carbon during reduction of the iron oxide can be avoided, the purity of the H₂ upon subsequent oxidation will improve. One method of avoiding the deposition of carbon is to introduce steam with the reducing gas (Ishida *et al.*, 1998). Figure 7.3 showed that for experiments with a fuel of high moisture content (Fig. 7.3(a)) or when steam was co-fed with the reducing gas (Fig. 7.3(b)), the resulting H₂ had a contamination of [CO] ≲ 50 ppmv. However, even experiments with the Russian sub-bituminous fuel gave H₂ with [CO] ≲ 200 ppmv, a significant improvement in purity compared to conventional
methods such as the steam reforming of methane. The high moisture content of the German lignite might also explain the lower levels of CH$_4$ and H$_2$ in the gasifier outlet compared to the effluent gas from the gasification of the Russian and UK sub-bituminous coals, as seen in Fig. 7.2. Steam could also prevent the deposition of sulphurous species during reduction and could explain why the experiment with the UK sub-bituminous coal (1.1 wt. % S), where steam was co-fed with the reducing gas, produced a lower total quantity of SO$_2$ compared to that with the Russian sub-bituminous coal (0.9 wt. % S). From thermodynamics (McBride et al., 2002) at 1073 K and 10$^5$ Pa, the formation of FeS is inhibited by steam, which permits gaseous species H$_2$S and SO$_2$ to be formed instead. Importantly, since SO$_2$ was only observed during oxidation with air, and was not released during oxidation with steam; the H$_2$ was free from SO$_2$. Finally, based on the SO$_2$ released during oxidation with air, it appears that a small fraction, < 0.5 mol. %, of the sulphur entering the bed during reduction was fixed. Quantifying the contamination of the H$_2$ produced by H$_2$S was, however, outside the scope of the present study.

Previous experiments in Chapters 2, 3 and 4 demonstrated that reduction to Fe resulted in a decrease in the quantity of H$_2$ produced with cycle number, with almost no H$_2$ being produced after 10 cycles. In some cases here, however, reduction proceeds beyond FeO so that the metal is present as a mixture of Fe and FeO, as shown in Fig. 7.4 by points above the dashed horizontal line. The quantity of H$_2$ produced, however, shows no indication of a decrease after 5 cycles. Investigation of how much of the iron oxide can be reduced to Fe before the detrimental effects associated with complete reduction to Fe are observed would therefore be interesting for further research.

In the original steam-iron process, oxidation of the metal oxide to Fe$_2$O$_3$ in air during each cycle was not proposed by Messerschmitt (1910) and was only later incorporated by Lane (1913). Currently other groups, e.g. Galvita et al. (2008a) and Li et al. (2009), do not include oxidation with air in their research. From Fig. 7.3(a) at the start of oxidation with air, all of the incoming O$_2$ is consumed and a stream of pure N$_2$ with [CO] $\lesssim$ 10 ppmv is produced. This gas could in theory be captured and used for the N$_2$ purge between reduction and oxidation steps. Figure 7.3 also showed that the introduction of air permits accumulated carbonaceous and sulphurous species to be eliminated from the surface of the metal oxide. Since oxidation in air also provides useful heat, c.f. the enthalpy for reaction (7.3), it is recommended to incorporate this step into the overall reaction scheme.
7.5 Conclusions

The production of separate streams of pure H$_2$ and CO$_2$ from a solid fuel was demonstrated using the redox reactions (7.1)-(7.3) of iron oxide in a packed bed at 1073 K. The conclusions were as follows:

- During the initial stage of reduction, CO$_2$ is produced with little H$_2$ or CO slip which would be suitable for sequestration.

- Pure H$_2$ with [CO] $\lesssim 50$ ppmv can be obtained from low-rank coal.

- This H$_2$ is free from SO$_2$, since SO$_2$ was only released during oxidation with air.

- Contaminants found in syngas which are gaseous above 273 K apparently do not adversely affect the iron oxide material as stable quantities of pure H$_2$ were produced over 5 cycles.

- Since oxidation with air removes contaminants, e.g. sulphurous and carbonaceous species deposited during reduction, and generates useful heat and pure N$_2$ for purging, it should be included in the operating cycle.

Overall, it has been demonstrated that crude syngas produced by the gasification of low-rank coals can be upgraded to pure H$_2$, representing a substantial increase in calorific value, whilst capturing CO$_2$, a greenhouse gas.
Chapter 8

Development and validation of a lattice Boltzmann model

8.1 Introduction

A detailed model of the production of hydrogen in a packed bed requires the simultaneous solution of equations for the conservation of mass, momentum and energy. Historically, simple 1D advection-diffusion-reaction models have been applied to packed beds. Here, the bed is considered to be a pseudo-homogeneous medium and bulk parameters representing, e.g. average flow per unit cross-section or average rate of reaction per unit volume, are used. Integration of the descriptive partial differential equations is generally not feasible by analytical methods, so numerical integration using e.g. finite differences is employed. A 1D mass conservation model was presented for the reduction of iron oxide in Chapter 5. Two-dimensional models, accounting for axial and radial gradients, have also been developed (Froment, 1967).

To resolve fully the flow field, however, more detailed models are required. Table 8.1 lists a hierarchy of strategies for modelling fluid flows arranged by Knudsen number, $Kn$, a ratio of the mean free path of a molecule to the characteristic length scale. For $Kn < 0.01$, a fluid comprised of individual molecules can be treated as a continuum. Here, the frequency of contacts between molecules is significantly higher than that between molecules and physical boundaries and the Navier-Stokes equation can be applied. As the characteristic length decreases, the continuum assumption breaks down, and for $Kn > 1$, molecules must be treated as discrete entities.

The lattice Boltzmann method (LB) (Succi, 2001) is based on kinetic theory of gases and
Table 8.1: Hierarchy of modelling strategies for resolving fluid flow at different length scales.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Fluid</th>
<th>Mathematics</th>
<th>Method (Abbreviation)</th>
<th>Length (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>macroscopic</td>
<td>simplified continuum</td>
<td>advection/dispersion Eq.</td>
<td>plug flow, packed bed reactors (PFR, PBR); computational fluid dynamics (CFD)</td>
<td>$10^{-1} - 10^{-1}$</td>
</tr>
<tr>
<td>$(0 &lt; Kn &lt; 0.01)$</td>
<td>continuum</td>
<td>Euler Eqs.</td>
<td>computational fluid dynamics (CFD)</td>
<td>$10^{-1} - 10^{-5}$</td>
</tr>
<tr>
<td>mesoscopic</td>
<td>continuum: atomic distribution functions</td>
<td>Boltzmann Eq.</td>
<td>lattice Boltzmann method (LB)</td>
<td>$10^{-3} - 10^{-6}$</td>
</tr>
<tr>
<td>$(Kn &lt; 0.1)$</td>
<td>atomic</td>
<td>Liouville Eq.</td>
<td>direct simulation Monte Carlo (DSMC)</td>
<td>$10^{-6} - 10^{-8}$</td>
</tr>
<tr>
<td>transition</td>
<td>atomic</td>
<td>streaming/collision rules</td>
<td>lattice gas cellular automata (LGCA)</td>
<td>$&lt; 10^{-7}$</td>
</tr>
<tr>
<td>$(0.1 &lt; Kn &lt; 10)$</td>
<td>molecular dynamics (MD)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>microscopic</td>
<td>atomic</td>
<td>Newton’s law</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(Kn &gt; 1)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

can be used to resolve fluid flow over a wide range of length scales as shown in Table 8.1. In packed beds at moderate fluid velocities, the LB method has proved to be effective in predicting fluid dynamic quantities such as velocity (Freund et al., 2003; Sullivan et al., 2007), pressure drop (Zeiser, 2007) and drag force (Yu et al., 2003). The kinetic formulation of the LB method permits the incorporation of a wide range of physical phenomena such as multicomponent flows (Asinari, 2008; Flekkøy, 1993), particle laden flows (Ladd, 1994), bubbles (Inamuro et al., 2004), surface wetting (Raiskinmäki et al., 2000), flow at low Knudsen number (Toschi and Succi, 2005), turbulence (Teixeira, 1998), and compressible flows (Yu and Zhao, 2000; Asinari and Ohwada, 2009). Detailed comparison between experiment and LB results with reactive flows has received less attention and remains a promising area of research.

The lattice Boltzmann (LB) method has several advantages for modelling reactive fluid flow through porous media. Thus, (i) it is inherently discrete and all computations are local so that it can be implemented on several processors in parallel with little information exchange required at each time step. (ii) It uses linear advection and collision operators, but still recovers the incompressible Navier-Stokes equations in the low Mach number limit, thereby avoiding the computationally-difficult solution of either the Boltzmann or the Navier-Stokes equations. (iii) Advection is calculated in a discrete velocity space with arithmetic operations to avoid rounding errors. (iv) It accounts for irregularly-shaped boundaries in a straightforward way. The LB method is, in fact, suitable for direct numerical simulation (DNS) of incompressible, or slightly-compressible, flows with $(Ma < 0.1)$ (Chen and Doolen, 1998). The disadvantages of the LB approach include the computational cost, the difficulty of including temperature gradients for non-isothermal flows and the mathematical imprecision of much of the lattice Boltzmann literature. Indeed, the lattice Boltzmann method can only be considered a competitive
technique for incompressible, single-phase, isothermal flows or for problems approximated as such. In the present Chapter, a three-dimensional lattice Boltzmann model is presented to model the reduction of (i) a single particle and (ii) a packed bed of Fe$_2$O$_3$ to Fe$_3$O$_4$ with a dilute mixture of CO+CO$_2$+N$_2$. The bulk fluid is taken to be a single phase, gaseous N$_2$, at a fixed temperature and the reactive species, CO, is incorporated as a passive scalar. Model predictions are validated with experimental results.

8.2 The lattice Boltzmann method

8.2.1 Lattice gas cellular automata and lattice Boltzmann methods

The dynamics of a simple continuum fluid are governed by the conservation of mass and momentum, given by the continuity and Navier-Stokes equation:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{8.1}
\]

\[
\rho [\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u}] = -\nabla P + \nabla \cdot \mathbf{T}, \tag{8.2}
\]

where $\partial_t = \partial/\partial t$, $\rho$ is the mass density, $\mathbf{u}$ is the velocity of the bulk fluid, $P$ is the pressure, $\nu$ is the kinematic viscosity and $\mathbf{T}$ is the deviatoric stress tensor. Unlike traditional methods which rely on a top-down approach to discretise Eqs. (8.1) and (8.2), e.g. using finite difference, finite element or finite volume methods, the lattice Boltzmann method is a bottom-up approach (Chen and Doolen, 1998), as outlined in Fig. 8.1. Macroscopic parameters such as, density and momentum, are derived from a mass distribution function.

The lattice Boltzmann method has its origin in lattice gas cellular automata (LGCA) (Wolfram, 1986) and consists of three basic elements:

- a domain of interconnected sites, the lattice,

- state variables defined at each site, such as a real-valued mass distribution function, $f_i$,

- a set of update rules, defined locally, consisting of two steps: (streaming) permitting information exchange between neighbouring sites and (collision) defining the interaction of the state variables at each site.

In the present dissertation, the lattice Boltzmann equation will be presented as a particular discretisation of the continuous Boltzmann equation, though historically it evolved from LGCA.
...Continuous partial differential equations
· mass (continuity)
· momentum (Navier-Stokes)

Discrete

Discrete

LGCA, LB

Figure 8.1: Overview of the modelling of fluid flow. (a) Traditionally, top-down methods were used to discretise the partial differential equations governing fluid motion. (b) Recently, bottom-up approaches based on kinetic theory which recover the same macroscopic partial differential equations have attracted growing interest (WebofKnowledge, 2009).

For the interested reader, an overview of the lattice Boltzmann method is given by Succi (2001) and Chen and Doolen (1998); a good introduction into the mathematics of the method is provided by Wolf-Gladrow (2000); a simple introduction into writing lattice Boltzmann code is presented in Sukop and Thorne (2006).

8.2.2 The continuous Boltzmann equation

Since it is known that the Navier-Stokes equation can be derived from the Boltzmann equation (Wolf-Gladrow, 2000), it is reasonable to use the Boltzmann equation as a starting point for modelling fluid flow. The Boltzmann equation describes the mass distribution of single particles \( f \equiv f(x, v, t) \) in a fluid as a function of particle position, \( x \), particle velocity, \( v \), and time, \( t \):

\[
\frac{\partial f(x, v, t)}{\partial t} + \mathbf{v} \cdot \nabla f(x, v, t) = \Omega(x, v, t),
\]  

(8.3)

\[
\mathbf{v} = \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix}, \quad \nabla f = \begin{bmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial z} \end{bmatrix}
\]
where $\Omega$ is a collision integral describing interactions with other particles. The simplest form of the collision operator involves the Bhatnagar-Gross-Krook (BGK) (Bhatnagar et al., 1954) approximation, which expresses $\Omega$ as a linear relaxation towards an equilibrium:

$$\frac{\partial f}{\partial t} + v \cdot \nabla f = -\frac{1}{\tau'} (f - f^{(eq)}),$$

(8.4)

the local Maxwell-Boltzmann distribution function:

$$f^{(eq)}(x, v, t) = \rho \left( \frac{m}{2\pi k_B T} \right)^{\frac{D}{2}} \exp \left[ -\frac{m}{2k_B T} (v - u)^2 \right].$$

(8.5)

Here, $u$ and $T$ are the macroscopic velocity and absolute temperature of the bulk fluid, $k_B$ is Boltzmann’s constant, $m$ is the mass of a single, monatomic particle and $D$ is the dimension of space, e.g. 3 for 3D. The conserved macroscopic variables $\rho$ and $u$ are the microscopic velocity moments of $f$ and $f^{(eq)}$:

$$\rho = \int f dv = \int f^{(eq)} dv$$

(8.6)

$$\rho u = \int v f dv = \int v f^{(eq)} dv.$$  

(8.7)

The microscopic velocity set $v$ comprises the velocities of all single particles; the macroscopic velocity of the bulk fluid, $u$, is thus related to $v$ by summing over all particles, as shown in Eq. (8.7).

### 8.2.3 Derivation of the discrete lattice Boltzmann equation

Evaluating Eq. (8.4) over the continuous velocity space $x = \mathbb{R}^D = \mathbb{V}$ and $v = \mathbb{R}^D = \mathbb{V}$, where $D$ is again the dimension of the velocity space, is computationally impracticable, and so a finite velocity set $v_i$ over which evaluation will take place is chosen. For lattice Boltzmann models, the Cartesian cube is typically taken as the basis for the velocity set. Here, each point defined at $(0,0,0)$ has six nearest neighbours $(\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1)$, twelve second nearest neighbours $(\pm 1, \pm 1, 0), (\pm 1, 0, \pm 1), (0, \pm 1, \pm 1)$, and eight third nearest neighbours $(\pm 1, \pm 1, \pm 1)$ (D’Humières et al., 2002). The notation DDQQ is used to denote the dimension, $D$, and number of axisymmetric velocities, $Q$, of the chosen model. As shown in Fig. 8.2, which shows components of the mass distribution function, $f_i$, aligned according to lattice velocity, the D2Q9 model uses the velocities with squared moduli 0 and 1 lying in the 2D
plane (D’Humiéres et al., 2002); the D3Q15 model uses velocities with squared moduli 0, 1 and 3; the D3Q19 model uses the velocities with squared moduli 0, 1, and 2. In this work, the D3Q19 lattice is considered as shown in Fig. 8.2(a).

The choice of a discrete \( v_i \) permits the discretisation of physical space, \( x_i \), if only those \( x_i \) accessible by moving along the discrete \( v_i \) are considered. After fixing the velocity space, the continuous distribution function \( f(x_i,v_i,t) \) need only be written as a function of \( x_i \) and \( t \). Dropping the subscript \( i \) denoting the property of being discrete from all but the leading variable, the discrete distribution function becomes \( f_i(x,t) \). Thus, Eq. (8.4) can be written as:

\[
\frac{\partial f_i}{\partial t} + v_i \cdot \nabla f_i = -\frac{1}{\tau'} \left( f_i - f_i^{(eq)} \right).
\]  

(8.8)
Discretisation of Eq. (8.8) with respect to time is performed by defining the total derivative,

\[ \frac{D}{Dt} \equiv \frac{\partial}{\partial t} + v_i \cdot \nabla, \]  

(8.9)

which permits Eq. (8.8) to be written explicitly as

\[ \frac{Df_i}{Dt} = -\frac{1}{\tau'} \left( f_i - f_i^{(\text{eq})} \right). \]  

(8.10)

The left hand side of Eq. (8.10) can be evaluated using a truncated Taylor series expansion for small \( t \), which yields the familiar result:

\[ \frac{Df_i(t)}{Dt} = \frac{f_i(t + \Delta t) - f_i(t)}{\Delta t} + O(\Delta t). \]  

(8.11)

Combining Eqs. (8.10) and (8.11) and multiplying through by \( \Delta t \) yields the discrete lattice Boltzmann equation:

\[ f_i(x + v\Delta t, t + \Delta t) - f_i(x, t) = -\frac{1}{\tau} \left[ f_i(x, t) - f_i^{(\text{eq})}(x, t) \right] + O(\Delta t^2), \]  

(8.12)

where \( \tau \equiv \tau' / \Delta t \) is the dimensionless relaxation time. Importantly, Eq. (8.12) is explicit in time and is accurate up to first order in \( \Delta t \) (Wolf-Gladrow, 2000). It can be shown (Appendix 5; Sterling and Chen, 1996) that the discretisation error of \( O(\Delta t^2) \) can be incorporated into the viscosity during the derivation of the Navier-Stokes equations, effectively making Eq. (8.12) accurate to second, rather than first, order in time.

To ensure that the macroscopic variables, \( \rho \) and \( \mathbf{u} \) are recovered by the discrete Boltzmann equation, the following definitions analogous to Eqs. (8.6)-(8.7) are used (He and Luo, 1997c):

\[ \rho = \sum_i f_i = \sum_i f_i^{(\text{eq})} \]  

(8.13)

\[ \rho \mathbf{u} = \sum_i f_i \mathbf{v}_i = \sum_i f_i^{(\text{eq})} \mathbf{v}_i. \]  

(8.14)

To summarise, the discrete lattice Boltzmann equation with linearised BGK collision operator (8.12) has been derived from the continuous Boltzmann equation by assuming a discrete microscopic velocity set and approximating the time derivative with a numerical Euler scheme. The rigorous derivation of the Navier-Stokes and continuity equation from the lattice Boltzmann equation is presented in Appendix 5.
8.2.4 Multiple relaxation time collision operators

Ignoring terms of $O(\Delta t^2)$, the lattice Boltzmann equation with the linear BGK collision operator was given in Eq. (8.12) as:

$$f_i(x + v\Delta t, t + \Delta t) - f_i(x, t) = -\frac{1}{\tau} \left[ f_i(x, t) - f_i^{(eq)}(x, t) \right],$$  \hspace{1cm} (8.15)

or alternatively in vector notation,

$$f(x + v\Delta t, t + \Delta t) - f(x, t) = -S[f(x, t) - f^{(eq)}(x, t)],$$ \hspace{1cm} (8.16)

where $f(x, t) = [f_0(x, t), \ldots, f_{n-1}(x, t)]^T$, $S = \text{diag}(1/\tau, \ldots, 1/\tau)$ and $n$ is the number of discrete velocities, e.g. 19 in the D3Q19 model. Here, the relaxation of $f$ to $f^{(eq)}$ is governed by a single time constant $\tau$.

To increase the flexibility of the lattice Boltzmann approach, a more general collision operator with multiple relaxation times (MRT) has been introduced (D’Humieres et al., 2002; Lallemand and Luo, 2003). With MRT operators, collisions take place in moment space, $\mathcal{M}$, rather than in velocity space, $\mathcal{V}$. A transformation matrix, $\mathbf{M}$, provides the linear mapping such that

$$\mathbf{m} = \mathbf{M}f \quad \quad \mathbf{m}^{(eq)} = \mathbf{M}f^{(eq)},$$ \hspace{1cm} (8.17)

where it is noted that the square matrix, $\mathbf{M}$, must be consistent with the size of $f$. A particular example of $\mathbf{M}$ is given for the D3Q19 model in Appendix 5, section A5.2. The concept of the lattice Boltzmann equation with a MRT collision operator is most straightforwardly explained through manipulation of Eq. (8.16):

$$f(x + v\Delta t, t + \Delta t) - f(x, t) = -\mathbf{S}\mathbf{M}^{-1}\mathbf{M}[f(x, t) - f^{(eq)}(x, t)],$$ \hspace{1cm} (8.18)

giving,

$$f(x + v\Delta t, t + \Delta t) - f(x, t) = -\hat{\mathbf{S}}[\mathbf{m}(x, t) - \mathbf{m}^{(eq)}(x, t)],$$ \hspace{1cm} (8.19)

where,

$$\hat{\mathbf{S}} = \text{diag}(s_1, s_2, \ldots, s_n),$$ \hspace{1cm} (8.20)

is defined and Eq. (8.17) as well as the property, $\mathbf{I} = \mathbf{M}^{-1}\mathbf{M}$, have been used. Note that
the MRT collision operator will reduce to the BGK collision operator for the special case, \( \hat{S} = \text{MSM}^{-1} = S = \text{diag}(1/\tau, 1/\tau, \ldots, 1/\tau) \) for any choice of transformation matrix \( M \). Defining \( \hat{S} = \text{diag}(s_1, s_2, \ldots, s_n) \), however, means that the MRT collision model has \( s_1, s_2, \ldots, s_n \) adjustable relaxation rates rather than a single relaxation time \( \tau \). These additional tunable parameters provide several advantages over the single relaxation time (BGK) operator. For example, specific relaxation times can be optimised to improve the model stability and permit the simulation of higher \( Re \) number flow.

### 8.2.5 Transport of a passive scalar

The previous discussion, when considered with Appendix 5, has shown how the lattice Boltzmann equation (8.19) can be used to model single-phase flow of an incompressible or slightly-compressible fluid. For chemical engineering applications, however, transport of chemical species is of fundamental importance. The behaviour of a passive scalar in a fluid, *i.e.* a scalar which itself does not influence the underlying fluid momentum, is governed by the macroscopic advection and diffusion equation:

\[
\frac{\partial \rho_s}{\partial t} + \nabla \cdot (u \rho_s) - D_s \nabla^2 \rho_s = 0,
\]

(8.21)

where \( \rho_s \) is a scalar quantity of arbitrary units, \( D_s \) is its diffusivity, and \( u \) is the macroscopic velocity of the bulk fluid, defined as before by Eq. (8.14). In the present dissertation, chemical species have been incorporated using a passive scalar approach with separate distribution functions \( f_{i,s} \) for each scalar \( s \) considered. Here, the quantity of passive scalar is conserved, but not the momentum. Therefore, the passive scalar approach of the present LB model is only exact for situations with chemical species of identical molecular mass and no net consumption or production, but can be extended to situations where the reactive species are substantially diluted in an inert fluid.

To incorporate advection and diffusion of a scalar into a lattice Boltzmann type model, the approach of Flekkøy (1993) and Sullivan (2006) was used. Unlike the Navier-Stokes equation (8.2), the advection and diffusion equation (8.21) only has terms up to first order in \( u \). As a result, the number of discrete velocities required to recover the correct macroscopic behaviour can be significantly reduced compared to that required for the Navier-Stokes equations. For example, to recover the advection and diffusion equation up to \( O(u^2) \), a reduced velocity set, \( D2Q5 \) in 2D and \( D3Q7 \) in 3D, is sufficient and a reduced equilibrium distribution function.
which includes terms only up to first order in \( u \) is required (Sullivan, 2006). Reducing the number of velocity directions and truncating the equilibrium distribution function permits a significant increase in computational efficiency with almost no loss in computational accuracy. The evolution of the \( f_{i,s} \) is governed by:

\[
f_{i,s}(x + v \Delta t, t + \Delta t) - f_{i,s}(x, t) = -\frac{1}{\tau_s} \left( f_{i,s}(x, t) - f_{i,s}^{(eq)}(x, t) \right),
\]

(8.22)

which is the lattice Boltzmann equation (8.12) with BGK collision operator. In this work, the D3Q7 velocity set shown in Fig. 8.2(b) with \( f_{i,s}^{(eq)} = w_i \rho_s \left[ 1 + 4 \frac{(v_i \cdot u)}{c^2} \right] \),

(8.23)

where

\[
w_i = \begin{cases} 
\frac{1}{4} & i = 0 \\
\frac{1}{8} & i = 1, \ldots, 6 \end{cases}
\]

(8.24)

was used with Eq (8.22). As in Eqs. (8.13) and (8.14), the moments of \( f_{i,s} \) are given by:

\[
\rho_s = \sum_i f_{i,s} = \sum_i f_{i,s}^{(eq)}
\]

(8.25)

\[
\rho_s u_s = \sum_i f_{i,s} v_i = \sum_i f_{i,s}^{(eq)} v_i.
\]

(8.26)

Sullivan (2006) has shown that this choice of \( f_{i,s}^{(eq)} \) recovers the advection and diffusion equation (8.21) with an error of the order \( O(u^2) \) and diffusivity,

\[
D_s = \frac{1}{4} (\tau_s - 1).
\]

(8.27)

### 8.2.6 Reaction

To incorporate chemical reactions into the lattice Boltzmann model, the approach of Sullivan (2006) was used which permits product species to be both diffused and also advected at the correct macroscopic velocity, \( u \). Following Sullivan (2006), the change in density is calculated just prior to evaluation of the \( f_{i,s}^{(eq)} \) as:

\[
\Delta \rho_s = F(\rho_1, \ldots, \rho_s, \ldots, x, t),
\]

(8.28)
where \( F(\rho_1, \ldots, \rho_s, \ldots, x, t) \) is the function corresponding to the chosen rate expression. For example, \( F = -k_i \rho_s \Delta t + O(\Delta t^2) \) would represent a first order reaction where \( k_i \) is the rate constant, \( \rho_s \) is the concentration of reactant species \( s \) and \( \Delta t \) is the time step. After calculating \( F \), evaluation of \( f_{i,s}^{\text{eq}} \) in Eq. (8.23) is then performed using \( \rho_s + \tau_s \Delta \rho_s \) in place of \( \rho_s \) to give:

\[
f_{i,s}^{\text{eq}} = w_i (\rho_s + \tau_s \Delta \rho_s) \left[ 1 + 4 \frac{(v_i \cdot u)}{c^2} \right].
\] (8.29)

Inserting Eq. (8.29) into Eq. (8.22) and summing over all \( i \), then gives:

\[
\sum_i \left[ f_{i,s}(x + v \Delta t, t + \Delta t) - f_{i,s}(x, t) \right] = \sum_i -\frac{1}{\tau_s} \left[ f_{i,s}(x, t) - (\rho_s + \tau_s (\rho_s|_{\tau_{i+1}} - \rho_s)) w_i \left( 1 + 4 \frac{(v_i \cdot u)}{c^2} \right) \right] \nonumber
\]

\[
= -\frac{\rho_s}{\tau_s} + \frac{\rho_s}{\tau_s} + \rho_s|_{\tau_{i+1}} - \rho_s = \Delta \rho_s,
\] (8.30)

which recovers the correct \( \Delta \rho_s \) at each time step as desired. Greater accuracy in the method can be achieved by evaluating \( F \) up to higher order in \( \Delta t \). In the present dissertation evaluation up to first order in \( \Delta t \), as in the previous example, was found to give satisfactory results.

