Immobilised Solvent Systems for Carbon Capture

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Thank you

Τω δε δυναμενω υπερ παντα ποιησαι υπερεκπέρεσσου

ων αιτουμεθα η νουμεν
Declaration

This is to certify that:

- This thesis compromises only my own original work, except where explicitly indicated otherwise.

- This thesis is less than 100,000 words in length, exclusive of tables, bibliographies and appendices.

Thomas Moore

April 2019
Acknowledgements

For the last four years, I have been given the freedom - by friends and family and supervisors and organisations - to do the one thing every academic longs to do deep down in their soul: to sit back, think, and work on interesting ideas and problems. The results of this time I am neither eager nor qualified to judge, though I take joy in the fact that certain ideas have been well received, and look likely to be developed further into the future. I am proud of the ideas and analysis contained herein, but only as a parent is proud of their child - it gives me pleasure to call this work ‘mine’, but I know in reality it is gift upon gift upon gift.

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only understood the significance of an off-handed observation (‘that wouldn’t work
for phase-change solvents,’ ‘I’m not sure you can get away with that energy balance,’
‘Are you sure it isn’t diffusion limited’ . . . ) weeks, months or even years later. In
their humility and their diligence, I am reminded of Bumstead’s description of Gibbs
[2],

   His modesty with regard to his work was proverbial among all who knew
   him, and it was entirely real and unaffected. There was never any doubt
   in his mind, however, as to the accuracy of anything which he published,
   nor indeed did he underestimate its importance; but he seemed to re-
   gard it in an entirely impersonal way and never doubted, apparently,
   that what he had accomplished could have been done equally well by
   almost anyone who might have happened to give his attention to the
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S. D. G.

πασα δοσις αγαθη, και παν δωρημα τελειον, ανωθεν εστιν, καταβαινον απο του Πατρος των φωτων.
List of Publications

Published Articles


Conference Proceedings and Presentations


Planned Publications

Three articles are currently being prepared for submission, based on the contents of chapter 3.6, chapters 5.1 – 5.4, and chapter 5.5. A collaborative paper is also
planned based on the work described in chapter 4.7. Please contact the author for further details on these works.
Executive Summary

Microencapsulated solvents (MECS) are a novel approach to carbon capture, with the potential to reduce unit operation volumes by 1-2 orders of magnitude, and to allow a wide range of solvents to be contacted with a flue gas stream in a practical way. In this technology, small droplets of a solvent which selectivity absorbs CO\textsubscript{2} are encapsulated inside thin polymer shells, which immobilise the liquid but allow CO\textsubscript{2} to easily pass through. The capsules have diameters of 100\,\mu m – 600\,\mu m, which corresponds to a surface area 1 – 2 orders of magnitude greater than the specific area of a fluid flowing over random or structured packing in a traditional absorber. A fluidised bed containing fine MECS could plausibly be over 10 times smaller than a traditional absorber, and may allow solvents with slow absorption kinetics to capture CO\textsubscript{2} in a practical way. MECS could also contain viscous or precipitating solvents, such as functionalised ionic liquids or CO\textsubscript{2}-binding organic liquids, which may otherwise be difficult to contact to a flue gas stream. Ultimately, it is hoped that microencapsulation of non-aqueous solvents could lead to energy savings relative to a traditional, amine based process.

This study is divided into three parts. First, the intrinsic mass transfer properties of MECS are analysed, and compared with a traditional absorber in a rigorous way. Second, a novel material for CCS, ‘Solvent Impregnated Polymers’ (SIPs), is described. SIPs have many of the desirable properties of MECS but are manufactured in a much more scaleable way. Finally, the energetic savings MECS and SIPs could provide are analysed. The key findings of this thesis are summarised in dot point form at the end of this executive summary.

Mass Transfer into MECS

This body of work was motivated by the following question:

Does the fact that the liquid inside a MECS particle is stationary significantly reduce the gas flux, relative to a traditional absorption column,
in which the liquid is continuously mixed?

By reformulating the surface renewal theory of Danckwerts, expressions were derived for the enhancement in flux which mixing in an absorber provides for a concentrated chemical solvent in the pseudo-first order regime. Some care had to be taken when selecting appropriate $k_L$ correlations, but it was ultimately found that the suppression of liquid mixing inside MECS containing concentrated chemical solvents in the pseudo-first order regime would not significantly reduce the gas flux. MECS containing physical solvents were also analysed, and, somewhat surprisingly, it was found that microencapsulation of these solvents could increase the gas flux under many circumstances. This occurs because the reduction in spatial scales increases the concentration gradients within the solvent.

The analysis was then extended to focus on the specific absorption rate per unit volume of absorber. It was found that MECS containing chemical solvents could be expected to increase the absorption rate by about an order of magnitude, while MECS containing physical solvents could absorb gas up to 2 orders of magnitude faster than a traditional absorber. In this analysis, appropriate correlations for the effective surface area, $a$, in various random and structured packings were selected. Modern structured packings have very large surface areas, and it was found that earlier papers in the MECS literature had underestimated these areas by approximately a factor of four, which had led to overly optimistic predictions for the increase in absorption rate that MECS could provide.

To this point, it had been assumed that the liquid inside a MECS was stationary, but this may not be accurate if the MECS particles are fluidised. Experimental methods and computational fluid dynamics calculations were used to show that the movement and compression of MECS containing concentrated chemical solvents will not significantly increase the rate of mass transfer.

Finally, the relationship between liquid mixing and gas flux into chemical solvents was reconsidered from a different and more general perspective. This relationship is of importance to several emerging technologies which aim to increase the gas flux
by agitating the chemical solvent. However, the earlier analysis had only considered solvents in the pseudo-first order regime. In these solvents the flux into a stationary fluid approaches a steady state value, which may be compared with the steady-state value in an agitated solvent to calculate an ‘enhancement factor’ due to mixing (rather than the more common enhancement factor due to reaction). However, this is not in general possible, as for most stationary chemical solvents the flux is time-dependent. In this section, a new quantity, the sensitivity to liquid mixing, $\xi$, is proposed. The sensitivity is defined such that if an increase in agitation would increase the flux into a physical solvent by some factor $1 + d\alpha > 1$ (where $d\alpha$ is a small positive number), then the increase in flux into a chemical solvent with identical physical properties would be $1 + \xi d\alpha$. Values of $\xi$ may be calculated numerically for an arbitrary chemical solvent, and the process is demonstrated for several systems using both the film theory and a steady-state eddy diffusivity theory. For chemical solvents with moderately fast kinetics in the pseudo-first order reaction regime, $\xi \approx 0$, which is consistent with the earlier finding that liquid mixing will have little effect on these systems. However, for solvents in a more general second-order regime, increased mixing is useful for solvents with either very slow or very fast kinetics. For slow solvents, mixing assists transport of unreacted molecules to the bulk, while for fast solvents, mixing assists transport of reactive species in the liquid to the surface.

**Solvent Impregnated Polymers for CCS**

A major challenge with the MECS motif is the manufacture of the particles on an industrial scale as, at present, they are manufactured in microfluidic devices at the rate of a few grams per hour. In this work, a novel and more scaleable means of immobilising liquid solvents inside high surface area solids is presented: solvent impregnated polymers (SIPs).

The manufacture of SIPs follows a simple, three stage process. First, a concentrated (typically 50/50wt%) solvent-in-polydimethyl siloxane (PDMS) emulsion
is created via shear emulsification. Second, this emulsion is either cast as a thin film or dispersed as a double emulsion to create fine particles. Third, the PDMS is crosslinked \textit{in situ} via heat or UV-light, in order to create a solid gel material, in which microscopic droplets of liquid solvent are embedded within a PDMS matrix.

SIPs containing potassium carbonate solutions, an ionic liquid, and a nanoparticle organic hybrid material (NOHM) were synthesised, and the SIPs containing potassium carbonate solutions were stable in a humid gas stream, and through multiple CO2 absorption/regeneration cycles. SIP layers as thin as 200 µm were manufactured, and these materials have surface areas comparable to MECS.

A model for mass transfer into SIPs was developed from first principles, and was in good agreement with experimentally measured uptake curves into SIPs containing K2CO3 solutions. Non-dimensionalisation of the model revealed that, for chemical solvents which would typically operate in the pseudo-first order regime, immobilisation of the solvent inside a SIP material would, under a range of practical conditions, increase the average gas flux into the material by a factor of 2 – 4. This increase was made possible by the very high CO2 permeability of the continuous PDMS phase, which is approximately two orders of magnitude greater than in most solvents for CCS, and provides a low-resistance pathway for CO2 to tunnel into the material and react with the immobilised solvent droplets. Initially, the flux into a SIP can be 1 – 2 orders of magnitude greater than the flux into a MECS or neat liquid, but the formation of a saturated zone near the material surface quickly slows down absorption. This saturated zone does not form inside MECS containing solvents in the pseudo-first order reaction regime, and this tradeoff between enhanced permeability increasing the flux and the formation of a saturated zone decreasing the flux leads to the more modest increase of 2 – 4 in the average flux over an entire absorption run. On the other hand, immobilising chemical solvents which exist in the diffusion-with-instantaneous reaction regime can lead to much greater enhancement in the average flux, as such solvents are already limited by diffusion through a saturated zone, and in this case the average gas flux approximately increases in proportion
with the square root of the permeability. These effects were demonstrated experi-
mentally using SIPs containing NOHMs, which are strongly diffusion limited. For
these materials, a 50-fold increase in the gas flux was observed, relative to a neat
liquid (the same improvement would also be expected relative to a MECS particle).
When combined with a 1-2 order of magnitude increase in the specific surface area,
SIPs containing such solvents could reasonably be expected to provide an increase
in the specific absorption rate of over three orders of magnitude.

Mass transfer into NOHMs was in good agreement with a simpler, diffusion-
limited version of the more general mass transfer model which had been previously
generated. This model required much less information about the specific chem-
istry inside the immobilised solvent droplets (such information was not available for
NOHMs) and was numerically simpler to evaluate. By non-dimensionalising each
model, it was shown that the simpler model will give identical predictions to the
complex model for the large majority of SIPs which would occur in practice.

**Thermodynamic Analysis of SIPs/MECS**

Throughout the development of SIPs and MECS, the hope that they could enable
the use of solvents with superior thermodynamic properties has repeatedly been
expressed. Water-lean solvents such as ionic liquids or CO₂-binding organic liquids
may lead to reduced sensible heat and evaporative loads during solvent regenera-
tion. However, in recent years, the sophistication and efficiency of amine-based CCS
processes has improved markedly, to the point where there is, at present, relatively
little room remaining for further thermodynamic improvements. Furthermore, while
SIPs and MECS could allow thermodynamically efficient solvents to be used in CCS
processes, they are also likely to have relatively poor sensible heat recovery effi-
ciencies. The heat load of the cross heat exchanger in a CCS process is typically
several times larger than the head supplied within the stripper, and so even a small
decrease in sensible heat recovery efficiency could have detrimental effects on the
thermodynamic performance of the process. In this final body of work, the energy
savings that an optimised SIP or MECS based process could *in principle* achieve were evaluated.

An idealised equilibrium model of a CCS process utilising SIPs or MECS was developed. Equilibrium, counter-current contacting was assumed in the absorber, and the sensible heat recovery efficiency in the cross heat exchanger, $\lambda$, was treated as a variable within the system. Both aqueous and non-aqueous solvents were considered. Several different idealised stripper arrangements were modelled, including regeneration in pure CO2 (in either a single stage or multiple stages of varying pressure) and regeneration using steam in a stripper with multiple equilibrium stages. The vapor-liquid equilibrium for each solvent was modelled via an ideal solution model, though the standard entropy and enthalpy of absorption and the reaction stoichiometry itself were all variables within the system. For each idealised process, and for a given value of $\lambda$, the minimal equivalent work requirements were optimised *over all operating conditions* and *over all thermodynamic properties of the solvent*. These were then compared with the equivalent work requirements of a simple stripper and an advanced flash stripper using piperazine, taken from the recent work of Lin and Rochelle [*Chem. Eng. J.*, 283, pp.1033-1043 (2016)].

For the aqueous solvent, the equivalent work requirements (for optimised process conditions and solvent properties) asymptoted to the work requirements of a simple stripper using piperazine (but performed worse than an advanced flash stripper) if sensible heat recovery of 90% were achievable. The good agreement with the simple stripper is unsurprising, as a number of studies have shown that amines are close to optimal for carbon capture, and no attempt was made to recover the lost work associated with steam exiting the stripper. If this heat could be fully recovered, the optimised MECS process would be competitive with an advanced flash stripper, but would be unlikely to outperform it. Furthermore, while 90% sensible heat recovery is reasonable in an aqueous amine system, such an efficiency is unlikely to be possible in a solid-solid system, especially in processes operating below 100°C. If a lower heat recovery is assumed, the optimised SIPs or MECS process fails to outperform
even the simple stripper.

For non-aqueous solvents regenerated in pure CO\textsubscript{2}, there are no energy losses associated with the condensation of steam exiting the stripper. However, the very large partial pressure of CO\textsubscript{2} in the regeneration unit requires a very large change in the partial pressure with temperature, and, because of the Gibbs-Helmholtz equation, this is only achievable for non-aqueous solvents with very large enthalpies of absorption. Furthermore, there is evidence in the literature to suggest that the negative entropy of absorption into various ionic liquids is smaller than that in aqueous amines, and is dominated by the phase change of the CO\textsubscript{2} molecule. Using the small negative entropies found in the literature, sufficiently large enthalpies of absorption cannot be used without absorption becoming an effectively irreversible process.

When restrictions were placed on the magnitude of the negative entropy of absorption into the non-aqueous solvent, the optimised process was only able to outperform the advanced flash stripper with unrealistic sensible heat recovery efficiencies on the order of 92 – 96 %.

When the restrictions on the negative entropy of absorption were lifted, the energy efficiency of the process improved, however even in the best possible cases, in which the negative entropy of absorption exceeded the values found in any other solvents, and in which multiple regeneration stages were used in order to produce a high-pressure CO\textsubscript{2} stream in order to reduce compression duties, with 80% sensible heat recovery efficiency, the total equivalent work of the SIPs or MECS process would be at best \(\sim 10\%\) less than for an advanced flash stripper.

These findings are a reflection of the excellent thermodynamic efficiency of modern amine processes, and the very small amount of room they leave for improvement.

Several other processing configurations are discussed, including vacuum regeneration and regeneration of non-aqueous solvents using various stripping agents to reduce the CO\textsubscript{2} partial pressure during regeneration. However, such measures are unlikely to lead to processes with equivalent work requirements substantially less than those in an advanced amine system. The use of SIPs or MECS containing solvents which may be regenerated using low-grade waste- or electrically-generated
heat is discussed.

Finally, the relationship between the standard entropy and enthalpy of absorption in an ‘optimal’ chemical solvent is discussed. It is shown, through theoretical calculations, optimised process simulations, and comparison with solvents used in practice, that an optimal solvent must have a sufficiently large enthalpy of absorption (to facilitate the pressure swing the temperature) coupled with an appropriately sized entropy of absorption, in order to balance enthalpy and ensure the absorption is reversible at operating temperatures and pressures. While the role of an appropriate enthalpy of absorption is widely acknowledged within the literature, the need for a balancing entropy of absorption has not been stressed in the same way. It is argued that ionic liquids with small negative entropies of absorption (as is common in practice) are unlikely to lead to energy savings in a practical process.

**Key Findings**

- The flux of gas into MECS containing concentrated chemical solvents in the pseudo-first order reaction regime is likely to be comparable to the flux of gas in an absorption column.

- The flux of gas into MECS containing physical solvents may be larger than in an absorption column.

- An order of magnitude increase in the specific absorption rate can be expected for MECS containing concentrated chemical solvents in the pseudo-first order regime, and a two order of magnitude increase may be achievable when encapsulating physical solvents.

- The surface area increase which MECS can provide over a traditional absorption column is roughly 4 times smaller than earlier estimates [3] had suggested, though the increase in area will still exceed an order of magnitude for fine MECS particles.
• A sensitivity to liquid mixing, $\xi$, is introduced, and is used to evaluate the potential benefits of increased mixing in a number of solvent systems. Increased mixing will increase the gas flux for solvents with very slow and very fast (i.e. instantaneous) kinetics, but not for solvents in the pseudo-first order reaction regime.

• A new material, solvent impregnated polymers (SIPs), is proposed for carbon capture. These have surface areas similar to MECS, but are much simpler to manufacture and have enhanced mass transfer properties.

• Several SIPs are synthesised containing a range of solvents, including various carbonate solutions, an ionic liquid, and a nanoparticle organic hybrid material.

• SIPs containing carbonate solutions were stable in a humid environment, and also over multiple stages of absorption and regeneration.

• A model for mass transfer into SIPs was developed, and shown to be in good agreement with experimental data.

• Non-dimensionalisation of the model revealed that, because of the large permeability of the continuous PDMS phase, SIPs could be expected to increase the gas flux. An increase by up to a factor of 4 is expected for solvents in the pseudo-first order reaction regime, while much greater increases may be achievable for solvents in the instantaneous reaction regime.

• Mass transfer experiments into a SIP containing a nanoparticle organic hybrid material for direct air capture showed a remarkable 50-fold increase in the gas flux, relative to the neat liquid (the NOHM absorbed $\text{CO}_2$ via an instantaneous reaction mechanism.) As in the MECS motif, this increase in the flux could be complemented by an increase in the surface area of the material.

• The mass transfer model was shown to collapse to a simple, diffusion-limited model for the large majority of SIPs which could be used in practice. This
model predicted the absorption rate into the SIP containing NOHMs with reasonable accuracy.

- A theoretical analysis of SIPS and MECS containing various aqueous and non-aqueous solvents in an idealised post-combustion CCS process found that relatively minimal energy savings could be expected, even if optimal solvent properties and process conditions were selected. This was primarily due to the very high efficiency of existing, optimised amine systems (which leave relatively little room for improvement) and the relatively poor sensible heat recovery efficiency achievable using solid-solid systems.

- A theoretical analysis of the ‘optimal’ solvent for carbon capture found that optimal solvents must strike a balance between the enthalpy and entropy of absorption, in order to ensure absorption is reversible over the pressure and temperature ranges which occur within a process. The results suggest that ionic liquids with relatively small negative entropies of absorption are unlikely to be optimal for carbon capture.

- An extensive list of recommendations for future work was prepared, and is presented in Section 6.2 of this thesis.
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1 Introduction

Carbon capture and storage (CCS) is a key technology for the reduction of greenhouse gas emissions and for the removal of CO₂ from the atmosphere [4]. At present, the best developed technologies for CCS use aqueous amines such as monoethanolamine or piperazine to capture CO₂, which is then stripped from the solvent using steam [32]. However, a large number of other technologies are under ongoing development, including alternative non-aqueous or precipitating solvents [33], solid sorbents [34], membrane processes [35], chemical looping combustion [36] and oxyfuel combustion [37] (see Chapter 2 for a more complete review.)

Microencapsulated Solvents (MECS) are a new approach to carbon capture, which may reduce unit operation volumes and allow slow, precipitating or viscous solvents to be used in a practical way [3]. MECS are small capsules, a few hundred microns in diameter, with a thin polymer shell and a liquid core composed of a solvent (such as aqueous monoethanolamine, or an aqueous K₂CO₃ solution) which selectively absorbs CO₂ (see Figure 1.1). The specific surface area of these capsules is 10 – 100 times greater than the specific surface area of a liquid in a traditional absorption column, and if the shell is composed of a polymer which is permeable to CO₂ (such as polydimethyl siloxane (PDMS)), this increase in area could be expected to lead to a 1 – 2 order of magnitude increase in the specific gas absorption rate. It is hoped that MECS may allow novel solvents to be used for carbon capture, leading, ultimately, to smaller unit operations and reduced energy loads and costs.

1.1 Overview of Thesis

This thesis focusses on several aspects of MECS and related technologies, which we refer to collectively as ‘immobilised solvent systems’. The chapters of this thesis cover a range of interrelated topics. In chapter 3, the enhancement in flux which MECS could provide is evaluated; in chapter 4 the question of upscaling the manufacture of these materials is tackled; finally, in chapter 5, the energy savings these materials could deliver is assessed. While it is difficult to suggest a single research
question governing the entirety of this work, the common goal throughout has been to answer practical questions about MECS, and to seek practical solutions where possible.

In the literature review, a discussion of climate change and recent developments in CCS deployment and research provide important context for the development of MECS. The literature on MECS (which has grown rapidly in the last few years) and similar composite sorbent materials is then reviewed.

Chapter 3 focusses on the fundamental absorption kinetics into MECS. It seeks to quantify, in a rigorous way, whether the increase in surface area in MECS is likely to lead to a commensurate increase in mass transfer rates. It is not obvious that this will be the case, as the lack of liquid mixing inside the capsules, the presence of the shell, and the transition to a reaction-limited regime may all limit the increase in flux MECS may provide. The chapter ends with a broader discussion on the role of liquid mixing in increasing the gas flux into chemical solvents, the results of which may be applied to a number of technologies beyond microencapsulation.

Chapter 4 moves from the micro-scale to the bench-scale, and discusses whether MECS, or a material like them, could be manufactured in a more scaleable way. MECS are currently manufactured at a rate of a few grams per hour, and the cre-
ation of many tonnes of MECS (as would be required for a practical CCS operation) may prove prohibitively difficult. In this chapter, a novel material for CCS, ‘solvent impregnated polymers’ (SIPs), is proposed. SIPs are a gel material, rather than a capsule, and are manufactured via a simple, one-pot method which is much more scalable than the manufacture of MECS. They may have surface areas comparable to MECS, and their structure is shown to enhance the gas flux by up to 50 times, relative to a neat solvent or a MECS particle. The immobilisation of a number of liquid solvents is demonstrated, including several potassium carbonate solutions, an ionic liquid, and a nanoparticle organic hybrid material. The development, validation, simplification and analysis of models for mass transfer into SIPs forms a large portion of this chapter.

Chapter 5 considers the use of SIPs and MECS on an industrial scale, and discusses whether these technologies could be expected to lead to significant energy savings, relative to a modern, amine based process. An idealised SIP or MECS based process is analysed, and both process conditions and the thermodynamic properties of the solvent are optimised in order to minimise the equivalent work requirements. The various simplifications within the analysis consistently favour SIPs and MECS, so these calculations put an upper bound on the efficiency gains these technologies could allow. This chapter ends with a broader discussion on the interrelated roles of the standard enthalpy and standard entropy of absorption in an ‘optimal’ solvent for CCS.
2 Literature Review

2.1 Overview

This thesis focusses on two hybrid materials for carbon capture - Microencapsulated solvents (MECS) and Solvent Impregnated Polymers (SIPs) - which, in a sense, combine each of the major strands of carbon capture into a single technology. They have the thermodynamics and kinetics of liquid solvents, the unit operation and materials handling characteristics of solid adsorbents, and shells or supports made from popular membrane materials. Compounding this, this thesis will discuss the details of mass transfer into traditional absorption columns, the effect of liquid agitation on absorption kinetics, the synthesis and stability of concentrated emulsion and gel systems, the exergetic efficiency of existing carbon capture processes, and the search for an optimal solvent for carbon capture. It will not be possible to review all of the literature relevant to each of these topics within this section.

This section begins with a discussion on the role of carbon capture as a CO₂ mitigation strategy, before an overview of existing technologies and the various challenges they face is provided. After this, Microencapsulated Solvents (MECS), which form the impetus (if not the eventual bulk) of this work, are introduced. The literature on MECS has grown very quickly since the seminal Nature Communications article of Vericella et al. [3], and a number of non-trivial (and non-obvious) problems with the technology have become apparent. Various competing solid-sorbents for carbon capture are then discussed, before the literature on the chemistry and kinetics of CO₂ uptake into concentrated K₂CO₃ solutions, which are modelled in both Chapter 3 and Chapter 4 of this work, is reviewed.

2.2 Climate Change and Global CO₂ Emissions

In 2018, the International Panel on Climate Change (IPCC) released a special report, at the request of the 21st Conference of Parties of the United Nations Framework Convention on Climate Change to adopt the Paris Agreement, entitled ‘Global
Warming of 1.5 °C’ [39]. This report systematically outlined the effects of increased global warming from 1.5 °C (the aspirational target of the Paris agreement) to 2 °C. It discussed the negative effect of climate change on the frequency of extreme weather events, sea level rise, agricultural production, wildfires, access to fresh water, ocean acidification, sensitive ecosystems, the spread of disease, heat-related morbidity and mortality, migration, conflict, and many other systems. The world is on track for well over 2 °C of warming [40], however the IPCC concluded that even this will leave ‘greater proportions of people exposed and susceptible to poverty in Africa and Asia’ and that ‘risks across energy, food, and water sectors could overlap spatially and temporarily, creating new – and exacerbating current – hazards, exposures, and vulnerabilities that could affect increasing numbers of people and regions (medium confidence).’ Small island states and economically disadvantaged populations are particularly at risk (high confidence).’ [39]

Countless papers have been published on the science of climate change and its (predominantly negative) impacts, going back to the classical calculations of Arrhenius [41]. Unfortunately, it is impossible to discuss this field here. The interested reader is referred to the aforementioned IPCC special report on 1.5 °C of Global Warming [39], and the three AR5 reports, published again by the IPCC in 2013 – 2014 [40, 4, 42]. These provide an excellent, authoritative and readable summary of the physical science, the human impacts, and the available mitigation and adaptation strategies. For a deeper discussion on the moral nature of the climate change crisis, see [43, 44, 45].

Even as scientists, policy makers and the general public have become aware of the magnitude of the threat of climate change, relatively little concrete action has been taken to reduce emissions of greenhouse gases, which continue to accelerate (total greenhouse gas emissions increased by 1.6% in 2017, and another 2% in 2018 [46]). Over 40% of all emissions from the burning of fossil fuels have been released since the establishment of United Nations Framework Convention on Climate Change in 1992 [46]. Deep cuts are difficult, as emissions are embedded in many disparate parts of
the global economy. This is best illustrated by the Sankey diagram shown in Figure 2.1, which is based on the paper of Bajzelj et al. [5]. Significant greenhouse gas emissions are associated with food production, heating, transportation, electrical power, industrial activities, and many other sectors (see also Figure 2.2, in which total greenhouse gas emissions are broken down by sector.) Unfortunately, efforts to constrain emissions across an entire economy (whether through a carbon tax, a carbon trading scheme, or otherwise) have proven politically unpopular [47]. Climate action is further complicated by the fact that unilateral action by one country may leave it at a competitive disadvantage against economies with less stringent restrictions [48]. International treaties, meanwhile, are non-binding at present, and will not succeed in meeting their stated temperature targets if they are not drastically ramped up [49]. The future trajectory of global emissions is deeply and disturbingly uncertain at present.

2.3 The Application of Carbon Capture and Storage

One means of reducing global CO₂ emissions is carbon capture and storage (CCS), whose main areas of application are:
Figure 2.2: Breakdown of total greenhouse gas emissions by sector. AFOLU refers to emissions due to agricultural, forestry and other land use changes. ‘Industry’ refers to industrial emissions, of which roughly 2/3 are not directly due to heat or electricity production. Sourced from [4].

- The supply of carbon-neutral baseload power when coupled with fossil fuels.
- The reduction of emissions from industrial sources, such as steel or cement manufacturing.
- Negative emissions technologies.

The future role of CCS in supplying baseload power is unclear at present. While the technology is well developed, without a carbon tax or other financial incentive (such as the use of CO₂ in enhanced oil recovery) CCS is a purely loss-making enterprise, which no company could be expected to engage in. The development of a centralised system of gas pipelines and storage sites will also require significant financial incentives, and the lack of such systems in many countries is a hurdle the technology must overcome [50]. CCS also has a scale problem: while $50 million could be used to build a ‘full scale’ solar plant which supplies carbon-neutral electricity to the grid, a significantly greater investment would be required to build a ‘full scale’ post-combustion CCS facility on a coal-fired power plant. Even if CCS is competitive, or cheaper, on a per-tonne of CO₂ basis, the high cost-of-entry is a
major obstacle (especially, again, without a universal carbon tax.) The failure of several prominent CCS demonstration plants [51], the cancellation of a number of high-profile sources of funding [52], and the promotion of ‘clean coal’ by groups otherwise opposed to climate change action have all harmed the technology’s reputation [53]. Finally, the drastic fall in the cost of renewable energies, and particularly solar and wind, has arguably undercut some of the economic arguments for CCS, especially given that further price drops are predicted over the coming decade [54]. At present, the development of renewable energy is on track to meet the targets of the Paris agreement, while CCS is not [55]. Of course, renewable energy and storage technologies have their own issues. The diffuse nature of renewables means that many countries simply don’t have enough land area to supply their own power [56]. The possibility of capturing sunlight on farmland (using solar collectors which allow photosynthetically-relevant light to pass through to the crops below) is a plausible means of overcoming the land-limitation in many countries [57], but such technologies are still in their infancy. Another possibility is for renewable-rich countries such as Australia to export renewable energy in the form of liquid fuels such as H₂ or NH₃. However, like CCS, this is only feasible with a sufficient economic driving force [58]. Grid-scale storage also remains expensive, though a number of promising technologies are under active development [59, 60]. Overall, the relatively slow market infiltration of CCS relative to renewables, the scaleable nature of renewable infrastructure, the tendency of governments to use incentives and rebates rather than to allow market forces to select the cheapest options, and the continued decrease in the cost of renewables all suggest that the role of large-scale CCS in supplying carbon-neutral baseload power may be smaller than has been previously projected [61].

The role of CCS in reducing emissions from industrial processes such as steel or cement manufacturing is much clearer, as, in many cases, it is the only viable means of significantly reducing the technology’s emissions. Whether CCS will actually be applied to these technologies depends largely on whether appropriate economic
incentives can be put into place. As previously noted, there is a disincentive for individual countries to tax industrial carbon emissions, and global, industry-wide solutions may be required, though these may be difficult to achieve in practice. Nevertheless, there has been significant research on processes specifically designed to capture carbon from the flue gases of cement and steel plants [62].

Negative emissions technologies are another application area of CCS, though these technologies are largely unproven at scale. The most prominent approaches are direct capture of CO₂ from air (DAC), capture and storage of CO₂ from the combustion of biological materials (BECCS), and mineral weathering. DAC is the subject of a great deal of research and development [63, 64, 65] however the seminal paper of House et al. [64] argues that DAC is likely to cost about $1000/tonne of CO₂, several times the projected cost of a number of new technologies. Certainly, if CCS from concentrated carbon sources is currently proving uneconomical, it is unclear why capture from air should be expected to be economical in the near future. The viability of BECCS is also unclear at present, and issues remain around land-use and fugitive emissions [66]. A recent paper [67] on hydrogen production via renewably-sourced electricity combined with enhanced mineral weathering suggested costs as low as $3/tCO₂, though these numbers seem rather hard to believe at present.

The uncertainty in the development of negative emissions technologies is deeply concerning, as the majority of models proposed by the IPCC require the development of a large-scale negative emissions industry (on the same scale as the present-day oil and gas industry) in the second half of the 21st century, in order to reach a 2°C temperature target [68, 69, 6]. The large scale of the projected negative emissions is shown in Figure 2.3. Even if the world follows a pathway with only a fraction of the negative emissions the IPCC projects, CCS will still play a very large role in controlling global CO₂ levels.
Figure 2.3: Median behaviour of all scenarios from the IPCC’s AR5 report [4] which limit the global temperature to 2°C with 66% likelihood. Figure taken from [6].

2.4 Technologies for Carbon Capture and Storage

A wide range of technologies are available for CCS, and they cannot all be discussed in depth here. For more details, the interested reader is directed to the recent review of Bui et al. [32] (whose extensive list of authors spans the entire field) and the excellent textbooks of Smit et al. [70] and Wilcox [71].

Broadly speaking, CCS technologies may be broken down into solvent, adsorbent, and membrane-based processes, and are also often divided into post-combustion capture (i.e. capture from the flue gas of a process) and pre-combustion capture (i.e. capture prior to combustion, typically from a pressurised syngas stream.) Other options include chemical looping combustion [36], in which oxygen for combustion is supplied by oxidised solids in a high-temperature fluidised bed, and oxyfuel combustion [37, 72], in which combustion occurs in a pure O₂ environment. Both of these technologies lead to the production of pure CO₂ streams, and may also be more thermodynamically efficient if issues with material selection can be overcome [73, 74].

An excellent (if slightly dated) review on polymeric membranes for post-combustion CCS is given by Powell and Qiao [35]. In this thesis, dense polymeric membranes
with high CO₂ permeabilities will be sought (selectivity is less important for MECS and SIPs) and in reviewing several hundred polymers, Powell and Qiao [35] found that polydimethylsiloxane (PDMS) had among the highest CO₂ permeabilities (its CO₂ permeability is around 3000 barrer; the only polymers with greater permeability were polyacetylenes such as poly(1-trimethylsilylpropyne), with permeabilities up to 28 000 barrer, though these are less stable than PDMS [35]). Unfortunately, the permeability of CO₂ through polymeric membranes often decreases in the presence of N₂. For example, Scholes et al. [75] observed a 2 – 3 fold decrease in the CO₂ permeability between a pure CO₂ system and a 90% N₂/10% CO₂ mixture.

A large number of solid sorbents are being developed for CCS, including zeolites, silica materials, metal-organic frameworks (MOFs) and activated carbons. A comprehensive review is provided by Lee et al. [34], and an interesting perspective was written by Webley [76]. Various composite solid sorbents will be discussed in section 2.6.

A very large number of liquid solvents are available for post-combustion CCS. The most prominent is 30wt% monoethalamine (MEA), which, for many years, was the de facto standard against which all hypothetical solvents were compared [70]. More recently, concentrated piperazine systems, with various innovative process designs, have been proposed as the new ‘standard’ for the state-of-the-art [77], though 40wt% MEA (with various additives) has also been investigated [78]. Aqueous carbonate solutions have also been investigated for carbon capture [79, 80, 81]. These have lower enthalpies of absorption than amines (though this isn’t necessarily an advantage, see [82]) and precipitation of KHCO₃ may be exploited to reduce the reboiler duties during regeneration if handling issues can be overcome [83]. A disadvantage of carbonate systems is their relatively slow absorption kinetics, and the development of promoters for these systems is an active field of research [84, 85]. Another area of research is non-aqueous solvents, including ionic liquids which absorb CO₂ physically or in which CO₂ reacts with various functional groups [86], CO₂-Binding Organic Liquids (CO₂BOLs) [87, 88] or Nanoparticle Organic Hybrid
Materials (NOHMs) [89]. Non-aqueous solvents may have reduced sensible heat duties (as their sensible heat capacities are typically roughly half that of H₂O) and may have reduced reboiler duties as there is no evaporation of water from the top of the stripper. Another active area of research is phase-change solvents, in which the absorption of CO₂ induces the formation of either a multiphase liquid-liquid or solid-liquid system, such that the majority of the absorbed CO₂ is stored in only one phase. An advantage of these systems is that only the CO₂-rich phase needs to be regenerated, which may reduce the sensible heat losses if a high sensible heat recovery efficiency can be maintained. Heldebrant et al. [33] provided a comprehensive review and assessment of non-aqueous solvents for carbon capture, which ultimately concluded that such systems have the potential to be more efficient than aqueous solvents. However, this has not been without controversy, as other researchers have pointed out that concentrated aqueous amine systems with integrated recovery of the heat of condensation are already approaching the thermodynamic optimum, once the minimal energy for separation and compression and the unrecovered exergetic losses in the absorber are accounted for [27].

This final point deserves further attention, as it is directly relevant to the various immobilised solvent systems discussed in this thesis, and in the author’s opinion it has not been fully appreciated by parts of the CCS community. In 2009, Knuutila et al. [90] published an interesting study on the use of sodium carbonate slurries for CO₂ capture, and argued that such systems could reduce the energy requirements from 3.8 GJ t⁻¹ of CO₂ captured (then a standard value cited for concentrated MEA systems; the US Department of Energy suggested 3.6 GJ t⁻¹ in 2010 [91]) to 3.22 GJ t⁻¹ of CO₂ captured. At the time, this appeared to be a reasonable improvement. However, in the last few years, the development of concentrated amine systems and various sophisticated stripper designs (which allow for the direct production of high pressure CO₂ (reducing compression duties) and recovery of the lost work of condensation) have drastically reduced this number. In 2016, Lin et al. [27] predicted that a process utilising concentrated piperazine with an Advanced
Flash Stripper could have a heat duty as low as 2 GJ t\(^{-1}\) CO\(_2\), and a later pilot plant operation [92] reported operational heat duties of 2.1 GJ t\(^{-1}\) - over 40% less than the standard value from 2010. Even greater efficiencies have been found in simulations of an Advanced Flash Stripper with aqueous ammonia [93, 94], though these have not been tested at a pilot-plant scale. Similar efficiencies have also been claimed for carbonate systems [32], though it is unclear if these can be achieved in practice, as the low heat of absorption may prevent production of a high-pressure CO\(_2\) stream from the stripper [95]. Other amine processes have also claimed regeneration energies as low as 2 GJ t\(^{-1}\) (see Table 4 of [32]) though again it is unclear whether these can be realised in practice. In any case, the value of 2.1 GJ t\(^{-1}\) (or, more precisely, 32 kJ of equivalent work per mol of CO\(_2\) captured) which has been demonstrated at pilot scale is already close to the thermodynamic optimum: Lin et al. [27] reported a remarkable 74% thermodynamic efficiency for the solvent regeneration process, and estimated that the overall thermodynamic efficiency of the whole process exceeded 50%. Remaining thermodynamic inefficiencies are largely associated with the low-temperature exothermic reactions in the absorber, which will be difficult to recover as the lost work is of so poor quality, and remaining inefficiencies in the cross-heat exchanger, which will also be difficult to reduce. Existing processes leave remarkably little room for optimisation and improvement.

The rapid improvement of amine systems over the last 10 years has arguably rendered much of the research into alternative solvents of more questionable value. It is unfortunate that, rather than acknowledging this challenge, recent papers and reviews in the water-lean solvent literature consistently continue to reference older papers and quote the value of 3.6 GJ t\(^{-1}\) of CO\(_2\) from the USDOE referenced above, without acknowledging that modern amine systems use over 40% less energy [33, 96, 97]. This makes it difficult to fairly evaluate various solvents, accounting for energy use, cost, stability, toxicity, and other relevant factors. The efficiency of amine systems also brings into question the persuasiveness of the arguments in favour of the immobilised solvents discussed in this work, as early calculations on
their potential energy savings also cited the USDOE estimates [98], and the rapid development of amine systems has left relatively little room for improvement that these systems could exploit. The implications of this will ultimately be discussed in Chapter 5 of this thesis.

2.5 Microencapsulated Solvents for Carbon Capture.

Microencapsulated Solvents (MECS) are a relatively new approach to carbon capture, first developed in a series of papers by a research group centred at Lawrence Livermore National Laboratory [3, 99, 100, 101]. In this technology, small capsules (100 – 500 µm in diameter) are manufactured with a thin (10 – 50 µm) polymer shell and a liquid core containing a solvent which selectively absorbs carbon dioxide (see Figure 2.4). Various solvents have been successfully encapsulated, including concentrated K2CO3 solutions [3], and various ionic liquids and CO2-binding organic liquids [100]. The most common shell material is PDMS, which, as mentioned above, has a very large CO2 permeability, though other shell materials have been used [100, 101]. MECS may be used to encapsulate solvents which are too viscous, volatile or corrosive to be used in a traditional process, such as various ionic liquids and highly concentrated amine solutions. They may also be used to encapsulate precipitating solvents, which may otherwise be difficult to handle. Finally, the very large surface areas of MECS (1-2 orders of magnitude greater than in a traditional absorber [3, 38]) may increase gas uptake rates, which in turn may substantially reduce unit volumes, and allow solvents which absorb CO2 slowly to be used in a practical way. Preliminary mass transfer experiments by Vericella et al. [3] demonstrated that a simple reaction-diffusion model can successfully predict uptake rates into MECS, and showed that, at least for MECS with a PDMS shell containing dilute K2CO3 (a relatively slow solvent) resistance in the PDMS shell is not rate limiting.

A major challenge with the MECS motif is the upscaling of the manufacture of the particles to industrial scales. MECS were originally manufactured in mi-
crofluidic devices assembled by hand (see Figure 2.5). These devices, which were first developed by Utada et al. [7], may be used to produce a continuous stream of monodisperse, double-emulsion droplets. When manufacturing MECS, the inner fluid is a solvent for CCS, the middle fluid is a UV-curable PDMS, and the outer fluid is an aqueous solution. After the monodisperse W/O/W emulsion has been manufactured, it is exposed to high-intensity UV light in order to cure the PDMS and create solid capsules. The microfluidic device may be used to manufacture up to \( \sim 100 \) droplets per second, however this only corresponds to a rate of a few grams of MECS per hour. Various approaches are available for upscaling the manufacture of microcapsules, including membrane emulsification [102], emulsion ripening [103] and liquid marbles [104]. An alternative approach is the creation of high-surface area gel materials via single-emulsion methods; this forms a large part of this thesis (see Chapter 4 and [105]) and similar materials have been developed independently by researchers at Lawrence Livermore [106].

A large number of papers on MECS have emerged in the years following the original *Nature Communications* article of Vericella et al. [3]. The popularity of MECS can probably be attributed to the fact that they are seen as an *enabler* for the many non-aqueous solvent systems which have been developed in recent years.

Several articles have reported on the encapsulation of novel solvents for carbon capture. After their original paper [3], which discussed the encapsulation of
various K₂CO₃ solutions, the group at Lawrence Livermore have reported the encapsulation of various ionic liquids, CO₂-BOLs, and Na₂CO₃ solutions promoted with cyclen and sarcosine [100, 107]. In order to produce stable MECS, they were forced to develop several new shell formulations, including a PDMS mixture with a UV-catalysed thiolene crosslinking mechanism, which was able to crosslink in the presence of solvents containing amine groups, and an acrylate mixture they termed ‘SiTRIS’. The acrylate mixture was more stable for some systems, however its CO₂ permeability was 400 barrer (almost 10 times smaller than the PDMS), and in a later work they found this shell material to be rate-controlling for a number MECS containing ionic liquids [101]. Knipe et al. [107] also showed that MECS containing ionic liquids and Na₂CO₃ solutions were stable over multiple cycles of absorption and regeneration, however MECS containing the CO₂-BOL tended to leak fluid over time. Other groups have also developed novel MECS systems. Wang et al. [108] reported the encapsulation of nanoparticle organic hybrid materials (NOHMs) inside a PDMS shell. They were able to accomplish encapsulation using a printed PDMS chip (rather than a hand assembled microcapillary device) and developed a computational fluid dynamics (CFD) simulation to aid in the design of the chip. The MECS absorbed CO₂ 10 times faster than a neat NOHM liquid. Recently, Yew et al. [109] have demonstrated the production of MECS using an ‘off-the-shelf’ microfluidic device, which may be much simpler to assemble than those considered by Vericella et al. [3]. They were able to synthesise MECS with diameters
of 600 μm and shells as thin as 20 μm. These shell thicknesses are comparable to those reported by Vericella et al., and are much thinner than those achieved by other simplified methods of creating microcapsules [110]. Song et al. [111] demonstrated the microencapsulation of ‘tunable’ and phase-change ionic liquids, similar to those developed in a series of papers by Seo et al. [112, 28]. They showed the MECS were stable over ∼10 cycles of absorption and regeneration. Nabavi et al. [113] synthesised MECS containing K2CO3 solutions with concentrations ranging from 5-30 wt%, and analysed several fundamental aspects of the capsules. After analysing the particle morphology via SEM, they developed and validated a simple model for the osmotic swelling of the particles when placed in water. They discussed the optimal parameters and methods for UV-curing of the silicone, and also showed that the capsules could be fully regenerated even after exposure to temperatures as high as 460 °C. Finally, they showed that the microfluidic device could produce uniform particles for time periods on the order of 50 minutes.

A number of authors have attempted to model the behaviour of MECS processes. In an early work, Raksajati et al. [114] developed a techno-economic analysis of a CCS process utilising MECS containing concentrated MEA solutions. They developed simple process simulations for MECS in fluidised bed and fixed bed absorbers, and found that the cost of the MECS system would be 1.6 – 2 times greater than that of a traditional MEA process, mainly due to membrane resistance, increased sensible heat losses (they considered a heat recovery efficiency of 60%), and increased equipment and capital costs. Of course, it could be argued that MEA is not the best solvent to encapsulate, given its large sensible heat capacity and intrinsically fast kinetics. However Raksajati et al.’s results are stronger than they initially appear, as their benchmark MEA case required 4.35 GJ t⁻¹ CO2 captured, and modern amine systems require less than half this much energy [92]. Furthermore, several simplifications within their model strongly favoured MECS. Most notably, the conversion in the fluidised bed containing MECS was based on a plug-flow assumption, which can overestimate conversion by up to a factor of 10000 [115].
A similar analysis was conducted by Hornbostel et al. \[116\], who developed a multi-scale model of a large-scale CCS process utilising MECS containing Na$_2$CO$_3$ solutions. They developed and experimentally validated a model for CO$_2$ absorption into Na$_2$CO$_3$ capsules, and suggested several innovative design ideas to reduce pressure drops within the process. They found that when ‘standard’ capsules (i.e. capsules which could currently be produced) were used, energy requirements were greater than those in an MEA process. However, when they considered ‘improved’ capsules, with smaller shell fractions and greater Na$_2$CO$_3$ concentrations, the energy requirements were less than those for an MEA process. While these results appear promising, this study also considered an MEA benchmark which required substantially more energy than a modern amine process. They assumed an equivalent work of 36 kJ mol$^{-1}$ CO$_2$ without compression of CO$_2$ to 150 bar; in a modern process, only 32 kJ mol$^{-1}$ of CO$_2$ is required for both capture and compression \[27\]. If this baseline is used, their MECS perform substantially worse than the amine-based process.

A number of researchers have analysed the fundamental mass transfer properties of MECS. Moore et al. \[38\] demonstrated that the gas flux into MECS containing concentrated chemical solvents will be similar to the flux in an absorber, despite the fact that the liquid inside the capsules is stationary (strictly speaking, this only held for chemical solvents in the pseudo-first order reaction regime). They also suggested that microencapsulation would be well suited to physical solvents, as in these systems the reduction in spatial scales would lead to an increase in both the surface area and the gas flux. Finn et al. \[117\] developed and validated a rigorous model for the transport of water across the shells of MECS containing carbonate solutions. They found that significant dehydration could be expected under absorber conditions, and rehydration in a humid gas stream will be difficult, as very fine control of the relative humidity will be required to prevent the capsules swelling or buckling. There is also some concern that the physical compression of the capsules, as would occur in collisions in a fluidised bed or at the bottom of a packed bed, could increase the
pressure inside the capsules and ‘squeeze’ the solvent out of them over time.

Wang et al. [118] built an Eulerian-Eulerian CFD model for MECS of various sizes in a single-stage fluidised bed. The bed was 6.8 m high and had a diameter of 1.3 m, and the capsules contained concentrated Na$_2$CO$_3$ solutions (the dynamics of CO$_2$ absorption and reaction were based on the model of Finn et al. [117].) Lean capsules were continuously fed into the bed (and saturated capsules removed) and the authors were interested in the bed’s steady-state behaviour. With 120 micron MECS, the single bed could capture almost all of the CO$_2$ from a flue gas stream flowing at 0.7 kg s$^{-1}$, though only 65% could be captured at a gas flow rate of 1.45 kg s$^{-1}$. The outlet solid conversion was not reported, but it is likely that multiple beds would need to be run in a counter-current operation in order to ensure large chemical conversion in the rich sorbent. One concern with their analysis relates to the underlying Eulerian-Eulerian model, which is based on the work of Sarkar et al [119], and does not account for the tendency of MECS to stick together. This is especially likely to be significant with smaller MECS, and may have a detrimental effect on the fluidisation. Nevertheless, this is still a striking result, as a traditional absorber containing an unpromoted K$_2$CO$_3$ solution would be over 100 m high [79]. This result probably represents the most compact carbonate-based CCS absorber ever rigorously modelled.

### 2.6 Composite Sorbents for CCS

Apart from MECS, several other composite sorbent systems have been developed which combine multiple carbon capture motifs in the one material. For example, facilitated transport membranes have been investigated for many years [120]. In these systems, liquid solvent droplets are immobilised inside a membrane material. The solvent enhances both the selectivity and the effective permeability of the membrane, as the solvent reacts chemically with the CO$_2$, which may then be transported in the form of the dissolved CO$_2$ molecules (as in all membranes) and also in the form
of the reaction products (such as bicarbonate ions), which may have solubilities\(^1\) many orders of magnitude greater than the physically absorbed CO\(_2\).

Solvent impregnated resins are another popular composite sorbent material. In these systems, a reactive solvent such as poly-ethylene amine (PEI) is immobilised inside a high surface area resin [121, 122]. Most commonly, the resin is soaked in the solvent for a period up to several days, and the liquid is held in place by physical adsorption and capillary forces. Many such resins have been manufactured, and they often have CO\(_2\) capacities comparable with aqueous amines [123, 124]. However, diffusion of CO\(_2\) through the impregnated solvent is often slow and rate-limiting, and leaching of the solvent has been reported in a number of studies [125]. Chemically tethering the solvent onto a silica or alumina support is one means of improving the stability, and this has been demonstrated for a number of systems [126, 127, 128]. Yet another possibility is to directly graft amine groups onto a porous polymer support [125].

In the literature, the relatively low heat capacity of these solid sorbents (typically around \(1.5\text{kJkg}^{-1}\text{K}^{-1}\) [125]) is often claimed as an advantage [126]. The essential idea is that water is a relatively inefficient ‘support’ for reactive amine groups, as its very large sensible heat capacity makes achieving a temperature swing difficult, and so, all else being equal, a low-\(c_p\) solid support would be superior. Of course, in practice what matters is not the total sensible heat of the sorbent, but the sensible heat that cannot be recovered from the hot, lean sorbent. It seems likely that heat recovery from solid sorbents will be substantially less efficient than from liquid solvents\(^2\), and if this is the case, the reduction in the total sensible heat may not lead to significant energy savings. A second advantage is the lack of evaporation of water during regeneration, however this is also less relevant, given the excellent recovery of this heat in modern processes [27]. A third potential benefit of these materials is that regeneration may occur at temperatures as low as 60\(^\circ\)C [129].

\(^{1}\)Of course, increasing the effective solubility will tend to increase the effective permeability.  
\(^{2}\)In a liquid, around 90\% of the sensible heat is recovered [70], while both [114] and [116] assumed 60\% recovery for a solid system. It may be possible to do a little better than this; see Chapter 5 of this thesis.
The possibility of using waste heat or a heat pump to regenerate the solvent could then plausibly lead to energy savings, and a number of systems have been proposed [130]. An issue with these technologies is that regeneration in pure CO₂ is relatively difficult because of the large CO₂ partial pressure, while regeneration in steam is impossible without pulling a strong vacuum. Vacuum-assisted steam regeneration has itself been proposed, with claimed heat duties as low as 1.5 GJ t⁻¹. However, these heat duties do not account for the work required to pull the vacuum [129, 130]. Another approach is to use a condensable stripping gas, such as pentane, to reduce the partial pressure of CO₂ above the sorbent [131]. However, this gas would need to be completely condensed out of the product CO₂ stream before being reboiled again. It will be difficult to recover the heat of condensation, as the stripping agent will only condense from the CO₂ at a temperature below its boiling point (compression of the entire stream could solve this, but will bring its own energy load.) Without clever process integration, it is likely that the energy required to boil the stripping agent will overwhelm any gains from using a superior sorbent.

A number of liquid solvents have also been developed which can be regenerated at temperatures as low as 50°C [132, 133, 134]. These solvents may have handling issues or slow kinetics, and the very large partial pressure swing with temperature implies (via the Gibbs-Helmholtz equation [82]) that the enthalpy required to drive the endothermic desorption of the CO₂ must be very large. Nevertheless, microencapsulation of such solvents would represent an alternative means of creating a solid sorbent which is regenerable at low temperatures. To the author’s knowledge this has not yet been demonstrated.³

Unfortunately, as has also been observed in the water-lean solvent and the MECS literature, even very recent papers which attempt to assess the parasitic energy load of processes utilising novel solid sorbents regularly compare their results with previous-generation MEA systems. For example, in 2016, Zhang et al. [135] estimated reboiler duties of 2.46 GJ t⁻¹ CO₂ using a PEI/silica adsorbent, which they

³Though it is unsuccessfully attempted in Chapter 4 of this work.
compare favourably with a value of 3.6 – 3.9 GJ t\(^{-1}\) CO\(_2\) for an aqueous amine system, rather than a more modern value of 2.1 GJ t\(^{-1}\) [92]. In 2018, Lara et al. [136] estimated equivalent work requirements of 40.9 kJ mol\(^{-1}\) of CO\(_2\) captured, which they compared favourably with the ‘general consensus’ of the amine scrubbing literature (no references were given; a reasonable value is 32 kJ mol\(^{-1}\) [27].) On the other hand, several pilot-plant and commercial-scale demonstrations for such materials are in development [137], and it is certainly possible that these materials could be competitive when combined with sophisticated process integration.

Other composite sorbent systems include Molecularly Imprinted Adsorbents [138], porous liquids [139] and high internal phase polymer foams [140]. These systems are all at an early stage of development, and each can claim their own advantages over a traditional process. The future development of these materials is unclear at this time.

2.7 CO\(_2\) Absorption into K\(_2\)CO\(_3\) Solutions.

Aqueous potassium carbonate was among the first solvents to be encapsulated inside MECS [3]. It was chosen because of its relatively low heat of absorption\(^4\) (\(\Delta h \approx -25\) kJ mol\(^{-1}\), compared with \(\Delta h \approx -85\) kJ mol\(^{-1}\) in MEA [82]) and the fact that two of the issues the solvent faces - the precipitation of bicarbonate at high loadings and the slow absorption rate of CO\(_2\) - could each be mitigated by microencapsulation. Much of the modelling work in Chapters 3 and 4 of this thesis will require knowledge of the physical and chemical properties of K\(_2\)CO\(_3\) solutions, and these are reviewed here.

When CO\(_2\) is absorbed into a carbonate solution with pH \(\geq 9\), it reacts with hydroxide ions to form bicarbonate [15]:

\[
CO_2 + OH^- \rightleftharpoons HCO_3^-. \quad (2.1)
\]

\(^4\)There is an argument to be made that this is actually a disadvantage of these solvents, as it limits the thermal pressure swing; see [82], and also Chapter 5 of this thesis.
The bicarbonate then re-equilibrates via the buffer reaction:

\[ \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^- . \] (2.2)

Reaction (2.2) is typically much faster than Reaction (2.1), and may be treated as instantaneous. Hence, the overall reaction is:

\[ \text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCO}_3^- . \] (2.3)

and the reaction rate is governed by the rate-limiting step, Reaction (2.1):

\[ -r_{\text{CO}_2} = k_{\text{OH}^-}[\text{CO}_2][\text{OH}^-] . \] (2.4)

Many correlations exist for the second order reaction rate constant, \( k_{\text{OH}^-} \). Five such correlations are plotted at infinite dilution in Figure 2.6. The agreement is quite reasonable, however the recent work of Ye and Lu [12] is substantially lower than all other correlations, probably because they extrapolated their infinite-dilution value from data at relatively high concentrations (5-30 wt% K\text{2CO}_3.) In regards to high concentration data, Thee, et al. [80] found a mean variation of less than 8% between their own value for \( k_{\text{OH}^-} \) in 30wt% K\text{2CO}_3, and the values predicted by Astarita, et al. [9] and Knuutila, et al. [8], over a temperature range from 40-80\(^\circ\)C. The equation of Astarita et al. [9] is applicable over a range of CO\(_2\) loadings.

In Figure 2.7, four correlations for the Henry’s constant of CO\(_2\) in K\text{2CO}_3 solutions are plotted. It is difficult to directly measure the physical solubility of CO\(_2\) in solution, as it quickly reacts away, so researchers have instead used the N\text{2O}-analogy: because of their similar molecular structures, the ratio of the solubility of CO\(_2\) to the solubility of N\text{2O} in a given aqueous solution is assumed to be the same as the ratio in water at the same temperature [141]. The four correlations in Figure 2.7 give quite different predictions for the change in solubility as the concentration of K\text{2CO}_3 increases. The correlation of Knuutila et al. [13] is the most recent, and
Figure 2.6: Values of $k_{\text{OH}^-}$ at infinite dilution, as predicted by Knuutila et al. [8], Astarita [9], Kucka et al. [10], Pohorecki and Moniuk [11], and Ye and Lu [12].

is based on experimental data up to 4.5 molar K$_2$CO$_3$ and over a temperature range from 20°C to 80°C. It has also been widely used since it was published [109, 3]. It is an extension of the model of Weisenberger and Schumpe [14], which is only valid up to 2 mol/L (and is in reasonable agreement with Knuutila’s model in this range). The data on which the correlations of Astarita et al. [9] and Danckwerts [15] are based are not given in their texts, and it seems unlikely they would be valid over a wider range than the more recent correlations. For these reasons, the correlation of Knuutila, et al. [13] is considered the most accurate for modelling concentrated potassium carbonate solutions.

Because CO$_2$ reacts with OH$^-$ upon entering the K$_2$CO$_3$ solution, an accurate estimate of the pH (as determined by the equilibrium of Reaction 2.2) is essential for predicting the reaction rate. Early researchers found empirical relationships between the concentration-based equilibrium constant, $K_c$, and the ionic strength of the solution [142]. More recently, Cents et al [143] suggested the equilibrium constant,

$$K_2 = \frac{c_{\text{CO}_3^{2-}}}{c_{\text{HCO}_3^-}c_{\text{OH}^-}}$$

(2.5)
Figure 2.7: Henry’s constant of CO$_2$ in K$_2$CO$_3$ solutions at a range of concentrations, $H$, divided by Henry’s constant of CO$_2$ in water. $T = 298.15$ K. Data sourced from Knuutila et al. [13], Weisenberger and Schumpe [14], Danckwercts [15] and Astarita [9].

could be related to its value at infinite dilution by:

$$\frac{K_2}{K_2^\infty} = \frac{1.01\sqrt{c_{K^+}}}{1 + 1.49\sqrt{c_{K^+}}} \quad (2.6)$$

More recent work has involved regressing rigorous activity coefficient models with large quantities of experimental data [144, 145].

The literature on the density of potassium carbonate solutions, CO$_2$ diffusivity and viscosity is in substantial agreement. Correia et al. [146] made many measurements of the K$_2$CO$_3$ density, and these are in excellent agreement with the model of Sohnel and Novotny [147]. Regarding viscosity, the average deviation between the correlation of Correla and Kestin [146] and the data points listed in Fair et al. [148] is less than 3.5%. The thermal conductivity of various K$_2$CO$_3$ solutions was measured by Akhmedova-Azizova et al. [149]. Regarding CO$_2$ diffusivity, the diffusivity of CO$_2$ in pure water was given by Versteeg and Van Swaalj [150]. To relate this to diffusivity in K$_2$CO$_3$ solutions, some researchers use the Stokes-Einstein equation.
[8], while others use the modified version of Joosten and Danckwerts [151]:

\[
\frac{D_{\text{sol}}}{D_{w}} = \left( \frac{\mu_{w}}{\mu_{\text{sol}}} \right)^{0.82}
\]

(2.7)

Where the subscripts ‘\(w\)’ and ‘\(\text{sol}\)’ refer to pure water and potassium carbonate solutions respectively. The variation is less than 20% in all concentrations up to 30wt% \(\text{K}_2\text{CO}_3\).

2.8 Further References

The classic work on absorption of gases into reactive liquids is Danckwerts’ *Gas-Liquid Reactions* [15], and other good texts include *Mass Transfer with Chemical Reaction* [152] and *Gas Treating with Chemical Solvents* [9], both by Astarita. For the fundamentals of chemical thermodynamics, Denbigh [153] is clear and concise, while Sandler [154] and Gmehling [155] cover many of the activity coefficient models in common use in the field. The following papers have also proven helpful throughout the course of this work, and in many ways they form the starting-points for the ideas that follow.

- Hegeley et al [156]. An excellent survey on the literature of mass transfer correlations for packed absorption columns. The ultimate conclusion is that *great care* must be taken when using a ‘general purpose’ correlation to estimate enhancement factors.

- Oexmann et al. [82]. Clearly outlines the reason why a reduced enthalpy of absorption does not imply a reduced regeneration energy.

- Ho et al. [157]. An interesting article on absorption into liquid emulsion membranes, which allowed for a significant simplification when modelling absorption into SIPS.

- Lin et al. [27, 92]. The rapid development of aqueous amine CCS processes should be much more widely known. These papers are a testament to the
power of the thoughtful use of simulations to refine a process *in silico*.

- House et al. [64]. A mildly polemical argument against relying too heavily on significant price reductions in direct air capture technology. Best read in conjunction with other mildly polemical papers on DAC [6, 68].
3 Enhancement in Specific Absorption Rate by Solvent Microencapsulation

Note. This chapter is an expanded version of a previously published paper by Moore et al. [38]. Specifically, sections 3.1 – 3.5 are expanded versions of material published in this paper, while the extension to this work discussed in section 3.6 has not previously been published.

Chapter Overview & Summary

The original question which motivated this work was as follows:

How does mass transfer into a MECS particle compare with mass transfer in a traditional absorption column? In particular, under what circumstances does the mixing of a solvent flowing over random or structured packing in a traditional absorber increase the rate of gas absorption, compared with a MECS, in which the encapsulated chemical solvent is stationary.

The rate of absorption into agitated chemical solvents has been studied for many years (see Danckwerts [15] for a good introduction). However, in these studies, the primary focus has been on determining the enhancement of the flux due to reaction, and the enhancement due to mixing has not received the same, explicit attention.\(^5\)

To begin answering these questions, the surface renewal theory of Danckwerts was reformulated, in order to find an expression for the increase in gas flux into a concentrated chemical solvent in an absorber, relative to the same solvent sitting stationary inside a MECS capsule. Obviously, the enhancement in flux due to mixing depends on the degree of mixing in the absorber, which may be related to the liquid-phase mass transfer coefficient, \(k_L\). However, it was found that different ‘general purpose’ correlations for \(k_L\), each in widespread use and widely cited, gave qualitatively different predictions (e.g. for CO\(_2\) absorption into a concentrated

\(^5\)A few papers which discussed this briefly are cited the start of Section 3.6.
K2CO3 solution, some correlations suggested mixing in an absorber would lead to a four-fold increase in the flux, while others suggested no increase under the same conditions.) The large discrepancy between these popular correlations is often unacknowledged in the literature, though we did find some older references [15, 158] and an excellent, recent survey [156] which discuss the issues in depth. From these sources, appropriate $k_L$ correlations were selected, and it was found that the lack of liquid mixing inside MECS containing concentrated chemical solvents operating in the pseudo-first order reaction regime would not significantly reduce the gas flux.

The analysis was then applied to physical solvents, for which it was found that the flux into MECS containing physical solvents would under many circumstances be significantly greater than in an absorber, because the small scale of the particles would increase the magnitude of the concentration gradients within the liquid.

The analysis was then extended, in order to estimate the increase in specific absorption rate (i.e. absorption rate per unit volume of absorber) that MECS could provide, compared with a traditional absorber modelled via the $k_L$ and $a$ correlations previously identified as the most accurate. This analysis was, of necessity, less precise, and various assumptions were made regarding the volume fraction of MECS inside the absorber and the mean concentration driving forces. Overall, an absorption rate increase of up to an order of magnitude was observed for MECS containing concentrated chemical solvents, while physical solvents performed better because of the increase in gas flux, and the specific absorption rate was up to two orders of magnitude greater. MECS were compared with absorbers containing both random and structured packings, and one of the more interesting results of the analysis was that the effective surface area for mass transfer, $a$, inside absorbers containing modern structured packings is much larger than has so far been assumed in the MECS literature. These results suggest that previous studies had overestimated the increase in surface area that MECS could provide (compared to a traditional absorber) by up to a factor of four.

After this, the analysis turned to the dynamics of mass transfer inside individual
MECS particles. Both experimental methods and computational fluid dynamics (CFD) calculations were used to assess the degree to which the fluid inside a MECS is truly stationary, especially when the MECS are used in a fluidised bed. Ultimately, it was concluded that particle collisions are unlikely to affect the gas flux into MECS containing concentrated chemical solvents. The magnitude of gas-side resistance was also calculated, and it was found it was likely to be negligible for all systems considered.

While the above material was principally devoted to the analysis of MECS, the core idea of reworking classical mass transfer theories in order to systematically analyse the effect of increased liquid agitation on the rate of absorption into chemical solvents is applicable to a number of emerging technologies for CCS (e.g. pulsation in a hollow fibre membrane, and various approaches designed to enhance mixing in flow over structured packings.) However, the analysis above only applied to a solvent in the pseudo-first order reaction regime, as in this case the gas flux into a stationary fluid quickly asymptotes to a constant value, which may be taken as the reference case against which the faster flux into agitated liquids can be compared. This is not true of other absorption regimes, and in such cases an ‘enhancement’ due to mixing is more difficult to define. In the final section of this chapter, an alternative quantity, the sensitivity of the gas flux to liquid mixing, $\xi$, is proposed. This quantity may be calculated numerically for a chemical solvent in any absorption regime, and may be used to quantify the effect that a small increase in the liquid mixing would have on the solvent. In particular, if a small increase in the degree of liquid agitation would increase the flux into a physical solvent by some factor $1 + d\alpha > 1$ (where $d\alpha$ is a small positive number), then the same change will increase the flux into a chemical solvent with the same physical properties by a factor $1 + \xi d\alpha$. Expressions for $\xi$ are developed for a number of chemical solvents. The findings for solvents in the pseudo-first order reaction regime are consistent with those developed above (i.e. $\xi \approx 0$ provided the solvent is not impractically slow). For the more general

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6And was published, largely as presented below, with that emphasis [38].
second-order reaction regime, on the other hand, increased mixing is useful when the reaction is either very slow or very fast. In the former case, mixing assists in moving dissolved gas molecules to the bulk where they can react, while in the later case, mixing is useful as it brings reactive molecules in the solvent to the surface where they can react. Three different chemical systems were analysed, using both the thin-film and eddy-diffusivity theories.

3.1 Introduction

Microencapsulated solvents (MECS) possess two potential advantages over traditional absorption columns. They may facilitate solvent handling, by immobilising viscous, volatile, precipitating, corrosive or toxic solvents, which could not otherwise be used. And they may increase mass transfer rates by enlarging the area available for absorption - it has been estimated that MECS have 1–2 orders of magnitude more surface area than the liquid in an absorber [3], and this could lead to comparable increases in gas absorption rates. The dual benefit of enhanced mass transfer and solvent immobilisation is particularly well suited to advanced solvents, such as ionic liquids or precipitating potassium carbonate systems, which typically have excellent thermodynamic properties, but which may be highly viscous, precipitate solids, or absorb CO₂ slowly [159, 112, 100].

However, increased surface area is not the only difference between mass transfer in MECS and in traditional packed columns. As a liquid flows down a packed column it is continually mixed. This process carries spent solvent at the surface to the bulk and replaces it with fresh solvent, and this ‘surface renewal’ can increase the gas flux [15]. On the other hand, in a MECS particle, the proximity of the capsule walls increases the significance of viscous forces, limiting radial fluid flow and surface renewal effects. Other differences include the shell of a MECS particle (which provides an extra layer of mass transfer resistance) [99], differences in liquid holdup between the two operations, and the fact that, for the smallest MECS particles, absorption may be reaction controlled, in which case increasing the surface area
does not further improve mass transfer [160].

To date, only the simplest comparisons between gas absorption in microencapsulated sorbents and in traditional packed columns can be found in the literature. Raksajati et al. [114] assumed that the mass transfer coefficient, $k_L$, for absorption into MECS could be calculated using a correlation valid for a packed column, but it is unclear whether these correlations can be applied to MECS particles, given the large differences in fluid flow patterns between the two operations. Both Vericella et al. [3] and Stolaroff et al. [100] compared the flux of gas into stationary MECS particles with the flux into a stationary liquid film with the same specific surface area as a liquid in a packed column. However they did not quantify how well a stationary liquid film models the liquid flowing down a packed column. Stolaroff et al. [101] measured gas absorption into MECS containing ionic liquids and carbonate solutions inside a flow-through, fixed-bed absorber. They found that mass transfer rates were similar to those into static MECS particles, and were in good agreement with a simple resistance in series absorption model, however they did not seek to compare their system with a traditional operation.

In this chapter, a careful comparison is made between mass transfer in MECS and in traditional absorption columns, and the degree to which shell resistance or suppression of liquid agitation could reduce the gas flux is analysed at a fundamental level. The comparison accounts for the large surface area of MECS particles, the suppression of liquid mixing inside the particles, the presence or absence of reactions inside the liquid solvent, the presence of the capsule shells, and the difference in liquid holdup between a traditional absorber and an absorber containing MECS. In section 3.2, surface renewal theories are used to derive general expressions for the difference in the specific absorption rate into MECS and in a traditional absorber for both chemical and physical solvents, and in section 3.3 these are applied to two particular cases: absorption of CO2 into an aqueous K2CO3 solution, and absorption of CO2 into Selexol. In section 3.4, the effect of gas-phase mass transfer resistance is quantified, and in section 3.5 computational fluid dynamics simulations
and experiments are used to quantify the degree of liquid mixing inside fluidised MECS particles, and the effect this may have on gas absorption. Finally, in section 3.6 a more general means of quantifying the sensitivity of the gas flux to changes in the degree of agitation of the solvent is presented.

### 3.2 Analysis of Mass Transfer

The purpose of this section is to derive two expressions. First, an expression is derived for the ratio of the flux of gas in an absorption column to the flux into a MECS:

$$\frac{J_{\text{Column}}}{J_{\text{MECS}}} \equiv M. \tag{3.1}$$

Second, an expression is derived for the ratio of the specific absorption rate (absorption rate per unit volume of absorber) into a MECS and into an absorption column,

$$\frac{\bar{R}_{\text{MECS}}}{\bar{R}_{\text{Column}}} \equiv \Gamma. \tag{3.2}$$

Deriving these expressions requires detailed knowledge of the mass transfer mechanisms into both MECS (which are relatively simple) and into absorption columns (which are relatively complex, but well studied). Two industrially relevant cases are studied: first mass transfer with pseudo-first order reaction is considered in sections 3.2.1 – 3.2.3, and the analysis is then repeated for mass transfer without reaction (i.e. for a physical solvent) in section 3.2.4.\(^7\) Expressions which account for shell resistance are then presented, before the physical significance and applicability of $M$ and $\Gamma$ is discussed.

The goal of the proceeding analysis is to develop an understanding of *intrinsie*, or particle-scale, mass transfer into MECS, and how this compares with a fluid flowing in an absorber. Hence, idealised systems (such as a single MECS in an environment of constant gas partial pressure) are analysed, in order to understand the extent to

\(^7\)Steady-state expressions for $M$ and $\Gamma$ cannot be derived for more general reaction regimes (e.g. absorption with second-order reaction), however an alternative means of evaluating the sensitivity of the solvent to liquid mixing, which may be applicable to a number of technologies beyond microencapsulation, is discussed in section 3.6.
which suppression of liquid mixing, surface area increase, shell resistance, and other factors affect the rate of gas uptake inside these particles.

3.2.1 Mass Transfer into MECS: Pseudo-First Order Reaction

Consider a gas brought into contact with a stationary MECS particle containing a chemical solvent in which a particular component of the gas (such as CO$_2$) dissolves and reacts according to a reversible first order or pseudo-first order chemical reaction, with reaction rate constant $k$ (Figure 3.1). Suppose the gas phase is large and well mixed (so that the partial pressure of the absorbed gas remains constant), the absorption is liquid-phase controlled (as is common for many processes; conditions for which this assumption is reasonable are discussed in section 3.4) and convective liquid movement inside the particles can be ignored (see section 3.5). Then mass transfer inside the liquid core of the MECS particles is governed [161] by the spherical reaction-diffusion equation,

$$\frac{\partial c}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D r^2 \frac{\partial c}{\partial r} \right) - k (c - \bar{c}),$$

where $c$ is the concentration of unreacted gas in the liquid, and $\bar{c}$ is the concentration of unreacted gas which would be at equilibrium with the bulk liquid composition.$^8$

For irreversible reactions, $\bar{c} = 0$, while for reversible reactions $\bar{c}$ will increase with the degree of solvent saturation. Because the partial pressure of the absorbed gas is held constant, the concentration at the polymer-gas interface is fixed.

Under these conditions, it is not difficult to show that (irrespective of the initial concentration profile inside the MECS) the gas flux into the liquid solvent in the MECS will quickly asymptote to the following, quasistatic value (see Bird, Stewart and Lightfoot [161], Fogler [162], and Levenspiel [160], who discuss similar problems

$^8$It should be emphasised that $c$ refers to the concentration of physically dissolved gas (e.g. for CO$_2$ absorption into K$_2$CO$_3$, $c$ refers to the local CO$_2$ concentration, not the local concentration of CO$_2$ stored chemically inside HCO$_3^-$ ions.) While the concentration of physically dissolved gas in a chemical solvent is often thermodynamically negligible, it is kinetically all-important.
without the polymer shell; a careful derivation is provided in Appendix 3.1):

\[ J_{\text{MECS}} = \alpha \Delta c \frac{D}{r} (\coth \phi - 1) \]  

(3.4)

where \( \Delta c \equiv c^* - \bar{c} \), in which \( c^* \equiv H_{\text{liq}} p_i \) is the concentration of unreacted gas which would be present at the solvent surface if the shell were removed (here \( H_{\text{liq}} \) is the Henry’s constant in the liquid, and \( p_i \) is the partial pressure of the absorbed gas.) In general \( c^* \) will not equal the concentration at the outer polymer surface, as the Henry’s constant for the shell and the liquid will be different. \( \alpha \equiv (c_i - \bar{c})/\Delta c \) quantifies the significance of shell resistance (e.g. \( \alpha = 0.9 \) corresponds to a 10% reduction in flux due to shell resistance; see Section 3.2.5), and

\[ \phi \equiv \sqrt{kr^2/D} \]  

(3.5)

is the Thiele Modulus of the system, which quantifies the relative rates of diffusion and reaction (\( \phi \gg 1 \) implies diffusion is slow relative to reaction and controls the absorption rate, and vice versa for \( \phi \ll 1 \).) For an unsaturated, diffusion-controlled particle (\( \phi \to \infty \)) with minimal shell resistance, Eq. (3.4) reduces to the much simpler:

\[ J = c^* \sqrt{Dk} \]  

(3.6)

Vericella et al. [3] have demonstrated that, when shell resistance is accounted for, this expression is in good agreement with experimental data for absorption of CO2 into MECS containing 3wt% K\(_2\)CO\(_3\). The time required for the flux to asymptote to Eq. (3.6) (after, for example, a change in the external gas concentration) is on the order of \( \min(r^2/D, k^{-1}) \). As shown in the examples below, this is often much less than 1 second, and so even in an environment of variable gas concentration (e.g. a fluidised bed), the flux at any one time and location can often be well approximated by Eq. (3.6).

If these stationary MECS particles of radius \( r \) were exposed to a gas in a unit
operation with liquid holdup\(^9\) equal to \(1 - \varepsilon\) then the absorption rate of gas per unit volume of absorber would be equal to:

\[
\bar{R}_{\text{MECS}} = \frac{J_{\text{MECS}}}{r} = \alpha(1 - \varepsilon)k\Delta c \left( \frac{\phi \coth \phi - 1}{\phi^2/3} \right)
\]  

(3.7)

Even though this expression was derived for stationary MECS particles, it will be shown in section 3.5 that it is also valid for MECS particles placed in a fluidised bed, as particle collisions would not generate enough liquid mixing to significantly affect the mass transfer rate.

### 3.2.2 Mass Transfer in a Packed Column: Pseudo-First Order Reaction

Mass transfer inside a traditional packed column is considerably more complicated. The liquid surface area available for mass transfer is difficult to quantify, as is the effect of the mixing of the liquid as it flows over the packing material. At present, rigorously modelling all of the transport phenomena occurring inside an absorption column is computationally challenging [163, 164]. Instead, empirical

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\(^9\)Note that in this work the liquid holdup is defined as the fraction of total absorber volume occupied by the liquid solvent (whether packing is present or otherwise) and the unit operation ‘voidage’, \(\varepsilon\), is the fraction of remaining space occupied by the gas phase, any packing material, and the shells of the particles. Similarly, \(r\) is the radius of the inner liquid core, rather than the total radius of the particle, see Figure 3.1.
equations have been developed which take into account both physical properties of the liquid (viscosity, gas diffusivity, etc.) and properties of the absorption process (packing type and size, Reynold's number, etc.) These equations predict a $k_L$ value, which is the liquid side mass transfer coefficient for a purely physical solvent, defined by

$$J_{\text{Physical Column}}^{\text{Physical}} = k_L(c^* - c_{\text{bulk}}) \approx k_L(c^* - c_{av}).$$  \hspace{1cm} (3.8)

Here, $c_{\text{bulk}}$ is the concentration of gas in the bulk of the liquid, while $c_{av}$ is the average concentration in the entire fluid (both the bulk and the thin surface film). In most cases these are effectively equal, as the surface film is typically much thinner than the liquid depth.

If the solute gas reacts with the flowing solvent, it can further enhance the mass transfer rate, and Eq. (3.8) is no longer valid. Many idealised mathematical models of the fluid flowing down an absorption column have been developed, and these can be used to relate the mass transfer enhancement due to reaction to the reaction kinetics, the physical properties of the liquid, and also the absorption rate under the same hydrodynamic conditions but with no reaction occurring, as quantified by $k_L$. The most popular are the surface renewal model of Danckwerts [18], the penetration theory of Higbie [17], and the two-film theory of Whitman [16]. For a gas absorbed by a solvent with which it undergoes a reversible pseudo-first order chemical reaction, Danckwerts’ surface renewal theory predicts the flux will be given by:

$$J_{\text{Column}} = k_L \Delta c \sqrt{1 + \frac{Dk}{k_L^2}} = k_L \Delta c \sqrt{1 + \frac{Ha^2}{2}}$$  \hspace{1cm} (3.9)

where $Ha \equiv \sqrt{Dk/k_L}$ is the Hatta number for a pseudo-first order reaction, which represents the ratio of gas that reacts at the surface to gas that is convectively transported to the bulk. Even though the theories of Whitman and of Higbie are based on very different physical idealisations, their predictions for $J$ differ by less than 3% over the whole range $0 < Ha < \infty$ (see Figure 3.2); Danckwerts’ expression
Figure 3.2: Comparison of the surface renewal theories of Whitman [16], Higbie [17] and Danckwerts [18] for the case of absorption with pseudo-first order reaction. was chosen for its algebraic simplicity.

The rate of absorption of gas per unit volume of absorber is given by:

\[
\bar{R}_{\text{Column}} = J_{\text{Column}} \cdot a = a k_L \Delta c \sqrt{1 + Ha^2} \tag{3.10}
\]

where \( a \) is the effective liquid surface area available for mass transfer per unit volume of absorber.\(^{10}\)

### 3.2.3 Mass Transfer Enhancement: Expressions for \( M \) and \( \Gamma \) with Pseudo-First Order Reaction

Eq. (3.4) to Eq. (3.10) can be used to compare mass transfer rates inside MECS particles and packed columns. In order to provide a fair comparison between the

\(^{10}\)Both \( k_L \) and \( a \) may be predicted using general-purpose mass transfer correlations regressed from experimental data. However, as discussed at some length in section 3.3.2, a great deal of care must be taken when selecting such correlations to ensure they are appropriate to the system under consideration.
two technologies, it is assumed throughout that the mean driving force for mass transfer, $\Delta c$, is the same in each case (a discussion of this point will be delayed until Section 3.2.6.) Based on these expressions, the ratio of the flux in an absorber to the flux into a MECS particle is given by:

$$M \equiv \frac{J_{\text{Column}}}{J_{\text{MECS}}} = \frac{1}{\alpha} \left( \frac{\phi}{\phi \coth \phi - 1} \right) \sqrt{1 + \text{Ha}^{-2}}$$  \hspace{1cm} (3.11)

In the (physically common) limit of $\alpha \rightarrow 1$ and $\phi \rightarrow \infty$, this expression reduces to

$$M = \sqrt{1 + \text{Ha}^{-2}}.$$  \hspace{1cm} (3.12)

This is a physically reasonable result. As mentioned above, the Hatta number may be thought of as the ratio of gas that reacts at the liquid surface to gas that is convectively transported to the bulk of the solvent. Thus, when the Hatta number is large liquid mixing should have little effect on the gas flux, and it would be expected that $M \sim 1$, while when the Hatta number is small (and so convective motion plays an important role in gas absorption) it would be expected that microencapsulation would reduce the gas flux, and so $M \gg 1$. Clearly, Eq. (3.12) is consistent with these intuitions. At least for the case of absorption with pseudo-first order reaction, liquid mixing is much more likely to be a significant factor for solvents with slow kinetics, for which convective transport to the bulk is more important.\(^{11}\)

Rather than comparing the flux of gas in a packed column with the flux into MECS, a fairer comparison would be to consider the specific absorption rate per unit volume of absorber, $\bar{R}$, as given by Eq. (3.7) and (3.10). MECS have very large specific surface areas, so the specific absorption rate could be large even if the gas flux is suppressed. The enhancement in specific absorption rate that MECS can

\(^{11}\)Interestingly, it turns out that liquid mixing is also important for solvents with very fast kinetics: fast enough to move out of the pseudo-first order reaction regime and into the instantaneous reaction regime. Intuitively, this is because, for these solvents, liquid mixing enhances the transport of reactive species towards the surface, where they react with the gas. No solvents considered in the following analysis have kinetics this fast, however this situation is discussed in section 3.6.
provide is given by:

\[
\Gamma \equiv \frac{\bar{R}_{\text{MECS}}}{\bar{R}_{\text{Column}}} = \left( \frac{\alpha(1 - \varepsilon)}{\sqrt{1 + Ha^{-2}}} \left( \frac{k}{Da^2} \right)^{1/2} \right) \left( \frac{\phi \coth \phi - 1}{\phi^2/3} \right)
\] (3.13)

Though no single parameter can be constructed to unambiguously compare these two different technologies, the relative specific absorption rate, \(\Gamma\), accounts for both the enhanced surface area of MECS, and any differences in mass transfer mechanisms and liquid holdup. In order to quantify \(\Gamma\) a correlation is required for \(k_L\) and for \(a\): these provide the base case against which the MECS technology can be compared.

It is interesting to note that only the final term in Eq. (3.13) depends upon the radius of the particles; this term is plotted in Figure 3.3 (note that, with physical properties kept constant, \(\phi\) can be considered a dimensionless radius.) In the limit as particles become very small (\(\phi < 0.1\)), the improvement provided by microencapsulation plateaus. At this point, the particles are so small that the absorption is reaction controlled, so further increases in surface area do not increase the absorption rate. Because the second term asymptotes to 1 as \(\phi \to 0\), the maximal possible improvement MECS can provide is given by the first bracketed term in Eq. (3.13). For large particles (\(\phi > 10\)), the second term asymptotes to \(3/\phi\). Under these conditions, absorption is diffusion controlled, and \(\Gamma\) is proportional to the specific surface area of the MECS. Eq. (3.13) can be rearranged to more clearly highlight the factors that contribute to the differences between \(\bar{R}_{\text{Column}}\) and \(\bar{R}_{\text{MECS}}\):

\[
\Gamma = \left[ \frac{\alpha}{\sqrt{1 + Ha^{-2}}} \frac{\phi \coth \phi - 1}{\phi} \right] \left[ \frac{3(1 - \varepsilon)/r}{a} \right]
\] (3.14)

\[
\Gamma = \alpha \times \left( \frac{1}{\alpha M} \right) \times \left( \frac{a_{\text{MECS}}}{a} \right)
\] (3.15)

\[
\Gamma = \alpha \times \left( \frac{1}{\sqrt{1 + Ha^{-2}}} \right) \times \left( \frac{\phi \coth \phi - 1}{\phi} \right) \times \left( \frac{a_{\text{MECS}}}{a} \right)
\] (3.16)

\[
\Gamma = \alpha \times \left( \frac{1}{\sqrt{1 + Ha^{-2}}} \right) \times \left( \frac{\phi \coth \phi - 1}{\phi} \right) \times \left( \frac{a'_{\text{MECS}}}{a'} \right) \times \left( \frac{1 - \varepsilon}{h} \right)
\] (3.17)

In Eq. (3.15), \(\Gamma\) is divided into three factors - the effect of shell resistance, \(\alpha\), the
effects of suppression of liquid motion and transition to reaction control, $1/\alpha M$, and the relative specific surface area on a unit volume basis, $a_{\text{MECS}}/a$. These terms may be further factorised. In Eq. (3.16), $1/\alpha M$ is broken into its two contributing factors - the reduction in flux due to suppression of liquid mixing, $1/\sqrt{1 + Ha^{-2}}$, and the term that accounts for the transition from diffusion control (under which $\Gamma$ grows in proportion with the MECS specific surface area) to reaction control (under which $\Gamma$ is independent of surface area.) In Eq. (3.17), the last term is further broken down into the relative specific surface area on a volume of solvent basis and the relative liquid holdup inside each unit operation. The magnitude of the various contributions to $\Gamma$ will be investigated in section 3.3.

3.2.4 Alternative Reaction Mechanism: Physical Solvents

The derivation of a time-independent expression for $\bar{R}_{\text{MECS}}$, and hence for $\Gamma$, is only possible when the concentration of the reactive species remains homogeneous in
space (as occurs in the case of diffusion with pseudo-first order reaction.) When this is not the case, the flux into a static solvent is time-dependent, and also depends on the particle's history. For pseudo-first order reactions, however, the only condition is that the partial pressure of gas not change too quickly: provided partial pressure fluctuations have periods substantially longer than $\mathcal{O}(\min(r^2/D, k^{-1}))$, the flux will be well approximated by the asymptotic expression Eq. (3.4).

The restriction to solvents which undergo first order or pseudo-first order reactions is not as limiting as it may at first seem. Such solvents are very common industrially: when the concentration of the reactive species in a solvent is much greater than the physical concentration of dissolved gas, a pseudo-first order approximation is often valid, even if the fundamental reaction kinetics are of a different order in the reactive species (e.g. CO$_2$ absorption into K$_2$CO$_3$ solutions) [18]. In such cases the concentrations of any reactive species in the solvent change slowly enough for spatial inhomogeneities to be smoothed out, and they can be lumped into a single, pseudo-first order rate constant. This rate constant may change over time as the reactive species are slowly depleted.

On the other hand, purely physical solvents do not exhibit pseudo-first order behaviour under any conditions. However, they are widely used in industry, and it would be useful to extend the above analysis to this common case. Furthermore, the analysis above suggests that the suppression of liquid mixing is particularly significant for solvents with slow reactions: when the Hatta number is small, convective transport to the bulk is much more significant than surface reactions. Physical solvents could be considered the limiting case of slow reactions, and so the suppression of liquid mixing inside MECS which contain physical solvents could be much more significant than for chemically reactive systems.

While the analytic approach taken above is impossible here (in general the flux into a MECS particle containing a physical solvent, $J_{\text{MECS}}^\text{Physical}$, is a function of time and also the particle's history), it is well known that, for spherical solid particles which adsorb gas, the gas flux can be well approximated by the linear driving force
(LDF) model. Despite its simplicity, this model appears capable of capturing most of the important dynamic behaviour of solid adsorbent particles, and it has been used in the design of both packed beds [165] and fluidised beds [166]. When applied to a static MECS particle containing a physical solvent (which is governed by the same diffusion equation) the LDF model gives:

\[ J_{\text{MECS}}^{\text{Physical}} = k_{\text{LDF}}(c_i - c_{av}) = \alpha' k_{\text{LDF}} (c^* - c_{av}) \]  

(3.18)

where \( \alpha' \equiv (c_i - c_{av})/(c^* - c_{av}) \) once again quantifies the shell resistance. Glueckauf [167] suggested that \( k_{\text{LDF}} \approx 5D/r \), and other researchers have found this to be a useful (if slightly conservative) value [168, 165]. Substituting this into Eq. (3.18) gives:

\[ J_{\text{MECS}}^{\text{Physical}} = \frac{5 \alpha' D}{r} (c^* - c_{av}). \]  

(3.19)

Eq. (3.19) can now be directly compared with Eq. (3.8), to calculate the degree to which liquid mixing enhances the gas flux, and to calculate the enhancement in specific absorption rate that can be achieved. Following the same procedure, and again assuming that the driving force, \((c^* - c_{av})\), is the same for a process utilising MECS and a traditional packed column:

\[ M_{\text{Physical}} = \frac{J_{\text{Column}}^{\text{Physical}}}{J_{\text{MECS}}^{\text{Physical}}} = \frac{k_L r}{5 \alpha' D} \]  

(3.20)

\[ \Gamma_{\text{Physical}} = \frac{\bar{R}_{\text{MECS}}^{\text{Physical}}}{\bar{R}_{\text{Column}}^{\text{Physical}}} = \frac{J_{\text{MECS}}^{\text{Physical}}}{J_{\text{Column}}^{\text{Physical}}} \cdot \frac{3(1 - \varepsilon)/r}{a} = \frac{15 \alpha' (1 - \varepsilon) D}{r^2 k_L a} \]  

(3.21)

It is interesting to observe that the flux in Eq. (3.19) is dependent on the particle radius, and is larger for smaller particles. This is in contrast to MECS containing chemically reactive solvents in the diffusion-controlled regime, for which the flux is independent of particle radius. For diffusion-controlled chemical solvents, the characteristic spatial scale over which the concentration changes is the thickness of the thin surface layer inside which gas reacts away. This is of order \( \sqrt{D/k} \), and is independent of particle radius [15]. On the other hand, for physical solvents, the
characteristic spatial scale is the radius \( r \), and smaller particles will have larger concentration gradients than larger particles with the same degree of saturation. That the flux should scale with \( 1/r \) can be seen by nondimensionalising the spherical diffusion equation for a particle placed in an environment of constant partial pressure. The time-evolution of this system is governed by [161]:

\[
\frac{\partial c}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D r^2 \frac{\partial c}{\partial r} \right)
\] (3.22)

and consider the simplest boundary conditions: \( c = c_0 \) at \( t = 0 \) and \( c = c_i \) for \( t > 0 \) at the liquid surface. If this equation is non-dimensionalised, the dimensionless time takes the form:

\[
\bar{t} = \frac{t}{r^2/D}
\] (3.23)

and the radius appears in no dimensionless groups. Hence, if the radius is changed but everything else is held constant, the time to achieve some arbitrary degree of saturation, \( t_{\text{sat}} \), scales with \( r^2 \). Because the total number of moles of gas absorbed, \( n \), scales with \( r^3 \), the rate of gas absorption into a single particle scales as \( n/t_{\text{sat}} \propto r \). As the surface area scales with \( r^2 \), the gas flux scales with \( 1/r \), and is larger for smaller particles.

Thus, for the case of physical solvents, decreasing particle size has two potential benefits: it increases the specific surface area, and, by reducing spatial scales (and hence increasing the magnitude of all concentration gradients) it can also lead to higher gas flux. It is unclear at present whether suppression of liquid mixing will be as significant as either of these effects.

3.2.5 Shell Resistance

The effect of shell resistance was analysed by Vericella et al. [3], and was found to be minor (\( \alpha \approx 0.9 \)) for large (\( \sim 400 \mu m \) diameter capsules) containing a K\(_2\)CO\(_3\) solution. They modelled absorption into MECS as a resistance in series problem, so
that
\[ \alpha = \frac{R_{\text{solvent}}}{R_{\text{solvent}} + R_{\text{shell}}} \]  
(3.24)

where resistance is defined by \( R = \Delta c/J \) (see Appendix 3.II for a careful derivation).

Solvent-side resistances are given by the expressions described previously. From Eq. (3.4), for solvents undergoing a pseudo-first order reaction,

\[ R_{\text{solvent}} = \left[ \frac{D}{r} (\phi \coth \phi - 1) \right]^{-1} \]  
(3.25)

and from Eq. (3.19), for physical solvents,

\[ R_{\text{solvent}} = \frac{r}{5D}. \]  
(3.26)

For a spherical shell, the resistance takes the form (see Appendix 3.II)

\[ R_{\text{shell}} = \frac{Hz}{P_{\text{shell}}} \frac{r}{r + z} \]  
(3.27)

where \( P_{\text{shell}} \) is the shell permeability, and \( z \) its thickness. \( \alpha \) primarily depends on the shell thickness (which can vary from 10 – 50 µm), the shell permeability, and the rate at which the neat solvent absorbs the gas.

3.2.6 Significance of \( M \) and \( \Gamma \)

In order to derive general expressions for the gas flux ratio, \( J_{\text{Column}}/J_{\text{MECS}} = M \), and the specific absorption rate ratio, \( \bar{R}_{\text{MECS}}/\bar{R}_{\text{Column}} = \Gamma \), it was assumed that the mean driving force for mass transfer, \( \Delta c \), was the same for both MECS-based systems and traditional packed columns. In reality this is unlikely to be the case, as the mean \( \Delta c \) value depends upon the process design and the internal gas and liquid flow patterns in a complex way. However, this does not invalidate the above analysis. There is always a tradeoff between reducing \( \Delta c \) to minimise irreversibility and maximise the cyclic solvent capacity, and maximising \( \Delta c \) to minimise absorber volume. If the mean value of \( \Delta c \) is different in the two cases, the process with greater \( \Delta c \) will only
Figure 3.4: Gas and solid concentration profiles inside (a) single-stage and (b) multiple-stage fluidised beds used for gas purification. $\bar{c}$ is the concentration of gas in the liquid, and $c^* = H_{liq}p_i$ is the concentration at equilibrium with the gas composition.

Improve its kinetic performance at the cost of reduced thermodynamic efficiency or greater solvent circulation rates. To see this, consider the extreme example of gas scrubbing using a single-stage fluidised bed (Figure 3.4a.) Because of the severe solid back-mixing (so severe, in fact, that the solid phase is often modelled as a mixed flow reactor [166]), the maximum solid loading in the bed cannot be greater than the loading that is at equilibrium with the clean, outlet gas. Because of this limitation, the mean driving force for mass transfer, $\Delta c$, will be very large, and the rate of absorption will be correspondingly greater - but this is not without cost. The low solid conversion will lead to much larger circulation rates, and the large driving force will lead to significantly greater exergetic losses in the absorber. Compare this with a multi-stage fluidised bed, for which the mean driving force will be lower, but the solid circulation rates will be smaller as well (Figure 3.4b.) In fact, this tradeoff may be seen even in the design of a traditional absorption column, where increased circulation rates may be used to reduce absorber volume, but only at the cost of greater pumping and reboiler heat duties.
Thus, in order to fairly evaluate the kinetic enhancement microencapsulation can provide, it was assumed that the MECS-based process and the traditional absorption column were designed so that the mean driving force was identical for each case. This provides a fair means of evaluating the enhancement in absorption rate that microencapsulation may provide, ensuring that no technology is improving its kinetics by sacrificing its thermodynamics. The analysis above was intentionally presented in an abstract way, with reference to intrinsic absorption mechanisms and rates rather than actual absorption rates in a particular unit operation. Intrinsic mass transfer mechanisms were analysed because the motivating question for this work - whether suppression of liquid mixing or shell resistance inside MECS would significantly reduce the gas flux - was itself an intrinsic question, making no reference to the particular unit operations used to expose MECS to a gas stream. Nevertheless, $\Gamma$ also provides a reasonable estimate for the ratio of the volume of a traditional absorption column and a multi-stage fluidised bed containing MECS, provided they are designed so the mean value of $\Delta c$ is similar in each case.

### 3.3 Example Systems

In the previous section, general expressions were derived for the relative flux and specific absorption rate into MECS particles and into an agitated liquid flowing inside an absorption column. In order to numerically evaluate these expressions, they are now applied to two specific solvent systems for the absorption of carbon dioxide: a 30wt% K$_2$CO$_3$ solution, and Selexol®. These systems are widely used industrially, and are chemical and physical solvents respectively.

#### 3.3.1 Potassium Carbonate for Carbon Capture

The original context in which MECS were developed was the encapsulation of carbonate solutions for CO$_2$ capture [99]. Carbonate solutions are an obvious candidate for microencapsulation: they have favourable thermodynamic properties, but absorb CO$_2$ slowly and may precipitate bicarbonate at high loadings. Concentrated
carbonate solutions react with CO₂ to produce bicarbonate:

\[ \text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- \]  
\[ \text{H}_2\text{O} + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- + \text{OH}^- \]  

The carbonate/bicarbonate buffer ensures the pH remains around 9-10, and because Eq. (3.29) may be regarded as instantaneous, hydroxide ions are constantly supplied for Eq. (3.28), at a concentration that only depends on the [HCO₃⁻]/[CO₃²⁻] ratio [15]. In concentrated carbonate solutions the concentrations of HCO₃⁻ and CO₃²⁻ change slowly enough to remain spatially homogeneous, so the system is governed by diffusion with pseudo-first order reaction [15]. Unpromoted carbonate solutions represent a useful limiting case, in that they have slower kinetics than most CCS solvents with low enough viscosity to be used in a packed column (e.g. promoted carbonates, amine-based solvents). Thus they typically operate at relatively low Hatta numbers, and so the reduction in gas flux due to the suppression of liquid motion and surface renewal effects inside the small capsules (relative to liquid flowing down a traditional absorption column) will be more significant in these systems than in most others. An unpromoted 30wt% K₂CO₃ system is considered below.

### 3.3.2 Mass Transfer Correlations

In order to evaluate the difference in gas flux, \( M \), and the overall absorption rate, \( \Gamma \), between a traditional packed column and MECS particles, a correlation for \( k_L \) is required, along with an estimate of the specific liquid surface area, \( a \). Many such correlations can be found in the literature (see, for instance, the review papers of Wang et al. [169] and Hegely et al. [156]) Table 3.1 summarises a number of widely used correlations: the correlation of Shulman et al. [19] was recommended by Treybal [170] (who also provided the correlation for \( a \) based on Shulman’s data); the correlation of Onda et al. [20] has been widely used [171, 79], and was recommended in *Perry’s Chemical Engineering Handbook* [148]; the correlation of Hanley and Chen
[23] is implemented in the popular ASPEN process simulation software, and both Rocha et al. [22] and Billet and Shultes [21] have been cited several hundred times. Even though these correlations have been widely used and recommended, a great deal of care must be taken when using them to assess enhancement factors associated with chemical reactions or (as in the present case) liquid mixing.

Table 3.1: General-purpose correlations for the liquid-phase mass transfer coefficient and effective mass-transfer area.

<table>
<thead>
<tr>
<th>Source</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onda et al. [20]</td>
<td>[ k_L = 0.0051(a_d d_p)^{0.4} \left( \frac{\mu g}{\rho} \right)^{1/3} \left( \frac{L}{a_d \mu} \right)^{2/3} \left( \frac{\mu}{\rho D} \right)^{-1/2} ]</td>
</tr>
<tr>
<td>Shulman et al. [19] &amp; Treybal [170]</td>
<td>[ a = q_1 \left[ \frac{808 G}{\sqrt{g}} \right] L^{9.1} ]</td>
</tr>
<tr>
<td>Billet and Shultes [21]</td>
<td>[ k_L = q_1 \left( \frac{\mu g}{\mu} \right)^{1/6} \left( \frac{D}{d_h} \right)^{1/2} \left( \frac{L}{p_{in}} \right)^{1/3} ]</td>
</tr>
<tr>
<td>Hanley and Chen [23]</td>
<td>[ a = q_1 \left( \frac{\mu g}{\mu} \right)^{9.2} \left( \frac{D}{d_h} \right)^{9.7} \left( \frac{L}{p_{in}} \right)^{9.1} ]</td>
</tr>
<tr>
<td>Rocha et al. [22]</td>
<td>[ k_L = 2 \left( \frac{q_1 D L}{\pi S \rho e h_L \sin \alpha} \right)^{1/2} ]</td>
</tr>
<tr>
<td>Tsai et al. [24]</td>
<td>[ a = \frac{29.12 (W e \cdot F r)^{0.15} S^{0.359}}{R e^{0.2} e^{0.6} (1 - 0.93 \cos \gamma) \sin^{0.3} \alpha} ]</td>
</tr>
</tbody>
</table>

\[ a_e \] are packing-dependent constants listed in Appendix 3.111.

In Figure 3.5, the correlations of Onda, of Billet and Shultes, and of Shulman were each used to analyse a packed column containing 1/2-inch ceramic Raschig Rings, which would use a 30wt% K$_2$CO$_3$ solution to remove CO$_2$ from a flue gas stream (see Table 3.2 for the relevant material parameters). The correlations of Billet
Table 3.2: Physical Properties of 30wt% K₂CO₃ solution at 313 K.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ</td>
<td>1286 kg m⁻³</td>
<td>Sohnel and Novotny [147]</td>
</tr>
<tr>
<td>µ</td>
<td>1.72 × 10⁻³ Pas</td>
<td>Correia et al. [146]</td>
</tr>
<tr>
<td>𝐃</td>
<td>1.0 × 10⁻⁹ m² s⁻¹</td>
<td>Versteeg and Van Swaaij [150], Correia et al. [146]</td>
</tr>
<tr>
<td>σ</td>
<td>0.087 N m⁻¹</td>
<td>Wilcox et al. [172]</td>
</tr>
<tr>
<td>σₑ</td>
<td>0.061 N m⁻¹</td>
<td>Wilcox et al. [172]</td>
</tr>
<tr>
<td>k</td>
<td>11.5 s⁻¹</td>
<td>Astarita [9], assuming pH = 10</td>
</tr>
</tbody>
</table>

and Shultes and of Shulman et al. predict that suppression of liquid mixing inside MECS particles could decrease the gas flux by around 2 – 4 times (i.e. 𝛼𝑀 ≈ 2 – 4) while the Onda correlation predicts only a modest decrease, with 𝛼𝑀 ≈ 1.2. If the former were accurate, suppression of liquid mixing would be critically important, and would significantly counteract the increase in surface area that MECS may provide. It would also bring into question an assumption made by Vericella et al. [3] and Stolaroff et al. [100], that a static pool of liquid is a good model of the fluid in an absorber. On the other hand, if Onda et al. [20] were trusted instead, the flux into MECS would be comparable with a packed column (so the increase in absorption rate would be comparable to the increase in surface area), and the static pool of Vericella et al. [3] and Stolaroff et al. [100] would be a reasonable model system. Figure 3.6 is a similar plot for a tower containing the structured packing Mellapak 500Y; the differences in the value of 𝛼𝑀 are less pronounced, but still significant.

In order to understand this discrepancy, the physical methods used to derive these correlations must be considered. It is clear from Figures 3.5 and 3.6 that the correlations give similar predictions for 𝑘𝐿𝑎 but disagree on how this should be factored into 𝑘𝐿 and 𝑎 separately. Values for 𝑎 inside a packed column are difficult to measure experimentally, and many general-purpose correlations (such as Billet and Shulites [21]) are fitted to 𝑘𝐿𝑎 data, which can force unrealistic values for 𝑎 [24]. On top of these practical difficulties, there is also no universally accepted definition of 𝑎. Some authors define 𝑎 as the fraction of the total packing area
that is covered in liquid [20]. This definition does not take into account the fact that liquid trapped in pockets of packing can become saturated, and its surface area useless for gas absorption purposes. For this reason, some authors define \( a \) as an effective area for mass transfer, calculated either by measuring \( k_G a \) values (gas-side coefficients) in situations where \( k_G \) is known [19], or by systematically varying \( k \) (by adding a catalyst) and analysing the increase in \( k_L a \) using surface renewal theories [15]. The difficulty with these approaches is that the effective area depends upon the capacity of the solvent to absorb gas. Physical solvents with low gas solubility tend to saturate quite quickly, and so pockets of useless solvent form easily. Chemical solvents tend to have higher capacities relative to their absorption rates, so even stagnant pockets which trap liquid for long periods of time are likely to remain useful for gas absorption. In light of this, Danckwerts [15] suggested that, for concentrated chemical solvents such as 30wt% \( \text{K}_2\text{CO}_3 \), it is most appropriate to assume that all wetted area is useful for mass transfer, and so the effective area \( a \) should be set equal to the entire wetted area of the packing. Thus for chemical solvents Danckwerts recommended the Onda correlation be used instead of the Shulman correlation (which was correlated using physical absorption data.) This is supported by the fact that the wetted area predicted by Onda et al. closely matches the area given by Danckwerts and Sharma [142], who measured the effective area for absorption into a chemically reactive solvent.

Regarding structured packing, Tsai et al. [24] found the general-purpose correlation of Rocha et al. [22] gave incorrect predictions for aqueous systems (the errors in effective surface area were similar to those shown in Figure 3.6). It was suggested this could be because Rocha et al. used large amounts of data from distillation columns containing non-aqueous solutions. Hanley and Chen [23] and Tsai et al. [24] give quantitatively similar predictions, but Hanley and Chen’s correlation predicts a decrease in area with increasing liquid velocity: an unintuitive result not found in most correlations. As Tsai et al. measured the surface area using a reactive aqueous solvent, their predictions would appear most applicable to the carbonate
Given that the correlations of Onda et al. and Tsai et al. provide the most appropriate measurements for $a$, Figures 3.5 and 3.6 show that the flux of CO$_2$ into MECS containing 30wt% K$_2$CO$_3$ will only be moderately less than the flux inside a packed column. Thus, in this case, microencapsulation will not significantly reduce the gas flux, and a static, thin layer of solvent is a reasonable model for the fluid inside an absorption column.

The addition of promoters to K$_2$CO$_3$ will increase the Hatta number, which will further reduce the effect of liquid mixing. Indeed, these results suggest it is unlikely that suppression of liquid mixing inside MECS will be significant for any chemical CCS solvents which operate within the pseudo-first order reaction regime, as most solvents either have faster reaction kinetics than unpromoted K$_2$CO$_3$ (and so the Hatta number will be larger, and hence $M$ smaller) or else are too viscous to be used in a standard packed column (in which case the comparison is vacuous.) The pseudo-first order reaction regime encompasses most reversible solvents for CCS, including carbonates and amines [15]. However, irreversible solvents, such as concentrated NaOH solutions, which are currently being considered for direct air capture of CO$_2$ [173], typically operate in the instantaneous reaction regime [15], and for such solvents the degree of liquid mixing may be significant (see section 3.6.)

### 3.3.3 Shell Resistance, Specific Surface Area and Liquid Holdup

As noted by Vericella et al. [3], shell resistance is not particularly significant for this system. Taking $L = 25\mu$m, and considering a PDMS shell with a CO$_2$ permeability of 3000 barrer [174, 175], then Eq. (3.24)–Eq. (3.27) give $\alpha = 0.94$ (i.e. the presence of the shell reduces the gas flux by 6%; see also Figure 3.9 below.) For solvents that absorb gas more quickly, such as promoted K$_2$CO$_3$ or the physical solvent Selexol, shell resistance will be more significant.

The final factor that can affect $\Gamma$ (c.f. Eq. (3.15)) is the relative surface area, which can be broken down into the surface area per unit volume of solvent and
Figure 3.5: Values of $a$, $k_L$, $k_{La}$ and $\alpha_M$ for 30wt% K$_2$CO$_3$ flowing down a packed column containing 1/2-inch Raschig Rings, as a function of liquid flow rate, $L$, using the correlations of Shulman et al. [19], Onda et al. [20] and Billet and Shultes [21].
Figure 3.6: Values of $a$, $k_L$, $k_{La}$ and $\alpha M$ for 30wt% K$_2$CO$_3$ flowing down a packed column containing the structured packing Mellapak 500Y, as a function of liquid flow rate, $L$, using the correlations of Rocha et al. [22], Hanley and Chen [23] and Tsai et al. [24]. Note that Tsai et al. only provides a prediction for $a$, so values of $k_L$ and $\alpha M$ were calculated based on the average of the $k_{La}$ predictions of Rocha et al. and Hanley and Chen.
the liquid holdup inside the unit operation. Vericella et al. [3] only considered the first factor: they assumed the surface area per unit volume of solvent in a packed column was equal to 1000 m$^2$m$^{-3}$, and compared this with the much higher values for MECS. While this is a reasonable first estimate, a more rigorous approach is to use correlations for $a$. For example, in the K$_2$CO$_3$ system discussed above, the specific surface area per unit volume of absorber of Mellapak 500Y with a liquid flowrate of 5 kg m$^{-2}$s$^{-1}$ is approximately 360 m$^2$m$^{-3}$ (see Figure 3.6.) If the liquid layer were 1 mm thick (as assumed by Vericella et al.) then, as

$$h = \text{Liquid thickness} \times a,$$  \hspace{1cm} (3.30)

the liquid holdup, $h$, inside the column would be 36%. Suess and Spiegel [176] developed the following correlation for liquid holdup for Mellapak 500Y when $L/\rho < 40$ m$^3$m$^{-2}$h$^{-1}$:

$$h = 1.69 \times 10^{-4}a_t^{0.83} \left( \frac{L}{\rho} \cdot \left[ \frac{\text{m}^2\text{h}}{\text{m}^3} \right] \right)^{0.37} \left( \frac{\mu}{\mu_{\text{water},20^\circ\text{C}}} \right)^{0.25},$$  \hspace{1cm} (3.31)

where $L/\rho$ should be measured in m$^3$m$^{-2}$h$^{-1}$. According to this correlation, for a liquid flow rate of 5 kg m$^{-2}$s$^{-1}$, the holdup of a K$_2$CO$_3$ solution is 8.9%. Rearranging Eq. (3.30), the liquid film thickness will be closer to 0.25 mm: 4 times thinner than originally assumed. This calculation, which is based on validated surface area and liquid holdup correlations, suggests that in comparing MECS with a traditional absorption column, Vericella et al. may have significantly overestimated the increase in specific surface area MECS may provide. However, it does not invalidate their experimental approach of using a 1mm thin film to simulate an absorption column. This is because, as absorption is strongly diffusion controlled in unpromoted K$_2$CO$_3$, the initial absorption rate per unit area is independent of film thickness.

In Figure 3.7, the increase in surface area per unit volume of absorber that MECS can provide, $a_{\text{MECS}}/a$, is plotted against particle diameter for various packings, assuming various $\varepsilon$ values. The chosen voidages are typical of fluidised bed operations.
though $\varepsilon = 0.8$ is also a reasonable value for a bed of MECS supported in a porous packing. Following Vericella et al. [3], the increase in area per unit volume of solvent is also plotted, assuming the liquid in the packed bed is 1mm thick. The equation for this line is:

$$\Lambda \equiv \frac{3/r}{1000 \text{ m}^2 \text{ m}^{-3}}.$$  \hspace{1cm} (3.32)

The increase in surface area on a reactor-volume basis is generally smaller than $\Lambda$. Indeed, if the largest MECS particles ($r = 300 \mu m$) were placed in a fluidised bed with $\varepsilon = 0.95$, then the surface area on a unit volume of absorber basis would be almost identical to that of a traditional absorber containing Mellapak 500Y, even though the calculation of Vericella et al. would suggest a 10-fold increase in specific surface area in this case. In general, the assumption of a 1mm thin layer appears relatively optimistic, and for Mellapak 500Y it leads to an overestimation of the enhancement in surface area by a factor of 3-10. While the large surface areas inside the packed columns could in principle be due to very large liquid holdups, liquid holdups are typically $<15\%$ for these packings [176, 158], so the discrepancy is instead predominantly due to thinner than expected liquid films.

### 3.3.4 Absorption Rate per Unit Volume of Absorber

In Figure 3.8, all the above factors are combined to give the overall increase in specific absorption rate, $\Gamma$, as a function of MECS diameter. $\Lambda$, as defined in Eq. (3.32), is also plotted. The enhancement plateaus for very small particles as mass transfer becomes reaction controlled, but for the smallest MECS which are currently manufactured (with diameters of about 100$\mu$m) mass transfer is still close to diffusion controlled ($\phi = 5.3$ in this case.) The transition to the reaction-controlled regime will be even less significant for promoted carbonate solutions or other solvents with faster reaction kinetics. In Figure 3.9, the various contributions to $\Gamma$ highlighted in Eq. (3.16) are plotted separately for one particular system. The four contributions are the ratio of the specific surface areas on a volume of reactor basis, $a_{\text{MECS}}/a$, the effect of shell resistance, $\alpha$, the effect of suppression of liquid mixing, $1/\sqrt{1 + Ha^{-2}}$, and...
Figure 3.7: The increase in surface area on a unit volume of absorber basis which MECS can provide relative to a packed column, $a_{\text{MECS}}/a$, plotted against particle diameter for various packing types. Also plotted is the increase in surface area per unit volume of solvent assuming a 1mm thin layer of liquid in the packed column, $a'_{\text{MECS}}/1000\text{m}^2\text{m}^{-3}$. M500Y: Mellapak 500Y. Raschig: 1/2 Inch Raschig Rings. $\varepsilon$: voidage inside absorber containing MECS particles. Operating Conditions: 30wt% K2CO3 flowing at 5 kg m$^{-2}$ s$^{-1}$. 
and the transition from the diffusion controlled to the reaction controlled regime, 
\((\phi \coth \phi - 1)/\phi\). Because Figure 3.9 is a log-log plot, the 4 independent contributions 
graphically sum to the overall value of \(\Gamma\). It may be seen that both the suppression 
of liquid mixing and the presence of shell resistance have a relatively minor influence 
on the value of \(\Gamma\): each affect its value by \(< 10\%\).

Overall, the difference between \(\Gamma\) and \(\Lambda\) shown in Figure 3.8 is similar to that 
shown in Figure 3.7, and can largely be attributed to the large liquid surface areas 
in packed columns. For small MECS with diameters of 100\(\mu\)m, the improvement 
microencapsulation can provide ranges from 7 – 60, and the value of \(\Lambda\) at this point 
is at the very top of this range. In general, \(\Lambda\) is a relatively optimistic estimate 
for the enhancement in specific absorption rate MECS can provide, and it may 
overestimate the improvement by as much as a factor of 10. While further work 
should be undertaken to design and size specific processes utilising MECS, these 
results suggests that, for chemically reactive solvents, the improvement in specific 
absorption rate may not be as significant as has been claimed to date.

3.3.5 Selexol for \(\text{CO}_2\) Removal

If a gas is absorbed by a MECS particle containing a physical solvent, the flux does 
not asymptote to a constant expression, however the dynamics are well approxi-
mated by the linear driving force model, Eq. (3.19). Unlike the diffusion-controlled 
MECS containing chemically reactive solvents discussed above, the flux into physi-
cal solvents depends on the particle radius. The flux is larger for smaller particles, 
as concentration gradients increase as particle size is reduced. Given that the di-
ameters of MECS particles may be smaller than the thickness of the liquid flowing 
down an absorption column, this effect may lead to an increase in gas flux. On 
the other hand, physical solvents may also be considered the limiting case of very 
slow chemically reactive solvents, and it has been found that suppression of liquid 
mixing (and associated convective mass transfer) is particularly significant for such 
solvents. The relative weight of these competing factors can only be assessed on a
Figure 3.8: $\Gamma$ vs particle diameter for various packing types and values of $\varepsilon$. Also plotted is the increase in surface area per unit volume of solvent assuming a 1mm thin layer of liquid in the packed column, $a'_{\text{MECS}}/1000\text{m}^2\text{m}^{-3}$. M500Y: Mellapak 500Y. Raschig: 1/2 Inch Raschig Rings. $\varepsilon$: voidage inside absorber containing MECS particles. Operating Conditions: 30wt% K$_2$CO$_3$ flowing at 5 kg m$^{-2}$ s$^{-1}$. 
Figure 3.9: Various contributions to $\Gamma$, broken down according to the factorisation of Eq. (3.16). ‘Area Increase’ refers to the area increase provided by MECS, $a_{\text{MECS}}/a$; ‘Shell Resistance’ refers to the reduction in flux due to the MECS’ shell, $\alpha$; ‘Suppression of Liquid Mixing’ refers to the reduction in flux due to suppression of liquid mixing, $1/\sqrt{1 + Ha^{-2}}$; ‘Transition to Reaction Control’ refers to the reduction in flux due to the transition to reaction control, $(\phi \coth \phi - 1)/\phi$; ‘$\Gamma$’ refers to the overall value of $\Gamma$, which is the multiplicative product of all other terms. Conditions are identical to the curve for Mellapak 500Y, $\varepsilon = 0.9$ in Figure 3.8.
Table 3.3: Physical Properties of Selexol at 30°C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ</td>
<td>1030 kg m⁻³</td>
<td>Li et al. [179]</td>
</tr>
<tr>
<td>µ</td>
<td>6.35 × 10⁻³ Pa s</td>
<td>Li et al. [179]</td>
</tr>
<tr>
<td>D</td>
<td>7.4 × 10⁻¹⁰ m² s⁻¹</td>
<td>Poling et al. [180]</td>
</tr>
<tr>
<td>σ</td>
<td>0.035 N m⁻¹</td>
<td>Li et al. [179]</td>
</tr>
<tr>
<td>σ_c</td>
<td>0.061 N m⁻¹</td>
<td>Wilcox et al. [172]</td>
</tr>
<tr>
<td>H</td>
<td>1.5 × 10⁻³ mol Pa⁻¹ m⁻³</td>
<td>Kohl and Nielsen [177]</td>
</tr>
</tbody>
</table>

The absorption of CO₂ from a CH₄/CO₂ mixture into MECS containing the physical solvent Selexol is analysed below; relevant material properties are summarised in Table 3.3. Selexol is a mixture of polyethylene glycol dimethyl ethers, which is widely used to remove acid gases from high-pressure (2-14MPa) gas streams [177]. While MECS containing physical solvents such as Selexol have not yet been manufactured, there is no reason in principle why they could not be, and, just as for chemical solvents, the increase in surface area could lead to substantial reductions in unit size. MECS with shell thicknesses equal to 10% of their diameter were compared with a packed column containing metal IMTP-40, which is often used in Selexol-based acid gas treating operations [178]. The correlation of Hanley and Chen [23] was used to predict $k_L$ and $α$: this correlation was specifically regressed using data from IMTP packings, and was in good agreement with experimental data for several physical solvent systems.

In Figure 3.10, values of $M$ are plotted against MECS diameter for various liquid flow rates. As opposed to chemical solvents (for which $M ≥ 1$) the flux of gas into the smallest MECS particles containing Selexol was larger than the flux into a comparable absorption column. In this case, the reduction in particle size, with associated increase in concentration gradients, is more significant than the suppression of liquid mixing, and microencapsulation would increase both the specific surface area and the gas flux. This is in spite of the fact that, because this solvent absorbs gas quite quickly, shell resistance is particularly significant, with $α ≈ 0.5$ in this case. For solvents which absorb gas more slowly, shell resistance will
be less significant, and the enhancement that microencapsulation can provide will be correspondingly greater. In Figure 3.11, the increase in specific absorption rate into MECS, $\Gamma$, is plotted against particle diameter for various values of $\varepsilon$. $\Lambda$, as defined by Eq. (3.32), is also plotted. It can be seen that, for the smallest MECS particles, microencapsulation would increase the specific gas absorption rate by even more than $\Lambda$ predicts, and for the smallest particles the increase would be 50-150-fold. This is in contrast to the case of the chemically reactive K$_2$CO$_3$ solution shown in Figure 3.8, for which $\Lambda$ was a relatively optimistic estimate. The increase in gas flux is an improvement not accounted for in a naive surface area comparison.

To date, research into MECS has focussed on chemical solvents, however these results suggest that microencapsulation could be more effective for physical solvents, especially for the smallest MECS particles. The dual benefit of enhanced area and enhanced flux means that the specific gas absorption rate increases as $1/r^2$, rather than $1/r$. The formation of small MECS containing ionic liquids which physically absorb carbon dioxide [181] should continue to be investigated.

Throughout this analysis, it was assumed that both gas-phase resistance and internal liquid motion were insignificant; the validity of these assumptions are discussed in the following two sections.

### 3.4 Gas-Phase Resistance

Absorption from dilute gas streams is gas-side controlled whenever $k_G/(EHk_L) \ll 1$, and liquid-side controlled for $k_G/(EHk_L) \gg 1$, where for physical solvents the enhancement factor due to reaction, $E$, is equal to 1, while for chemical solvents undergoing pseudo-first order reactions, Danckwerts [18] predicts $E = \sqrt{1 + Ha^2}$.

Both Onda et al. [20] and Shulman et al. [19] developed correlations for $k_G$, and their predictions were in much better agreement than their $k_L$ correlations, only varying by $\pm 15\%$ over the range $100 < Gd/\mu_G(1 - \varepsilon') < 10,000$ [20]. In Table 3.4, values of $k_G/(EHk_L)$, calculated via the correlation of Onda et al., are listed for the various systems analysed above. In all cases considered this ratio was orders
Figure 3.10: \( M \) values for CO\(_2\) absorption into Selexol solvent as a function of particle radius, for various liquid flow rates, \( L \), in the absorption column. Steel IMTP-40 packings are used. To maintain consistency with the chemical solvent case, a decrease in \( M \) is associated with an increase in flux into the MECS particles, see Eq. (3.20).
Figure 3.11: $\Gamma$ values for CO2 absorption into Selexol solvent as a function of particle radius, for various column voidages, $\varepsilon$, assuming $L = 5 \text{ kg m}^{-2} \text{ s}^{-1}$. Steel IMTP-40 packings are used.
Table 3.4: Values of $k_G/\langle EHk_L \rangle$ for various solvent systems.

<table>
<thead>
<tr>
<th>System</th>
<th>$k_G/\langle EHk_L \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selexol, IMPT-40</td>
<td>194</td>
</tr>
<tr>
<td>Unpromoted 30wt% K$_2$CO$_3$, pH = 9, 1/2-Inch Raschig Rings</td>
<td>6395</td>
</tr>
<tr>
<td>Unpromoted 30wt% K$_2$CO$_3$, pH = 10, 1/2-Inch Raschig Rings</td>
<td>3160</td>
</tr>
</tbody>
</table>

of magnitude greater than 1, and so the assumption of liquid phase control is very reasonable in these absorption columns. This should also be the case for MECS particles, as even though gas-phase mass transfer resistance into MECS may be different to that in a column, it is unlikely to be orders of magnitude larger.

### 3.5 Internal Liquid mixing

It was assumed in the analysis above that internal motion of the liquid inside MECS is not significant enough to influence the rate of gas absorption. This assumption should be valid for static MECS placed in a packed column. While it is possible for convective currents, caused by the formation of density gradients, thermal gradients, surface tension effects or solvent evaporation, to form spontaneously in static liquids during gas absorption, models based upon pure diffusion with reaction have been shown to be reasonable for many static liquids [15], and the presence of the solid MECS shell will only suppress convective motion further. On a practical level, stacking $\sim$100 µm MECS directly into a packed column is infeasible, as the pressure drop would be far too large. However it may be possible to pelletize MECS inside porous supports. Such an approach could help to solve several issues related to heat recovery and solids handling, and it is a plausible pathway for the industrial application of MECS for which the analysis above is completely valid.

On the other hand, if MECS particles are fluidised, it is possible that changes in angular velocity and compression of the shells during particle collisions could lead to mixing inside the particles, and could influence the rate of mass transfer. For the case of chemically reactive solvents, it seems unlikely that mass transfer will be influenced by particle movement. It was shown above that, even for a solvent with
relatively slow reaction kinetics placed inside an absorption column, liquid mixing did not significantly affect mass transfer. The Hatta number of the liquid inside a MECS particle should be larger than in an absorption column, as the capsule walls will tend to suppress liquid motion, and so $M$ would be even closer to unity in this case. This is supported by the experiments of Vericella et al. [3], who fluidised MECS containing 3wt% K$_2$CO$_3$ in a stream of CO$_2$. The MECS contained thymol blue, so that the CO$_2$ loading could be visualised. In videos of their experiment, some particles were heavily fluidised, while others were immobile, clumped together at the top or bottom of the column. However, all particles changed colour at the same rate, independent of the degree of particle motion.