### 8.2.7 Implementation

Implementation of the lattice Boltzmann equations, (8.19) and (8.22), involves two basic steps: streaming and collision. Where ' denotes the post-collision values:

- **collision**
  - for BGK: \( f_{i,s}'(x, t) = f_{i,s}(x, t) - \frac{1}{\tau_s} \left[ f_{i,s}(x, t) - f_{i,s}^{\text{eq}}(x, t) \right] \),
  - for MRT: \( f'(x, t) = f(x, t) - M^{-1} \hat{S} \left[ m(x, t) - m^{eq}(x, t) \right] \).

- **streaming**
  - \( f_{i,s}(x + v \Delta t, t + \Delta t) = f_{i,s}'(x, t) \),
  - \( f_i(x + v \Delta t, t + \Delta t) = f_i'(x, t) \).

A computational flow chart giving an overview of the lattice Boltzmann algorithm is given in Fig. 8.3.

Because the lattice Boltzmann equation is explicit in time and only involves local interactions among the distribution functions during streaming, it is inherently suited for parallel computing. Consequently, a parallel version of the program was developed in Fortran 90. The non-blocking message passing interface (MPI) commands MPI_Isend and MPI_Irecv were
Figure 8.3: Computational flowsheet for the lattice Boltzmann method.
used. After each time step, the $f_i$ or $f_{i,s}$ for the boundary nodes of each domain were exchanged and all domains synchronised prior to the start of the next time step. In the present dissertation, the fluid flow and passive scalar programs were decoupled. Thus, the flow profile through a geometry was first calculated before models for mass transport and reaction kinetics were overlayed.

8.2.8 Boundary conditions and initial conditions

Four types of boundary conditions, arranged in order of increasing complexity and increasing accuracy, were used in this work: periodic, equilibrium, zero flux outlet, halfway bounce-back and non-equilibrium bounce-back. In the following, the notation $f_i(x, t) = f_i(x, y, z, t)$ and $f_{i,s}(x, t) = f_{i,s}(x, y, z, t)$ is used to denote the $x, y$ and $z$ location of $f_i$ and $f_{i,s}$, respectively, in the 3D domain. The domain is comprised of an integer number of nodes bounded by $1 \leq x \leq L_x$, $1 \leq y \leq L_y$ and $1 \leq z \leq L_z$.

**Periodic.** Periodic boundary conditions are implemented during streaming and treat the domain as continuous. For example, for flow in the positive $x$ direction the outflowing $f_i(L_x, y, z, t)$ becomes the inflowing $f_i(1, y, z, t + 1)$ for a fluid, or, for a passive scalar, $f_{i,s}(L_x, y, z, t)$ (Sukop and Thorne, 2006).

**Equilibrium.** The equilibrium boundary condition is typically implemented after streaming and involves using the specified $\rho$ or $\rho_s$ and $\mathbf{u}$. For flow simulations, $\rho$ and $\mathbf{u}$ are used with Eqs. (A5.26) and (A5.27) to calculate $\mathbf{m}^{eq}$; next, $\mathbf{f}^{eq} = \mathbf{M}^{-1}\mathbf{m}^{eq}$ is used; then, $\mathbf{f} = \mathbf{f}^{eq}$ is set. For a passive scalar, $\rho_s$ and $\mathbf{u}$ are used with Eq. (8.23) to evaluate $f_{i,s}^{eq}$; next, $f_{i,s} = f_{i,s}^{eq}$ is set. This boundary method is for Dirichlet type boundaries and, while initially dismissed as too simplistic, has recently been shown to achieve good accuracy in low $Re$ flows (Mohamad and Succi, 2009).

**Zero flux outlet.** To impose zero flux at the outlet of a domain, a simple Neumann type boundary condition is used. For example, for flow in the positive $z$ direction, the zero flux is incorporated by specifying:

$$f_i(x, y, L_z, t) = f_i(x, y, L_z - 1, t)$$  \hspace{1cm} (8.31)

$$f_{i,s}(x, y, L_z, t) = f_{i,s}(x, y, L_z - 1, t),$$  \hspace{1cm} (8.32)

for fluid flow (8.31) or flow of a passive scalar (8.32), respectively. That is the outlet nodes
are copied from the preceding nodes in the flow direction. This boundary condition is derived from Taylor expansion of $df_i/dz$ or $df_{i,s}/dz$ up to first order in $\Delta z$ and is therefore accurate to first order in lattice spacing.

**Halfway bounce-back.** The halfway bounce-back boundary condition is a no-slip boundary condition for a solid lattice node. It is carried out after the collision step. The $f_i$ or $f_{i,s}$ are reversed according to their respective lattice velocities. The reversed $f_i$ are then streamed to neighbouring nodes in the following time step. If the true location of the boundary is considered to be halfway between the solid and fluid node, this scheme can be shown to be second order accurate (Cornubert *et al.*, 1991; He *et al.*, 1997) with respect to grid spacing for regular boundaries, *i.e.* when the solid boundary is not stair-stepped. Because it can be easily implemented on any geometry, the halfway bounce-back condition is often applied even to curved boundaries (Gallivan *et al.*, 1997).

**Non-equilibrium bounce-back.** For fluid flow, the non-equilibrium bounce-back boundary condition of Zou and He (1997) was used to fix velocity boundaries. For flow in the positive $z$ direction with the D3Q19 velocity set, after streaming, the values of $\rho, f_5, f_{11}, f_{12}, f_{15}$ and $f_{16}$ are unknown. As shown from Fig. 8.2(a), these values are relevant to the $z$ direction and must be determined. Specifying $u$ to be equal to the desired inlet value, the unknown $\rho$ can be solved by adding Eq. (8.13) to the negative of Eq. (8.14) evaluated in the $z$ direction and rearranging to solve for $\rho$. Next, to close the system and solve for the unknown $f_i$’s, it is assumed that the bounce-back rule is correct for the non-equilibrium part (Zou and He, 1997) of the particle distribution (for example, $f_5 - f_5^{(eq)} = f_6 - f_6^{(eq)}$), giving overall:

$$\rho = \frac{[f_0 + f_1 + f_2 + f_3 + f_4 + f_7 + f_8 + f_9 + f_{10} + 2(f_6 + f_{13} + f_{14} + f_{17} + f_{18})]}{(1 - u_z)}$$

$$f_5 = f_6 + (f_5^{eq} - f_6^{eq}) = f_6 + \frac{1}{3}\rho u_z$$

$$f_{11} = f_{14} + (f_{11}^{eq} - f_{14}^{eq}) = f_{14} + \frac{1}{6}\rho (u_z + u_x)$$

$$f_{12} = f_{13} + (f_{12}^{eq} - f_{13}^{eq}) = f_{13} + \frac{1}{6}\rho (u_z - u_x)$$

$$f_{15} = f_{18} + (f_{15}^{eq} - f_{18}^{eq}) = f_{18} + \frac{1}{6}\rho (u_z + u_y)$$

$$f_{16} = f_{17} + (f_{16}^{eq} - f_{17}^{eq}) = f_{17} + \frac{1}{6}\rho (u_z - u_y).$$

For a passive scalar, a non-equilibrium bounce-back boundary condition to fix the concentration was employed following Zou and He (1997). For flow in the positive $z$ direction with
the D3Q7 velocity set, \( \rho_s \) at the inlet can be fixed by rearranging Eq. (8.25) to give:

\[
f_{5,s} = \rho_s - (f_{0,s} + f_{1,s} + f_{2,s} + f_{3,s} + f_{4,s} + f_{6,s}).
\tag{8.34}
\]

Setting the velocity using Eq. (8.33) and setting the inlet density with Eq. (8.34), effectively fixes the inlet flux, \( \rho, u \), of species, \( s \).

Thus, periodic and halfway bounce-back boundaries do not require any macroscopic variables as inputs. Equilibrium boundaries require the macroscopic variables \( \rho \) and \( u \) for fluid simulations, or \( \rho_s \) and \( u \) for simulations with a passive scalar. Non-equilibrium bounce-back boundaries required \( u \) for fluid simulations and \( \rho_s \) for simulations with a passive scalar.

**Initial conditions.** The initial conditions for the hydrodynamic lattice Boltzmann model in the present work were determined from the initial macroscopic variables, \( \rho \) and \( u \). Using Eq. (A5.26) with Eq. (A5.27) substituted for the specified moments, \( m^{eq}(\rho, u) \) was calculated. Then,

\[
\left. f(x, t) \right|_{t=0} = f^{eq}(\rho, u) = M^{-1}m^{eq}(\rho, u),
\tag{8.35}
\]

was used to generate the starting values for the distribution function. Similarly, for a simulation involving a passive scalar the initial condition was determined from \( \rho_s \) and \( u \) by using Eq. (8.23) and setting \( f_s(x, t) \big|_{t=0} = f_s^{eq}(\rho_s, u) \).

### 8.2.9 Conversion of lattice units to real units

Parameters in lattice units are related to corresponding parameters in physical units through scaling factors in length, \( \Delta x \), time, \( \Delta t \) and mass, \( \Delta m \) (Maier et al., 1998). The lattice resolution \( \Delta x \) gives the physical length corresponding to the distance between nodes in m/(lattice unit); \( \Delta t \) gives the physical time corresponding to each time step in s/(time step); \( \Delta m \) gives the physical mass associated with each unit volume of the lattice in kg/(lattice unit)\(^3\) since \( \rho_0 = 1 \) was chosen as the equilibrium density. Writing physical units on the left hand side and lattice units, denoted by the subscript LB, on the right hand side, examples of scalings are as follows:

\[
L_x = L_{\text{c,LB}} \Delta x
\]

\[
u = \nu_{\text{LB}} \frac{\Delta x^2}{\Delta t}
\]

\[
\rho = \rho_{\text{LB}} \frac{\Delta m}{\Delta x^3}.
\tag{8.38}
\]
For a simulation, the choice of parameters is performed as follows:

1. Given the parameters for the problem of interest in physical units,

2. Choose a scaling $\Delta x$ and $\Delta t$.

3. Calculate $|u_{LB}|$ using Eq. (8.37) and the physical velocity $u$. Check that $|u_{LB}| < 0.15$ in lattice units for the simulation. Proceed if this condition is satisfied; otherwise, return to step (1) and make a new choice for $\Delta x$ and $\Delta t$.

4. Calculate the relaxation parameters for the variables of interest, e.g. $s_{10}$ and $\tau_s$, using Eq. (8.37), $\nu$ and $D_s$ in physical units, and Eqs. (A5.84) and (8.27) to evaluate $\nu_{LB}$ and $D_{s, LB}$, respectively. Check that the relaxation parameters obtained lie within the range of stability and within the range that permits satisfactory accuracy for the given lattice Boltzmann model. Proceed if these conditions are met; otherwise, return to step (1) and make a new choice for $\Delta x$ and $\Delta t$.

Later, in sections 8.4.5 and 8.4.6, Tables 8.3 and 8.4 give explicit details of the scalings used for simulations in this dissertation.

### 8.3 Validation of the lattice Boltzmann model

#### 8.3.1 Validation of hydrodynamics

To verify the accuracy of the hydrodynamic calculations in the D3Q19 lattice Boltzmann program, Poiseuille flow in a channel was simulated. The analytical solution to the Navier-Stokes equation (A5.89) for Poiseuille flow between two plates with $u = 0$ at the boundaries is given by a parabolic velocity profile:

$$u_z = \frac{4u_{z, \text{max}}}{(L_x - 2)^2} \left( x - \frac{3}{2} \right) \left( L_x - \frac{1}{2} - x \right)$$  \hspace{1cm} (8.39)

$$u_{z, \text{max}} = \frac{F_z (L_x - 2)^2}{8 \rho \nu}$$  \hspace{1cm} (8.40)

where $u_{z, \text{max}}$ denotes the maximum centerline velocity, $F_z$ is the driving force, $(L_x - 2)$ is the effective channel width, $\nu = 1/3 \times (1/s_{10} - 1/2)$ is the kinematic viscosity, $\rho = 1$ is the mass density, and $x$ is the lattice position consistent with the simulation set-up in Fig. 8.4(a). The odd form of Eq. (8.39) is owing to the halfway bounce-back boundary condition and the
Figure 8.4: (a) Simulation geometry for Poiseuille flow in a channel with \( L_x = 17 \). The true channel width is \((L_x - 2)\). (b) Velocity profile for Poiseuille flow using halfway bounce-back boundary conditions with the D3Q19 MRT model and \(1/s_{10} = 1.0\). The velocity was normalised by \( u_{z,\text{max}} \) from the simulation. The solid line represents the analytical solution.

definition of the computational domain: the first lattice node in a three dimensional domain is defined as \( x = y = z = 1 \) rather than \( x = y = z = 0 \). The lattice dimensions were \( L_x = L_z = 1 \), and \( L_x \) was varied over \( 5 \leq L_x \leq 53 \). In addition for each value of \( L_x \), the relaxation time was varied over \( 0.51 < 1/s_{10} < 2.5 \). Thus, in the simulation the parameters which varied were channel width, \((L_x - 2)\), and relaxation time, \(1/s_{10}\), i.e. viscosity; all other parameters were fixed. Halfway bounce-back boundary conditions were used in the \( x \) direction at the walls so that the boundary between the solid and fluid was one half of a lattice spacing from each respective node as shown in Fig. 8.4(a). Hence, for a domain with \( L_x = 17 \) nodes the true channel width is only \( L_x - 2 = 15 \). In the \( z \) direction (flow direction) and \( y \) direction, periodic boundary conditions were used. The domain was initialised with \( \rho = 1 \) and \( u = 0 \) everywhere. The simulations were run for \( 10^5 - 1.5 \times 10^6 \) time steps, where larger times were required for lower values of the relaxation time, \(1/s_{10}\), until the convergence criterion of

\[
\sum_{x=2}^{(L_x-1)} \frac{|u_z(x,t) - u_z(x,t-1)|}{u_z(x,t)} < 10^{-10},
\]

was met in all cases.

The force to accelerate the fluid, \( \mathbf{F} = (0, 0, F_z)^T \), was incorporated in two steps to reduce numerical error (Lallemand and Luo, 2003; Ginzbourg and Adler, 1994):

Step 1, Streaming of \( f_i \);

Step 2, Compute moments \( m_i \) from \( f_i \);
Step 3, \( j' = j + \frac{1}{2}F\Delta t; \)
Step 4, Compute \( m_{i}^{(eq)} \) from \( \rho, j' \);
Step 5, Collision: relaxation of the moments to give \( j'' \);
Step 6, \( j''' = j'' + \frac{1}{2}F\Delta t; \)
Step 7, Compute \( f_i \) from the moments \( m_i \).

The force, \( F_z \), was varied to give \( u_{c,max} = 0.05 \) from Eq. (8.40) in all cases. The momentum, \( j' \), with one-half of the force added, \( i.e. \) after step 3 and before step 4, was used as the output.

Fig. 8.4(b) shows that the simulated values of \( u_c \) for \( 1/s_{10} = 1 \) were in good agreement with the parabolic analytical solution. Similar plots were obtained for \( 1/s_{10} = 0.51, 0.55 \) and 2.5. In addition, \( u_x < 10^{-15}, u_y < 10^{-16} \), and \( \rho = 1.0 \pm 10^{-6} \) in all cases. The relative error in the centreline velocity, shown in Fig. 8.5, was determined by taking the absolute value of the difference between the analytical centreline velocity from Eq. (8.40) and the centreline velocity from the LB simulation, and dividing by the analytical centreline velocity. In theory, this error should be zero since \( F_z \) was chosen to give \( u_{c,max} = 0.05 \). However, higher errors are observed for lower values of the relaxation time, \( 1/s_{10}, \ i.e. \) higher \( Re \), and for smaller channel widths. This dependence on \( Re \) is a result of the low \( Ma \) requirement in Appendix 5. For small channel widths, the centreline velocity was underpredicted by the lattice Boltzmann simulation. Figure 8.5 demonstrates that for \( 0.51 \leq 1/s_{10} \leq 2.5 \) errors in the centreline

Figure 8.5: Relative error in the maximum centreline velocity, \( u_{c,max} \), from simulations \( versus \) the width of the channel, \( (L_x - 2) \). From the slope, error is second order with respect to grid spacing.
velocity are < 11% for a channel of width 3, while errors are < 4% for a channel of width 5. Figure 8.5 also confirms that the halfway bounce-back boundary condition is accurate up to second order in grid spacing, as the errors conform to a line of slope $-2$ on the $\log_{10} - \log_{10}$ plot. However, second order accuracy is only achievable with halfway bounce-back boundary conditions when the boundary is regular and does not have a stair step pattern. For irregular boundaries, the order of the error lies between 1 and 2 (Yu et al., 2003).

### 8.3.2 Validation of mass transport

To verify the accuracy of mass transport with the D3Q7 lattice Boltzmann program, the decay of a 1D convected sinusoidal concentration wave was modelled (Flekkøy, 1993; Sullivan et al., 2007). The time-dependent solution of the advection diffusion equation (8.21) for this problem in a periodic domain is given by Flekkøy (1993):

$$
\rho_s(x, t) = \frac{\rho_{s,\text{max}}}{2} \left[ 1 + e^{-k_D^2 D_s t} \sin k_D (x - u_x t) \right],
$$

where $x$ is the direction in which the domain extends, $k_D = \frac{2\pi}{L_x}$, $L_x$ is the number of lattice nodes, $u_x$ is the macroscopic velocity of the bulk fluid in the $x$ direction, and $\rho_{s,\text{max}}$ is the maximum initial concentration. The diffusion coefficient, $D_s$, can be determined using:

$$
D_s = \frac{1}{k_D^2} \ln \frac{A(0)}{A(t)}, \quad A(t) = \int \left| \rho_s(x, t) - \frac{\rho_{s,\text{max}}}{2} \right|.
$$

For simulations, the integral on the right-hand side of Eq. (8.43) was calculated using the trapezium rule. The domain was $L_x = 128$, $L_y = L_z = 1$. The relaxation time was varied in the range $0.50001 < \tau_s < 10.5$, giving diffusion coefficients of $2.5 \times 10^{-6} < D_s < 2.5$ in lattice units. A value of $\rho_{s,\text{max}} = 1$ was fixed. For each value of $\tau_s$, three different steady uniform velocity fields of $u_x = 0.0, 0.1$ and 0.2 were employed. Thus, the parameters which varied were the relaxation time, $\tau_s$, and the velocity, $u_x$; all other parameters were fixed. Simulations were run for a total of $10^4$ time steps. Periodic boundary conditions were used in all directions. The initial condition for the mass density was determined from Eq. (8.42) with $t = 0$.

Figure 8.6(a) shows the concentration, $\rho_s(x, t)$ as a function of lattice position $x$, at various times for a simulation with $\tau_s = 1$ and $u_x = 0$. Good agreement between the analytical concentration profile and that predicted from the LB method is apparent. The relative error was calculated as the absolute value of the difference between the analytical solution, Eq. (8.27),
Figure 8.6: (a) Comparison between the analytical solution and LB results for the diffusive decay of a sinusoidal concentration profile, \( \rho_s(x, t) \) against \( x \) after 0, 2500, 5000, 7500 and \( 10^5 \) time steps. Here, \( \tau_s = 1 \) and \( u_x = 0 \). (b) Relative error in the diffusion coefficient, \( D_s \), as a function of \( (\tau_s - 1/2) \) for \( u_x = 0.0, 0.1 \) and 0.2. The shaded region corresponds to values of \( \tau_s \) used in sections 8.4.5 and 8.4.6.
and that calculated from Eq. (8.43), divided by the analytical solution. Figure 8.6(b) shows the relative error in $D_s$ as a function of $\tau_s$ for the three different velocities, $u_x$. Here, for $0 < Pe < 10^6$ relative errors < 4% in $D_s$ were obtained. For simulations using double precision (8 byte, 64 bit), a value of $\tau_s = 1/2$ gave a finite diffusivity in lattice units of $4 \times 10^{-6}$ and $6 \times 10^{-6}$ for $u_x = 0$ and $u_x = 0.2$, respectively. For $\tau_s > 5$, $\rho_s$ had equilibrated to a uniform density equal, within machine precision, to $1/2$ after $t = 10^5$ time steps; therefore, errors were independent of $u_x$. The shaded region $0.51 \leq \tau_s \leq 1.0$ and $0.0 \leq u_x \leq 0.15$, corresponds to values used in the remainder of this dissertation.

### 8.3.3 Validation of reaction

Next, to verify the rate of reaction in the D3Q7 lattice Boltzmann program, a uniform concentration field undergoing a simple first order reaction was used:

$$\frac{d\rho_s(t)}{dt} = -k_i \rho_s(t).$$

(8.44)

The solution of the ODE given in Eq. (8.44) is:

$$\rho_s(t) = \rho_s(0)e^{-k_i t} \quad \text{or} \quad k_i = -\frac{1}{t} \ln \left[ \frac{\rho_s(t)}{\rho_s(0)} \right],$$

(8.45)

where $\rho_s(0)$ is the initial concentration. A domain of $L_x = L_y = L_z = 3$ was used with periodic boundary conditions. Based on Eq. (8.30), the error in $k_i$ is independent of velocity, $u$, and relaxation time, $\tau_s$. For the simulations, $u = 0$ and $\tau_s = 1$ were used. The rate constant, the only parameter not fixed, was varied over the range $10^{-10} < k_i < 0.1$. Simulations were run over $10^5$ time steps. The relative error in $k_i$ was calculated as the absolute value of the difference between the theoretical value for $k_i$ and that calculated from Eq. (8.45), divided by the theoretical value for $k_i$. Figure 8.7 shows the relative error in $k_i$ against the theoretical value of $k_i$. For $k_i < 10^{-4}$, the relative error is $< 10^{-4}$; for $k_i > 10^{-4}$, the error increases as a result of the first-order forward Euler approximation to $\Delta \rho_s$. The shaded region corresponds to the values of $k_i$ used in sections 8.4.5 and 8.4.6 with error $< 0.035$. Thus, the method for incorporating reaction in the lattice Boltzmann model for the current study gives satisfactory error estimates over a wide range of parameters.

Overall, sections 8.3.1-8.3.3 have used theoretical test problems with analytical solutions to demonstrate that hydrodynamics, mass transport and reaction can be accurately simulated with
Figure 8.7: Relative error in the rate constant, $k_i$, from simulations *versus* theoretical $k_i$. The shaded region corresponds to the values of $k_i$ used later in sections 8.4.5 and 8.4.6.

the lattice Boltzmann program implemented in this work. Next, verification of hydrodynamics, mass transport and reaction for systems containing a single sphere will be performed.

### 8.4 Comparison of the lattice Boltzmann model with experiments

#### 8.4.1 Flow past a single sphere

To verify flow past a single sphere with the D3Q19 lattice Boltzmann model, the drag force as a function of $Re$ was calculated. The domain size was $L_x = L_y = L_z = 50$. A single sphere was generated on the lattice Boltzmann grid by defining as solid all nodes (integer $x, y, z$) satisfying:

$$
\left( x - \frac{L_x + 1}{2} \right)^2 + \left( y - \frac{L_y + 1}{2} \right)^2 + \left( z - \frac{L_z + 1}{2} \right)^2 \leq r^2,
$$

(8.46)

with $r = 4.8$. The non-integer value of $r$ was found to give better results consistent with Mei *et al.* (2002). The centre of the sphere was off the lattice, *i.e.* not a lattice node. The sphere, shown in Fig. 8.8, was 10 lattice nodes across and contained a total of 480 nodes. Considering each node to have unit volume, the effective diameter of an equal-volume sphere was $d_p = 9.714$, giving $L_x/d_p \approx 5$. 

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Flow was in the positive $z$ direction. At the inlet, the constant velocity boundary condition given by Eq. (8.33) was used to set $U$. At the outlet boundary, the no-flux condition of Eq. (8.31) was specified. In the $x$ and $y$ directions, periodic boundary conditions were applied. Halfway bounce-back boundary conditions were used at the interface between the solid sphere and fluid; no special treatment for the curved geometry was considered. The domain was initialised with $\rho = 1$ and $u = 0$ everywhere, except at the inlet, where the inlet velocity condition was used. For the simulations, the parameter $1/s_{10} = 0.6$ was used to fix the kinematic viscosity from Eq. (A5.84) in all simulations except those with $Re = \{20, 50, 100, 150\}$ where $1/s_{10} = \{0.55, 0.56, 0.53, 0.52\}$ was used. The inlet velocity, $U$, was varied over $0.0001 \leq U \leq 0.1$. Thus, the parameters which were varied to alter the $Re$ number were $s_{10}$ and $U$; all other parameters were fixed. Simulations were run for $10^5$ time steps until steady state was obtained. The Reynolds number was defined as:

$$Re = \frac{Ud_p}{\nu}, \quad (8.47)$$

where $U$ is the superficial inlet velocity.

Fig. 8.8 shows the velocity, $u_z$, for flow past a sphere with a diameter of 10 lattice nodes.
or, equivalently, with \( d_p = 9.714 \) at \( Re = 20 \). The velocity near the surface of the sphere and in the wake of the sphere is nearly zero. A velocity increase from the inlet velocity is observed around the sphere and is necessary to accommodate for the constriction in the incompressible flow.

To determine the drag coefficient, \( C_d \), the momentum-exchange method of Mei et al. (2002) was used. As per Mei et al. (2002), the scalar array \( w_s(x) \) is defined to take a value of 0 for a fluid node and 1 for a solid node. The scalar array \( w_b(x) \) is 0 everywhere except for those solid boundary nodes, \( x_b \), which border the fluid. For a given non-zero velocity \( v_i \), \( v_i^- \) denotes the velocity in the opposite direction, so that \( -v_i = v_i^- \). For a solid boundary node, \( x_b \), with \( w_b(x_b) = 1 \) and \( w_s(x_b) = 1 \), the momentum exchanged with all neighbouring fluid nodes over a single time step \( \Delta t = 1 \) is then given by:

\[
\sum_{i \neq b} v_i \left[ f_i'(x_b, t) - f_i^-(x_b + v_i^- \Delta t, t) \right] \left[ 1 - w_s(x_b + v_i^- \Delta t) \right].
\] (8.48)

The total force acting on a solid body can then be calculated by summing Eq. (8.48) over all boundary nodes belonging to it:

\[
F = \sum_{x_b} \sum_{i \neq b} v_i \left[ f_i'(x_b, t) - f_i^-(x_b + v_i^- \Delta t, t) \right] \left[ 1 - w_s(x_b + v_i^- \Delta t) \right],
\] (8.49)

where the force is evaluated after the collision step. To summarise, the momentum exchanged between a solid body and the surrounding fluid can be calculated using those \( f_i \) which stream between solid and fluid phases in a given time step.