In order to investigate the effect of larger particle strains on gas uptake rate, 500 $\mu$m MECS containing 3wt% K$_2$CO$_3$ and thymol blue, supplied by Lawrence Livermore National Laboratory, were analysed in the apparatus shown in Figure 3.12. A number of MECS were placed inside region A where they could be compressed by manually moving the right glass rod. Several more MECS were placed in region B, where they would not undergo any compression. The entire junction was flooded with CO$_2$, and the MECS particles in region A were manually compressed at $\sim 2.5$ Hz with Cauchy strains between 30-80% until CO$_2$ absorption was complete. As shown in Figure 3.13, the rate of colour change was identical for particles in region A and region B, indicating that even extremely large particle strains would not affect the rate of mass transfer into even a relatively slow, non-viscous chemically reactive solvent. For more viscous solvents, or solvents with faster chemical kinetics, liquid mixing should be even less significant.

While it seems likely that MECS motion will not influence gas absorption in particles containing chemically reactive solvents, it is unclear if this would also be true for MECS containing physical solvents, for which liquid mixing is typically a more significant factor. No experimental data analogous to that above is available for this case. Below we present the results of some preliminary calculations.

Liquid mixing inside a spherical MECS particle can be induced by changes in the
Figure 3.12: Testing the effect of particle compression on gas absorption. Particles in region A are crushed as the right piston is manually moved, while particles in region B are not compressed. Both regions are exposed to identical CO$_2$ partial pressures, and gas uptake is monitored by observing particle colour change.

Figure 3.13: MECS particles changing colour as they absorb CO$_2$. The rate of colour change is identical for particles manually compressed between two glass plates (left) and uncompressed particles placed in the same gas environment. Compression frequency $\approx 2.5$ Hz, compressive strain $\approx 30 - 80\%$. 
angular velocity and by particle compression during collisions. In order to investigate
the former, a 3D, dynamic model of a spherical ball of liquid was created using the
simulation software arb [182]. The model simultaneously solved the Navier-Stokes
equations and the convection-diffusion-reaction equation, and was used to study how
changes in the angular velocity of the surface of the liquid (analogous to changes in
the angular velocity of a rigid MECS shell during a collision) influenced liquid flows
inside the particle and the rate of gas absorption. Details of the simulation may be
found in Appendix 3.IV. Both pure diffusion and diffusion with first order chemical
reaction were studied over $10^{-1} < Re < 10$, $1 < \phi < 10^2$ (for the chemical system)
and $10 < R^2\omega/D < 10^3$ (this last dimensionless parameter represents the relative
timescales for the mass transfer and momentum transfer problems.) When the
angular velocity of the shell was regularly changed, complex flow patterns developed
inside the fluid (Figure 3.14). However, in all cases tested, the radial component of
the velocity was at least 3 orders of magnitude smaller than the mean fluid velocity
(see Figure 3.15.) Unsurprisingly (given this finding) the shell rotation also had no
significant effect on the rate of gas absorption - the numerical solutions with liquid
motion differed from the analytical solution for a static fluid [25] by on average less
than 0.3% (see Figure 3.16).

Particle compression could also cause liquid motion inside MECS. By extending
the linear elastic theory of Hertz [183] and Reissner [184], Berry et al. [185] derived
the following equation, valid for $0 < z/R \leq 1$, for the force with which a hollow
elastic shell will resist deformation:

$$F \sqrt{3(1 - \nu^2)} = \varepsilon \beta_1 \left(\frac{C \delta}{z}\right)^{\beta_2}.$$  \hspace{1cm} (3.33)

Here $z$ is the shell thickness, $\delta$ the shell deformation, and $R$ the particle radius. The
linear elastic theory gives reasonable predictions until buckling occurs at approxi-
mately $\delta/z = 3$ [186], however, as Eq. (3.33) does not account for the presence of
the viscous liquid inside the capsules, particle compression will be overestimated.
$\beta_1$ and $\beta_2$ are constants that depend on $z/R$, while, following Reissner [184], $C = 1$
Figure 3.14: Simulated velocity field inside a dynamically rotating spherical ball of fluid with regular changes in its surface angular velocity. This image corresponds to $t = 3.6$ in Figure 3.15. Even though relatively complex flow patterns can form inside the sphere, the radial component of the velocity is always negligible, and the rate of gas absorption is not influenced by the liquid motion. Re = 10.

Figure 3.15: The volume-averaged radial component of the velocity, $|\mathbf{u} \cdot \mathbf{r}|$, divided by the volume averaged magnitude of the velocity, $|\mathbf{u}|$, for a sphere of liquid with a rotating surface. The sphere is initially stationary, and at $t = 0$ its shell is set in motion. At times 2.5, 3.0 and 3.5 the shell’s angular velocity is randomly changed (dotted lines), inducing the complex flow patterns shown in Figure 3.14. Nevertheless, $|\mathbf{u} \cdot \mathbf{r}|/|\mathbf{u}| \ll 1$ at all times. Re = 10
Figure 3.16: Mean value of absorbed gas concentration gradient, $|\partial \bar{c}/\partial \bar{r}|$, at the surface of two rotating spheres of liquid with $\text{Re} = 10$ and $\text{Re} = 1$, and a static sphere with $\text{Re} = 0$. The gas absorbs and reacts via a first order reaction, and for $\text{Re} = 0$ an analytical solution was used [25]. Shell velocities are identical to those in shown Figures 3.14 and 3.15, except that in the $\text{Re} = 1$ case the magnitude of $\omega$ is reduced by a factor of 10. The maximum difference between $\text{Re} = 1$ and $\text{Re} = 10$ is less than 0.002%, and the mean difference between $\text{Re} = 10$ and the analytical solution at $\text{Re} = 0$ is 0.25%. $\phi = 1$, $R^2 \omega/D = 100$. 
for the single-sided compression which occurs when a MECS particle collides with a wall or another particle. By integrating Newton’s second law with the force term given by Eq. (3.33), the maximum particle deformation, $\delta_{\text{max}}$, can be calculated as a function of $z/R$ and the initial particle velocity, $v_0$ (see Appendix 3.V for details of this calculation.) The results are shown in Figure 3.17, in which $\delta_{\text{max}}/D$ is plotted against $v_0$.

Meissner and Kusik [187] showed that in a fluidised bed containing 200 µm particles of sand, particle velocities were comparable to the gas superficial velocity. The correlation of Wen and Yu [188] predicts that minimum fluidisation of 100–500µm particles with $\rho = 1300 \text{ kg m}^{-3}$ will occur at gas velocities of $0.5 - 10 \text{ cm s}^{-1}$, and the phase diagram of Grace [189] predicts that for these particles the bubbling fluidisation regime will persist for gas velocities 1-2 orders of magnitude larger than minimum fluidisation, with the onset of turbulent fluidisation above that. These results suggest that particle velocities in fluidised beds containing MECS are likely to be on the order of magnitude of $1 \text{ m s}^{-1}$, and possibly even larger for vigorous fluidisation of bigger MECS particles.

Despite the large gas velocities, the strains shown in Figure 3.17 are significantly less than those experienced by the MECS which were compressed in the experiment above, and it is still expected that, for chemically reactive solvents, compressions should not influence the gas flux. For physical solvents, on the other hand, it is difficult to make any absolute conclusions. It is plausible that regular, sudden strains of 10-20% coupled with instantaneous changes in particle angular velocity could lead to significant liquid motion which could enhance mass transfer. Further experimental or modelling work is required to determine if the flux may be affected by liquid motion in this case.
Figure 3.17: Maximum deformation of MECS particles during a collision with a wall, as a function of relative shell thickness, $z/D$, and particle velocity before the collision, $v_0$. 
3.6 Sensitivity to Liquid Mixing: A General Approach

In sections 3.2 – 3.3, the effect of suppression of liquid mixing inside MECS was studied for two common cases: a chemical solvent in the pseudo-first order reaction regime, and a physical solvent. A large number of industrially-relevant systems fall within these domains, however other regimes, such as the instantaneous reaction regime used to model CO2 absorption into concentrated NaOH solutions, are also common. In the above analysis, more general reaction regimes were not considered because they did not lead to simple expressions for the flux into MECS particles. For example, for a second order reaction between a gas A and a reactive species in the liquid, B,

\[ A + B \xrightarrow{k_2} C \]  

(3.34)

the flux depends not only on the average concentration of B, but also on its concentration profile, which itself depends on the particle’s history. It is therefore difficult to find simple expressions for \( J_{\text{MECS}} \) which can be compared with the flux in an absorption column, \( J_{\text{Column}} \), in order to quantify the effect of liquid mixing.

Nevertheless, the analysis above indicates that some solvents (such as physical solvents or solvents in the slow pseudo-first order reaction regime) are quite sensitive to liquid mixing, while others (such as solvents in the fast pseudo-first order reaction regime) are not. Even if general, steady-state expressions for \( J_{\text{MECS}} / J_{\text{Column}} \) cannot be derived, it would be helpful to find some way of quantifying whether the flux into a particular chemical solvent is likely to be affected by changes in the degree of liquid mixing. This also has implications beyond microencapsulation, as a large number of traditional and emerging gas absorption technologies rely on liquid agitation enhancing the gas flux. For example, Roy et al. [190] recently created structured metal packings with a striped hydrophobic coating, in order to stimulate liquid mixing to increase the rate of CO2 absorption into concentrated chemical solvents. Similarly, Hosseini et al. [191] recently demonstrated that high-frequency pulsation of a chemical solvent flowing on the shell side of a hollow-fibre membrane significantly increased gas flux. Agitated gas-liquid [192] and liquid-liquid [193, 194]
contactors have also been widely used for many decades. Many studies have investigated the relationship between agitation rates and $a$ or $k_L$ [195, 196, 197], however to the author’s knowledge the relationship between liquid agitation and the gas flux has not been systematically investigated over a range of chemical absorption regimes.

In this section, a parameter which quantifies the sensitivity of gas flux to changes in the degree of liquid mixing is introduced. This parameter may be numerically calculated using widely-used theories of absorption into agitated liquids, including the surface renewal theory [18], the penetration theory [17], the film theory [16], or the eddy diffusivity theory [198]. The analysis may be applied to a chemical solvent with arbitrarily complex chemical kinetics, in order to help map out the parameter regimes in which enhanced liquid agitation (via pulsation, surface coatings, or otherwise) would increase the gas flux, or in which suppression of liquid mixing (via microencapsulation or otherwise) is likely to decrease the gas flux. This information may then be used to guide parameter selection prior to a detailed design.

After the theory is developed, it is used to analyse three cases of increasing complexity: an irreversible second order reaction, which may be analysed using an empirical expression for the enhancement factor; a reversible second order reaction, which is analysed via the film theory; and the absorption of CO2 into a dilute K2CO3 solution, which is analysed via a steady-state eddy diffusivity model, accounting for coupled ionic diffusion effects.

### 3.6.1 Theoretical Development

Consider an agitated physical solvent absorbing a gas species, under conditions in which gas-phase mass transfer resistance may be ignored. For such a system, the gas flux, $J$, will depend upon the degree of liquid agitation, and an increase in agitation will tend to increase both the flux and the liquid-side mass transfer coefficient, $k_L$, according to:

$$J = k_L \Delta c.$$  \hfill (3.35)
It is clear that, if $\Delta c$ and other physical parameters remain constant, $J$ will be proportional to $k_L$: a 1% increase in $k_L$ due to enhanced agitation will correspond to a 1% increase in $J$. Mathematically, this is equivalent to the statement that the following parameter, $\xi$, is equal to unity:

$$
\xi \equiv \left( \frac{\partial J/J}{\partial k_L/k_L} \right)_{\Delta c,D} = \left( \frac{\partial \log J}{\partial \log k_L} \right)_{\Delta c,D} = 1. \quad (3.36)
$$

In what follows, $\xi$ shall be referred to as the sensitivity of the flux to liquid agitation. The sensitivity relates the fractional increase in flux, $dJ/J$, to the fractional increase in liquid-phase mass transfer coefficient, $dk_L/k_L$, caused solely by enhanced liquid agitation, all else held constant. For a physical solvent $\xi$ is not particularly interesting, as it is always equal to 1. For a chemical solvent, it is defined as:

$$
\xi \equiv \left( \frac{\partial \log J}{\partial \log k_L} \right)_{\alpha_i} = \left( \frac{\partial \log J}{\partial \log k_L} \right)_{c^*,w_0,D_i,k}. \quad (3.37)
$$

where $\alpha_i$ is used to indicate that all physical and chemical properties (all boundary concentrations, diffusivities, reaction rate constants, etc.) are held constant, so the flux is only influenced by the degree of liquid agitation. If $\xi \approx 1$, the solvent behaves as a physical solvent, and as the liquid is agitated the flux increases in proportion to the mass transfer coefficient. However, if $\xi \approx 0$, the flux is insensitive to the degree of liquid agitation. The utility of $\xi$ is that it may be numerically calculated for a solvent with arbitrary chemical kinetics in order to systematically assess the sensitivity of gas flux to liquid agitation in various absorption regimes.

### 3.6.2 Irreversible 2nd-Order Reaction

Consider a gas, $A$, absorbed by an agitated liquid in which it reacts with a dissolved species, $B$, according to the following irreversible second-order reaction:

$$
A + zB \xrightarrow{k_2} \text{Products}. \quad (3.38)
$$
If liquid-side resistance is mass transfer limiting, the flux of gas is given by:

\[ J = E k_L c^* \] (3.39)

where the enhancement factor, \( E \), is typically written as a function of the following dimensionless parameters [15]:

\[ E_i = 1 + \frac{w_0 D_2}{z c^* D_1} \] (3.40)

\[ M = \frac{k_2 w_0 D_1}{k_L^2} \] (3.41)

where \( w_0 \) is the bulk concentration of \( B \), \( c^* \) is the surface concentration of \( A \), \( E_i \) is the enhancement factor for instantaneous reaction, and \( M \) is the square of the Hatta number. A large number of correlations for \( E \) were surveyed by Wellek et al. [199], and the following explicit correlation was recommended:

\[ \frac{1}{(E-1)^{1.35}} = \frac{1}{(E_i-1)^{1.35}} + \frac{1}{(E_1-1)^{1.35}} \] (3.42)

where

\[ E_1 = \frac{\sqrt{M}}{\tanh \sqrt{M}}. \] (3.43)

For this system, the sensitivity of the gas flux to changes in liquid mixing is defined as:

\[ \xi = \left( \frac{\partial \log J}{\partial \log k_L} \right)_{D_1,D_2,k_2,c^*,w_0}. \] (3.44)

It is not difficult to show (see Appendix 3.VI) that, when \( E = E(E_i, M) \),

\[ \xi = 1 - 2 \left( \frac{\partial \log E}{\partial \log M} \right)_{E_i}. \] (3.45)

Substituting in Eq. (3.42) and Eq. (3.43) gives

\[ \xi(E_i, M) = 1 - \frac{1}{E} \left( \frac{E - 1}{E_1 - 1} \right)^{2.35} \left( \frac{\sqrt{M}}{\tanh \sqrt{M}} - \frac{M}{\sinh^2 \sqrt{M}} \right) \] (3.46)
Figure 3.18: Sensitivity to liquid mixing, $\xi$, as a function of $E_i$ and $\sqrt{M}$.

where $E_1$ is defined by Eq. (3.43) and $E$ may be evaluated via Eq. (3.42).

Values of $\xi$ are plotted in Figure 3.18. For very small $M$ (slow pseudo-first order reaction, with $\sqrt{M} < 1/10$) and for very large $M$ (instantaneous reaction, with $\sqrt{M} > 10E_i$), $\xi \approx 1$ and absorption will be sensitive to liquid mixing. These are the absorption regimes in which pulsation in a hollow fibre or surface modification of a structured packing would be a rational design choice. However, for large $E_i$ and intermediate $M$ (the fast pseudo-first order reaction regime, with $E_i > 100$ and $3 < \sqrt{M} < E_i/2$), $\xi \approx 0$, and increased liquid agitation will have negligible effect on the gas flux.

The decrease in $\xi$ with $M$ on the left hand side of Figure 3.18 is consistent with sections 3.2 – 3.3, in which it was found that increasing the reaction rate decreased the sensitivity of the gas flux to liquid agitation for solvents in the pseudo-first order reaction regime, until ultimately, for solvents such as concentrated aqueous K$_2$CO$_3$ in the fast pseudo-first order reaction regime, liquid agitation has negligible effect. However, the present analysis is not confined to the pseudo-first order regime, and it suggests that if the reaction rate is increased even further, liquid agitation once again becomes significant (c.f. the increase in $\xi$ for large values of $M$.) In this regime,
the reaction is so fast that the pseudo-first order assumption is no longer valid, and agitation assists in transport of reactive species from the bulk to the liquid surface. These findings suggest that liquid agitation is likely to be significant for solvents with very fast kinetics, such as the absorption of CO₂ into concentrated NaOH solutions currently being considered for direct air capture [173]. Microencapsulation of such solvents will likely lead to a significant reduction in the gas flux.

3.6.3 General Reaction Kinetics via Film Theory

Many chemical solvents of practical interest contain multiple reactive species undergoing simultaneous reactions with various rates and degrees of reversibility. In complex systems such as these, ξ may be calculated numerically via the film theory in a straightforward manner. Because

\[ k_L = \frac{D_1}{\delta} \]

in the film theory [15], Eq. (3.44) becomes

\[ \xi = \left( \frac{\partial \log J}{\partial \log k_L} \right)_{\alpha_i} = - \left( \frac{\partial \log J}{\partial \log \delta} \right)_{\alpha_i} \]

(3.48)

where \( \delta \) is the film thickness, and \( \alpha_i \) denotes all the diffusivities, reaction rates and boundary concentrations. Eq. (3.48) may be evaluated by numerically solving the steady state differential equations for diffusion and reaction inside the thin film [15] and calculating the rate of change of \( \log J \) with \( \log \delta \), all else kept constant.

Consider, for example, the absorption of species A into a liquid containing species B, C and D in which it reacts according to the following reversible reaction:

\[ A + B \xrightleftharpoons{\frac{k_1}{k_2}} C + D \]

(3.49)
The film theory predicts that absorption is governed by the following set of simultaneous differential equations:

\[ D_A \frac{\partial^2 c_A}{\partial x^2} = D_B \frac{\partial^2 c_B}{\partial x^2} = -D_C \frac{\partial^2 c_C}{\partial x^2} = -D_D \frac{\partial^2 c_D}{\partial x^2} = k_1 c_A c_B - k_1 c_C c_D / K \]  

(3.50)

With boundary conditions

\[ c_A|_{x=0} = c_A^*; \quad \partial_x c_B|_{x=0} = \partial_x c_C|_{x=0} = \partial_x c_D|_{x=0} = 0 \]  

(3.51)

\[ c_B|_{x=\delta} = c_B^0; \quad c_C|_{x=\delta} = c_C^0; \quad c_D|_{x=\delta} = c_D^0; \quad c_A|_{x=\delta} = c_A^0 c_D^0 / K c_B^0; \]  

(3.52)

where \( K \equiv k_1 / k_2 \). This boundary value problem was non-dimensionalised and solved numerically using the \texttt{bvp4c} algorithm in Matlab [200] (see Appendix 3.VII) and the gas flux was calculated using

\[ J = -D_A \frac{\partial c_A}{\partial x} \bigg|_{x=0}. \]  

(3.53)

Values of \( \xi \) were then calculated via a finite difference approximation to Eq (3.48), for the conditions considered by Glasscock and Rochelle [26] (see Figure 3.19). Once again, the regimes in which enhanced liquid agitation will increase gas flux may be clearly seen. The results are qualitatively similar to the previous section. As the solvent become more concentrated (i.e. as \( c_B^0 / c_A^* \) increases), liquid agitation becomes less significant over a wider range of regimes. This is because, for such concentrated solvents, the pseudo-first order assumption is valid, and agitation plays no role in assisting the transport of reactive species from the bulk to the surface. For very slow and very fast reactions, agitation is significant: in the former case it assists the transport of unreacted absorbed gas to the bulk, while in the latter case it assists the transport of reactive species to the surface.
Figure 3.19: Values of $\xi$ for absorption with reversible reaction as a function of $c_0^B/c_0^A$ and $\sqrt{M} = \sqrt{k_2c_0^B D_A/k_L}$. Absorption conditions, taken from Glasscock and Rochelle [26]: $D_B = D_C = D_D = 0.5D_A$, $c_0^C = c_0^D = 0$, $K = 350$.

### 3.6.4 Eddy Diffusivity Theory for Absorption of CO$_2$ in Dilute K$_2$CO$_3$

The film theory has a long and respectable pedigree in chemical engineering [16, 15, 152]. However, while for systems in the pseudo-first order reaction regime considered above the film theory is in good agreement with other theories, in systems with more complex kinetics it can give incorrect predictions, and more sophisticated models may be required to accurately capture the physics [26]. The boundary layers predicted and observed by Prandtl at fluid-solid boundaries [201, 202] do not occur in the liquid at a free interface, and so the physical meaning of the liquid film is unclear [198]. Further, Glasscock and Rochelle [26] found that, for complex absorption processes such as the uptake of CO$_2$ by MDEA, unsteady-state penetration, unsteady-state surface renewal, and steady-state eddy diffusivity theories are in excellent agreement, while the film theory predicts fluxes which differ by up to a factor of two. Reactive absorption often involves the simultaneous diffusion of multiple ionic species, and a realistic model must also account for the coupling
imposed by the condition of electroneutrality.\footnote{For example, when HCl diffuses into pure water, the mobile protons are ‘held back’ by the slow-moving chloride ions. A microscopic discrepancy in the anion and cation concentration profiles sets up an electric field that slows the protons and speeds up the chloride ions, with the net effect that the whole ensemble progresses in unison. See Newman [203] or Deen [204].}

To demonstrate how these complicating effects could be modelled, $\xi$ will be calculated for CO$_2$ absorption into a dilute K$_2$CO$_3$ solution, using a model which accounts for both eddy diffusivity and coupled ionic diffusion. The results will then be compared with the predictions of section 3.3.

In the steady-state eddy diffusivity theory considered by Glasscock and Rochelle [26] (and originally developed by King [198] and Prasher and Fricke [205]), the diffusivity of a species, $i$, is supposed to be the sum of a molecular diffusivity term, $D_i$, and an ‘eddy diffusivity’, $D_e$, which is assumed to take the form:

$$D_e = ax^m + b$$

where $x$ is the distance from the gas-liquid interface, and $a$, $b$ and $m$ are non-negative parameters. The eddy diffusivity term accounts for the transport of species in turbulent eddies, which (if the eddies move randomly and are of appropriate size) will cause diffusive flux analagous to molecular diffusion. It is common to assume that $D_e = 0$ near the interface, where turbulent eddies are damped by viscous forces, and this implies $b = 0$ [198, 205]. Meanwhile, experimental evidence suggests that $m = 2$ is a reasonable value for the exponent [26, 205]. These assumptions lead to the following steady-state, single parameter eddy diffusivity model:

$$\frac{\partial}{\partial x} \left( (D_i + ax^2) \frac{\partial c_i}{\partial x} \right) = r_i$$

where $r_i$ is the rate of reaction of species $i$. For an absorbed gas, $A$, the boundary conditions are

$$c_A|_{x=0} = c_A^{\text{surface}}, \quad c_A|_{x=\infty} = c_A^{\text{bulk}},$$

$$c_A|_{x=0}$$

$$c_A|_{x=\infty}$$
while for a non-volatile reactive species, $i$, the boundary conditions are

$$\partial_x c_i|_{x=0} = 0; \quad c_i|_{x \to \infty} = c_{i}^{\text{bulk}}. \quad (3.57)$$

The unknown parameter, $a$, plays an analogous role to the film thickness in the film theory or surface lifetime in the penetration theory. For purely physical absorption of a gas, $A$, Eq. (3.55) – (3.57) may be solved [205], in order to relate $a$ to the liquid-side mass transfer coefficient:

$$k_L = \frac{2}{\pi} \sqrt{a D_A}. \quad (3.58)$$

Hence, as with other, single-parameter models, $k_L$ data obtained using general-purpose correlations may be used\textsuperscript{14} to predict gas flux for reactive absorption.

The eddy diffusivity model may also be modified to account for coupled ionic diffusion. If the diffusion of ions obeys Fick’s Law, and if the electrical mobility is related to the molecular diffusivity via the Nernst-Einstein equation, then the transport of ions is governed by a modified Nernst-Planck equation [26]:

$$\frac{\partial}{\partial x} \left( (D_i + a x^2) \frac{\partial c_i}{\partial x} \right) - Z_i D_i \frac{F}{k_B T} \frac{\partial}{\partial x} \left( c_i \frac{\partial E}{\partial x} \right) = r_i \quad (3.59)$$

where $Z_i$ is the charge number of species $i$, $F$ the Faraday constant, $k_B$ the Boltzmann constant, and $E$ the electrical field induced by the difference in ionic diffusivity of the anions and cations present in the solution. The Nernst-Planck equation is the low-concentration limit of the generalised Maxwell-Stefan equations, which should be used for concentrated multicomponent electrolyte solutions [206]. Following Glasscock and Rochelle [26], the eddy diffusivity does not appear in the second term of Eq. (3.59), because the random movement of ions due to turbulent eddies is assumed to be independent of any electrical fields present. The condition that the net flux of charge is zero, $\sum Z_i J_i = 0$, may be used to derive the Henderson

\textsuperscript{13}Eq. (3.58) is analogous to Eq. (3.47), which relates $\delta$ and $k_L$ in the film theory.

\textsuperscript{14}Of course, as stressed in section 3.3.2, care must be taken when selecting $k_L$ correlations.
equation for the electric field strength (see Appendix 3.VIII):

\[ E = \frac{k_B T \sum_i Z_i D_i \nabla c_i}{F \sum_i Z_i^2 D_i c_i} \quad (3.60) \]

Eqs. (3.59) and Eq. (3.60) may then be solved simultaneously to determine the steady-state concentration profiles of all species present, and the gas flux at the surface may be calculated. Because Eqs. (3.59) – (3.60) will preserve charge neutrality, in practice one of Eqs. (3.59) is typically replaced by a simple charge balance of the form:

\[ \sum Z_i c_i = 0. \quad (3.61) \]

Eq. (3.56), (3.57), (3.59), (3.60) and (3.61) were used to model the absorption of CO2 into a dilute K2CO3 solution. Details of the carbonate chemistry and relevant material properties have been discussed previously (see section 3.3 and 2.7), and are also discussed in Appendix 3.VIII, along with details of the numerical solution of the transport equations. The gas flux was calculated from the concentration gradient at the surface,

\[ J = -D_{CO2} \frac{\partial c_{CO2}}{\partial x} \bigg|_{x=0} \quad (3.62) \]

and the sensitivity, \( \xi \), was calculated using a finite difference approximation of Eq. (3.48).

Figure 3.20 shows the variation in \( \xi \) with Hatta number and total K2CO3 concentration for absorption of CO2 at 0.1 bar and 20°C over a physically reasonable range of range of \( k_L \) values (based on the \( k_L \) values considered in section 3.3.2, the Hatta number for a practical column will be between 3 – 10.) The overall trend is the same as in Figures 3.18 and 3.19, and the results are also consistent with the findings of section 3.3. For small Hatta numbers (the slow pseudo-first order regime) agitation is significant. As the Hatta number is increased, and the systems move to the fast pseudo-first order reaction regime, agitation is less significant, and \( \xi \) decreases. For even larger Hatta numbers, however, the pseudo-first order assumption breaks down (though for more concentrated solvents, this pseudo-first order regime
Figure 3.20: Values of $\xi$ for absorption of CO$_2$ into various K$_2$CO$_3$ solutions at 20°C, calculated using the eddy diffusivity model and the Nernst-Planck equation. $p_{CO2} = 0.1$ bar; $T = 20$°C; loading = $c_{OH}^\text{bulk}/k^\text{bulk}_{K^+} = 0.3$. To obtain a range of $\sqrt{D_{CO2}k_2c_{OH}}/k_L$ values, $k_L$ was varied from $1.5 \times 10^{-3}$ m s$^{-1}$ to $7 \times 10^{-7}$ m s$^{-1}$.

is maintained for greater Ha values) and agitation again becomes significant.

The curve for 30wt% K$_2$CO$_3$ should be treated with some skepticism, as the model was designed for dilute K$_2$CO$_3$ solutions. However, it should be accurate in the pseudo-first order regime, and so under practical operating conditions around Ha $\approx$ 5, the true value should not differ significantly from the model’s prediction of $\xi \approx 0.05$. Hence, for CO$_2$ absorption into concentrated K$_2$CO$_3$ solutions under practical operating conditions, the gas flux will be relatively insensitive to liquid agitation, and an increase in $k_L$ due to liquid mixing would lead to an increase in gas flux on the order of 20 times smaller than would occur for a physical solvent.

The results of this section and sections 3.2 – 3.3 both indicate that microencapsulation is most suitable for systems in the fast pseudo-first order reaction regime, and this should be accounted for when considering systems to which microencapsulation could be applied. Technologies designed to increase gas absorption rates via

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15 In the pseudo-first order regime, the complex model collapses to the much simpler model considered in section 3.3, and all relevant physical parameters are expected to be accurate up to 30wt% K$_2$CO$_3$. 

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liquid agitation, on the other hand, should target either slower pseudo-first order reactions, or systems with faster reactions or lower concentrations of reactants, which are not in the pseudo-first order reaction regime.

### 3.7 Conclusions

This chapter provided a number of practical insights into the difference between mass transfer in MECS and in a traditional absorption column. Expressions for $M = J_{\text{MECS}} / J_{\text{Column}}$ suggested that suppression of liquid mixing in MECS is unlikely to reduce the gas flux for chemical solvents in the pseudo-first order reaction regime, provided the reaction rate is at least as fast as that of CO$_2$ in 30wt% K$_2$CO$_3$ (which itself is a relatively slow reaction.) This was supported by calculations of the sensitivity, $\xi$, which approached 0 for solvents in the fast pseudo-first order regime, and was roughly equal to 0.05 for a 30wt% K$_2$CO$_3$ solution. However, the calculation of $\xi$ showed that if the reaction is very fast - so fast that the pseudo-first order assumption is no longer valid - then liquid agitation again becomes significant, and microencapsulation may lead to significant reductions in the gas flux.

The calculation of $\Gamma = \bar{R}_{\text{MECS}} / \bar{R}_{\text{Column}}$ suggested that, for chemical solvents, the increase specific absorption rate which MECS may provide ranged from $\sim 7 - 60$, depending on the diameter of the MECS and the specifics of the units being compared. The increase in surface area estimated by Vericella et al. [3] was at the very top of this range, and may be a little optimistic. The difference between $\Gamma$ and the rough area estimate had little to do with liquid agitation or shell resistance (both of which had negligible influence on $\Gamma$), but was instead related to the estimate for the surface area in an absorber. Modern structured packings have extremely high surface areas, and rigorous correlations for the effective area suggested that the liquid films inside the absorber were around 4 times thinner than Vericella et al. had assumed.

For physical solvents it was found that $J_{\text{MECS}}$ may be greater than $J_{\text{Column}}$ for the smallest MECS particles, because the reduction in spatial scales increases concen-
tration gradients within the liquid. This in turn led to values of $\Gamma = \bar{R}_{\text{MECS}} / \bar{R}_{\text{Column}}$ of between 50 – 150; significantly larger than for chemical solvents. Future work should focus on immobilising such liquids.

CFD simulations revealed that changes in the angular momentum of the particle shells will not significantly affect the mass transfer rate into MECS. However, vigorously fluidised particles could be expected to undergo strains as large as 10-20% during a collision, and this could induce irregular liquid mixing. Experiments on a chemical solvent with relatively slow reaction kinetics, 30wt% K$_2$CO$_3$, revealed that even under much larger strains, mass transfer rates are unaffected by particle motion. This should also remain true for solvents with faster kinetics operating with larger Hatta numbers. On the other hand, it is unclear at present whether particle collisions will affect mass transfer into MECS containing physical solvents, and this case should be investigated through further experimental or modelling work.

Overall, this study suggests microencapsulation could be expected to increase gas absorption rates by approximately an order of magnitude for chemical solvents, and up to 2 orders of magnitude for physical solvents. Further work is required to determine whether this intensification can lead to economically competitive processes.
Appendix 3.I. Mass Transfer into a MECS Particle.

Consider the MECS particle shown in Figure 3.21, which is absorbing a gas species which reacts with a reactive species in the liquid according to a reversible first-order or pseudo-first order chemical reaction. Assuming the liquid core is stationary and the diffusion obeys Fick’s Law, the concentration profile\(^ {16} \) of gas inside the liquid, \( c \), will evolve according to the spherical reaction-diffusion equation [161]:

\[
\frac{\partial c}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D r^2 \frac{\partial c}{\partial r} \right) - R_{\text{net}}
\]  

(3.63)

where \( R_{\text{net}} \) is the net rate of consumption of gas per unit volume of solvent. Because the reaction is reversible, the reaction rate, \( R_{\text{net}} \), may be expressed as the difference between the forward and reverse reaction rates, \( R_{\text{net}} = R_f - R_r \), where \( R_f \) is the rate of consumption of gas, and \( R_r \) is the rate of production of gas due to the reverse reaction. Because the reaction is first or pseudo-first order, the rate of the forward reaction is proportional to the concentration of gas,

\[
R_f = kc
\]  

(3.64)

where \( k \) is the first-order rate constant. In general, the reverse reaction rate, \( R_r \), depends on the loading of the solvent. Suppose the local gas concentration is changed from \( c \) to the concentration in dynamic equilibrium with the solvent, \( \bar{c} \). Then the rate of the forward reaction would be \( R_f = k \bar{c} \), and the rate of the backwards reaction would be exactly the same (to ensure chemical equilibrium):

\[
R_r = k \bar{c}.
\]  

(3.65)

\(^{16}\)As stressed in section 3.3.2, \( c \) is the concentration of free, unreacted gas molecules. For example, when CO\(_2\) is absorbed into a 30wt\% K\(_2\)CO\(_3\) solution, the solution can absorb up to around 10\% of its weight in CO\(_2\). However, almost all of this is stored chemically, as CO\(_2\) molecules react with carbonate to form bicarbonate ions. The concentration of unreacted CO\(_2\) molecules moving inside the liquid is orders of magnitude smaller. Yet this ‘free’ concentration is precisely what determines the rate of reaction and the rate of diffusion of the gas.
Now, if it is assumed that the reverse reaction is independent of the concentration of physically dissolved gas (i.e. of the value of $c$) then it is reasonable to take $R_r = k\bar{c}$ even when $c \neq \bar{c}$, and in this case the general, net reaction rate will equal

$$R_{net} = k(c - \bar{c}) \quad (3.66)$$

even far from equilibrium. This expression is widely used [15, 161], but the assumption that $R_r$ is independent of $c$ is rarely highlighted. In practice, this assumption is usually reasonable, as the physical solubility of the solvent is typically many orders of magnitude smaller than the chemical solubility. At high pressures, however, Eq. (3.66) may be inaccurate.

Combining Eq. (3.63) with Eq. (3.66) gives

$$\frac{\partial c}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( Dr^2 \frac{\partial c}{\partial r} \right) - k(c - \bar{c}) \quad (3.67)$$

Shell resistance will temporarily be ignored, and so the concentration at the fluid boundary will be at equilibrium with the gas partial pressure, which is assumed to be constant:

$$c|_r = c^* = H_{\text{liq}} p_i \quad (3.68)$$
where $H_{\text{liq}}$ is the Henry’s constant in the liquid, and $p_i$ is the partial pressure of the absorbed gas.

The pseudo-first order assumption implies that the chemical composition of the solvent is constant in space, and so $\tilde{c}(r, t) = \bar{c}(t)$. Furthermore, because the physical solubility is much smaller than the chemical solubility, $\bar{c}$ tends to change relatively slowly over time. If it is assumed to be quasistatic (i.e. if it is assumed that $dc/dt \ll \partial c/\partial t$ whenever $c(t, x)$ is far from any quasistatic equilibrium) then $\bar{c}$ may be eliminated from the pde altogether. Defining $c' \equiv c - \bar{c}$ gives:

\[
\frac{\partial c'}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D r^2 \frac{\partial c'}{\partial r} \right) - k c'. \tag{3.69}
\]

with boundary condition $c'|_{r=}= c^* - \bar{c}$. It is well known that this ostensibly time-dependent equation has an asymptotic solution, at which the rate of diffusion into the particle exactly matches the rate of reaction. This may be found by setting $\partial c'/\partial t = 0$ and solving the resulting ordinary differential equation via the substitution $u = c' \times r$ (see Fogler [162], p. 822.) Irrespective of the initial concentration profile, after time on order $O(\min(r^2/D, k^{-1}))$ the flux will have asymptoted to the following quasistatic value:

\[
J = (c^* - \bar{c}) \frac{D}{r} (\phi \coth \phi - 1) \tag{3.70}
\]

where $\phi$ is the Thiele modulus inside the fluid,

\[
\phi = r \sqrt{\frac{k}{D}}. \tag{3.71}
\]

To this point, shell resistance has been ignored. However, shell resistance may be accounted for by multiplying the quasistatic flux in Eq. (3.70) by a fudge factor, $\alpha < 1$:

\[
J_{\text{MECS}} = \alpha (c^* - \bar{c}) \frac{D}{r} (\phi \coth \phi - 1) \tag{3.72}
\]

Expressions for $\alpha$ are derived in the following section.
Appendix 3.II. Shell Resistance.

Following the original article on MECS by Vericella et al. [3], absorption into MECS is modelled as a resistance-in-series problem: diffusion through the shell followed by diffusion (and possibly reaction) inside the liquid. This is clearly reasonable for the physical system at hand. In this work, shell resistance is quantified by a fudge factor $\alpha$. It’s simplest to explain $\alpha$ by example: if $\alpha = 0.85$ for some MECS, then the shell reduces the flux by 15%, relative to a hypothetical MECS of the same size and composition but with no shell resistance. The advantage of $\alpha$ is that it allows the shell resistance to be handled in a single constant, rather than constantly carrying resistance-in-series expressions in the form of Eq. (3.83), below, in every equation. The derivation of a resistance-in-series expression is complicated by two factors: the curvature of the system (which causes the steady-state flux to change radially) and the relative solubilities of the shell and liquid.

To begin, consider the simple, classical resistance-in-series problem for electric current. Imagine two resistors in series, with resistance $R_1$ and $R_2$, and let the initial, intermediate and final voltage be $V_0$, $V_1$ and $V_2$ respectively. Then the current through the system is given by:

$$ I = \frac{V_0 - V_1}{R_1} = \frac{V_1 - V_2}{R_2} $$

(3.73)

Rearranging these two equations gives

$$ I = \frac{V_0 - V_2}{R_1 + R_2} $$

(3.74)

The situation is exactly analogous for the MECS system. However, the concentration driving forces in the polymer shell and in the liquid solvent cannot be compared directly, because the two materials have different gas solubilities (this also...
occurs in the film theory [16].) $V_0$, $V_1$ and $V_2$ must be replaced by the concentrations at the gas-shell interface, $c_{\text{shell}}^*$, the gas concentration in the polymer at the shell-liquid interface $c_{i,\text{shell}}$, the gas concentration in the liquid at the shell liquid interface $c_i$, and the gas concentration in the liquid bulk, $\bar{c}$. The two interface concentrations are related by the two Henry’s constants:

$$\frac{c_{i,\text{shell}}}{c_i} = \frac{H_{\text{shell}}}{H_{\text{liq}}}$$  

(3.75)

Analogous with the electrical resistance example, the flux of gas at the shell-liquid interface, $J_{\text{int}}$, may be expressed in terms of either the shell resistance and shell driving force, or the solvent resistance and solvent driving force:

$$J_{\text{int}} = \frac{c_{\text{shell}}^* - c_{i,\text{shell}}}{R_{\text{shell}}} = \frac{c_i - \bar{c}}{R_{\text{solvent}}}.$$  

(3.76)

In the case of a solvent with pseudo-first order reaction, we have (see Eq. (3.70) above, which was derived without shell resistance, in which case $c^* = H_{\text{liq}}p_i = c_i$):

$$J_{\text{int}} = \frac{D}{r} (\phi \coth \phi - 1) (c_i - \bar{c}) = \frac{c_i - \bar{c}}{R_{\text{solvent}}}.$$  

(3.77)

and so

$$R_{\text{solvent}} = \left( \frac{D}{r} (\phi \coth \phi - 1) \right)^{-1}$$  

(3.78)

For the shell-side resistance, the situation is a little more complicated, as the curvature of the shell must be accounted for. However, diffusion through a spherical shell is a well-known problem, and it’s straightforward to show (see the methods discussed in Carslaw and Jaeger [207]) that the steady-state flux at the inside layer of the shell is given by:

$$J_{\text{int}} = \frac{D_{\text{shell}}}{z} \frac{r + z}{r} \left( c_{\text{shell}}^* - c_{i,\text{shell}} \right)$$  

(3.79)

where $r$ is the internal radius of the shell and $z$ the shell thickness. Note that Eq.
(3.79) and Eq. (3.77) both refer to the gas flux at the shell-fluid interface: Eq. (3.79) refers to the flux from the shell towards the interface, while Eq. (3.77) refers to the flux away from the interface and into the fluid. If no gas accumulates or reacts on this interface, the two expressions must be equal. However, it is difficult at present to compare them, as the driving force in (3.77) is \((c_i - \bar{c})\) and the driving force in Eq. (3.79) is \((c_{shell}^* - c_{i,shell})\). This may be changed by substituting Eq. (3.75) into Eq. (3.79):

\[
J_{int} = \frac{D_{shell} H_{shell}}{H_{liq} z} \frac{r + z}{r} \left( \frac{H_{liq} c_{shell}^*}{H_{shell}} - \frac{H_{liq} c_{i,shell}}{H_{shell}} \right) = P_{shell} \frac{r + z}{H_{liq} z} \frac{c^* - c_i}{r} \quad (3.80)
\]

where \(P_{shell} = D_{shell} H_{shell}\) is the permeability of the membrane, and \(c^* = H_{liq} c_{shell}^*/H_{shell} = H_{liq} p_i\), as defined in Appendix 3.I. Just as in the electrical resistance case, this may be rearranged to

\[
J_{int} = \frac{c^* - c_i}{\frac{Hz}{P_{shell}} \frac{r}{r + z}} = \frac{c^* - c_i}{R_{shell}} \quad (3.81)
\]

where

\[
R_{shell} = \frac{Hz}{P_{shell}} \frac{r}{r + z} \quad (3.82)
\]

Both Eq. (3.77) and Eq. (3.81) refer to the same flux (the flux of molecules at the solid-liquid interface) and both express the driving force in the same way (in terms of concentrations in the liquid phase) and so they may be algebraically rearranged to give

\[
J = \frac{c^* - \bar{c}}{R_{solvent} + R_{shell}} \quad (3.83)
\]

or, as used in this work:

\[
J = \alpha \frac{c^* - \bar{c}}{R_{solvent}} \quad (3.84)
\]

where

\[
\alpha = \frac{R_{solvent}}{R_{solvent} + R_{shell}} \quad (3.85)
\]

The use of \(\alpha\) as a shell-resistance fudge factor leads to slightly simpler algebraic expressions. For a chemical solvent, \(\alpha\) may be evaluated via Eq. (3.78), Eq. (3.82)
and Eq. (3.85). For a physical solvent, the resistance may be derived in the same way. From Eq. (3.19), it follows that

\[ R_{\text{solvent, Physical}} = \frac{c_i - \bar{c}}{J_{\text{int, Physical}}} = \left( \frac{5\alpha' D}{r} \right)^{-1}. \tag{3.86} \]

and this should be used in place of Eq. (3.78) when evaluating \( \alpha' \).

Note that, in this work, the flux is defined as the flux into the inner fluid, and not into the outer polymer shell, and in turn the particle ‘radius’ refers to the radius of the liquid core, and not the overall radius (see Figure 3.1.) This nomenclature is simpler than talking about the overall radius for small particles, as there’s no need to worry that the shell thickness will ever be set to a value greater than the overall radius (i.e. \( z > r + z \)). It also leads to simpler flux expressions, and is more natural in the common case in which mass transfer resistance in the fluid dominates. This radius, \( r \), also defines the volume of the MECS capable of absorbing significant quantities gas, and this simplifies the expressions comparing MECS with absorbers, as the ‘volume fraction’ of MECS and of liquid in an absorber refer, in each case, to the volume of liquid. For these reasons, when the analysis is conducted in terms of overall particle radius, rather than the radius of the liquid core, several physically-meaningless factors are introduced, which only confuse the analysis. Furthermore, even though the language is slightly unintuitive (and is different to the language of Vericella et al. [3], who talked about the total particle diameter), in practice it’s a purely academic choice, as the discrepancy between \( r \) and the overall radius is typically < 10%.
Appendix 3.III Constants used for Correlations.

Below we list all correlations cited in Table 3.1, along with the values of the constants $q_i$ which were used.

**Onda et al. [20]**

$$k_L = 0.0051(a_t d_p)^{0.4} \left( \frac{\mu g}{\rho} \right)^{1/3} \left( \frac{L}{a_w \mu} \right)^{2/3} \left( \frac{\mu}{\rho D} \right)^{-1/2}$$  \hspace{1cm} (3.87)

$$\frac{a_w}{a_t} = 1 - \exp \left[ -1.45 \left( \frac{\sigma_c}{\sigma} \right)^{0.75} \left( \frac{L}{a_t \mu} \right)^{0.1} \times \left( \frac{L^2 a_t}{\rho^2 g} \right)^{0.05} \left( \frac{L^2}{\rho \sigma a_t} \right)^{0.2} \right]$$  \hspace{1cm} (3.88)

**Shulman et al. [158] and Treybal [170]**

$$\frac{k_L d_s}{D} = 25.1 \left( \frac{d_s L}{\mu} \right)^{0.45} \left( \frac{\mu}{\rho D} \right)^{0.5}$$  \hspace{1cm} (3.89)

$$a = q_1 \left[ \frac{808 G}{\sqrt{\rho G}} \right]^{q_2} L^{q_3}$$  \hspace{1cm} (3.90)

$$q_1 = \begin{cases} 28.01 & \text{if } L < 2 \\ 14.69 & \text{if } L \geq 2 \end{cases}$$  \hspace{1cm} (3.91)

$$q_2 = \begin{cases} 0.2323 L - 0.3 & \text{if } L < 2 \\ 0.01114L + 0.148 & \text{if } L \geq 2 \end{cases}$$  \hspace{1cm} (3.92)

$$q_3 = \begin{cases} -1.04 & \text{if } L < 2 \\ -0.11 & \text{if } L \geq 2 \end{cases}$$  \hspace{1cm} (3.93)

**Billet and Shultes [21]**

$$k_L = q_1 \left( \frac{\rho g}{\mu} \right)^{1/6} \left( \frac{D}{d_h} \right)^{1/2} \left( \frac{L}{\rho a_t} \right)^{1/3}$$  \hspace{1cm} (3.94)

$$\frac{a}{a_t} = 1.5(a_t d_h)^{-0.5} \left( \frac{L d_h}{\mu} \right)^{-0.2} \times \left( \frac{L^2 d_h}{\sigma \rho} \right)^{0.75} \left( \frac{L^2}{g d_h \rho^2} \right)^{-0.45}$$  \hspace{1cm} (3.95)

$$q_1 = 1.367$$  \hspace{1cm} (3.96)
Hanley and Chen [23]

\[
\frac{k_L d_e}{D} = q_1 \left( \frac{d_h L}{\mu} \right)^{q_2} \left( \frac{\mu}{\rho D} \right)^{q_3}
\]

(3.97)

\[
\frac{a}{a_t} = q_4 \left( \frac{\rho V}{\rho} \right)^{q_5} \left( \frac{\mu V}{\mu} \right)^{q_6} \times Re_{L}^{q_7} Fr_{L}^{q_8} We_{L}^{q_9} Re_{V}^{q_{10}} \left( \frac{\cos \theta}{\cos \pi/4} \right)^{q_{11}}
\]

(3.98)

\[
q_1 = 0.33; \quad q_2 = 1.0; \quad q_3 = 1/3; \quad q_4 = 0.539; \quad q_5 = -0.033; \quad q_6 = 0.090
\]

(3.99)

\[
q_7 = -0.153; \quad q_8 = -0.2; \quad q_9 = 0.2; \quad q_{10} = 0.145; \quad q_{11} = 4.078
\]

(3.100)

Rocha et al. [22]

\[
k_L = 2 \left( \frac{q_1 D L}{\pi S \rho \varepsilon h_L \sin \alpha} \right)^{1/2}
\]

(3.101)

\[
\frac{a}{a_t} = F_{SE} \frac{29.12 (W_e \cdot Fr)^{0.15} S^{0.359}}{Re^{0.2} \varepsilon^{0.6} (1 - 0.93 \cos \gamma) \sin^{0.3} \alpha}
\]

(3.102)

Tsai et al. [24]

\[
\frac{a}{a_t} = 1.34 \left( \frac{\rho}{\sigma} \right)^{g^{1/3}} \left( \frac{L}{\rho \ L_p} \right)^{4/3}
\]

(3.103)
Appendix 3.IV Advection-Diffusion-Reaction inside a Rotating Sphere of Fluid.

It is possible that sudden changes in the angular velocity of the shell of a fluidised MECS particle could induce mixing in the capsule that would increase the rate of mass transfer. In order to test this, a 3D, dynamic, multiphysics simulation of a rotating MECS capsule which was chemically absorbing gas was constructed using the open source simulation software arb [182]. Arb may be used to solve a wide range of transport problems, which are defined by specifying the relevant ordinary or partial differential equations directly (in a notation quite close to the mathematical equations), with no need to convert the equations to a variational form (as required by some comparable solvers [208].) General geometries may be modelled by constructing meshes using the open source software Gmsh [209].

In this work, arb was used to simultaneously solve the Navier-Stokes equations and an advection-diffusion or an advection-diffusion-reaction equation inside a rotating sphere. A spherical mesh was created using Gmsh. The differential equations to be solved were (in dimensional form):

- The incompressible Navier-Stokes momentum equation:

\[
\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{u} \quad (3.104)
\]

- The continuity equation:

\[
\nabla \cdot \mathbf{u} = 0 \quad (3.105)
\]

- The advection-diffusion-reaction equation:

\[
\frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{u}) = D \nabla^2 c - kc \quad (3.106)
\]

where \( k = 0 \) for the pure advection-diffusion problem.

The boundary conditions specified that
• $c = c^*$ on the boundary:

$$c|_{r=R} = c^*$$  \hspace{1cm} (3.107)

• The angular velocity of the surface of the sphere changes according to some function $\omega(t)$, with mean magnitude $O(\omega)$:

$$\mathbf{u}|_{r=R} = \omega \times \mathbf{r}$$  \hspace{1cm} (3.108)

Note that this implies that $\mathbf{u}$ has no radial component at the surface:

$$(\mathbf{u} \cdot \mathbf{r})|_{r=R} = 0.$$  \hspace{1cm} (3.109)

These equations were non-dimensionalised by defining the following variables:

$$\bar{r} = \frac{r}{R}; \quad \bar{\mathbf{u}} = \frac{\mathbf{u}}{\omega R}; \quad \bar{t} = \frac{t}{1/\omega}; \quad \bar{p} = \frac{p}{\rho \omega^2 R^2}; \quad \bar{c} = \frac{c}{c^*}; \quad \bar{\omega} = \frac{\omega}{\omega}.$$  \hspace{1cm} (3.110)

These variables were specifically chosen in reference to the Navier-Stokes equation, so that standard code developed within arb could be used without modification. Hence, with these dimensionless variables, the Navier-Stokes equation reduces to the simple expression:

$$\frac{\partial \bar{\mathbf{u}}}{\partial \bar{t}} + (\bar{\mathbf{u}} \cdot \nabla)\bar{\mathbf{u}} = -\nabla \bar{p} + \frac{1}{Re} \nabla^2 \bar{\mathbf{u}}$$  \hspace{1cm} (3.111)

where $Re = \omega R^2 / \nu$. The continuity equation is unchanged:

$$\nabla \cdot \bar{\mathbf{u}} = 0$$  \hspace{1cm} (3.112)

while the advection-diffusion-reaction equation reduces to:

$$\left(\frac{\omega R^2}{D}\right) \left(\frac{\partial \bar{c}}{\partial \bar{t}} + \nabla \cdot (\bar{c} \bar{\mathbf{u}})\right) = \nabla^2 \bar{c} - \phi^2 \bar{c}$$  \hspace{1cm} (3.113)

where $\phi^2 = kR^2 / D$ is the Thiele modulus for absorption and reaction, and $\omega R^2 / D$
is a term that appears because the typical time-scale in the system was chosen on
the basis of the momentum transfer and not the mass transfer - it may be thought
of as a ratio of the typical time for fluid flow and the typical time for diffusion.

The boundary conditions then become:

\[ \bar{c}|_{r=1} = 1 \]  \hspace{1cm} (3.114)

\[ \bar{u}|_{r=1} = \bar{\omega} \times \bar{r} \] \hspace{1cm} (3.115)

Eq. (3.111) – Eq. (3.115) were numerically solved in arb for a wide range of values
within the ranges \( 10^{-1} < \text{Re} < 10, \ 1 < \phi < 100, \ 1 < \omega R^2/D < 100 \). The mean
concentration gradient at the interface, \( \partial \bar{c}/\partial \bar{r} \), and the mean radial component of
\( \bar{u} \) inside the fluid were both recorded over time, and were used in Figures 3.15 and
3.16.
Appendix 3.V. Compression of Capsules During Collisions.

In Figure 3.17, the relative maximum deformation of a MECS capsule colliding with a wall, \( \delta_{\text{max}}/D \), is plotted against the initial velocity of the capsule, \( v_0 \), and the relative shell thickness of the capsule, \( z/D \). The purpose of this appendix is to show that, for a given MECS particle, \( \delta_{\text{max}}/D \) depends only on \( v_0 \) and \( z/D \), and to provide details on the calculation method for Figure 3.17.

For a capsule colliding with a wall, Newton’s second law relates the reactive force to the particle acceleration:

\[
\frac{d^2\delta}{dt^2} = -\frac{F}{m}
\]  

(3.116)

where \( \delta \) is the deformation of the particle during the collision. The exact meaning of ‘particle deformation,’ \( \delta \), is a little difficult to define, especially for one-sided collisions (c.f. Berry et al. [185].) In this work, \( \delta \) is defined as the distance the particle’s centre of mass has travelled from the moment of initial contact with the wall. This ensures that Eq. (3.116) holds exactly, and is consistent with the definition of Berry et al. [185] for small particle strains, provided \( C = 1 \) is specified for single-sided collisions. Rearranging the force expression of Berry et al. [185] given in Eq. (3.33) and substituting this into Eq. (3.116) gives

\[
\frac{d^2\delta}{dt^2} = -E\beta_2 \left( \frac{C\delta}{z} \right)^{\beta_1} \left( \frac{z/R}{R} \right)^3 \frac{4R^2}{3(1-\nu^2)} \frac{3}{4\pi\rho R^3} \]  

(3.117)

and

\[
= \left( -\frac{3E\beta_2C^{\beta_1}}{\pi\rho \sqrt{3(1-\nu^2)}} \right) \left( \frac{z}{R} \right)^{3-\beta_1} \left( \frac{\delta}{R} \right)^{\beta_1} \frac{1}{R^2} \]  

(3.118)

The initial conditions are \( \delta = 0 \) at \( t = 0 \) and \( d\delta/dt = v_0 \) at \( t = 0 \). A natural non-dimensionalisation is to define

\[
\bar{\delta} \equiv \frac{\delta}{R}
\]  

(3.119)

\[
\bar{t} = \frac{t}{R/v_0}
\]  

(3.120)
Then, defining (for convenience)

\[ A \equiv -\frac{3E\beta_2C^{\beta_1}}{\pi\rho\sqrt{3(1-\nu^2)}} \]  

which only depends on the material properties of the MECS,

\[
\frac{d^2\bar{\delta}}{dt^2} = \frac{A}{v_0^2} \left(\frac{z}{R}\right)^{3-\beta_1} \bar{\delta}^{\beta_1}
\]  

with initial conditions

\[ \bar{\delta}_{t=0} = 0; \quad \frac{d\bar{\delta}}{dt}\bigg|_{t=0} = 1 \]  

Clearly, the evolution of \( \bar{\delta} = \delta/R \) depends only on \( v_0, z/R \) and the material properties of the MECS. In particular, with these dimensionless values kept constant, \( \delta_{\text{max}}/R \) is independent of \( R \). In order to create Figure 3.17, Eq. (3.122) was numerically integrated from the initial conditions given by Eq. (3.123), and the maximum deformation, \( \delta_{\text{max}}/D \), was calculated as a function of \( v_0 \) and \( z/D \). The following numerical values were used:

- For \( z/D = 0.05 \): \( C = 1.0, \beta_1 = 1.14, \beta_2 = 1.12 \), from Berry et al. [185].
- For \( z/D = 0.1 \): \( C = 1.0, \beta_1 = 1.26, \beta_2 = 1.34 \), from Berry et al. [185].
- For \( z/D = 0.15 \): \( C = 1.0, \beta_1 = 1.36, \beta_2 = 1.50 \), from Berry et al. [185].
- For a PDMS shell, \( E = 5 \times 10^5 \) Pa, from Armani et al. [210], and \( \nu = 0.5 \), from Mark [211].
- A mean capsule density of \( \rho = 1000 \text{ kg m}^{-3} \) was used.
Appendix 3.VI Relationship Between $\xi$ and Enhancement Factor, $E$

For a chemical solvent, the enhancement factor, $E$, is defined by the following equation:

$$J = Ek_L \Delta c.$$ (3.124)

For the irreversible reaction considered in section 3.6.2, $E$ is typically written in terms of two dimensionless groups [15]:

$$E_i = 1 + \frac{w_0 D_2}{zc^* D_1}$$ (3.125)

$$M = \frac{k_2 w_0 D_1}{k_2 L}$$ (3.126)

where $E_i$ is the enhancement factor for instantaneous reaction, and $M$ is the square of the Hatta number. When $E = E(E_i, M)$, the enhancement factor may be related to the sensitivity to liquid mixing, $\xi$, in the following way:

$$\xi = \left(\frac{\partial \log J}{\partial \log k_L}\right)_{D_1, D_2, k_2, c^*, w_0} = 1 + \left(\frac{\partial \log E}{\partial \log k_L}\right)_{D_1, D_2, k_2, c^*, w_0} \frac{\partial M}{\partial k_L}$$

$$= 1 + 2 \left(\frac{\partial \log E}{\partial \log M}\right)_{E_i}$$ (3.127)

We now consider the expression for $E$ given by Wellek et al. [199], which was in good agreement with a number of studies:

$$\frac{1}{(E - 1)^{1.35}} = \frac{1}{(E_i - 1)^{1.35}} + \frac{1}{(E_1 - 1)^{1.35}}$$ (3.128)

where

$$E_1 = \frac{\sqrt{M}}{\tanh \sqrt{M}}$$ (3.129)
At constant $E_i$, we take the total derivative of both sides of Eq. (3.128) to get

$$d \left( \frac{1}{(E - 1)^{1.35}} \right) = d \left( \frac{1}{(E_i - 1)^{1.35}} \right)$$

(3.130)

$$\frac{1.35}{(E - 1)^{2.35}} dE = \frac{1.35}{(E_i - 1)^{2.35}} dE_i = \frac{1.35}{(E - 1)^{2.35}} \frac{dE_i}{dM} dM$$

(3.131)

$$\frac{1.35}{(E - 1)^{2.35}} dE = \frac{1.35}{(E_i - 1)^{2.35}} \frac{1}{2} \left( \frac{1}{\sqrt{M} \tanh \sqrt{M}} - \frac{1}{\sinh^2 \sqrt{M}} \right) dM$$

(3.132)

$$\left( \frac{\partial E}{\partial M} \right)_{E_i} = \left( \frac{E - 1}{E_i - 1} \right)^{2.35} \frac{1}{2} \left( \frac{1}{\sqrt{M} \tanh \sqrt{M}} - \frac{1}{\sinh^2 \sqrt{M}} \right)$$

(3.133)

$$\left( \frac{\partial \log E}{\partial \log M} \right)_{E_i} = \frac{1}{E} \left( \frac{E - 1}{E_i - 1} \right)^{2.35} \frac{1}{2} \left( \frac{\sqrt{M}}{\tanh \sqrt{M}} - \frac{M}{\sinh^2 \sqrt{M}} \right)$$

(3.134)

Substituting this into Eq. (3.127), we may evaluate $\xi$ via:

$$\xi(E_i, M) = 1 - 2 \left( \frac{\partial \log E}{\partial \log M} \right)_{E_i} = 1 - \frac{1}{E} \left( \frac{E - 1}{E_i - 1} \right)^{2.35} \left( \frac{\sqrt{M}}{\tanh \sqrt{M}} - \frac{M}{\sinh^2 \sqrt{M}} \right),$$

(3.135)

where $E$ may be calculated from the rearranged Eq. (3.128):

$$E = 1 + \left( \frac{1}{(E_i - 1)^{1.35}} + \frac{1}{(E_i - 1)^{1.35}} \right)^{-1/1.35}$$

(3.136)

and where $E_1$ is calculated from Eq. (3.129).
Appendix 3.VII Non-Dimensionalisation of ODEs for Reversible Reaction via Film Theory

As described in section 3.6.3, for absorption of gas $A$ with the reversible reaction

$$A + B \xrightleftharpoons[k_2]{k_1} C + D$$ (3.137)

the film theory provides the following system of ODEs:

$$D_A \frac{\partial^2 c_A}{\partial x^2} = D_B \frac{\partial^2 c_B}{\partial x^2} = -D_C \frac{\partial^2 c_C}{\partial x^2} = -D_D \frac{\partial^2 c_D}{\partial x^2} = k_1 c_A c_B - k_1 c_C c_D / K$$ (3.138)

With boundary conditions

$$c_A|_{x=0} = c_A^*; \quad \partial_x c_B|_{x=0} = \partial_x c_C|_{x=0} = \partial_x c_D|_{x=0} = 0$$ (3.139)

$$c_B|_{x=\delta} = c_B^0; \quad c_C|_{x=\delta} = c_C^0; \quad c_D|_{x=\delta} = c_D^0; \quad c_A|_{x=\delta} = c_A^0 c_D^0 / c_B c_B^0;$$ (3.140)

where $K \equiv k_1 / k_2$.