Next, for the simulated system,

\[
C_d = \frac{|F_z|}{\frac{\rho}{2} U^2 \pi \left( \frac{d_p}{2} \right)^2},
\] (8.50)

was calculated with \( \rho = 1 \) and \( d_p = 9.714 \). For \( Re < 0.1 \), i.e. Stokes’ flow,

\[
C_d = \frac{24}{Re} \quad Re < 0.1,
\] (8.51)

whilst for larger \( Re \), the empirical equation:

\[
C_d = \left( \sqrt{\frac{24}{Re}} + 0.5407 \right)^2 \quad Re < 6000,
\] (8.52)
Figure 8.9: Drag coefficient, $C_d$, as a function of Reynolds number, $Re$, for laminar flow past a sphere. Correlations are lines; simulations results are shown by (●).

from Bird et al. (2007) can be used. Figure 8.9 shows that $C_d$ derived from the lattice Boltzmann simulations agrees with the $C_d$ predicted from Eqs. (8.51) and (8.52) for a sphere with as few as 10 lattice nodes in diameter and further validates the hydrodynamic results of the current lattice Boltzmann model.

### 8.4.2 Effectiveness factor for a single sphere

To validate the D3Q7 lattice Boltzmann program, the effectiveness factor for a first-order, irreversible reaction in a porous, spherical catalyst pellet was calculated. The analytical solution is given by (Thiele, 1939) as outlined in Appendix 4:

$$
\eta = \frac{3}{\phi^2} (\phi \coth(\phi) - 1) \quad \phi = \frac{d_p}{2 \sqrt{D_s}}.
$$

(8.53)

It is assumed that the heat of reaction is negligible. Spheres of varying diameter were constructed using Eq. (8.46) with $r = \{2.8, 4.8, 9.8, 24.8, 49.8\}$, giving effective diameters in lattice units of $d_p = \{5.519, 9.714, 19.549, 49.634, 99.594\}$. The domain size was varied so that the sphere was circumscribed by at least one fluid node in all directions. An equilibrium boundary condition was used to fix the concentration of the exterior fluid by specifying $\rho_s = 1$ and $\mathbf{u} = 0$ for all fluid nodes after each streaming step. The initial conditions were $\rho_s = 0, \mathbf{u} = 0$ for solid nodes and $\rho_s = 1, \mathbf{u} = 0$ for fluid nodes. The macroscopic fluid velocity used as input
to the D3Q7 model was \( u = 0 \) over the entire domain for all time. For the present simulations \( \tau_s \) was fixed to 1 or 0.55 and \( k_i \) was varied to give \( \phi = d_p/2 \times \sqrt{k_i/D_s} = \{0.01, 0.1, 1, 10, 100\} \). Thus, the parameters which varied were \( k_i \) and \( d_p \); only for \( \phi = 10 \) in Fig. 8.10(b) was \( \tau_s \) also changed. All other parameters were fixed. Simulations were run for \( 10^5 \) time steps to permit a constant, steady state concentration profile to evolve within the catalyst pellet.

The observed rate at steady state was evaluated as:

\[
k_i \sum_x \rho_s(x) w_s(x),
\]

where \( w_s(x) \) is a scalar array which takes the value of 0 or 1 for fluid or solid nodes, respectively. The effectiveness factor from simulations was then calculated using:

\[
\eta = \frac{k_i \sum_x \rho_s(x) w_s(x)}{k_i \sum_x w_s(x)},
\]

where \( \rho_s(x) = 1 \) in the surrounding fluid has been used in the denominator. Figure 8.10(a) shows the effectiveness factor calculated using Eq. (8.55) against Thiele modulus, \( \phi \). In all cases in Fig. 8.10(a), \( \tau_s = 1 \). Good agreement between simulations and the analytical solution for \( \phi \leq 10 \) is observed. The relative error in the effectiveness factor was found to be < 2.2 % for \( \phi \leq 1 \); the error increased with increasing \( \phi \), and decreased with increasing \( d_p \).

The increasing error with increasing \( \phi \) can be explained by two factors. First, to increase \( \phi \) at a fixed \( d_p \) and \( \tau_s \), \( k_i \) must be increased as shown by Eq. (8.53) and using Eq. (8.27) to evaluate \( D_s \). However, increasing \( k_i \) for this first-order reaction will eventually result in \( O(k_i \rho_s) = O(\Delta \rho_s) \approx O(\rho_s) \). Once the change in \( \rho_s \) over a single time step is of the order of the existing \( \rho_s \), the forward Euler method used in section 8.2.6 to incorporate \( \Delta \rho_s \) will produce errors. Indeed, at \( \phi = 100 \), only the sphere with \( d_p = 99.594 \) in Fig. 8.10(a) returned positive \( \rho_s \) over the entire domain; therefore, only this point has been plotted. Errors can be reduced by either reducing \( k_i \) or by using a more accurate scheme for numerical integration (Sullivan, 2006), e.g. Runge-Kutta. Figure 8.10(b) shows that better results were indeed obtained for simulations with \( \tau_s = 0.55 \) and \( k_i \) values one tenth those for simulations with \( \tau_s = 1 \). Second, as \( \phi \) is increased the reaction only occurs near the boundary of the sphere. For large \( \phi \) if the grid spacing \( \Delta x \) is not kept less than the width of the front \( \sqrt{D_s/k_i} \), substantial errors as a result of the low accuracy of the equilibrium boundary conditions will be incurred. Overall, it has been shown that the present method for incorporating mass transfer and reaction can accurately
predict the behaviour of catalyst pellets over a wide range of Thiele moduli, provided suitable values for $k_i$, $\tau_s$, i.e. the diffusivity, and the grid spacing are chosen.

### 8.4.3 Mass transfer to the surface of a particle

To verify mass transfer to the surface of a sphere, the D3Q7 lattice Boltzmann model for mass transport of passive scalar was used together with the D3Q19 lattice Boltzmann model for hydrodynamics. The computational domain was of dimension $L_x = L_y = L_z = 50$, and the effective diameter of the sphere was $d_p = 9.714$. The steady state macroscopic velocity field from the hydrodynamic simulations in section 8.4.1 was used as input for the mass transfer simulations with the velocity of solid nodes set to zero and was fixed for all time. Boundary and initial conditions will not be repeated.

For mass transport, the constant concentration boundary condition given by Eq. (8.34) such that $\rho_s = 1$ was used at the inlet ($z = 1$). At the outlet ($z = L_z$), a zero flux boundary given by Eq. (8.32) was used. In the $x$ and $y$ directions, periodic boundary conditions were applied. Any mass entering the sphere was destroyed by setting $f_{i,s} = 0$ for all $i$ within the sphere prior to each streaming step. The initial conditions were $\rho_s = 0$ everywhere, except at the inlet where the inlet boundary condition, $\rho_s = 1$ was used. For simulations, the parameters which varied were $U$, the inlet velocity of the bulk fluid, $1/s_{10}$, the viscosity of the bulk fluid, and $\tau_s$. 

---

**Figure 8.10:** (a) Effectiveness factor, $\eta$, as a function of Thiele modulus, $\phi$, for a first order reaction in a sphere of effective diameter, $d_p$. (b) Effectiveness factor, $\eta$, at $\phi = 10$ for spheres of varying diameter, $d_p$. For $\tau_s = 0.55$ the values of $k_i$ used in simulations were smaller than those required for $\tau_s = 1$ for the same value of $\phi$ and better agreement with the analytical solution was observed.
Table 8.2: Parameters used in simulations to produce Fig. 8.11.

<table>
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<tr>
<th>Parameter</th>
<th>U</th>
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<th>Re</th>
<th>Sc</th>
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<td>0.55</td>
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<td>0.56</td>
</tr>
</tbody>
</table>

Figure 8.11: Sherwood number, $Sh$, as a function of Reynolds number, $Re$. Here, the Schmidt number, $Sc = 1$.

the diffusivity of the passive scalar; all other parameters were fixed. Table 8.2 lists the input parameters used to produce Fig. 8.11. Simulations were run for $10^5$ time steps.

The rate was related to a mass transfer coefficient using the following expression at steady state:

$$k_g A_s (c_{out} - c_s) = \sum_{x,y} \rho_s(x, y, 1) u_z(x, y, 1) - \sum_{x,y} \rho_s(x, y, L_z) u_z(x, y, L_z),$$

(8.56)

where $k_g$ is the mass transfer coefficient, $A_s = \pi d_p^2 = \pi (9.714)^2$ is the surface area of the sphere, $c_{out} = \rho_s \approx 1$ is the concentration in the bulk and $c_s = \rho_s \approx 0$ is the concentration at the surface of the sphere. The Sherwood number, Reynolds number, and Schmidt number were defined as follows:

$$Sh = \frac{k_g d_p}{D_{mix}}, \quad Re = \frac{U d_p}{\nu}, \quad Sc = \frac{\nu}{D_{mix}},$$

(8.57)
where $D_{m} = D_{s}$ is the diffusivity of the scalar in the bulk fluid mixture. To compare the simulated values of $k_{g}$ with values from the literature, the most common correlation for $S h(Re, Sc)$ given by Ranz and Marshall (1952) for $Re \geq 0$ was used:

$$S h = 2.0 + 0.6Re^{1/2}Sc^{1/3},$$

(8.58)

where it is noted that the original correlation was for the Nusselt number, the heat transfer analogue of the Sherwood number (Bird et al., 2007). For $Re > 3.5$, Whitaker (1972) subsequently gave the correlation:

$$S h = 2.0 + (0.4Re^{1/2} + 0.06Re^{2/3})Sc^{0.4},$$

(8.59)

as an alternative to Eq. (8.58). Figure 8.11 shows the calculated Sherwood number based on $k_{g}$ determined from simulations against Reynolds number compared to the correlations of Eqs. (8.58) and (8.59). The non-linear increase in $S h$ with $Re$ is captured; however, the present LB simulations underpredict $S h$. Better results for $S h$ might be obtained by either increasing the size of the sphere or by enforcing $\rho_{s} = 1$ for the bulk fluid on all six sides of the 3D cubic domain, not just at the inlet.

Next, rather than eliminating the passive scalar entering the sphere, reaction and diffusion
within the sphere was incorporated for the flow with $Re = 20$. Thus, rather than setting $f_{i,s} = 0$ for all $i$ within the sphere prior to each streaming step, the entering $f_{i,s}$ were streamed over the entire sphere. The effective diffusivity within the sphere was set to a value half that of the molecular diffusion in the fluid by setting $\tau_s = 0.55$ in the fluid and $\tau_s = 0.525$ within the sphere. The boundary and initial conditions were identical to those used previously to produce the point corresponding to $Re = 20$ in Fig. 8.11. The rate constant, $k_i$, was then varied between $10^{-6}$ and 1; all other parameters were fixed as specified by column 3 of Table 8.2 for flow at $Re = 20$. Figure 8.12 shows the rate, calculated using Eq. (8.56), against the rate constant, $k_i$. Three distinct kinetic regimes are apparent. In regime (1), intrinsic kinetics are rate limiting and any increase in $k_i$ results in a commensurate increase in the rate. As such, the dashed line in regime (1) has a slope of unity. In regime (2), intraparticle diffusion begins to limit the rate and the slope decreases to approximately half that from the kinetically controlled regime (1). In regime (3), mass transfer to the particle surface is limiting. Here, increasing $k_i$ does not result in an increase in the rate. The intercept of the horizontal dashed line in regime (3) with the ordinate corresponds to the value of the rate calculated using the left hand side of Eq. (8.56), with $k_g$ determined from the correlation of Ranz and Marshall, Eq. (8.58). The numerical increase in $k_i$ is tantamount to an increase in temperature in experimental work; and plots similar to Fig. 8.12 have been observed for experimental gas-solid reactions in porous catalyst, e.g. Fig. 11.2 in Satterfield (1980).

### 8.4.4 Flow in a packed bed

Next, flow through a packed bed was investigated with the D3Q19 lattice Boltzmann model. A computational domain of $L_x = L_y = 102$ and $L_z = 800$ lattice nodes was used. In total, 297 particles, each approximately 20 lattice nodes across were placed into the centre of the domain between lattice nodes $252 \leq z \leq 538$. The position of the particles was determined with a discrete element model (Third et al., 2010) by dropping sheets of spheres into a cylinder and tapping. A schematic diagram of the packed bed is shown in Fig. 8.13(a).

Figure 8.13(b) shows the position of the centre of the 297 spheres in the $x - y$ plane. Two distinct rings and one central point can be seen. This is a typical packing arrangement for a system with $d_{bed}/d_p = 5$. The scatter of the location of the centre of the spheres increases towards the centre. Figure 8.13(c) shows the position of the centre of the spheres in the $x - z$ and $y - z$ planes. The centres corresponding to the initial row of spheres are located between
Figure 8.13: (a) Diagram of the packed bed comprising 297 particles each with \( d_p \approx 20 \); the tube had a diameter of \( d_p \approx 100 \). The computational domain consisted of \( L_x = L_y = 102 \) and \( L_z = 800 \) nodes. (b) Position, in the \( x-y \) plane, of the centre points of the 297 spheres comprising the packed bed shown in (a). (c) Position, in the \( x-z \) (+) and \( y-z \) (○) planes, of the centres of the spheres forming an initial portion of the packing. (d) Porosity as a function of position, \( z \), for a slice in the \( x-y \) plane (black) and the average of all preceding slices (red). (e) Mean porosity as a function of radial position (○) and corresponding results from Zeiser (2008)(■). Here, \( r = 0 \) is defined to as the axis of the bed. All dimensions are in lattice units (lu); conversion to physical units for results in section 8.4.6 is performed using \( \Delta x = 10^{-4} \text{ m}/(\text{lattice unit}) \).
Figure 8.14: Cross-section of flow through the bed at $z = 400$ corresponding to the centre of the packing for (a) $Re = 5$ (b) $Re = 10$ (c) $Re = 15$ (d) $Re = 20$. The velocity, $u_z$, given in lattice units increases with $Re$.

$L_z = 262 - 263$; increasing scatter in the location of the centrepoints is evident with increasing $z$. Figure 8.13(d) shows the porosity of a single slice in the $x - y$ plane as a function of position $z$ as well as the porosity averaged over all preceding slices in the $x - y$ plane as a function of position $z$. The porosity at $L_z = 251.5$, i.e. the start of the packing, was manually set to 0 owing to the halfway bounce-back boundary conditions. The mean porosity within the packing, calculated as the integer number of fluid nodes divided by the total number of nodes within the tube between $252 \leq z \leq 538$, was $\varepsilon = 0.429$, compared to a theoretical porosity from the DEM simulations of $\varepsilon = 0.413$. The difference is a result of discretisation of both the tube and the particles. Figure 8.13(e) shows the porosity as a function of radial position and was in good agreement with the results of Zeiser (2008).

For fluid flow, a non-equilibrium boundary condition (Zou and He, 1997) was used to fix the superficial inlet velocity, $U$, using Eq. (8.33). No special treatment of corner or edge nodes at the inlet was necessary. At the outlet, the zero flux boundary condition of Eq. (8.31) was applied after streaming. Halfway bounce-back boundaries were applied between fluid and solid nodes, i.e. between both the fluid and the tube and between the fluid and the solid particles. The superficial velocity at the inlet was ramped in a linear fashion over $5 \times 10^4$
Figure 8.15: Pressure, $P/P_{out}$ as a function of dimensionless length, $z/d_p$, showing a linear pressure drop through the packing.

time steps from a starting value of 0. The initial condition was $\rho = 1$ and $u = 0$ over the entire domain. The Reynolds number was defined as $Re = Ud_p/\nu$, where $d_p$ is the effective particle diameter, $U$ is the superficial velocity at the inlet, and $\nu$ is the kinematic viscosity. The flow through the packing was investigated at $Re = \{5, 10, 15, 20\}$ by setting $1/s_{10} = 0.55$ and varying $U = \{0.0042, 0.0083, 0.0125, 0.0167\}$. Thus, the only parameter which varied was $U$; all other parameters were fixed. Simulations were run until steady state for a total of $2 \times 10^5$ time steps.

The uniform velocity profile at the inlet changed to a parabolic velocity profile prior to the packing, then became distorted as the fluid passed through the interstices. High velocity flow through the interstices is evident from Fig. 8.14 which shows the velocity, $u_z$, through a central cross-section of the bed at $z = 400$ for $Re = \{5, 10, 15, 20\}$. As $Re$ increases, the maximum magnitude of the velocity, $u_z$, increases.

The pressure drop through the packing was linear and is shown in Fig. 8.15. As a comparison, the pressure drop from the correlation of Zhavoronkov et al. (1949), which is similar to the correlation of Ergun and Orning (1949), but accounts for low ratios of tube to particle diameter was calculated as outlined in Freund et al. (2003). Agreement in the pressure drop, $\Delta P/L$ where $L$ is the length of the packed bed and $P$ is the pressure from Eq. (A5.90), with
the simulated results was better than 0.6 % for all four values of Re using $\varepsilon = 0.413$, the true porosity predicted from the DEM simulation.

### 8.4.5 Reaction of a single particle

Next experimental results and simulations with the D3Q7 lattice Boltzmann model for the reduction of a single, spherical particle of Fe$_2$O$_3$ to Fe$_3$O$_4$ via reaction (1.9):

$$3 \text{Fe}_2\text{O}_3 + \text{CO} \rightleftharpoons 2 \text{Fe}_3\text{O}_4 + \text{CO}_2, \quad \Delta H_{1023K}^o = -44.3 \text{kJ/mol} \quad (8.60)$$

were compared. The relevant physical parameters for the current problem were determined as follows. The diameter of the particle of Fe$_2$O$_3$ was 2 mm. From Table 5.1, the effective diffusivity of CO within a particle at 1023 K was $D_{e,\text{CO}} = 2.5 \times 10^{-5}$ m$^2$/s. From Eq. (5.19), the intrinsic rate constant was $k_i = 2.4 \times 10^7 \exp(-75000/RT) = 3550$ s$^{-1}$. The concentration of CO in the gas surrounding the particle was 0.6 mol/m$^3$. The molar density of reactive Fe$_2$O$_3$ initially present was determined using the mass density of Fe$_2$O$_3$ (5150 kg/m$^3$) and porosity of the particles ($\varepsilon_p = 0.6$) as follows:

$$n_{\text{Fe}_2\text{O}_3}\big|_{t=0} = \frac{5150 \text{ kg}}{\text{m}^3} \times \frac{1 \text{ kmol Fe}_2\text{O}_3}{159.7 \text{ kg}} \times \frac{(1-0.6)}{1} \times \frac{0.8}{1} = 10.3 \text{ kmol/m}^3,$$

where the factor of 0.8 comes from the experimental observation that maximum conversions of $\sim$ 80 % are achieved, as shown in Fig 5.9. Thus, for the current problem $\phi = d_p/2 \times \sqrt{k_i/D_{e,\text{CO}}} = 20$.

For the experiments, mechanically-mixed particles of Fe$_2$O$_3$ were prepared as described in Chapter 2, section 2.2. For reduction experiments, the fluidised bed, sampling line and analysers described in Chapter 5, section 5.2 were used. In all cases, the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ was studied at 1023 K and $10^5$ Pa, using mixtures of CO+CO$_2$+N$_2$ (respectively, 5, 15 and 80 vol. %) during reduction to give $c_{\text{CO}} = 0.6$ mol/m$^3$; during oxidation, air (21 O$_2$, 79 vol. % N$_2$) was used. From thermodynamics (Barin and Knacke, 1973), these compositions will generate Fe$_3$O$_4$ and Fe$_2$O$_3$, respectively. The total flowrate of gas through the fluidised bed was fixed at $1.6 \times 10^{-4}$ m$^3$/s, giving $U/U_{mf} = 7$ as shown in Table 5.1. As in Chapter 5, the fluidised bed could be assumed to be well-mixed.

In a typical experiment, particles of Fe$_2$O$_3$ with $d_p = 2$ mm were counted, weighed and then
Table 8.3: Table relating the parameters in physical units to lattice units. Here, \( \Delta x = 4 \times 10^{-5} \text{ m/(lattice unit)} \), \( \Delta t = 1 \times 10^{-5} \text{ s/(time step)} \), \( \Delta n/\Delta x^3 = 0.6 \text{ mol/m}^3 \).

<table>
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</thead>
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</tr>
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</tr>
<tr>
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<td>10320</td>
</tr>
<tr>
<td>( k_i )</td>
<td>2.4 \times 10^7 \exp(-75000/RT)</td>
</tr>
<tr>
<td>( D_{e,CO} )</td>
<td>2.5 \times 10^{-5}</td>
</tr>
</tbody>
</table>

dropped into the fluidised bed operated at 1023 K. In each case, 20 particles corresponding to \( \sim 0.15 \text{ g} \) of \( \text{Fe}_2\text{O}_3 \) were introduced to the bed and resulted in an initial change in the effluent CO by \( < 0.5 \text{ vol. \%} \) or \( < 10 \% \) of the inlet value. After a specified time, the inlet gas to the bed was switched to inert \( \text{N}_2 \) to prevent further reaction using solenoid valves controlled by a timer. The bed was subsequently cooled to room temperature under the flow of \( \text{N}_2 \); the reacted particles were then sieved to separate them from the inert \( \text{Al}_2\text{O}_3 \) bed material which had a smaller diameter, \( d_p = 300, -425 \mu \text{m} \). Reacted particles were fixed in an acrylic resin (Kleer-Mount, MetPrep) and cross-sectioned by light sanding for analysis with an optical microscope (Leica DM/LM) at 5\( \times \) magnification in dark field mode. Image analysis to measure the location of the phase boundary between \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) was performed with conventional software (analySIS Image Processing).

For the lattice Boltzmann simulations, the domain size was \( L_x = L_y = L_z = 52 \). A single particle was initialised using Eq. (8.46) with \( r = 24.8 \) in lattice units, giving a sphere 50 nodes across or 2 mm in physical units. Thus, the particle was enclosed by a minimum of one fluid node in every direction. No flow was modelled, i.e. the hydrodynamic D3Q19 model was not used; rather, only the D3Q7 model for a passive scalar for CO was employed as outlined in section 8.2.5 using a distribution, \( f_{i,CO} \). A separate variable, \( n_{\text{Fe}_2\text{O}_3}(\mathbf{x}, t) \), was used to follow the conversion of the \( \text{Fe}_2\text{O}_3 \). Because the \( \text{Fe}_2\text{O}_3 \) is not advected, however, a separate distribution function for \( \text{Fe}_2\text{O}_3 \) was not required.

As in section 8.4.2, equilibrium boundary conditions were used to set \( \rho_{CO}(\mathbf{x}, t) = 0.6 \text{ mol/m}^3 \) over all fluid nodes for all time. Additionally, \( \mathbf{u}(\mathbf{x}, t) = 0 \) was set over the entire domain for all time. Thus, only the D3Q7 model was required, not the D3Q19 model. The initial conditions were \( \rho_{CO}(\mathbf{x}, 0) = 0.6 \text{ mol/m}^3 \), \( n_{\text{Fe}_2\text{O}_3}(\mathbf{x}, 0) = 0 \) for fluid nodes, whilst for the solid nodes of the
sphere $\rho_{\text{CO}}(x, 0) = 0$, $n_{\text{Fe}_2\text{O}_3}(x, 0) = 10.3 \text{ kmol/m}^3$ was used. Conversion between physical and lattice units was performed as outlined in section 8.2.9. The parameters used for the simulation are summarised in Table 8.3.

The rate of reduction of $\text{Fe}_2\text{O}_3$ to $\text{Fe}_3\text{O}_4$ was previously given in units of mol/(s g) by Eq. (5.19):

$$r' = \frac{2.4 \times 10^7 \exp\left(\frac{-75000}{R T}\right)}{\rho_{\text{Fe}_2\text{O}_3}} \left(c_{\text{CO}} - \frac{c_{\text{CO}_2}}{K_p}\right) \left(1 - \frac{X}{0.8}\right)^{0.4}. \quad 0 \leq X \leq 0.8 \quad (8.62)$$

Based on the large equilibrium constant at 1023 K, $K_p = 1.47 \times 10^5$, the back reaction is however negligible. Additionally, the exponent, 0.4, was set to unity to simplify the rate expression. In the model, the conversion $X$ at each lattice point was determined using:

$$X(x, t) = 0.8 \left(1 - \frac{n_{\text{Fe}_2\text{O}_3}(x, t)}{n_{\text{Fe}_2\text{O}_3}(x, 0)}\right), \quad (8.63)$$

with $n_{\text{Fe}_2\text{O}_3}(x, 0) = 10.3 \text{ kmol/m}^3$. Therefore, the overall expression for the rate of reaction as a function of conversion for the lattice Boltzmann model was in units of (mol/s m$^3$):

$$\frac{d\rho_{\text{CO}}(x, t)}{dt} = -k_i \rho_{\text{CO}}(x, t) \left(1 - \frac{X}{0.8}\right) = -k_i \rho_{\text{CO}}(x, t) \left(\frac{n_{\text{Fe}_2\text{O}_3}(x, t)}{n_{\text{Fe}_2\text{O}_3}(x, 0)}\right), \quad (8.64)$$

and was incorporated as outlined in section 8.2.6. It should be noted that the factor of 0.8 in Eqs. (8.61) and (8.63) permits a consistent definition of conversion, $X$, for both experiments and the LB simulation, i.e. the initial conversion is $X = 0$ and the final conversion is $X = 0.8$ in both cases. The simulation was run for a total of $6 \times 10^6$ time steps corresponding to 60 s. Finally it should be noted that the problem’s symmetry was exploited and only one eighth of a particle was actually modelled.

Figure 8.16 shows the experimental cross-section and corresponding cross-section from the D3Q7 lattice Boltzmann simulation for the reduction of a single sphere of $\text{Fe}_2\text{O}_3$ to $\text{Fe}_3\text{O}_4$ as a function of time, $t$. Initially, at $t = 0$ the particle is entirely $\text{Fe}_2\text{O}_3$ and $X = 0$. As the reaction progresses, the front between $\text{Fe}_2\text{O}_3$ and $\text{Fe}_3\text{O}_4$ moves progressively towards the centre of the particle. Qualitatively good agreement between the model and simulation is observed by comparing the experimental and model predictions at $t = 10, 30$ and 40 s. Quantitatively, the thickness of the $\text{Fe}_3\text{O}_4$ shell at $t = 10, 30$ and 40 s determined from simulations using the arbitrary cut-off of $X = 0.4$ gave 280, 480 and 620 $\mu$m. For comparison, the experimental boundaries estimated from the intersection of black and red phases at identical times from the
Figure 8.16: Experimental cross-section (left) and lattice Boltzmann simulation (right) for reduction of a particle of Fe$_2$O$_3$ ($X = 0$) to mostly Fe$_3$O$_4$ ($X = 0.8$) in CO+CO$_2$+N$_2$ (5, 15, 80 vol %, respectively) at 1023 K. The physical parameters were $D_{c, CO} = 2.5 \times 10^{-5}$ m$^2$/s, $k_t = 2.4 \times 10^7 \exp(-75000/RT) = 3550$ s$^{-1}$ and $d_p = 2$ mm. Scalebar = 500 µm.
Figure 8.17: Conversion, $X$, versus time, $t$, for the reduction of a sphere, $d_p = 2 \text{ mm}$, of Fe$_2$O$_3$ to mostly Fe$_3$O$_4$ ($X = 0.8$) at 1023 K and $10^5 \text{ Pa}$ measured using experimental CO consumption ($\times$), experimental CO$_2$ production ($\times$) and the LB simulation ($\bullet$). The time to reach the final conversion to Fe$_3$O$_4$, $X = 0.8$, is $t^* = 48 \text{ s}$.

For the model, a cut-off of $X = 0.65$ gave the thicknesses of the Fe$_3$O$_4$ shells to be 200, 400 and 560 $\mu\text{m}$. For long times ($t = \infty$), the particle is reduced mostly to Fe$_3$O$_4$ and $X = 0.8$ in the simulations. From experiments, the time to reach the final conversion to Fe$_3$O$_4$ was independent of the mass of particles used for batches 0.05 – 0.2 g or 5 – 26 particles and was equal to $t^* \approx 48 \pm 4 \text{ s}$, as shown in Fig. 8.17. Here, final conversions of $X = 0.85$ for CO$_2$ and $X = 0.90$ for CO were obtained. The simulation gave $X > 0.79$ for $t^* = 48 \text{ s}$, in good agreement.

### 8.4.6 Reaction in a packed bed

Next, experimental and model results for the reduction of a packed bed of Fe$_2$O$_3$ to Fe$_3$O$_4$, similar to that described in Chapter 2, sections 2.2 and 2.3.1, were compared. The reactor was made from 316 stainless steel tubing (I.D. 10 mm; total length 450 mm). A stainless steel plate (1 mm thick) supported the bed: the plate contained 6 evenly spaced holes in a circular pitch, each with a diameter of 1 mm. The packed bed consisted of 12 g or $\sim 1500$
particles of Fe$_2$O$_3$ with $d_p = 2$ mm; a layer of 2 g of Al$_2$O$_3$ with $d_p = +1.4, -1.7$ mm was placed on either side of the reactive iron. Stainless steel thermocouples (O.D. 1.5 mm, type K) were positioned every 30 mm along the packed bed by welding fittings (Swagelok) to the steel tube, as shown in Fig. 8.18(a). The temperature of the thermocouples was recorded at a frequency of 1 Hz (Measurement Computing, USB-Temp). The reactor was placed in a tubular furnace to heat to the desired temperature of 1023 K. To obtain a uniform temperature along the length of the reactor, insulation was placed between the furnace wall and the reactor at both the top and bottom of the heated section. To avoid dampening of temperature fluctuations owing to the furnace control system: the bed was heated to 1023 K in air, the temperature was allowed to stabilise, and then the furnace was switched to a setting to provide constant power during the experiment. The gas sampling line and analyser set-up was identical to that in Chapter 5 for reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$. The flowrate of the reducing gas with composition CO+CO$_2$+N$_2$ respectively, 5, 15 and 80 vol. % to give $c_{CO} = 0.6$ mol/m$^3$ was $1.4 \times 10^{-5}$ m$^3$/s. This corresponded to $Re = Ud_p/\nu = 10$, where $U = 0.61$ m/s is the superficial velocity at the inlet at 1023 K and $10^5$ Pa, $d_p = 2$ mm is the particle diameter and $\nu = 1.28 \times 10^{-4}$ m$^2$/s is the kinematic viscosity of the inlet gas, which was assumed to be equal to that of pure N$_2$ and calculated from Hirschfelder et al. (1954). An identical flowrate of air (21 O$_2$, 79 N$_2$ vol. %) was used during oxidation to return the Fe$_3$O$_4$ to Fe$_2$O$_3$. Between oxidation and reduction stages, the reactor was purged with N$_2$ for 60 s. A total of 4 cycles of reduction and oxidation were performed.

Figure 8.18(b) shows the composition of the effluent as a function of time for cycles 2-4. At $t = 0$ s, the reducing gas is switched on. All of the entering CO was consumed in the reduction reaction for $t < 500$ s. For $t > 500$ s, the CO rapidly increased before reaching its inlet value of $c_{CO} = 0.6$ mol/m$^3$ at $t = 700$ s. The effluent concentration profile thus suggests that reduction in the packed bed is characterised by a sharp reaction front which propagates down the reactor and ultimately breaks through over $500 < t < 700$ s. The experimental results demonstrate satisfactory reproducibility: the breakthrough profile of CO is nearly identical over the three cycles studied. Results for cycle 1 are not included owing to the anomalous behaviour observed during reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ in cycle 1, as described in Chapter 5.

Thermocouple measurements were used to track the progress of the reaction front. Figure 8.18(c) shows the temperature measured by three thermocouples spaced $\sim 30$ mm apart along the length of the bed as a function of time for cycles 2-4. The increase in the reactor temperature is sequentially observed for $T_1$, followed by $T_2$, then $T_3$, where $T_1$, $T_2$ and
Table 8.4: Table relating the parameters in physical units to lattice units. Here, $\Delta x = 10^{-4}$ m/(lattice unit), $\Delta t = 1.37 \times 10^{-6}$ s/(time step), $\Delta m/\Delta x^3 = 0.34 \text{ kg/m}^3$ and $\Delta n/\Delta x^3 = 0.6$ moles/m$^3$.

<table>
<thead>
<tr>
<th>Physical</th>
<th>Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>Value</td>
</tr>
<tr>
<td>$L_x$</td>
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</tr>
<tr>
<td>$L_y$</td>
<td>0.0102</td>
</tr>
<tr>
<td>$L_z$</td>
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</tr>
<tr>
<td>$d_p$</td>
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</tr>
<tr>
<td>$\rho$</td>
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</tr>
<tr>
<td>$U$</td>
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</tr>
<tr>
<td>$\nu$</td>
<td>0.000122</td>
</tr>
<tr>
<td>$\rho_{CO}$</td>
<td>0.6</td>
</tr>
<tr>
<td>$n_{Fe_2O_3}$</td>
<td>10320</td>
</tr>
<tr>
<td>$k_i$</td>
<td>2.4 $\times 10^7$ exp(−75000/R T)</td>
</tr>
<tr>
<td>$D_{m,CO}$</td>
<td>$1.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>$D_{s,CO}$</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

$T_3$ were thermocouples located progressively further along the length of the bed, as shown in Fig. 8.18(a). The mean rise in temperature for the three thermocouples over cycles 2-4, representing a total of 9 measurements, was 21.0 ± 1.5 K.

The lattice Boltzmann simulation was carried out in two stages. First, the D3Q19 lattice Boltzmann model was used to calculate a steady state velocity field through a representative packing of solid particles, 2 mm in diameter. Second, the D3Q7 lattice Boltzmann model with mass transport and reaction was used to model the consumption of the dilute reactant, CO, as a passive scalar. Thus, the final steady state velocity field from the D3Q19 model was used as input for the D3Q7 model. The two models were not coupled at each time step; rather the predetermined D3Q19 result fixed the macroscopic bulk velocity field in the D3Q7 model.

For the D3Q19 lattice Boltzmann model, details of the simulation set-up, boundary conditions and initial conditions were presented in section 8.4.4 for flow at $Re = 10$ and will not be repeated. Parameters used for the flow simulation are given in Table 8.4. It should be noted that the number of particles in the simulation (297) is considerably lower than the number of particles in the experiment (~ 1500). Once the sharpness of the experimental front between Fe$_2$O$_3$ and Fe$_3$O$_4$ had been observed, it was decided to simulate only a portion of the experimental packed bed.

For the D3Q7 lattice Boltzmann model, the domain size was $L_x = L_y = 102$, $L_z = 800$, identical to that for the D3Q19 flow simulation. The distribution of fluid and solid nodes was also identical. As in section 8.4.5, a variable, $n_{Fe_2O_3}$, was used to track the conversion
Figure 8.18: (a) Schematic diagram of the packed bed showing the thermocouples spaced 30 mm apart. (b) Concentration of CO in the effluent gas as a function of time for the reduction of a packed bed of 16 g of Fe$_2$O$_3$ to Fe$_3$O$_4$ using CO+CO$_2$+N$_2$ (5, 15, 80 vol %, respectively or $c_{\text{CO}}$ = 0.6, $c_{\text{CO}_2}$ = 1.8, $c_{\text{N}_2}$ = 9.6 mol/m$^3$) at 1023 K. (c) Corresponding temperature excursion during reduction as a function of time measured by the thermocouples.
of solid nodes from $\text{Fe}_2\text{O}_3$ to $\text{Fe}_3\text{O}_4$. The reactant species, CO, was assigned a distribution function, $f_i,\text{CO}$, capable of participating in streaming and collision steps. At the inlet, the non-equilibrium boundary condition of Eq. (8.34) (Zou and He, 1997) was used to fix the inlet density, $\rho_{\text{CO}} = 0.6 \text{ mol/m}^3$. No special treatment of corner or edge nodes at the inlet was necessary. At the outlet, the zero flux boundary condition of Eq. (8.32) was applied after streaming. Halfway bounce-back boundary conditions were applied between the fluid and those solid nodes forming the tube, so that mass was conserved within the tube. No boundary condition was applied between the fluid and those solid nodes comprising particles; rather, the $f_i,\text{CO}$ were permitted to freely stream between fluid and particle nodes. The local relaxation time was however varied depending on whether a node comprised a solid particle or the fluid, so as to vary the internal and external molecular diffusivities, as shown in Table 8.4. For CO, the initial condition was $\rho_{\text{CO}} = 0$ over the entire domain except at the inlet where the inlet boundary condition $\rho_{\text{CO}} = 0.6 \text{ mol/m}^3$ was applied. For solid particles, the initial condition was $n_{\text{Fe}_2\text{O}_3} = 10.3 \text{ kmol/m}^3$. Fluid nodes and those comprising the tube, were initiated with $n_{\text{Fe}_2\text{O}_3} = 0$. The initial velocity condition was simply the predetermined flow field, $\mathbf{u}$, from the D3Q19 model with $\mathbf{u}$ set to 0 for all solid nodes. The flow field, $\mathbf{u}$, was held constant during the D3Q7 simulation. The parameters used in the D3Q7 lattice Boltzmann model are listed in Table 8.4 along with conversions between physical and lattice units. The first-order reduction reaction was incorporated using Eq. (8.64) as in section 8.4.5 just prior to the equilibrium step. Details on implementing the reaction were given in section 8.2.6. Simulations were run for a total of $4.5 \times 10^6$ time steps, corresponding to 6.15 s. The notable assumptions of the present lattice Boltzmann model were: (i) the reduction is considered isothermal, (ii) the change in momentum associated with the conversion of CO to $\text{CO}_2$ is negligible, and therefore only the momentum of the bulk gas, assumed to have identical properties to pure $\text{N}_2$, is conserved and (iii) solids do not change size upon reduction from $\text{Fe}_2\text{O}_3$ to $\text{Fe}_3\text{O}_4$.

Figure 8.19 shows a cross-sectional slice of (a) the location of the solid nodes, (b) the longitudinal velocity, $u_z$ and (c) the concentration of CO after $t = 0.27$ s, all in lattice units. From Fig. 8.19(c) it is evident that the domain of interest is given by a narrow boundary corresponding to the consumption of CO at the start of the packing. Given the sharp reaction front, the particle does not see a uniform concentration of CO at the surface, a problem often overlooked in conventional models of packed beds. To reduce computational time, therefore, it was decided to shrink the domain to those nodes lying between $200 < z < 600$ in lattice units, i.e. to effectively cut the regions of inflow and outflow from the D3Q7 lattice Boltzmann model,
Figure 8.19: Instantaneous profiles showing (a) the location of solid nodes, (b) the longitudinal velocity, \( u_z \), and (c) the concentration of reactant species, \( \rho_{\text{CO}} \) in the \( x-z \) plane in lattice units after \( t = 0.27 \) s. Conversion to physical units as outlined in section 8.2.9 requires \( \Delta x = 10^{-4} \) m/(lattice unit), \( \Delta t = 1.37 \times 10^{-6} \) s/(time step) and \( \Delta n/\Delta x^3 = 0.6 \) moles/(lattice unit)^3.
since the velocity field had already been set over \(1 \leq z \leq 800\) with the D3Q19 model. Finally, to avoid lengthy simulation times owing to the small time step, \(\Delta t\) and to compare the time-dependent experiments with the instantaneous concentration profile along the reactor length, a change in reference frame based on the speed of the reaction front was necessary. Using the distance between thermocouples (30 mm) and the times between temperature maxima, \(\Delta t_{12}\), \(\Delta t_{23}\) and \(\Delta t_{13}\) in Fig. 8.18(c), the speed of the reaction front was measured to be:

\[
\frac{dx}{dt} = 0.154 \pm 0.01 \text{ mm/s.} \tag{8.65}
\]

To convert the time-dependent profile given in Fig. 8.18(b) to a profile with respect to reactor position, \(z\), the abscissa in Fig. 8.18(b) was multiplied by \(-dx/dt\) from Eq. (8.65) and offset so as to intersect the model predictions at half the maximum \(c_{\text{CO}}\) value.

Figure 8.20 shows the experimental effluent concentration as a function of position, \(z\), as well as the prediction from the lattice Boltzmann model. The value of concentration, \(\rho_{\text{CO}}\), from the LB simulation was determined by averaging over all fluid nodes on the inside of the cylinder. From Fig. 8.20 the modelled front is sharper than the experimentally-determined front at both \(t = 0.27\) s and \(t = 6.15\) s. However, from the lattice Boltzmann simulations, the front becomes more diffuse from \(t = 0.27\) s to \(t = 6.15\) s. Additionally, a slight increase in the concentration of CO between the inlet and the start of the packing is observed. This is a result of the compressibility error of the model and is more pronounced for simulations involving the entire domain \((1 \leq z \leq 800)\) compared to the truncated domain \((200 \leq z \leq 600)\). For a true comparison between model results and experiments, longer times must be simulated and are the focus of ongoing research.

When comparing the experimental concentration profile with that predicted from the simulation, the response time of the sampling line and infrared analyser for CO, and the response time of the thermocouples and acquisition system for \(T\) must be considered. The response time of the sampling line and analyser was estimated by flowing the reaction mixture, \(\text{CO} + \text{CO}_2 + \text{N}_2\) with 5, 15 and 80 vol. \%, respectively, through an inert bed of 16 g of \(\text{Al}_2\text{O}_3\) particles of \(d_p = +1400, -1700\) \(\mu\text{m}\) heated to 1023 K. A step change in the inlet concentration was approximated by automatically switching the solenoid valves to a flow of pure \(\text{N}_2\). By measuring the decay in the CO signal at the specified flowrate, the response time was determined to be \(\tau_{\text{CO}}^\text{mix} = 1\) s. Deconvolution of the signal did not therefore alter the shape of the front observed in Fig. 8.18(a) which takes \(\sim 200\) s to break through. Similarly, experiments to approximate
Figure 8.20: Concentration profile for the reduction of a packed bed of Fe₂O₃ to Fe₃O₄ in CO+CO₂+N₂ (5, 15, 80 vol %, respectively) at 1023 K obtained by rescaling the abscissa in Fig. 8.18 by the speed of the front, \( \frac{dx}{dt} = 0.15 \text{ mm/s} \).
the response time of the thermocouples and acquisition system were performed by rapidly moving the thermocouples between boiling water and an ice water bath, and *vice versa*, whilst vigorously stirring. The response time of the thermocouples was determined to be \( \sim 0.3 \) s and did not, therefore, alter the temperature results.

### 8.5 Conclusions

A lattice Boltzmann model which uses a multiple relaxation time approach to model fluid flow and a single relaxation time approach for a passive scalar to incorporate mass transfer was developed. The model was validated on a variety of test cases and the conclusions were as follows:

- The LB model accurately captures the physics of (i) Poiseuille flow between two parallel plates, (ii) the diffusive decay of a sinusoidal concentration wave, (iii) a first order reaction in a well-mixed reactor and (iv) the relationship between the effectiveness factor and Thiele modulus for a reacting spherical catalyst pellet. In all cases, excellent agreement between the model and analytical solutions was observed and it can be concluded that model correctly captures the fundamentals of advection, diffusion and reaction for dilute systems at low *Ma* number.

- The LB model accurately predicted (i) flow past a single sphere and the resulting drag force, (ii) the pressure drop through a packed bed, and (iii) a lower than first order increase in Sherwood number with increasing Reynolds number for mass transfer to the surface of a sphere. Since analytical solutions do not exist for these test cases, the LB model was validated with established empirical correlations.

In general, lattice Boltzmann implementations do not consider reactive solids and further development was required.

- The LB model was successfully extended to gas-solid reactions where the solid composition changes with time, while the solid boundaries remain fixed.

Direct comparison of the model with experimental measurements was then performed for the reduction of spherical particles of \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \) in a mixture of \( \text{CO}+\text{CO}_2+\text{N}_2 \) at 1023 K and \( 10^5 \) Pa. The conclusions were as follows:
• The LB model correctly and quantitatively predicted the phase boundary between Fe$_2$O$_3$ and Fe$_3$O$_4$ for the reduction of a single particle.

• The LB model predicted a sharp front between Fe$_2$O$_3$ and Fe$_3$O$_4$ for the reduction of a packed bed of iron oxide; however, longer simulation times, which will be pursued in further research, are required for a substantive comparison between experiment and theory.

• The LB model permitted non-uniform mass transfer to a single particle in a packed bed with a sharp reaction front to be captured, a problem often overlooked by conventional modelling approaches.

Overall, the extension of the lattice Boltzmann method to gas-solid reactions has been demonstrated and appears a promising approach for capturing the fundamental physics involved in such processes.
Chapter 9

Conclusions

Given the current dependence on and large reserves of carbonaceous fuels, efficient conversion of these fuels to useful energy without the release of CO\(_2\) is necessary. The production of pure H\(_2\), a secondary and environmentally-benign energy vector, at a distributed scale is also pertinent. In the present dissertation, both of these issues have been investigated with respect to the redox reactions of iron and its oxides with CO and CO\(_2\) and with H\(_2\) and H\(_2\)O. These problems require multi-scale approaches, and experimental and numerical investigations from the particle scale to the reactor scale have been presented.

Particles of iron oxide were investigated for their ability to produce H\(_2\) with the simultaneous capture of CO\(_2\) using both packed and fluidised bed reactors over the temperature range, 873-1173 K. A variety of preparation techniques from physical chemistry were applied including: the mechanical mixing of oxide powder (pure Fe\(_2\)O\(_3\)) in Chapter 2, the wet-impregnation of Fe\(_2\)O\(_3\) with a support (based on Al, Cr, Mg and Si) in Chapter 3 and the sol-gel preparation of Fe\(_2\)O\(_3\) and Al\(_2\)O\(_3\) composites in Chapter 4. The conclusions were as follows:

- Pure iron oxide, either Fe\(_2\)O\(_3\) or Fe\(_3\)O\(_4\), undergoing repeated redox cycling to FeO, \(i.e.\) the Fe\(^{2+}\) cation, does not require chemical modification with a support. Stable conversions of H\(_2\) were achieved over 40 cycles.

- For reduction of either Fe\(_2\)O\(_3\) or Fe\(_3\)O\(_4\) to metallic Fe, the yield of H\(_2\) dramatically drops over ten cycles regardless of the reaction temperature - either 873, 1023 or 1173 K. Stable yields of hydrogen could only be obtained for reduction to Fe by the addition of Cr\(_2\)O\(_3\) or Al\(_2\)O\(_3\). Best results were achieved for the case of 40 wt. % Al\(_2\)O\(_3\) and 60 wt. % Fe\(_2\)O\(_3\), with stable conversions over 40 cycles.

- The ability of Al addition to improve the yield of H\(_2\) over repeated cycles was shown to
be definitively linked to the formation of the aluminate, FeO·Al₂O₃. The presence of a significant amount of FeO·Al₂O₃ was quantitatively confirmed using a Rietveld analysis on an X-ray diffraction (XRD) pattern.

- The element added as an oxide support, either Al, Cr, Mg or Si, cannot be considered inert. The prevailing assumption in chemical looping literature to treat additives as inert is therefore false.

- Providing some Fe₂O₃ was present near the gas outlet to the bed, all of the entering reactant CO was converted to CO₂ suitable for sequestration. Even for residence times as low as \( t = 0.2 \) s, the reduction Fe₂O₃ to Fe₃O₄ and simultaneous oxidation of CO to CO₂ via reaction (1.9) was sufficiently fast to entirely convert the entering CO.

- The hydrogen from experiments involving reduction to FeO was pure, with CO contaminations < 25 ppmv for temperatures 873-1173 K. By contrast reduction to Fe resulted in severe carbon deposition with CO contaminations up to 10000 ppmv. This observation is consistent with the thermodynamics for the Boudouard reaction (1.18).

An investigation into the kinetic rates was undertaken in Chapters 5 and 6 for the reduction of Fe₂O₃ with mixtures of CO+CO₂+N₂ in a well-mixed fluidised bed:

\[
\begin{align*}
3 \text{Fe}_2\text{O}_3 + \text{CO} & \rightleftharpoons 2 \text{Fe}_3\text{O}_4 + \text{CO}_2 \quad (9.1) \\
1.2 \text{Fe}_3\text{O}_4 + \text{CO} & \rightleftharpoons 3.8 \text{Fe}_{0.947}\text{O} + \text{CO}_2. \quad (9.2)
\end{align*}
\]

The present study provides a new contribution since it determined the rate in a regime predominantly controlled by intrinsic kinetics and presented the rate over multiple cycles. Additionally, the possibility of increasing the rate of reaction (9.2) by the addition of a small amount, 0.01 mol %, Ce was pursued. The conclusions were as follows:

- The order of reaction for CO was found to be unity for both reduction reactions (9.1) and (9.2).

- The activation energy for the reduction of Fe₂O₃ to Fe₃O₄ was found to be constant and equal to 75 kJ/mol over cycles 2-10. The pre-exponential factor for reduction of Fe₂O₃ to Fe₃O₄ was constant and equal to \( A = 2.4 \times 10^7 \text{ s}^{-1} \) over cycles 2-10.

- The activation energy for reduction of Fe₃O₄ to Fe₉₄₇O was approximately constant and equal to 94 kJ/mol over cycles 2-10. The pre-exponential factor decreased for the
reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O from $A = 4.3 \times 10^7$ s$^{-1}$ in cycle 2 to $A = 1.2 \times 10^7$ s$^{-1}$ in cycle 10, a drop of 70%, suggesting a morphological change such as a decrease in active surface area.

• The presented rate parameters were validated using a 1D model which predicted, successfully, the reduction of a packed bed of unmodified iron oxide.

• The addition of 1 mol % Ce assisted in preventing the destruction of active surface area during sintering. Particles of Fe$_2$O$_3$ with 1 mol % Ce added, showed an increase in the surface area of 2× corresponding to a subsequent increase in the rate of reaction (9.2) by 2×. Hence, it seems that the reduction of Fe$_3$O$_4$ to Fe$_{0.947}$O is limited by surface phenomena for grains < 500 nm.

The redox reactions involving iron and its oxides were investigated not only with simulated syngas from cylinders, but also with syngas from the gasification of coal which contains contaminants such as hydrocarbons, SO$_x$, H$_2$S and NO$_x$. The findings were as follows:

• During the initial stage of reduction, CO$_2$ and H$_2$O are produced with little slip of CO or H$_2$. Upon condensation of the H$_2$O, this CO$_2$ would be suitable for sequestration.

• Pure H$_2$ can be produced from syngas originating from the gasification of a low-rank coal, representing a significant increase in calorific value. Contamination levels were: [CO] < 50 ppmv and [SO$_2$] ≈ 0 ppmv.

• Contaminants in syngas which are gaseous above 273 K apparently do not adversely affect the iron oxide material as stable quantities of pure H$_2$ were observed over 5 cycles.

• Since oxidation with air removes contaminants, e.g. sulphurous and carbonaceous species deposited during reduction, and generates useful heat and pure N$_2$ for purging, it should be included in the operating cycle.

The choice of which transitions and which temperatures to use for the proposed process in an industrial application is not straightforward. From the presented research, the overall recommended sequence for the production of pure H$_2$ with simultaneous capture of CO$_2$ is as follows:

1. *Production of CO$_2$ with oxide reduction*. Syngas from the gasification of coal or biomass with steam or CO$_2$ via reactions (1.7) and (1.8) in Table 1.2, is converted to a stream
of CO$_2$ and H$_2$O via reactions (1.9)-(1.10) or (1.12)-(1.13) in Table 1.2 by passing it through a packed bed of particles of Fe$_2$O$_3$. Condensing out the H$_2$O from the off-gas yields a pure stream of CO$_2$ suitable for sequestration. The concentration gradient along the reactor would enable Fe$_{0.947}$O to exist at the gas inlet of the packed bed, while still maintaining Fe$_2$O$_3$ in the packed bed towards the gas outlet.

2. *Production of H$_2$ with partial reoxidation of metal oxide.* After the partial reduction of the iron oxide in the bed, passing steam through the reactor would generate hydrogen and reoxidise the reduced iron oxide to Fe$_3$O$_4$ via reaction (1.16) in Table 1.2.

3. *Complete reoxidation of metal oxide with air.* The reoxidation to Fe$_2$O$_3$ in air produces a stream of N$_2$ with residual O$_2$, reaction (1.17) in Table 1.2. Once the entire packed bed has been regenerated to Fe$_2$O$_3$, the cycle could begin anew at step 1.

If maximising the yield of H$_2$ is the primary objective and concerns about heat integration and the purity of the H$_2$ can be ignored, reduction to Fe in step (1) could be performed. However, the iron oxide would then need to be modified by the addition of Al to maintain high conversions over multiple cycles.