We choose the following dimensionless variables:

$$\bar{c}_A = c_A / c_A^*; \quad \bar{c}_B = c_B / c_B^0; \quad \bar{c}_C = c_C / c_B^0; \quad \bar{c}_D = c_D / c_B^0; \quad \bar{x} = x / \delta$$ (3.141)

The equations then reduce to:

$$\frac{\partial^2 \bar{c}_A}{\partial \bar{x}^2} = \left( \frac{D_A c_B^0 k_1}{k_2^2 L} \right) \left( \bar{c}_A \bar{c}_B - \left( \frac{c_B^0}{c_A^*} \right) \left( \frac{1}{K} \right) \bar{c}_C \bar{c}_D \right)$$ (3.142)

$$\frac{\partial^2 \bar{c}_B}{\partial \bar{x}^2} = \left( \frac{D_A c_B^0 k_1}{k_2^2 L} \right) \left( \frac{D_A}{D_B} \right) \left( \bar{c}_A \bar{c}_B - \left( \frac{c_B^0}{c_A^*} \right) \left( \frac{1}{K} \right) \bar{c}_C \bar{c}_D \right)$$ (3.143)

$$\frac{\partial^2 \bar{c}_C}{\partial \bar{x}^2} = - \left( \frac{D_A c_B^0 k_1}{k_2^2 L} \right) \left( \frac{D_A}{D_C} \right) \left( \bar{c}_A \bar{c}_B - \left( \frac{c_B^0}{c_A^*} \right) \left( \frac{1}{K} \right) \bar{c}_C \bar{c}_D \right)$$ (3.144)

$$\frac{\partial^2 \bar{c}_D}{\partial \bar{x}^2} = - \left( \frac{D_A c_B^0 k_1}{k_2^2 L} \right) \left( \frac{D_A}{D_D} \right) \left( \bar{c}_A \bar{c}_B - \left( \frac{c_B^0}{c_A^*} \right) \left( \frac{1}{K} \right) \bar{c}_C \bar{c}_D \right)$$ (3.145)
and the boundary conditions become:

\[
\begin{align*}
\bar{c}_A|_{x=0} &= 1; & \partial_x \bar{c}_B|_{x=0} = \partial_x \bar{c}_C|_{x=0} = \partial_x \bar{c}_D|_{x=0} &= 0 \\
\bar{c}_B|_{x=1} &= 1; & \bar{c}_C|_{x=1} &= c^0_C/c^0_B; & \bar{c}_D|_{x=1} &= c^0_D/c^0_B; & \bar{c}_A|_{x=1} &= \left(\frac{c^0_C}{c^0_B}\right) \left(\frac{c^0_D}{c^0_B}\right) \left(\frac{1}{K}\right) \left(\frac{c^0_B}{c^0_A}\right)
\end{align*}
\]

These are solved using a boundary value problem solver provided by Matlab, \texttt{bvp4c}, which utilises a three-stage Lobatto IIIa formula [200], under the conditions described in the caption to Figure 3.19.
Appendix 3.VIII Absorption of CO2 into a Dilute K2CO3 Solution via Eddy Diffusivity Theory

As discussed in section 3.3, the absorption of CO2 into a K2CO3 solution is governed by the following simultaneous chemical reactions:

$$\text{CO}_2 + \text{OH}^- \xrightleftharpoons{\frac{k_1}{k_1/K_1}} \text{HCO}_3^-$$  \hspace{1cm} (3.148)

$$\text{H}_2\text{O} + \text{CO}_3^{2-} \xrightleftharpoons{K_2} \text{HCO}_3^- + \text{OH}^-$$  \hspace{1cm} (3.149)

The second reaction is a fast proton transfer which is assumed to be in instantaneous local equilibrium at all times. The overall reaction is:

$$\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \iff 2\text{HCO}_3^-$$  \hspace{1cm} (3.150)

Provided that the concentration of OH$^-$ is much smaller than carbonate or bicarbonate concentrations, the rates of production of CO$_2$, CO$_3^{2-}$ and HCO$_3^-$ per unit volume of liquid are given by:

$$\mathcal{R}_{\text{CO}_2} = \mathcal{R}_{\text{CO}_3^{2-}} = -\mathcal{R}_{\text{HCO}_3^-} = -k_1(c_{\text{CO}_2}c_{\text{OH}^-} - c_{\text{HCO}_3^-}/K_1)$$  \hspace{1cm} (3.151)

Absorption into a concentrated K$_2$CO$_3$ solution was previously considered in section 3.3. For such solutions the reaction is pseudo-first order, and when predicting the absorption rate only the diffusion and reaction of CO$_2$ need be considered (as the concentration of all other species are constant in space.) A more general analysis of this system, however, must account for the simultaneous diffusion of CO$_2$ and of K$^+$, CO$_3^{2-}$ and HCO$_3^-$ ions, whose concentration may change in space and time, while always maintaining charge-neutrality throughout the solution. This will be modelled here.

Material properties used in this work are listed in Table 3.5. Henry’s constants for 3wt% and 10wt% K$_2$CO$_3$ were calculated using Weisenberger and Schumpe’s
Table 3.5: Properties of Dilute K\textsubscript{2}CO\textsubscript{3} solution at 293 K.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value/Correlation</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$10^{14.40-2095/T+0.185} \text{ L mol}^{-1} \text{s}^{-1}$</td>
<td>Astarita [9]</td>
</tr>
<tr>
<td>$K_1$</td>
<td>$6.12 \times 10^4 \text{ mol}^{-1}$</td>
<td>Danckwerts [15]</td>
</tr>
<tr>
<td>$K_2$</td>
<td>$0.162 \text{ mol m}^{-3}$</td>
<td>Danckwerts [15]</td>
</tr>
<tr>
<td>$D_{\text{CO}_2}$</td>
<td>$1.0 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$</td>
<td>Versteeg et al. [150], Correia et al. [146]</td>
</tr>
<tr>
<td>$D_{\text{HCO}_3^-}$</td>
<td>$0.94 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$</td>
<td>Kigoshi et al. [212]</td>
</tr>
<tr>
<td>$D_{\text{CO}_3^{2-}}$</td>
<td>$0.7 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$</td>
<td>Kigoshi et al. [212]</td>
</tr>
<tr>
<td>$D_{K^+}$</td>
<td>$2.0 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$</td>
<td>Friedman et al. [213]</td>
</tr>
<tr>
<td>$H_{\text{CO}_2}^\text{Water}$</td>
<td>$3.54 \times 10^{-7} \exp(2044/T) \text{ mol m}^{-3} \text{ Pa}^{-1}$</td>
<td>Versteeg and Van Swaalj [150]</td>
</tr>
</tbody>
</table>

[14] correlation, while for 30wt% K\textsubscript{2}CO\textsubscript{3} the correlation of Knutila et al. [13] was used (see the discussion in section 2.7.)

Assuming the steady state eddy-diffusivity theory is valid, and supposing that the relative diffusion of the various ionic species induces an electric field, $E$, then the diffusion and reaction of the various species are given by the Nernst-Planck equations:

\begin{align}
0 &= \nabla ((D_{\text{CO}_2} + ax^2) \nabla c_{\text{CO}_2}) - k_1 (c_{\text{CO}_2} c_{\text{OH}^-} - c_{\text{HCO}_3^-} / K_1) \tag{3.152} \\
0 &= \nabla ((D_{\text{HCO}_3^-} + ax^2) \nabla c_{\text{HCO}_3^-}) + D_{\text{HCO}_3^-} \frac{F}{k_B T} \nabla (c_{\text{HCO}_3^-} E) + 2k_1 (c_{\text{CO}_2} c_{\text{OH}^-} - c_{\text{HCO}_3^-} / K_1) \tag{3.153} \\
0 &= \nabla ((D_{\text{CO}_3^{2-}} + ax^2) \nabla c_{\text{CO}_3^{2-}}) + 2D_{\text{CO}_3^{2-}} \frac{F}{k_B T} \nabla (c_{\text{CO}_3^{2-}} E) - k_1 (c_{\text{CO}_2} c_{\text{OH}^-} - c_{\text{HCO}_3^-} / K_1) \tag{3.154} \\
0 &= \nabla ((D_{K^+} + ax^2) \nabla c_{K^+}) - D_{K^+} \frac{F}{k_B T} \nabla (c_{K^+} E) \tag{3.155} \\
 c_{\text{OH}^-} &= K_2 \frac{c_{\text{CO}_3^{2-}}}{c_{\text{HCO}_3^-}} \tag{3.156} 
\end{align}

In the 5 equations above there are 6 unknown functions, as the electric field, $E$, has been introduced without providing a corresponding equation. As the electric field is induced by the need to maintain charge neutrality, it is natural to specify it by requiring that there is no net flux of charge at any point in space:

\begin{equation}
0 = \sum_i Z_i J_i \tag{3.157} 
\end{equation}
where $Z_i$ is the charge number of $i$ and $J_i$ is the flux of species $i$ in the solution (expressions for $J_i$ are contained implicitly within Eq. (3.152) – (3.155).) As an extra equation has been provided, Eq (3.152) – (3.157) are now a fully specified system of differential equations (modulo appropriate boundary conditions), however they are inconvenient to use, as $E$ is implicitly defined. Instead, Eq. (3.157) and the flux expressions implied by Eq. (3.153) – (3.155) may be used to derive an explicit expression for $E$:

$$0 = \sum J_i Z_i$$

$$= -(D_{K^+} + ax^2) \frac{dc_{K^+}}{dz} + D_{K^+} \frac{F}{k_B T} c_{K^+} E$$

$$- [-(D_{HCO_3^-} + ax^2) \frac{dc_{HCO_3^-}}{dz} - D_{HCO_3^-} \frac{F}{k_B T} c_{HCO_3^-} E]$$

$$- 2[-(D_{CO_3^{2-}} + ax^2) \frac{dc_{CO_3^{2-}}}{dz} - 2D_{CO_3^{2-}} \frac{F}{k_B T} c_{CO_3^{2-}} E]$$

$$E = \frac{k_B T (D_{K^+} + ax^2) \frac{dc_{K^+}}{dz} - (D_{HCO_3^-} + ax^2) \frac{dc_{HCO_3^-}}{dz} - 2(D_{CO_3^{2-}} + ax^2) \frac{dc_{CO_3^{2-}}}{dz}}{D_{K^+} c_{K^+} + D_{HCO_3^-} \frac{F}{k_B T} c_{HCO_3^-} + 4D_{CO_3^{2-}} \frac{F}{k_B T} c_{CO_3^{2-}}}$$

This equation may be further simplified via the condition of charge neutrality, which this system will satisfy at all locations and times:

$$0 = \sum_i Z_i c_i = -c_{HCO_3^-} - 2c_{CO_3^{2-}} + c_{K^+}$$

Eq. (3.159) then reduces to:

$$E = \frac{k_B T}{F} \frac{D_{K^+} \frac{dc_{K^+}}{dz} - D_{HCO_3^-} \frac{dc_{HCO_3^-}}{dz} - 2D_{CO_3^{2-}} \frac{dc_{CO_3^{2-}}}{dz}}{D_{K^+} c_{K^+} + D_{HCO_3^-} \frac{F}{k_B T} c_{HCO_3^-} + 4D_{CO_3^{2-}} \frac{F}{k_B T} c_{CO_3^{2-}}}$$

This is the standard Henderson formula [214] for the electric field in a dilute ionic solution. It may be thought of as an extension of the classical equation of Vinograd

\[17\] It is physically obvious that, with appropriate boundary conditions, the above system of equations will satisfy the condition of charge neutrality. If charge neutrality is satisfied at $t = 0$, Eq. (3.157) implies that charge neutrality will also be satisfied at all times $t > 0$. Hence any stable, steady-state solution to Eq (3.152) – (3.157) would be expected to satisfy charge neutrality.
and McBain [215] for binary ionic diffusion. It has been derived here to demonstrate that it is valid even in the presence of eddy diffusion.\(^{18}\)

The Henderson equation and the charge balance may replace any of Eq (3.152) – (3.157), to produce a fully specified system of equations that may be solved numerically in a straightforward manner. In this work, Eq. (3.161) and Eq. (3.160) were substituted for Eq. (3.155) and Eq. (3.157), and so Eq. (3.152), (3.153), (3.154), (3.156), (3.160) and (3.161) were solved simultaneously for the unknown functions \(c_{CO_2}\), \(c_{HCO_3^-}\), \(c_{CO_3^{2-}}\), \(c_{OH^-}\), \(c_{K^+}\) and \(E\). Eq. (3.156), (3.160) and (3.161) will be substituted into the 3 differential equations, Eq. (3.152), (3.153), (3.154), producing a set of three simultaneous ODE boundary value problems. The three sets of boundary conditions follow from the eddy-diffusivity theory:

\[
c_{CO_2}|_{x=0} = c_{CO_2}^*; \quad c_{CO_2}|_{x=\infty} = c_{CO_2}^{\text{bulk}} = \frac{2c_{CO_2}^{\text{bulk}}}{K_1K_2} \left( \frac{c_{HCO_3^-}^{\text{bulk}}}{c_{K^+}^{\text{bulk}}} \right) \left( 1 - \frac{c_{HCO_3^-}^{\text{bulk}}}{c_{K^+}^{\text{bulk}}} \right)^2 \tag{3.162}
\]

\[
\partial_x c_{HCO_3^-}|_{x=0} = 0; \quad c_{HCO_3^-}|_{x=\infty} = c_{HCO_3^-}^{\text{bulk}} = c_{K^+}^{\text{bulk}} \times \left( \frac{c_{HCO_3^-}^{\text{bulk}}}{c_{K^+}^{\text{bulk}}} \right) \tag{3.163}
\]

\[
\partial_x c_{CO_3^{2-}}|_{x=0} = 0; \quad c_{CO_3^{2-}}|_{x=\infty} = c_{CO_3^{2-}}^{\text{bulk}} = \frac{c_{K^+}^{\text{bulk}}}{2} \left( 1 - \frac{c_{HCO_3^-}^{\text{bulk}}}{c_{K^+}^{\text{bulk}}} \right) \tag{3.164}
\]

The expression for \(c_{CO_2}^{\text{bulk}}\) follows from the charge balance, Eq. (3.160), while the expression for \(c_{CO_2}^{\text{bulk}}\) may be derived by substituting the expressions in Eq. (3.163), (3.164) and (3.156) into the equilibrium expression associated with Reaction (3.148):

\[
K_1 = \frac{c_{HCO_3^-}^{\text{bulk}}}{c_{OH^-}^{\text{bulk}} c_{CO_2}^{\text{bulk}}} \tag{3.165}
\]

The 4 variables which need to be specified are the concentration of CO\(_2\) at the boundary, \(c_{CO_2}^*\), the mass transfer coefficient, \(k_L\), which determines \(a\) via Eq. (3.58), and the loading, \(c_{HCO_3^-}^{\text{bulk}}/c_{K^+}^{\text{bulk}}\), and total concentration, \(c_{K^+}^{\text{bulk}}\), in the bulk of the solvent.

\(^{18}\)The Henderson formula has been used within the eddy diffusivity model before [26], but these authors did not explicitly verify its validity.
Numerical Details

A little algebra is required to convert this to a form that can be used by Matlab. Writing $D_1 \equiv D_{CO_2}$, $D_2 \equiv D_{HCO_3}^-$, $D_3 \equiv D_{CO_3^{2-}}$ and $D_4 \equiv D_{K^+}$, the system of equations to be solved (Eq. (3.152), (3.153), (3.154), (3.156), (3.160) and (3.161)) are:

\begin{align*}
0 &= \frac{d}{dx} \left( (D_1 + ax^2) \frac{dc_{CO_2}}{dx} \right) - k_1 (c_{CO_2}c_{OH^-} - c_{HCO_3^-} / K_1) \quad \text{(3.166)} \\
0 &= \frac{d}{dx} \left( (D_2 + ax^2) \frac{dc_{HCO_3^-}}{dx} \right) + D_2 \frac{F}{k_BT} \frac{d}{dx} (c_{HCO_3^-} E) + 2k_1 (c_{CO_2}c_{OH^-} - c_{HCO_3^-} / K_1) \quad \text{(3.167)} \\
0 &= \frac{d}{dx} \left( (D_3 + ax^2) \frac{dc_{CO_3^{2-}}}{dx} \right) + 2D_3 \frac{F}{k_BT} \frac{d}{dx} (c_{CO_3^{2-}} E) - k_1 (c_{CO_2}c_{OH^-} - c_{HCO_3^-} / K_1) \quad \text{(3.168)}
\end{align*}

\begin{align*}
&c_{K^+} = 2c_{CO_3^{2-}} + c_{HCO_3^-} \quad \text{(3.169)} \\
&c_{OH^-} = K_2 \frac{c_{CO_3^{2-}}}{c_{HCO_3^-}} \quad \text{(3.170)} \\
&E = \frac{k_BT}{F} \frac{D_4 \frac{dc_{K^+}}{dx} - D_2 \frac{dc_{HCO_3^-}}{dx} - 2D_3 \frac{dc_{CO_3^{2-}}}{dx}}{D_4 c_{K^+} + D_2 c_{HCO_3^-} + 4D_3 c_{CO_3^{2-}}} \quad \text{(3.171)}
\end{align*}

Eq. (3.169) – (3.171) must now be substituted into Eq. (3.166) – (3.168) and algebraically rearranged into the form which Matlab accepts:

\[
\dot{y} = f(x, y) \quad \text{(3.172)}
\]

In this problem, the following $y_i$ shall be solved for:

\[
y_1 = c_{CO_2}; \quad y_2 = c_{HCO_3^-}; \quad y_3 = c_{CO_3^{2-}}; \quad y_4 = \dot{y}_1; \quad y_5 = \dot{y}_3; \quad y_6 = \dot{y}_5 \quad \text{(3.173)}
\]

Eq. (3.166) now becomes

\begin{align*}
0 &= \frac{d}{dx} \left( (D_1 + ax^2) \frac{dy_1}{dx} \right) - k_1 (y_1 c_{OH^-} - y_3 / K_1) \quad \text{(3.174)} \\
0 &= \left( (D_1 + ax^2) \frac{d^2y_1}{dx^2} + 2ax \frac{dy_1}{dx} \right) - k_1 \left( \frac{K_2 y_1 y_5}{y_3} - \frac{y_3}{K_1} \right) \quad \text{(3.175)}
\end{align*}
\[ 0 = (D_1 + ax^2)\dot{y}_2 + 2axy_2 - k_1 \left( \frac{K_2y_1y_5}{y_3} - \frac{y_3}{K_1} \right) \quad (3.176) \]

\[ \dot{y}_2 = \frac{k_1 \left( \frac{K_2y_1y_5}{y_3} - \frac{y_3}{K_1} \right) - 2axy_2}{D_1 + ax^2} \quad (3.177) \]

Equation (3.167) and (3.168) are a little more difficult, as they each contain a \( dE/dx \) term. Eq. (3.167) becomes

\[ 0 = \frac{d}{dx} \left( (D_2 + ax^2) \frac{dy_3}{dx} \right) + D_2 \frac{F}{k_BT} \frac{d}{dx} (y_3E) + 2k_1 \left( \frac{K_2y_1y_5}{y_3} - \frac{y_3}{K_1} \right) \quad (3.178) \]

\[ 0 = (D_2 + ax^2)\dot{y}_4 + 2axy_4 + D_2 \frac{F}{k_BT} y_4E + D_2 \frac{F}{k_BT} \frac{dy_3}{dx} + 2k_1 \left( \frac{K_2y_1y_5}{y_3} - \frac{y_3}{K_1} \right) \quad (3.179) \]

and Eq. (3.168) becomes

\[ 0 = \frac{d}{dx} \left( (D_3 + ax^2) \frac{dy_5}{dx} \right) + 2D_3 \frac{F}{k_BT} \frac{d}{dx} (y_5E) - k_1 \left( \frac{K_2y_1y_5}{y_3} - \frac{y_3}{K_1} \right) \quad (3.180) \]

\[ 0 = (D_3 + ax^2)\dot{y}_6 + 2axy_6 + 2D_3 \frac{F}{k_BT} y_6E + 2D_3 \frac{F}{k_BT} \frac{dy_5}{dx} - k_1 \left( \frac{K_2y_1y_5}{y_3} - \frac{y_3}{K_1} \right) \quad (3.181) \]

The only complicated part here is then \( dE/dx \), which will need to be evaluated:

\[ \frac{dE}{dx} = \frac{d}{dx} \left( \frac{K_BT}{F} \left( \frac{dc_{k^+}}{dx} - \frac{dc_{HC03^-}}{dx} - 2 \frac{dc_{CO3^2-}}{dx} \right) \right) \quad (3.182) \]

\[ \frac{dE}{dx} = \frac{d}{dx} \left( \frac{K_BT}{F} \left( \frac{dc_{k^+}}{dx} + \frac{dc_{HC03^-}}{dx} + 4 \frac{dc_{CO3^2-}}{dx} \right) \right) \quad (3.183) \]

\[ \frac{dE}{dx} = \frac{k_BT}{F} \frac{(D_4 - D_2) \frac{dy_4}{dx} + 2(D_4 - D_3) \frac{dy_6}{dx}}{(D_4 + D_2)y_4 + 2(D_4 + 2D_3)y_6} \quad (3.184) \]
Substituting this into Eq. (3.179) gives:

\[
0 = \left( D_2 + ax^2 \right) \ddot{y}_4 + 2ax \dot{y}_4 + D_2 \frac{F}{k_B T} y_4 E
\]

\[
+ D_2 \frac{F}{k_B T} y_5 \left[ \frac{k_B T}{F} \left( (D_4 - D_2) \dot{y}_4 + 2(D_4 - D_3) \dot{y}_6 \right) \right]
- \frac{k_B T}{F} \left( (D_4 - D_2) \dot{y}_4 + 2(D_4 - D_3) \dot{y}_6 \right) \left( (D_4 + D_2) \dot{y}_4 + 2(D_4 + 2D_3) \dot{y}_6 \right)
+ 2k_1 \left( \frac{K_2 y_1 y_5}{y_3} - \frac{y_3}{K_1} \right)
\]

\[
(3.185)
\]

\[
0 = \left( D_2 + ax^2 \right) \ddot{y}_4 + 2ax \dot{y}_4 + D_2 \frac{F}{k_B T} y_4 E
\]

\[
+ \frac{D_2 y_3 (D_4 - D_2)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \dot{y}_4 + \frac{2D_2 y_3 (D_4 - D_3)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \dot{y}_6
\]

\[
- D_2 y_5 \left( (D_4 - D_2) \dot{y}_4 + 2(D_4 - 2D_3) \dot{y}_6 \right) \left( (D_4 + D_2) \dot{y}_4 + 2(D_4 + 2D_3) \dot{y}_6 \right)
+ 2k_1 \left( \frac{K_2 y_1 y_5}{y_3} - \frac{y_3}{K_1} \right)
\]

\[
(3.186)
\]

\[
0 = \left[ D_2 + ax^2 + \frac{D_2 y_3 (D_4 - D_2)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \right] \ddot{y}_4
\]

\[
+ \left[ \frac{2D_2 y_3 (D_4 - D_3)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \right] \dot{y}_6 + \left[ 2ax \dot{y}_4 + D_2 \frac{F}{k_B T} y_4 E \right]
\]

\[
- D_2 y_5 \left( (D_4 - D_2) \dot{y}_4 + 2(D_4 - 2D_3) \dot{y}_6 \right) \left( (D_4 + D_2) \dot{y}_4 + 2(D_4 + 2D_3) \dot{y}_6 \right)
+ 2k_1 \left( \frac{K_2 y_1 y_5}{y_3} - \frac{y_3}{K_1} \right)
\]

\[
(3.187)
\]

which may be written as

\[
0 = \alpha \ddot{y}_4 + \beta \dot{y}_6 + \gamma
\]

\[
(3.188)
\]

And doing the same for (3.181) gives

\[
0 = \left( D_3 + ax^2 \right) \ddot{y}_6 + 2ax \dot{y}_6 + 2D_3 \frac{F}{k_B T} y_6 E
\]

\[
+ 2D_3 \frac{F}{k_B T} y_5 \left[ \frac{k_B T}{F} \left( (D_4 - D_2) \dot{y}_4 + 2(D_4 - D_3) \dot{y}_6 \right) \right]
- \frac{k_B T}{F} \left( (D_4 - D_2) \dot{y}_4 + 2(D_4 - D_3) \dot{y}_6 \right) \left( (D_4 + D_2) \dot{y}_4 + 2(D_4 + 2D_3) \dot{y}_6 \right)
- k_1 \left( \frac{K_2 y_1 y_5}{y_3} - \frac{y_3}{K_1} \right)
\]

\[
(3.189)
\]
\[ 0 = (D_3 + ax^2) \dot{y}_6 + 2axy_6 + 2D_3 \frac{F}{k_B T} y_6 E \]
\[ + \frac{2D_3 y_5 (D_4 - D_2)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \dot{y}_4 + \frac{4D_3 y_5 (D_4 - D_3)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \dot{y}_6 \]
\[ - 2D_3 y_5 \frac{((D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5)^2 ((D_4 + D_2) y_4 + 2(D_4 + 2D_3) y_6)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \]
\[ - k_1 \left( \frac{K_2 y_1 y_5}{y_3} - \frac{y_3}{K_1} \right) \]

(3.190)

\[ 0 = \left[ \frac{2D_3 y_5 (D_4 - D_2)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \right] \dot{y}_4 + \left[ \frac{D_3}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \right] \dot{y}_6 \]
\[ + ax^2 + \frac{4D_3 y_5 (D_4 - D_3)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \dot{y}_6 \]
\[ + \left[ \frac{2axy_6 + 2D_3 \frac{F}{k_B T} y_6 E - 2D_3 y_5 \frac{(D_4 - D_2) y_4 + 2(D_4 - D_3) y_6}{((D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5)^2}}{(D_4 + D_2) y_4 + 2(D_4 + 2D_3) y_6} \right] \]
\[ \times ((D_4 + D_2) y_4 + 2(D_4 + 2D_3) y_6) - k_1 \left( \frac{K_2 y_1 y_5}{y_3} - \frac{y_3}{K_1} \right) \]

which may be written as

\[ 0 = \delta \dot{y}_4 + \lambda \dot{y}_6 + \xi \]

(3.192)

The solution to Eq. (3.188) and (3.192) is

\[ \dot{y}_4 = \frac{\beta \xi - \gamma \lambda}{\alpha \lambda - \beta \delta} \]
\[ \dot{y}_6 = \frac{\alpha \xi - \gamma \delta}{\beta \delta - \alpha \lambda} \]

(3.193)

Overall, then, the system of ODEs to be solved are:

\[ \dot{y}_1 = y_2 \]
\[ \dot{y}_2 = \frac{k_1 \left( \frac{K_2 y_1 y_5}{y_3} - \frac{y_3}{K_1} \right) - 2axy_2}{D_1 + ax^2} \]
\[ \dot{y}_3 = y_4 \]
\[ \dot{y}_4 = \frac{\beta \xi - \gamma \lambda}{\alpha \lambda - \beta \delta} \]
\[ \dot{y}_5 = \dot{y}_6 \]
\[ \dot{y}_6 = \frac{\alpha \xi - \gamma \delta}{\beta \delta - \alpha \lambda} \]
where
\[ \alpha = D_2 + ax^2 + \frac{D_2 y_3 (D_4 - D_2)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \]  
(3.200)
\[ \beta = \frac{2D_2 y_3 (D_4 - D_3)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \]  
(3.201)
\[ \gamma = 2axy_4 + D_2 \frac{F}{k_B T} y_4 E - D_2 y_3 \frac{(D_4 - D_2) y_4 + 2(D_4 - D_3) y_6}{((D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5)^2} \times ((D_4 + D_2) y_4 + 2(D_4 + 2D_3) y_6) + 2k_1 \left( \frac{K_2 y_1 y_5}{y_3} - \frac{y_3}{K_1} \right) \]  
(3.202)
\[ \delta = \frac{2D_3 y_5 (D_4 - D_3)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \]  
(3.203)
\[ \lambda = D_3 + ax^2 + \frac{4D_3 y_5 (D_4 - D_3)}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \]  
(3.204)
\[ \xi = 2axy_6 + 2D_3 \frac{F}{k_B T} y_6 E - 2D_3 y_5 \frac{(D_4 - D_2) y_4 + 2(D_4 - D_3) y_6}{((D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5)^2} \times ((D_4 + D_2) y_4 + 2(D_4 + 2D_3) y_6) - k_1 \left( \frac{K_2 y_1 y_5}{y_3} - \frac{y_3}{K_1} \right) \]  
(3.205)
with
\[ E = \frac{k_B T}{F} \frac{(D_4 - D_2) y_4 + 2(D_4 - D_3) y_6}{(D_4 + D_2) y_3 + 2(D_4 + 2D_3) y_5} \]  
(3.206)
The boundary conditions are
\[ y_1 |_{x=0} = c_{\text{CO}_2}^* \]  
(3.207)
\[ y_1 |_{x \to \infty} = c_{\text{CO}_2}^{\text{bulk}} = \frac{2c_{\text{K}^+}^{\text{bulk}}}{K_1 K_2} \left[ \frac{c_{\text{HCO}_3^-}^{\text{bulk}}}{c_{\text{K}^+}^{\text{bulk}}} \right] \]  
(3.208)
\[ y_3 |_{x \to \infty} = c_{\text{HCO}_3^-}^{\text{bulk}} = c_{\text{K}^+}^{\text{bulk}} \times \left( \frac{c_{\text{HCO}_3^-}^{\text{bulk}}}{c_{\text{K}^+}^{\text{bulk}}} \right) \]  
(3.209)
\[ y_4 |_{x=0} = 0 \]  
(3.210)
\[ y_5 |_{x \to \infty} = c_{\text{CO}_3^{2-}}^{\text{bulk}} = c_{\text{K}^+}^{\text{bulk}} \left( \frac{1 - c_{\text{HCO}_3^-}^{\text{bulk}}}{c_{\text{K}^+}^{\text{bulk}}} \right) \]  
(3.211)
\[ y_6 |_{x=0} = 0 \]  
(3.212)
These have been expressed in terms of the CO2 boundary concentration, \( c_{\text{CO}_2}^* \), the bulk potassium concentration, \( c_{\text{K}^+}^{\text{bulk}} \), and the bulk CO2 loading, \( c_{\text{HCO}_3^-}^{\text{bulk}} / c_{\text{K}^+}^{\text{bulk}} \). The
only other variable is $a$ from the expression for eddy diffusivity, which may be related to $k_L$ by

$$a = \frac{\pi^2 k_L^2}{4 \overline{D}_{CO2}} = \frac{\pi^2 k_L^2}{4 \overline{D}_1}$$

(3.214)

These equations were solved in Matlab using the built-in boundary value problem solver, \texttt{bvp4c} [200]. The flux of CO$_2$ was calculated via Eq. (3.62), and $\xi$ was calculated via a finite difference approximation to Eq. (3.48).
Notation

- $a$ - Effective area in absorption column on unit volume of absorber basis, $m^2 m^{-3}$ absorber.

- $a'$ - Effective area in absorption column on unit volume of solvent basis, $m^2 m^{-3}$ solvent.

- $a_{MECS}$ - Specific surface area of MECS on unit volume of absorber basis, $m^2 m^{-3}$ absorber.

- $a'_{MECS}$ - Specific surface area of MECS on unit volume of solvent basis, $m^2 m^{-3}$ solvent.

- $a_t$ - Total packing area, $m^2 m^{-3}$ absorber.

- $a_w$ - Wetted packing area, $m^2 m^{-3}$ absorber.

- $\bar{c}$ - Physical gas concentration in bulk of chemically reactive solvent, mol m$^{-3}$

- $c^* \equiv H_{pCO_2}$ - Physical gas concentration in liquid at equilibrium with gas, mol m$^{-3}$

- $c_{av}$ - Average physical gas concentration in physical solvent, mol m$^{-3}$

- $c_{bulk}$ - Physical gas concentration in bulk of physical solvent, mol m$^{-3}$

- $c_i$ - Physical gas concentration at liquid surface; for MECS, this is the concentration at the liquid surface inside the polymer shell, mol m$^{-3}$

- $C'$ - Dimensionless constant in Eq. (3.33)

- $\Delta c$ - Difference in physical gas concentration between liquid surface and liquid bulk, mol m$^{-3}$

- $D$ - MECS diameter, m

- $\mathcal{D}$ - Gas diffusivity, m s$^{-2}$
• $d_h \equiv 4\varepsilon/a_t$ - Hydraulic diameter of packing, m

• $d_p$ - Nominal diameter of packing (i.e. 0.0254 m for 1/2-inch Raschig Rings), m

• $d_s$ - Diameter of sphere with same surface area as packing, m

• $E$ - Electric field strength, NC$^{-1}$

• $E$ - Enhancement in flux provided by chemical reaction

• $E_i$ - Enhancement in flux provided by instantaneous chemical reaction

• $F$ - Force required to compress thin-walled capsule, N

• $F$ - Faraday’s constant, 96 485.332 89 C

• $\text{Fr}$ - Froude Number

• $F_{SE}$ - Surface enhancement factor

• $g$ - Gravitational constant, m s$^{-2}$

• $G$ - Gas flow rate, kg m$^{-2}$ s$^{-1}$

• $H$ - Henry’s constant, mol Pa$^{-1}$ m$^{-3}$

• $H_a$ - Hatta number

• $h$ - Liquid holdup, m$^3$ liquid m$^{-3}$ absorber

• $J$ - Flux into liquid, mol m$^{-2}$ s$^{-1}$

• $J_{\text{MECS}}$ - Flux into MECS, mol m$^{-2}$ s$^{-1}$

• $J_{\text{Column}}$ - Flux into liquid in packed column mol m$^{-2}$ s$^{-1}$

• $j_D$ - Mass transfer factor

• $k$ - Pseudo-first order chemical reaction rate constant, s$^{-1}$
- $k_B$ - Boltzmann Constant, $1.38 \times 10^{-23} \text{ JK}^{-1}$
- $k_L$ - Liquid phase mass transfer coefficient, m s$^{-1}$
- $k_G$ - Gas phase mass transfer coefficient, mol s$^{-1}$ m$^{-2}$ Pa$^{-1}$
- $k_{LDF}$ - Linear driving force constant, m s$^{-1}$
- $L$ - Liquid flow rate, kg m$^{-2}$ s$^{-1}$
- $L_p$ - Wetted perimeter of packing, m
- $M$ - Ratio of gas flux in packed column to gas flux in MECS
- $M$ - Square of the Hatta number
- $M_M$ - Molar mass, kg mol$^{-1}$.
- $P_{BM}$ - Log mean partial pressure of inert gas, Pa
- $p_{CO_2}$ - CO$2$ partial pressure, Pa
- $p_{i}^{\text{bulk}}$ - Partial pressure of species $i$ in bulk, Pa
- $p_{i}^{*}$ - Partial pressure of species $i$ at gas-liquid interface, Pa
- $P_{\text{shell}}$ - Permeability of MECS shell to gas, mol s$^{-1}$ m$^{-1}$ Pa$^{-1}$
- $q_i$ - Packing-dependent constant in correlation
- $r$ - Radius of liquid sphere inside MECS particle, m
- $R$ - Radius of capsule (including wall thickness), m
- $R_{\text{Column}}$ - Rate of absorption of gas in absorber per unit volume of absorber, mol s$^{-1}$ m$^{-3}$ absorber.
- $R_{\text{MECS}}$ - Rate of absorption of gas into MECS per unit volume of absorber, mol s$^{-1}$ m$^{-3}$ absorber.
- Re - Reynolds number, defined as $\rho \omega r^2 / \mu$ for spinning MECS particle.
- $\mathcal{R}$ - Resistance to mass transfer, $\text{s m}^{-1}$

- $v_0$ - MECS velocity prior to collision, $\text{m s}^{-1}$

- $w_0$ - Concentration of reactive species in bulk of chemical solvent, $\text{mol m}^{-3}$

- $\text{We}$ - Weber number

- $z$ - Shell thickness, $\text{m}$

- $Z_i$ - Charge number of ion $i$

**Greek Letters**

- $\alpha = (c_i - \bar{c})/\Delta c$ - Fractional reduction in flux due to shell resistance in chemical solvent.

- $\alpha' = (c_i - c_{av})/\Delta c$ - Fractional reduction in flux due to shell resistance in physical solvent.

- $\beta_i$ - Dimensionless constants in Eq. (3.33).

- $\delta$ - Compression of MECS particle, $\text{m}$

- $\varepsilon$ - Unit operation voidage, $\text{m}^3$ liquid-free space $\text{m}^{-3}$ absorber

- $\mathcal{E}$ - Young’s Modulus, $\text{Pa}$

- $\Gamma$ - Ratio of specific absorption rate into MECS to specific absorption rate in an absorption column, on a unit volume of absorber basis.

- $\xi$ - Sensitivity of gas flux to liquid mixing.

- $\Lambda$ - Increase in surface area per unit volume of solvent, compared with a 1 mm layer of liquid.

- $\phi \equiv \sqrt{kr^2/\mathcal{D}}$ - Thiele modulus.

- $\mu$ - Viscosity, $\text{Pa s}$
• \( \rho \) - Density, kg m\(^{-3}\)

• \( \sigma \) - Surface tension, N m\(^{-1}\)

• \( \sigma_c \) - Critical surface tension of packing, N m\(^{-1}\)

• \( \nu \) - Poisson’s ratio

• \( \omega \) - Angular velocity of spinning MECS, s\(^{-1}\)
4 Solvent Impregnated Polymers for Carbon Capture

Note. This chapter is an expanded version of a manuscript by Moore et al. [105], which has been previously published. Specifically, sections 4.1 – 4.5 and various Appendices it cites are almost exact replicas of the paper and its supplementary materials, while various extensions of this work, which have not yet been published, are discussed in sections 4.6 – 4.7.

Chapter Overview and Summary

In the previous chapter, the intrinsic kinetics of MECS were analysed, and it was found that, in spite of the difference in fluid flow patterns and the presence of the shell, they could reasonably be expected to increase specific absorption rates by 1-2 orders of magnitude. In this chapter, we focus on a second, practical question: can we manufacture MECS, or materials similar to them, at scale? MECS are currently made in microfluidic devices, at a rate of a few grams per hour. The manufacture of tens to hundreds of tonnes of MECS (as required for a full scale CCS process) will involve a scale-up on the order of 7 – 8 orders of magnitude, which will be difficult even if production can be automated and parallelised. This concern leads to the following question:

Can other materials be developed which, like MECS, allow a wide range of liquid solvents to be trapped inside a high-surface area solid, but which may be manufactured at scale in a more straightforward manner?

In this chapter, we report the development of a novel class of materials for carbon capture, which we refer to as a ‘Solvent Impregnated Polymers’, or SIPs. The manufacture of SIPs is exceptionally straightforward, and they are much more versatile than both MECS and other comparable composite solid systems. The first step in the manufacturing process is to create a concentrated (typically ∼50/50wt%) solvent-in-PDMS emulsion via shear emulsification. These emulsions are
typically quite stable, as the viscosity of the PDMS discourages Ostwald ripening and droplet collisions, though PDMS-based surfactants may also be used to stabilise the material. Once this emulsion has been manufactured, it may be cast as a thin film or dispersed as a double emulsion in an aqueous solution. Finally, the PDMS is cross-linked in situ (typically via application of heat or UV light) to create either a solid thin film or small solid particles, in which micron-scale droplets of a solvent for CCS are immobilised inside a continuous, solid PDMS matrix.

The method by which SIPs are manufactured requires only shear emulsification followed by casting, which are inherently much more scalable than the microfluidic processes required to manufacture MECS. SIPs may be cast into sheets as thin as 200 µm, with surface areas comparable to MECS. We report the manufacture of SIPs containing various carbonate solutions and a volatile ionic liquid which may be regenerated at low temperature. MECS containing carbonate solutions were stable through multiple cycles of absorption and regeneration, and did not lose water when exposed to a humid air stream.

Beyond the scalability and simplicity of their production, a second, significant advantage of SIPs relates to their mass transfer properties. The solvent droplets within a SIP are dispersed inside PDMS, which has a CO₂ permeability 1-2 orders of magnitude greater than most liquid solvents. For this reason, during absorption the continuous polymer phase acts as a low-resistance pathway by which gas can diffuse into the material and react with a greater quantity of the immobilised solvent than would occur during absorption into MECS or a neat liquid. This effect will typically increase the initial gas flux into SIPs, compared to equivalent MECS or a neat liquid, by 1-2 orders of magnitude. Unfortunately, in many liquid systems this initial increase is not indicative of the increase in the average flux over the whole absorption run. In a MECS or a neat liquid, depleted solvent is free to diffuse into the bulk, and fresh solvent to the surface. However, during absorption into a SIP, when the immobilised droplets near the surface become saturated, they are fixed in place, and cannot be replaced by fresh solvent. Hence a saturated zone forms...
near the surface and propagates into the material over time, decreasing the gas flux relative to a neat liquid.

In order to better understand these phenomena, a model for mass transfer into SIPs was developed and validated against CO$_2$ uptake curves into several SIP systems. The model was then non-dimensionalised, in order to compare the flux into SIPs with the flux into a MECS (or a neat liquid) containing a chemical solvent in the pseudo-first order reaction regime. It was found that for SIPs with reasonable properties and reasonable dimensions, the average gas flux (over an entire absorption run) could be expected to be up to 4-5 times greater. The increase in flux could complement a 1-2 order of magnitude increase in specific surface area, and the two would be multiplied together to give the total increase in absorption rate per unit volume of material.

The above work has previously been published; in the second half of this chapter, we report on two recent developments which have not yet been published.

First, we show that the complex, PDE-based model used to predict the absorption rate into SIPs collapses, under a range of circumstances, to a much simpler, diffusion-limited model, which has previously been used to model liquid emulsion membranes. This occurs when diffusion through the saturated zone described above is rate-controlling, in which case the PDE-model reduces to a simpler ODE which may be solved analytically. By non-dimensionalising the simple and complex models, we demonstrate that the diffusion-limited model is valid for a very large range of absorption regimes, and accurately predicts the time to reach 80% saturation provided diffusional resistance in the system is large enough to increase the absorption time by a factor of 6, relative to a reaction-controlled system with no diffusional resistances at all. As diffusional resistance in a reactive liquid and solid sorbent is typically much greater than this, we expect the simpler, diffusion-limited model to be accurate for the large majority of SIPs.

Second, we report on recent work, in which nanoparticle organic hybrid materials (NOHMs) for carbon capture have been successfully immobilised inside SIP
materials. Mass transfer experiments into these materials show a remarkable 50-fold increase in the gas flux, relative to a neat NOHM liquid. The reason this enhancement in the flux is much greater than the ~ 5-fold increase predicted previously is that NOHMs do not exist in the pseudo-first order absorption regime. Because they are so viscous, and the reactive molecules inside them have such low mobility, a saturated zone forms near the surface of the NOHMs and propagates into the material over time, just as it does inside SIPs. Hence, there is no tradeoff between either enhancing permeability, on the one hand, or forming a saturated zone on the other: the saturated zone exists for both NOHMs and SIPs. Hence, the fact that the permeability of CO$_2$ inside the SIP is several orders of magnitude greater than in the NOHM leads to a very large increase in the average absorption rate. Furthermore, the simple diffusion-limited model was shown to give a reasonable prediction for the rate of absorption into SIPs containing NOHMs, even though very little information about the chemical kinetics inside the NOHMs was available.
4.1 Introduction

The accumulation of carbon dioxide in the atmosphere is changing the earth’s climate at an unprecedented rate. If dangerous climate change is to be avoided, the rate of global anthropogenic CO₂ emissions must be drastically reduced over the coming decades [40]. One means of reducing CO₂ emissions is carbon capture and storage (CCS). CCS can reduce the CO₂ released by the combustion of fossil fuels, and is also a primary means of reducing emissions from industrial processes, which are responsible for roughly 30% of world emissions [4]. CCS is also the basis for many negative emissions technologies (NETs). Most policy scenarios put forward by the Intergovernmental Panel on Climate Change (IPCC) assume large-scale deployment of NETs in the second half of the 21st century, even though the technology is largely unproven today [68, 6, 69]. However, in spite of its importance and the need for rapid technological progress, the development of CCS has been hampered by project delays and funding cuts, even as the uptake of renewables continues in line with IPCC scenarios [55, 51, 32].

In the last few years, a number of novel classes of solvent have been investigated for carbon capture, including ionic liquids [86], CO₂-binding organic liquids [216], piperazine [217], and precipitating potassium carbonate systems [84, 218]. These systems typically have thermodynamic advantages over traditional solvents such as monoethanolamine (MEA), including lower regeneration energy, lower regeneration temperature or higher CO₂ capacity [112, 132]. However, they may have properties, such as high viscosity, high volatility, corrosivity, the precipitation of solids, or slow absorption of CO₂, that make gas-liquid contacting difficult. One novel approach to utilising these thermodynamically favourable materials is the microencapsulation of liquid solvents (MECS) inside small capsules a few 100 microns in diameter [3, 100]. The very high specific surface area of these capsules could allow slow solvents to be utilised in a practical way, and the isolation of the liquid from its environment may render problematic liquid properties irrelevant. The most significant practical challenge that MECS face is their manufacture on a large scale. They are currently
produced in microfluidic devices at a rate of a few grams per hour, and even the most optimistic predictions for large-scale manufacture inside microfluidic devices do not exceed tens to hundreds of tonnes per year [219]. As CCS operations generally use absorbers with volumes of several hundred cubic meters [220], it's likely that the mass of particles required will be at or above the upper limit of what could be produced by a parallellised microfluidic droplet assembly.

In this chapter, an alternative, novel means of immobilising liquid solvents is proposed, which may enhance mass transfer and is highly scalable. A concentrated (∼50/50wt%) solvent-in-polydimethyl siloxane (PDMS) emulsion is first created via shear emulsification (see Figure 4.1). The emulsion is then cast into a flat film, or further emulsified into a double emulsion in an aqueous phase to generate fine particles. The PDMS is then crosslinked using heat or UV light to produce a solid gel. These ‘solvent impregnated polymers’ (SIPs) are manufactured by a simple, one-pot method which may prove more scalable than the microfluidic devices used to create MECS particles, and like MECS they could provide a pathway for solvents with inconvenient fluid properties to be used for CCS or other gas separation processes. Mass transfer can be enhanced by shaping the solid gel into very small particles or thin sheets with surface area comparable to MECS. Furthermore, as PDMS has a relatively high CO₂ permeability, it can, under certain circumstances, enhance the flux of gas by acting as a pathway along which the gas can tunnel deeper into the material before interacting with the immobilised liquid solvent droplets. Like MECS, when shaped into small particles SIPs could be contacted with a gas in a supported packed bed or a fluidised bed, though the flexible nature of the manufacturing process opens up alternative schemes, including coating SIPs onto the walls of a monolith or structured packing for high-surface area, low-pressure drop gas-solid contacting.

SIPs may be compared with a large number of alternate composite materials. They are structurally similar to colloidal ionic liquid gels [221, 222], though these have not previously been used as high-surface area sorbent materials for gas sepa-
Figure 4.1: Synthesis of SIPs particles and thin sheets.

ration. They have similar capacities to solvent impregnated resins [223, 224] and amine impregnated resins [122], which may be manufactured in a straightforward manner using commercially available resins. However, the fact that the solvent is physically embedded inside the SIP, rather than held by capillary or surface forces, may allow greater flexibility in solvent and polymer selection. The use of PDMS in the continuous phase may also improve mass transfer in SIPs, as the polymers used in commercial resins typically have lower CO₂ permeabilities [122]. Molecularly imprinted polymers (MIPs) are another high surface area polymer material, which may be manufactured via bulk [138] or suspension [225] polymerisation. However, MIPs have relatively low CO₂ capacities (they typically hold < 0.4 mmol CO₂/g material at 0.1 bar of CO₂ [138, 225, 113]) and SIPs containing concentrated chemical solvents would be expected to absorb several times more CO₂. Other composite sorbents with similar properties include amine-modified solid sorbents [121], porous liquids [139], and high internal phase polymer foams [140]. An advantage of SIPs over each these technologies is the simplicity of their manufacture. Because the solvent is held physically inside the SIP, there is no need to ensure a chemical binding between a reactive sorbent and a structural support. This may allow for faster screening of systems, and also for independent optimisation of solvent and polymer selection, with less concern for chemical compatibility than would otherwise be required.

The SIP motif could in principle be applied to a wide range of gas separations and
solvents, though, following Vericella et al. [3], this work focuses on the immobilisation of a concentrated potassium carbonate solution. This is a promising solvent for CCS, with excellent thermodynamic properties, but it is hampered by slow absorption kinetics and the precipitation of solid bicarbonate at high CO$_2$ loadings [159]. Immobilising K$_2$CO$_3$ solutions inside high surface area solids could address both of these problems. The immobilisation of a volatile ionic liquid, DMEDAH Formate, is also demonstrated. This ionic liquid has remarkable thermodynamic properties: it is able to absorb $\sim$11 wt% CO$_2$ at room temperature, and then release it at 40°C [132], and so may allow freely-available waste heat from a process to be used for gas desorption if its practical drawbacks - slow absorption kinetics, volatility, and high viscosity - can be overcome.

4.2 Experimental Methods

4.2.1 Materials

Semicosil® 949 UV was provided by Wacker Chemie AG. KE-103® and KE-106® were purchased from Shin-Etsu Chemical Co., Ltd.. Sylgard® 184, 5225C Formulation Aid, ES-5612 Formulation Aid, ES-5600 Silicone Glycerol Emulsifier and 9011 Silicone Elastomer Blend were purchased from Dow Corning. SMS-042 and DMS-V31 were purchased from Gelest, Inc.. K$_2$CO$_3$ (>99.5%) was purchased from UCID Co. Ltd. Jiangsu, China). 2,2-Dimethoxy-2-phenylacetophenone (DMPA) and Eosin Y were purchased from Sigma-Aldrich. DMEDAH Formate was synthesised and supplied by the Defence Science and Technology Group at the Australian Department of Defence.

4.2.2 Emulsion Synthesis

The process for manufacturing precursor emulsions was identical for all K$_2$CO$_3$-based SIPS listed in Table 4.2 in Appendix 4.I. Multi-part PDMSs were mixed according to the manufacturer’s specifications, and approximately 10 g was placed in a 70 mL polypropylene container. Appropriate masses of any stabilising agents (see
Table 4.2) were then added, and the mixture was stirred for approximately 20 s using a Dremmel® 3000 drill with a 3/4” steel brush attachment at 5000 RPM. The drill speed was then increased to the maximum speed of 35000 RPM. A potassium carbonate solution, which had been made up to the desired mass fraction (between 3-30wt%) and placed on a scale, was then added dropwise to the PDMS using a 5 mL plastic dropper as the solution was vigorously stirred. The aqueous solution was added at a rate of approximately 2 g min$^{-1}$ to the PDMS emulsion until the desired mass fraction was achieved. The emulsion was further stirred at 35000 RPM for 1 min, and was then placed in a 80 kPa vacuum and allowed to degas. When bubbles stopped evolving from the material surface, the container was removed and sealed.

To manufacture the ionic liquid-based SIP, 5 g of SMS-042 was placed in a glass beaker and weighed, and 10 mg of the UV-activated initiator 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was added. The beaker was then placed in an ultrasonic bath for 30 min, in order to dissolve the DMPA. After this, 5 g of DMS-V31 was added to the beaker, and the PDMSs were thoroughly stirred until they were combined. The PDMS was then transferred to a 70 mL polypropylene container, and the mass of PDMS transferred was measured. The addition of the stabilising agent, 5225C Formulation Aid, and the formation of a 50wt% emulsion containing DMEDAH Formate in PDMS, then proceeded as per the previous paragraph.

### 4.2.3 Thin Film Synthesis

A sample of the UV-curable emulsion was transferred to a 6 cm ID polystyrene Petri dish, the mass of sample added was recorded, and a lid was placed over the dish. The Petri dish was then manually shaken in a horizontal circular motion to facilitate spreading of the emulsion into a thin film. Once a thin film had been produced, the lid of the Petri dish was sealed to the base by wrapping 3 layers of parafilm tightly around the circumference, and the Petri dish was placed under UVC light to crosslink for ~12 h overnight. Samples were placed approximately 5 cm below a 30 W Philips
TUV G30T8 lamp.

4.2.4 Particle Synthesis

An emulsion containing 75wt% of Shin-Etsu’s KE-103®, 1wt% 9011 Silicone Elastomer Blend, and 25wt% of a 3wt% K2CO3 solution containing 25 mg L−1 of thymol blue was synthesised according to the methods described in ‘Emulsion Synthesis’. 80 mL of a 3wt% K2CO3 solution and 0.8 g of Tween® 20 were then added to a 100 mL glass beaker, which was placed on a hot plate and heated to 50°C. A 1 cm magnetic stir bar was then placed in the water and stirred at high speed (∼1500 RPM) and approximately 1 g of the emulsion was added dropwise to the water, forming a double emulsion. The solution was left to stir for 2 h, after which the PDMS had thermally cross-linked and small solid particles had formed.

4.2.5 Mass Transfer Measurements

Mass transfer into SIP sheets was measured using a constant-volume vessel connected to a buffer tank, both of which were held in an incubator at constant temperature. A piece of SIP on a plastic Petri dish, manufactured according to the ‘Thin Film Synthesis’ section, was placed inside the vessel and flooded with 1 atm of N2. The buffer tank was filled with pure CO2 at about 5 bar, and both vessels were left in the incubator to thermally equilibrate at 40°C overnight. The SIP was then exposed to CO2 by briefly opening a valve connecting the vessel to the buffer tank. The total pressure inside the vessel was recorded over time using a UNIK 5000 digital pressure transducer purchased from GE Measurement, and the moles of CO2 absorbed at any point in time was calculated from the difference between the initial pressure, just after the CO2 was added, and the present pressure.

The solubility and diffusivity of CO2 into Semicosil® 949 UV in 1 atm of N2 was also measured using the constant-volume apparatus. A 3 g sheet of crosslinked Semicosil® 949 UV was first prepared in a 6 cm ID polystyrene Petri dish. Mass transfer of CO2 into this sheet was then measured using the same methodology and
conditions described in the previous paragraph. The vessel was flooded with N\textsubscript{2} at 1 atm, and left to equilibrate at 40\degree C overnight. It was then exposed to CO\textsubscript{2} from a buffer tank, and the uptake of CO\textsubscript{2} was inferred from the decrease in pressure over time. The solubility and diffusivity were then calculated by fitting the CO\textsubscript{2} uptake curve to the analytical solution to the diffusion equation in a finite one-dimensional slab.

In order to estimate the vessel and buffer tank volumes, the vessels were pressurised to 2 bar and then equilibrated with a second reference vessel of known volume. The vessel volumes were estimated using the ideal gas law. This measurement was taken 6 times for each vessel, and the overall coefficient of variation was 0.35%.

### 4.2.6 Stability Experiments

For cyclical CO\textsubscript{2} absorption/desorption stability experiments, a 10 g piece of SIP containing 50wt\% Semicosil\textsuperscript{®} 949 UV, 1wt\% 9011 Silicone Elastomer Blend, and 50wt\% of a 30wt\% K\textsubscript{2}CO\textsubscript{3} solution was synthesised on a 6 cm polystyrene ID Petri dish according to the methods described in ‘Thin Film Synthesis’. A \~7 g piece of SIP was cut out, carefully removed and weighed. For CO\textsubscript{2} absorption, CO\textsubscript{2} gas was bubbled through 80\degree C water and continuously flowed through a 5 L plastic vacuum chamber operated at positive pressure. The SIP sample was placed inside the vacuum chamber and exposed to a humid CO\textsubscript{2} stream for 3 h. The sample was then removed from the vessel and its mass measured. For regeneration, the sample was placed in a 90\degree C to 100\degree C solution of 30wt\% K\textsubscript{2}CO\textsubscript{3} for 3 hours. Milli-Q\textsuperscript{®} water was added to the solution over time in order to maintain a constant water level. The sample was then removed and placed in an isotonic 30wt\% K\textsubscript{2}CO\textsubscript{3} solution overnight. It was then removed from this solution, carefully dried, and its mass was recorded before the beginning of the next absorption experiment.

For humid air stability experiments, two 2 g samples of SIP containing 50wt\% Semicosil\textsuperscript{®} 949 UV, 1wt\% 9011 Silicone Elastomer Blend, and 50wt\% of a 30wt\% K\textsubscript{2}CO\textsubscript{3} solution were synthesised on 6 cm ID polystyrene Petri dishes according to
the methods described in ‘Thin Film Synthesis’. Their initial masses were measured. One sample was placed in a desiccator, while another was placed in the same humid vessel as used for CO₂ absorption/desorption experiments, except that N₂ was flowing through the vessel rather than CO₂. A digital hygrometer placed inside the vessel confirmed that the relative humidity in the vessel was greater than 95% throughout the experiment. Approximately once per hour the samples were removed, their masses were measured, and they were placed back in their respective environments.

For cyclical CO₂ absorption/desorption stability experiments for the SIP containing DMEDAH Formate, a NETZSCH TG 209 F1 Libra® Thermogravimetric analyser (TGA) was used. A small piece of SIP was placed in the TGA crucible, and was sequentially exposed to CO₂ at 30 °C and N₂ at 60 °C. 20 minutes was allocated for the temperature adjustment, and 60 minutes for isothermal gas exposure; all gas flow rates were set to 20 mL min⁻¹.

4.2.7 Imaging

For confocal microscopy imaging, SIPs were manufactured in a similar manner to that described in ‘Thin Film Synthesis’, except that 0.001wt% of the dye Eosin Y was added during the manufacturing of the emulsion. The emulsion was also placed directly onto a glass cover slip inside the Petri dish, and solidified on top of this slip during crosslinking. The solid SIP was imaged with a Nikon A1R confocal microscope with a 60×1.4NA oil immersion objective. For imaging the emulsions, an Olympus BX51 microscope was used, with an Olympus LUCPlanFLN PH2 Phase Achromat Objective, with a total magnification of 400x.

4.3 Results and Discussion

4.3.1 SIP Manufacture

A typical precursor emulsion, containing 50wt% of an aqueous K₂CO₃ solution dispersed in a UV-curable PDMS by shear emulsification, is shown in Figure 4.2a.
Figure 4.2: (a) Uncrosslinked emulsion containing 50wt% of a 30wt% K₂CO₃ solution, 50wt% Semicosil® 949 UV and 1wt% 9011 Silicone Elastomer Blend. (b, c) SIP containing 50wt% of a 10wt% K₂CO₃ solution, 50wt% Semicosil® 949 UV and 1wt% 9011 Silicone Elastomer Blend, before (b) and after (c) crosslinking. (d) Piece of SIP of identical composition to emulsion in (a) (e,f) SIP particles containing 25wt% of a 3wt% K₂CO₃ solution with 25 mg L⁻¹ thymol blue, 75wt% KE-103® and 1wt% 9011 Silicone Elastomer Blend before (e) and after (f) exposure to CO₂.

The microscopic structure of an emulsion before and after crosslinking of the polymer is shown in Figures 4.2b and 4.2c. No significant change in the internal droplet size or morphology was observed during crosslinking. The internal particle size was strongly dependent on the polymer, solvent and stabilising agents used, and materials were created with mean internal particle size ranging from 1µm to several 100µm (see Figures 4.16 and 4.17 in Appendix 4.I.) A number of stable SIPs were synthesized using various PDMSs and stabilising agents, and with K₂CO₃ concentrations from 3-30wt%; a complete list may be found in Table 4.2 in Appendix 4.I.

Figure 4.2d shows a stable piece of SIP containing 50wt% of a 30wt% K₂CO₃ solution, formed by casting an emulsion in a Petri dish and crosslinking the PDMS under UV light. Uniform SIPs as thin as ~200µm could be manufactured in this way, and these materials have a total surface area of 5000 m² m⁻³ to 10 000 m² m⁻³, comparable to MECS particles. Figures 4.2e and 4.2f show SIP particles containing a 3wt% K₂CO₃ solution with 25 mg L⁻¹ of thymol blue, before and after exposure to
a stream of pure CO$_2$. SIP particles were manufactured by dispersing the emulsion in a stirred aqueous phase to create a double emulsion, and then crosslinking the PDMS \textit{in situ}. For simplicity, a heat-curing PDMS was used. The mean particle size was around 2 mm (see Figs 4.18 and 4.19 in Appendix 4.I). This is substantially larger than the typical size of MECS particles (100 $\mu$m to 600 $\mu$m) though it may be possible to reduce this size with higher shear or by reduction of the emulsion viscosity.