An LB model capable of resolving: (i) fluid flow through a packed bed (ii) mass transfer to the surface of a spherical particle of iron oxide and (iii) reaction and diffusion within a particle of iron oxide was developed in Chapter 7 and first comparisons with experimental results were performed. It was found that

- The LB model showed excellent agreement with analytical solutions for the test cases: (i) Poisueille flow between two parallel plates, (ii) the decay of a sinusoidal concentration wave and (iii) a first order reaction in a well-mixed reactor.

- Further validation of the model with experimental measurements was performed for: (i) flow past a single sphere and the resulting drag force, (ii) the effectiveness factor in a reacting spherical catalyst pellet and (iii) mass transfer to the surface of a sphere. The LB model accurately predicted the drag force and effectiveness factor, and correctly predicted a non-linear increase in Sherwood number with increasing Reynolds number. However, the values of the Sherwood number predicted were generally lower than those given by established correlations (Bird et al., 2007) and could be a result of the small diameter of the sphere, $d_p = 10$ in lattice units.
• Comparison between the the LB model and experimental results for the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ in CO+CO$_2$+N$_2$ was achieved by considering the conversion profile of a single particle, $d_p = 100$ in lattice units. The LB method quantitatively captured the boundary between Fe$_2$O$_3$ and Fe$_3$O$_4$ phases.

• A further comparison involving the reduction of a packed bed of Fe$_2$O$_3$ particles ($d_p = 20$ in lattice units) to Fe$_3$O$_4$ in CO+CO$_2$+N$_2$ was conducted using a passive scalar approach. Agreement between the model and experiments was observed for the concentration profile in the packed bed.
Chapter 10

Future Work

The stabilisation of the production of hydrogen by Fe$_2$O$_3$ and Al$_2$O$_3$ composites has been shown both for impregnated particles and those prepared by the sol-gel process. However, the mechanism by which Al$_2$O$_3$ stabilises the iron oxide requires further investigation. The exact amount of Al$_2$O$_3$ required for stability and how rapidly, if at all, the Al$_2$O$_3$ is incorporated into the iron oxide lattice compared with the rapid sintering of pure Fe$_2$O$_3$ must be determined. If a single or even a few reduction and oxidation cycles are sufficient to form a homogeneous mixture of Fe and Al, then the more costly and labour-intensive sol-gel technique may be unnecessary. The use of redox cycling rather than the sol-gel technique to produce a material with specified homogeneity could have a significant impact on industrial processes.

In the future, catalyst supports not used in the present investigation, ZrO$_2$ and TiO$_2$, will also be investigated as candidates for stabilising the repeated reduction to Fe. In particular, ZrO$_2$ is an interesting candidate since it has a high melting temperature, $T_m \approx 2973$ K (Barin and Knacke, 1973) and is inert, i.e. should not form any intermediates with the iron species.

Longer LB simulations for the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ in a packed bed will be pursued using the Hades cluster (Dept. of Engineering) with InfiniBand communication across 4 nodes each containing 8 CPU’s. Despite the small time step on the order of $O(10^{-6}$ s) for the current simulations, the continuing rapid advance in computation will make the application of LB methods to transient gas-solid systems a reality in the future. The extension of the LB model to include further reduction steps, e.g. reactions (1.10)-(1.11), will therefore become feasible.

An inherent feature of the LB method is that it can be used to develop closure correlations for coarser modelling strategies. To be more specific, consider the mass transfer coefficient, $k_{g,CO}$. The present LB model does not require $k_{g,CO}$ as an input, but naturally incorporates
the physical effect of $k_{g, CO}$ through the molecular diffusivity and hydrodynamics of the flow. The LB method has already been successfully applied to provide a drag force correlation for fluidised bed models (Beetstra et al., 2007) and to provide axial or radial dispersion coefficients (Khirevich et al., 2007) for packed bed models. Determining correlations for mass and heat transfer coefficients in packed structures is therefore a natural extension, and only preliminary research in this area exists. Creating a correlation for the Sherwood number, $Sh$, for porous structures, where established empirical correlations such as those for a single sphere are lacking, is possible and would provide a fundamental contribution to scientific literature.

The development of a multiple-relaxation time (MRT) model for the advection and diffusion of a passive scalar in 2D and 3D will be pursued. The simplicity of the D2Q5 and D3Q7 lattices make such a development a good starting point for addressing the theory, rather than simply the application, of lattice Boltzmann models. A simple MRT model for a passive scalar would be a useful tool for engineers and physicists.
Appendix 1

Thermodynamics

A1.1 Calculation of thermodynamic properties

The Gibbs free energy of species \( i \) at a reference temperature, \( T \), can be calculated using:

\[
G^\circ_i(T) = H^\circ_i(T) - TS^\circ_i(T),
\]  

(A1.1)

where \( H^\circ_i \) and \( S^\circ_i \) are, respectively, the enthalpy and entropy of the pure substance at temperature, \( T \), and pressure, \( P^\circ \). The standard state is defined by a reference temperature \( T = 298.15 \) K and pressure, \( P^\circ = 10^5 \) Pa; gases are considered ideal, and condensed species are considered to be purely crystalline or purely liquid. All thermodynamic properties are listed as molar quantities. Using standard thermodynamic tables (Barin and Knacke, 1973; McBride et al., 2002) for the molar heat capacity at constant pressure, which is typically estimated by a polynomial of the form (Barin and Knacke, 1973):

\[
C^\circ_{p,i}(T) = a_i + b_iT + c_iT^{-2} + d_iT^2,
\]  

(A1.2)

the enthalpy and entropy can be obtained by integration:

\[
H^\circ_i(T) = \int C^\circ_{p,i}(T)dT = a_iT + \frac{b_iT^2}{2} - \frac{c_i}{T} + \frac{d_iT^3}{3} + e_i
\]  

(A1.3)

\[
S^\circ_i(T) = \int \frac{C^\circ_{p,i}(T)}{T}dT = a_i\log T + b_iT - \frac{c_i}{2T^2} + \frac{d_iT^2}{2} + e_i,
\]  

(A1.4)

where \( a_i, b_i, c_i \) and \( d_i \) are fitted coefficients and \( e_i \) is a constant of integration which is different for Eqs. (A1.3) and (A1.4) and includes, e.g. in Eq. (A1.3) the enthalpy of formation and enthalpy of any phase transitions.
A1.2 Equilibrium

At a fixed temperature and pressure, a system is at equilibrium if the total Gibbs free energy of the system is at a global minimum (Denbigh, 1957). The total Gibbs free energy of a system, \( G \), is defined as:

\[
G = \sum_i \bar{G}_i n_i,
\]

(A1.5)

where \( s \) is the total number of molecularly distinct species, \( n_i \) is the number of moles of species \( i \) and \( \bar{G}_i \) is the partial molar Gibbs free energy, or chemical potential, of species \( i \). Furthermore,

\[
\bar{G}_i(T) = G_i^\circ(T) + RT \log \frac{f_i}{f_i^\circ},
\]

(A1.6)

where \( G_i^\circ \) is the Gibbs free energy of species \( i \) at temperature, \( T \), and reference pressure, \( P^\circ \). \( f_i \) is the fugacity of \( i \) and \( f_i^\circ \) is the fugacity of pure \( i \) in the reference state. For a gas at low to moderate pressures, the fugacity can be approximated by \( f_i = y_i P \phi_i \), where \( y_i \) is the molar fraction of \( i \) in the gaseous mixture, \( \phi_i \) is the fugacity coefficient used to capture deviations from ideal gas behaviour, and \( P \) is the total pressure of the system. For a gas in which molecular interactions are negligible, e.g. at high temperatures and low pressures as considered in this work, the ideal gas assumption holds and \( \phi_i = 1 \). Thus for gases,

\[
\bar{G}_i(T) = G_i^\circ(T) + RT \log \frac{y_i P}{P^\circ},
\]

(A1.7)

where \( P \) is the total pressure of the system, \( P^\circ \) is the reference pressure and it is noted that \( \bar{G}_i \) is a function of \( n_i \) since \( y_i = n_i / \sum n_i \) where summation is only over the gaseous species. Unlike that of a gas, the fugacity for a pure solid or immiscible liquid is only weakly dependent on pressure and the following approximation is used:

\[
\bar{G}_i(T) = G_i^\circ(T).
\]

(A1.8)

To solve for the minimum Gibbs free energy, the first order necessary condition (FONC),

\[
dG = \sum_i n_i d\bar{G}_i + \sum_i \bar{G}_i dn_i = 0,
\]

(A1.9)

must be satisfied. From the Gibbs-Duhem equation \((-SdT + VdP - \sum n_i d\bar{G}_i = 0)\) at a constant
temperature and pressure, this simplifies to:

\[
dG = \sum_i \bar{G}_i dn_i = 0
\]

(A1.10)

The second order sufficient condition for a minimum is then \(d^2 G = \sum_i (\bar{G}_i dn_i + \bar{G}_i d^2 n_i) > 0\).

In general, two mathematical approaches for determining the minimum Gibbs free energy exist: (i) the method of independent reactions and (ii) the constrained minimisation of the free energy. Both give equivalent results; however, as the number of species and potential reactions increases, the method of constrained minimisation is preferred.

### A1.2.1 Method of independent reactions

In practice the method of independent reactions can be applied to any number of reactions; however, for simplicity only a single reaction will be considered. Take the general reaction given by:

\[
v_1 M_1 + \cdots + v_{j-1} M_{j-1} \rightleftharpoons v_j M_j + \cdots + v_s M_s
\]

where the \(v_j\) represent the stoichiometric coefficients and \(M_j\) are the distinct molecular species of which there are \(s\) in total. For mathematical summation, the \(v_j\) are defined to be negative for substances on the left of the equation and positive for those on the right. Reaction (A1.11) describes any chemical reaction, including those in Table 1.2. The state of \(M_j\) is not constrained and could be either liquid, gas, etc. For any substance which is inert, \(v_j = 0\). Considering the reaction stoichiometry,

\[
\frac{dn_1}{v_1} = \frac{dn_2}{v_2} = \cdots = \frac{dn_s}{v_s}
\]

(A1.12)

That is, the change in the number of moles of species \(i\) is not independent of the change in number of moles of other species. This dependency permits the elimination of all of the \(dn\)’s from Eq. (A1.10) with the exception of one, say \(dn_1\), to give:

\[
\left(\bar{G}_1 + \frac{v_2}{v_1} \bar{G}_2 + \cdots + \frac{v_s}{v_1} \bar{G}_s\right) dn_1 = 0.
\]

(A1.13)

Therefore, multiplying through by \(v_1\) gives the simple relation for the FONC

\[
\sum_i v_i \bar{G}_i = 0,
\]

(A1.14)
which is the starting point for determining the equilibrium for reaction (A1.11).

Defining the equilibrium constant,
\[ K_p \equiv \prod_i \left( \frac{y_i P_i}{P^o} \right)^{\nu_i} = \prod_i (p_i)^{\nu_i}, \]  
(A1.15)

where the product summation is only over the gaseous species, \( P^o \) has been chosen to have the value of unity (e.g. 1 bar) consistent with convention and \( P \) is chosen to have identical units to \( P^o \) such that the ratio \( P/P^o \) is dimensionless, and using Eq. (A1.7), Eq. (A1.14) can be rewritten as
\[ -RT \log K_p = \sum_i \nu_i G^o_i. \]  
(A1.16)

Thus, the equilibrium which satisfies the FONC of Eq. (A1.14) is defined by the equilibrium constant in Eq. (A1.16). In practice, this definition of \( K_p \) can be thought of as the product
\[ K_p = \prod_i \left( \frac{f_i}{f^o_i} \right)^{\nu_i} = e^{-\sum_i \nu_i G^o_i/RT}. \]  
(A1.17)

Since for solids and immiscible liquids \( f_i/f^o_i = 1 \), the product summation need only be carried out for the gaseous species, whereas the algebraic summation is over all the substances in their standard state at temperature, \( T \), and reference pressure, \( P^o = 10^5 \) Pa. Since \( G^o_i \) refers to the reference pressure, \( P^o \), \( G^o_i \) is only a function of \( T \). Accordingly, \( K_p \) is only a function of \( T \).

A1.2.2 Worked example

The equilibrium constant for reaction (1.10), reproduced here for the convenience of the reader,
\[ \text{Fe}_2\text{O}_3 + \text{CO} \rightleftharpoons 3\text{FeO} + \text{CO}_2, \]  
(A1.18)

will now be derived for a temperature of 1023 K and pressure of \( 10^5 \) Pa. Table A1.1 lists the Gibbs free energy for each of the four species in reaction (A1.18) relative to the standard state given by the reference temperature, \( T = 298.15 \) K, and pressure, \( P^o = 10^5 \) Pa. The values of \( H^o_{1023 \text{K}}, S^o_{1023 \text{K}} \) and \( G^o_{1023 \text{K}} \) were calculated as previously outlined in section A1.1. The change in Gibbs free energy for the overall reaction can then be calculated using the reported values for the individual species, listed in Table A1.1, and the stoichiometric coefficients from reaction (A1.18). Subtracting the Gibbs free energy of the reactants from that of the products
Table A1.1: Enthalpy, entropy and Gibbs free energy for reactant and product species from reaction (A1.18). The overall enthalpy, entropy and Gibbs free energy for the reaction is also listed.

<table>
<thead>
<tr>
<th>Species</th>
<th>Fe$_3$O$_4$</th>
<th>Fe$_{0.947}$O</th>
<th>CO</th>
<th>CO$_2$</th>
<th>∑</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_1^{1023}$ K (kJ/mol)</td>
<td>-968.8</td>
<td>-227.6</td>
<td>-88.1</td>
<td>-359.2</td>
<td>27.1</td>
</tr>
<tr>
<td>$S_1^{1023}$ K (J/(mol K))</td>
<td>390.5</td>
<td>122.4</td>
<td>235.3</td>
<td>270.2</td>
<td>31.3</td>
</tr>
<tr>
<td>$G_1^{1023}$ K (kJ/mol)</td>
<td>-1368.3</td>
<td>-352.7</td>
<td>-328.8</td>
<td>-635.7</td>
<td>-5.3</td>
</tr>
</tbody>
</table>

gives:

$$
\Delta G_1^{1023} = \sum_i \nu_i G_i = (-635.7 - 3.8 \times 352.7) - (-1.2 \times 1368.3 - 328.8) = -5.3 \frac{kJ}{mol},
$$

(A1.19)

shown by the final column in Table A1.1. Next, the equilibrium constant for the reaction is calculated using Eq. (A1.17):

$$
K_p = \frac{p_{CO_2}}{p_{CO}} = e^{-\sum \frac{\nu_i G_i}{RT}} = e^{\frac{5324}{RT}} = 1.87.
$$

(A1.20)

Thus, for $\frac{p_{CO_2}}{p_{CO}} < 1.87$ CO and Fe$_3$O$_4$ will be consumed; for $\frac{p_{CO_2}}{p_{CO}} > 1.87$ CO$_2$ and Fe$_{0.947}$O will be consumed.

### A1.2.3 Method of constrained minimisation of the Gibbs free energy

For the method of constrained minimisation of the Gibbs free energy, two constraints must be considered along with the FONC of Eq. (A1.10), viz. (i) the non-negativity of each molecular species and (ii) atomic conservation:

(i) $n_i \geq 0$  
(ii) $b_j - \sum_i a_{ij} n_i = 0,$

(A1.21)

where $b_j$ is the number of moles of element $j$ entering the system and $a_{ij}$ is the number of atoms of $j$ in one molecule of species $i$.

The constrained minimisation problem can be solved using Lagrange’s method of undetermined multipliers with an objective function given by a combination of Eqs. (A1.5) and (A1.21):

$$
F = G + \sum_j \lambda_j \left( b_j - \sum_i a_{ij} n_i \right) + \sum_i \gamma_i n_i,
$$

(A1.22)
where $b$ is the total number of distinct atomic species and $\lambda_j$ and $\gamma_i$ are the Lagrange multipliers. The constrained minimum is found using the Karush-Kuhn-Tucker (KKT) equations, which provide the necessary conditions for an extremum in a constrained optimisation problem (Edgar et al., 2001):

\[
\frac{\partial F}{\partial n_i} = \frac{\partial G}{\partial n_i} - \sum_j^m \lambda_j a_{ij} + \gamma_i = 0 \tag{A1.23}
\]

\[
\lambda_j \left( b_j - \sum_i^s a_{ij} n_i \right) = 0 \quad j = 1 \ldots b \tag{A1.24}
\]

\[
\gamma_i \geq 0. \quad i = 1 \ldots s \tag{A1.25}
\]

In this dissertation, the KKT equations were solved numerically using \textit{fmincon} in the MATLAB\textsuperscript{®} programming language which attempts to compute the Langrange multipliers directly by collecting second order information about the minimisation problem using a numerical approximation of the Hessian of the Langrangian given by:

\[
\frac{\partial^2 F}{\partial n_i^2} = \frac{\partial^2 G}{\partial n_i^2}. \quad (A1.26)
\]

The algorithm then updates values of the initially-guessed Lagrange multipliers using a quasi-Newton time-stepping scheme.
Appendix 2

Experimental measurements

This Appendix describes the physical principles underlying the measuring techniques used during experiments in this dissertation. It is separated into two categories: (i) techniques for the characterisation of a gas (e.g. infrared spectroscopy and thermal conductivity) and (ii) techniques for the characterisation of a porous solid (e.g. gas adsorption, mercury intrusion, X-ray diffraction and scanning electron microscopy).

A2.1 Infrared spectroscopy

Infrared (IR) spectroscopy operates on the principle that every molecule is made up of a unique configuration of chemical bonds. Each bond has a characteristic frequency at which it will absorb energy and translate it into vibrational motion. For a normal mode of vibration to be infrared active, i.e. to give rise to an observable infrared band, there must be a change in dipole moment of the molecule associated with vibration. Therefore, diatomic gases without dipole moments such as N₂, H₂ and O₂ are not detectable by IR spectroscopy (Colthup et al., 1964). To identify organic gases (e.g. CO, CO₂, CH₄) and certain inorganic gases (e.g. SO₂), electromagnetic radiation within the mid-infrared spectrum with wave numbers of 450 – 4000 cm⁻¹ or equivalent wavelengths of 2.5 – 22.2 µm can be used, so long as unique, non-overlapping frequencies exist by which each species in the mixture can be identified.

In a typical gas-phase IR analyser, a monochromatic light is directed into a cell containing the sample; the transmittance is measured by a detector of InGaAs or PbSe. At a specified wavelength, a transmittance of 1 indicates the absence of the species; a transmittance of 0 indicates the species is present in such quantity that all of the light is absorbed. The transmittance, Tr, and absorbance, Abs, are related by Abs = −log₁₀(Tr). Figure A2.1 shows the IR
Figure A2.1: Absorbance versus wavelength for CO, CO₂ and a typical background scan.

spectra for CO and CO₂ as well as a typical background scan of the atmosphere (NIST, 2010). Identification of the C=O bond in CO₂ is apparent at 2380 cm⁻¹, the doublet for CO at 2120 and 2180 cm⁻¹. The background scan shows aberration from the smooth spectrum owing to H₂O and CO₂ in the atmosphere. Infrared analysers (Easyline, ABB) with response times of < 3 s were used in experiments.

A2.2 Thermal conductivity

For a monatomic gas obeying the Lennard-Jones 6-12 potential, the thermal conductivity can be calculated from (Fahien, 1983):

\[ \lambda_0 = 8.322 \times 10^{-4} \frac{\sqrt{T/M_i}}{\sigma^2 \Omega} \quad \text{(W/m K)}, \]  
(A2.1)

where the collision integral, \( \Omega \), can be evaluated as

\[ \Omega = \frac{1.16145}{T^*^{0.14874}} + 0.52487e^{-0.7732T^*} + 2.16178e^{-2.43787T^*}, \]  
(A2.2)

for \( 0.4 < T^* < 1.4 \), where

\[ T^* = T \frac{k_b}{\xi}. \]  
(A2.3)
Here,

\[
\begin{align*}
T & \quad \text{Absolute temperature} \quad (\text{K}) \\
M_i & \quad \text{Molecular mass of species } i \quad (\text{kg/kmol}) \\
\sigma & \quad \text{Collision diameter from the Lennard-Jones function} \quad (\text{nm}) \\
\frac{k_B}{\xi} & \quad \text{Lennard-Jones parameter} \quad (\text{K}^{-1})
\end{align*}
\]

For polyatomic gases, a correction factor must be applied to determine the thermal conductivity (Fristrom and Westenberg, 1965),

\[
\lambda_i = \lambda_0 \left( 0.115 + \frac{0.178}{4.184} \times C_{p,i}^c \right),
\]

(A2.4)

where \(C_{p,i}^c\) can be calculated from Eq. (A1.2) and has units (J/mol K). The thermal conductivity of a mixture of \(n\) components can be determined from Bird et al. (2007):

\[
\lambda_{\text{mix}} = \sum_{i} y_i \lambda_i \frac{\sum_{j} y_j \Phi_{ij}}{\sum_{j} y_j},
\]

(A2.5)

with

\[
\Phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{\frac{1}{2}} \left[ 1 + \left( \lambda_i / \lambda_j \right) \left( M_j / M_i \right)^{\frac{1}{2}} \right]^2.
\]

(A2.6)

Thermal conductivities for selected gases at 300 K and 1000 K are listed in Table A2.2 and agree with experimental results reported in Fristrom and Westenberg (1965) to within 5 %, except for CO\(_2\). Since the thermal conductivity of H\(_2\) is approximately one order of magnitude larger than that for the other gases, measuring the thermal conductivity of a mixture provides a suitable method for determining its content of H\(_2\). Using Eqs. (A2.5) and (A2.6) demonstrated that increasing the composition of CO or CO\(_2\) in a mixture of N\(_2\) and H\(_2\) results in a change in thermal conductivity which is approximately linear with composition of the introduced species; corrections to the measured value of H\(_2\) were therefore straightforward once the value of CO or CO\(_2\) had been measured with IR spectroscopy. In experiments, the thermal

| Table A2.2: Thermal conductivity (W/m K) of various gases at 300 K and 1100 K. |
|------------------|--------|--------|--------|--------|--------|--------|--------|        |
| Species, \(i\)   | H\(_2\) | CO     | CO\(_2\)| N\(_2\) | O\(_2\) | CH\(_4\) |        |
| \(\lambda_i\) (300 K) | 0.1757 | 0.0251 | 0.0162 | 0.0247 | 0.0256 | 0.0340 |        |
| \(\lambda_i\) (1100 K) | 0.4628 | 0.0721 | 0.0691 | 0.0720 | 0.0719 | 0.1777 |        |
conductivity of the gas was measured using a silicon micromechanic sensor (TCS208F) within a designated analyser (Caldos27, ABB). The total volume of the diffusion cavity was 0.2 mm$^3$ and response times, ignoring the sampling line, were < 0.5 s.

A2.3 Determination of morphology using gas adsorption

An isotherm is a measure of the equilibrium quantity of pure gas adsorbed on to a solid surface as a function of its relative pressure, $P/P_{\text{sat}}$, where $P_{\text{sat}}$ is the saturation pressure of the gas at fixed temperature. The BET equation (Brunauer et al., 1938) assumes that adsorption of the first layer of gas molecules is governed by the characteristic heat of adsorption, while adsorption of subsequent layers is governed by the heat of liquefaction, since molecules in higher layers only contact like neighbours. The linear BET equation provides a good approximation to the surface area for $P/P_{\text{sat}} < 0.3$, i.e. before pores have been completely filled with adsorbate. Since the surface area is given in units of m$^2$/g, accurate determination of the mass of particles used is necessary and was performed, after degassing the samples externally under a flow of He at 363 K for 1 h and then at 383 K for 1 h, using a balance with a precision of $10^{-4}$ g.

At $P/P_{\text{sat}} = 1$, physical adsorption and capillary condensation will ensure that all pores are filled. Measuring the volume of gas released at decreasing relative pressures and recognising that smaller pores will exhaust gas at lower values of $P/P_{\text{sat}}$, the BJH equation (Barrett et al., 1951) can be employed to determine the distribution of pore sizes. The BJH equation is a composite of BET and capillary theory and assumes cylindrical pores. Because calculations near the limits of $P/P_{\text{sat}} = 0$ and $P/P_{\text{sat}} = 1$ are not practicable, an arbitrary cut-off of 0.01 < $P/P_{\text{sat}} < 0.95$ is used, which for N$_2$ corresponds to pores with mean diameters within the range 2 – 200 nm. A gas adsorption analyser (Tristar 3000, Micromeritics), operated at 77 K with N$_2$ gas, was used in all adsorption experiments.

A2.4 Mercury intrusion porosimetry

Porosity and pore size distributions for pores with mean radii between 4 nm and 100 µm were determined using mercury porosimetry (Micromeritics, Autopore IV). Since Hg is a non-wetting liquid at 298 K, i.e. it forms a contact angle > 90° with most solids, it will only enter a capillary under an applied pressure. Following Washburn (1921) and assuming the porous
solid is comprised of cylindrical capillaries, a force balance on a single pore relates the pressure of Hg to capillary pressure:

\[ P = \frac{-2\gamma \cos \theta}{r_e}, \]  

(A2.7)

where \( P \) is the pressure of the mercury at the inlet to the pore, \( \gamma \) is the surface tension of mercury, \( \theta \) is the contact angle, and \( r_e \) is the radius of the cylindrical pore. The pore size distribution is determined from the volume intruded at each incremental pressure: the total porosity is determined using the volume of the particles and the total volume intruded. The particles were degassed prior to analysis; parameters for the triply-distilled mercury of \( \theta = 130^\circ \) and \( \gamma = 0.49 \text{ N/m} \) were assumed.

### A2.5 X-ray diffraction

Diffraction provides a method for measuring the interatomic distance, \( d \), of a unit cell of a crystal, since X-rays (typical wavelength 2-25 nm) will interfere constructively when Bragg’s law,

\[ n\lambda = 2d \sin \theta, \]  

(A2.8)

is satisfied, as shown in Fig. A2.2. Here, \( \lambda \) is the wavelength of the X-ray and \( n \) is an integer describing the order of diffraction. Since \( \theta \) is the angle of both incidence and reflection, interference patterns are reported as a function of \( 2\theta \). To perform quantitative XRD on a powder, the powder must be randomly oriented in space. Scanning through a range of \( 2\theta \) values will then permit interference from all of the Bragg reflection planes to be measured. The interference pattern provides a unique fingerprint for the identification of a crystalline phase; the intensity of the interference pattern provides an indication of the quantity of each crystalline phase. Using the method of relative intensity ratios (RIR), quantitative measurements to within \( \pm 10 \) wt. % are possible if all of the existing phases have been identified; the method of Rietveld refinement, which matches not only intensities, but also peak positions, can achieve quantitative measurements to within \( \pm 5 \) wt. %. Amorphous phases cannot be distinguished using XRD.