### 4.3.2 CO$_2$ Uptake and Stability

The stability of a SIP film containing 50wt\% of a 30wt\% K$_2$CO$_3$ solution was tested over multiple cycles of CO$_2$ absorption and thermal regeneration; the mass of the sample after each step is shown in Fig 4.3a. The sample was exposed to a saturated CO$_2$ stream to minimise water evaporation (c.f. Fig 4.3b.), however there was still significant experimental variation in the absorption measurements, likely due to condensation of small quantities of water onto the material’s surface. However, when the material was thermally regenerated it consistently returned to the same mass, suggesting that the absorption and regeneration cycles were not affecting the quantity of K$_2$CO$_3$ stored inside the SIP. Further, in this experiment the sample was not exposed to the gas for long enough to reach saturation, and over multiple cycles there was no evidence of any decrease in the rate of uptake of CO$_2$.

In an industrial setting, gas-streams containing CO$_2$ are often saturated in water, and SIPs must remain stable in that environment. Fig 4.3b shows the change in mass over time of two films of SIP exposed to saturated and dry N$_2$ in a flow-through apparatus. The mass is relative to the mass of the \textit{emulsion} prior to crosslinking, and starts at approximately 0.97 because a small amount of water escaped during the crosslinking process. In humid air the sample mass was stable over time, while in dry air water evaporated from the sample quite quickly. Samples dried in a desiccator for a week were fully regenerated when soaked in an isotonic solution. While these preliminary experiments are positive, further work is required to demonstrate that
Figure 4.3: (a) Cyclic CO2 absorption and regeneration experiments for piece of SIP containing 50wt% of a 30wt% K2CO3 solution. Dotted lines show minimum and maximum theoretical loading; the maximum loading corresponds to 1.25 mmol CO2/g sorbent. The droplets of concentrated K2CO3 solution inside the SIP provide ∼95% of the theoretical CO2 capacity. Error bar shows variation in uptake during absorption experiments. (b) Humid air stability experiments for a piece of SIP containing 50wt% of a 30wt% K2CO3 solution.

SIPs are stable over many more cycles, and also when they are regenerated using steam, which would likely be used in practice.

4.3.3 Encapsulation of a Protic Ionic Liquid

The volatile protic ionic liquid DMEDAH formate could not be encapsulated using the UV-curing and heat-curing PDMSs that had been used for K2CO3 solutions, as the amine groups in the IL inhibited the crosslinking of the polymer [100]. Instead, a thiol-ene based PDMS crosslinking reaction was used. It was hoped that encapsulation of this volatile ionic liquid would minimise evaporation, and would provide a pathway for its utilisation in a practical setting. Unfortunately, while a solid gel was formed by this method (Figure 4.4a), during gravimetric CO2 absorption/regeneration experiments most of the ionic liquid evaporated out of the material within 24 h (Figure 4.4b). While PDMSs with a greater density of functional groups could probably be used to produce a more stable gel, it seems unlikely that encapsulation could ever completely prevent the evaporation of a volatile, non-aqueous solvent. Furthermore, while it is reasonable to imagine SIPs being exposed to gas streams saturated in water, there is always going to be a driving force for
the evaporation of non-aqueous solvents from these materials. On the other hand, DMEDA Formate is a particularly volatile ionic liquid, as the proton transfer reaction is only partially complete [132]. SIPs containing ionic liquids with lower vapor pressure would be expected to be considerably more stable [222].

Figure 4.4: (a) Piece of SIP containing 50wt% of protic ionic liquid DMEDA Formate. (b) Cyclic CO₂ absorption and regeneration experiment for SIP containing DMEDA Formate.

4.3.4 Mass Transfer Model: Development and Validation

Gas absorption into SIP sheets differs from absorption into a neat liquid in several respects (see Figure 4.5a.) Gas molecules entering the material may either diffuse through the immobilised liquid droplets or through the continuous PDMS matrix. In many cases, the CO₂ permeability inside the PDMS is far greater than inside the solvent. For example, the CO₂ permeability inside a 40wt% K₂CO₃ solution is about $8 \times 10^{-15}$ mol Pa$^{-1}$ m$^{-1}$ s$^{-1}$, while in the PDMS it is approximately $1 \times 10^{-12}$ mol Pa$^{-1}$ m$^{-1}$ s$^{-1}$, two orders of magnitude larger (the diffusivity of PDMS are taken from [175]; see Appendix 4.V for physical properties of carbonate systems.). Under these conditions, PDMS provides a low-resistance pathway, allowing the gas to penetrate more deeply into the material, react with more solvent, and be absorbed more quickly.

On the other hand, mass transfer into SIP materials is inhibited by the formation of a saturated zone which propagates away from the solid surface. Unlike in a neat liquid (where fresh solvent can diffuse to the surface and used solvent can diffuse
away) in a SIP, droplets of exhausted solvent are held in place by the surrounding polymer, and gas must diffuse through them in order to reach the fresh solvent beneath. This saturated zone is similar to the ash layer that forms in a shrinking core model [160], and is most significant for thicker SIP layers.

In order to better understand and quantify mass transfer, a theoretical model was developed and independently validated using gas uptake measurements. It was assumed that a second order reaction took place between the gas and a reactive species in the liquid (for example, for CO₂ absorption into K₂CO₃ solutions, the primary reactive species would be OH⁻.) A shell balance was used to derive the following, volume-averaged equations:

\[
\frac{\partial c}{\partial t} = D_{\text{eff}} \nabla^2 c - k_{2\text{eff}} c w \tag{4.1}
\]

\[
\frac{\partial w}{\partial t} = f(c, w, \xi) \tag{4.2}
\]

where \( D_{\text{eff}} \) and \( k_{2\text{eff}} \) are given by:

\[
D_{\text{eff}} = \frac{D_s \varepsilon S_s + D_l (1 - \varepsilon)}{\varepsilon S_s + \xi (1 - \varepsilon)} \tag{4.3}
\]

\[
k_{2\text{eff}} = \frac{k_2 (1 - \varepsilon)}{\varepsilon S_s + \xi (1 - \varepsilon)} \tag{4.4}
\]

c and \( w \) are the gas and reactive species concentration in the liquid phase, respectively (c.f. Fig 4.5a), and \( f(c, w, \xi) \) (the rate of change of the reactive species concentration inside the immobilised droplets) is a function that depends on the specific chemistry of the solvent (see section 5.5 and Appendices 4.II – 4.V for a detailed development of the model and the calculations described below.) \( \xi \) is an **effectiveness factor**, which accounts for the reduction in reaction due to local diffusional resistance in the liquid droplets [226]:

\[
\xi = \frac{\phi' \coth \phi' - 1}{(\phi')^2/3} \tag{4.5}
\]
where $\phi'$ is the local Thiele modulus,[226]

$$
\phi' = r_{\text{droplet}} \sqrt{\frac{k_2 w}{D_l}}. 
$$

(4.6)

The model does not account for local diffusional resistance inside the continuous polymer layer, as the permeability of the polymer is significantly greater than the permeability of the liquid for the SIPs considered in this work. Furthermore, if the reaction is fast enough for the concentration profiles in both the liquid and solid phases to vary at the microscopic level, then on the macroscopic level the system approximates a moving front model with instantaneous reaction, of the kind considered by Ho et al. [157]. Under these conditions, diffusion of gas to the moving reaction front is rate controlling, and accurately modelling the local diffusional resistance in the polymer is unnecessary (see section 4.6 for a further discussion on this point.)

To validate the model, CO$_2$ uptake experiments were conducted at 40 °C in a fixed-volume vessel. Thin layers of SIP containing 50wt% of 3wt% and 10wt% K$_2$CO$_3$ solutions were analysed. The diffusivity and permeability of CO$_2$ in the PDMS Semicosil® 949 UV at 40 °C were calculated from CO$_2$ uptake measurements taken in the same constant-volume vessel, and other material parameters (including material properties, reaction rate constants, and vapor-liquid equilibrium data required for the calculation of $f(c, w)$) were estimated using published correlations and data (see Appendix 4.IV - 4.V) CO$_2$ reacts according to the following mechanism [15]:

$$
\text{CO}_2 + \text{OH}^- \longrightarrow \text{HCO}_3^- 
$$

(4.7)

$$
\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^- 
$$

(4.8)

Reaction 4.8 may be assumed to be at instantaneous equilibrium at all times [15], and so Reaction 4.7 is rate controlling. In concentrated solutions, the chemistry may be complicated by the precipitation of bicarbonate at high loadings. However, for the dilute solution considered below, this will not occur [72].
Figure 4.5: (a) Gas absorption into a SIP sheet and a neat liquid. \(c(t,x)\) and \(w(t,x)\) are concentration profiles of the absorbed gas and the reactive species respectively. (b,c) Comparison between measured and modelled CO\(_2\) uptake rates for SIPs containing (b) 50wt\% of a 3wt\% K\(_2\)CO\(_3\) solution and (c) 50wt\% of a 10wt\% K\(_2\)CO\(_3\) solution. (d) Plot of the theoretical enhancement in mean gas flux SIPs can provide, \(J_{\text{SIP}}/J_{\text{Liq}}\), for various values of the liquid Thiele modulus, \(\phi\), and the relative permeability of the polymer, \(P_s/P_l\). Grey lines show the mean value of \(J_{\text{SIP}}/J_{\text{Liq}}\), calculated for 8 hypothetical \(f(c,w)\) functions, and the shaded regions show the standard deviation from the mean. In this plot, \(L/r_{\text{drop}} = \infty\), however \(J_{\text{SIP}}/J_{\text{Liq}}\) varied by less than 4\% for values of \(L/r_{\text{drop}} > 10\) (e) SIP thickness for which \(J_{\text{SIP}}/J_{\text{Liq}} = 1\) (black lines) and for which \(J_{\text{SIP}}/J_{\text{Liq}}\) is maximised (gray lines), as a function of \(\sqrt{D_l/k_2u_0}\) and and \(P_s/P_l\), assuming \(L/r_{\text{droplet}} = \infty\). Predicted values for 30wt\% K\(_2\)CO\(_3\) and 40wt\% K\(_2\)CO\(_3\) solutions are highlighted.
As can be seen in Figures 4.5b and 4.5c, the model developed from first principles was in good agreement with the experimental absorption data, and accurately predicted both the absorption kinetics and the total CO₂ capacity of the material. For these calculations, the local particle size distribution was estimated from Figure 4.2c, however the model was quite insensitive to changes in the local Thiele modulus. This is because for this system macroscopic diffusion through the saturated zone (see Figure 4.5a) is rate controlling [157], and under these circumstances the absorption rate is independent of the local Thiele modulus.

### 4.3.5 Mass Transfer Model: Analysis

The model accurately predicted mass transfer rates into several SIP materials, even though it was not regressed against experimental data. This suggests that the underlying approach of modelling SIPs using the known properties of each phase is valid (as is the case for many other composite materials [227].) On this basis, the model’s predictions for a variety of polymer and solvent compositions were analysed to gain insight into mass transfer mechanisms and to guide material selection.

The most immediate problem is to determine how the flux of gas into SIPs compares with the flux into the neat solvent alone. This comparison is directly relevant to the comparison of SIPs with alternative technologies, as shell resistance in MECS and liquid mixing in a traditional column do not significantly influence the gas flux for most chemical solvents [15, 38]. Using the model described by Eq. (4.1) - (4.6), absorption into a thin slice of SIP was compared with direct absorption into a neat, stationary layer of solvent of identical composition to the liquid held inside the SIP. The liquid thickness was chosen so that the two materials had identical gas capacity, and the liquid solvent was modelled as absorption with pseudo-first order reaction: a reasonable approximation for many solvents of industrial interest [18]. For each system, the mean gas flux, \( \bar{J} \), was calculated over an entire absorption run, starting with 10% gas saturation and ending at 80%.

By nondimensionalising the differential equations governing each system, the
parameters that affect the ratio of the mean gas fluxes, $\bar{J}_{\text{SIP}}/\bar{J}_{\text{Liq}}$, were identified. For solvents whose chemical solubility was much greater than their physical solubility (a condition that holds for the large majority of chemical solvents), this ratio depended upon only four dimensionless parameters: the polymer volume fraction in the SIP, $\varepsilon$, the relative size of the internal droplets, $L/r_{\text{droplet}}$, the ratio of the permeability of the polymer to the permeability of the liquid, $P_s/P_l$, and the Thiele modulus of the liquid,

$$\phi \equiv L \sqrt{\frac{k_2 w_0}{D_l}},$$

(4.9) where $w_0$ was chosen as the mean reactive species concentration over the whole range of liquid loadings present in the system, in order to best approximate the dynamics inside the reaction zone (details may be found in Appendix 4.III).

With $\varepsilon$ held at 0.5, $\bar{J}_{\text{SIP}}/\bar{J}_{\text{Liq}}$ was calculated as a function of $P_s/P_l$, $L/r_{\text{droplet}}$ and $\phi$ for a number of hypothetical solvent chemistries over a wide range of values. The mean value of $\bar{J}_{\text{SIP}}/\bar{J}_{\text{Liq}}$ over all runs is plotted in Figure 4.5d; the shaded area represents the standard deviation among the different solvent chemistries considered. Somewhat surprisingly, $\bar{J}_{\text{SIP}}/\bar{J}_{\text{Liq}}$ was relatively independent of the specific solvent chemistry: the average standard deviation was less than 0.1. Similarly, $\bar{J}_{\text{SIP}}/\bar{J}_{\text{Liq}}$ was insensitive to the specific value of $L/r_{\text{droplet}}$: provided $L/r_{\text{droplet}} > 10$ (i.e. provided there was reasonable separation between the macroscopic and microscopic length scales) variations in $L/r_{\text{droplet}}$ did not change $\bar{J}_{\text{SIP}}/\bar{J}_{\text{Liq}}$ by more than 3% (in making Figure 4.5d, $L/r_{\text{droplet}} = \infty$ was used.) This is because in these systems mass transfer is typically controlled by diffusion through the saturated zone, not the local dynamics inside the reaction zone (as predicted on intuitive grounds by Ho et al. [157].) Hence, Fig 4.5d can be viewed as an approximate phase diagram, valid for all SIPS containing chemical solvents. Provided the Thiele modulus and the relative permeability of the polymer and liquid can be estimated, it may be used to assess whether SIP materials of a given thickness will absorb gas faster or slower than an equivalent liquid film. In Fig 4.5e, the Thiele modulus, $\phi = L \sqrt{\frac{k_2 w_0}{D_l}}$, is expanded into two separate, dimensional terms to more concretely demonstrate the results of
this calculation. Solid black lines show the ‘break-even’ SIP thicknesses as a function of $\frac{P_s}{P_l}$ and $\sqrt{D/k_2w_0}$ - above this thickness, the flux of gas into SIPs is less than into a neat liquid, and below it is greater. Grey lines show the SIP thickness for which $\bar{J}_{\text{SIP}}/\bar{J}_{\text{Liq}}$ is maximised (i.e. the maxima on the curves in Fig 4.5d).

Fig 4.5d highlights the trade-off between enhanced gas permeability and the formation of a saturated zone. It is clear that increasing $\frac{P_s}{P_l}$ always increases $\bar{J}_{\text{SIP}}/\bar{J}_{\text{Liq}}$, however a large value of $\frac{P_s}{P_l}$ doesn’t guarantee that the flux into the SIP will be greater than the flux into the liquid. When $\phi$ is very small (so the absorption is reaction controlled) the diffusional resistance has no influence on the gas flux, so $\bar{J}_{\text{SIP}}/\bar{J}_{\text{Liq}} = 1$. For very large $\phi$, the material thickness is much greater than the thickness of the zone in which the reaction occurs, and a reaction front is established inside the SIP which progresses into the material (c.f. Figure 4.5a.) Even though the initial flux into the SIP may be greater, over time the resistance provided by the saturated zone outweighs the enhanced gas permeability, and the greater the Thiele modulus (i.e. the greater the material thickness relative to the reaction front thickness) the poorer the SIP will perform. For moderate values of $\phi$ and large values of $\frac{P_s}{P_l}$, the flux of gas into a SIP may be substantially greater than the flux into an equivalent neat liquid. Such an increase in flux could by complemented by an increase in surface area for fine SIP particles or films, as is the case for MECS, which have roughly an order of magnitude greater surface area than the liquid in a traditional packed column [38]. For SIPs, the combined effect of increased flux and increased surface area could be expected to increase the absorption rate per unit volume of material by up to 1-2 orders of magnitude.

Because the relative flux depends upon the relative permeability of the polymer and solvent, and not the relative diffusivity, SIPs would be expected to provide greater enhancement in mass transfer for more concentrated solvents, in which salting-out effects often reduce the physical gas solubility by 1-2 orders of magnitude [13]. For example, for a PDMS-based SIP containing 3wt% K$_2$CO$_3$, $\frac{P_s}{P_l}$ is only approximately 2, and so immobilisation is unlikely to increase the mean gas flux (the
diffusivity of PDMS is taken from [175]; see Appendix 4.V for physical properties of carbonate systems.) On the other hand, for a PDMS-based SIP containing a 40wt% K₂CO₃ solution, \( P_s/P_l \approx 120 \), and solvent immobilisation could increase the gas flux by up to a factor of four, provided that \( \phi \approx 10 \), which corresponds to a thickness of \( \sim 150 \mu m \) for this solvent (c.f. Figure 4.5e). SIPs containing solvents with faster reaction kinetics will need to be even thinner in order to achieve significant improvements in the gas flux, especially if the internal droplet size is large enough for significant local diffusional resistance to occur. This underscores the need for further work to develop finer SIP particles and thinner SIP sheets.

### 4.3.6 Industrial Application

SIPs represent a novel approach to immobilising liquid solvents inside high surface area solids for gas separation. The primary benefit of SIPs over MECS is the scalability of their manufacturing process: they are produced via a simple one-pot method, which could be expanded to an industrial scale in a straightforward manner. The ease of manufacture could also allow for simpler screening and material development. SIPs are very versatile: they could be shaped into particles which could be placed in a fluidised bed, or thin films to coat a monolith through which flue gas could flow with minimal pressure drop. Finally, they may also exhibit improved mass transfer properties over MECS or static fluids, with substantially increased gas flux for appropriately sized materials. However this last point may prove a major limitation, as the mean gas flux into SIPs is strongly dependent on the material thickness, and very thin materials may be required ensure the entire volume of material is utilised for gas absorption in a reasonable amount of time. While SIP sheets as thin as 200 \( \mu m \) were manufactured, SIP particles were \( \sim 2 \) mm, significantly larger than MECS, and further work is required to test more sophisticated casting techniques and to develop finer SIP particles. The solvent fraction inside SIPs is also likely to be lower than inside MECS, as increasing it above 50wt% runs the risk of inducing a phase inversion in the emulsion or producing a gel with poor mechanical stability.
This in turn is likely to lead to greater sensible heat losses.

Both the SIPs and MECS motifs face a number of practical challenges. Without careful process design, the pressure drop through a bed of SIPs or MECS particles will be prohibitively large, and the time-scales for heating and cooling the bed may be greater than the time-scales for absorption and regeneration. Sensible heat recovery is likely to be less efficient and more complicated than in an amine-based process, and it is unclear at present whether either SIPs or MECS have the mechanical or chemical durability to withstand long-term process operations. Finally, any reduction in capital costs from reduced absorber volume is likely to be outweighed by increased material costs. For these reasons, it’s unlikely to be economical to immobilise solvents that are presently used in traditional columns (such as 30wt% monoethanolamine) inside SIPs or MECS [114]. It is more realistic to think of SIPs and MECS as solvent enabling technologies. Of course, this means these technologies are only as good as the solvents that can be placed inside them. If solvent immobilisation is to be applied in practice, it will be with solvents with novel thermodynamic properties. This is why the immobilisation of DMEDAH Formate - an ionic liquid that could be regenerated with waste heat alone - was attempted in this work, and similar research has been conducted demonstrating immobilisation of ionic liquids into MECS [100]. Further work is needed to identify the thermodynamically optimal solvents for these systems, and to demonstrate that they can be successfully immobilised inside stable materials. Solvent-based gas separations beyond CCS should also be considered.

4.4 Conclusion

In the sections above, a novel, high surface area gel material was proposed for carbon capture. This material, SIPs, is similar to MECS, but is produced by a more scalable method. High surface area SIP particles and sheets containing aqueous solutions of K2CO3 and the ionic liquid DMEDAH Formate were manufactured. SIPs containing K2CO3 were stable in humid air and through multiple absorption/regeneration
cycles, while the SIP containing DMEDAH Formate was not stable, losing over half of the IL it contained during a single, 24 hour absorption/regeneration run when regenerated at 60°C. Mass transfer into several SIPs containing K₂CO₃ solutions was measured, and found to be in good agreement with a volume-averaged model developed from first principles. This model was then non-dimensionalised, and it was found that the mean gas flux into SIPs may be greater than the flux into a neat liquid, but only when the SIP has an intermediate thickness. Overall, SIPs represent a promising new approach to large scale gas separations such as carbon capture. Further work is required to identify the most promising solvents and gas-solid contacting processes for the SIPs or MECS motifs, and to refine the SIPs manufacturing process, with a particular emphasis on creating particles and sheets with greater specific surface area.
Note. Section 4.5, and the various appendices it references, were originally published as supplementary materials for [105]. However, an argument can be made that the model developed here is needlessly complicated, as it asymptotically collapses to a much simpler, diffusion-limited model in most systems of practical interest. This is discussed in section 4.6, which has not been published previously.

4.5 Model Derivation

We now derive a model for mass transfer into a solvent impregnated polymer (SIP) containing a chemical solvent.

4.5.1 Assumptions

- We ignore changes in density, temperature, gas solubility and diffusivity that may occur during the absorption process.

- The diameter of solvent droplets are much less than the length scale over which macroscopic changes occur, so a continuum model is justified.

- The solvent reacts with the gas via a second order reaction - first order in both the reactive species in the solvent and in the absorbed gas.

- Interfacial mass transfer resistance at the internal polymer-liquid surfaces is ignored. Thus the concentrations of gas at the interface are related by:

\[
\frac{c_s}{S_s} = \frac{c_l}{S_l} \tag{4.10}
\]

- The solvent is perfectly trapped inside the polymer matrix, and so no solvent escapes the material or diffuses within it.

- Diffusional resistance inside the immobilised droplets is accounted for via an effectiveness factor,

\[
\xi = \frac{\phi' \coth \phi' - 1}{(\phi')^2/3} \tag{4.11}
\]
where

\[ \phi' = r_{\text{drop}} \sqrt{k_2 w/D_l} \]  

is the local Thiele modulus [226]. The rate of reaction inside a droplet is equal to the rate of reaction if the concentration profile were constant in space, multiplied by the effectiveness factor. Because diffusional resistance inside the droplets is considered significant, the concentration of gas inside the droplets is not constant in space, and inside each droplet it is less than the concentration at the surface of the droplet, \( c_l \) (see Figure 4.7c in section 4.6).

- Diffusional resistance inside the polymer is ignored, and so the concentration inside the polymer is considered constant on a local scale, and is equal to \( c_s \). This is reasonable, as the permeability in the polymer is typically much greater than the permeability in the liquid. Furthermore, local diffusional resistance in the polymer is only significant when the reaction is fast, and under these conditions the model will collapse to a moving front model which is not controlled by the local diffusional or reaction resistance (see Ho et al. [157] and section 4.6).

Figure 4.6: A thin slice of SIP, indicating coordinate choice, volume fraction definition, and direction of gas flux.
4.5.2 Mass Balance

Consider the thin linear slice of SIP shown in Figure 4.6. Assume it has unit cross-sectional area. Then the rate of change of physical or free gas molecules (e.g. unreacted CO$_2$ molecules) in this slice is:

$$\Delta x \varepsilon \frac{\partial c_s}{\partial t} + \Delta x \xi (1 - \varepsilon) \frac{\partial c_l}{\partial t}$$

(4.13)

where $\xi$ is given by Eq. (4.11) - this appears in Eq. (4.13) because the average concentration of free gas molecules inside a droplet is reduced by a factor of $\xi$ when there is local diffusional resistance. This may be simplified to:

$$\left(\varepsilon \frac{S_s}{S_l} + \xi (1 - \varepsilon)\right) \frac{\partial c_l}{\partial t} \Delta x$$

(4.14)

The net diffusive flow of free gas molecules into this slice may be approximated by:

$$D_s \varepsilon \left(-\frac{\partial c_s}{\partial x} \bigg|_{x} - \left(-\frac{\partial c_s}{\partial x} \bigg|_{x+\Delta x}\right) + D_l (1 - \varepsilon) \left(-\frac{\partial c_l}{\partial x} \bigg|_{x} - \left(-\frac{\partial c_l}{\partial x} \bigg|_{x+\Delta x}\right)\right)$$

(4.15)

which may also be simplified to:

$$\left(D_s \varepsilon \frac{S_s}{S_l} + D_l (1 - \varepsilon)\right) \left(-\frac{\partial c_l}{\partial x} \bigg|_{x} - \left(-\frac{\partial c_l}{\partial x} \bigg|_{x+\Delta x}\right)\right).$$

(4.16)

Strictly speaking, the net rate of diffusion through the liquid droplets will depend on $\xi$ in a way that is difficult to quantify, and Eq. (4.16) will be inaccurate for $\xi \ll 1$. However, it turns out that when $\xi \ll 1$, accurate quantification of the diffusive flux through the immobilised droplets is usually unnecessary, and the use of Eq. (4.16) leads to negligible error. This is discussed further in section 4.6.3.

The net rate of reaction of free gas molecules inside the slice is:

$$-k_2 \xi w c_l (1 - \varepsilon) \Delta x$$

(4.17)

where $w$ is the concentration of the reactive species inside the liquid which reacts.
with the free gas (e.g. for absorption of CO2 into an alkaline carbonate solution, \( w \) is the concentration of OH\(^-\)). This is typically a space- and time-dependent variable, and its dynamics will be discussed later in this section; for now note that the active species does not diffuse (as it is trapped inside the individual liquid droplets) and also that the relation between the rate of gas reaction and the depletion of reactive species can be complex, especially if other reactions, such as buffers, occur simultaneously. Because the droplets are microscopic, \( w \) will be assumed to be constant inside each droplet (this is equivalent to a pseudo-first order assumption inside each droplet, which at such small scales will be reasonable for all but the fastest chemical reactions.)

Combining all these terms, and dropping the subscript of \( c_l \), the mass balance gives:

\[
\left( \varepsilon \frac{S_s}{S_l} + \xi (1 - \varepsilon) \right) \frac{\partial c}{\partial t} \Delta x = \left( D_s \varepsilon \frac{S_s}{S_l} + D_l (1 - \varepsilon) \right) \left( \frac{\partial c}{\partial x} \bigg|_{x+\Delta x} - \frac{\partial c}{\partial x} \bigg|_{x} \right) - k_2 \xi wc (1 - \varepsilon) \Delta x
\]

(4.18)

Divide by \( \Delta x \) and take \( \Delta x \to 0 \), and we get

\[
\left( \varepsilon \frac{S_s}{S_l} + \xi (1 - \varepsilon) \right) \frac{\partial c}{\partial t} = \left( D_s \varepsilon \frac{S_s}{S_l} + D_l (1 - \varepsilon) \right) \nabla^2 c - k_2 \xi wc (1 - \varepsilon)
\]

(4.19)

Or, to clear up the mess,

\[
\frac{\partial c}{\partial t} = D_{\text{eff}} \nabla^2 c - \xi k_2^{\text{eff}} wc
\]

(4.20)

where

\[
D_{\text{eff}} = \frac{D_s \varepsilon \frac{S_s}{S_l} + D_l (1 - \varepsilon)}{\varepsilon \frac{S_s}{S_l} + \xi (1 - \varepsilon)}
\]

(4.21)

and

\[
k_2^{\text{eff}} = \frac{k_2 (1 - \varepsilon)}{\varepsilon \frac{S_s}{S_l} + \xi (1 - \varepsilon)}
\]

(4.22)

Now \( w \) is the concentration of reactive species, and (as this has no spatial mobility
within the material) it may be modelled by:

\[ \frac{\partial w}{\partial t} = f(c, w, \xi). \]  

(4.23)

Note that \( w \) also changes in space, so \( \partial \) is appropriate. The expression for \( f(\cdot) \) depends on the chemistry of the particular solvent. For a simple, second order chemical reaction (e.g. the reaction of CO\(_2\) with OH\(^-\) ions in an NaOH solution) \( w \) would be the concentration of OH\(^-\) ions, and \( f(c, w, \xi) \) would take the form:

\[
f(c, w, \xi) = \frac{\partial w}{\partial t} = \frac{\partial [\text{OH}^-]}{\partial t} = -k_2\xi(w) \times cw
\]

(4.24)

where \( \xi(w) \) is given by Eqs. (4.11) and (4.12), and \( k_2 \) is the second-order reaction rate constant. If local diffusional resistance in the small droplets may be ignored, \( \xi \approx 1 \) and this expression reduces to:

\[
f(c, w) = \frac{\partial w}{\partial t} = -k_2cw
\]

(4.25)

More complicated expressions need to be derived if there are other reactions present which influence the concentration of the reactive species, \( w \). An appropriate \( f(\cdot) \) for the reaction of CO\(_2\) with OH\(^-\) in a K\(_2\)CO\(_3\)-KHCO\(_3\) buffer solution, which was used in the creation of Figures 4.5b and 4.5c, is derived in Appendix 4.IV.

Overall, Eqs. (4.11), (4.12), (4.20), (4.21), (4.22) and (4.23) together describe the evolution of the concentration profile of the dissolved gas, \( c \), and the reactive species with which it reacts, \( w \), inside the SIP. Provided appropriate boundary conditions and initial conditions are provided, and provided an expression is derived (for the particular chemistry under consideration) for the rate of change of \( w \) with time, \( f(\cdot) \), these equations may be numerically integrated to predict the rate of uptake of gas into a SIP. In order to create Figures 4.5b and 4.5c above, these equations were numerically integrated, using the function \( f(\cdot) \) derived in Appendix 4.IV, and the physical parameters for carbonate solutions and PDMS discussed in Appendix 4.V.
Appendix 4.II, an efficient method-of-lines discretisation for these pde’s is described, and details of the integration method are provided. In Appendix 4.III, these PDE’s are non-dimensionalised, and the mean gas flux into a SIP is compared with the mean gas flux into a neat liquid with the same capacity, in order to produce the phase diagram shown in Figure 4.5d above. Each of these appendices are presented as-is from the supplementary information of [105].

4.6 A Simplified, Diffusion-Controlled Model

4.6.1 Classification of Microscopic Absorption Regimes

In section 4.5, a coupled set of partial differential equations was derived and used to model absorption into a SIP. This model was derived from first principles, and provided a good fit for several experimentally-measured uptake curves. However, it is quite computationally expensive, especially for solvents with very fast reactions, for which the moving reaction zone (see Figure 4.5a) is very thin, and a very fine spatial discretisation is required to accurately model the system. Fortunately, with a little thought about the physical processes occurring within a SIP material, it is possible to show that this complex model collapses to a much simpler, diffusion-controlled model in many situations of practical interest.19

In Figure 4.7, the microscopic concentration profile inside a single, immobilised droplet and the surrounding polymer are shown for three possible absorption regimes.20

Figure 4.7(a) shows the simplest case, regime 1, in which the concentration profiles are both locally constant, and local diffusional resistance is negligible in both phases. This corresponds to the case of $\xi \approx 1$ in section 4.5, and the model developed in that section should be accurate for this regime.

Figure 4.7(c) shows regime 3, in which there is significant diffusional resistance

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19I am indebted to Prof. Hatton at MIT for several of the insights that follow. I probably could have reached the same conclusions if I had more closely heeded the eternal wisdom of my supervisors. Never again shall I forbear from making a log-log plot.

20A fourth regime, in which local diffusional resistance is significant in the polymer but not the liquid, will only occur if $\mathcal{P}_s/\mathcal{P}_l \ll 1$, and it’s unlikely that a SIP with this property would be manufactured.
in the immobilised liquid, but not in the surrounding polymer. This was also modelled in section 4.5. For such systems, the local rate of reaction is reduced by the diffusional resistance in the spherical droplet, and this may be accounted for via a local effectiveness factor, $\xi$, given by Eqs. (4.11) and (4.12). Because there is no diffusional resistance within the polymer, no extra ‘effectiveness factor’ is required to account for diffusional resistance external to the spherical droplet, which is fortunate because the geometry of the polymer is much more complicated than the geometry of the liquid droplet. The model developed in section 4.5 should also be valid for this regime, with the following caveat. In developing this model, it was assumed that the diffusive flux through the spherical droplets was proportional to the local gradient of $c_l$ - the concentration at the droplet’s surface (see Eq. (4.16)). This will not always be true, as the reaction inside the droplets can influence the net rate at which gas molecules diffuse through them (i.e. the diffusion and reaction processes are not linearly independent, and cannot in general be decoupled via some kind of ‘superposition principle’). Fortunately, the situations in which the use of Eq. (4.16) will lead to significant errors are quite extreme edge cases, and are discussed in section 4.6.3. For almost all systems, the model developed in the previous sections will also accurately model systems within regime 3.

For very fast chemical reactions, there may be large local concentration gradients in both the immobilised droplets and also the surrounding polymer, and we refer to this as regime 2 (Figure 4.7b). No simple ‘effectiveness factor’ can be derived...
for the effect of diffusional resistance in the external polymer phase, because the geometry is too complicated. Instead, modelling such systems accurately would in principle require a computationally intensive, non-local multi-scale model. In practice, however, this is unnecessary, for the following reason. If the reaction rate is fast enough for there to be significant concentration gradients in both the liquid solvent and the solid polymer at the local, microscopic level, then at the macroscopic level the reaction will be so fast as to appear instantaneous. Under these conditions, it is not necessary to accurately model the complex concentration profiles within the spheres and the polymer, because these processes are not rate controlling. Instead, the ‘reaction zone’ of Figure 4.5a collapses to an infinitesimally thin moving ‘reaction front’, and diffusion of gas to this reaction front controls the rate of absorption. In this case, a simple shrinking core or moving front model is appropriate.

The existence of large concentration gradients in both phases was emphasised in the previous paragraph. If the local concentration gradients are large in the liquid but small in the solid (as may occur for systems with $P_s/P_l \gg 1$, Figure 4.7c) then a moving reaction front model may be inaccurate, as the large permeability of the solid phase may ‘smear’ out the reaction zone over a large region of space.

In summary, SIPs may operate within three different absorption regimes:

Regime 1. $\phi' \ll 1$: No local diffusional resistance. The concentration profile is locally constant in both phases (see Figure 4.7a.) The model described previously is accurate, and $\xi = 1$.

Regime 2. $\phi' \geq 1$, $P_s/P_l \gg 1$. Local diffusional resistance in both phases (see Figure 4.7b.) Will approximate instantaneous reaction on the macroscopic level.

Regime 3. $\phi' \geq 1$, $P_s/P_l \gg 1$. Local diffusional resistance in liquid droplets only (see Figure 4.7c.) May not approximate instantaneous reaction on the macroscopic level, but the model developed previously will accurately predict the rate of absorption in most cases (see section 4.6.3).
4.6.2 A Diffusion-Controlled Moving Front Model

The model developed in section 4.5 is expected to be valid for regimes 1 and regime 3, as these are the regimes for which it was derived. At first glance, regime 2 appears more difficult to model, as the local diffusional resistance in the polymer will be quite complex, and it was not accounted for in the model developed in section 4.5. However, as was observed above, on a macroscopic scale the reaction will be effectively instantaneous for the parameters for which regime 2 is valid ($\phi' \geq 1$, $P_s/P_l \gg 1$), and the system may be accurately modelled as diffusion with instantaneous reaction, with mass transfer resistance dominated by diffusional resistance through the saturated zone (see Ho et al. [157], who made precisely this assumption on intuitive grounds when modelling a liquid emulsion membrane.) Furthermore, the model described in section 4.5 would also be expected to collapse to diffusion with instantaneous reaction under these conditions, as for very fast reactions it will also predict a very narrow reaction zone. If this were the case, the model developed previously would in fact be accurate for all 3 regimes considered above. It wouldn’t matter that it doesn’t account for local diffusional resistance in the polymer phase, because such resistance would only occur precisely when such local resistances are not rate controlling (instead, macroscopic diffusion to a thin reaction zone would be controlling, and the model would correctly capture this process.)

In this section, we quantify these intuitive ideas by developing a simple moving-front model\(^\text{21}\) for regime 2, and show that it asymptotes to the more complex model developed in section 4.5 in the appropriate limits (in fact, provided there is reasonable separation of the microscopic and macroscopic scales, this collapse occurs in systems in which the local reaction rate is not that fast, and whose local concentration profiles qualitatively look more like those of regime 3.) We will also show that this simpler model will be accurate for a wide range of physically-relevant systems.

Consider a SIP with linear geometry, containing a solvent which reacts very quickly with the absorbed gas, such that the ‘reaction zone’ of Figure 4.5a collapses

\(^{21}\)Of a similar form to that proposed by Ho et al. [157].
to a thin ‘reaction front’ (see Figure 4.8), whose movement is controlled by the rate
at which gas can diffuse through the saturated zone trailing behind it. Suppose that
the partial pressure of the gas is constant. Then the velocity of the front is given
by:
\[
\frac{dz}{dt} = \frac{\text{Flux at Reaction Front}}{\text{Capacity of Material}} = -\left. \frac{\partial c}{\partial z} \right|_{z'=z} \left( \frac{(1-\varepsilon)P_l + \varepsilon P_s}{S_l} \right) \frac{1}{(1 - \varepsilon)(N + c^*) + \varepsilon S_s c^*}
\]
(4.26)

where \(N\) is the volumetric chemical capacity of the liquid solvent at the gas partial
pressure. Under many circumstances (and especially for SIPs containing a concentra-
ted chemical solvent), the moving front will move slow enough to be treated as
quasi-static (see Ho et al. [157]), in which case the flux through the saturated zone
is constant at each point in space, and the concentration profile is linear (see Figure
4.8), giving:

\[
\frac{dz}{dt} = \frac{c^*}{z S_l(N + c^*)(1 - \varepsilon) + \varepsilon S_s c^*}((1 - \varepsilon)P_l + \varepsilon P_s) \equiv \frac{1}{z N_{\text{SIP}}} \left( \frac{p^*}{(1 - \varepsilon)P_l + \varepsilon P_s} \right)
\]
(4.27)

where \(N_{\text{SIP}}\) is the overal volumetric capacity of the SIP and \(p^*\) is the gas partial
pressure at the surface. This may be integrated from \(z = 0\) at \(t = 0\) to give:

\[
z = \sqrt{\frac{2}{N_{\text{SIP}}} \left( \frac{p^*}{(1 - \varepsilon)P_l + \varepsilon P_s} \right) t}
\]
(4.28)

If the total thickness of the SIP is \(L_{\text{SIP}}\), then the fractional uptake of the SIP (i.e.
the moles of gas absorbed divided by the moles of gas which will be absorbed at
\(t = \infty\)) is given by:

\[
\gamma \equiv \frac{z}{L_{\text{SIP}}} = \sqrt{\frac{2}{N_{\text{SIP}} L_{\text{SIP}}^2} \left( \frac{p^*}{(1 - \varepsilon)P_l + \varepsilon P_s} \right) t}
\]
(4.29)

Or, more simply,

\[
\gamma = \sqrt{C_1 t}
\]
(4.30)

where

\[
C_1 = \frac{2}{N_{\text{SIP}} L_{\text{SIP}}^2} \left( \frac{p^*}{(1 - \varepsilon)P_l + \varepsilon P_s} \right)
\]
(4.31)
Figure 4.8: Diagram of concentration profile, $c(t,z)$, inside a diffusion-controlled SIP, in which the ‘reaction zone’ of Figure 4.5a has collapsed to a infinitesimally thin moving reaction front. In a linear geometry with a quasi-static moving front, the concentration profile in the saturated zone will be linear.

Similarly simple equations may be derived for spherical SIP particles.

Clearly, using Eqs. (4.30) and (4.31) would be much simpler than solving the set of PDE’s derived in section 4.5. It’s important to understand exactly when this model is valid, and under what circumstances the complex model developed previously collapses to this simple expression.

In order to answer these questions, the simple model described by Eqs. (4.30) and (4.31) was non-dimensionalised, and compared with a dimensionless form of the model developed in section 4.5 (see Appendix 4.VI). In particular, the dimensionless time, $t k_2 c^*$, to reach 80% saturation was calculated for each model; their predictions are compared in Figure 4.9. The relevant dimensionless groups were $P_s/P_l$, $\phi'$, $L_{\text{SIP}}/r_{\text{droplet}}$ and $\varepsilon$. The voidage is held constant at $\varepsilon = 0.5$, and lines of constant $P_s/P_l$ and $L_{\text{SIP}}/r_{\text{droplet}}$ are plotted for various values of $\phi'$. Note that $\phi'$ is defined by Eq. (4.12). For these calculations, a simple second-order irreversible reaction was assumed, and so $f(\cdot)$ was of the same form as in Eq. (4.24).

As expected, the models converge at large $\phi'$, at which point the reaction rate is effectively instantaneous, and the local concentration profiles would be expected to
be of the form shown in Figure 4.7b. $L_{\text{SIP}}/r_{\text{droplet}}$ is the ratio between the macro-
scopic and microscopic length scales: a realistic value of 100 is plotted, along with
values of 10 and 1000. In Figure 4.9b, the local concentration profile inside a SIP
droplet and the surrounding polymer are plotted at four different conditions shown
in Figure 4.9a. These were chosen because they are all points at which the two
models begin to diverge. It is clear that at each of these points the local concen-
tration profile in the polymer phase is relatively flat: $\partial \bar{c}/\partial \bar{r} < 0.1$ in each case.\textsuperscript{22}

Hence, at the points where the two models diverge, the system will be in regime 3,
and the model described in section 4.5 (which does not account for concentration
gradients in the polymer) would be expected to be accurate at each of these points.

For smaller values of $\phi'$ (i.e. for values to the left of these points, at which the two
models diverge) the concentration gradients in the polymer will be even smaller, and
the more sophisticated model of section 4.5 should remain accurate. However, the
simple model given by Eqs. (4.30) – (4.31) will not be accurate for these systems;
instead, the reaction zone will be of a finite width, and absorption will not be con-
trolled by diffusion through the saturated zone alone. On the other hand, for values
of $\phi'$ to the right of the marked points, the two models give identical predictions,
and the behaviour of the system will approximate diffusion with instantaneous reaction.\textsuperscript{23} Under these conditions local concentration gradients in the polymer will not
be rate controlling (instead, diffusion of gas to the narrow reaction front will be rate

\textsuperscript{22}$\partial \bar{c}/\partial \bar{r}$ is a dimensionless spatial derivative in the polymer at the polymer/droplet boundary.
It represents the fractional change in the concentration of gas in the polymer which would occur
over a distance equal to the radius of the droplet. $\partial \bar{c}/\partial \bar{r} \ll 1$ implies the concentration is approxi-
mately constant on the individual droplet scale. See Appendix 4.VII for details on the calculation
methodology.

\textsuperscript{23}It may be objected that just because the PDE-based model collapses to the simpler, moving
front model doesn’t mean that the system itself will behave this way: the PDE-based model ignores
local diffusional resistance in the polymer, after all, and if this were accounted for absorption into
the droplets would be slower, and may not be fast enough for the system to collapse to the moving
front (or ‘instantaneous reaction’) case. However, the fact that the values of $\partial \bar{c}/\partial \bar{r}$ in Figure 4.9b
are so small implies that even if the model were to account for local diffusional resistance in the
solid, the local absorption rate would not change significantly. Hence the real system will transition
to the instantaneous reaction regime at approximately the same points in Figure 4.9a, and both
the PDE-based model and the simple model given by Eqs. (4.30) – (4.31) will be approximately
accurate at these points. Of course, this argument will not hold for $L_{\text{SIP}}/r < 10$ and $P_s/P_t \gg 1$, for
which the $\partial \bar{c}/\partial \bar{r}$ are likely to be larger (note the trend in Figure 4.9b), but this is to be expected,
as for such systems the internal droplets will be of comparable size to the material itself, and a
composite model would not be expected to be accurate.
Figure 4.9: (a) Comparison of times to reach 80% saturation according to a moving front model, as described by Eq. (4.30) – (4.31) (dotted lines) and a model which accounts for a finite reaction rate, as described in section 4.5 (solid lines.) Various lines of constant $P_s/P_l$ and constant $L_{SP}/r_{droplet}$ are plotted. $\varepsilon = 0.5$. (b) Microscopic concentration profiles in a droplet and the surrounding solid are shown for 4 representative points, labelled $i$ – $iv$. Dimensionless concentration gradients, $\partial \bar{c}/\partial \bar{r}$, at the surface of the droplet in the external phase are also given. See Appendix 4.VII for the calculation methodology. i) $P_s/P_l = 5$, $\phi' = 0.15$. ii) $P_s/P_l = 100$, $\phi' = 0.7$. iii) $P_s/P_l = 20$, $\phi' = 2$. iv) $P_s/P_l = 100$, $\phi' = 7$. 

controlling) and the PDE-based model will be accurate, even though it doesn’t explicitly account for local diffusional resistance in the polymer. Hence the PDE-based model could be expected to be accurate for all conditions shown, which encompasses the full range of parameters likely to occur in practice.

The simpler, moving-front model, on the other hand, will only be accurate when the more sophisticated model collapses onto it. But as shown in Figure 4.9a, this will occur for a very wide range of systems. In particular, it is clear that, over a very wide range of parameters, for an irreversible second-order reaction the sophisticated PDE-based model collapses to the moving front model when the time to achieve 80% saturation exceeds around $10/k_2c^*$. This is a surprisingly small amount of time, as the time for the reaction to occur with no diffusional resistance at all is equal to $-\ln(1 - 0.8)/k_2c^* \approx 1.6/k_2c^*$, which the various solid curves in Figure 4.9a converge to at very low reaction rates. Diffusional resistance in most reactive solid or liquid systems will usually slow down the average absorption rate by much more than a
factor of $10/1.6 \approx 6$. It seems likely that the moving front model will be valid for the large majority of SIPs, only excepting those which are very thin, which have very slow intrinsic reaction kinetics (e.g. slow precipitation reactions), or which have very high permeabilities within the PDMS.

The simple, diffusion controlled model would be expected to collapse to the more complex, PDE-based model for the K$_2$CO$_3$ based systems investigated in Figure 4.5. As shown in Figures 4.10 and 4.11, this is indeed the case, as the uptake curves predicted by Eqs. (4.30) and (4.31) closely follow the more complex PDE model described previously. The slight discrepancy between the two models suggests that reaction resistance has a small influence on the absorption rate at high loadings, which is unsurprising given the very slow kinetics of K$_2$CO$_3$ solutions at high CO$_2$ loadings. The only parameters required for Eq. (4.30) and (4.31) were the permeabilities of the polymer and carbonate solution, and the chemical capacity, thickness and polymer volume fraction of the SIP, each of which were known from the more complex simulation described in section 4.5. Numerical values are provided in Table 4.1. From these values, $C_1$ was calculated via (4.31), and from this the change in overall conversion, $\gamma$, with time may be calculated from Eq. (4.30). $\gamma(t)$ was then
Figure 4.11: Comparison between PDE-based model and diffusion limited model for absorption into SIP containing 10wt% K₂CO₃. Conditions identical to those in Figure 4.5c.

Table 4.1: Numerical parameters required for the curves plotted in Figures 4.10 and 4.11 multiplied by the equilibrium absorption capacity of the PDE-based models in order to create the curves in Figures 4.10 and 4.11.

<table>
<thead>
<tr>
<th></th>
<th>( P_s ) (mol s(^{-1}) m(^{-1}) Pa(^{-1}))</th>
<th>( P_l ) (mol s(^{-1}) m(^{-1}) Pa(^{-1}))</th>
<th>( N_{\text{SIP}} ) (mol m(^{-3}))</th>
<th>( L_{\text{SIP}} ) (mm)</th>
<th>( \varepsilon )</th>
<th>( P' ) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3wt% K₂CO₃</td>
<td>( 7.6 \times 10^{-13} )</td>
<td>( 5.1 \times 10^{-13} )</td>
<td>92</td>
<td>2.13</td>
<td>0.5</td>
<td>38.2</td>
</tr>
<tr>
<td>10wt% K₂CO₃</td>
<td>( 7.6 \times 10^{-13} )</td>
<td>( 2.0 \times 10^{-13} )</td>
<td>312</td>
<td>0.93</td>
<td>0.5</td>
<td>54.7</td>
</tr>
</tbody>
</table>

Overall, the very simple diffusion-limited model given by Eq. (4.30) and (4.31) provides a very reasonable prediction for the average rate of absorption into these SIPs. In section 4.7, this simple model will be used to accurately predict the flux into a SIP containing a solvent (a Nanoparticle Organic Hybrid Material, or NOHM) whose physical and chemical properties are almost completely unknown. For this SIP, the construction of a more detailed model would be impossible.

4.6.3 On the Accuracy of the Model for Regime 3.

The model derived in section 4.5 should be completely accurate for regime 1 (for which \( \xi \approx 1 \)) and will collapse to a moving-front model valid for regime 2 when only a small amount diffusional resistance is present. These regimes will cover the large
majority of physically-relevant systems. Nevertheless, the validity of the model for regime 3 is a little harder to discern, and we discuss it here for the sake of completeness.

First, it must be emphasised that systems in regime 3 will not necessarily have moving-front behaviour, as the very large permeability of the polymer phase may ‘smear’ out the reaction zone (see Figure 4.5a) over a large region of space. Hence, in general, a more complex, PDE-based model will be necessary.

The model derived in section 4.5 was designed to be valid for regime 3. In particular, the reduction in the local reaction rate due to local diffusional resistance in the spherical droplets was accounted for via an effectiveness factor, $\xi$. However, a few concerns could reasonably be raised about the mass balance.

Most notably, diffusional flux of gas through the immobilised liquid droplets was assumed to be of the form (see Eq. (4.16)):

$$ J = -\frac{\partial c_l}{\partial x} D_l $$

where $c_l$ is the concentration at the droplet surface, which is greater than the concentration in the droplet bulk because of the local diffusional resistance (see Figure 4.7). It is worth considering what is physically happening inside the material. Each microscopic immobilised droplet inside a SIP is sitting within an environment in which there is a ‘background’ concentration gradient, which is driving the gas into the SIP. During absorption, the concentration of physically dissolved gas on one side of a droplet will be slightly larger than on the other side, and this will result in a net flux through the droplet. Because the droplets are microscopic, the actual difference between the concentration on each side will be extremely small - perhaps on one side $c_l$ will be 1% greater than on the other. But, again because the droplets are so small, this may correspond to a significant concentration gradient at the macroscopic scale.

The question then becomes - how does the presence of a chemical reaction affect the flux through a microscopic droplet with slightly different concentrations on each boundary? When the profile inside the droplet is approximately linear ($\xi \approx 1$, see
Figure 4.7a) the flux will just be given by Eq. (4.32). But if a fast chemical reaction occurs so that $\xi < 1$, the difference in the flux on each side of the droplet may change, and in general, for the same asymmetric boundary conditions, the difference in flux on each side will be greater the faster the chemical reaction.

It may be possible to model these effects accurately, and to account for the role of the reaction in enhancing the net diffusive flux through the liquid phase, but the author was unable to derive a closed-form expression for the case of a 3-dimensional spherical droplet. However, this is not a serious concern. Consider the following scenarios:

1. The permeability of the polymer phase is much larger than the permeability of the immobilised droplets.

2. Mass transfer in the SIP is controlled by diffusion through the saturated zone.

Both of these are likely to occur in practice. Point 1 is one of the motivational ideas behind the SIP motif: by immobilising liquids inside high-permeability polymers, we can potentially increase the gas flux. Indeed, because of the formation of the saturated zone, if point 1 does not hold, the flux into the SIP will likely be significant smaller than the flux into a neat liquid. Point 2 is also likely to occur for the large majority of SIPs.

Provided either one of these points is valid, then any inaccuracies that follow as a consequence of ignoring the effect of chemical reaction on the net flux through the immobilised liquid droplets will be negligible. For point 1, this is because the exact value of the flux inside the droplets is irrelevant, as diffusion will be dominated by diffusion through the polymer phase. For point 2, Eq. (4.16) will be reasonable, as $\xi \approx 1$ in the saturated zone (as the droplets are depleted and little reaction occurs) and this is what will control the absorption rate. Hence, for most practical SIPs, Eq. (4.16) should be reasonable.

Indeed, an even stronger argument can be made. If point 1 is false (so $P_s \approx P_l$) then the SIP will either fall into regime 1 (in which case the model in section 4.5
will be valid) or regime 2 (in which case, provided there is reasonable separation of length scales, diffusion through the saturated zone dominates, and again the model is valid.) In either case, Eq. (4.16) should be reasonable. On the other hand, if point 1 is true, then, as argued above, accurately modelling the permeability through the immobilised liquid is irrelevant, as it is much smaller than the permeability through the polymer.

We would have liked to have made these intuitive arguments more rigorous, by developing a more detailed model, which accounts for the interplay between reaction rate and the net diffusive flux through the reactive immobilised droplets, and comparing this with the simpler model. However, as noted above, this proved mathematically difficult. Nevertheless, it seems very likely that the simple expression for the flux through the immobilised liquid droplets will be sufficient for the large majority of cases. The only conceivable systems in which it might be slightly erroneous are those with moderately greater permeabilities in the polymer (maybe $P_s = 5P_l$) and moderately fast reaction (maybe $\xi \approx 0.5$). Even here, it seems unlikely that significant errors would be introduced.
4.7 Immobilisation of NOHMs

Note. The SIPs discussed in this section were first synthesised while the author was visiting the group of Dr. Alissa Park at Columbia University, using materials and equipment supplied by them, and using NOHMs they had previously synthesised. The mass transfer data in Figure 4.13 was later measured by Guanhe Rim, and is included here by permission.

4.7.1 Nanoparticle Organic Hybrid Materials for CCS

Nanoparticle organic hybrid materials (NOHMs) are a novel, tunable solvent for CCS and direct air capture (DAC) [228, 229]. NOHMs are manufactured by ionically or covalently grafting functionalised polymer chains onto a surface-modified inorganic nanoparticle. In pure form (i.e. when not dissolved in a solvent such as water), these materials may be solids or viscous liquids, depending on the nanoparticles and polymer chains used. They have negligible vapor pressure (likely even lower than ionic liquids, which usually have some finite vapor pressure [230]) and by selecting polymer chains such as polyethylene amine (PEI) which react with CO2, they may exhibit excellent CO2 capacities, often exceeding 6 mol kg$^{-1}$, or 20 wt% (see Figure 4.13 below.) They may also prove simpler to tune than ionic liquids, as the functional groups responsible for carbon capture are relatively independent of the groups responsible for the grafting of the chain onto the nanoparticles. If NOHMs can be manufactured with sufficiently large enthalpies of absorption (to ensure a large pressure swing with temperature) balanced by appropriate entropies of absorption (to ensure reversible absorption at practical partial pressures) they may also prove useful for direct air capture (see Chapter 5 for a more complete discussion of these thermodynamic ideas.) Unfortunately, at present NOHMs have impractically slow sorption kinetics. It appears that this is caused primarily by severe diffusion resistance related to their high viscosity, as the intrinsic kinetics of the reaction of CO2 with the PEI chains should be very fast.\textsuperscript{24} NOHMs are also very viscous when used

\textsuperscript{24}There also appears to be some other, more complicated surface or autocatalytic effects which are not fully understood: these are discussed below.
in their pure form. In an attempt to overcome these limitations, microencapsulation of NOHMs inside high surface area MECS was recently demonstrated [108]. The MECS were created using a diluted NOHM/water mixture, and the water was then evaporated, leaving deformed MECS containing pure NOHMs. MECS containing NOHMs exhibited specific absorption rates approximately 10 times faster than neat NOHM liquids; this was attributed to the increase in specific surface area.

As noted in the literature review (Chapter 2), it seems increasingly unlikely that novel solvents such as NOHMs will be able to significantly outperform advanced amine processes, at least when regenerated at high temperatures using steam (see Chapter 5 for a more complete discussion of these ideas.) However, the tunability of NOHMs suggests they may be a plausible candidate for low-temperature regeneration and for direct air capture if handling and mass transfer issues can be overcome. Furthermore, the advantages of NOHMs (low vapor pressure and tunability) and also their disadvantages (severely diffusion-limited mass transfer and high viscosity) are perfectly suited to the SIP motif, which could be used to increase the specific surface area, and would also be expected to increase the gas flux under many circumstances, as the PDMS will significantly decrease the diffusional resistance. In this section, the immobilisation of a PEI-based NOHM is demonstrated, and mass transfer into the material is measured and modelled.

4.7.2 Experimental Methods

NOHMs containing a silica nanoparticle on which PEI chains were grafted (NOHM-PEI) were synthesised according to the methods described in [229]. The NOHM-PEI was diluted in 50wt% water; in this form it existed as a viscous, non-Newtonian fluid. This solution was then dispersed as a 50wt% emulsion inside the UV-curable PDMS Tegorad 2650 sourced from Evonik, using the shear-emulsification methodology described in section 4.2. Tegorad 2650 has emerged as a promising shell material in the MECS literature due to its high CO2 permeability and short crosslinking times [107]. No surfactants were required to stabilise the emulsion. The emulsion was
then dried in a vacuum for several hours to allow the water to evaporate, leaving an emulsion containing roughly 33wt% NOHM-PEI dispersed in 66wt% PDMS. This emulsion was then crosslinked in an oxygen-free environment under UV light, creating a solid SIP gel. Crosslinking occurred within \(~10\) seconds.

Mass transfer measurements were conducted on a 1 mm thin piece of SIP containing 33wt% NOHM-PEI and 66wt% Tegorad 2650 using a Thermogravimetric Analyser (TGA). The SIP was dried in a pure N\(_2\) at 1 atm to remove any residual water. Once the mass had stabilised the SIP was exposed to pure CO\(_2\) at 1 atm. The uptake of CO\(_2\) was measured gravimetrically over time. The TGA was also used to measure the uptake rate into a neat NOHM-PEI film which was 1.5 mm thick, and had the same surface area as the SIP sample.

4.7.3 Results

A photograph of a SIP material containing 33wt% NOHM-PEI shaped into a thin film is shown in Figure 4.12. One of the advantages of the SIP motif is the ease with which it can be applied to novel solvents, and the immobilisation of NOHMs is a good example of this in practice. The manufacture of the material was straightforward, and very little trial-and-error was required to create a stable material. However, the creation of a stable SIP containing 50wt% NOHM-PEI has proved more difficult, and work is ongoing to find appropriate stabilising agents.

Physically, the material was similar to the SIPs described in section 4.1 – 4.4, with the notable difference that it was not sticky. It is unclear whether this was caused by the PDMS used or the lack of water in the system. This is encouraging for direct air capture applications, as the accumulation of dust during passive absorption of CO\(_2\) is a major challenge for such systems [231]. Fluidisation of fine particles of this particular SIP is also likely to be simpler than fluidisation of the stickier SIPs discussed in section 4.1 – 4.4 or of fine MECS.

In Figure 4.13, the uptake of CO\(_2\) into a 1 mm SIP sheet containing 33wt% NOHM-PEI is compared with the uptake into a 1.5 mm layer of pure NOHM-PEI.
liquid with the same surface area. The two curves were both normalised by the mass of the SIP (i.e. the moles of CO₂ absorbed was, in each case, divided by the same number: the mass of the SIP) so the relative shape of the two curves is exactly the same as for a plot of the total moles absorbed into each material over time. The rate of absorption into the SIP was about 50 times greater than into the neat liquid (1.8 mol kg⁻¹ in 2 hours, compared to 0.09 mol kg⁻¹ in 5 hours.)

4.7.4 Discussion

Even though mass transfer into NOHMs is poorly understood, mass transfer into a SIP containing NOHMs is quite straightforward to model. This is because, as with most SIPs, mass transfer is likely to fall into the diffusion-limited regime discussed in section 4.6. Furthermore, because the CO₂ permeability of the NOHMs is likely to be at least 2 orders of magnitude less than in the PDMS [232], diffusive mass transfer through the NOHMs in the saturated zone can be ignored, and only the permeability of the Tegorad 2650 is required. The chemical capacity of the material can be inferred from the equilibrium loading of the SIP. With this information, $C_1$ may be calculated (see section 4.6) via:

$$C_1 = 2 \frac{p^*}{N_{SIP} L_{SIP}^2} \frac{(1 - \varepsilon)P_1 + \varepsilon P_s}{P_s}$$ (4.33)
Figure 4.13: Experimentally measured gas uptake curves into a 1 mm layer of SIP containing 33wt% NOHM-PEI and 66wt% Tegorad 2650, and a neat 1.5 mm layer of NOHM-PEI. Each material had identical surface area, and to create each curve the total moles of CO$_2$ absorbed was divided by the mass of the SIP. Because the SIP contained 33wt% NOHM-PEI, the total capacity of the NOHM-PEI itself was approximately 6 mol kg$^{-1}$. Data collected by Guanhe Rim; used by permission.

and the conversion may be then be calculated via:

$$\gamma = \sqrt{C_1 t}$$  \hspace{1cm} (4.34)

For this particular system, the most accurate available estimates for the parameters are$^{25}$

- $p^* = 1$ bar
- $P_s = 1.1 \times 10^{-12}$ mol m$^{-1}$ Pa$^{-1}$ s$^{-1}$ [107]
- $\varepsilon = 0.72$
- $N = 2175$ mol m$^{-3}$ SIP
- $L_{SIP} = 1$ mm

$^{25}$These estimates are based on a measured NOHM density of 1273 kg m$^{-3}$, a PDMS density of 965 kg m$^{-3}$ and a total CO$_2$ capacity of 2 mol kg$^{-1}$ SIP.
Figure 4.14: Model predictions for the degree of saturation of SIP containing 33wt% NOHM-PEI, plotted against experimental uptake data collected by Guanhe Rim. ‘Simple Model’ refers to the parameters calculated above, with $C_1 = 7.52 \times 10^{-5} \text{s}^{-1}$. ‘Best Fit’ refers to the parameters determined by the line of best fit, corresponding to a lag time of 17 minutes and a SIP thickness of 0.72 mm.

Assuming single-sided absorption into the SIP sheet, this gives $C_1 = 7.52 \times 10^{-5} \text{s}^{-1}$, which may be substituted into Eq. (4.34) to calculate the conversion.

The model’s predictions for this value of $C_1$ are plotted as the ‘Simple Model’ alongside the experimental mass transfer data in Figure 4.14. The diffusion-limited model provides a reasonably accurate prediction for the rate of uptake into the SIP, even though almost no information about the immobilised NOHM was available.

The very slow initial absorption in the experimental data is related to known autocatalytic effects within PEI systems, and is even clearer in the uptake curve into the pure NOHM-PEI shown in Figure 4.13; this will be discussed below. The difference between the data and the simple model near the end of the run may be caused by double-sided absorption into the material, which is probably unavoidable when a solid sample is exposed to a pure gas, even if it is placed on a flat surface. It may also be the result of experimental uncertainty, as relatively small changes in the parameters listed above can significantly change the model’s predictions. Cer-
tainly, the relatively abrupt decrease in gas flux at around 2 hours is indicative of a diffusion-limited, moving front model; this occurs in a linear geometry when the thin moving front ‘collides’ with the bottom of the material and absorption abruptly finishes.

Because of the lag introduced by the autocatalytic reaction effects, the above model was modified to the form:

\[ \gamma = \sqrt{C_1(t - t_0)} \]  

(4.35)

where \( t_0 \) was a lag-time introduced to account for the slow initial reaction rate. The parameters \( C_1 \) and \( t_0 \) were fit to the experimental uptake curve by creating a plot of \( \gamma \) vs \( \sqrt{t - t_0} \), and selecting a value of \( t_0 \) for which the linear region of the plot passed through the origin (see Figure 4.15). Incidentally, the linear behaviour of this plot is strong evidence of diffusion-limited mass transfer throughout the majority of the absorption run. The best fit, which is shown in Figure 4.14 as the ‘Best Fit’ line, provides a very good prediction from around 10% to around 90% conversion. It corresponds to a lag time of \( t_0 = 17 \text{ min} \) and, a SIP thickness of 0.72 mm using the physical parameters listed in the dot points at the start of this section. This thickness is not much smaller than the actual value (around 1 mm), and the deviation may simply be a result of the uncertainty in the various terms that contribute to \( C_1 \).

Alternatively, the smaller predicted value of \( L_{SIP} \) may reflect a degree of double-sided absorption within the system. Overall, with very little data on the SIP material, the diffusion-controlled model was able to predict the absorption rate to within a reasonable accuracy. Further details on the complicated reaction kinetics inside the SIPs would be required before a more accurate model could be built.

The observed 50-fold increase in the gas flux is substantially greater than the increase that had previously been predicted for SIP materials (see Figure 4.5d, in which a 2-5 fold increase in the flux was predicted). This is obviously a very encouraging result, however it begs the question of exactly how such a large increase in the flux could occur. The permeability of the NOHM is much lower than the
Figure 4.15: Experimentally measured values of $\gamma$ vs $\sqrt{t - t_0}$ for uptake of CO2 into SIP containing 33wt\% NOHM-PEI. Delay of $t_0 = 17$ min introduced to account for region of very slow reaction at the start of the uptake curve. $t_0$ was selected to ensure the line of best fit through the linear region passed through the origin. Slope of line of best fit = $1/\sqrt{C_1} = 1.4\, \text{h}^{1/2}$, corresponding to $C_1 = 1.42 \times 10^{-4}\, \text{s}^{-1}$, which is roughly double the value estimated from the available data, and would correspond to a 0.72 mm SIP, all other parameters held constant.
permeability of the PDMS, but a reasonable estimate, based on experiments by [232], is that $P_s/P_l \approx 100$, which is within the bounds of the predictions of Figure 4.5d.

The very large increase in the gas flux is probably due to the relatively low mobility of the polymer chains inside the NOHM. The model on which Figure 4.5d was based compared SIPs to a neat solvent in the pseudo-first order regime, so that depleted solvent was free to diffuse to the bulk and fresh solvent to the surface. Absorption into NOHMs, on the other hand, is likely to look much more like absorption into SIPs. Because the polymer chains have relatively little mobility, a saturated zone is likely to form near the material surface, and propagate into the material over time. Hence the ‘tradeoff’ that was talked about in section 4.3 is not relevant here, as both the SIP and the neat liquid will have reduced flux due to the formation of a saturated zone. The diffusion-limited model suggests that the increase in the mean gas flux into the SIP will be proportional to $\sqrt{P_s/P_l}$. This will be on the order of 1 – 2 orders of magnitude for this system, which is consistent with the observed increase in the flux. Somewhat counterintuitively, a NOHM may be thought of as existing in the diffusion with instantaneous reaction regime [15], which is more typically used to model very fast processes such as the absorption of CO2 into NaOH. In this regime, a saturated zone forms at the surface and propagates into the material, just as occurs in a SIP. Because a saturated zone is present in both the neat liquid and the SIP, the SIP motif could be expected to lead to increases in the gas flux by a factor on the order of $\sqrt{P_s/P_l}$ when such solvents are immobilised, which is much greater than the increase in flux shown in Figure 4.5d when immobilising solvents in the pseudo-first order regime. The immobilisation of other viscous solvents which absorb gas slowly yet exist within the instantaneous reaction regime should be pursued further.

A second explanation lies in the initial region of the uptake curves shown in Figure 4.13. In both neat NOHMs and SIPs containing NOHMs, the initial uptake rate is very slow, and for the pure NOHM in Figure 4.13, absorption only really
begins after an hour of exposure. This behaviour is very unusual in reactive sorption, as in most cases the initial uptake rate is much faster than at any other time. Identical behaviour has been observed in other solids containing immobilised PEI [233], and it has been suggested that the increase in rate from $t = 0$ could be due to the presence of an autocatalytic reaction. They suggest that CO$_2$ absorbed on the PEI chain accelerates the reaction of other CO$_2$ molecules, much as the existence of precipitated solids accelerates the precipitation of more solids during a crystalisation process. Certainly, the chemical kinetics reported by Monazam et al. [233] are consistent with such a mechanism, though it is still unclear what particular reactions are occurring. Irrespective of what is actually happening within the NOHM-PEI, it is clear that its surface must be exposed to CO$_2$ for some time before absorption can begin. The massive surface area of the immobilised NOHM droplets inside the SIP (roughly 2 orders of magnitude greater than the area of the SIP itself) appear to accelerate whatever autocatalytic processes are inhibiting the initial uptake of CO$_2$. While a small degree of reaction-limitation is observed at the beginning of the uptake curves for the SIPS, for the majority of the run moving-front, diffusion-controlled behaviour appears to dominate the absorption into the SIP.

4.7.5 Application and Further Work

The immobilisation of NOHMs is one of the most exciting applications of the SIP motif to date, and the 50-fold increase in the gas flux is a significant step towards allowing NOHMs to be used in a practical process. If fine SIP films or particles containing NOHMs could be manufactured with surface areas comparable to MECS, this could lead to a further 1-2 orders of magnitude increase in the uptake rate over the use of diluted NOHMs in a traditional absorption process. The overall increase in the specific absorption rate could conceivably be 3-4 orders of magnitude.

There are also a number of approaches available to increase the gas flux into SIPS containing NOHMs. For one, it may be possible to increase the free volume inside the PDMS by diluting it in a solvent such as hexane at the start of the SIP-
manufacturing process. Once the SIP has been crosslinked, the hexane could be evaporated away, leaving a PDMS with greater free volume, and potentially much greater permeability. A second means of increasing the gas flux would be to intentionally introduce air bubbles within the emulsion prior to crosslinking. The diffusivity of CO2 inside these empty spaces within the material would be at least 3 orders of magnitude larger than the diffusivity in the solid, and if a sufficient volume fraction of air were included, this could significantly increase the gas uptake rate. Nozad et al. [234] investigated the thermal conductivity of multi-phase solids in which the dispersed phase had much greater thermal conductivity than the continuous phase, and found that the presence of a dispersed phase with infinite conductivity could increase the effective conductivity by a factor of 5-10 when the volume fraction of the dispersed phase was 50 – 80%. The presence of gaseous voids within a SIP would have a comparable effect on the CO2 permeability of the material. However, such voids would also decrease the volumetric capacity of the material, and if thicker materials were required this would partially counteract the increase in the material’s permeability. A much more efficient approach would be to introduce connected void spaces within the SIP, rather than independent, isolated droplets. It is unclear how this could be done chemically, though it may be possible to create such voids physically with a needle or fine punch. It is unlikely these approaches could be applied to SIPs containing aqueous solvents, as the condensation of water in the void spaces is likely reduce the mass transfer rate. Another approach would be to place a small volume fraction of metal-organic framework (MOF) sheets or rods into the PDMS, as these have been shown to increase the CO2 permeability of PDMS by a factor of 2 – 4 [235].

The SIP motif is a promising, flexible and simple means of improving mass transfer rates into NOHMs and similar liquids with severe diffusional limitations. The 50-fold increase in the gas flux achievable using SIPs is a very promising result. Of course, the uptake rates shown in Figure 4.13 are still relatively slow, though because absorption is diffusion controlled, there is considerably scope for increas-
ing the uptake rate by creating SIPs with surface areas comparable to MECS.\textsuperscript{26} Implementing some of the ideas discussed in the previous paragraph could further reduce the absorption time. At present, the application of SIPs containing NOHMs specifically designed for direct air capture is the subject of ongoing investigation.

4.8 Conclusions

Solvent Impregnated Polymers (SIPs) have been proposed as a novel material for carbon capture and storage and direct air capture applications. The immobilisation of concentrated K$_2$CO$_3$ solutions, a volatile ionic liquid, and a nanoparticle organic hybrid material (NOHM) have each been demonstrated. Mass transfer into SIPs has been successfully modelled, and the conditions under which absorption collapses to a diffusion-controlled regime are understood. The average gas flux into a SIP over the course of an entire absorption run may be up to 5 times greater than the flux into a MECS or a neat liquid when aqueous chemical solvents in the pseudo-first order regime are immobilised, and an increase of over 50 times was observed for the immobilisation of a viscous, non-aqueous solvent operating in an instantaneous-reaction regime.

SIPs are a promising approach to carbon capture and other large-scale gas separation problems, and could in principle reduce unit operation volumes by several orders of magnitude. A model of a fluidised bed containing MECS with an encapsulated K$_2$CO$_3$ solution was over 10 times smaller than a traditional absorber utilising the same solvent [118]. The enhanced flux into SIPs could reduce these volumes further, and the scalable nature of their manufacturing method means the required quantities of material could likely be made.

There is certainly a great deal of promise within the SIP motif. However, we will refrain from making too many recommendations for future research until the thermodynamics of SIPs inside a carbon capture process is discussed in the following chapter.

\textsuperscript{26}Recent experiments, not included here, have shown that cutting a SIP sheet into 1 mm cubes can reduce the time to saturation by a factor of 2 – 3, compared to the neat 1 mm film.
Appendix 4.I. Supporting Tables and Figures

Manufactured SIPs

A number of stable SIPs were manufactured using various PDMSs, stabilising agents, and solvents. These are summarised in Table 4.2 below. Several emulsions were labelled as ‘low viscosity’ - while the viscosity was not measured, these emulsions flowed freely with a viscosity comparable to glycerol. The emulsions containing KE-103 were used for manufacturing particles.

<table>
<thead>
<tr>
<th>SIP</th>
<th>PDMS</th>
<th>Aqueous Solvent</th>
<th>Solvent wt%</th>
<th>Stabilising Agent (wt% in Emulsion)</th>
<th>Crosslinking</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIP1</td>
<td>Semicosil 949 UV</td>
<td>Water</td>
<td>50%</td>
<td>9011 (1%)</td>
<td>UV Light</td>
<td></td>
</tr>
<tr>
<td>SIP2</td>
<td>Semicosil 949 UV</td>
<td>3wt% K$_2$CO$_3$</td>
<td>50%</td>
<td>9011 (1%)</td>
<td>UV Light</td>
<td>Optionally add 0.25g/L of thymol due to the aqueous phase to visualize CO$_2$ uptake.</td>
</tr>
<tr>
<td>SIP3</td>
<td>Semicosil 949 UV</td>
<td>30wt% K$_2$CO$_3$</td>
<td>50%</td>
<td>9011 (1%)</td>
<td>UV Light</td>
<td></td>
</tr>
<tr>
<td>SIP4</td>
<td>Semicosil 949 UV</td>
<td>30wt% K$_2$CO$_3$</td>
<td>40%</td>
<td>Ethanol (2.5%)</td>
<td>UV Light</td>
<td>Small particle size and low viscosity emulsion.</td>
</tr>
<tr>
<td>SIP5</td>
<td>KE-103</td>
<td>30wt% K$_2$CO$_3$</td>
<td>50%</td>
<td>9011 (1%)</td>
<td>Heat</td>
<td></td>
</tr>
<tr>
<td>SIP6</td>
<td>KE-103</td>
<td>30wt% K$_2$CO$_3$</td>
<td>50%</td>
<td>Ethanol (2.5%)</td>
<td>Heat</td>
<td></td>
</tr>
<tr>
<td>SIP7</td>
<td>Sylgard 184</td>
<td>30wt% K$_2$CO$_3$</td>
<td>50%</td>
<td>Ethanol (2.5%)</td>
<td>Heat</td>
<td></td>
</tr>
<tr>
<td>SIP8</td>
<td>KE-103</td>
<td>3wt% K$_2$CO$_3$</td>
<td>25%</td>
<td>Ethanol (1.25%)</td>
<td>Heat</td>
<td></td>
</tr>
<tr>
<td>SIP9</td>
<td>KE-103</td>
<td>30wt% K$_2$CO$_3$</td>
<td>25%</td>
<td>Ethanol (1.25%)</td>
<td>Heat</td>
<td>Optionally add 0.25g/L of thymol blue to the aqueous phase to visualize CO$_2$ uptake.</td>
</tr>
<tr>
<td>SIP10</td>
<td>Semicosil 949 UV</td>
<td>10wt% K$_2$CO$_3$</td>
<td>50%</td>
<td>9011 (1%)</td>
<td>UV Light</td>
<td>Low viscosity emulsion.</td>
</tr>
<tr>
<td>SIP11</td>
<td>Semicosil 949 UV</td>
<td>DMEDAH Formate</td>
<td>50%</td>
<td>5223C (1%)</td>
<td>UV Light</td>
<td>Solid DMPA was dissolved in SMS-042 using a sonicator before polymers were mixed.</td>
</tr>
<tr>
<td></td>
<td>50wt% SMS-042</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Summary of manufactured solvent impregnated polymers.
Internal Particle Size Distribution

The internal droplet size inside SIPs varied substantially depending on the PDMS, stabilising agent and solvent used. In Figure 4.16 below, the microscopic structure of 2 stable SIPs with particle size ranging from 1 µm to several 100 µm are compared; the SIP shown in Figure 4.2 of the paper is also reproduced. The left-hand column shows images of the precursor emulsions, while the right-hand column shows images of the crosslinked emulsions. The internal particle size distribution for each of these materials was estimated using the image-analysis software ImageJ, and is shown in Figure 4.17.

Figure 4.16: (a)-(c) are microscopic images of precursor emulsions for SIP10, SIP4 and SIP8 in Table 4.2 respectively. (d)-(f) are images of crosslinked SIP gels for SIP10, SIP4 and SIP8 respectively.
Figure 4.17: Volume averaged particle size distributions for (a) SIP10, (b) SIP4 and (c) SIP8 from Table 4.2, calculated via image analysis on photographs of emulsions using ImageJ.

SIP Particles

Figure 4.18 shows typical SIP particles, manufactured according to the methods discussed in section 4.2. Figure 4.19 shows the particle size distribution for a batch of particles, calculated by estimating the diameter of several 1000 particles using ImageJ.

Figure 4.18: SIP particles composed of SIP8 in Table 4.2.
Appendix 4.II: Numerical Solution

The equations derived in section 4.5 were solved via a method of lines (MOL) approach using the DifferentialEquations.jl suite in Julia. The implementation was based on the excellent monograph of Hundsdorfer and Verwer [236].

- To model absorption into a flat SIP inside a petri dish, we modelled the SIP surface via a Dirichlet condition, and the bottom of the material via a Neumann condition [237].

- A second order spatial discretisation was used: these are commonplace for diffusion problems, and indeed almost identical systems have been modelled via exactly this approach before (c.f. Hundsdorfer and Verwer [236], particularly p. 64 and p. 206).

- The stiff CVODE_BDF() solver inside DifferentialEquations.jl, which interfaces with the popular backwards differentiation formulas in the CVODE solver [238], was used. A stiff solver was required, as MOL discretisations of diffusion problems are often stiff (c.f. Hundsdorfer and Verwer [236], p. 64). An alternative stiff solver, Rodas4(), which uses a 4th order stably-stiff Rosen-
brock method, was used in the dimensionless analysis described in Appendix 4.III. Though it was substantially slower, as a pure-Julia implementation it proved more stable when implementing a continuous callback.

The PDE’s were discretised on a vertex-centred grid with points labelled $j = 1, \ldots, m+1$. The Neumann condition held at the boundary at point 1, while the Dirichlet condition held at the boundary at point $m+1$. The point spacing was $h = L/m$ (where $L$ was the material thickness). For $j = 2, \ldots, m-1$:

$$\dot{c}_j(t) = \frac{D_{\text{eff}}}{h^2}(c_{j-1} - 2c_j + c_{j+1}) - k_{2}^{\text{eff}}c_jw_j$$  \hspace{1cm} (4.36)

For the Neumann condition, we consider a ghost point at point $j = 0$ with concentration equal to $c_2$:

$$\dot{c}_1(t) = \frac{D_{\text{eff}}}{h^2}(2c_2 - 2c_1) - k_{2}^{\text{eff}}c_1w_1$$  \hspace{1cm} (4.37)

For the Dirichlet condition, note that $c_{m+1} = S_l p$, where $p$ is the gas partial pressure, so

$$\dot{c}_m = \frac{D_{\text{eff}}}{h^2}(c_{m-1} - 2c_m + S_l p) - k_{2}^{\text{eff}}c_mw_m$$  \hspace{1cm} (4.38)

And of course, for all $j = 1, \ldots, m+1$,

$$w_j = f(c_j, w_j).$$  \hspace{1cm} (4.39)

We can approximate the gas flux into the material using a second-order one-sided finite difference approximation:

$$J_{\text{surface}} = \left(\frac{S_l p - 2c_m + \frac{1}{2}c_{m-1}}{h}\right) \left( D_s \varepsilon S_s + D_l (1 - \varepsilon) \right)$$  \hspace{1cm} (4.40)

Integrating $J_{\text{surface}}$ from time $t = 0$ with no gas in the material to saturation (with all physical properties set to 1 and $f = -cw$), the relative error in total gas absorption (compared to that predicted by the changes in concentration inside the material) is less than $10^{-3}$ for $m = 100$. In general $m$ was chosen so that halving the grid-size
had negligible effect on the solution.
Appendix 4.III: Dimensional Analysis

As discussed in section 4.3, the SIP motif represents a tradeoff between improved gas flux increasing mass transfer, and decreased gas flux due to the presence of a saturated-zone building from the material surface (in the limit in which diffusional resistance through the saturated-zone dominates, the model collapses to the moving front model considered by Ho et al. [157]). To quantify these effects, the model was put into dimensionless form, and was compared with a similar, dimensionless model for absorption into a static liquid. For a fair comparison, we compare a thin SIP layer with a liquid with identical surface area, and with volume chosen such that the total gas capacity of each are the same. We then calculate the time, \( t_\gamma \), to reach some arbitrary degree of saturation \( \gamma \) (with \( 0 \leq \gamma \leq 1 \)), and we find the properties of each system that determine the ratio of these absorption times. We then apply these predictions to several hypothetical SIP materials. In what follows, we consider the simplest SIP chemistry: the gas reacts with 1-1 stoichiometry in a 2nd order reaction with the active species, \( w \). The initial concentration of active species is \( w_0 \), and it is depleted over time as the reaction continues (i.e. it is not replaced by a buffer reaction.) We will then extend the dimensional analysis to SIPS with other chemistries.

Material Geometry

If the static liquid has thickness \( L \), then a SIP material with the same gas capacity will have thickness:

\[
L_{\text{SIP}} = L \left( (1 - \varepsilon) + \frac{c^*/w_0}{c^*/w_0 + \frac{S_s}{S_l}} \right)^{-1}
\]  

(4.41)
Transport Equations

In general, absorption into a SIP can be modelled via:

$$\frac{\partial c}{\partial t} = D^\text{eff} \nabla^2 c - k^\text{eff}_2 \xi wc \tag{4.42}$$

$$\frac{\partial w}{\partial t} = f(c, w, \xi). \tag{4.43}$$

where $\xi$ is an effectiveness factor defined by Eq. (4.11) and (4.12). For this analysis we consider the simplest scenario, in which we start with a fixed quantity of reactive species, which is consumed as it reacts with the gas with 1 : 1 stoichiometry. Then

$$\frac{\partial w}{\partial t} = -k_2 \xi wc \tag{4.44}$$

Assuming we start with no gas absorbed, the initial and boundary conditions are:

$$c|_{t=0} = 0; \quad w|_{t=0} = w_0; \quad c_x|_{x=0} = 0; \quad c|_{x=L_{\text{SIP}}} = c^*.$$  \tag{4.45}

The pde’s describing absorption of gas into a static fluid are similar; for the absorbing gas, we have:

$$\frac{\partial c}{\partial t} = D_l \frac{\partial^2 c}{\partial x^2} - k_2 cw. \tag{4.46}$$

We make the same assumptions about the solvent chemistry as before: the only difference is that in this case the reactive species is free to diffuse inside the liquid. In many systems of industrial interest we can make a pseudo-first order assumption: we suppose $w$ changes slowly enough for spatial inhomogeneties in $w$ to be smoothed out. For the second-order system under consideration, this will occur whenever $w_0 \gg c^*$, in other words when chemical solubility is much greater than physical solubility: a very common situation. (More rigorously, in an infinitely deep liquid the pseudo-first order assumption is valid whenever $\sqrt{\frac{\pi k_2 t w_0}{4}} \ll \frac{w_0}{c^*}$ [15]. Because of the different scaling of $w_0$ on either side of the inequality, this is equivalent to $w_0 \gg c^*$ provided the material is not too thick and the reaction is not too fast.)
Under this regime, \( w \) only depends on time, and varies according to:

\[
\frac{dw}{dt} = -k_2 w \frac{1}{L} \int_0^L c(x) dx. \tag{4.47}
\]

The boundary and initial conditions are

\[
c|_{t=0} = 0; \quad c|_{x=0} = 0; \quad c|_{x=L} = c^*; \quad w|_{t=0} = w_0. \tag{4.48}
\]

**Dimensionless Form of Transport Equations**

We now transform each equation into a dimensionless form. The dimensionless variables for the static liquid are defined as follows:

\[
c = c^* \tilde{c}; \quad w = w_0 \bar{w}; \quad t = (k_2 c^*)^{-1} \bar{t}; \quad x = L \bar{x}. \tag{4.49}
\]

With these definitions, equations (4.46)-(4.48) become:

\[
\alpha \frac{\partial \tilde{c}}{\partial \bar{t}} = \frac{1}{\phi^2} \nabla^2 \tilde{c} - \bar{c} \bar{w} \tag{4.50}
\]

\[
\frac{\partial \bar{w}}{\partial \bar{t}} = -\bar{w} \int_0^1 \tilde{c} \bar{d} \bar{x} \tag{4.51}
\]

\[
\tilde{c}|_{\bar{t}=0} = 0; \quad \tilde{c}|_{\bar{x}=0} = 0; \quad \tilde{c}|_{\bar{x}=1} = 1; \quad \bar{w}|_{\bar{t}=0} = 1. \tag{4.52}
\]

where

\[
\alpha \equiv \frac{c^*}{w_0} \tag{4.53}
\]

and

\[
\phi \equiv \sqrt{\frac{k_2 w_0 L^2}{D_l}} \tag{4.54}
\]

is the *Thiele Modulus*, which represents the relative significance of diffusion and reaction resistance.

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We choose the following dimensionless variables for the SIP material:

\[ c = c^* \tilde{c}; \quad w = w_0 \tilde{w}; \quad t = (k_2 c^*)^{-1} \tilde{t}; \quad x = L_{\text{SIP}} \tilde{x}. \]  

(4.55)

The only difference is the change in the length scaling; we intentionally keep the time scaling consistent with the pure liquid case, in order to simplify the comparison of the absorption rates of the systems. With these dimensionless variables, equations (4.42), (4.44) and (4.45) become:

\[ \alpha \beta \frac{\partial \tilde{c}}{\partial \tilde{t}} = \frac{1}{\tilde{\phi}^2} \nabla^2 \tilde{c} - \xi \tilde{c} \tilde{w} \]  

(4.56)

\[ \frac{\partial \tilde{w}}{\partial \tilde{t}} = -\xi \tilde{c} \tilde{w} . \]  

(4.57)

\[ \tilde{c}|_{\tilde{t}=0} = 0; \quad \tilde{c}|_{x=0} = 0; \quad \tilde{c}|_{x=1} = 1; \quad \tilde{w}|_{x=0} = 1. \]  

(4.58)

where \( \alpha \) is as above,

\[ \beta = \frac{k_2}{k_2^{\text{eff}}} \]  

(4.59)

and

\[ \tilde{\phi} = \sqrt{\frac{k_2^{\text{eff}} w_0 L_{\text{SIP}}^2}{D^{\text{eff}}}} \]  

(4.60)

is again the Thiele modulus of the material. The effectiveness factor is not a constant, as \( w \) may vary in space and time. Instead, it is given by:

\[ \xi = \frac{\phi' \coth \phi' - 1}{(\phi')^2/3} \]  

(4.61)

where

\[ \phi' = r_{\text{droplet}} \sqrt{\frac{k_2 w}{D_l}} = \left( \frac{r_{\text{droplet}}}{L} \right) \phi \sqrt{w} \]  

(4.62)

where \( \frac{r_{\text{droplet}}}{L} \) is a new dimensionless parameter, which quantifies the degree of separation between the microscopic and macroscopic scales. Overall, the dimensionless parameters describing absorption into the liquid are \( \alpha \) and \( \phi \), and the parameters describing absorption into the SIP are \( \alpha, \beta, \phi, \tilde{\phi} \) and \( r_{\text{droplet}}/L \).
Comparison of Saturation Times

We are interested in the ratio of the times, $t_\gamma$, required for each system to reach some arbitrary degree of saturation, $\gamma$:

$$ \Psi \equiv \frac{t_{\gamma_{\text{liq}}}}{t_{\gamma_{\text{SIP}}}}. $$

(4.63)

This ratio will determine which material absorbs gas fastest: because the materials have identical capacities, it may also be thought of as the ratio of the mean gas fluxes over the course of the gas absorption process. Because we have chosen the same dimensionless time scaling for each of our systems:

$$ \Psi = \frac{t_{\gamma_{\text{liq}}}}{t_{\gamma_{\text{SIP}}}}. $$

(4.64)

Now, as can be seen from the non-dimensionalised equations, each of these $\bar{t}_\gamma$ values depends upon several dimensionless parameters:

$$ \Psi = \frac{t_{\gamma_{\text{liq}}}(\gamma, \alpha, \phi)}{t_{\gamma_{\text{SIP}}}(\gamma, \alpha, \beta, \phi, \phi, r_{\text{droplet}}/L)} $$

(4.65)

We can eliminate $\gamma$ immediately by simply stipulating a reasonable value, such as 80% saturation ($\gamma = 0.8$). This still leaves $\alpha$, $\beta$, the two Thiele moduli and $r_{\text{droplet}}/L$. The Thiele moduli may be related by:

$$ \bar{\phi}^2 = \frac{k_2^e w_0 L_{\text{SIP}}^2}{D_{\text{eff}}} = \left( \frac{k_2 w_0 L^2}{D_l} \right) \left( \frac{1 - \varepsilon}{\varepsilon \frac{P_s}{P_l} + (1 - \varepsilon)} \right) \left( (1 - \varepsilon) + \varepsilon \frac{\alpha}{\alpha + 1} \frac{S_s}{S_l} \right)^{-2} $$

(4.66)

However, for this practical chemical system, $\alpha \ll 1$, and so

$$ \bar{\phi}^2 \approx \phi^2 \left( \frac{1}{\varepsilon \frac{P_s}{P_l} + (1 - \varepsilon)} \right) \frac{1}{(1 - \varepsilon)} $$

(4.67)

or, more abstractly,

$$ \bar{\phi} \approx \bar{\phi} (\varepsilon, \phi, P_s/P_l) $$

(4.68)
Overall then,

$$\Psi = \Psi(\alpha, \beta, \varepsilon, \phi, \frac{P_s}{P_l}, r_{\text{droplet}}/L). \quad (4.69)$$

However, consider the role of $\alpha$ and $\beta$ in equations (4.56) and (4.50). In each case they are multipliers of the $\partial c/\partial t$ term. However, for systems with first-order reaction with diffusion, the concentration profile quickly asymptotes towards a stable quasi-steady state where $\partial c/\partial t \approx 0$, so that $\bar{\phi}^{-2}\nabla^2 \bar{c} \approx \bar{c} \bar{w}$. Given that $\alpha \ll 1$ and $\beta = \mathcal{O}(1)$, this asymptotic adjustment will happen extremely quickly (much faster than any changes in $w$) and the only effect of changing $\alpha$ or $\beta$ will be to slightly increase or decrease the already very small time in which the concentration profile, $c$, takes to respond to changes in $w$. This will have negligible influence on the evolution of the concentration profiles and the gas uptake rate over time.

Numerical experiments confirmed this physical reasoning: starting from $\alpha = 10^{-2}$, $\beta = 1$, changing the value of either $\alpha$ or $\beta$ by an order of magnitude only changed $\Psi_{0.8}$ by $\pm 1\%$.

Given this, it is clear that for a wide range of systems of practical interest:

$$\Psi = \Psi(\varepsilon, \phi, \frac{P_s}{P_l}, r_{\text{droplet}}/L). \quad (4.70)$$

The relationship between $\Psi$ and $\varepsilon$ is not particularly interesting ($\varepsilon$ is constrained for practical reasons) and so we hold $\varepsilon = 0.5$. In this case,

$$\Psi = \Psi(\phi, \frac{P_s}{P_l}, r_{\text{droplet}}/L). \quad (4.71)$$

Numerical experiments suggest that $\Psi$ is not sensitive to changes $r_{\text{droplet}}/L$ for the large majority of SIPS. In particular, provided the internal droplets inside the SIP are $\sim 20$ times smaller than the macroscopic thickness of the SIP itself, then variations in $r_{\text{droplet}}/L$ do not significantly change the absorption rate. This is unsurprising, as mass transfer in SIPS is typically controlled by macroscopic diffusion through the saturated zone shown in Figure 4.5, rather than by microscopic diffusion inside the reaction zone. Hence Ho et al. [157], when modelling a similar system, ignored
local reaction and diffusional resistances altogether; the more complex model developed here collapses to their simpler model for a wide range of SIPs (for further discussion, see section 4.6.) The insensitivity of the model to changes in $r_{\text{droplet}}/L$ for constant $\phi$ (i.e. for constant $L$, so we are really considering changes in $r_{\text{droplet}}$ alone) may also be seen indirectly in Figure 4.9a, as decreasing $\phi'$ by a factor of 10 (i.e. making $r_{\text{droplet}}$ 10 times smaller) and increasing $L_{\text{SIP}}/r_{\text{droplet}}$ by a factor of 10 (i.e. keeping the overall material thickness, $L_{\text{SIP}}$ the same) has negligible effect on the absorption rate for almost all systems, because the various curves are, approximately at least, horizontal translations of each other.)

Hence, under most circumstances, $\Psi = \Psi(\phi, P_s/P_l)$. This is a very interesting result. It suggests that the improvement in the gas flux a SIP could provide over a static liquid depends upon only two factors: the relative permeability of the solid compared to the liquid (presumably the larger this is, the better for the SIP) and the Thiele modulus (which will capture the significance of the presence of the saturated zone, and also the case of $\phi \ll 1$, where reducing diffusional resistance will not increase the gas flux.)

The dimensionless equations for the SIP derived above were solved using the same discretisation scheme described in Appendix 4.II, with the coefficients in the PDE and the initial conditions replaced by the relevant dimensionless numbers. The discretisation of the dimensionless equation for the static liquid was similar, except the $\dot{w}_i$ terms were replaced by the single term:

$$\dot{\bar{w}} = -\frac{\bar{w}}{m} \left(\frac{1}{2}(c_1 + c_{m+1}) + \sum_{i=2}^{m} c_i\right). \tag{4.72}$$

**General Nondimensionalisation of Transport Equations.**

For more complicated chemistries, the relationship between $\partial w/\partial t$ and $c$, $w$ and the initial conditions may be much more complicated. In such cases, a dimensionless analysis can be simplified by considering the solvent loading, $\lambda$, rather than the active species concentration. The solvent loading is simply the amount of gas absorbed in
the liquid, divided by the total chemical capacity of the gas. For chemical solvents, the physical solubility of the gas is typically ignored when calculating the loading. For a second order reaction, no matter what other chemical reactions are occurring, the change in loading can always be expressed as:

\[ \frac{\partial \lambda}{\partial t} = \frac{k_2 \xi w}{N} \]  

(4.73)

where \( N \) is the total amount of gas that can be chemically absorbed into the material per unit volume. If the reactive species concentration, \( w \), is expressed in terms of the loading, then the differential equations for the SIP become:

\[ \frac{\partial c}{\partial t} = D_{\text{eff}} \nabla^2 c - k_{\text{eff}} \xi w(\lambda)c \]  

(4.74)

\[ \frac{\partial \lambda}{\partial t} = \frac{k_2 \xi w(\lambda)}{N}. \]  

(4.75)

with initial conditions,

\[ c|_{t=0} = 0; \quad \lambda|_{t=0} = \lambda_0; \quad c_x|_{x=0} = 0; \quad c|_{x=L_{\text{SIP}}} = c^*. \]  

(4.76)

For the liquid,

\[ \frac{\partial c}{\partial t} = D_l \frac{\partial^2 c}{\partial x^2} - k_2 cw(\lambda). \]  

(4.77)

\[ \frac{d\lambda}{dt} = \frac{k_2 w(\lambda)}{N} \frac{1}{L} \int_0^L c(x)dx. \]  

(4.78)

The boundary and initial conditions are

\[ c|_{t=0} = 0; \quad c_x|_{x=0} = 0; \quad c|_{x=L} = c^*; \quad \lambda|_{t=0} = \lambda_0. \]  

(4.79)

For the SIP, the following dimensionless variables are defined:

\[ t = \left( \frac{k_2 c^* w_0}{N} \right)^{-1} \bar{t}; \quad c = c^* \bar{c}; \quad x = L_{\text{SIP}} \bar{x} \]  

(4.80)
where \( w_0 \) is a ‘typical’ reactive species concentration, which will be defined below.

Then the differential equations become:

\[
\alpha \beta \frac{\partial \bar{c}}{\partial \bar{t}} = \frac{1}{\phi^2} \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} - \xi \bar{c} \bar{w}(\lambda)
\] (4.81)

\[
\frac{\partial \lambda}{\partial \bar{t}} = \xi \bar{c} \bar{w}(\lambda)
\] (4.82)

\[
\bar{c}|_{\bar{t}=0} = 0; \quad \bar{c}|_{\bar{x}=0} = 0; \quad \bar{c}|_{\bar{x}=1} = 1; \quad \lambda|_{\bar{t}=0} = \lambda_0.
\] (4.83)

where \( \bar{w} \equiv w/w_0, \alpha \equiv c^*/N, \) and otherwise all other variables are the same as above:

\[
\beta = \frac{k_2}{k_2^{\text{eff}}}
\] (4.84)

and

\[
\bar{\phi} = \sqrt{\frac{k_2^{\text{eff}} w_0 L_{\text{SIP}}^2}{D_{\text{eff}}}}
\] (4.85)

For the liquid, the dimensionless variables are

\[
t = \left( \frac{k_2 c^* w_0}{N} \right)^{-1} \bar{t}; \quad c = c^* \bar{c}; \quad x = L \bar{x}
\] (4.86)

giving the following dimensionless equations,

\[
\alpha \frac{\partial \bar{c}}{\partial \bar{t}} = \frac{1}{\phi^2} \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} - \bar{c} \bar{w}(\lambda)
\] (4.87)

\[
\frac{\partial \lambda}{\partial \bar{t}} = \bar{w}(\lambda) \int_0^1 \bar{c} d\bar{x}
\] (4.88)

\[
\bar{c}|_{\bar{t}=0} = 0; \quad \bar{c}|_{\bar{x}=0} = 0; \quad \bar{c}|_{\bar{x}=1} = 1; \quad \lambda|_{\bar{t}=0} = \lambda_0.
\] (4.89)

where everything is the same as in the SIP, and

\[
\phi = \sqrt{\frac{k_2 w_0 L^2}{D_l}}
\] (4.90)

As before, \( \alpha = c^*/N \) can be expected to be much less than unity for most practi-
cal chemical solvents. This means the analysis above is completely applicable, and
\[ Ψ_γ = Ψ_γ(ε, P_s/P_l, ϕ, r_{droplet}/L). \]
Apart from \( ε, P_s/P_l, r_{droplet}/L \) and \( ϕ \), the relative flux into the liquid and into the SIP depends only upon what may be called the ‘chemistry’ of the solvent: the function \( w(λ) \). Physically, this represents the relationship between the solvent loading, \( λ \), and the reactive species concentration in the solvent, \( w \). However, it turns out that \( Ψ \) is relatively independent of \( w(λ) \) if the quantity \( w_0 \) is chosen appropriately. To demonstrate this, we consider 8 hypothetical ‘chemistries’ (i.e. \( w(λ) \) functions):

- Direct consumption of active species: \( w(λ) = 1 - λ \)
- \( K_2CO_3 \) Solutions (see Appendix 4.IV): \( w(λ) = K_{eq}^{1-λ} \)
- Buffer of form \( w ↔ 2B \): \( w(λ) = (1 - λ)^2 \)
- \( w(λ) = 1 - λ + \sin(πλ) \)
- \( w(λ) = 1 - λ + \sin(5πλ) \)
- \( w(λ) = 1 - λ^2 \)
- \( w(λ) = 1 - \sqrt{λ} \)
- \( w(λ) = 1 - λ^{0.1} \)

Normalised versions of these are plotted in Figure 4.20. Some of these correspond to physical chemistries, while others are hypothetical relationships, chosen to capture as wide a range of relationships between the solvent loading and the active species concentration as possible (though all were required to satisfy \( w(λ = 1) = 0 \).) For each of these chemistries, and for each value of \( ϕ \) and \( P_s/P_l \) in the phase diagram, Eqs. (4.81) – (4.88) were solved numerically using the methods described in Appendix 4.II. A continuous callback was built into the DE solver in order to find the exact time at which \( ξ = 0.8 \), and \( Ψ \) was recorded for each run. The plot was insensitive to the specific choice of \( α \) and \( β \), and values of 0.01 and 1 were used. \( λ_0 \) was
Figure 4.20: 8 hypothetical ‘chemistries’ used to create phase diagram for increase in gas flux which SIPs can provide (Figure 4.5d). $\lambda$ is the chemical loading of the solvent, and $w(\lambda)$ is the concentration of the species which reacts with the absorbed gas. All lines functions have been normalised to have unit area.

set equal to 0.1, primarily to avoid divide-by-zero errors in some $w(\lambda)$ functions. $w_0$ was set to the mean value of $w(\lambda)$ on the interval $\lambda \in [0.1, 1.0]$

\[
w_0 = \int_{0.1}^{1} w(\lambda) d\lambda \quad (4.91)
\]

This choice was made so that the Thiele modulus, $\phi = \sqrt{k_2 w_0 L^2 / D_t}$ would most accurately reflect the dynamics inside the reaction zone. With this choice of $w_0$, the value of $\Psi$ was found to be largely independent of the shape of $w(\lambda)$, and near-identical phase diagrams were created for the wide range of chemistries plotted in Figure 4.20. Without this adjustment (e.g. setting $w_0 = w(\lambda_0)$) the different chemistries do not converge to the same phase diagram.
Appendix 4.IV: Absorption of Carbon Dioxide into Carbonate Solutions.

Absorption of CO\textsubscript{2} into K\textsubscript{2}CO\textsubscript{3}-KHCO\textsubscript{3} buffer solutions is governed by the following chemistry [15]:

\[
\text{CO}_2 + \text{OH}^- \longrightarrow \text{HCO}_3^-
\]  
(4.92)

\[
\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-
\]  
(4.93)

The second buffer reaction is considered to be instantaneous, and so the overall reaction is:

\[
\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \longrightarrow 2\text{HCO}_3^-
\]  
(4.94)

with reaction rate given by:

\[
\dot{r} = -k_2[\text{CO}_2][\text{OH}^-].
\]  
(4.95)

This chemistry is slightly more complicated than that discussed above. Our first task is to derive the function \(f(\cdot, \cdot)\), giving the rate of change of reactive species,

\[
\frac{\partial[\text{OH}^-]}{\partial t} = f([\text{CO}_2], [\text{OH}^-]).
\]  
(4.96)

We first define the \textit{loading} of carbon dioxide in the solvent:

\[
\lambda \equiv \frac{0.5[\text{HCO}_3^-]}{0.5[\text{HCO}_3^-] + [\text{CO}_3^{2-}]} = \frac{[\text{HCO}_3^-]}{[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]} = \frac{[\text{HCO}_3^-]}{2[\text{CO}_3^{2-}]^0}
\]  
(4.97)

where \([\text{CO}_3^{2-}]^0\) is the equivalent carbonate concentration (i.e. the concentration of carbonate if all CO\textsubscript{2} were removed and all HCO\textsubscript{3}\textsuperscript{−} were converted back to CO\textsubscript{3}\textsuperscript{2−}).

For example, if a 3 M solution of K\textsubscript{2}CO\textsubscript{3} were created, then \([\text{CO}_3^{2-}]^0\) would be 3 M, irrespective of the progression of (4.94). The loading measures the overall
progression of (4.94), and the rate of change of loading is given by:

\[
\frac{\partial \lambda}{\partial t} = \frac{1}{2[\text{CO}_3^{2-}]} \frac{\partial [\text{HCO}_3^-]}{\partial t} = \frac{k_2[\text{CO}_2][\text{OH}^-]}{[\text{CO}_3^{2-}]^0}
\]  

(4.98)

Furthermore, for the fast equilibrium reaction,

\[
K_{eq} = \frac{[\text{OH}^-][\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}.
\]

(4.99)

This may be written

\[
\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{[\text{OH}^-]}{K_{eq}}
\]

(4.100)

while (4.97) may be rearranged to give:

\[
\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{1 - \lambda}{2\lambda}
\]

(4.101)

and so overall

\[
[\text{OH}^-] = K_{eq} \frac{1 - \lambda}{2\lambda}
\]

(4.102)

This is the function \( w(\lambda) \) considered in the dimensional analysis above. If we rearrange (4.102), we get

\[
\lambda = \frac{K_{eq}}{2[\text{OH}^-] + K_{eq}}.
\]

(4.103)

Taking the derivative of this last equation,

\[
\frac{\partial \lambda}{\partial t} = \frac{\partial[\text{OH}^-]}{\partial t} \left( \frac{-2K_{eq}}{2[\text{OH}^-] + K_{eq}} \right)
\]

(4.104)

and comparing this with (4.98) gives:

\[
f(c, w) = \frac{\partial[\text{OH}^-]}{\partial t} = -\left( \frac{k_2(2[\text{OH}^-] + K_{eq})^2}{2K_{eq}[\text{CO}_3^{2-}]^0} \right) [\text{CO}_2][\text{OH}^-] = -\left( \frac{k_2(2w + K_{eq})^2}{2K_{eq}[\text{CO}_3^{2-}]^0} \right) cw
\]

(4.105)

This is our expression for \( f(c, w) \), assuming that \( \xi \approx 1 \). If local diffusional resistance
is significant, \( f(\cdot) \) becomes

\[
f(c, w, \xi) = -\xi \left( \frac{k_2(2w + K_{eq})^2}{2K_{eq}[\text{CO}_3^{2-}]} \right) cw
\]

(4.106)

Second-order Reaction Rate Constant $k_{OH}$ in K$_2$CO$_3$ Solutions

Carbon dioxide reacts with hydroxide ions in the K$_2$CO$_3$ solution according to the following reaction:

$$\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$$

The second order rate constant for this reaction, $k_{OH}^-$, is, according to Astarita et al. [9], given by

$$k_{OH}^- = 10^{13.635 - 2895/T + 0.08I}$$

where $T$ is the temperature in Kelvin, $I$ the ionic strength in molL$^{-1}$, and $k_{OH}^-$ has units of L mol$^{-1}$ s$^{-1}$.

Density of K$_2$CO$_3$ Solutions

Novotny and Sohnel [147] provide functions for the density of salt solutions at various temperatures and concentrations:

$$\rho(t, c) = \rho_w(t) + (A + Bt + Ct^2)c + (D + Et + Ft^2)c^{3/2}$$

where $t$ is the temperature in Celsius, $c$ is the concentration in molL$^{-1}$, $\rho_w$ is the density of pure water in kg m$^{-3}$, and $A, B, \ldots, F$ are constants. For the density of water, the function of Kell (1975) was used:

$$\rho(\text{kg/m}^3) = \frac{999.83952 + 16.945176t - 7.9870401 \times 10^{-3}t^2 - 46.170461 \times 10^{-6}t^3}{1 + 16.897850 \times 10^{-3}t} + \frac{105.56302 \times 10^{-9}t^4 - 280.5423 \times 10^{-12}t^5}{1 + 16.897850 \times 10^{-3}t} \quad (4.107)$$

where $t$ is again in degrees Celsius.
Viscosity of K\textsubscript{2}CO\textsubscript{3} Solutions

The viscosity of potassium carbonate solutions was calculated using the correlation of Correia et al. [146]:

\[ \mu(t, m) = \mu(t, 0) \left( 1 + \sum_{i=0}^{2} \sum_{j=0}^{2} f_{ij} t^i m^{j+1} \right) \]

Note that \( f_{ij} \) is a matrix of constants, \( t \) is temperature in degrees Celsius and their concentration unit, \( m \), is molality, in mol/kg, see p. 203 of their paper. This calculation required a correlation for the viscosity of pure water as a function of temperature, and this is provided by Kestin, Sokolov and Wakeham [239]:

\[ \log \left( \frac{\mu(t)}{\mu(20^\circ C)} \right) = \frac{20 - t}{t + 96} \left( 1.2378 - 1.303 \times 10^{-3} (20 - t) + 3.06 \times 10^{-6} (20 - t)^2 + 2.55 \times 10^{-8} (20 - t)^3 \right) \]

where once again, \( t \) is the temperature in Celsius.

Diffusivity of CO\textsubscript{2} in K\textsubscript{2}CO\textsubscript{3} Solutions

The diffusivity of carbon dioxide in potassium carbonate solutions is calculated from the diffusivity of CO\textsubscript{2} in pure water as measured by Versteeg and Van Swaalj [150]:

\[ D_{CO_2} = 2.35 \times 10^{-6} \exp(-2119/T) \]

where \( T \) is the temperature in Kelvin. This is modified for potassium carbonate solutions using the Stokes-Einstein relation, which simply states that \( D \propto 1/\mu \)

Solubility of CO\textsubscript{2} in K\textsubscript{2}CO\textsubscript{3} Solutions

We use the model of Weisenberger and Shumpe [14] to predict the solubility of CO\textsubscript{2} into dilute K\textsubscript{2}CO\textsubscript{3} solutions. For more concentrated solutions, the parameters of Knuutila [13] are more appropriate.
The solubility, $S_l$, in units mol Pa$^{-1}$ L$^{-1}$, are given by

$$S_l = S_{water} 10^{\sum (h_i + h_G)c_i}$$

where $S_{water}$ is the solubility of the gas in pure water, $h_i$ are the ion specific coefficients, $c_i$ are the molar concentrations of the dissolved ions, and

$$h_G = h_{G,0} + (T - 298.15K)h_T$$

is the temperature-dependent parameter for the gas. For CO2 dissolving in K2CO₃, Weisenberger and Shumpe [14] give

- $h_{i,K} = 0.0922$ mol/L
- $h_{i,CO} = 0.1423$ mol/L
- $h_{G0} = -0.172$ mol/L
- $h_T = -0.338 \times 10^{-3}$ mol/L.K

while Knuutila et al. [13] gave parameters:

- $h_{i,K} = 0.0971$ L/mol
- $h_{i,CO} = 0.1423$ L/mol
- $h_{G0,N2O} = -0.0085$ L/mol
- $h_{T,N2O} = -0.01809 \times 10^{-3}$ L/mol.K

Note that Knuutila’s parameters are for N2O, but they can be adjusted to CO2 using the N2O-analogy, which states that

$$\frac{S_{CO2 \ In \ Salt \ Soln.}}{S_{N2O \ In \ Salt \ Soln.}} = \frac{S_{CO2 \ In \ Water}}{S_{N2O \ In \ Water}}$$

Finally, we need an expression for the solubility of CO2 in water. The solubility, $x_2$, in units of mole fraction per atm, of CO2 in water is given by Wilhelm et al.
\[ R \ln x_2 = A + B/T + C \ln(T) + DT \]

where, for CO₂,

- \( A = -317.658 \text{ cal/K.mol} \)
- \( B = 17371.2 \text{ cal/mol} \)
- \( C = 43.0607 \text{ cal/K.mol} \)
- \( D = -0.00219107 \text{ cal/K}^2.\text{mol} \)
- \( R = 1.987 \text{ cal/K.mol} \)

This gives almost identical results to the expression of Versteeg and Van Swaalj [150].

**Equilibrium Constant**

The equilibrium constant

\[ K_{eq} = \frac{[OH^-][HCO_3^-]}{[CO_2^-]} \]

is given, at infinite dilution, by Hikita et al [241]:

\[ K_{eq}^\infty = 10^{-1568.9/T+2.5866+6.737 \times 10^{-3}T} \]

Where \( K_{eq}^\infty \) has units mol m\(^{-3}\). It is common practice to describe VLE in these systems in terms of activity coefficient models such as the eNRTL model. However, the thermodynamic non-ideality can be corrected for by modifying the concentration-based equilibrium constant according to (Cents et al. [143]):

\[ \log_{10} \frac{K_{eq}^\infty}{K_{eq}} = \frac{1.01 \sqrt{c_{K^+}}}{1 + 1.49 \sqrt{c_{K^+}}} + 6.1 \times 10^{-2} c_{K^+} \]

where \( c_{K^+} \) is the concentration of potassium ions in mol/L.
Appendix 4.VI Non-Dimensionalisation of Moving Front Model

This appendix outlines the calculation methodology for Figure 4.9a. We consider absorption with an irreversible second order reaction, so that the chemical capacity of the material is equal to the initial concentration of reactive species, \( w_0 \). We assume that the physical solubility of the gas is much less than the chemical solubility, \( c^* \ll w_0 \), as this assumption was required for the dimensionless analysis of the PDE model, which is invoked here. This assumption has the added bonus of putting the quasi-static assumption on a more firm footing (see [157].)

In the diffusion-controlled model, an instantaneous reaction front moves into the material at rate:

\[
\frac{dz}{dt} = \frac{\text{Flux at Reaction Front}}{\text{Capacity of Material}} = -\left. \frac{\partial c}{\partial z'} \right|_{z'=z} \frac{(1-\varepsilon)P_l + \varepsilon P_s}{s_l} \frac{S_l}{(1-\varepsilon)(w_0 + c^*) + \varepsilon S_s c^*} \tag{4.108}
\]

Assuming that \( c^*/w_0 \ll 1 \), this reduces to

\[
\frac{dz}{dt} = -\frac{1}{w_0 S_l} \left( P_l + \frac{\varepsilon}{1-\varepsilon} P_s \right) \left. \frac{\partial c}{\partial z'} \right|_{z'=z} \tag{4.109}
\]

\( c^*/w_0 \ll 1 \) also implies that a quasi-steady state approximation will be accurate [157], and so

\[
\frac{dz}{dt} = \frac{c^*}{z w_0 S_l} \left( P_l + \frac{\varepsilon}{1-\varepsilon} P_s \right) \tag{4.110}
\]

Non-dimensionalising with the following variables:

\[
z = \tilde{z} L_{\text{SIP}}; \quad t = \tilde{t}/k_2 c^*; \quad c = \tilde{c} c^*; \quad w = \tilde{w} w_0 \tag{4.111}
\]

gives

\[
\frac{k_2 c^* L^2_{\text{SIP}}}{D_l} \frac{d\tilde{z}}{d\tilde{t}} = \frac{c^*}{\tilde{z} w_0 P_l} \left( P_l + \frac{\varepsilon}{1-\varepsilon} P_s \right) \tag{4.112}
\]

\[
(\phi'')^2 \frac{d\tilde{z}}{d\tilde{t}} = \frac{1}{\tilde{z}} \left( 1 + \frac{\varepsilon}{1-\varepsilon} \frac{P_s}{P_l} \right) \tag{4.113}
\]
where
\[
(\phi'')^2 = \frac{k_2w_0L_{\text{SIP}}^2}{D_l}.
\] (4.114)

This may be integrated from \(\bar{z} = 0\) at \(\bar{t} = 0\) to give
\[
\bar{z} = \sqrt{\frac{2}{(\phi'')^2} \left( 1 + \frac{\varepsilon}{1 - \varepsilon} \frac{P_s}{P_l} \right)} \bar{t}
\] (4.115)

The time required for the material to reach some degree of fractional saturation, \(\gamma\), with \(0 \leq \gamma \leq 1\), is given by
\[
\bar{t}_{\text{sat}, \gamma} = \gamma^2 (\phi'')^2 \left( 1 + \frac{\varepsilon}{1 - \varepsilon} \frac{P_s}{P_l} \right)^{-1}
\] (4.116)

this is a function of \(\phi'', P_s/P_l\) and \(\varepsilon\) alone. We now require a similar function for the PDE-based model.

The model described in section 4.5 may also be non-dimensionalised using the same dimensionless variables (see Appendix 4.III). The equations then reduce to:
\[
\left( \frac{k_2}{k_{\text{eff}}^2} \right) \left( \frac{c^*}{w_0} \right) \frac{\partial \bar{c}}{\partial \bar{t}} = \frac{1}{(\phi_{\text{eff}})^2} \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} - \xi \bar{c} \bar{w}
\] (4.117)
\[
\frac{\partial \bar{w}}{\partial \bar{t}} = -\xi \bar{c} \bar{w}
\] (4.118)

where
\[
(\phi_{\text{eff}})^2 = \frac{L_{\text{SIP}}^2 k_{\text{eff}}^2 w_0}{D_{\text{eff}}} = \frac{L_{\text{SIP}}^2 w_0 k_2}{D_l} \left( \frac{(1 - \varepsilon)}{(1 - \varepsilon) + \varepsilon S_s/S_l} \right) \left( \frac{D_l(1 - \varepsilon) S_l + \varepsilon S_s)}{(1 - \varepsilon) P_l + \varepsilon P_s} \right).
\] (4.119)
\[
(\phi'')^2 = (\phi'')^2 \left( \frac{(1 - \varepsilon) P_l}{(1 - \varepsilon) P_l + \varepsilon P_s} \right) = (\phi'')^2 \left( 1 + \frac{\varepsilon}{1 - \varepsilon} \frac{P_s}{P_l} \right)^{-1} = f(\phi'', P_s/P_l, \varepsilon)
\] (4.120)

It is reasonable to assume \(c^*/w_0 \ll 1\) and \(k_2/k_{\text{eff}}^2 \approx 1\), and so the prefactor to the \(\partial c/\partial t\) term in Eq. (4.117) is very small. As discussed previously, when these values are small, a quasi-steady state is quickly approached for which \(\partial c/\partial t \approx 0\). Under these conditions, the model is insensitive to changes in \(c^*/w_0\) and \(k_2/k_{\text{eff}}^2\), and
numerical experiments show these may be varied by an order of magnitude without significantly affecting the model’s predictions.

Overall, Eq. (4.117) – (4.118) are dependent on only \( \phi'' \), \( P_s/P_l \), \( \varepsilon \) and \( \xi \) (or, equivalently, \( \phi' \), see Eq. (4.11).) If these 4 variables are specified, \( \bar{t}_\gamma \) may be calculated for the PDE-based model. Recall that, for the diffusion limited model described by Eq. (4.116), \( \bar{t}_\gamma \) could be calculated given \( \phi'' \), \( P_s/P_l \) and \( \varepsilon \). Hence, specification of \( \phi'' \), \( P_s/P_l \), \( \varepsilon \) and \( \phi' \) allow the diffusion-limited and PDE-model’s dimensionless saturation times to be calculated via (4.116) and (4.117) – (4.118), respectively. In generating Figure 4.9a, we specify values of \( \phi' \), \( P_s/P_l \), \( \varepsilon \) and \( L_{SIP}/r_{\text{droplet}} \), which is equivalent as \( \phi'' = \phi' \times (L_{SIP}/r_{\text{droplet}}) \).
Appendix 4.VII: Concentration Gradients in Internal Droplets and the Surrounding Polymer.

In this appendix, details are provided on the calculation of the local concentration profiles in Figure 4.9b.

Absorption into an immobilised droplet of a chemical solvent of radius $R$ inside a SIP is governed by the following PDE:

$$
\frac{\partial c}{\partial t} = \frac{D_l}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) - kc; \quad c\rvert_{r=R} = c^*; \quad \partial_r c\rvert_{r=0} = 0 \quad (4.121)
$$

Because the droplets are microscopic, the reaction may be approximated as pseudo-first order (with reaction rate constant $k$) for all but the fastest reactions. The quasistatic solution to this PDE, in terms of $\bar{c} = c/c^*$ and $\bar{r} = r/R$, is (see Fogler [226]):

$$
\bar{c} = \frac{1}{\bar{r}} \sinh(\phi \bar{r}) \sinh \phi; \quad (4.122)
$$

This function was used to plot the internal concentration profiles in Figure 4.9b.

The concentration profiles in the solid phase in Figure 4.9b obey Laplace’s equation,

$$
\nabla^2 c_s = 0 \quad (4.123)
$$

A solution to the spherically symmetric Laplace equation is:

$$
c_s = \frac{A}{r} + B. \quad (4.124)
$$

As $r \to \infty$, $c_s \to c_s^*$, and so $B = c_s^*$. Meanwhile, the flux of gas must be the same across the boundary:

$$
D_s \frac{\partial c_s}{\partial r}\rvert_{r=R} = D_l \frac{\partial c}{\partial r}\rvert_{r=R} \quad (4.125)
$$

$$
D_s \frac{\partial c_s}{\partial r} = -D_s \frac{A}{R^2} = D_l \frac{c^*}{R} (\phi \coth \phi - 1) \quad (4.126)
$$

If mass transfer resistance inside the liquid dominates (as occurs in all systems shown
in Figure 4.9b), then \( c^*/c_s^* \approx S_l/S_s \), and, defining \( \bar{c}_s \equiv c_s/c_s^* \), Eq. (4.126) reduces to

\[
\frac{\partial \bar{c}_s}{\partial \bar{r}} \bigg|_{\bar{r}=1} \approx \frac{\phi \coth \phi - 1}{P_s/P_l}
\]

(4.127)

and

\[
\bar{c}_s = 1 - \frac{1}{\bar{r}} \frac{\phi \coth \phi - 1}{P_s/P_l}
\]

(4.128)

Eq. (4.127) and (4.128) were used to estimate \( \partial \bar{c}_s/\partial \bar{r} \) and the profile for \( \bar{c}_s \) in Figure 4.9b, respectively.
Notation

- \( c \) - Physical gas concentration, \( \text{mol m}^{-3} \)
- \( D_{\text{eff}} \) - Effective diffusivity inside SIP, \( \text{m}^2 \text{s}^{-1} \)
- \( D_s \) - Diffusivity of gas inside solid, \( \text{m}^2 \text{s}^{-1} \)
- \( D_l \) - Diffusivity of gas inside liquid, \( \text{m}^2 \text{s}^{-1} \)
- \( \bar{J} \) - Average gas flux into material, \( \text{mol s}^{-1} \text{m}^{-2} \)
- \( k_{2\text{eff}} \) - Effective second-order rate constant inside SIP, \( \text{m}^3 \text{mol}^{-1} \text{s}^{-1} \)
- \( k_2 \) - Second-order rate constant inside liquid, \( \text{m}^3 \text{mol}^{-1} \text{s}^{-1} \)
- \( L \) - Thickness of liquid layer, \( \text{m} \)
- \( L_{\text{SIP}} \) - Thickness of SIP layer, \( \text{m} \)
- \( P_s \) - Permeability of gas inside solid, \( \text{mol m}^{-1} \text{Pa}^{-1} \text{s}^{-1} \)
- \( P_l \) - Permeability of gas inside liquid, \( \text{mol m}^{-1} \text{Pa}^{-1} \text{s}^{-1} \)
- \( S_s \) - Solubility of gas inside solid, \( \text{mol m}^{-3} \text{Pa}^{-1} \)
- \( S_l \) - Solubility of gas inside liquid, \( \text{mol m}^{-3} \text{Pa}^{-1} \)
- \( r_{\text{droplet}} \) - Mean radius of droplets inside SIP, \( \text{m} \)
- \( t \) - Time, \( \text{s} \)
- \( w \) - Concentration of reactive species, \( \text{mol m}^{-3} \)
- \( w_0 \) - Average concentration of reactive species over all gas loadings, \( \text{mol m}^{-3} \)
- \( \varepsilon \) - Polymer fraction inside SIP
- \( \xi \) - Local effectiveness factor
- \( \phi \) - Thiele modulus
- \( \phi' \) - Local Thiele modulus
5 Thermodynamic Analysis of SIPs and MECS

Chapter Overview & Summary

In Chapter 3, particle-scale sorption kinetics were analysed, while in Chapter 4, bench-scale manufacturing methods were developed. Continuing along the same trajectory, in this chapter, process-scale applications of SIPs and MECS will be modelled.