For the X-ray diffractometer used (Philips model PW1830/00, in air at 298 K), the sample and X-ray source (Cu-K\( _\alpha \)) were fixed, while the detector arm was rotated through an angle of \( 20^\circ \leq 2\theta \leq 80^\circ \) at a rate of 0.01°s\(^{-1}\).
A2.6 Scanning electron microscopy

Scanning electron microscopy (SEM) permits the imaging of bulk specimens with nanometre resolution and improved depth of focus compared to optical microscopes. In SEM, electrons are thermally emitted from a metal filament with a high melting point, such as tungsten, in a vacuum ($10^{-4}$ Pa) and focused to a spot size of $\sim 5$ nm using electromagnetic lenses (Reimer, 1998). Deflector plates are then used to direct the beam on to the sample to permit raster scanning of a rectangular portion of the surface of a specimen. The incident electrons of high energy will interact with the specimen and e.g. (i) cause secondary, lower-energy electrons to be emitted from the specimen, (ii) be reflected as high-energy back-scattered electrons or (iii) produce characteristic X-rays from electron interactions within the sample. In this dissertation, (i) secondary electron imaging (SEI) was used and (iii) the atomic composition was determined using energy dispersive X-ray spectroscopy (EDS, Oxford INCAPentaFET-x3). On a JSM-5800LV microscope, a beam energy of 15 kV was used to produce a spot size of $\sim 7$ nm with a typical resolution of 100 nm, as shown in Fig. 3.8. A field emission gun scanning electron microscope (FEG-SEM, JSM-6340F), which produced a more coherent electron beam with a smaller spot size ($< 2$ nm) and operated at 5 kV, offered an improved resolution of $\sim 10$ nm, as shown in Fig 4.1. For imaging, the specimen must be electrically conductive as well as grounded so as to avoid the accumulation of charge (Goldstein et al., 2003). Here, a conductive phenolic resin (Conducto-Mount, Metprep) was used to mount samples.

Figure A2.2: Schematic illustration of Bragg’s law showing two constructively-interfering X-rays.
Appendix 3
Temperature change during oxidation

To determine the temperature rise during the oxidation of Fe₃O₄ to Fe₂O₃ in air, reaction (1.17) in Table 1.2, reproduced below for convenience, is used:

\[ 2 \text{Fe}_3\text{O}_4 + \frac{1}{2} \text{O}_2 \rightleftharpoons 3 \text{Fe}_2\text{O}_3, \quad \Delta H^{\circ}_{1023 \text{ K}} = -238 \text{ kJ/mol} \quad (A3.1) \]

where the enthalpy is for the reaction as written. Conservation of energy within the packed bed dictates:

\[ \Delta H^{\circ}_{1023 \text{ K}} = \text{Mass} \times C_p \times \Delta T, \quad (A3.2) \]

where the fact that the specific heat capacity at constant pressure is nearly constant for most substances on a mass basis and can be approximated by that for air, $C_p = 1000 \text{ J/(kg K)}$, has been used. In Eq. (A3.2), Mass denotes the mass of the bed affected by the change in temperature, and it has been assumed that $C_p$ and $\Delta H^{\circ}_{1023 \text{ K}}$ are approximately constant with temperature, which holds for small temperature excursions. Rearranging Eq. (A3.2) gives the familiar result:

\[ \Delta T = \frac{\Delta H^{\circ}_{1023 \text{ K}}}{\text{Mass} \times C_p}. \quad (A3.3) \]

Choosing 2 mol Fe₃O₄ as a basis as per reaction (A3.1), the total mass of solid and gaseous species involved is 4.4 kg, as shown in Fig. A3.1. Thus, the total temperature rise for the oxidation reaction is:

\[ \Delta T = \frac{238}{4.4 \times 1} = 54 \text{ K}, \quad (A3.4) \]

sufficiently small to justify the assumption of constant $C_p$ and $\Delta H^{\circ}_{1023 \text{ K}}$. The above analysis assumes that 1 g of iron oxide and 8 g of sand are all at the same temperature.
Figure A3.1: (a) Schematic diagram of the initial packed bed. (b) Calculation of the total mass in the system, including sand, for oxidation of 2 mol of Fe$_3$O$_4$ to 3 mol of Fe$_2$O$_3$.
Appendix 4
Determining the reaction rate

Reaction (1.9) and the corresponding rate expression can be written as:

$$3 \text{Fe}_2\text{O}_3 + \text{CO} \rightleftharpoons 2 \text{Fe}_3\text{O}_4 + \text{CO}_2$$  \hspace{1cm} (A4.1)

$$-\frac{dc_{\text{CO}}}{dt} = \frac{dc_{\text{CO}_2}}{dt} = k_i c_{\text{CO}} - k_{-i} c_{\text{CO}_2},$$  \hspace{1cm} (A4.2)

where $k_i$ and $k_{-i}$ are the intrinsic rate constants for the forward and reverse reaction, respectively. The derivation of the effectiveness factor and Thiele modulus will now be demonstrated for this specific case. However, an analogous analysis can be performed for any of the iron oxide reduction and oxidation steps in Table 1.2 and, more generally, for any gas solid reaction of the form of Eq. (A4.1) with first order kinetics.

Reaction of a single particle of Fe$_2$O$_3$ will occur via the following five steps: (i) mass transfer of reactant CO from the bulk phase to the particle surface, (ii) diffusion of CO through the porous particle, (iii) reaction of CO to form CO$_2$ and simultaneous, conversion of Fe$_2$O$_3$ to Fe$_3$O$_4$, (iv) diffusion of product CO$_2$ through the porous particle, and (v) mass transfer of CO$_2$ from the particle surface into the bulk phase. The following assumptions are made:

- no changes in the volume of the solid occur during the course of the reaction,
- temperature variations are minimal so that the isothermal approximation holds,
- the effective diffusivities, mass transfer coefficients and intrinsic rate constants are constant throughout the course of the reaction,
- the particles are uniform spheres,
- the change in concentration with respect to time within a sphere is negligible compared
to the change in concentration with respect to radial position, therefore, the pseudo-steady-state hypothesis holds.

**A4.1 Relationship between intraparticle diffusion and chemical reaction**

In a single reacting sphere, a mole balance on the spherical shell from $r$ to $r + \Delta r$ for reactant CO yields:

$$4\pi r^2 D_{e,CO} \left. \frac{dc_{CO}}{dr} \right|_{r + \Delta r} - 4\pi r^2 D_{e,CO} \left. \frac{dc_{CO}}{dr} \right|_r - 4\pi r^2 \Delta r \left( k_i c_{CO} - k_{-i} c_{CO_2} \right) = 0$$  \hspace{1cm} (A4.3)

Similarly, for product CO$_2$:

$$D_{e,CO_2} \left( \frac{dc_{CO_2}}{dr} \right)^2 + (k_i c_{CO} - k_{-i} c_{CO_2}) = 0.$$  \hspace{1cm} (A4.5)

Finiteness of $c_{CO}(r)$ and $c_{CO_2}(r)$ at $r = 0$ is required. Additionally, the following boundary condition holds:

$$c_{CO}(r) = c_{CO_s} \quad \begin{cases} r = R, \end{cases}$$

$$c_{CO_2}(r) = c_{CO_2 s}$$

where $c_{CO_s}$ and $c_{CO_2 s}$ are the concentration of CO and CO$_2$ at the surface of the sphere, $r = R$, respectively, and are assumed to be constant.

**A4.2 Solving for $c_{CO}(r)$ and $c_{CO_2}(r)$**

To solve Eqs. (A4.4) and (A4.5) for the intraparticle concentrations, $c_{CO}(r)$ and $c_{CO_2}(r)$, let $u_{CO} = r c_{CO}$ and $u_{CO_2} = r c_{CO_2}$. Rewriting Eqs. (A4.4) and (A4.5) gives for CO and CO$_2$:

$$D_{e,CO} \frac{d^2 u_{CO}}{dr^2} - (k_i u_{CO} - k_{-i} u_{CO_2}) = 0$$  \hspace{1cm} (A4.7)

$$D_{e,CO_2} \frac{d^2 u_{CO_2}}{dr^2} + (k_i u_{CO} - k_{-i} u_{CO_2}) = 0.$$  \hspace{1cm} (A4.8)
Further differentiation and elimination gives:

\[
\begin{align*}
\frac{d^4u_{\text{CO}}}{dr^4} - P \frac{d^2u_{\text{CO}}}{dr^2} &= 0, \\
\frac{d^4u_{\text{CO}_2}}{dr^4} - P \frac{d^2u_{\text{CO}_2}}{dr^2} &= 0,
\end{align*}
\]

where

\[P = \left( \frac{k_i}{D_{e,\text{CO}}} + \frac{k_{-i}}{D_{e,\text{CO}_2}} \right).\]

Integration of these fourth order differential equations will give four constants of integration. For the case of \(u_{\text{CO}}\):

\[
\begin{align*}
u_{\text{CO}} &= a_1 + b_1 r + c_1 e^{r \sqrt{P}} + e_1 e^{-r \sqrt{P}}, \\
c_{\text{CO}} &= a_1 \frac{r}{r} + b_1 \frac{c_1}{r} e^{r \sqrt{P}} + e_1 \frac{r}{r} e^{-r \sqrt{P}}.
\end{align*}
\]

Mathematically, the restriction that the concentrations at \(r = 0\) are finite implies \(a_1 = 0\); also, \(c_1 = -e_1\) otherwise the exponential terms are non-finite. Using

\[
\sinh(r \sqrt{P}) = \frac{e^{r \sqrt{P}} - e^{-r \sqrt{P}}}{2},
\]

gives for \(\text{CO}\) and \(\text{CO}_2\), respectively:

\[
\begin{align*}
c_{\text{CO}} &= b_1 + \frac{2c_1}{r} \sinh r \sqrt{P}, \\
c_{\text{CO}_2} &= b_2 + \frac{2c_2}{r} \sinh r \sqrt{P}.
\end{align*}
\]

Here, it is noted that \(b_1\) and \(b_2\), and \(c_1\) and \(c_2\) are not independent, rather substituting into Eq. (A4.4) or (A4.5) and comparing terms:

\[
\begin{align*}
b_2 &= b_1 \frac{k_i}{k_{-i}}, \\
c_2 &= -\frac{D_{e,\text{CO}}}{D_{e,\text{CO}_2}} c_1.
\end{align*}
\]
Therefore,

\[ \begin{align*}
    c_{CO} &= b_1 + \frac{2c_1}{r} \sinh r \sqrt{P} \\
    c_{CO_2} &= \frac{k_i}{k_{-i}} b_1 - \frac{2c_1}{r} \frac{D_{e,CO}}{D_{e,CO_2}} \sinh r \sqrt{P}. 
\end{align*} \tag{A4.19} \tag{A4.20} \]

Next, the constants \( b_1 \) and \( c_1 \) are solved for by evaluating Eqs. (A4.19) and (A4.20) at the boundary, \( r = R \), using Eq. (A4.6). This gives

\[ \begin{align*}
    b_1 &= \frac{c_{CO_2,s} + \frac{D_{e,CO}}{D_{e,CO_2}} c_{CO,s}}{\left( \frac{k_i}{k_{-i}} + \frac{D_{e,CO}}{D_{e,CO_2}} \right)} \\
    c_1 &= \frac{R}{2 \sinh R \sqrt{P}} \cdot \frac{k_i}{k_{-i}} c_{CO,s} - c_{CO_2,s} \left( \frac{k_i}{k_{-i}} + \frac{D_{e,CO}}{D_{e,CO_2}} \right). \tag{A4.21} \tag{A4.22} 
\end{align*} \]

With these constants and Eqs. (A4.19) and (A4.20), the values of \( c_{CO} \) and \( c_{CO_2} \) within the particle are now defined.

### A4.3 Effectiveness factor and Thiele modulus

Next, following Levenspiel (1972), the effectiveness factor, \( \eta \), is defined as the ratio of the observed rate of reaction over the intrinsic rate of reaction in the absence of mass transfer limitations due to intraparticle diffusion:

\[ \eta = \frac{4\pi \int_0^R r^2 \left[ k_i c_{CO}(r) - k_{-i} c_{CO_2}(r) \right] dr}{4\pi \int_0^R r^2 \left[ k_i c_{CO,s} - k_{-i} c_{CO_2,s} \right] dr}. \tag{A4.23} \]

The denominator in Eq. (A4.23) is easily evaluated and gives:

\[ 4\pi \int_0^R r^2 \left( k_i c_{CO,s} - k_{-i} c_{CO_2,s} \right) dr = \frac{4\pi R^3}{3} \left( k_i c_{CO,s} - k_{-i} c_{CO_2,s} \right). \tag{A4.24} \]

The numerator in Eq. (A4.23) is evaluated using Eqs. (A4.19) and (A4.20) as follows:

\[ \begin{align*}
    4\pi \int_0^R r^2 \left[ k_i c_{CO}(r) - k_{-i} c_{CO_2}(r) \right] dr &= 4\pi \int_0^R r^2 \left[ k_i \left( b_1 + \frac{2c_1}{r} \sinh r \sqrt{P} \right) \right] \\
    &- 4\pi \int_0^R r^2 \left[ k_{-i} \left( \frac{k_i}{k_{-i}} b_1 - \frac{2c_1}{r} \frac{D_{e,CO}}{D_{e,CO_2}} \sinh r \sqrt{P} \right) \right]. \tag{A4.25} 
\end{align*} \]
Terms with $b_1$ cancel and substituting for $c_1$ after integration by parts then gives:

\[ 4\pi \int_0^R r^2 [k_i c_{\text{CO}}(r) - k_{-i} c_{\text{CO}_2}(r)] \, dr = \frac{4\pi R (k_i c_{\text{CO}_3} - k_{-i} c_{\text{CO}_2,s})}{P} \left[ R \sqrt{P} \coth(R \sqrt{P}) - 1 \right]. \]  

(A4.26)

Using the two integral results, i.e. Eqs. (A4.24) and (A4.26), in Eq. (A4.23), defining $\phi \equiv R \sqrt{P}$, and canceling terms then gives:

\[ \eta = \frac{3}{\phi^2} \left[ \phi \coth(\phi) - 1 \right] \]  

(A4.27)

\[ \phi = R \sqrt{\frac{k_i}{D_{e,\text{CO}}} + \frac{k_{-i}}{\text{CO}_2}}. \]  

(A4.28)

Note that for a negligible back reaction, i.e. $k_{-i} = 0$, Eq. (A4.27) is obtained with $\phi = R \sqrt{k_i/D_{e,\text{CO}}}$.

### A4.4 Relationship between the intraparticle and outlet concentrations

From the pseudo-steady-state assumption, the rate at which CO enters the sphere must be equal to the rate of reaction within the sphere and the rate of CO$_2$ leaving the sphere. Writing these rates in units of mol/(s g of particle as Fe$_2$O$_3$) gives:

\[ r' = \frac{k_{g,\text{CO}} (c_{\text{CO},p} - c_{\text{CO},s}) 4\pi R^2}{\frac{4\pi R^3}{3} \rho_{\text{Fe}_2\text{O}_3}} \]  

(A4.29)

\[ r' = \frac{(k_i c_{\text{CO},s} - k_{-i} c_{\text{CO}_2,s}) \eta}{\rho_{\text{Fe}_2\text{O}_3}} \]  

(A4.30)

\[ r' = \frac{k_{g,\text{CO}_2} (c_{\text{CO}_2,s} - c_{\text{CO}_2,p}) 4\pi R^2}{\frac{4\pi R^3}{3} \rho_{\text{Fe}_2\text{O}_3}}, \]  

(A4.31)
where \( c_{CO,p} \) and \( c_{CO_2,p} \) are the concentration of CO and CO\(_2\) in the particulate phase, respectively. Rearranging Eqs. (A4.29)-(A4.31) gives:

\[
\begin{align*}
\frac{r'R_{Fe_2O_3}}{3k_{g,CO}} &= c_{CO,p} - c_{CO,s} \\
\frac{r'R_{Fe_2O_3}}{\eta} &= k_i c_{CO,s} - k_{-i} c_{CO_2,s} \\
\frac{r'R_{Fe_2O_3}}{3k_{g,CO_2}} &= c_{CO_2,s} - c_{CO_2,p}.
\end{align*}
\]

(A4.32)

(A4.33)

(A4.34)

Summing Eqs. (A4.32)-(A4.34) after multiplying Eq. (A4.32) by \( k_i \) and Eq. (A4.34) by \( k_{-i} \) enables one to write the rate, \( r' \), in terms of the concentrations of the particulate phase only:

\[
\frac{r'R_{Fe_2O_3}}{k_i} \left( \frac{k_i R}{3k_{g,CO}} + 1 + \frac{k_{-i} R}{3k_{g,CO_2}} \right) = k_i c_{CO,p} - k_{-i} c_{CO_2,p}.
\]

(A4.35)

After dividing by \( k_i \) and rearranging, Eq. (A4.35) becomes:

\[
\frac{r'}{R_{Fe_2O_3}} = k \left( c_{CO,p} - c_{CO_2,p} \right) K_p
\]

(A4.36)

where \( K_p = k_i/k_{-i} \). Assuming a well-mixed fluidised bed reactor, such that the concentration in the particulate phase is equal to the concentration at the outlet, \( i.e. \ c_{CO,p} = c_{CO,out} \) and \( c_{CO_2,p} = c_{CO_2,out} \), Eq. (A4.36) can be rewritten:

\[
\frac{r'}{R_{Fe_2O_3}} = \frac{k}{R_{Fe_2O_3}} \left( c_{CO,out} - c_{CO_2,out} \right) K_p.
\]

(A4.37)

(A4.38)

Note that Eq. (A4.38) with \( k \) given by Eq. (A4.37) is the relation used in Chapter 5, section 5.3, to evaluate the rate of reduction of iron oxide. While derived for the case of a single sphere, Eq. (A4.38) gives the rate in units of mol/(s g of particle as Fe\(_2\)O\(_3\)) and is therefore a general rate expression for any number of particles.
Appendix 5

Lattice Boltzmann method

In the following, the derivation of the discrete equilibrium function, transformation matrix, and continuity and Navier-Stokes equations will be outlined. While the derivations are specific to the D3Q19 model, derivations for other LB models, e.g. D2Q9 or D3Q15, follow in an analogous and straightforward manner.

A5.1 Derivation of the discrete equilibrium distribution

The equilibrium distribution function in continuous space and time was the Maxwell-Boltzmann distribution, given by Eq. (8.5) for the BGK approximation. However, a discrete equilibrium distribution, $f_{eq}^i$, for the LB equation is required as shown by Eq. (8.12). Taylor expansion (He and Luo, 1997c) of the Maxwell-Boltzmann distribution, Eq. (8.5), with respect to the macroscopic velocity, $\mathbf{u}$, gives:

$$f_{eq} = f|_{u=0} + \frac{\partial f}{\partial \mathbf{u}}|_{u=0} (\mathbf{u}) + \frac{\partial^2 f}{\partial \mathbf{u}^2} |_{u=0} (\mathbf{u})^2 + O(\mathbf{u}^3)$$

$$= \rho \left( \frac{m}{2\pi k_B T} \right)^{D/2} \exp \left( -\frac{m \mathbf{v} \cdot \mathbf{u}}{k_B T} \right) \left[ 1 + \frac{m \mathbf{v} \cdot \mathbf{u}}{k_B T} + \frac{m^2 (\mathbf{v} \cdot \mathbf{u})^2}{2(k_B T)^2} - \frac{m \mathbf{u}^2}{2k_B T} \right] + O(\mathbf{u}^3). \quad (A5.1)$$

Greater accuracy in $f_{eq}^i$ with respect to $\mathbf{u}$ can be obtained by expansion to higher orders in $\mathbf{u}$ if required. An analogous equation to Eq. (A5.1) in discrete space is then:

$$f_{eq}^i = \rho w_i \left( 1 + \frac{m \mathbf{v}_i \cdot \mathbf{u}}{k_B T} + \frac{m^2 (\mathbf{v}_i \cdot \mathbf{u})^2}{2(k_B T)^2} - \frac{m \mathbf{u}^2}{2k_B T} \right) + O(\mathbf{u}^3), \quad (A5.2)$$

where the $w_i$ can be considered weighting factors which will be constant once the dimension, D, and velocity set, Q are chosen, that is, once the D-dimensions and Q-velocities in the DDQQ model have been specified.
To determine the $w_i$, the assumption of a closed system at equilibrium such that the macroscopic velocity, $\mathbf{u} = 0$, is sufficient and gives:

$$\rho_0 \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left( \frac{-m v_i^2}{2k_B T} \right) = f^{(eq)} \bigg|_{u=0}$$  \hspace{1cm} (A5.3)

$$\rho_0 w_i = f^{(eq)} \bigg|_{u=0},$$  \hspace{1cm} (A5.4)

for the continuous (A5.3) and discrete (A5.4) cases, respectively, where $\rho_0$ is the mean mass density of the system, i.e. the density of the system at equilibrium. The $w_i$ can then be determined by requiring the moments of the discrete lattice Boltzmann equilibrium distribution to be equal to the moments of the continuous Maxwell-Boltzmann distribution, both evaluated at $\mathbf{u} = 0$, up to fourth order. Thus, substituting $a = m/(2k_B T)$ into the Maxwell-Boltzmann distribution, Eq. (8.5), and taking the moments up to fourth order gives for the three-dimensional, $D = 3$, case:

$$\int f^{(eq)} \bigg|_{u=0} d\mathbf{v} = \rho_0 \left( \frac{a}{\pi} \right)^{\frac{3}{2}} \int e^{(-av_i^2)} dv_x \int e^{(-av_i^2)} dv_y \int e^{(-av_i^2)} dv_z = \rho_0 = \rho_0 \sum_i w_i$$  \hspace{1cm} (A5.5)

$$\int v_x f^{(eq)} \bigg|_{u=0} d\mathbf{v} = \rho_0 \left( \frac{a}{\pi} \right)^{\frac{3}{2}} \int v_x e^{(-av_i^2)} dv_x \int e^{(-av_i^2)} dv_y \int e^{(-av_i^2)} dv_z = 0 = \rho_0 \sum_i w_i v_{ix}$$  \hspace{1cm} (A5.6)

$$\int v_x^2 f^{(eq)} \bigg|_{u=0} d\mathbf{v} = \rho_0 \left( \frac{a}{\pi} \right)^{\frac{3}{2}} \int v_x^2 e^{(-av_i^2)} dv_x \int e^{(-av_i^2)} dv_y \int e^{(-av_i^2)} dv_z = \frac{\rho_0}{2a} = \rho_0 \frac{k_B T}{m} = \rho_0 \sum_i w_i v_{ix}^2$$  \hspace{1cm} (A5.7)

$$\int v_x^3 f^{(eq)} \bigg|_{u=0} d\mathbf{v} = \rho_0 \left( \frac{a}{\pi} \right)^{\frac{3}{2}} \int v_x^3 e^{(-av_i^2)} dv_x \int e^{(-av_i^2)} dv_y \int e^{(-av_i^2)} dv_z = 0 = \rho_0 \sum_i w_i v_{ix}^3$$  \hspace{1cm} (A5.8)

$$\int v_x^4 f^{(eq)} \bigg|_{u=0} d\mathbf{v} = \rho_0 \left( \frac{a}{\pi} \right)^{\frac{3}{2}} \int v_x^4 e^{(-av_i^2)} dv_x \int e^{(-av_i^2)} dv_y \int e^{(-av_i^2)} dv_z = \frac{3\rho_0}{4a^2} = 3 \rho_0 \left( \frac{k_B T}{m} \right)^2 = \rho_0 \sum_i w_i v_{ix}^4$$  \hspace{1cm} (A5.9)

$$\int v_x^2 v_y f^{(eq)} \bigg|_{u=0} d\mathbf{v} = \rho_0 \left( \frac{a}{\pi} \right)^{\frac{3}{2}} \int v_x^2 e^{(-av_i^2)} dv_x \int v_y e^{(-av_i^2)} dv_y \int e^{(-av_i^2)} dv_z = \frac{\rho_0}{4a^2} = \rho_0 \left( \frac{k_B T}{m} \right)^2 = \rho_0 \sum_i w_i v_{ix}^2 v_{iy}$$  \hspace{1cm} (A5.10)

where the integrals have been evaluated using the standard integrals listed in Table A5.3. It
Table A5.3: Table of standard integrals (Young, 2006).

<table>
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<th>n</th>
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<tbody>
<tr>
<td>0</td>
<td>$\sqrt{\frac{2}{\pi}}$ odd 0</td>
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<tr>
<td>2</td>
<td>$\frac{1}{2} \sqrt{\frac{2}{\pi}}$ 4</td>
<td>$rac{1}{2} \sqrt{\frac{2}{\pi}}$</td>
<td></td>
</tr>
</tbody>
</table>

is noted that in Eqs. (A5.5)-(A5.10), odd moments vanish; this holds for all odd moments not just those listed. Additionally, it is noted that Eqs. (A5.5)-(A5.10) hold for the 2D case as well, where the term $\int e^{(-av^2)}dv_z$ in the evaluation of $\int f^{eq}|_{u=0}dv$ would be dropped and $D = 2$ would be used. The derivation of the equilibrium distribution up to this point has been general.

To solve for the $w_i$, however, a specific lattice and hence a specific set of $v_i$ must be chosen. Considering the D3Q19 lattice in Fig. 8.2(a), the lattice velocities are:

$v_{ix} = [0, 1, -1, 0, 0, 0, 1, -1, 1, -1, 0, 0, 0, 0]^T c$
$v_{iy} = [0, 0, 0, 0, 0, 0, 1, -1, 1, -1, 0, 0, 0, 0]^T c$
$v_{iz} = [0, 0, 0, 0, 0, 0, 1, 1, 1, 1, 1, 1, -1, -1]^T c$

where multiplication by $c = \Delta x/\Delta t$, with $\Delta x$ = (m/lattice unit) and $\Delta t$ = (s/time step), permits conversion from lattice units to physical units. From the symmetry of the lattice, it can further be seen that the $w_i$ will be identical for directions with identical lattice speeds, $|v_i|$. Thus, $w_0 = W_0$, $w_1 = w_2 = w_3 = w_4 = w_5 = w_6 = W_1$ and $w_7 = \ldots = w_{18} = W_2$ is assumed.

Evaluating the right hand sides of Eqs. (A5.5)-(A5.10) with substitution of Eq. (A5.11) gives:

\[
\begin{align*}
0 \text{ moment:} & \quad \sum_i w_i = W_0 + 6W_1 + 12W_2 = 1 \\
2 \text{ moment:} & \quad \sum_i w_i v_{ix}^2 = 2W_1 c^2 + 8W_2 c^2 = \left(\frac{k_B T}{m}\right) \\
4 \text{ moment:} & \quad \sum_i w_i v_{ix}^4 = 2W_1 c^4 + 8W_2 c^4 = 3 \left(\frac{k_B T}{m}\right)^2 \\
& \quad \sum_i w_i v_{ix}^2 v_{iy}^2 = 4W_2 c^4 = \left(\frac{k_B T}{m}\right)^2 
\end{align*}
\]

The four independent equations (A5.12-A5.15) can be used to solve for the four unknowns:

\[
W_0 = \frac{1}{3}, \quad W_1 = \frac{1}{18}, \quad W_2 = \frac{1}{36}, \quad c^2 = \frac{k_B T}{m},
\]

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where generally $c^2 = \Delta x / \Delta t = 1$ is used.

Thus, the overall discrete equilibrium distribution for the D3Q19 model with error of order $O(u^3)$ is given by evaluating Eq. (A5.2) with Eq. (A5.16),

$$f_i^{(eq)} = w_i \rho \left[ 1 + 3 \vec{v}_i \cdot \vec{u} / c^2 + \frac{9}{2} (\vec{v}_i \cdot \vec{u})^2 / c^4 - \frac{3}{2} \frac{u^2}{c^2} \right],$$  
(A5.17)

where

$$w_i = \begin{cases} 
\frac{1}{3}, & i = 0 \\
\frac{1}{18}, & i = 1, 2, 3, 4 \\
\frac{1}{36}, & i = 5, 6, ..., 18 
\end{cases}$$
(A5.18-20)

For fluids with little variation in $\rho$, e.g. slightly-compressible flows, the equilibrium distribution function Eq. (A5.17) is sometimes written as:

$$f_i^{(eq)} = w_i \rho + w_i \rho_0 \left[ 3 \vec{v}_i \cdot \vec{u} / c^2 + \frac{9}{2} (\vec{v}_i \cdot \vec{u})^2 / c^4 - \frac{3}{2} \frac{u^2}{c^2} \right],$$
(A5.21)

with the same $w_i$ as before. This expression has been shown to reduce numerical errors due to the compressibility of the fluid (He and Luo, 1997b).

Finally, it is noted that Eq. (A5.16) has implications for the speed of sound, $c_s$, in the lattice model. If the definition of the isothermal speed of sound, $c_s^2 = \left( \frac{\partial P}{\partial \rho} \right)_T$, is used with the equation of state for an ideal gas, $PV = nRT$, then

$$c_s^2 = \left( \frac{\partial P}{\partial \rho} \right)_T = \frac{RT}{mN_A} = \frac{k_B T}{m} = \frac{c^2}{3},$$
(A5.22)

where $P$ is the pressure, $\rho$ is the mass density, $T$ is the temperature which is assumed constant, $V$ is the volume of the system containing $n$ moles of monatomic gas, $R$ is the universal gas constant, $m$ is the mass of a single monatomic particle and $N_A$ is Avogadro’s number. Hence, for the current lattice Boltzmann model with $c^2 = 1$ the speed of sound is $c_s = \sqrt{1/3}$.

To summarise, the discrete analogue to the Maxwell-Boltzmann equilibrium distribution has been fully derived for a discrete lattice and is given by either Eq. (A5.17) for weakly-compressible flows or Eq. (A5.21) for incompressible flows.
\section*{A5.2 Transformation matrix for collisions with multiple relaxation times}

Depending on the discrete velocity set chosen, the transformation matrix $M$ for the collision operator with multiple relaxation times can be constructed from linear combinations of the discrete velocities, $v_i$. The rows of $M$ must be linearly independent and are typically chosen to be mutually orthogonal such that $\sum_k M_{ik} M_{jk} = 0$, where $M_{ik}$ corresponds to the element on row $i$ and column $k$ of $M$. An example of the construction of $M$ is given in Bouzidi et al. (2001). For the D3Q19 model, D’Humières et al. (2002) give,

\begin{align*}
M_{1i} &= |v_i|^0; \quad M_{2i} = 19 |v_i|^2 - 30c^2; \quad M_{3i} = \frac{1}{2} \left( 21 |v_i|^4 - 53c^2|v_i|^2 + 24c^4 \right); \quad M_{4i} = v_{ix}; \\
M_{5i} &= (5 |v_i|^2 - 9c^2) v_{ix}; \quad M_{6i} = v_{iy}; \quad M_{7i} = (5 |v_i|^2 - 9c^2) v_{iy}; \quad M_{8i} = v_{iz}; \\
M_{9i} &= (5 |v_i|^2 - 9c^2) v_{ix}; \quad M_{10i} = 3v_{ix}^2 - |v_i|^2; \quad M_{11i} = (3 |v_i|^2 - 5c^2) (3v_{ix}^2 - |v_i|^2); \\
M_{12i} &= v_{iy}^2 - v_{iz}^2; \quad M_{13i} = (3 |v_i|^2 - 5c^2) (v_{iy}^2 - v_{iz}^2); \quad M_{14i} = v_{ix} v_{iy}; \quad M_{15i} = v_{ix} v_{iz}; \\
M_{16i} &= v_{ix} v_{iz}; \quad M_{17i} = (v_{iy}^2 - v_{iz}^2) v_{ix}; \quad M_{18i} = (v_{iz}^2 - v_{ix}^2) v_{iy}; \quad M_{19i} = (v_{ix}^2 - v_{iy}^2) v_{iz};
\end{align*}

(A5.23)

For $c = 1$, an assumption that will apply from this point through Eq. (A5.79), the transformation matrix, $M$, is given by:

\begin{align*}
M = \begin{bmatrix}
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
12 & -4 & -4 & -4 & -4 & -4 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
o & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
o & -4 & 4 & 0 & 0 & 0 & 0 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 \\
o & 0 & 0 & 0 & 1 & -1 & 0 & 1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\
o & 0 & 0 & 0 & -4 & 4 & 0 & 0 & 1 & -1 & 1 & -1 & 0 & 0 & 0 & 1 & -1 & 1 -1 \\
o & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & -1 & -1 & 1 & -1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\
o & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\end{bmatrix}
\end{align*}
It is noted that while the individual rows of \( \mathbf{M} \) are orthogonal, they are not normalised.

The moments, \( \mathbf{m} \), are related to the distribution functions, \( \mathbf{f} \), through the transformation matrix, \( \mathbf{M} \), as given by Eq. (8.17). For consistency with the literature, each element of \( \mathbf{m} \) is labeled according to standard convention (D’Humières et al., 2002):

\[
\mathbf{m} = \mathbf{Mf} = [\rho, e, e_2, j_x, q_x, j_y, q_y, j_z, q_z, 3p_{xx}, 3\pi_{xx}, p_{ww}, \pi_{ww}, p_{xy}, p_{yz}, p_{zx}, m_x, m_y, m_z]^T, \quad (A5.24)
\]

so that \( m_1 = \rho \) is the density, \( m_4 = j_x \) is the momentum in the \( x \)-direction, etc. This labeling makes the derivation of the Navier-Stokes equation in section A5.3 easier to understand.

Similarly, the equilibrium functions in moment space, \( \mathbf{m}^{(eq)} \), are then related to those in velocity space, \( \mathbf{f}^{(eq)} \), through Eq. (8.17) as follows:

\[
\mathbf{m}^{(eq)} = \mathbf{M}^{(eq)} \mathbf{f}^{(eq)} = [\rho, e^{(eq)}, e_2^{(eq)}, j_x^{(eq)}, q_x^{(eq)}, j_y^{(eq)}, q_y^{(eq)}, j_z^{(eq)}, q_z^{(eq)}, 3p_{xx}^{(eq)}, 3\pi_{xx}^{(eq)}, p_{ww}^{(eq)}, \pi_{ww}^{(eq)}, p_{xy}^{(eq)}, p_{yz}^{(eq)}, p_{zx}^{(eq)}, m_x^{(eq)}, m_y^{(eq)}, m_z^{(eq)}]^T. \quad (A5.25)
\]

Thus, it is evident that for the conserved moments, \( \rho, j_x, j_y \) and \( j_z \), i.e. the mass density and the momentum in the \( x, y \) and \( z \) directions, respectively, the following relation holds: \( [m_i - m_i^{(eq)}] = 0 \) for \( i = \{1, 4, 6, 8\} \).

Expressions for the non-conserved or kinetic moments can be constructed through matrix multiplication of the transformation matrix, \( \mathbf{M} \), and the local discrete Maxwellian, \( \mathbf{f}^{(eq)} \), in Eq. (A5.21) and results in:

\[
e^{(eq)} = -11\rho + 19\left(\frac{j_x^2 + j_y^2 + j_z^2}{\rho_0}\right); \quad e_2^{(eq)} = 3\rho - \frac{11}{2}\left(\frac{j_x^2 + j_y^2 + j_z^2}{\rho_0}\right); \quad q_x^{(eq)} = -\frac{2}{3}j_x;
\]
\[
q_y^{(eq)} = -\frac{2}{3}j_y; \quad q_z^{(eq)} = -\frac{2}{3}j_z; \quad p_{xx}^{(eq)} = \frac{1}{3}\left(\frac{2j_x^2 - (j_y^2 + j_z^2)}{\rho_0}\right); \quad \pi_{xx}^{(eq)} = -\frac{1}{2}p_{xx}^{(eq)};
\]
\[
p_{ww}^{(eq)} = \frac{(j_y^2 - j_z^2)}{\rho_0}; \quad \pi_{ww}^{(eq)} = -\frac{1}{2}p_{ww}^{(eq)}; \quad p_{xy}^{(eq)} = \frac{j_xj_y}{\rho_0}; \quad p_{yz}^{(eq)} = \frac{j_yj_z}{\rho_0}; \quad p_{zx}^{(eq)} = \frac{j_xj_z}{\rho_0};
\]
\[
m_x^{(eq)} = 0; \quad m_y^{(eq)} = 0; \quad m_z^{(eq)} = 0, \quad (A5.26)
\]

where \( j_x = \rho_0u_x, j_y = \rho_0u_y \) and \( j_z = \rho_0u_z \). Here it is clear that the choice, \( \rho_0 = 1 \), simplifies the denominators in Eq. (A5.26). Optimisation with respect to the linear stability of the model (D’Humières et al., 2002; Lallemand and Luo, 2000) gives the equilibrium values in
Eq. (A5.26), except:

\[ e_2^{(eq)} = - \frac{475}{63} \frac{(j_x^2 + j_y^2 + j_z^2)}{\rho_0}; \quad \pi_{xx}^{(eq)} = 0; \quad \pi_{ww}^{(eq)} = 0. \]  

(A5.27)

Either choice of equilibrium moments, Eq. (A5.26) or alternatively Eq. (A5.26) with Eq. (A5.27) substituted for the specified moments, can be used to derive the Navier-Stokes equations in the following section. For the current dissertation, the optimised equilibrium moments, Eq. (A5.26) with Eq. (A5.27) substituted for the specified moments, were used in simulations; however, the equilibrium moments given by Eq. (A5.26) will be used to derive the Navier-Stokes equation.

The collision matrix \( \hat{S} \) containing the inverse of the relaxation times, \( \text{i.e.} \) the relaxation rates, is (D’Humières et al., 2002):

\[
\hat{S} \equiv \text{diag} \left( s_1, s_2, s_3, s_4, s_5, s_6, s_7, s_8, s_9, s_{10}, s_{11}, s_{12}, s_{13}, s_{14}, s_{15}, s_{16}, s_{17}, s_{18}, s_{19} \right) \quad (A5.28)
\]

\[ \equiv \text{diag} \left( 1.0, 1.19, 1.4, 1.0, 1.2, 1.0, 1.2, 1.0, 1.2, s_{10}, 1.4, s_{12}, 1.4, s_{14}, s_{15}, s_{16}, 1.98, 1.98, 1.98 \right)^T. \]

The relaxation rates for the conserved moments \( \rho, j_x, j_y \) and \( j_z \) are in principle inconsequential since the collision term \( [m_i - m_i^{eq}] = 0 \) for \( i = \{1, 4, 6, 8\} \) as previously highlighted. Only for the incorporation of a body force (Lallemand and Luo, 2003; Premnath and Abraham, 2007) or for multiple component simulations are the \( s_i \) corresponding to the conserved momentum important. In the present simulations, these relaxation rates were set to 1.

### A5.3 Derivation of the continuity and Navier-Stokes equations

In this section, the continuity and Navier-Stokes equations for the lattice Boltzmann model will be derived using a Chapman-Enskog multiscale analysis for the D3Q19 model with multiple relaxation times as in Premnath and Abraham (2007). Although a straightforward extension to include body forces is possible, the following derivation, for simplicity, will not consider body forces. As in He and Luo (1997b), three expansions are introduced. First, a Taylor expansion
is given by:

\[ f(x + v\Delta t, t + \Delta t) = \sum_{m=0}^{\infty} \frac{\Delta t^m}{m!} D^m f(x, t). \quad (A5.29) \]

Second, two Chapman-Enskog expansions are introduced:

\[ f(x, t) = \sum_{n=0}^{\infty} \varepsilon^n f^{(n)}(x, t) \quad (A5.30) \]
\[ \partial_t = \sum_{n=0}^{\infty} \varepsilon^n \partial_t^n. \quad (A5.31) \]

Additionally, the definitions

\[ D_t \equiv \text{diag}(\partial_t, \partial_t + v_1 \cdot \nabla, \partial_t + v_2 \cdot \nabla, \ldots) \quad (A5.32) \]
\[ D_{t_n} \equiv \text{diag}(\partial_{t_n}, \partial_{t_n} + v_1 \cdot \nabla, \partial_{t_n} + v_2 \cdot \nabla, \ldots) \quad (A5.33) \]
\[ \partial_t \equiv \frac{\partial}{\partial t} \quad (A5.34) \]

are used. Thus,

\[ D_t^2 \equiv \text{diag} \left[ \partial_t, \partial_t, \partial_t + 2\partial_t(v_1 \cdot \nabla) + (v_1 \cdot \nabla)^2, \partial_t, \partial_t, \partial_t + 2\partial_t(v_2 \cdot \nabla) + (v_2 \cdot \nabla)^2, \ldots \right], \quad (A5.35) \]

which will be important later for evaluation of Eq. (A5.29). The lattice Boltzmann equation in vector notation:

\[ f(x + v\Delta t, t + \Delta t) - f(x, t) = -S \left[ f(x, t) - f^{(eq)}(x, t) \right], \quad (A5.36) \]

can then be rewritten using Eq. (A5.29) and subsequently Eqs. (A5.30) and (A5.31) as:

\[ \Delta t D_t f(x, t) + \frac{\Delta t^2}{2} D_t^2 f(x, t) + O(\Delta t^3) = -S \left[ f(x, t) - f^{(eq)}(x, t) \right] \]

\[ \Delta t D_{t_i} f^{(0)}(x, t) + \Delta t \varepsilon \partial_t f^{(0)}(x, t) + \Delta t \varepsilon D_{t_i} f^{(1)}(x, t) + \frac{\Delta t^2}{2} D_{t_i}^2 f^{(0)}(x, t) + O(\Delta t^3) = -S \left[ f^{(0)}(x, t) - f^{(eq)}(x, t) + \varepsilon f^{(1)}(x, t) + \varepsilon^2 f^{(2)}(x, t) \right]. \quad (A5.38) \]
Assuming a small time step (He and Luo, 1997b), so that \( O(\Delta t) = O(\varepsilon) \), and separating terms based on orders of \( \Delta t \) and \( \varepsilon \), then gives:

\[
O(0) : \quad f^{(0)}(x, t) = f^{(eq)}(x, t) \quad (A5.39)
\]

\[
O(1) : \quad \Delta t D_0 f^{(0)}(x, t) = -\varepsilon S f^{(1)}(x, t) \quad (A5.40)
\]

\[
O(2) : \quad \Delta t \varepsilon \partial_t f^{(0)}(x, t) + \Delta t \varepsilon D_0 \left( I - \frac{1}{2} \hat{S} \right) f^{(1)}(x, t) = -\varepsilon^2 S f^{(2)}(x, t), \quad (A5.41)
\]

where Eq (A5.40) has been substituted in to Eq. (A5.41) and \( I \) is the identity matrix. Premultiplying Eqs. (A5.39)-(A5.41) by the transformation matrix \( M \) gives:

\[
O(0) : \quad m^{(0)}(x, t) = m^{(eq)}(x, t) \quad (A5.42)
\]

\[
O(1) : \quad \Delta t M D_0 M^{-1} m^{(0)}(x, t) = -\varepsilon S M^{-1} M f^{(1)}(x, t)
\]

\[
O(2) : \quad \Delta t \varepsilon \partial_t m^{(0)}(x, t) + \Delta t \varepsilon M D_0 M^{-1} \left( I - \frac{1}{2} \hat{S} \right) M^{-1} M f^{(1)}(x, t) = -\varepsilon^2 S M^{-1} M f^{(2)}(x, t)
\]

where \( m = Mf \) from Eq. (8.17), \( \hat{S} = S M^{-1} \), \( I = M^{-1} M \) and the distributive property of matrix multiplication have been used. Next, the multiple relaxation time definition \( \hat{S} = \text{diag}(s_1, s_2, \ldots, s_{19}) \) is set.

The present derivation has been general up to this point, i.e. it was independent of the choice of the discrete velocity set. To evaluate Eqs. (A5.42)-(A5.44), however, the velocity set of the particular lattice Boltzmann model, in this case the D3Q19 model, is required. From Eq. (A5.43), the components of the first-order equations in moment space yield 19 equations, which were straightforwardly determined using, e.g. the symbolic toolbox of Matlab®:

\[
\Delta t \left[ \partial_t \rho + \left( \partial_x j_x + \partial_y j_y + \partial_z j_z \right) \right] = 0 \quad (A5.45)
\]

\[
\Delta t \left[ \partial_t \left( -11 \rho + 19 \frac{(j_x^2 + j_y^2 + j_z^2)}{\rho_0} \right) + \frac{5}{3} \left( \partial_x j_x + \partial_y j_y + \partial_z j_z \right) \right] = -\varepsilon s_2 \varepsilon^{(1)} \quad (A5.46)
\]

\[
\Delta t \left[ \partial_t \left( 3 \rho - \frac{11}{2} \frac{(j_x^2 + j_y^2 + j_z^2)}{\rho_0} \right) - \frac{2}{3} \left( \partial_x j_x + \partial_y j_y + \partial_z j_z \right) \right] = -\varepsilon s_3 \varepsilon^{(1)} \quad (A5.47)
\]
where division by $\Delta t$, Eq. (A5.45) and Eqs. (A5.48), (A5.50) and (A5.52) are the Euler equations governing conservation of mass and momentum, respectively, for an inviscid fluid up to first order in the Chapman-Enskog expansion. Note that since $m_i = m_i^{(eq)}$ for the conserved
moments, as shown by comparing Eqs. (A5.24) and (A5.25), the right hand sides of the above equations for conserved moments, i.e. Eqs. (A5.45), (A5.48), (A5.50) and (A5.52), have been set to zero.

The components for the second order equations in moment space can then be obtained from Eq. (A5.44) in a similar fashion. For the derivation of the macroscopic flow equations, only the second order equations for the conserved moments are necessary; therefore, only these equations have been listed:

\[
\Delta t \rho = 0 \tag{A5.64}
\]

\[
\Delta t \left( \partial_t j_x + \partial_x \left( \frac{1}{57} \left[ 1 - \frac{1}{2} s_2 \right] e^{(1)} + \left[ 1 - \frac{1}{2} s_{10} \right] p_{xx}^{(1)} \right) + \partial_y \left( \left[ 1 - \frac{1}{2} s_{14} \right] p_{xy}^{(1)} \right) \right) = 0 \tag{A5.65}
\]

\[
\Delta t \left( \partial_t j_x + \partial_x \left( \left[ 1 - \frac{1}{2} s_{14} \right] p_{xx}^{(1)} \right) \right) + \partial_y \left( \frac{1}{57} \left[ 1 - \frac{1}{2} s_2 \right] e^{(1)} - \frac{1}{2} \left[ 1 - \frac{1}{2} s_{10} \right] p_{xx}^{(1)} + \frac{1}{2} \left[ 1 - \frac{1}{2} s_{12} \right] p_{ww}^{(1)} \right) + \partial_z \left( \left[ 1 - \frac{1}{2} s_{16} \right] p_{xz}^{(1)} \right) = 0 \tag{A5.66}
\]

\[
\Delta t \left( \partial_t j_x + \partial_x \left( \left[ 1 - \frac{1}{2} s_{16} \right] p_{xz}^{(1)} \right) \right) + \partial_y \left( \left[ 1 - \frac{1}{2} s_2 \right] e^{(1)} - \frac{1}{2} \left[ 1 - \frac{1}{2} s_{10} \right] p_{xx}^{(1)} - \frac{1}{2} \left[ 1 - \frac{1}{2} s_{12} \right] p_{ww}^{(1)} \right) = 0 \tag{A5.67}
\]

Adding the first and second order equations for the conserved moments, i.e. Eqs. (A5.45) and (A5.64), Eqs. (A5.48) and (A5.65), Eqs. (A5.50) and (A5.66), and Eqs. (A5.52) and (A5.67), and using \( \partial_t \approx \partial_0 + \varepsilon \partial_1 \) from Eq. (A5.31) gives after division by \( \Delta t \):

\[
\partial_0 \rho + \nabla \cdot (u \rho_0) = 0 \tag{A5.68}
\]

\[
\partial_1 j_x + \partial_x \left( \frac{1}{5} \rho + \frac{j_x}{\rho_0} + \varepsilon \frac{1}{57} \left[ 1 - \frac{1}{2} s_2 \right] e^{(1)} + \varepsilon \left[ 1 - \frac{1}{2} s_{10} \right] p_{xx}^{(1)} \right) + \partial_y \left( \frac{j_x j_y}{\rho_0} + \varepsilon \left[ 1 - \frac{1}{2} s_{14} \right] p_{xy}^{(1)} \right) + \partial_z \left( \frac{j_x j_z}{\rho_0} + \varepsilon \left[ 1 - \frac{1}{2} s_{16} \right] p_{xz}^{(1)} \right) = 0 \tag{A5.69}
\]
\[ \partial_t j_y + \partial_x \left( \frac{j_y j_x}{\rho_0} + \varepsilon \left[ 1 - \frac{1}{2} s_{14} \right] \rho^{(1)} \right) \]
\[ + \partial_y \left( \frac{j_y^2}{\rho_0} + \varepsilon \frac{1}{57} \left[ 1 - \frac{1}{5} s_1 \right] \rho^{(1)} - \varepsilon \frac{1}{2} \left[ 1 - \frac{1}{5} s_{10} \right] \rho^{(1)} + \varepsilon \frac{1}{2} \left[ 1 - \frac{1}{5} s_{12} \right] \rho^{(1)} \right) \]
\[ + \partial_z \left( \frac{j_y j_z}{\rho_0} + \varepsilon \left[ 1 - \frac{1}{5} s_{15} \right] \rho^{(1)} \right) = 0 \] (A5.70)
\[ \partial_t j_z + \partial_x \left( \frac{j_z j_x}{\rho_0} \right) = 0 \]
\[ \partial_t j_z + \partial_y \left( \frac{j_z j_y}{\rho_0} + \varepsilon \left[ 1 - \frac{1}{5} s_{16} \right] \rho^{(1)} \right) \]
\[ + \partial_z \left( \frac{j_z^2}{\rho_0} + \varepsilon \frac{1}{57} \left[ 1 - \frac{1}{5} s_1 \right] \rho^{(1)} - \varepsilon \frac{1}{2} \left[ 1 - \frac{1}{5} s_{10} \right] \rho^{(1)} - \varepsilon \frac{1}{2} \left[ 1 - \frac{1}{5} s_{12} \right] \rho^{(1)} \right) = 0. \] (A5.71)

If the compressible form of the equilibrium distribution, i.e. Eq. (A5.17) for \( \mathbf{f}^{(eq)} \), had been used instead of the incompressible form, Eq. (A5.21) for \( \mathbf{f}^{(eq)} \), the recovered continuity equation would have been \( \partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0 \). To recover incompressible flow, i.e. \( \nabla \cdot \mathbf{u} \), thus requires small temporal variation in \( \rho \), so that \( \partial_t \rho \approx 0 \). The assumption of small temporal variation in \( \rho \) will always hold for flows in steady state. Additionally, it can be shown (Martinez et al., 1994) that \( \partial_t \rho = O(\mathbf{u}^2) \). In Eqs. (A5.69)-(A5.71), the variables \( e^{(1)}, p_{xx}^{(1)}, p_{ww}^{(1)}, p_{xy}^{(1)}, p_{yz}^{(1)}, p_{xz}^{(1)} \) are unknowns. Expressions for these variables can be obtained by rearranging Eqs. (A5.46), (A5.54), (A5.56), (A5.58), (A5.59) and (A5.60), respectively, and employing the continuity and momentum equations, i.e. Eq. (A5.45) and Eqs. (A5.48), (A5.50) and (A5.52), to give (Premnath and Abraham, 2007; McCracken and Abraham, 2005):

\[ e^{(1)} = -\frac{\Delta t}{\varepsilon} \frac{38}{3 s_2} (\partial_x j_x + \partial_y j_y + \partial_z j_z) = -\frac{38}{3 s_2} \nabla \cdot \mathbf{j} \approx e - e^{(eq)} \] (A5.72)
\[ p_{xx}^{(1)} = -\frac{\Delta t}{\varepsilon} \frac{2}{9 s_{10}} (\partial_x (2 j_x) - \partial_y j_y - \partial_z j_z) \approx p_{xx} - p_{xx}^{(eq)} \] (A5.73)
\[ p_{ww}^{(1)} = -\frac{\Delta t}{\varepsilon} \frac{2}{3 s_{12}} (\partial_x j_y - \partial_z j_z) \approx p_{ww} - p_{ww}^{(eq)} \] (A5.74)
\[ p_{xy}^{(1)} = -\frac{\Delta t}{\varepsilon} \frac{1}{3 s_{14}} (\partial_x j_y + \partial_y j_x) \approx p_{xy} - p_{xy}^{(eq)} \] (A5.75)
\[ p_{yz}^{(1)} = -\frac{\Delta t}{\varepsilon} \frac{1}{3 s_{15}} (\partial_x j_z + \partial_z j_x) \approx p_{yz} - p_{yz}^{(eq)} \] (A5.76)
\[ p_{xz}^{(1)} = -\frac{\Delta t}{\varepsilon} \frac{1}{3 s_{16}} (\partial_x j_z + \partial_z j_x) \approx p_{xz} - p_{xz}^{(eq)} \] (A5.77)

where terms of order \( O(\mathbf{u}^3) \) and higher have been neglected to be consistent with the small velocity expansion of \( \mathbf{f}^{(eq)} \) in Eq. (A5.2) up to the order of \( O(\mathbf{u}^2) \).
Substituting Eqs. (A5.72)-(A5.77) into Eqs. (A5.69)-(A5.71), with $\Delta t = 1$ and

$$
\zeta = \frac{2}{9} \left( \frac{1}{s_2} - \frac{1}{2} \right) \tag{A5.78}
$$

$$
\nu = \frac{1}{3} \left( \frac{1}{s_i} - \frac{1}{2} \right), \quad i = 10, 12, 14, 15, 16 \tag{A5.79}
$$

the momentum equations simplify to:

$$
\partial_s j_x + \partial_s \left( j_x \frac{j_x}{\rho_0} \right) + \partial_s \left( j_x \frac{j_x}{\rho_0} \right) = -\partial_s \left( \frac{1}{3} \rho \right) + \partial_s \left( 2 \nu \left[ \partial_s j_x - \frac{1}{3} \nabla \cdot \mathbf{j} \right] + \zeta \nabla \cdot \mathbf{j} \right) 
+ \partial_s \left( \nu [\partial_s j_x + \partial_s j_y] \right) \tag{A5.80}
$$

$$
\partial_s j_y + \partial_s \left( j_y \frac{j_y}{\rho_0} \right) + \partial_s \left( j_y \frac{j_y}{\rho_0} \right) = -\partial_s \left( \frac{1}{3} \rho \right) + \partial_s \left( \nu [\partial_s j_y + \partial_s j_z] \right) 
+ \partial_s \left( 2 \nu \left[ \partial_s j_y - \frac{1}{3} \nabla \cdot \mathbf{j} \right] + \zeta \nabla \cdot \mathbf{j} \right) 
+ \partial_s \left( \nu [\partial_s j_y + \partial_s j_z] \right) \tag{A5.81}
$$

$$
\partial_s j_z + \partial_s \left( j_z \frac{j_z}{\rho_0} \right) + \partial_s \left( j_z \frac{j_z}{\rho_0} \right) = -\partial_s \left( \frac{1}{3} \rho \right) + \partial_s \left( \nu [\partial_s j_z + \partial_s j_x] \right) + \partial_s \left( \nu [\partial_s j_z + \partial_s j_y] \right) 
+ \partial_s \left( 2 \nu \left[ \partial_s j_z - \frac{1}{3} \nabla \cdot \mathbf{j} \right] + \zeta \nabla \cdot \mathbf{j} \right). \tag{A5.82}
$$