This chapter focuses on the thermodynamic (or energetic) gains that SIPs or MECS could theoretically provide. These materials could contain non-aqueous solvents, with lower heat capacities and no waste energy from water evaporation during regeneration. They could also contain more concentrated solvents, which, due to their high viscosity or solid precipitation, couldn’t easily be used in a traditional process. Ultimately, though, any SIP or MECS system, however novel, is still subject to the laws of thermodynamics.

In this chapter, energy requirements for post-combustion CCS for a number of hypothetical SIP and MECS systems are estimated, and the equivalent work, \( W_{eq} \), required for separation and compression is compared with that in a sophisticated amine process: an Advanced Flash Stripper containing 8M piperazine modelled by Lin and Rochelle [27]. The SIPs or MECS are assumed to contain various ideal solvents, whose thermodynamic properties are optimised to minimise the work requirements of the process. The process simulation is itself an idealised model which would, if anything, underestimate the energy requirements for the immobilised solvent systems.

The results, for both aqueous and non-aqueous solvents, consistently show that SIPs or MECS systems cannot significantly outperform an optimised amine system utilising an advanced flash stripper. In the best cases considered, energy savings of \( \sim 10\% \) were observed, however the assumptions made in these simulations were probably unrealistic. The main challenge SIPs or MECS face is the sensible heat load, which is increased by the polymer shells, and which is harder to recover in a solid-
solid system. A second challenge is the low entropy of absorption into non-aqueous solvents, which limits the allowable enthalpy of absorption, which in turn limits the swing of the partial pressure with temperature. Finally, the very high efficiency of modern amine processes, in which the ‘lost’ energy of water evaporation is largely recovered, and which approach the thermodynamic optimum for solvent regeneration, leave little room for improvement which even an idealised SIP or MECS system could exploit. These results suggest that SIPs or MECS regenerated by steam are unlikely to be energetically superior to an amine system. However, the application of SIPs or MECS to novel processes, which utilise electrically-generated low grade heat or freely available waste heat to regenerate solvents at lower temperatures, is more plausible, and is discussed in some depth.

As in the previous two chapters, this chapter ends with a small addendum, in which the optimal solvent for carbon capture is discussed. This is a topic that has been broached by many authors. However, while they have consistently focussed on the required enthalpy of absorption, the need for a counterbalancing entropy of absorption (in order to ensure the absorption is reversible over the operating partial pressure and temperature range) has not previously been highlighted. We argue, through theoretical calculations and the results of process simulations, that for a solvent to be useful in a practical process, it must satisfy certain simple restrictions on both $\Delta h^0$ and $\Delta s^0$ of absorption. We show that popular alkanolamines, including monoethanolamine (MEA), diethanolamine (DEA) and piperazine, all satisfy these criteria. However, many ionic liquids do not, as their entropies of absorption are not sufficiently large and negative.
5.1 Introduction

Thermodynamics provides the scientific foundation for process simulation [155]. By applying the laws of thermodynamics, energy and entropy flows may be tracked, equilibrium compositions predicted, and driving forces for rate-based simulations obtained [153]. Thermodynamics also provides guidance in the development of new materials, providing subtle relationships between material properties that restrict the phase-space of physically-achievable substances [242].

Beyond its ubiquitous role in process simulation packages and in checking the consistency of data, thermodynamics has also been used to analyse emerging technologies, including solar thermal hydrogen production [243] adsorptive storage of methane or CO₂ in activated carbon [244], direct air capture by moisture swing sorbents [245] and many other processes [246, 247, 248, 249, 250, 251, 252]. In the field of post combustion carbon capture with chemical solvents, thermodynamic modelling has been used to predict the properties of an ‘optimal’ solvent [253, 254, 255, 256, 95], and also to highlight non-obvious tradeoffs that exist between various solvent properties. For example, it has been pointed out in a number of studies that, for absorption of CO₂ into aqueous chemical solvents, a low enthalpy of absorption does not necessarily lead to lower reboiler heat duties [82, 257, 258]. The reason for this is straightforward, and follows from the Gibbs-Duhem equation [259, 260] which must be satisfied by all chemical solvents to ensure thermodynamic consistency:

\[ \left( \frac{\partial \log p_{CO_2}}{\partial T} \right)_{p,x_0} \approx \frac{\Delta h}{RT^2}. \] (5.1)

This equation implies that solvents with low enthalpies of absorption (in itself a favourable property, as less heat must be supplied to release CO₂ from the solvent during regeneration) have CO₂ partial pressures which are less sensitive to temperature. This means that larger solvent circulation rates or temperature swings are required for thermal regeneration, leading (in either case) to greater sensible heat loads and (under some conditions [82]) greater energy losses due to water evaporation.
Abstract thermodynamic analyses have consistently shown that concentrated aqueous amines are close to optimal for carbon capture [253, 255, 254]. Yet research into novel solvents (ionic liquids, CO2BOLs, promoted carbonates, etc.) and novel contacting methods\textsuperscript{27} is as active as ever, with little critical thought as to whether such solvents could prove better in practice [261, 262]. Undoubtedly, this is caused in part by an ignorance (noted by Oexmann [82]) of the subtle tradeoffs implied by the Gibbs-Helmholtz equation. On top of this, rigorous process simulations are difficult, and require more data than is often available for newly-synthesised solvents. The thermodynamic analyses themselves are often complex, and do not offer any simple and practical metrics which could replace naive parameters such as $\Delta h$, and be used to evaluate the energetic performance of candidate solvents in a straightforward manner. The complexity of the abstract analyses also brings into question the generality of their findings. For example, Mathias et al. [253] developed a detailed CCS process flowsheet, using a rigorous eNRTL activity coefficient model regressed on data for CO$_2$ absorption into MDEA. They developed a family of ‘hypothetical’ solvents by varying the standard enthalpy and Gibbs free energy of formation of the MDEA\textsuperscript{+} cation at infinite dilution in water, and identified the solvents with optimal performance. It is unclear whether the results of such a specific analysis may be applied more broadly - to different solvents with different chemistries and different processing configurations - in a meaningful & quantitative way. These analyses also do not make it clear exactly why traditional amines consistently perform best among the candidates considered, nor do they provide a clear answer on the extent to which research into novel solvents could lead to more efficient processes.

These issues are particularly relevant to SIPs & MECS. Because practical problems related to solvent handling and mass transfer rates may prove less relevant for these technologies, the best solvents to immobilise inside these materials are likely to correspond closely to the thermodynamic optimum. From the beginning, each of these technologies have been described as ‘solvent enabling’ technologies, and the

\textsuperscript{27}this thesis being a case in point
hope that they may lead to significant energy savings has been repeatedly expressed [3, 100]. However, both technologies have a significant thermodynamic drawback: sensible heat loads are likely to be significantly greater because of the presence of the polymer shell, and, compounding this, solid-solid sensible heat recovery is likely to be less efficient than in a liquid solvent system. It is essential that the effect of increased sensible heat losses is understood, as even a slight increase in sensible heat loads could overwhelm any gains from utilising thermodynamically favourable solvents.

The primary goal of this work is to conduct a thermodynamic analysis of SIPs- and MECS-based systems in order to determine whether they are likely to lead to energy savings. A simple process utilising SIPs or MECS will be analysed, and values of the relevant physico-chemical properties (heat capacity, CO₂ capacity, polymer weight fraction, sensible heat recovery efficiency, etc.) will be established in order for the process to be competitive with the modern, piperazine-based process utilising an advanced flash stripper considered by Lin and Rochelle [27]. Particular emphasis will be placed on determining the sensible heat recovery efficiency needed for a SIP or MECS process to be competitive. As in previous thermodynamic analyses, a range of hypothetical solvents will be analysed, including non-aqueous and aqueous systems with various chemistries.

A secondary goal of this work is to illuminate, as clearly as possible, the reasons why some solvents perform better in post-combustion capture than others. To this end, simple process configurations and thermodynamic models will be used throughout, in order to avoid obfuscating the basic results and to keep the analysis as general as possible. Ultimately, the large and negative entropies of absorption into aqueous amines²⁸ (which are of the appropriate size to balance out an optimal enthalpy of absorption) will be identified as the fundamental reason these solvents are near the thermodynamic optimum.

²⁸This may be caused by the ionisation of the amine and carbonate/carbamate groups, and the ordering of water molecules around them.
5.2 Analysis of MECS/SIPs Containing Non-aqueous Solvents

We will begin by considering SIPs or MECS containing non-aqueous chemical solvents. For such solvents, energy losses associated with evaporation of water during regeneration do not exist. A typical example is the class of functionalised ionic liquids developed by Seo et al. [28]. These ionic liquids are *tunable*, as by varying the aprotic hetercyclic anions the enthalpy of absorption of CO\(_2\), \(\Delta h\), may be adjusted. Such solvents have several thermodynamic advantages over traditional aqueous amines: they react with CO\(_2\) via a 1:1 molar stoichiometry,\(^{29}\) their sensible heat capacity is roughly half that of an aqueous solvent, and, as mentioned above, no energy is wasted by evaporation of water in the stripper. Thermodynamic models of these liquids have been developed and experimentally validated, and similar models should also be valid for other non-aqueous solvents which react via a 1:1 stoichiometry.

In Figure 5.1, a simplified block diagram of a CCS process is shown; this process will form the basis of the analysis of SIPs and MECS. The process has been kept as simple as possible. No assumptions will be made as to the unit operations utilised within each block; instead, various streams will be assumed to approach equilibrium around each block. The various units are described below.

- **Absorber.** The rich sorbent stream leaving the absorber is assumed to be at equilibrium the flue gas entering the absorber, which has a CO\(_2\) partial pressure of 0.1 bar. The CO\(_2\) partial pressure of the lean solvent is required to be less than 0.01 bar, to ensure the absorber is capable of capturing 90\% of the CO\(_2\) in the flue gas. A partial pressure lower than this is allowable, and in some cases may be beneficial, as deeper regeneration increases the cyclic capacity of the solvent. Physically, the absorber could represent several unit operations: it may be an ideal multi-stage fluidised bed, an ideal moving packed bed or,

\(^{29}\)rather than the 1:2 molar stoichiometry of concentrated monoethalamine solutions
if a liquid solvent were considered,\textsuperscript{30} it may represent a traditional absorption column with random or structured packing. Each of these unit operations approach the ideal, counter-current contactor which is modelled here.

- **Sensible Heat Recovery.** Sensible heat recovery will be critical in any SIPs or MECS based process. In this model a fractional heat recovery efficiency, $\lambda$, is specified, but no further assumptions are made about equipment used to recover this heat (as will be discussed in section 5.4, heat recovery efficiencies of 60-80% can reasonably be hoped for in a SIPs/MECS system.)

- **Regeneration.** Sorbent regeneration is assumed to take place in a pure CO\textsubscript{2} environment at constant temperature and pressure. The CO\textsubscript{2} stream exiting this unit is assumed to be at equilibrium with the lean solvent stream, which is also exiting the unit. In practice, heat may be supplied via heating coils or by the CO\textsubscript{2} itself. Regeneration in pure CO\textsubscript{2} is necessary if steam condensation is to be avoided, however the downside is that the large partial pressure of CO\textsubscript{2} in the gas phase reduces the driving force for regeneration. Regeneration under vacuum conditions was not considered in this work. However, regeneration in consecutive units at various CO\textsubscript{2} pressures (in order to recover high-pressure CO\textsubscript{2} and reduce the compression load) is considered in section 5.2.4. Regeneration of an aqueous solvent using steam requires a more complex model, which will be developed in section 5.3. Regeneration using a non-aqueous, condensable stripping gas will be discussed in section 5.4.

An external energy source must be provided at four points within this process (see Oexmann and Kather \cite{82}):

- Heat of absorption: the chemical stripping of CO\textsubscript{2} is an endothermic process, and heat equal to $-\Delta h$ must be supplied during regeneration.

- Lost sensible heat: sensible heat recovery always involves some loss of energy, especially if heat is to be exchanged between two solid streams. In this work,\textsuperscript{30}

\textsuperscript{30}The analysis will also be applicable to a traditional solvent process in the limit where the polymer fraction of the SIPs/MECS goes to 0.
Figure 5.1: Block diagram of process for absorption and regeneration of MECS or SIPs.

It is assumed that only a fraction $\lambda < 1$ of the sensible heat required to heat the cool, rich stream up to the regeneration temperature may be sourced from cooling the hot, lean stream. The remainder of the sensible heat will be supplied within the stripper, in order to heat the rich sorbent stream up to the regeneration temperature.

- Work of compression: work required to compress the CO$_2$ up to 150 bar for transport and injection. The greater the regeneration pressure, the less work is required.

- Pumping work: work required to move sorbent around and to pump it into the pressurised stripper.

The model used in this analysis was intentionally kept as simple as possible. A more sophisticated model, developed using specialist simulation software, may be more accurate for a specific process: it could account for finite driving forces in the absorber and stripper, or temperature changes in the absorber. However, this would come at the cost of greater complexity and reduced generality. The simplifications made in this model also consistently favour SIPs and MECS, and so the calculated energy requirements represent a lower bound on the more accurate values a rigorous simulation would provide.

In order to evaluate SIPs’ or MECS’ thermodynamic performance, the total equivalent work will be calculated. For the compressor and pump, the equivalent work is the work required to run each unit. The work required to compress CO$_2$ from $p_2$ to 150 bar using a series of intercooled compressors was found by Lin and
Rochelle [27] to be:

\[ W_c \left( \frac{J}{\text{mol CO}_2} \right) = -3480 \log p_2(\text{bar}) + 14850; \quad 1 \leq p_2(\text{bar}) < 20 \] (5.2)

The pumping work is difficult to quantify without making too many assumptions about the specific details of the capture process. However, for any process in which SIPs or MECS are moved between an absorption and a stripper unit, the minimum work required to move the sorbent into the pressurised stripper will be equal to:

\[ W_p = \dot{V}(p_2 - 1 \text{ bar}) \] (5.3)

where \( \dot{V} \) is the volumetric flow rate of the sorbent per mole of CO\(_2\) captured. However, if it is assumed that \( \rho_{\text{MECS}} \approx 1000 \text{ kg m}^{-3} \), this term is negligible in almost all of the simulations that follow (only for the multi-stage regeneration, in which SIPs/MECS were compressed to 10 bar, was the term larger than 1 kJ mol\(^{-1}\) CO\(_2\); this is consistent with other analyses [253, 27].) Hence, pumping work was ignored for all systems except those discussed in section 5.2.4.

The equivalent work for the heat flow into the stripper is determined by multiplying the total heat flow by a Carnot efficiency:

\[ W = Q \times \left( \frac{T_2 - T_{\text{sink}}}{T_2} \right) \] (5.4)

In Eq. (5.4), it is assumed that the heat is supplied at temperature \( T_2 \), rather than at a higher temperature (such as the temperature of the available steam.) Lin and Rochelle [27] included an inefficiency of 0.9 on the right hand side of Eq. (5.4), as they reasoned that steam used by the carbon capture process could not be converted into work with 100\% thermodynamic efficiency. However, we do not want to make the assumption that the heat of regeneration in the stripper is sourced from another available heat source (such as steam redirected from a power plant.) Low grade heat may instead come from a source of work via a heat pump, and this may prove more
economical for the regeneration of solvents at $<100^\circ C$, especially if there is an excess of electricity (potentially of renewable origin) available. Under such circumstances, the inefficiency of 0.9 (or whatever value would be appropriate for a large-scale heat pump) would be on the left hand side of Eq. (5.4). In order to remain technology neutral, we assume ideal conversion between heat and work in this analysis.\textsuperscript{31}

The equivalent work that must be supplied to overcome the enthalpy of absorption is:

\[ W_h \left( \frac{J}{\text{mol CO}_2} \right) = -\Delta h \left( \frac{T_2 - T_{\text{sink}}}{T_2} \right) \]  

(5.5)

Meanwhile, the work required to overcome the lost sensible heat is given by:

\[ W_s \left( \frac{J}{\text{mol CO}_2} \right) = \left( 1 - \lambda \right) \frac{T_2 - T_1}{n(\xi_{\text{rich}} - \xi_{\text{lean}})} \left( c_p^{\text{solv}} + c_p^{\text{poly}} \frac{1-f}{f} \right) \left( \frac{T_2 - T_{\text{sink}}}{T_2} \right) \]  

(5.6)

where $\lambda$ is the fraction of sensible heat recovered in the heat exchanger, $\xi$ is the (chemical) loading\textsuperscript{32} of the solvent ($0 < \xi < 1$), $c_p$ is a specific heat capacity (of either the solvent or the polymer), $n$ is the total chemical capacity of the solvent (mol CO\textsubscript{2} per kg of solvent) and $f$ is the weight fraction of solvent in the SIPS/MECS.

This may be rewritten as:

\[ W_s = \frac{T_2 - T_1}{\xi_{\text{rich}} - \xi_{\text{lean}}} \frac{T_2 - T_{\text{sink}}}{T_2} \beta \]  

(5.7)

where

\[ \beta = \frac{1 - \lambda}{n} \left( c_p^{\text{solv}} + c_p^{\text{poly}} \frac{1-f}{f} \right) \]  

(5.8)

Physically, $\beta$ represents the sensible heat energy lost per mole of CO\textsubscript{2} which may be absorbed by the solvent per unit temperature difference between the absorber and the stripper; Eq. (5.7) demonstrates that all the various thermal parameters of the solvent collapse to this one variable. The simplest way to calculate $\beta$ for a given

\textsuperscript{31}This choice only changes the final result by around 1 kJ mol\textsuperscript{-1}, and doesn’t influence the conclusions of this analysis.

\textsuperscript{32}In this work, loading is defined as the CO\textsubscript{2} stored chemically divided by the total chemical capacity of CO\textsubscript{2}. Hence, even for an amine system like MEA, for which the molar loading of CO\textsubscript{2} per mole of MEA doesn’t usually exceed 0.5, $\xi$, in this work, still varies from 0 to 1.
SIPs/MECS system is via the formula (equivalent to Eq. (5.8)):

\[
\beta = \frac{(1 - \lambda)c_{\text{sip}}^p}{n f} \tag{5.9}
\]

\(c_{\text{sip}}^p\) is the heat capacity of the SIP, and \(n f\) is the total molar CO\(_2\) capacity per kg of the SIP. Hence, if a material has a mean heat capacity of 2000 J kg\(^{-1}\) K\(^{-1}\) and is capable of storing up to 2 mol CO\(_2\)/kg SIP (an optimistic but realistic value, see Figure 5.4), then if the heat recovery efficiency was 90\% (\(\lambda = 0.9\)), \(\beta\) would equal 100 J K\(^{-1}\) mol\(^{-1}\). Hence, for a good SIP/MECS system, the fractional lost sensible heat may be approximated by \(1 - \lambda \approx \beta/1000\); this value should be borne in mind when analysing the figures that follow.

Overall, then,

\[
W_{\text{eq}} = W_c + W_h + W_s \tag{5.10}
\]

\[
W_{\text{eq}} \left( \frac{\text{J}}{\text{mol CO}_2} \right) = -3480 \log p_2(\text{bar}) + 14850 + \frac{T_2 - T_{\text{sink}}}{T_2} \left( -\Delta h + \frac{T_2 - T_1}{\xi_{\text{lean}} - \xi_{\text{rich}}} \beta \right) \tag{5.11}
\]

\(W_{\text{eq}}\) may be calculated provided the unit operation temperatures and pressures, \(-\Delta h\), and the rich and lean solvent loadings are known. This equivalent work may then be compared with the value of \(~31 \text{kJ mol}^{-1}\) CO\(_2\) calculated by Lin and Rochelle [27] for an optimised 8M piperazine system utilising an advanced flash stripper.

### 5.2.1 Thermodynamic Model of a Non-aqueous Solvent

The rich and lean loadings of the sorbent, required to evaluate Eq. (5.11), may be calculated from a thermodynamic model of the vapor-liquid equilibrium between CO\(_2\) and the liquid solvent (this is possible because it was assumed that the sorbent streams exiting the absorber and stripper were at equilibrium with the flue gas and CO\(_2\) product stream, respectively.) To begin, a simple model of a non-aqueous chemical solvent will be used. It is assumed that a 1-1 reaction occurs between the
molecules of a pure liquid, $A$, and absorbed CO$_2$:

$$A + CO_2 \rightleftharpoons B \quad (5.12)$$

If it is further assumed that the solvent is ideal (and, in particular, that it follows Raoult’s law) then it is not difficult to show (see Appendix 5.I) that:

$$p_{CO_2} = \frac{\xi/K}{1 - \xi} \quad (5.13)$$

where $\xi$ is the chemical loading of the solvent (i.e. $\xi = C_B/(C_A + C_B)$) and $K$ is an equilibrium constant given by:

$$K = \exp \left( -\frac{\Delta g^0}{RT} \right) = \exp \left( -\frac{\Delta h^0}{RT} + \frac{\Delta s^0}{R} \right) \quad (5.14)$$

A similar model was used by Seo et al. [28] to successfully model a family of 9 ionic liquids which reacted with CO$_2$ via Reaction (5.12). $\Delta h^0$ and $\Delta s^0$ refer to the standard enthalpy and entropy of reaction (5.12). In particular, because a Raoultian standard state was considered, these are equal to:

$$\Delta h^0 = h_{B}^{f,0} - h_{CO_2,1 \text{ bar}}^{f,0} - h_{A}^{f,0} \quad (5.15)$$

$$\Delta s^0 = s_{B}^{f,0} - s_{CO_2,1 \text{ bar}}^{f,0} - s_{A}^{f,0} \quad (5.16)$$

where the superscript $f0$ indicates standard enthalpies and entropies of formation.

It should be clear that $\Delta h^0$ is not necessarily equal to $\Delta h$ of absorption in a practical system. However, it has been shown that $\Delta h$ is quite independent of both loading and temperature in a number of systems, and under the first of these assumptions $\Delta h^0 \approx \Delta h$ (see Kim and Svendson [263], Mathias [247], and also Gabrielsen et al. [264], who made the same assumption). Hence, $\Delta h^0 = \Delta h$ may be taken as a constant parameter: a property of a given solvent, approximately independent of temperature and loading, which may theoretically be altered in the search for
an optimal solvent or SIPs/MECS system. Because of the tradeoffs inherent in the Gibbs-Helmholtz equation\textsuperscript{33} there will be an optimal value of $\Delta h$ for a given process.

The standard entropy of absorption, $\Delta s^0$, is a much more interesting parameter, which will be discussed in more depth in section 5.5. For now, it is noted that, when Seo et al. \textsuperscript{28} modelled absorption into their tunable ionic liquids using this model, they assumed that $\Delta s^0$ took on the constant value of $-130 \text{ J K}^{-1} \text{ mol}^{-1}$ for all ionic liquids which they modelled.\textsuperscript{34} Under this assumption, they found reasonable agreement between the value of $\Delta h^0$ predicted by density functional theory (DFT) calculations, and the value for which the model developed above gave the best fit to their VLE data. They claimed that $\Delta s^0$ could be kept constant because the change of entropy is dominated by the change of phase of CO\textsubscript{2} which, according to Trouton’s law, would contribute on the order of $-88 \text{ J K}^{-1} \text{ mol}^{-1}$ \textsuperscript{153}. This argument has been made elsewhere \textsuperscript{265, 254, 245} however it is not true for all solvents, as $\Delta s^0$ can deviate significantly from $-130 \text{ J K}^{-1} \text{ mol}^{-1}$ in aqueous or precipitating systems (see section 5.5). However, it is probably a reasonable assumption for a wide class of non-aqueous ionic liquids, and the good fit of the VLE data of Seo et al. \textsuperscript{28} for 9 different ionic liquids supports this assumption. Hence, to begin this analysis, $\Delta s^0$ will be held constant at $-130 \text{ J K}^{-1} \text{ mol}^{-1}$.

Under these assumptions, the vapor-liquid equilibrium of a non-aqueous chemical solvent is governed by only one parameter: the enthalpy of absorption, $\Delta h$. Hence the equivalent work in Eq. (5.11) is given by:

$$ W_{eq} = W_{eq}(T_1, T_2, p_1, p_2, T_{\text{sink}}, \Delta h, \beta) \quad (5.17) $$

Setting $T_1 = T_{\text{sink}} = 40^\circ C$ and $p_1 = 0.1$ bar leaves:

$$ W_{eq} = W_{eq}(T_2, p_2, \Delta h, \beta) \quad (5.18) $$

In other words, the work of separation depends only on the regeneration conditions,

\textsuperscript{33}There are also some more subtle relationships with the entropy of absorption, see section 5.5.
\textsuperscript{34}This value of $\Delta s^0$ was for a standard state of CO\textsubscript{2}(g) at 1 bar.
Figure 5.2: Optimised equivalent work for a typical SIPs-based process, broken down into the equivalent work to overcome the sensible heat losses and the enthalpy of absorption, and the work required to compress the CO$_2$ to 150 bar. \( \beta = 150 \text{J K}^{-1} \text{mol}^{-1} \), which corresponds to \( \sim 85\% \) sensible heat recovery for a reasonable solvent (see section 5.3). \( T_2 \) and \( p_2 \) optimised for each \( \Delta h_{\text{abs}} \) to minimise \( W_{\text{eq}} \).

the enthalpy of absorption, and the parameter \( \beta \), which quantifies all the relevant terms related to sensible heat loss. In order to search for the ‘optimal’ SIP or MECS system, the minimal value of \( W_{\text{eq}} \) over all possible values of \( T_2 \) and \( p_2 \) was calculated for a range of \( \Delta h \) values with \( \beta \) held constant\(^{35} \) at \( 150 \text{J K}^{-1} \text{mol}^{-1} \). The minimal equivalent work, along with the various contributions, is shown in Figure 5.2. It is clear that a tradeoff exists between reducing \( \Delta h \) and reducing the sensible heat losses; the optimal solvent appears to be at \( \Delta h \approx -50 \text{kJ mol}^{-1} \).\(^{36} \) This optimal value is relatively independent of \( \beta \).

In general, the smaller the value of \( \beta \), the less significant are the sensible heat losses within the process. A major goal of this work is to determine just how efficient sensible heat recovery would need to be in a SIP or MECS based process in order for it to be competitive with an amine-based system. In order to compare these\(^{35} \)This corresponds to 85\% sensible heat recovery from a SIP with total CO$_2$ capacity of 2 mol/kg SIP and net heat capacity of 2000 J K$^{-1}$ kg$^{-1}$ SIP.

\(^{36} \)This is substantially smaller than the value of -85 kJ/mol for MEA, which is often found to be optimal [254]; this discrepancy is related to the value of \( \Delta s^0 \) used in this analysis, and is discussed further in section 5.5.

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systems, the optimal value of $W_{eq}$ over all values of $T_2$, $p_2$ and $\Delta h$ was found for a range of $\beta$ values (i.e. for a given $\beta$, the minimal $W_{eq}$ over all regeneration conditions and solvents was found.) The same global optimima were found using a differential evolution algorithm and a BFGS algorithm [266, 267]. This minimal equivalent work is plotted in Figure 5.3 as a function of $\beta$, and the equivalent work of an optimised piperazine-based process [27] is also shown. It is clear that, over all regeneration conditions and non-aqueous chemical solvents considered, a SIPs or MECS based process will only be thermodynamically competitive provided $\beta \leq 80 \text{ J mol}^{-1} \text{ K}^{-1}$.

Hence, for a candidate SIP or MECS, the sensible heat recovery efficiency must be at least as large as:

$$\lambda \geq \lambda_{\text{min}} = 1 - \frac{80(n_f)}{c_p}$$

(5.19)

Minimal values of $\lambda$ are plotted in Figure 5.4 for a range of hypothetical SIPs or MECS containing various non-aqueous ionic liquids which react with CO$_2$ according to a 1-1 stoichiometry. It is clear that, for each of these systems, the sensible heat recovery efficiency will need to be between 92-96% for them to be competitive with modern amine-based processes.

This result is unsurprising. The energy required to heat a solvent from 40°C to 110°C often exceeds the enthalpy required to desorb the CO$_2$ (for 30wt% K$_2$CO$_3$, the former is around 300 kJ/kg solvent, while the latter is around 50 – 80 kJ/kg solvent, depending on the cyclic capacity.) Hence, small variations in the sensible heat recovery efficiency can overwhelm any gains from using more efficient solvents. This is exacerbated, in the case of SIPs/MECS, by the polymer shell, which significantly increases the sensible heat load, effectively neutralising one advantage (low $c_p$ values) ionic liquids have over aqueous solvents. The other advantage ionic liquids posses - no water evaporation in the stripper - is also largely negated by the sophisticated advanced flash stripper design, in which much of the heat of condensation is recovered. Finally, it will be seen below that the restriction of $\Delta s^0 = -130 \text{ J K}^{-1} \text{ mol}^{-1}$ limits the efficiency of the solvent process.

When considering the results shown in Figure 5.4, it should be remembered
Figure 5.3: Minimal equivalent work required to capture 1 mol of CO2 as a function of $\beta$, compared with the equivalent work required by an advanced flash stripper and a simple stripper. Both of these processes were analysed by Lin and Rochelle [27], and used an aqueous, 8 M piperazine solution. For a SIP/MECS with good CO2 capacity, sensible heat losses are on the order of $1 - \lambda \approx \beta/1000$.

Figure 5.4: Minimal sensible heat recovery efficiency, $\lambda$, required for a SIP- or MECS- based process to be competitive with an advanced flash stripper design [27]. The capacities of the ionic liquids are taken from [28, 29, 30]. $f = 0.5$, $c_{p}^{\text{PDMS}} = 1.5 \text{kJ kg}^{-1} \text{K}^{-1}$ [31]. $c_{p}^{\text{IL}} = 2000 \text{J kg}^{-1} \text{K}$. $\beta = 80 \text{J K}^{-1} \text{mol}^{-1}$. 

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that the predicted values of $\lambda$ represent lower bounds on the required sensible heat recovery efficiency. Throughout this analysis, any simplifying assumptions were consistently in favour of SIPs and MECS (for example, perfect equilibrium was assumed between streams exiting the absorber/stripper, pumping duties were ignored, and the heat source to the stripper was supplied at exactly the stripper temperature). The values of $\lambda$ shown in Figure 5.4 will already be challenging to obtain in a practical solid-solid heat recovery system (see section 5.4), and in reality even larger heat recovery efficiencies may be required. Compounding this, the values of $\lambda$ were simply for thermodynamic equality between a SIPs/MECS system and a traditional process; presumably significant energy savings would be required before these technologies could be feasible. These results suggest that it will be challenging for processes utilising SIPs or MECS containing non-aqueous solvents to be competitive with an amine based absorption process, at least if they react with a 1-1 molar stoichiometry and have $\Delta s^0 \approx -130 \text{ J mol}^{-1} \text{ K}^{-1}$.

### 5.2.2 Non-Aqueous Solvents with Alternative Chemistries

The analysis may easily be extended to non-aqueous solvents which react according to more complex stoichiometries. For example, non-aqueous ionic liquids functionalised with reactive amine sites may react [30] via a 1:2 stoichiometry similar to that of MEA:

$$\text{CO}_2 + 2 \text{RNH}_2 \rightleftharpoons \text{RNHCO}_2^- + \text{RNH}_3^+ \quad (5.20)$$

Consider a non-aqueous chemical solvent which reacts according to the following, more general stoichiometry:

$$\text{CO}_2(g) + m_1 \text{B} \rightleftharpoons m_2 \text{C} + m_3 \text{D} \quad (5.21)$$

where $m_1, m_2$ and $m_3$ are arbitrary constants. For an ideal solution in which all species are present in stoichiometric quantities, the partial pressure of CO$_2$ above
Figure 5.5: Isotherms at $T = 313 \text{K}$ for various chemistries of the form of Reaction (5.21).

this solvent is given by the function (see Appendix 5.1):

$$p_{\text{CO}_2}(\xi) = \frac{1}{K} \frac{(m_3 \xi)^{m_3}(m_2 \xi)^{m_2}}{(m_1(1 - \xi))^{m_1}} \left(m_1 + (m_2 + m_3 - m_1)\xi\right)^{m_1-m_2-m_3} \quad (5.22)$$

where $K$ is defined as in Eq. (5.14). Several of these isotherms are plotted in Figure 5.5. The analysis described above was repeated, but the optimisation was instead carried out over $m_1, m_2$ and $m_3$, as well as $T_2, p_2$ and $\Delta h$, for various values of $\beta$. For all values of $\beta$, the optimal stoichiometry was found to be a 1-1 solvent, with $m_1 = 1$ and $m_2 = 1$ and $m_3 = 0$ or $m_2 = 0$ and $m_3 = 1$. Hence, the conclusions of the previous section may be extended to non-aqueous solvents with a much broader range of stoichiometries.

5.2.3 Non-Aqueous Solvents with Variable Entropy of Absorption

To this point, it has been assumed that all non-aqueous solvents have a standard entropy of absorption of $-130 \text{J K}^{-1} \text{mol}^{-1}$. This has been based on the claim, made within the literature on chemically reactive ionic liquids, that the entropy of absorption is relatively constant and close to this value, because it is dominated by the phase change of the CO$_2$ molecule [265, 28, 254]. However, Wang et al. [245]
noted that the standard entropy of absorption can take on other, more negative values: $\Delta s^0 = -219 \text{ J K}^{-1} \text{ mol}^{-1}$ for CO$_2$ absorption onto solid Na$_2$CO$_3$, and $\Delta s^0$ also equals $-219 \text{ J K}^{-1} \text{ mol}^{-1}$ for CO$_2$ absorption into aqueous MEA$^{37}$[264]. In each case, the large negative value of $\Delta s^0$ is likely related to the role of water (either as a solvent or a reactant), and so these values may not invalidate the assumption of $\Delta s^0 = -130 \text{ J K}^{-1} \text{ mol}^{-1}$ for ionic liquids. Nevertheless, it is worthwhile determining how the process performance may be improved by varying the entropy of absorption.

The analysis was repeated for a general chemistry of the form of Eq. (5.21). The minimum value of $W_{eq}$ was found among the possible values of $p_2 \geq 1 \text{ bar}$, $T_2$, $m$, $n$, $q$, $\Delta h^0$, and $\Delta s^0$ was also allowed to vary, though it was restricted in various runs to values greater than $-150 \text{ J K}^{-1} \text{ mol}^{-1}$, $-200 \text{ J K}^{-1} \text{ mol}^{-1}$ and $-250 \text{ J K}^{-1} \text{ mol}^{-1}$. The results are shown in Figure 5.6. It is clear that allowing the entropy of absorption to be smaller than $-130 \text{ J K}^{-1} \text{ mol}^{-1}$ can produce more efficient solvent systems, and in all cases the optimal $\Delta s^0$ was on the lower boundary of the allowed domain. However, even for $\Delta s^0 \geq -250 \text{ J K}^{-1} \text{ mol}^{-1}$, the equivalent work values are only marginally smaller than those found in an advanced flash stripper process, and $W_{eq}$ will only be smaller if $\beta \leq 280 \text{ J mol}^{-1}$. As shown in Figure 5.7, in a practical SIPs/MECS system, this corresponds to sensible heat recovery on the order of 75-85%, which is on the upper end of what is likely to be achievable in a solid-solid system (see section 5.4). It is also unclear whether non-aqueous solvents with such large values of $-\Delta s^0$ could be synthesised.

In this system, there was no ‘optimal’ value for the entropy of absorption; instead, $W_{eq}$ continued to decrease as $-\Delta s^0$ increased. Physically, larger values of $-\Delta s^0$ enabled larger values of $-\Delta h^0$, which, in turn, enabled lower regeneration temperatures. The latter follows from the Gibbs-Helmholtz equation, which implies that the thermal sensitivity of the partial pressure, $\partial \log p / \partial T$, grows with $-\Delta h^0$. A large value of $\partial \log p / \partial T$ is particularly important for non-aqueous solvents regenerated in pure CO$_2$. Because there is no steam available to reduce the CO$_2$

$^{37}$In each case, $\Delta s^0$ was based on a standard CO$_2$ pressure of 1 bar.
Figure 5.6: Minimal equivalent work for several non-aqueous solvents with various restrictions on the allowable values of $\Delta s^0$ within the optimisation. Equivalent work values are compared against the Advanced Flash Stripper of Lin and Rochelle [27]. For a SIP/MECS system with good CO$_2$ capacity, sensible heat recovery is on the order of $1 - \lambda \approx \beta/1000$.

partial pressure, the equilibrium value of $p_{CO_2}$ in the lean solvent needs to vary from 0.01 bar at the absorber temperature to $> 1$ bar at the regeneration temperature. However, large values of $-\Delta h^0$ are only practical with sufficiently large values of $-\Delta s^0$, as the enthalpic driving force (which favours absorption) must be balanced by an equally large entropic driving force (which favours desorption) in order for the absorption process to be reversible. These ideas and their implications are discussed further in section 5.5.

5.2.4 Multiple Regeneration Stages.

A final way in which the equivalent work of regeneration of a non-aqueous solvent could be reduced is to conduct regeneration in multiple, consecutive stages in series, with the total CO$_2$ pressure decreasing from stage to stage. In the first few stages, high-pressure CO$_2$ is produced (reducing compression duties) while in the final stages lower pressures are used to remove more CO$_2$ (increasing the cyclic capacity of the sorbent.) At the most basic level, this arrangement leads to energy savings because it takes less energy to pressurise the SIPs/MECS than to compress the
Figure 5.7: Minimal sensible heat recovery efficiency, $\lambda$, required for a SIP- or MECS- based process to be competitive with an advanced flash stripper design [27], assuming $\Delta s^0 \leq -250$ J K$^{-1}$ mol$^{-1}$. The capacities of the ionic liquids are taken from [28, 29, 30]. $f = 0.5$, $c_p^{\text{PDMS}} = 1.5$ kJ kg$^{-1}$ K$^{-1}$ [31]. $c_p^{\text{IL}} = 2000$ J kg$^{-1}$ K [28]. $\beta = 280$ J K$^{-1}$ mol$^{-1}$.

A regeneration system consisting of three units in series at progressively lower pressures was modelled. The pressures in each stage were chosen so that each unit produced $1/3$ of the total CO$_2$ product. Hence, the pressure in the first stage was set so that the sorbent at equilibrium with the CO$_2$ generated in the stage had chemical loading $\xi_{\text{lean}} + (2/3)(\xi_{\text{rich}} - \xi_{\text{lean}})$, while sorbent leaving the second stage had chemical conversion $\xi_{\text{lean}} + (1/3)(\xi_{\text{rich}} - \xi_{\text{lean}})$. The stages were each at the same temperature, $T_2$, while, as before, the pressure of the final stage, $p_2$, (which, along with $T_2$, determines $\xi_{\text{lean}}$) was a variable to be set within system. Pumping duties were estimated based on the pressure in the first stage and $\rho_{\text{MECS}} = 1000$ kg m$^{-3}$, as all of the sorbent passed through this stage.

As before, the minimal value of $W_{eq}$ was calculated by optimising over $T_2$, $p_2$, $\Delta h^0$, $m$, $n$, $q$ and $\Delta s^0$, with $\Delta s^0$ restricted to greater than $-130$, $-150$, $-200$ and $-250$ J K$^{-1}$ mol$^{-1}$ (in each case, the optimal $\Delta s^0$ was the value on the boundary.)

As can be seen in Figure 5.8, multiple regeneration stages reduced the work re-
Figure 5.8: Minimal equivalent work requirements for various non-aqueous solvents regenerated using either one regeneration unit or three in series, compared against an Advanced Flash Stripper [27]. For a SIP/MECS system with good CO2 capacity, $1 - \lambda \approx \beta/1000$.

requirements by 1-3 kJ mol$^{-1}$ CO2. Furthermore, energy savings of up to $\sim 3$ kJ mol$^{-1}$ CO2 (relative to an advanced flash stripper) were possible when $-\Delta s^0 = 250$ J K$^{-1}$ mol$^{-1}$ and $\beta = 200$ JK$^{-1}$ mol$^{-1}$ (corresponding to 80% sensible heat recovery in a good SIPs/MECS system). However, for solvents with $\Delta s^0 \geq -130$ J K$^{-1}$ mol$^{-1}$ the equivalent work matched the advanced flash stripper at $\beta \approx 140$ J mol$^{-1}$ K$^{-1}$, which corresponds to 85–95% sensible heat recovery efficiency for the systems considered in Figures 5.4 and 5.7.

5.2.5 Summary: SIPs Containing Non-Aqueous Solvents

In this section, the work required to capture CO2 from a flue gas stream using SIPs or MECS containing non-aqueous chemical solvents was estimated. The analysis considered an idealised carbon capture process, in which streams exiting both the absorber and the stripper reached thermodynamic equilibrium. In spite of this and other favourable assumptions, the model predicted that substantial sensible heat recovery (typically on the order of $\sim 90\%$) would be required for a SIP/MECS systems to be competitive with an optimised amine-based process. These sensible
heat recovery efficiencies will be difficult to achieve in a solid-solid system (see Section 5.4.) This conclusion held true over a range of reaction stoichiometries, and also when a single regeneration unit was replaced by three units operating in series.

The only conditions under which the model predicted significant energy savings were for non-aqueous solvents with very large and negative $\Delta s^0$ and $\Delta h^0$ values regenerated at multiple pressures. These solvents underwent large partial pressure changes, allowing regeneration to occur at moderate temperatures and elevated pressures; the large partial pressure swing is particularly important for non-aqueous solvents regenerated in a pure CO2 environment. However, while large values of $-\Delta s^0$ have been observed in aqueous systems, there is evidence to suggest they are less likely to occur in non-aqueous solvents such as ionic liquids (see section 5.5). However, even if such solvents could be synthesised, they would only lead to energy savings on the order of 10%, compared with an advanced flash stripper, and those could only be achieved with reasonably efficient sensible heat recovery. If the various idealisations in the model considered here are also considered, it seems unlikely that a SIP or MECS system containing a non-aqueous chemical solvent could be used to significantly reduce the parasitic energy load of a carbon capture process.

While this analysis only considered ideal solvents, it is unlikely that the introduction of non-idealities would lead to solvents with significantly improved performance. Activity coefficients can change the shape of the isotherms of a given solvent (i.e. the composition-dependence of the partial pressure), but they are unable to change the temperature-dependence of the partial pressure (even in the most non-ideal system, this will still be governed by the Gibbs-Helmholtz equation.) A wide range of isotherms have already been considered in this analysis (see Figure 5.5), and even though the 1–1 stoichiometry was always optimal, experiments with a number of alternative isotherms (e.g. ‘MDEA’ chemistry, with $(m_1, m_2, m_3) = (1, 1, 1)$ or ‘MEA’ chemistry with $(m_1, m_2, m_3) = (2, 1, 1)$) only led to increases in $W_{eq}$ on the order of 1–2 kJ mol$^{-1}$. It seems likely that the trade-off between $\Delta h^0$ and the partial pressure swing will limit the minimal values of $W_{eq}$ in any non-ideal system, just as it has in
all of the ideal systems considered here.

By optimising over all possible thermodynamic properties of an ideal non-aqueous solvent, it has been shown that, in spite of their reduced sensible heat capacities and the lack of heat of condensation, these solvents are unlikely to be a ‘magic bullet’ for CCS, especially when coupled with SIPs or MECS, which increase the sensible heat load. It must be emphasised, however, that the difficulty of developing a process more efficient than an optimised amine system is simply the result of how close such processes are to the thermodynamic optimum, and how little room for improvement they leave. According to Lin and Rochelle ([27], Fig. 5) the sum of the minimum possible work of separation, the minimum possible work of compression, and the work lost in the absorber is between 20-25 kJ/mol CO₂. As no attempt has been made to recover heat or otherwise improve the efficiency of the absorber, this sets a lower bound on the possible values of \( W_{\text{eq}} \). In this light, the results of this analysis should not be viewed as failures of the SIP or MECS technologies. Instead, this analysis, and particularly Figure 5.8, shows how, under extreme and likely-unachievable conditions, an ideal SIP- or MECS-based process could extract out just a little more of the remaining efficiency gains that amine-based processes have been unable to exploit. In particular, the problem of the wasted heat of condensation has largely been resolved by the Advanced Flash Stripper design; this will be seen more clearly when aqueous solvents are considered in the next section.

5.3 SIPs or MECS Containing Aqueous Solvents

If SIPs or MECS containing non-aqueous chemical solvents are unlikely to lead to large energy savings, it would be surprising to find that aqueous solvents - with their evaporative energy loads and larger heat capacities - had better performance. However, aqueous solvents possess two unique advantages: the possibility of larger values of \( -\Delta s^0 \), and reduced CO₂ partial pressures in the stripper via steam regeneration. The potential value of the first point has already been encountered (see Figure 5.8). The second point refers to the fact that, because steam may be used to regenerate
the solvent over multiple counter-current equilibrium stages, the lean solvent may
exit the regenerator at equilibrium with a CO2/H2O mixture for which $p_{CO2} \ll
1$ bar. This means much lower lean loadings can be achieved without the need to
pull a vacuum or regenerate the sorbent at very high temperatures. In practice, a
balance must be struck between the depth of the regeneration and the steam flow
rate.

5.3.1 Process Model Development

An idealised process model (similar to that shown in Figure 5.1) was developed for
an aqueous solvent system. The model was similar to the one developed previously,
but there were a few differences in the modelling of the various unit operations.

- **Absorption:** As before, the partial pressure of CO2 above the rich sorbent
  exiting the absorber was set equal to $p_{CO2}$ in the flue gas, 0.1 bar, and the
  partial pressure in the lean sorbent was at least 10 times smaller than this, to
  allow for 90% CO2 capture. Water evaporation and temperature changes in
  the absorber were ignored.

- **Sensible Heat Recovery:** Only a fraction, $\lambda$, of the sensible heat in the
  hot, lean sorbent was transferred to the cool, rich sorbent, and the remaining
  energy required to heat the sorbent up to the inlet temperature in the stripper,
  $T_2$, was supplied by a heat source at the temperature of the steam, $T_{steam}$. The
difference in sensible heat capacity between the lean and rich solvent streams
was ignored. Hence, as in the non-aqueous analysis, the lost sensible heat was
numerically equal to:

$$Q_s \left( \frac{J}{\text{mol CO2}} \right) = \frac{T_2 - T_1}{\xi_{\text{lean}} - \xi_{\text{rich}}} \beta$$

(5.23)

where $\beta$ is defined by (see Eq. (5.8)):

$$\beta = \frac{1 - \lambda}{n} \left( c_{p}^{\text{solv}} + c_{p}^{\text{poly}} \frac{1 - f}{f} \right) = \frac{(1 - \lambda)c_{p}^{\text{SIP}}}{nf}$$

(5.24)
• **Regeneration:** The regeneration of an aqueous solvent is complicated by the presence of steam, which supplies the energy for regeneration and can also reduce the CO₂ partial pressure in the gas phase. In this work, the regeneration unit was modelled as a series of adiabatic, counter-current equilibrium stages operating at steady-state and constant pressure, \( p_{\text{regen}} \). In each stage, steam condensing from the gas to the liquid supplies the enthalpy of desorption to remove the CO₂. Mass and energy balances, along with a VLE model, were used to determine the outlet compositions and the temperatures of each stage. These must be solved simultaneously for all stages because of the counter-current nature of the flow. For simplicity, the solution is treated as ideal throughout the calculation; details on the simulation may be found in Appendix 5.II.

This unit-operation model is far more complicated than anything else within the process simulation. When van Neirop et al. [254], developed a similar, simplified thermodynamic model for a carbon capture operation, they used a much simpler model for the stripper. They assumed an outlet lean chemical loading of \( \xi_{\text{lean}} = 0.05 \), and assumed the steam flow rate was equal to the amount of steam required to supply the enthalpy of desorption, \( -\Delta h_{\text{abs}} \), plus the steam exiting with the CO₂ product, which they assumed to be at equilibrium with the hot, rich solvent. While such a simple model is enticing, it is insufficient on several fronts. First, by setting \( \xi_{\text{lean}} = 0.05 \) for all solvents, the model does not distinguish between solvents which are easy to regenerate (those with large values of \( -\Delta h^0 \propto \partial \log p_{\text{CO}_2}/\partial T \)), and solvents that are hard to regenerate (those with small values \( -\Delta h^0 \)), which is a central concern in this analysis. Even more concerningly, and related to the first issue, their model fails to account for the dual role that steam plays within a stripper, in supplying energy for regeneration and reducing the CO₂ partial pressure. When the steam flow rate is set to the *energetic* minimum (as suggested by van Neirop et al. [254]) there is often not enough steam in the column to
sufficiently reduce the CO₂ partial pressure in the gas phase near the bottom of the column, and small lean loadings cannot be achieved. Graphically, the operating line crosses above the equilibrium line, and regeneration to lean loadings is impossible. Experiments with the more complex model suggested that, for solvents with good thermodynamic properties, lean loadings of 0.05 – 0.15 can be achieved at the minimum steam flow rate, however for most hypothetical solvents considered in this work, even a stripper with many stages is unable to reduce the lean loading to near these values when operated with such little steam. A complex, multi-stage model of the stripper was developed because the authors could find no alternative, simple means of reliably estimating the steam required for regeneration. The complexity of the various ‘shortcut’ methods for stripper design available in the literature [268, 269] suggest that no such estimate is possible.

The two unknown variables within the model are the number of stages, \( N \), and the ratio of the molar flow rate of steam to the molar flow rate of chemically bound CO₂ entering with the solvent, \( \gamma \). As in the non-aqueous case, heat equal to \(-\Delta h_{\text{abs}}\) must be supplied by the steam to release each mole of absorbed CO₂. However, in the aqueous case, there is an extra energy contribution: the heat of evaporation for all the ‘waste’ steam exiting the unit. This is equal to

\[
Q_{\text{cond}} \left( \frac{J}{\text{mol CO}_2} \right) = \frac{y_w}{y_{CO_2}} \Delta h_{\text{vap}}
\]

where \( y_w \) and \( y_{CO_2} \) are the mole fractions of water and CO₂ in the gas leaving the stripper, and \( \Delta h_{\text{vap}} \) is the energy of vaporisation of water. After this water is condensed, the remaining CO₂ is compressed from the stripper pressure (it’s reasonable to ignore the pressure drop through the condenser [27]) to 150 bar via the same equation used previously:

\[
W_c \left( \frac{J}{\text{mol CO}_2} \right) = -3480 \log p_{\text{regen}}(\text{bar}) + 14850; \quad 1 \leq p_2(\text{bar}) < 20
\]

\(^{38}\)‘Good thermodynamic properties’ in the sense that \( \Delta h^0 \approx T \Delta s^0 \), see section 5.5.
If the stripper is operated at high pressure, work must also be supplied to compress the entering steam. An efficiency of 80% was assumed for the compressor, giving

\[
W_{c,w} \left( \frac{J}{\text{mol CO}_2} \right) = \left( \frac{\gamma_{\text{rich}}}{\xi_{\text{rich}} - \xi_{\text{lean}}} \right) \frac{RT_{\text{steam}}}{0.8} \log \left( \frac{p_{\text{renew}}}{1 \text{ bar}} \right)
\]  
(5.27)

As in the previous section, the total equivalent work was calculated as a sum of these various contributions, with heat flows converted to work flows via a Carnot efficiency based on the temperature of steam. Overall:

\[
W_{eq} \left( \frac{J}{\text{mol CO}_2} \right) = W_c + W_{c,w} + (Q_{\text{cond}} + Q_h + Q_s) \frac{T_{\text{steam}} - T_{\text{sink}}}{T_{\text{steam}}}
\]  
(5.28)

\[
W_{eq} \left( \frac{J}{\text{mol CO}_2} \right) = -3480 \log y_{\text{CO}_2} p_{\text{renew}} \text{ (bar)} + 14850
\]

\[
+ \left( \frac{\gamma_{\text{rich}}}{\xi_{\text{rich}} - \xi_{\text{lean}}} \right) \frac{RT_{\text{steam}}}{0.8} \log \left( \frac{p_{\text{renew}}}{1 \text{ bar}} \right)
\]

\[
+ \frac{T_{\text{steam}} - T_{\text{sink}}}{T_{\text{steam}}} \left( -\Delta h_{\text{abs}} + \frac{T_2 - T_1}{\xi_{\text{lean}} - \xi_{\text{rich}}} \beta + \frac{y_w}{y_{\text{CO}_2}} \Delta h_{\text{vap}} \right)
\]  
(5.29)

The stripper model also required explicit values for the mole fraction of water in the solvent, \(x_w\), and the solvent weight fraction, \(f\).

Overall, then,

\[
W_{eq} = W_{eq}(\xi_{\text{rich}}, \xi_{\text{lean}}, y_w, y_{\text{CO}_2}, \gamma, T_{\text{steam}}, p_{\text{renew}}, T_2, T_{\text{sink}}, \Delta h_{\text{abs}}, \Delta h_{\text{vap}}, x_w, f, \beta, N).
\]  
(5.30)

Of these variables, two will be held constant (\(T_{\text{sink}} = 313 \text{ K}, \Delta h_{\text{vap}} = -40 \text{ kJ/mol}\)), \(\xi_{\text{lean}}, y_w, y_{\text{CO}_2}\) will be calculated within the stripper model, and \(\xi_{\text{rich}}\) will be calculated from the VLE model discussed below. The rest will need to be explicitly specified.
5.3.2 Aqueous Solvent Thermodynamics

The aqueous solvent was modelled as an ideal solution with a Henrian standard state. The simple chemical reaction,

\[ \text{CO}_2(g) + A \rightleftharpoons B \]  

was considered, where \( A \) and \( B \) were species dissolved in the water. This stoichiometry provided the best performance for non-aqueous solvents, and was the only stoichiometry considered here. Because the solution was ideal, the partial pressure was given by:

\[ p_{\text{CO}_2} = \frac{\xi}{K (1 - \xi)} \]  

where \( \xi \) was the chemical loading of the solvent, and the equilibrium constant was given by:

\[ K = \exp \left( -\frac{\Delta h^0 - T \Delta s^0}{RT} \right) \]  

where \( \Delta h^0 \) and \( \Delta s^0 \) are the standard enthalpy and entropy of reaction; the standard state of \( A \) and \( B \) is at infinite dilution in water, while the standard state of \( \text{CO}_2 \) was an ideal gas at 1 bar.

5.3.3 Overall Work Requirement

With this thermodynamic model and the model for the regeneration unit, Eq. (5.30) reduces to

\[ W_{\text{eq}} = W_{\text{eq}}(T_{\text{steam}}, p_{\text{regen}}, T_2, \Delta h^0, \Delta s^0, x_w, f, \beta, N) \]  

Values of \( T_{\text{steam}}, p_{\text{regen}}, T_2, \Delta h^0 \) and \( \Delta s^0 \) which minimised \( W_{\text{eq}} \) were found for various values of \( \beta \) and \( N \) (Figure 5.9), with \( f = 0.9 \) (an optimistic value, which may be difficult to achieve in practice) and \( x_w = 0.9 \) (approximately equal to the value in 30wt% MEA). Unsurprisingly, the minimal work requirement reduced as the number of stages increased, and in the limit of many stages and \( \beta \approx 200 \text{JK}^{-1} \text{mol}^{-1} \), which corresponds to a reasonable heat recovery efficiency of 90% (reasonable for a solvent
system [70] but probably not for a MECS or SIP system, see section 5.4) the work requirements approach those of the simple stripper modelled by Lin and Rochelle [27]. For heat recoveries less efficient than those found in a solvent system, the process requires more work than even the simple stripper, let alone the advanced flash stripper.

The difference between $W_{eq}$ for the simple stripper and the advanced flash stripper may largely be attributed to the recovery of the heat of condensation (see Eq. (5.25)), which saves on the order of 4 kJ mol$^{-1}$ CO$_2$ (compare Figs. 6, 7 and 11 in [27]). The model considered in this work does not attempt the recovery of the heat of condensation, and the amount of lost work is on the order of 5 – 6 kJ mol$^{-1}$ (see Figure 5.10). If this could be recovered, the process would be competitive with the advanced flash stripper, provided reasonable ($\lambda \approx 0.9$) heat recovery could be achieved.

The optimal pressure varied from 1 – 1.5 bar, and the optimal steam temperature was always at the minimal value of 383 K, presumably because the Carnot efficiency factor outweighed any possible gains from using hotter steam. The optimal values of $\Delta h^0$ and $\Delta s^0$ were correlated in an interesting manner, which will be discussed in Section 5.5.

This analysis was repeated for an extremely-concentrated solvent with $x_w = 0.8$ (for 30wt% MEA, $x_w \approx 0.9$.) This system was able to outperform the simple stripper (see Figure 5.11.) Furthermore, the lost work of condensation was around 7 kJ/mol CO$_2$ (Figure 5.12), and if this could be recovered, and if the sensible heat recovery was as good as in a traditional solvent system (which would correspond to $\beta \sim 100$ JK$^{-1}$ mol$^{-1}$ for this system), then $W_{eq}$ could be reduced to around 26 kJ/mol CO$_2$, slightly lower than that in the advanced flash stripper reported by Lin et al. [27], and competitive with the ammonia-based advanced flash stripper process simulated by Jiang et al. [93]. This does, however, seems rather unrealistic.

39 Assuming $n_{SIP} = 2.5$ mol CO$_2$/kg sorbent (the capacity of 30wt% MEA) and $c_{p}^{SIP} \approx 4000$ J/kg.K, then $\beta = (1 - \lambda)c_{p}^{SIP}/n_{SIP} = 200$ JK$^{-1}$ mol$^{-1}$ corresponds to just under 90% sensible heat recovery. For $x_w = 0.8$, $n_{SIP}$ will be approximately twice as large, and so $\beta \sim 100$ JK$^{-1}$ mol$^{-1}$ will correspond to around 90% sensible heat recovery.
Figure 5.9: Minimal equivalent work to separate 1 mol of CO\textsubscript{2} from a 10 mol\% flue gas stream using SIPs/MECS containing an ideal aqueous solvent, compared to the equivalent work for a simple stripper and an Advanced Flash Stripper utilising 8M aqueous piperazine [27]. \(x_w = 0.9, f = 0.9\). \(\beta \approx 200 \text{JK}^{-1}\text{mol}^{-1}\) corresponds to \(\lambda \approx 0.9\) for a good SIP systems.

Figure 5.10: Value of \(W_{\text{cond}}\) for optimal solvent and process conditions at various values of \(N\). \(f = 0.9, x_w = 0.9\)
Figure 5.11: Minimal equivalent work to separate 1 mol of CO\textsubscript{2} from a 10% flue gas stream using SIPs/MECS containing a highly concentrated (capacity $\approx 12$ mol/kg H\textsubscript{2}O), ideal aqueous solvent, compared to the equivalent work for a simple stripper and an Advanced Flash Stripper utilising 8M aqueous piperazine [27]. $x_{w} = 0.8$, $f = 0.9$. $\beta \approx 200$ J K\textsuperscript{-1} mol\textsuperscript{-1} corresponds to $\lambda \approx 0.9$ for a good SIP systems.

Figure 5.12: Value of $W_{\text{cond}}$ for highly concentrated (capacity $\approx 12$ mol/kg H\textsubscript{2}O) under optimal solvent and process conditions, for various values of $N$. $f = 0.9$, $x_{w} = 0.8$
The development of the advanced flash stripper and other similar technologies demonstrates that the enthalpy of condensation can largely be recovered through clever process integration, and there is no reason to expect that an advanced SIP or MECS system couldn’t also be designed in which this heat is recovered. However, even if the recovery of heat of condensation were complete, and $5 - 6 \text{kJ mol}^{-1}\text{CO}_2$ of work was subtracted from the curves in Figure 5.9, the work requirements would still only be competitive with those found in an advanced amine process (and this itself could only be achieved with excellent sensible heat recovery, on the order of 90%; in reality, heat recovery in a solid sorbent process is likely to be around 60-80%, see section 5.4.) Even though the MECS and SIPs in this analysis contained an ‘optimal’ aqueous solvent, with perfectly tuned $\Delta h^0$ and $\Delta s^0$ values, they could not significantly improve on existing technologies. As discussed at the end of section 5.3.2, the difficulty in developing processes which utilise less energy than an optimised amine process is simply the result of the very high efficiency of these processes, and how little room they leave for improvement. Ultimately, these findings confirm what has been predicted, time and again, by the many studies [255, 254, 253] that have demonstrated that, among all aqueous solvents, amines are close to thermodynamically optimal for carbon capture.

5.4 Sensible Heat Recovery, and Implications for Future Research

The near-optimal performance of modern amine systems brings into question not just the value of SIPs or MECS, but the value of any further research into sorbents for post-combustion carbon capture. What’s the point of continuing to develop an expensive technology such as SIPs/MECS, when there are so few exergetic savings to be had? Of course, SIPs or MECS may find application in other fields, such as direct air capture as considered in section 4.7. However, we would like to tentatively suggest a few plausible routes by which SIPs/MECS could be used to capture CO$_2$ from various concentrated flue gas streams.
The large majority of aqueous solvent CCS systems rely on steam for regeneration of the solvent, and for this reason regeneration typically occurs at greater than 100°C. However, it is plausible that, in a few decades time, efficient renewable energy with grid-scale storage (perhaps of the kind considered by Genccer and Agrawal [60]) will lead to abundant and cheap electrical energy, and it may be cheaper to use this electrical energy to capture CO₂ from industrial processes, rather than using steam. This opens up the possibility of using a heat pump to regenerate the solvent. While heat pumps that generate steam can be manufactured, they are more commonly used to generate medium-grade heat (70 – 90°C) for residential warming [270], and it may be more efficient to use solvents which can be regenerated at such temperatures [132, 133, 134]. As shown in Chapters 3 and 4, SIPs or MECS may prove helpful in improving the rate of absorption into such materials. Furthermore, if electrical energy is much cheaper than steam, the fact that SIPs- or MECS-based processes don’t outperform an Advanced Flash Stripper design in an exergetic efficiency analysis is not a serious concern.