Here, $\zeta$ and $\nu$ are the kinematic bulk and shear viscosities, respectively. Writing Eqs. (A5.80)-(A5.82) explicitly in terms of $\Delta t$ and $c$, identical equations to Eqs. (A5.80)-(A5.82) would have been obtained, but with the transport coefficients defined as:

$$
\zeta = \frac{2}{9} \left( \frac{1}{s_2} - \frac{1}{2} \right) c^2 \Delta t \tag{A5.83}
$$

$$
\nu = \frac{1}{3} \left( \frac{1}{s_i} - \frac{1}{2} \right) c^2 \Delta t, \quad i = 10, 12, 14, 15, 16 \tag{A5.84}
$$

where $c = 1$ and $\Delta t = 1$ are typically used. For the correct viscous stress tensor, $s_{10} = s_{12} = s_{14} = s_{15} = s_{16}$ must be maintained. The left hand sides of Eqs. (A5.80)-(A5.82) can be expanded as

$$
\rho_0 \partial_s u_x + \rho_0 \left( u_x \partial_s u_x + u_x \partial_x \nabla u_x + u_x \partial_x \nabla u_x + \rho_0 \partial_s u_x \right) \tag{A5.85}
$$

$$
\rho_0 \partial_s u_y + \rho_0 \left( u_y \partial_s u_y + u_y \partial_x \nabla u_y + u_y \partial_x \nabla u_y + \rho_0 \partial_s u_y \right) \tag{A5.86}
$$

$$
\rho_0 \partial_s u_z + \rho_0 \left( u_z \partial_s u_z + u_z \partial_x \nabla u_z + u_z \partial_x \nabla u_z + \rho_0 \partial_s u_z \right), \tag{A5.87}
$$

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where the cancelation results from using continuity, $\nabla \cdot u = \partial_x u_x + \partial_y u_y + \partial_z u_z = 0$. Thus the overall macroscopic flow equations for the D3Q19 lattice Boltzmann model, representing the conservation of mass and momentum, respectively, are given by:

$$\nabla \cdot u = 0 + O(\epsilon^2) + O(Ma^2)$$  \hspace{1cm} (A5.88)

$$\rho_0[\partial_t u + u \cdot \nabla u] = -\nabla P + \nabla \cdot T + O(\epsilon^2) + O(Ma^3),$$  \hspace{1cm} (A5.89)

where $\rho_0$ is the constant density of the incompressible flow, $P$ is the pressure given by

$$P = c_s^2 \rho = \frac{c_s^2}{3} \rho,$$  \hspace{1cm} (A5.90)

and $T$ is the deviatoric part of the viscous stress tensor:

$$T_{ij} = \rho_0 \nu \left( \partial_j u_i + \partial_i u_j \right) - \frac{2}{3} \nabla \cdot u \delta_{ij} + \rho_0 \zeta \nabla \cdot u \delta_{ij},$$  \hspace{1cm} (A5.91)

where $\delta_{ij}$ is the Kronecker delta. In Eqs. (A5.88) and (A5.89) the error term, $O(\epsilon^2)$, originates from the higher order terms in the original expansions, Eqs. (A5.29)-(A5.31), where $O(\epsilon^2) = O(\Delta t^2)$ has been assumed. The term $O(Ma^2)$ in Eq. (A5.88) comes from $\partial_t = O(Ma^2)$ (Martinez et al., 1994). By contrast the error term, $O(Ma^3)$, in Eq. (A5.89) originates from higher order terms in Eqs. (A5.85)-(A5.87) as well as from the expansion of the equilibrium distribution function. In the present dissertation, the Mach number is defined as

$$Ma = \frac{|u|}{c_s} = \frac{|\mathbf{j}|}{\rho_0 c_s},$$  \hspace{1cm} (A5.92)

so that $O(u) = O(j) = O(Ma)$. Thus, the overall scheme is second order accurate in both time and space, since $O(\epsilon^2) = O(\Delta t^2)$ and the time step was chosen equal to the lattice spacing, $c = \Delta x/\Delta t = 1$, so that $O(\Delta x^2) = O(\Delta t^2)$. Since terms of $O(\Delta t^2)$ in the original lattice Boltzmann equation (8.12) are $O(\Delta t^2)$ in Eqs. (A5.88)-(A5.89), the low order discretisation error of $O(\Delta t^2)$ in Eq. (8.12) has effectively been absorbed into the transport coefficients, $\nu$ and $\zeta$ (Sterling and Chen, 1996). By having $\nu$ and $\zeta$ take the form $1/s_i - 1/2$ rather than simply $1/s_i$, Eq. (8.12) can be considered to have errors of order $O(\Delta t^3)$.

In general, the condition $Ma = |u|/c_s < 0.15$ is maintained in numerical simulations of the LB method (He and Luo, 1997b) to satisfy incompressibility and was observed in all simulations in this dissertation except those in Figs. 8.14(c) and (d). Finally, it is noted that if the
compressible form of the equilibrium distribution, \textit{i.e.} Eq. (A5.17) for $f^{(eq)}$, were used instead of the incompressible form, Eq. (A5.21) for $f^{(eq)}$, the result would have been the compressible form of the continuity and Navier-Stokes equations (Dellar, 2003).
Nomenclature

$a$  Index for curve fitting in Chapter 5
$a$  Constant, $= m/(2k_B T)$ in Appendix 5 \( (s^2/m^2) \)
$a_1$  Constant in Eq. A4.13 \( (mol/m^2) \)
$a_i$  Constant in Eq. A1.2 \( (J/(mol K)) \)
$a_{ij}$  Atoms of $j$ in one molecule of $i$ in Eq. A1.22
$A$  Pre-exponential factor \( (1/s) \)
$A_s$  Reactor cross-sectional area \( (m^2) \)
$Abs$  Absorbance of an X-ray beam
$b$  Number of distinct atomic species in Eq. A1.22
$b_1$  Constant in Eqs. 5.5 and A4.13 \( (mol/m^3) \)
$b_2$  Constant in Eq. A4.16 \( (mol/m^3) \)
$b_i$  Constant in Eq. A1.2 \( (J/(mol K^2)) \)
$b_j$  Number of moles of element $j$ in Eq. A1.22
$Bi$  Biot number, $= h d_p / 6 \lambda_p$
$c$  Lattice speed, $= \Delta x / \Delta t$ \( (m/s) \)
$c_1, c_2$  Constant in Eqs. 5.5, A4.13 and A4.16 \( (mol/m^2) \)
$c_{CO}, c_{CO_2}, c_{N_2}$  Concentration of CO, CO$_2$, N$_2$ \( (mol/m^3) \)
$c_{CO, in}, c_{CO_2, in}$  Concentration at reactor inlet \( (mol/m^3) \)
$c_{CO, out}, c_{CO_2, out}$  Concentration at reactor outlet \( (mol/m^3) \)
$c_{CO, p}, c_{CO_2, p}$  Concentration in particulate phase \( (mol/m^3) \)
$c_{CO, s}, c_{CO_2, s}$  Concentration at particle surface \( (mol/m^3) \)
$C_d$  Drag coefficient \( (J K)/mol) \)
$c_i$  Constant in Eq. A1.2 \( (J K)/mol) \)
$c_s$  Lattice speed of sound, $= \sqrt{k_B T/\bar{m}} = 1/ \sqrt{3}$ \( (m/s) \)
$C_p$  Mass specific heat capacity at constant pressure \( (J/(kg K)) \)
$C_{pi}$  Molar specific heat capacity at constant pressure \( (J/(mol K)) \)
for species $i$
$d$  Distance \( (m) \)
$d_{bed}$  Bed diameter \( (m) \)
$d_i$  Constant in Eq. A1.2 \( (J/(mol K^3)) \)
$d_p$  Particle diameter \( (m) \)
$d_{pore}$  Mean pore diameter \( (nm) \)
$D$  Packed bed dispersion coefficient \( (m^2/s) \)
$D$  Dimension, $= 2$ for 2D, $= 3$ for 3D
$D_{e, CO}, D_{e, CO_2}$  Effective diffusivity within porous particle \( (m^2/s) \)
$D_{k, CO}, D_{k, CO_2}$  Knudsen diffusivity within porous particle \( (m^2/s) \)
$D_{mix, CO}, D_{mix, CO_2}$  Diffusivity of CO and CO$_2$ in a gas mixture \( (m^2/s) \)
\[ D_s \] Diffusivity of scalar species \( s \) (m\(^2\)/s)

\[ \mathbf{D}_t, \mathbf{D}_n \] Total derivative in Eq. (A5.32), Eq. (A5.33) (1/s)

\[ \partial_t \] Partial derivative with respect to \( t = \partial/\partial t \) (1/s)

\[ \partial_x, \partial_y, \partial_z \] Partial derivative with respect to \( x, y, z; = \partial/\partial x, \partial y, \partial z \) (1/m)

\[ e_1 \] Constant in Eq. A4.13 (mol/m\(^2\))

\[ e \] Moment defined by Eq. (A5.24) (kg/m/s\(^2\))

\[ e_2 \] Moment defined by Eq. (A5.24) ((kg m)/s\(^4\))

\[ e_{i, eq} \] Equilibrium moment from Eq. (A5.26) (kg/(m s\(^2\)))

\[ e_2^{eq} \] Equilibrium moment from Eq. (A5.27) ((kg m)/s\(^4\))

\[ e_i \] Constant of integration in Eq. A1.3 (J/mol)

\[ e_i \] Constant of integration in Eq. A1.4 (J/(mol K))

\[ F \] Activation energy (J/mol)

\[ E \] Electric potential (V)

\[ E_{an} \] Electric potential difference between anode and normal hydrogen electrode (V)

\[ E_{cat} \] Electric potential difference between cathode and normal hydrogen electrode (V)

\[ f(X) \] Function of conversion, \( X \), in Chapter 5

\[ f \] Continuous mass distribution function ((kg s\(^3\))/m\(^3\) m\(^D\))

\[ f_{i, eq} \] Continuous equilibrium mass distribution function ((kg s\(^3\))/m\(^3\) m\(^D\))

\[ f_i \] Discrete mass distribution function (kg/m\(^3\))

\[ f_{i, eq} \] Discrete equilibrium mass distribution function (kg/m\(^3\))

\[ f_{i, s} \] Discrete distribution function for scalar \( s \) (mol/m\(^3\))

\[ f_{i, eq} \] Discrete equilibrium mass distribution function for scalar \( s \) (mol/m\(^3\))

\[ f_{i, s} \] Discrete post-collision distribution function (kg/m\(^3\))

\[ f_{i, s} \] Discrete post-collision distribution (mol/m\(^3\))

\[ f_i \] Fugacity of species \( i \) in Appendix 1, \( = y_i \rho_i \) (Pa)

\[ f_i^0 \] Fugacity of \( i \) in the reference state in Appendix 1 (Pa)

\[ \mathbf{f} \] Vectorised discrete mass distribution function ((kg s\(^3\))/m\(^3\) m\(^D\))

\[ \mathbf{f}^{(0)}, \ldots, \mathbf{f}^{(n)} \] Expansion parameters for \( \mathbf{f} \) in Eq. (A5.30) ((kg s\(^3\))/m\(^3\) m\(^D\))

\[ F \] Faraday constant, \( = 96 485.34 \) C mol\(^{-1}\) in Chapter 1 (C mol\(^{-1}\))

\[ F \] Lagrangian for minimisation of free energy in Appendix 1 (J)

\[ \mathbf{F} = (F_x, F_y, F_z)^T \] Force vector (N)

\[ G \] Total Gibbs free energy of a system (J)

\[ \bar{G}_i \] Chemical potential of species \( i \) (J/mol)

\[ G_i^0 \] Standard Gibbs free energy for species \( i \) at \( T, 10^5 \) Pa (J/mol)

\[ \Delta G_T^o \] Standard Gibbs free energy for reaction as written at \( T, 10^5 \) Pa (J/mol)

\[ h \] External heat transfer coefficient for reacting particle (W/(m\(^2\) K))

\[ H_0 \] Unfluidised bed height (m)

\[ H_i^0 \] Standard enthalpy for species \( i \) at \( T, 10^5 \) Pa (J/mol)

\[ \Delta H_T^o \] Standard enthalpy for reaction as written at \( T, 10^5 \) Pa (J/mol)

\[ I(n) \] Standard integral in Table A5.3 (m/s\(^n\)n + 1)

\[ \mathbf{I} \] Identity matrix, \( = \text{diag}(1, 1, \ldots, 1) \)

\[ \mathbf{j} = (j_x, j_y, j_z)^T \] Mass flux in \( x, y, z \) direction (kg/ (m\(^2\) s))

\[ k \] Rate constant, including mass transfer effects (1/s)
Initial value of $k_i$ at $X = 0, t = 0$ (1/s)

Boltzmann constant, $= 1.381 \times 10^{-23}$ (m² kg / (s² K))

Lennard-Jones parameter in Eq. (A2.3) (1/K)

Constant in Eq. (8.42), $= 2\pi/L_x$ (1/m)

Dimensionless force constant in Eq. (4.4), $= 0.22$

External mass transfer coefficient for a particle (m/s)

Forward and reverse intrinsic rate constant, chemical rate-controlled, $k_{-i} = k_i/K_p$ (1/s)

Forward intrinsic rate constant for surface reaction, chemical rate-controlled (m/s)

Knudsen number

Equilibrium constant, $= p_{CO_2}/p_{CO}$

Equilibrium constant for water-gas shift, $= p_{H_2}/p_{H_2O} \times p_{CO_2}/p_{CO}$

Length (m)

Length in x, y, and z direction (m)

Mass of single, monoatomic particle (kg)

Mass of CO, H₂ (kg)

Mass of fully oxidised carrier (kg)

Moments defined by Eq. (A5.24) (kg/s³)

Equilibrium moments from Eq. (A5.26), $= 0$ (kg/s³)

Discrete moment vector, $= \mathbf{Mf}$ (varied)

Element $i$ of discrete moment vector (varied)

Discrete equilibrium moment vector, $= \mathbf{Mf^{(eq)}}$ (varied)

Element $i$ of discrete equilibrium moment vector (varied)

Atomic species

Molecular species in Eq. (A1.11)

Mach number defined in Eq. (A5.92)

Molecular mass of CO, Fe₂O₃, H₂ (kg/kmol)

Molecular mass of species $i$, $j$ or general gas (kg/kmol)

Molar density (kmol/m³)

Transformation matrix (varied)

Nabla vector differential operator (1/m)

Moles of reactive iron oxide per unit volume particle (mol/m³)

Moles of H₂ (mol)

Moles of species $i$ (mol)

Number of successes, number of trials

Avogadro constant, $= 6.02214 \times 10^{23}$ (1/mol)

Nusselt number, $= \frac{hd_p}{\lambda_{mix}}$

Partial pressure of CO, CO₂, H₂, H₂O, O₂, species $i$ (Pa)

Moments defined by Eq. (A5.24) (kg/(m s²))

Equilibrium moments from Eq. (A5.26) (kg/(m s²))

Constant in Appendix 4, Eq. (A4.11) (1/m²)

Total pressure of a system (Pa)

Reference pressure, $10^5$ Pa (Pa)
$P_b$ Binomial probability, $[0,1]$  
$Pe$ Péclet number, $= vL/D$  
$P_{sat}$ Saturation pressure at fixed $T$ (Pa)  
$q$ Superficial volumetric flowrate of gas through reactor ($m^3/s$)  
$q_x, q_y, q_z$ Moments defined by Eq. (A5.24) ($kg/s^3$)  
$q_x^{(eq)}, q_y^{(eq)}, q_z^{(eq)}$ Equilibrium moments from Eq. (A5.26) ($kg/s^3$)  
$Q$ Number of discrete lattice velocities  
$r$ Radial position within particle (m)  
$r'$ Rate of reaction per unit mass of particle as Fe$_2$O$_3$ (mol/(s g))  
$r_e$ Effective radius of a cylindrical pore (m)  
$R$ External particle radius (m)  
$R$ Ideal gas constant (J/(mol K))  
$Re$ Reynolds number, $= \rho Ud_p/\mu = Ud_p/\nu$  
$Re_p$ Particle Reynolds number, $= \rho U_{mf}d_p/\mu \varepsilon_{mf}$  
$s_1, s_2, \ldots, s_{19}$ Dimensionless relaxation rates  
$S$ Total entropy of a system (J/K)  
$S_0$ Particle surface area divided by volume ($m^2/m^3$)  
$S_c$ Schmidt number, $= \mu_g/\rho D_{mix} = \nu/D_{mix}$ ($m^2/g$)  
$Sh$ Sherwood number, $= k_g d_p/D_{mix}$ (K)  
$S^i$ Standard entropy for species $i$ at $T$, $10^5$ Pa (J/(mol K))  
$S$ Dimensionless collision matrix, $= \text{diag}(1/\tau, \ldots, 1/\tau)$  
$S$ Dimensionless collision matrix, $= \text{diag}(s_1, \ldots, s_n)$  
$t$ Time (s)  
$\Delta t_{12}, \Delta t_{13}, \Delta t_{23}$ Time between temperature maxima (s)  
$T$ Absolute temperature (K)  
$T_1, T_2, T_3$ Temperature of thermocouple 1, 2 and 3 (K)  
$T_m$ Melting temperature (K)  
$Tr$ Transmittance of an X-ray beam, $= 10^{-Abs}$  
$T_{\infty}$ Fluidised bed bulk temperature (K)  
$T^*$ Dimensionless temperature, $= Tk_B/\xi$  
$T$ Deviatoric viscous stress tensor in Eq. (A5.91) (kg/(m s$^2$))  
$u_{CO}$ Variable, $= c_{COR}$ (mol/m$^2$)  
$u = (u_x, u_y, u_z)^T$ Velocity of bulk fluid (m/s)  
$u_s$ Velocity of bulk fluid of species $s$ (m/s)  
$U$ Superficial velocity of fluidising gas at inlet (m/s)  
$U_{mf}$ Value of $U$ at incipient fluidisation (m/s)  
$\nu$ Packed bed interstitial velocity in flow direction (m/s)  
$v = (v_x, v_y, v_z)^T$ Microscopic velocity (m/s)  
$v_s$ Discrete microscopic velocity, $= (v_{sx}, v_{sy}, v_{sz})^T$ (m/s)  
$v^*$ Velocity in opposite direction of $v_s$ (m/s)  
$V$ Total volume of a system ($m^3$)  
$w_0, w_1, \ldots, w_{18}, w_i$ Weighting constants in discrete equilibrium distribution function  
$w_b, w_s$ Scalar boundary arrays defined in section 8.4.1  
$W$ Total mass of particles of Fe$_2$O$_3$ added to reactor (kg)  
$W_0, W_1, W_2$ Weighting constants in Eq. (A5.16)  
$x$ Distance (m)  
$x_m$ Mole fraction of metal, $= (mol M/(mol Fe + mol M))$
Mass fraction of $\text{Al}_2\text{O}_3$, $x_w = (\text{g Al}_2\text{O}_3/(\text{g Fe}_2\text{O}_3 + \text{g Al}_2\text{O}_3))$

Spatial position vector $\mathbf{x} = (x, y, z)^T$ (m)

Position of boundary node $\mathbf{x}_b$ (m)

Conversion of solid reactant $(n_{\text{Fe}_2\text{O}_3,t=0} - n_{\text{Fe}_2\text{O}_3})/n_{\text{Fe}_2\text{O}_3,t=0} = 2n_{\text{Fe}_2\text{O}_3,t=0}/3 - n_{\text{Fe}_2\text{O}_3})/(2n_{\text{Fe}_2\text{O}_3,t=0}/3)$

Conversion of solid based on moles of CO consumed, CO$_2$ produced during reduction in $\text{N}_2+$CO+CO+2

Conversion of solid based on moles of H$_2$ produced during oxidation in $\text{N}_2$+steam

Moles of H$_2$ produced per mole of C$_{(s)}$ in Eq. (1.20)

Mole fraction of $i$, $j$, CO, CO$_2$ in gaseous mixture

Greek Symbols

$\beta$ Constant in Eq. (5.8), $= (1 - U/U_{mf})$

$\gamma$ Surface tension in Eq. (A2.7) (N/m)

$\gamma_i$ Lagrange multiplier in Eq. (A1.22) (J/mol)

$\delta$ Constant in Chapter 1, 0.05 < $\delta$ < 0.17

$\delta_{ij}$ Kronecker delta

$\varepsilon$ Small expansion parameter (s)

$\varepsilon_{\text{bed}}$ Packed bed porosity due to interstices

$\varepsilon_{mf}$ Fluidised bed porosity at $U_{mf}$

$\varepsilon_p$ Particle porosity

$\zeta$ Kinematic bulk viscosity (m$^2$/s)

$\eta$ Effectiveness factor for sphere, $= 3(\phi \coth \phi - 1)/\phi^2$

$\theta$ Angle (degrees)

$\lambda$ Wavelength (m)

$\lambda_0$ Thermal conductivity of monoatomic gas (W/(m K))

$\lambda_e$ Effective thermal conductivity of the porous particle (W/(m K))

$\lambda_i, \lambda_j$ Thermal conductivity of the gaseous species $i$, $j$ (W/(m K))

$\lambda_j$ Lagrange multiplier in Appendix 1, Eq. (A1.22) (J)

$\lambda_{mix}$ Thermal conductivity of gaseous mixture (W/(m K))

$\mu$ Viscosity of the gas (kg/(m s))

$\nu$ Kinematic shear viscosity, $= \mu/\rho$ (m$^2$/s)

$\nu_1, \ldots, \nu_s$ Stoichiometric integer coefficients in Eq. (A1.11)

$\pi_{xx}, \pi_{ww}$ Moments defined by Eq. (A5.24) (kg m)/s$^4$

$\pi_{xx}^{(eq)}, \pi_{ww}^{(eq)}$ Equilibrium moments from Eq. (A5.27) (kg m)/s$^4$

$\rho$ Mass density of gas (kg/m$^3$)

$\rho_0$ Mass density of gas in equilibrium (kg/m$^3$)

$\rho_{\text{CO}}$ Molar density of CO (mol/m$^3$)

$\rho_{\text{Al}_2\text{O}_3}$ Density of inert $\text{Al}_2\text{O}_3$ bed material (kg/m$^3$)

$\rho_{\text{Fe}_2\text{O}_3}$, $\rho_{\text{Fe}_3\text{O}_4}$ Initial particle density (particle mass/particle volume)

$\rho_s$ Density of scalar $s$ (mol/m$^3$)

$\sigma$ Collision diameter in Lennard-Jones potential (nm)

$\sigma_T$ Crushing stress (Pa)

$\tau$, $\tau_s$ Dimensionless relaxation time
\[ \tau' \] Relaxation time  
\[ \tau_{\text{mix}}, \tau_{\text{mix}}^{\text{CO}, \text{CO}_2} \] Mixing time constants of CO and CO\(_2\) analysers  
\[ \tau_p \] Tortuosity for particle in Chapter 5  
\[ \phi \] Thiele modulus, \( \phi = R[k_i/D_{e,\text{CO}} + k_i/(K_pD_{e,\text{CO}_2})]^{1/2} \)  
\[ \phi_i \] Fugacity coefficient  
\[ \Phi_{ij} \] Mixture coefficient in Eq. A2.6  
\[ \Omega \] Collision integral  
\[ ((\text{kg s}^D)/(\text{m}^3 \text{ m}^D \text{ s})) \]

**Acronyms**

- BET: Theory of Brunauer, Emmett and Teller (1938)
- BJH: Theory of Barrett, Joyner and Halenda (1951)
- CPU: Central processing unit
- DNS: Direct numerical simulation
- DSMC: Direct simulation Monte Carlo
- EDS: Energy dispersive X-ray spectroscopy
- FIB-SEM: Focused ion beam scanning electron microscopy
- I.D.: Interior diameter
- IR: Infrared radiation
- LB: Lattice Boltzmann
- LGCA: Lattice gas cellular automata
- MD: Molecular dynamics
- MPI: Message passing interface
- MRT: Multiple relaxation time
- NDIR: Non-dispersive infrared radiation
- NS: Navier-Stokes
- O.D.: Outer diameter
- PEM: Polymeric electrolyte membrane
- PBR: Packed bed reactor
- PFR: Plug flow reactor
- PROX: Preferential oxidation
- RIR: Relative intensity ratio
- SEM: Scanning electron microscopy
- STEM: Scanning transmission electron microscopy
- WGS: Water-gas shift
- XRD: X-ray diffraction
References


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