There is also some scope for improvement in the process used to regenerate non-aqueous solvent systems. As should be clear from the analysis above, when the sorbent is regenerated without steam in pure CO₂, the very high partial pressure of CO₂ reduces the efficiency of regeneration, especially for solvents with low $-\Delta s^0$ values. An interesting means of mitigating this problem, investigated by Wang et al. [131], is to use a non-aqueous, condensable stripping gas such as pentane during the CO₂ stripping. The stripping gas would flow in counter-current manner over the pre-heated, rich sorbent, reducing the CO₂ partial pressure (particularly above the sorbent leaving the stripper) and allowing for deeper regeneration. Of course, there are several challenges with this approach. In a steam stripper, only a small fraction of the steam supplied at the bottom of the stripper (where it is most important $p_{CO₂}$ be reduced) exits from the top, as most condenses within the unit. In the design of Wang et al. [131], significant condensation of the organic stripping agent into the non-aqueous solvent will probably harm the solvent’s performance, and so all
of the stripping gas entering the regeneration unit would also leave with the CO2 product. This stripping gas would then need to be completely condensed out of the CO2 product, and then reboiled. It will also be difficult to recover the heat of condensation, as it will be of very poor quality, and the temperature of condensation from the mixed-gas stream will also be lower than the boiling temperature of the pure stripping agent. Even with relatively low stripping flow rates, it seems likely that the enthalpy required to continually vaporise the stripping reagent (∼ 25 kJ mol⁻¹ for pentane, which corresponds to \( W_{eq} \approx 8 - 12 \text{kJ mol}^{-1} \) for a heat pump with coefficient of performance of 2-4⁴⁰) will be significant, and could easily outweigh any energy gains from increased cyclic capacity. Nevertheless, it is an interesting option, which, if it could be made to work, would be well suited to a SIPs/MECS system.

Of course, any such technology will still require a reasonably-efficient sensible heat recovery system. Fortunately, there are several plausible options available. A simple approach is to use an intermediate fluid, such as water, to first capture the heat from the hot, lean particles, and then transfer this heat to the cool, rich particles. The transfer could occur in a packed bed or a moving bed heat exchanger (MBHE) [272]. In the ideal case, the water would flow through the bed in plug flow, and an infinitely narrow moving thermal front would be established between the hot and cold particles. In practice, axial dispersion and radiative heat losses reduce the recovery efficiency, and the fact that two separate exchangers are required (one to cool the hot solids, a second to heat the cool solids) further reduces the net recovery. Saastamoinen [273] analysed a number of different systems, and found typical solid-solid heat recoveries of between 60-80%. If an appropriate intermediate medium can be found, ⁴¹ this degree of solid-solid heat recovery would be plausible.

A second option is to use a modified slurry-slurry system, in which SIPs or MECS are transported between the absorber and the stripper inside a carrying fluid, and

---

⁴⁰These are reasonable for a practical heat pump [271]; directly using the Carnot efficiency for heat supplied at temperatures as low as the boiling point of pentane (∼ 36 °C) is unrealistic, as the deviation from the Carnot efficiency grows quickly as \( T_2 \to T_{sink} \).

⁴¹This is far from an easy task. No gas will work: CO2 will absorb into the lean, cool sorbent, while anything else will strip CO2 from the hot, rich sorbent. Meanwhile, liquid water could induce osmotic swelling in the particles, and may be unsuited to non-aqueous solvents.
heat is exchanged between the two slurries in a traditional heat exchanger, which would have a recovery efficiency similar to a liquid-liquid exchanger ($\sim 90\%$ [70]). Before the slurry enters the stripper or absorber, the carrying fluid would be drained away, so only the particles need to be heated to the final regeneration temperature. After regeneration, the hot particles could be recombined with the carrying fluid and sent back towards the heat exchanger and the absorber. Because the carrying fluid increases the quantity of heat being transferred in the heat exchanger, a 10% inefficiency in the slurry-slurry exchanger will be equivalent to a greater loss (perhaps 15-20%, depending on the carrying fluid:particle ratio) of the specific heat energy of the particles. Nevertheless, if an appropriate carrying fluid could be found, this is a second, plausible means of achieving reasonable ($\sim 80\%$) sensible heat recoveries.

Sensible heat recoveries in the range of 60-80% are insufficient to allow SIPS or MECS to be significantly more efficient than amine-based processes. However, they do bring the $W_{eq}$ values within a factor of 50% of the Advanced Flash Stripper, even when non-aqueous solvents with $\Delta s^0 = -130 \text{ J K}^{-1} \text{ mol}^{-1}$ are used. The results of section 5.3 demonstrate that SIPS or MECS regenerated by steam are unlikely to significantly outperform an advanced amine process, even when the SIPS or MECS contain very concentrated solvents. If osmotic effects could be ignored, it is plausible that adding a few wt% of SIPS/MECS particles containing highly concentrated solvents into a traditional solvent process (to create a dilute particle/solvent slurry) could marginally increase the capacity of the solvent and reduce pumping/sensible heat duties (though the presence of the shell brings even this into question.) However, in reality, osmotic effects cannot be ignored, and such a hybrid process is probably impossible.

On the other hand the replacement of steam regeneration by low-temperature, waste- or electrically-generated heat could change the economics in favour of solvents designed to be regenerated at lower temperatures, especially for industrial processes in which excess steam is not readily available. It is likely that SIPS or MECS could assist in increasing mass transfer rates into such materials, given that MECS
may be able to reduce the volume of an absorber by an order of magnitude (see chapter 3 and [105, 118]) and SIPs may have even faster mass transfer than MECS (see chapter 4). These results suggest that future research into SIPs or MECS for carbon capture should not attempt to directly compete with steam-regenerated, amine-based processes, but should focus on sorbents that can be regenerated at lower temperatures without steam. The major unsolved questions relate to solvent selection, process design, and material stability.
5.5 On the Relationship Between the Standard Entropy and Enthalpy of Absorption in an Optimal Solvent.

Note: The following section is modified version of a separate body of work, tangentially related to the previous material. The goal of this section is to develop an understanding of the properties of an ‘optimal’ solvent for carbon capture, with a particular emphasis on the relationship between the standard enthalpy and entropy of absorption.

5.5.1 Introduction

As the number of novel liquid solvents for carbon capture and storage (CCS) has proliferated [262], many researchers have attempted to determine the properties of a thermodynamically ‘optimal’ solvent [253, 254, 255, 256, 95, 82]. These studies have emphasised the trade-off implied by the Gibbs-Helmholtz equation [153, 259]: the heat which must be supplied for desorption, $-\Delta h_{\text{abs}}$, cannot be decreased without also reducing the sensitivity of the partial pressure to temperature changes, $\partial \log P_{\text{CO}_2} / \partial T$, on which temperature swing regeneration depends. These studies have consistently found that existing solvents, and in particular alkanolamines already in widespread use, are close to thermodynamically optimal. Unfortunately, a number of interrelated problems have inhibited their widespread dissemination and use:

- **Complexity:** In order to accurately simulate a practical CCS process, several researchers have analysed rigorous but complex models developed in commercial software such as ASPEN [253, 82]. The complexity of these simulations can make identifying the important physical parameters difficult.

- **Specificity:** Researchers have considered specific chemistries and processes, most commonly taking a model developed for an aqueous amine and varying one or two thermodynamic parameters [253, 254, 95, 256, 255]. It is unclear how applicable these studies are to non-aqueous or precipitating solvents.
• **Lack of Physical Intuition:** While these studies have consistently found that alkanolamines are close to optimal, they do not provide insight as to why this should be the case.

• **Lack of Practical Recommendations:** For the reasons cited above, these studies have been unable to provide much practical guidance for chemists and engineers developing novel solvents. The lack of simple metrics by which solvents may be compared (such as are available in other fields: permeability and selectivity are ubiquitous in the membrane literature) and the lack of physical intuition for the properties of an optimal solvent can lead to confusion [82] and difficulty comparing alternative solvents; the latter may be partially responsible for the large number of solvents under development [261, 262].

In this section, the properties of an optimal solvent for carbon capture (or, indeed, for any analogous gas separation) will be analysed from a fundamental perspective. The need for a *sufficiently* large enthalpy of absorption coupled with an *appropriately sized* entropy of absorption will be stressed. While the role of the enthalpy of absorption in facilitating the temperature swing has been acknowledged in many works [82], the crucial role of a counterbalancing negative entropy of absorption has not previously been discussed. Theoretical calculations will be used to show that alkanolamines such as monoethanolamine (MEA) and diethanolamine (DEA) have an appropriate balance of enthalpy and entropy, and a simple process simulation will be used to show that such solvents are indeed optimal for carbon capture. The entropies of absorption observed in these amines are critical to their performance, and are much larger than those typically observed in ionic liquids and other non-aqueous solvents. It is suggested that these negative entropies may be related to the ordering of H$_2$O molecules around the ions produced during absorption. If this hypothesis is valid, nonaqueous solvents, even with their reduced specific heat capacities and lack of water loss during regeneration, may be unable to compete with aqueous solvents.
5.5.2 Optimal Enthalpy of Absorption

Vapor-liquid equilibrium (VLE) and enthalpy of absorption data for a chemical solvent are related by the Gibbs-Helmholtz equation (see [259, 153], and also Appendix 5.III for a careful derivation and discussion of the various assumptions implicit in this equation):

\[
\left. \frac{\partial \log p_i}{\partial T} \right|_{p,x_j} = \frac{\tilde{H}^\text{liq}_i - \tilde{H}^\text{gas}_i}{RT^2} \approx \frac{\Delta h^\text{abs}}{RT^2} \quad (5.35)
\]

This relation has profound implications for thermal swing absorption, as it implies that solvents with lower enthalpies of desorption also have partial pressures less sensitive to temperature swings. Physically, this holds because, when \( \tilde{H}^\text{gas}_i \) is much larger than \( \tilde{H}^\text{liq}_i \), the chemical potential of \( i \) in the gas is much more sensitive than the liquid to temperature changes, and a larger partial pressure change is required to counteract this difference in order to ensure that \( \mu^\text{gas}_i = \mu^\text{liq}_i \) continues to hold as the temperature is adjusted. Practically, this relation implies that every thermodynamically consistent chemical solvent must strike a compromise between reducing \(-\Delta h^\text{abs}\), on the one hand, and increasing \( \partial \log p_i / \partial T \) on the other. Too large a value of \(-\Delta h^\text{abs}\) will lead to prohibitive energy consumption to remove the CO2 from the solvent during regeneration, but too small a value will lead to larger circulation rates, greater sensible heat duties, and more water evaporation during regeneration [82].

A range of ‘reasonable’ \( \Delta h^\text{abs} \) values for post-combustion capture may be found by considering the integrated form of the Gibbs-Helmholtz equation:\footnote{It is reasonable to treat \( \Delta h^\text{abs} \) as roughly independent of temperature over this temperature range for a number of solvents - see Appendix 5.III.}

\[
\log \frac{p(T_2)}{p(T_1)} = \frac{\Delta h^\text{abs}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (5.36)
\]

The absorber and stripper temperatures may be set to \( T_1 = 313 \text{ K} \) and \( T_2 = 383 \text{ K} \), respectively. At the absorber temperature the lean and rich solvent must have partial pressures strictly less than 0.01 bar and 0.1 bar respectively, assuming 90% capture.
from a gas stream containing 10% CO₂ at atmospheric pressure. For a non-aqueous solvent regenerated without a vacuum in hot CO₂, \( p(T_2) \) in the lean sorbent must be at least 1 bar, and so, in this case, \( p(T_2)/p(T_1) \geq 100 \). The use of a non-aqueous, condensable stripping gas to reduce the required CO₂ partial pressure swing is not considered here (see section 5.4 and [131].) For a solvent regenerated using steam instead of CO₂, a smaller partial pressure swing is possible, and strictly speaking no partial pressure swing is required to sufficiently regenerate the lean sorbent, though in such a case exceptionally large steam flow rates would be required. In this work, a swing of \( p(T_2)/p(T_1) \geq 30 \) will be required for an aqueous solvent. This ensures a partial pressure of 2 to 3 bar is achievable at the top of the stripper, and provides a reasonable driving force at the bottom for regeneration to low lean loadings. A swing this large is certainly necessary if the stripper is to be operated at higher pressures, with the goal of reducing the compression duties of the process by producing high-pressure CO₂. For example, Lin and Rochelle [27] considered strippers operating at 8.5 and 11 bar, van Wagener et al. [274] considered strippers operating between 4 to 7 bar, while Jassim et al. [220] considered strippers operating at 2 to 4 bar, each with the explicit goal of reducing compression duties. A value of \( p(T_2)/p(T_1) = 1000 \) seems a reasonable upper bound, as beyond this value it’s unclear what process gains could be achieved. Hence, for non-aqueous solvents regenerated in CO₂, pressure changes of \( 100 \leq p(T_2)/p(T_1) \leq 1000 \) are considered, while for an aqueous solvent \( 30 \leq p(T_2)/p(T_1) \leq 1000 \).

Substituting these values into Eq. (5.36) gives a range of \( \Delta h_{\text{abs}} \) between \(-48 \text{ kJ mol}^{-1}\) and \(-98 \text{ kJ mol}^{-1}\) for the aqueous case, and \(-65 \text{ J K}^{-1} \text{ mol}^{-1} \leq \Delta h_{\text{abs}} \leq -98 \text{ J K}^{-1} \text{ mol}^{-1} \) for the non-aqueous case. These are consistent with the range covered by popular alkanolamines such as MDEA (\( \Delta h_{\text{abs}} = -50 \text{ kJ mol}^{-1} \)) and MEA (\( \Delta h_{\text{abs}} = -85 \text{ kJ mol}^{-1} \)) [264]. On the other hand, concentrated K₂CO₃ solutions have an enthalpy of absorption around \(-25 \text{ kJ mol}^{-1} \) [82]. While this is sometimes cited as an advantage for these solvents [261], Eq. (5.36) implies that this solvent will have only a 7-fold increase in the partial pressure between 40°C and 110°C (this is con-
sistent with experimental VLE data [145].) This will make regeneration difficult for such systems, and there is little scope for the production of high pressure CO₂ from the stripper. It should also be noted that processes which capture more than 90% CO₂ have recently attracted some interest [275], and, because of the large ratio of \( p(T_2)/p(T_1) \), such processes may require solvents with particularly large values of \(-\Delta h^{\text{abs}}\).

### 5.5.3 Optimal Entropy of Absorption

A sufficiently large enthalpy of absorption is not the only requirement for a solvent to be effective for carbon capture. Gas absorption always involves a compromise between the negative enthalpy of absorption (which favours absorption) and the negative entropy of absorption (which favours desorption.) For a solvent to be practical for carbon capture, it must have both a sufficiently large enthalpy of absorption (to facilitate the temperature swing) and an appropriately sized entropy of absorption, to counter-balance the enthalpy and ensure the solvent absorbs CO₂ reversibly under practical conditions. In what follows, it will be argued that, for a wide class of solvents, including all non-aqueous chemical solvents and many aqueous chemical solvents, the appropriate balance is struck when \( \Delta s^0 \approx \Delta h^0 / T \), where \( T \) is a typical temperature in the process.

The entropy of absorption is more difficult to quantify than the enthalpy of absorption, as, unlike the enthalpy (for which \( \Delta \bar{H}_i \approx \Delta h^{\text{abs}} = \Delta h^0 \)) the entropy varies with the solvent loading. Even in an ideal solution, the ‘differential’ entropy of absorption, \( \Delta \bar{S}_i \), depends on the equilibrium constant:

\[
\Delta \bar{S}_i = \Delta s^0 - R \log K, \tag{5.37}
\]

while, more generally, it depends on the temperature dependence of the activity
coefficients [153]:

$$\Delta S_i = \Delta s^0 - R \log K - RT \left( \log \frac{\Pi_{i} \gamma_{i}^{\text{prod}}}{\Pi_{i} \gamma_{i}^{\text{reac}}} \right) \bigg|_{p,x_j} \quad (5.38)$$

where $K$ is the equilibrium constant and $\bar{S}_i$ are the partial molar entropies of the various species. Hence, it is not obvious that the standard entropy of absorption, $\Delta s^0$, is useful for quantifying the required balance between the enthalpic and entropic driving forces.

For the overall reaction:

$$\text{CO}_2(g) + \alpha_1 A_1 + \alpha_2 A_2 + \cdots + \alpha_m A_m \rightleftharpoons \beta_1 B_1 + \cdots + \beta_n B_n \quad (5.39)$$

the equilibrium constant is of the form:

$$K = \frac{\Pi_{i=1}^{n} (a_{B_i})^{\beta_i}}{\Pi_{i=1}^{m} (a_{A_i})^{\alpha_i} (f_{CO2}/f_{CO2}^0)} \quad (5.40)$$

where the $a_i \equiv \gamma_i x_i$ are the activities of the various reactants and products in the solvent, $f_{CO2} \approx p_{CO2}$ is the fugacity of CO$_2$ above the solution, and $f_{CO2}^0 \approx p_{CO2}^0$ is the standard fugacity (or pressure) at which $\Delta s^0$ is calculated. In many chemical solvents, the various $A_i$ and $B_i$ are either present in stoichiometric quantities, or one species (typically H$_2$O) is present in such great excess it’s chemical potential may be taken as constant, and its activity is equal to unity and may be ommitted from Eq. (5.40). In what follows, it will be assumed that all $A_i$ and $B_i$ with activities appearing in Eq. (5.40) are present in stoichiometric quantities.

Rearranging the standard expression:

$$\Delta g^0 = \Delta h^0 - T \Delta s^0 = -RT \log K \quad (5.41)$$

gives the following relationship between the standard entropy and enthalpy of ab-
sorption, valid for any solution, ideal or otherwise:

\[
\frac{\Delta s^0}{R} = \frac{\Delta h^0}{RT} + \log K. \tag{5.42}
\]

We now argue that, under a range of circumstances, \( \log K \) would be expected to be much smaller than the other terms in Eq. (5.42) if the solvent is practically useful for post-combustion carbon capture.

The ‘practical’ values of \( \Delta h^0 \) provided above, \( 48 \) kJ/mol \( \leq -\Delta h^0 \leq 98 \) kJ/mol for an aqueous system and \( 65 \) kJ/mol \( \leq -\Delta h^0 \leq 98 \) kJ/mol for a non-aqueous system, correspond to \( 17 \leq -\Delta h^0/RT \leq 34 \) and \( 22 \leq -\Delta h^0/RT \leq 34 \) at \( T = 355 \) K, respectively.\(^{43}\) Suppose that Reaction (5.39) produces no new dissolved species in the solvent (i.e. is equimolar once water and CO\(_2\) are ignored, and so \( \sum_i \alpha_i = \sum_i \beta_i \) for all species appearing in Eq. (5.40).) Suppose also that the standard pressure, \( p_{CO_2}^0 \), is chosen so it is of the same order of magnitude as the CO\(_2\) partial pressures present in a CCS process (\( p_{CO_2}^0 = 1 \) bar is considered in this work). Then, in a solvent which would be useful in practice, the partial pressure of CO\(_2\) should equal the standard pressure (\( p_{CO_2} = p_{CO_2}^0 \)) at an intermediate temperature (\( T = 355 \) K will emerge organically from the analysis below) and an intermediate value of the chemical loading (perhaps at \( \xi = 0.1 \) or \( \xi = 0.8 \), but not at \( \xi = 10^{-3} \) or \( \xi = 0.999 \)). Then, because the loading takes on an intermediate value at \( p_{CO_2} = p_{CO_2}^0 \), the concentrations of the various reactants and products in the solvent, \( A_i \) and \( B_i \), which are all present in stoichiometric quantities, will all be of the same order of magnitude. Even if the solvent is not ideal, the various activities of the products and reactants should also be approximately of the same order of magnitude,\(^{44}\) and because \( \sum_i \alpha_i = \sum_i \beta_i \), they will approximately cancel from the numerator and denominator of Eq. (5.40). Finally, because \( p_{CO_2} = p_{CO_2}^0 \), this will also cancel from Eq. (5.40), and \( K \sim \mathcal{O}(1) \).

Obviously, this argument is inexact, and in a real system it may incorrectly predict the equilibrium constant by several orders of magnitude. For example, for

\(^{43}\)355 K is chosen as a ‘typical’ temperature in the process, but it will also spring quite organically from the analysis conducted below.

\(^{44}\)See section 5.5.5 for further discussion on non-idealities.
CO₂ absorption into piperazine, \( K \) varies from approximately 381.5 at 313 K to 10.5 at 355 K to 1.6 at 383 K, based on a standard pressure of \( p₀^{CO₂} = 1 \text{ bar} \) (see Appendix 5.VI, in which a number of values cited in this section are calculated. Note also that the relatively poor match at 313 K is a result of choosing \( p₀ = 1 \text{ bar} \), which is not a ‘typical’ CO₂ partial pressure at the absorber temperature; if a standard pressure of 1 kPa were used instead, \( K = 3.8 \) at 313 K.) However, even if \( K = 10^2 \) or even \( 10^3 \), \( \log K \) will only equal 4.6 or 6.9 respectively, and \( \Delta h^0/RT \) (with \( -\Delta h^0/RT \geq 17 \) or \( -\Delta h^0/RT \geq 22 \)) will be the dominant contribution to \( \Delta s₀ \) in Eq. (5.42). This will be especially likely in non-aqueous solvents, for which \( -\Delta h^0/RT \) is larger, and for which the activities are typically \( \mathcal{O}(1) \) because a Raoultian standard state is used.

Hence, to a first approximation, for a practical chemical solvent it would be expected that the appropriate balance between the entropy and enthalpy of absorption will be met when:

\[
\Delta s^0 \approx \frac{\Delta h^0}{T}.
\]

where \( T \) is a ‘typical’ temperature in the process, at which \( p_{CO₂} = p₀ \) would be expected to occur (in this work, \( T = 355 \text{ K} \) and \( p₀ = 1 \text{ bar} \).) If the solvent (a) has a reasonable value of \( \Delta h^0 \), (b) achieves a reasonable CO₂ partial pressure at intermediate chemical loadings, and (c) is equimolar in the reactive species in the solvent, then it will approximately satisfy this relationship.

Eq. (5.43) holds very well for both MEA, DEA and piperazine. At 355 K, \( \Delta h^0/(T\Delta s^0) \) equals 1.13, 0.98 and 1.10 for these systems, respectively, while at 383 K these values are 1.05, 0.90 and 1.02.⁴⁵ Each of these solvents satisfy the ‘equimolar’ criterion, as the total number of dissolved species in the solvent remains constant as CO₂ is absorbed. In each case, \( \Delta h^0 \approx T\Delta s^0 \) holds as a straightforward consequence of the practical nature of these solvents: the fact that \( -\Delta h^0 \) is large, and that ‘reasonable’ partial pressures occur at ‘reasonable’ temperatures.

Unfortunately, there is one notable exception to this otherwise simple and straightforward rule. Several non-ideal, aqueous solvents which don’t satisfy the equimolar

⁴⁵See Appendix 5.IV.
criterion fail to satisfy $\Delta h^0 \approx T \Delta s^0$. For example, MDEA, has a much greater standard entropy of absorption than would be expected from the $\Delta h^0$ value, with $\Delta h^0 / (\Delta s^0 \times 355 \text{ K}) = 0.64$. Absorption of CO$_2$ into MDEA is governed by the following reaction:

$$\text{CO}_2 + \text{MDEA} + \text{H}_2\text{O} \rightleftharpoons \text{MDEAH}^+ + \text{HCO}_3^-$$ (5.44)

This reaction is not equimolar in the dissolved reactive species, but instead involves an increase from 1 dissolved species (MDEA) to 2 (MDEAH$^+$ and HCO$_3^-$) as CO$_2$ is absorbed. Because of this increase, the activities in Eq. (5.40) will never completely cancel each other out, and there’s no reason to expect that $K \sim \mathcal{O}(1)$. Indeed, because there are more products than reactants, it would be expected that $K \ll 1$, and, according to Eq. (5.42), this will lead to $\Delta s^0$ values with a greater negative magnitude that would be expected from Eq. (5.43): exactly as is observed. The same argument may be made about CO$_2$ absorption into K$_2$CO$_3$ solutions, and the same behaviour is again observed: at 355 K, $\Delta h^0 / (\Delta s^0 \times 355 \text{ K}) = 0.58$ (see Appendix 5.IV.) Such deviations from Eq. (5.43) for non-equimolar reactions are only likely to occur in non-ideal aqueous solvents (for which the Henrian activities can be many orders of magnitude less than 1, both because the mole-fractions are small, and because the activity coefficients are also often much less than 1 [276]) which fail the equimolar criterion, and which have relatively low $-\Delta h^0$ and $-\Delta s^0$ values.

In general, if the CO$_2$ binds with a dissolved reactive species in the solvent, so the total number of dissolved species remains constant, Eq. (5.43) should approximately hold for a useful chemical solvent. On the other hand, if the CO$_2$ binds with water to form HCO$_3^-$ ions, Eq. (5.43) may underestimate the magnitude of $\Delta s^0$. Physically, this is because the increase in the number of dissolved species will lead to a positive entropy of mixing in the liquid, and so the standard entropy of reaction, $\Delta s^0$ must be even more negative in order to counterbalance both $-\Delta h^0$ and this added entropy of mixing effect.
In summary, a competitive non-aqueous chemical solvent for carbon capture would be expected to have

$$-\Delta h^0 \geq 65 \text{ kJ/mol},$$

(5.45)

and\textsuperscript{46} a competitive aqueous solvent should satisfy:

$$-\Delta h^0 \geq 50 \text{ kJ/mol}.$$  

(5.46)

These values must be balanced by an appropriately sized, negative entropy of absorption, to ensure the reaction is reversible at the correct range of CO\textsubscript{2} partial pressures:

$$\Delta s^0 \approx \Delta h^0 / T \quad \text{for equimolar reaction or non-aqueous solvent}$$

$$\Delta s^0 \leq \Delta h^0 / T \quad \text{for net gain in species (typically } \text{HCO}_3^- \text{)}$$

(5.47)

These findings may have negative implications for non-aqueous solvents such as chemically functionalised ionic liquids. These solvents typically have $\Delta s^0 \approx -130 \text{ J/mol.K}$, as the entropy change is dominated by the change of phase of CO\textsubscript{2} \textsuperscript{[28]}. On the other hand, the ‘reasonable’ range of $\Delta h^0$ values for a non-aqueous solvent ($65 \text{ kJ/mol} \leq -\Delta h^0 \leq 98 \text{ kJ/mol}$) corresponds, according to Eq. (5.43), to $183 \text{ J/mol.K} \leq -\Delta s^0 \leq 276 \text{ J/mol.K}$ at $T = 355 \text{ K}$. This suggests that such ionic liquids with $\Delta s^0 \approx -130 \text{ J/mol.K}$ may not have entropies of absorption negative enough to counterbalance a large enough enthalpy of absorption.

A simple process simulation will now be used to test whether Eq. (5.45), (5.46) and (5.47) are indeed close to optimal in an actual process.

\textbf{5.5.4 Optimal Thermodynamic Parameters for a Process Simulation}

The simplified process simulations used in this work are identical to those used in section 5.2 and 5.3 for a non-aqueous and an aqueous solvent, respectively, and they will not be described again here. We highlight the following properties of the

\textsuperscript{46}We suggest this more tentatively.
We consider a simplified process description, in which equilibrium is attained between streams leaving both the absorber and the stripper.

For the non-aqueous solvent, regeneration occurs in a single stage in pure CO₂.

For the aqueous solvent, steam is used to regenerate the solvent, using a stripper with \( N \) countercurrent equilibrium stages.

All solvents in this analysis are ideal solutions, for which the only thermodynamic variables are \( \Delta s^0 \) and \( \Delta h^0 \).

Figure 5.13 shows the optimal values for \( \Delta h^0 \) and \( \Delta s^0 \) (i.e. values of these parameters which led to processes with minimal \( W_{eq} \) requirements) for a number of the simulations which have been discussed in earlier sections of this chapter. The aqueous simulations refer to the SIP system whose \( W_{eq} \) values are shown in Figure 5.9, and \( N \) refers to the number of theoretical stages of separation. Several values of \( \beta \), from \( 70 \text{ J K}^{-1} \text{ mol}^{-1} \leq \beta \leq 300 \text{ J K}^{-1} \text{ mol}^{-1} \), are shown for each value of \( N \). The non-aqueous solvents refer to the systems discussed in Figure 5.6, for which \( \Delta s^0 \) values were restricted to being greater than -150, -200 and \( -250 \text{ J K}^{-1} \text{ mol}^{-1} \). The non-aqueous solvents with MDEA chemistry were calculated separately: the same restrictions on \( \Delta s^0 \) were applied, but the chemistry was also restricted to the form:

\[
\text{CO}_2 + B \rightleftharpoons C + D \cdot \tag{5.48}
\]

For all cases considered, the optimal values of \( \Delta h^0 \) and \( \Delta s^0 \) fell on the same straight line, exactly as predicted by the theory developed above. Furthermore, the gradient of this line was \( \sim 355 \text{ K} \), which is roughly equal to the average temperature within the process. Experimentally measured values for piperazine, MEA and DEA were also plotted, and again they each conformed to the general trend. These results support the theoretical ideas developed above, and strongly suggest that solvents
Figure 5.13: Plot of optimal values of $\Delta h^0$ and $\Delta s^0$ for a number of different simulations. $N = 1, 2, \ldots, 10$ refer to the process utilising an aqueous solvent whose $W_{eq}$ values were plotted in Figure 5.9; $N$ is the number of theoretical stages used for the regeneration process. Various points are shown for each simulation; these correspond to various values of $\beta$. The ‘Non-Aqueous’ solvents refer to the optimal non-aqueous solvent system whose $W_{eq}$ values are shown in Figure 5.6, under various restrictions on $\Delta s^0$. ‘Non-Aqueous MDEA’ refers to the optimal values for a non-aqueous solvent with MDEA chemistry. ‘Piperazine’, ‘MEA’ and ‘DEA’ each refer to experimentally determined values of the standard enthalpy and entropy of absorption at infinite dilution taken from the literature (see Appendix 5.IV). Infinite dilution molar standard state for ionic species, 1 bar ideal gas standard state for CO2.

with large enough enthalpies of absorption balanced by appropriately sized entropies of absorption are optimal for carbon capture.

It is interesting that the optimal $-\Delta h^0$ values are larger for the non-aqueous solvent (at least when $\Delta s^0$ is not restricted) and, for the aqueous solvent, they decrease as $N$ gets larger. This is a result of the difficulty of regenerating the solvent: for the non-aqueous solvent and for aqueous solvents with smaller values of $N$, regeneration is relatively difficult, because the lean solvent exiting the stripper is exposed to a gas stream with a larger CO2 partial pressure. For these systems, a large partial pressure swing is vitally important, and larger values of $-\Delta h^0$ facilitate this. On the other hand, for regeneration with more theoretical stages, a very large pressure swing is less critical, and the solvent instead benefits from the reduced
heat load from the enthalpy of desorption. Nevertheless, even with many theoretical stages, the model predicts the optimal solvent will still have enthalpies of absorption on the order of $\sim -60 \text{ kJ mol}^{-1}$, as the large partial pressure swing continues to assist in regeneration. These values are on the lower end for aqueous amines, but are much greater than the value of $\sim -25 \text{ kJ mol}^{-1}$ found in carbonate systems.

In Figure 5.14, a contour plot of the minimal values of $W_{\text{eq}}$ for a range of $\Delta h^0$ and $\Delta s^0$ values is plotted. This plot refers to a non-aqueous solvent regenerated in a single equilibrium stage in pure CO$_2$, and the surface was generated by optimising over the regeneration conditions and reaction stoichiometry ($p_2$, $T_2$ and $m_1$, $m_2$ and $m_3$) for various fixed values of $\Delta s^0$ and $\Delta h^0$. The need to balance the enthalpy and entropy of absorption is clear from this plot: solvents that strike this balance fall within a valley in which the work requirements are minimised. The variation when moving among these optimal solvents is much less than the variation in work requirements experienced when moving outside of this narrow zone. However, if a solvent were to differ from the optimal balance, it is preferrable that $-\Delta h^0$ be too large rather than too small. This is because when $-\Delta h^0$ is too large, relative to $-\Delta s^0$ (and so the solvent tends to absorb CO$_2$ too readily, at too low a partial pressure, and be harder to regenerate), it is relatively easy to adjust for this by varying the temperature in the regenator. When $-\Delta h^0$ is too small, relative to $\Delta s^0$, the CO$_2$ absorption is too weak, and lower temperatures in the absorber (not considered in this model) would be required. Compounding this, with too low a value of $-\Delta h^0$ it is more difficult to adjust for the sub-optimal partial pressures, because $\partial \log p/\partial T$ is smaller. Note also that the relatively-poor performance of non-aqueous solvents with $-\Delta s^0 = 130 \text{ J K}^{-1} \text{ mol}^{-1}$, compared to those with greater values of $-\Delta s^0$. The computational burden was too great for similar plots to be made for non-aqueous systems$^{47}$ at various values of $N$. Nevertheless, Figure 5.13 suggests that very similar behaviour is expected for the aqueous case, with the only difference being that a

\footnote{Figures 5.9 and 5.11 each took around a day to generate, and they involved the evaluation of only 4 points for each line. Thousands of such evaluations would be required to generate a surface similar to Figure 5.14}
global minima will be present on the plot, at the locations shown in Figure 5.13 for various values of \( N \).

After this work had been completed, the author became aware of a recent paper by Puxty et al. [277] on aromatic amines for CCS. These authors made a similar argument to that made above - that optimal solvents for carbon capture will require a balance of the standard enthalpy and entropy of absorption - in order to argue that aromatic amines (which may have very large negative entropies of absorption) may be good candidates for the development of next generation solvents with very large enthalpies of absorption (which, in turn, may facilitate the very large CO\(_2\) partial pressure swings crucial to the development of advanced stripping processes [95].) These authors formulated their arguments on intuitive grounds, and also included several plots similar to Figure 5.13, in which the standard enthalpy and entropy of common solvents all fell on the same line (however, they considered individual reactions, rather than the overall enthalpy and entropy of absorption; they also considered experimentally measured values for systems used in practice, rather than values calculated from optimised simulations as was done here.) This interesting paper complements and confirms the results of this analysis. In particular, the theoretical calculations and the results of the optimised simulations presented in this work confirm the intuitive arguments and chemical property data presented in Puxty et al. [277].

### 5.5.5 Non-Idealities

The arguments presented in the previous section were, strictly speaking, only valid for an ideal solution, and if the activity coefficients, \( \gamma_i \) are far from unity then the non-idealities in the system could, in principle, overpower the more ‘fundamental’ competing driving forces, the standard enthalpy and entropy of absorption and the entropy of mixing, all of which are accounted for within the ideal solution framework. And indeed, non-idealities in aqueous systems can be quite severe, with \( \gamma_i \) varying by up to 1-2 orders of magnitude [144]. However, they are often correlated, and
Figure 5.14: Contour plot of minimum possible $W_{eq}$ values (kJ/mol CO$_2$) for a range of $\Delta s^0$ and $\Delta h^0$ values in a non-aqueous solvent with arbitrary chemical stoichiometry regenerated in a single stage of pure CO$_2$. Standard state of CO$_2$: 1 bar.

so will at least partially cancel in Eq. (5.40), at least for an equimolar reaction. Furthermore, the good match of MEA, DEA and piperazine to the optimal curve in Figure 5.13 suggests that practical systems do in fact need to strike an appropriate balance between $\Delta h^0$ and $\Delta s^0$. A reasonable next step would be to optimise over the parameters of a thermodynamically consistent activity coefficient model such as the eNRTL model [278]. This would probably be computationally feasible, especially for a non-aqueous system or an aqueous system with small values of $N$, as modern black box optimisation algorithms are surprisingly insensitive to the number of dimensions in the problem [266, 279].

Non-idealities are unlikely to be significant for solvents with larger enthalpies and entropies of absorption (physically, this is because when these fundamental driving forces are greater, they more completely dominate the dynamics of the absorption process; mathematically, this follows from the order-of-magnitude of the various terms in Eq. (5.42).) They are also less likely to be significant in non-aqueous systems, as various non-aqueous ionic liquid systems have been shown to conform
quite closely to the ideal solution model [28, 265]. Future work on the design of ‘tunable’ solvents [28, 97] should explicitly consider the need to balance the standard entropy and enthalpies of absorption.

5.5.6 $\Delta s^0$ in Aqueous and Non-Aqueous Systems

Given the crucial role that $\Delta s^0$ plays in determining the performance of a chemical solvent, it is worth considering the physical effects that contribute to its value. According to Trouton’s law [153], the loss of translation degrees of freedom of the CO$_2$ molecule will reduce the entropy by about 88 J K$^{-1}$ mol$^{-1}$. However the standard entropy may vary significantly from this. For example, for the conversion of solid NaOH to solid NaHCO$_3$,

$$\text{CO}_2(\text{g}) + \text{NaOH}(\text{s}) \rightleftharpoons \text{NaHCO}_3(\text{s}) \quad (5.49)$$

the standard entropy of absorption is $-175$ J mol$^{-1}$ K$^{-1}$, while for the conversion of solid sodium carbonate to solid sodium bicarbonate,

$$\text{CO}_2(\text{g}) + \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{NaHCO}_3(\text{s}) \quad (5.50)$$

the standard entropy of absorption is $-218.7$ J mol$^{-1}$ K$^{-1}$ [245] (in each case, the standard state of the CO$_2$ molecules is an ideal gas at 1 bar.) On the other hand, when solid Ca(OH)$_2$ and Mg(OH)$_2$ absorb CO$_2$,

$$\text{CO}_2(\text{g}) + \text{Ca(OH)}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CaCO}_3(\text{s}) \quad (5.51)$$
$$\text{CO}_2(\text{g}) + \text{Mg(OH)}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{MgCO}_3(\text{s}) \quad (5.52)$$

their standard entropies of absorption are $-134.7$ J K$^{-1}$ mol$^{-1}$ and $-141.4$ J K$^{-1}$ mol$^{-1}$ [245]: much closer to the value of $-130$ J K$^{-1}$ mol$^{-1}$ suggested for non-aqueous ionic liquids [28]. Wang et al. [245] suggested the discrepancy may be related to the role water plays within the reaction. When liquid water is produced (as is the case for
Ca(OH)$_2$ and Mg(OH)$_2$) the entropy of the products tends to be greater, while if it is consumed, and immobilised inside a solid phase, (as is the case for Na$_2$CO$_3$), this tends to lead to a more negative entropy of absorption.

As shown in Figure 5.13, a number of aqueous amines have $\Delta s^0$ values around $-180$ to $-220$ J K$^{-1}$ mol$^{-1}$, much smaller that those in non-aqueous ionic liquids. One possible explanation for these large negative values relates to ionic effects inside the solution. In each of these systems, when CO$_2$ is absorbed, the number of moles of ions in the solution increases. These ions tend to order the water molecules around them, which, under some circumstances, may reduce the entropy of the solution [280, 281, 282]. It is unclear whether ordering effects of the same magnitude could occur inside a non-aqueous solvent.

5.5.7 Summary of Optimal Solvent Analysis

Ultimately, the results of this section may be summarised by saying that the standard Gibbs free energy of absorption, $\Delta g^0 = \Delta h^0 - T\Delta s^0$, should approximately vanish for a practical solvent, provided the standard states and temperature are comparable to those that exist in a real process. In one sense, this is an utterly unremarkable statement: if the Gibbs free energy were not near zero, absorption would be irreversible (or simply wouldn’t occur.) But this statement contains a few subtleties, and has several significant implications.

For one, the standard Gibbs free energy of absorption, $\Delta g^0$, is not equal to the differential Gibbs free energy of absorption, $\Delta G$. This is because $\Delta S$ is not equal to $\Delta s^0$, as mixing effects are significant even in ideal solutions (see Eq. (5.37) and (5.38)). Hence it is not completely obvious that ‘balancing’ the entropy and enthalpy of absorption is as straightforward as ensuring that $\Delta h^0 \approx T\Delta s^0$. However, order-of-magnitude arguments, simulation results, and comparisons with real systems all suggest that, under many circumstances, striking the appropriate balance is often as simple as setting $\Delta h^0 \approx T\Delta s^0$.

With this approximate equality in hand, the entropies of absorption in various
solvents may be compared, and the results are unfavourable for several systems. 
\[ \Delta s^0 = -130 \text{ J K}^{-1} \text{ mol}^{-1} \] corresponds to \[ \Delta h^0 = -46 \text{ kJ mol}^{-1} \] at \( T = 355 \text{ K} \) (the optimal line of Figure 5.13). With this enthalpy of absorption, regeneration would need to occur at 150°C in order to increase the partial pressure in the lean solvent from 0.01 bar at 40°C to 1 bar in the regeneration unit, and an even greater temperature swing would be required to produce pressurised CO\(_2\). Figures 5.13 and 5.14 also suggest that attempting to reduce the temperature swing by increasing \(-\Delta h^0\) without a commensurate increase in \(-\Delta s^0\) only leads to solvents with worse performance, as absorption becomes more irreversible in the working partial pressure range. If it is indeed true that the entropy of absorption into chemically-reactive ionic liquids is consistently around \(-130 \text{ J K}^{-1} \text{ mol}^{-1}\) [28, 265], this will likely prove a significant obstacle to the application of these materials. Further work is required to understand the physical causes for the low entropy of absorption in such systems, and to develop non-aqueous solvents with a greater entropic driving force for CO\(_2\) desorption.

In their landmark paper, Oexmann and Kather [82] argued that research into novel solvent systems for carbon capture had a ‘misguided focus’ on reducing the enthalpy of absorption, for precisely the reasons outlined here.\(^{38}\) While Oexmann and Kather were undoubtedly correct, this realisation has led to a vacuum within the research community, with no simple means of assessing the competitiveness of a newly-synthesised solvent. The results above suggest that, in a large range of aqueous and non-aqueous chemical solvent systems, reasonable performance can be expected when \(-\Delta h^0\) is sufficiently large (larger than around 50 kJ mol\(^{-1}\) and 65 kJ mol\(^{-1}\) for an aqueous and non-aqueous system, respectively) and \( T \Delta s^0 \approx \Delta h^0 \) at an intermediate temperature around 355 K, provided \( \Delta s^0 \) is measured relative to CO\(_2\) at 1 bar. While there are certainly exceptions to this general rule (non-ideal aqueous solvents which produce HCO\(_3^-\) being a clear example), in a large number of systems, this comparison is a simple first test, which may be used to estimate the

\(^{38}\)i.e. decreasing \( \Delta h^0 \) also reduces \( \partial \log p_{\text{CO}_2} / \partial T \).
usefulness of a newly synthesised solvent in a real process.

5.6 Conclusions

In section 5.1 – 5.4, it was found that even SIPs or MECS containing optimised solvents in an optimised and idealised process design were not significantly more energetically efficient than an integrated amine process. The most promising SIP or MECS systems were those containing non-aqueous solvents with large $-\Delta s^0$ values, as the large entropic driving force for desorption enabled a correspondingly large and negative enthalpic driving force for absorption, $-\Delta h^0$. This in turn allowed for large partial pressure swings and reduced regeneration temperatures. If SIPs or MECS are to be economically competitive, it is likely it will be in a process in which low-grade heat is used to regenerate novel solvents at low temperatures.

In section 5.5, the relationship between $\Delta h^0$ and $\Delta s^0$ was explored in more depth. It was found that an optimal solvent for carbon capture should approximately satisfy the following restrictions on the enthalpy and entropy of absorption:

$$-\Delta h^0 \geq 65 \text{ kJ/mol}, \quad \text{Non-Aqueous System} \quad (5.53)$$

$$-\Delta h^0 \gtrsim 50 \text{ kJ/mol}, \quad \text{Aqueous System} \quad (5.54)$$

$$\Delta s^0 \approx \frac{\Delta h^0}{T} \quad \text{if equimolar reaction or non-aqueous solvent} \quad (5.55)$$

$$\Delta s^0 \leq \frac{\Delta h^0}{T} \quad \text{if net gain in species (typically HCO}_3^-)$$

Ionic liquids for which $\Delta s^0 \approx -130 \text{ J K}^{-1} \text{ mol}$ will not satisfy these criteria, and such solvents may require unrealistic temperature swings when used in a real process.
Notation

- \( m_i \): Stoichiometric constant
- \( \gamma_i \): Activity coefficient
- \( a_i \): Activity
- \( \Delta h^0 \): Standard enthalpy of absorption, J mol\(^{-1}\)
- \( \Delta s^0 \): Standard entropy of absorption, J mol\(^{-1}\) K\(^{-1}\)
- \( \bar{S}_i \): Partial molar entropy of species \( i \), J mol\(^{-1}\) K\(^{-1}\)
- \( \bar{H}_i \): Partial molar enthalpy of species \( i \), J mol\(^{-1}\)
- \( \bar{G}_i \): Partial molar Gibbs free energy of species \( i \), J mol\(^{-1}\)
- \( p_{CO_2} \): CO\(_2\) partial pressure, Pa
- \( T \): Temperature, K
- \( T_{sink} \): Temperature of heat sink, K
- \( R \): Universal gas constant, 8.314 J K\(^{-1}\) mol\(^{-1}\)
- \( \lambda \): Sensible heat recovery efficiency
- \( p_1 \): Absorber pressure, Pa
- \( p_2 \): Regenerator pressure, Pa
- \( T_1 \): Absorber temperature, K
- \( T_2 \): Regenerator temperature, K
- \( W_{eq} \): Equivalent work of carbon capture process, J mol\(^{-1}\)CO\(_2\)
- \( W_c \): Work to compress CO\(_2\) to 150 bar, J mol\(^{-1}\)CO\(_2\)
- \( W_p \): Pumping work, J mol\(^{-1}\)CO\(_2\)
- $W_h$: Equivalent work due to enthalpy of desorption, J mol$^{-1}$CO$_2$
- $W_s$: Equivalent work due to lost sensible heat, J mol$^{-1}$ CO$_2$
- $W_{\text{cond}}$: Equivalent work due to condensation of water, J mol$^{-1}$ CO$_2$
- $W_{c,w}$: Work to compress steam entering stripper, J mol$^{-1}$CO$_2$
- $K$: Equilibrium constant
- $p^0$: Standard pressure, Pa
- $\beta$: Parameter which quantifies sensible heat recovery efficiency; defined by Eq. (5.8). J K$^{-1}$ mol$^{-1}$
- $c_p$: Specific heat capacity, J kg$^{-1}$ K$^{-1}$
- $n$: Total molar CO$_2$ capacity of solvent, mol kg$^{-1}$ solvent
- $N$: Number of theoretical stages of separation in stripper
- $f$: Weight fraction of solvent in SIP/MECS
- $\xi$: Total CO$_2$ loading, CO$_2$ Stored/Maximum CO$_2$ Stored
Appendix 5.I. Partial Pressures for Various Thermodynamic Models

In this appendix, expressions are derived for the relationship between partial pressure and composition for a number of ideal chemical solvents.

Consider the reaction

\[ \text{CO}_2(g) + B \rightleftharpoons C. \]  

(5.56)

between gaseous CO2 and an ideal liquid mixture composed of two species, B and C. The equilibrium constant is given by:

\[ K = \frac{x_C}{x_B(\frac{p_{CO2}}{p^0_{CO2}})} = \exp\left(\frac{-\Delta h^0 + T\Delta s^0}{RT}\right). \]  

(5.57)

and, assuming that the mole fraction of CO2(aq) is negligible, the chemical loading of the solvent (which, throughout this work, is defined for every solvent in such a way that it ranges from 0 to 1) is given by:

\[ \xi = x_C = 1 - x_B \]  

(5.58)

Substituting this into Eq. (5.57) and rearranging gives:

\[ p_{CO2}(\xi) = p^0_{CO2} \frac{\xi}{K} \frac{1}{1-\xi} \]  

(5.59)

and

\[ \xi(p_{CO2}) = \frac{K(p_{CO2}/p^0_{CO2})}{1 + K(p_{CO2}/p^0_{CO2})}. \]  

(5.60)

Now consider the more general reaction stoichiometry:

\[ \text{CO}_2(g) + m_1B \rightleftharpoons m_2C + m_3D \]  

(5.61)

which occurs in an ideal liquid solution composed of stoichiometric quantities of B,
C and D. The equilibrium constant is defined by:

\[ K = \frac{x_C^{m_2}x_D^{m_3}}{x_B^{m_1}(p_{CO2}/p_0^{CO2})} = \exp \left( \frac{-\Delta h^0 + T \Delta s^0}{RT} \right). \] (5.62)

The reaction conversion, \( \xi \), is the moles of CO2 that is chemically stored divided by the total chemical capacity for CO2. Because the species are present in stoichiometric quantity, the moles of CO2 stored is equal to \( n_C/m_2 \), while the total capacity is \( n_C/m_2 + n_B/m_1 \). Hence, the conversion is given by:

\[
\xi = \frac{n_C/m_2}{n_C/m_2 + n_B/m_1} = \frac{x_C/m_2}{x_C/m_2 + x_B/m_1} = \frac{x_C}{x_C + x_B \cdot m_2/m_1}
\]

Furthermore, we obviously have \( x_B + x_C + x_D = 1 \), and \( x_D = m_3x_C/m_2 \). Solving these simultaneously gives:

\[
x_C = \frac{m_2\xi}{m_1 + (m_2 + m_3 - m_1)\xi}
\]

\[
x_D = \frac{m_3\xi}{m_1 + (m_2 + m_3 - m_1)\xi}
\]

\[
x_B = \frac{m_1(1 - \xi)}{m_1 + (m_2 + m_3 - m_1)\xi}
\]

and so

\[
p_{CO2}(\xi) = \frac{p_{CO2}^0}{K} \frac{(m_3\xi)^{m_3}(m_2\xi)^{m_2}}{(m_1(1 - \xi))^{m_1}}(m_1 + (m_2 + m_3 - m_1)\xi)^{m_1-m_2-m_3}
\]

When the inverse function, \( \xi(p_{CO2}) \) was required, \( p_{CO2}(\xi) \) was inverted numerically using the simple but reliable Bisection() method from NLsolve.jl in julia v1.0. [283]
Appendix 5.II. Development of Stripper Model.

Regeneration with a Single Equilibrium Stage

Consider an equilibrium stage with two inlet streams and two outlet streams; the outlet streams, a liquid and a gas phase, are at thermodynamic equilibrium. The liquid stream is an aqueous chemical solvent, containing water and the reactive species $A$, which reacts with $\text{CO}_2$ according to the following reaction:

$$\text{CO}_2 + A \rightleftharpoons B \quad (5.63)$$

The four streams are:

- **Inlet Gas Stream**: Contains steam and $\text{CO}_2$, with molar flows $\dot{n}_{i}^{\text{w,g}}$ and $\dot{n}_{i}^{\text{CO}_2,g}$ respectively, and temperature $T_{g,i}$.

- **Inlet Liquid Stream**: Contains water, $A$ and $B$ (physically dissolved $\text{CO}_2$ is ignored), with molar flows $\dot{n}_{i}^{\text{w,l}}$, $\dot{n}_{i}^{A,l}$ and $\dot{n}_{i}^{B,l}$ respectively, and temperature $T_{l,i}$.

- **Outlet Gas Stream**: Contains steam and $\text{CO}_2$, with molar flows $\dot{n}_{f}^{\text{w,g}}$ and $\dot{n}_{f}^{\text{CO}_2,g}$ respectively, and temperature $T_{f}$.

- **Outlet Liquid Stream**: Contains water, $A$ and $B$ (physically dissolved $\text{CO}_2$ is ignored), with molar flows $\dot{n}_{f}^{\text{w,l}}$, $\dot{n}_{f}^{A,l}$ and $\dot{n}_{f}^{B,l}$ respectively, and temperature $T_{f}$.

**Mole Balances**

The following molar balances apply over the equilibrium stage:

- **Water Balance**:

$$\dot{n}_{i}^{\text{w,g}} + \dot{n}_{i}^{\text{w,l}} = \dot{n}_{f}^{\text{w,g}} + \dot{n}_{f}^{\text{w,l}} \quad (5.64)$$
• CO2 Balance:
\[
\dot{n}_i^{\text{CO2},g} + \dot{n}_i^{B,l} = \dot{n}_f^{\text{CO2},g} + \dot{n}_f^{B,l}
\]  (5.65)

• Reactive Species Balance:
\[
\dot{n}_i^{A,l} + \dot{n}_i^{B,l} = \dot{n}_f^{A,l} + \dot{n}_f^{B,l}
\]  (5.66)

**Enthalpy Balances**

The stage is assumed to be adiabatic, so \(\dot{H}_i = \dot{H}_f\). The enthalpy of each stream is calculated from the sum of the partial molar volumes of all species, \(\dot{H} = \sum_k \dot{n}_k H_k\). It is assumed that the gas and liquid are both ideal solutions, and so all \(\dot{H}_k\) are independent of the composition of the streams. For an ideal gas and a typical liquid, \(\dot{H}_k\) will also be independent of pressure, and so each \(\dot{H}_k = \dot{H}_k(T)\) alone, and may be written \(\dot{H}_k = \dot{H}_k(T_0) + c_{p,k}(T - T_0)\). For the Raoultian components (the gaseous components, and the water in the liquid) \(c_{p,k}\) will refer to the pure-component heat capacity, while for the Henrian components (A and B in the liquid) \(c_{p,k}\) will refer to the heat capacities in a dilute solution.

The enthalpies of the four streams are:

• Inlet Gas Stream:
\[
\dot{H}_i^g = \dot{n}_i^{w,g}(H^{w,g}(T_0) + c_{p,g}^{w,g}(T^g_i - T_0)) + \dot{n}_i^{\text{CO2},g}(\dot{H}^{\text{CO2},g}(T_0) + c_p^{\text{CO2},g}(T^g_i - T_0))
\]  (5.67)

• Inlet Solvent Stream:
\[
\dot{H}_i^l = \dot{n}_i^{w,l}(\dot{H}^{w,l}(T_0) + c_{p,l}^{w,l}(T^l_i - T_0)) \\
+ \dot{n}_i^{A,l}(\dot{H}^{A,l}(T_0) + c_{p,l}^{A,l}(T^l_i - T_0)) \\
+ \dot{n}_i^{B,l}(\dot{H}^{B,l}(T_0) + c_{p,l}^{B,l}(T^l_i - T_0))
\]  (5.68)
\[ \dot{H}_f^g = \dot{n}_f^{w,g} (\bar{H}_{w,g}(T_0) + c_p^{w,g}(T_f - T_0)) + \dot{n}_i^{CO2,g}(\bar{H}_{CO2,g}(T_0) + c_p^{CO2,g}(T_f - T_0)) \]

(5.69)

**Outlet Solvent Stream:**

\[ \dot{H}_i^l = \dot{n}_f^{w,l} (\bar{H}_{w,l}(T_0) + c_p^{w,l}(T_f - T_0)) + \dot{n}_i^{A,l}(\bar{H}_{A,l}(T_0) + c_p^{A,l}(T_f - T_0)) \]

(5.70)

\[ + \dot{n}_f^{B,l}(\bar{H}_{B,l}(T_0) + c_p^{B,l}(T_f - T_0)) \]

The overall enthalpy balance is:

\[ \dot{H}_i^g + \dot{H}_i^l = \dot{H}_f^g + \dot{H}_f^l \]

(5.71)

\[ \dot{n}_i^{w,g}(\bar{H}_{w,g}(T_0) + c_p^{w,g}(T_i^g - T_0)) + \dot{n}_i^{CO2,g}(\bar{H}_{CO2,g}(T_0) + c_p^{CO2,g}(T_i^g - T_0)) \]

\[ + \dot{n}_i^{w,l}(\bar{H}_{w,l}(T_0) + c_p^{w,l}(T_i^l - T_0)) + \dot{n}_i^{A,l}(\bar{H}_{A,l}(T_0) + c_p^{A,l}(T_i^l - T_0)) \]

\[ + \dot{n}_i^{B,l}(\bar{H}_{B,l}(T_0) + c_p^{B,l}(T_i^l - T_0)) \]

\[ + \dot{n}_f^{CO2,g}(\bar{H}_{CO2,g}(T_0) + c_p^{CO2,g}(T_f - T_0)) + \dot{n}_f^{w,l}(\bar{H}_{w,l}(T_0) + c_p^{w,l}(T_f - T_0)) \]

\[ + \dot{n}_f^{A,l}(\bar{H}_{A,l}(T_0) + c_p^{A,l}(T_f - T_0)) + \dot{n}_f^{B,l}(\bar{H}_{B,l}(T_0) + c_p^{B,l}(T_f - T_0)) \]

(5.72)

Just considering the water based terms at \( T_0 \),

\[ \dot{n}_i^{w,g}(\bar{H}_{w,g}(T_0)) + \dot{n}_i^{w,l}(\bar{H}_{w,l}(T_0)) = \dot{n}_f^{w,g}(\bar{H}_{w,g}(T_0)) + \dot{n}_f^{w,l}(\bar{H}_{w,l}(T_0)) \]

(5.73)

\[ (\dot{n}_i^{w,g} - \dot{n}_f^{w,g}) \bar{H}_{w,g}(T_0) = (\dot{n}_i^{w,l} - \dot{n}_f^{w,l}) \bar{H}_{w,l}(T_0) \]

(5.74)

From the water balance, \( \dot{n}_i^{w,g} - \dot{n}_f^{w,g} = \dot{n}_f^{w,l} - \dot{n}_i^{w,l} \equiv \Delta \dot{n}_w \), and so these terms in Eq. (5.72) reduce to:

\[ 0 = \Delta \dot{n}_w (\bar{H}_{w,l}(T_0) - \bar{H}_{w,g}(T_0)) \equiv \Delta \dot{n}_w (-\Delta h_{w,vap}(T_0)) \]

(5.75)

where \( \Delta h_{w,vap}(T_0) \) is the enthalpy of vaporisation of water at temperature \( T_0 \).
Now consider the terms in Eq. (5.72) involving the exchange of CO2 at temperature \( T_0 \):
\[
\dot{n}_i^{\text{CO2},g} \dot{H}^{\text{CO2},g}(T_0) + \dot{n}_i^{A,l} \dot{H}^{A,l}(T_0) + \dot{n}_i^{B,l} \dot{H}^{B,l}(T_0) \\
= \dot{n}_f^{\text{CO2},g} \dot{H}^{\text{CO2},g}(T_0) + \dot{n}_f^{A,l} \dot{H}^{A,l}(T_0) + \dot{n}_f^{B,l} \dot{H}^{B,l}(T_0)
\] (5.76)
\[
(\dot{n}_i^{\text{CO2},g} - \dot{n}_f^{\text{CO2},g}) \dot{H}^{\text{CO2},g}(T_0) + (\dot{n}_i^{A,l} - \dot{n}_f^{A,l}) \dot{H}^{A,l}(T_0) = (\dot{n}_f^{B,l} - \dot{n}_i^{B,l}) \dot{H}^{B,l}(T_0)
\] (5.77)

From the CO2 and reactive species balances, \( \dot{n}_i^{\text{CO2},g} - \dot{n}_i^{\text{CO2},g} = \dot{n}_i^{A,l} - \dot{n}_i^{A,l} = \dot{n}_i^{B,l} - \dot{n}_i^{B,l} \equiv \Delta \dot{n}_\text{CO2} \), and so these various terms reduce to:
\[
0 = -\Delta \dot{n}_\text{CO2}(\Delta h_{\text{CO2}}^{\text{abs}}(T_0))
\] (5.78)

where \( \Delta h_{\text{CO2}}^{\text{abs}}(T_0) \) is the enthalpy of absorption of CO2 at temperature \( T_0 \).

The various heat-capacity terms in Eq. (5.72) are:
\[
\dot{n}_i^{w,g} c_p^{w,g}(T_i^g - T_0) + \dot{n}_i^{\text{CO2},g} c_p^{\text{CO2},g}(T_i^g - T_0) + \dot{n}_i^{A,l} c_p^{A,l}(T_i^l - T_0) + \dot{n}_i^{B,l} c_p^{B,l}(T_i^l - T_0) \\
+ \dot{n}_i^{B,l} c_p^{B,l}(T_i^l - T_0) = \dot{n}_f^{w,g} c_p^{w,g}(T_f - T_0) + \dot{n}_f^{\text{CO2},g} c_p^{\text{CO2},g}(T_f - T_0) \\
+ \dot{n}_f^{A,l} c_p^{A,l}(T_f - T_0) + \dot{n}_f^{B,l} c_p^{B,l}(T_f - T_0)
\] (5.79)
\[
[\dot{n}_i^{w,g} c_p^{w,g} + \dot{n}_i^{\text{CO2},g} c_p^{\text{CO2},g}](T_i^g - T_0) + [\dot{n}_i^{A,l} c_p^{A,l} + \dot{n}_i^{B,l} c_p^{B,l}](T_i^l - T_0) \\
= [\dot{n}_f^{w,g} c_p^{w,g} + \dot{n}_f^{\text{CO2},g} c_p^{\text{CO2},g} + \dot{n}_f^{A,l} c_p^{A,l} + \dot{n}_f^{B,l} c_p^{B,l}](T_f - T_0)
\] (5.80)
\[
[\dot{n}_i^{w,g} c_p^{w,g} + \dot{n}_i^{\text{CO2},g} c_p^{\text{CO2},g}](T_i^g - T_0) + [\dot{n}_i^{A,l} c_p^{A,l} + \dot{n}_i^{B,l} c_p^{B,l}](T_i^l - T_0) \\
= [\dot{n}_i^{w,g} c_p^{w,g} + \dot{n}_i^{\text{CO2},g} c_p^{\text{CO2},g} + \dot{n}_i^{A,l} c_p^{A,l} + \dot{n}_i^{B,l} c_p^{B,l}](T_f - T_0) \\
+ [-\Delta \dot{n}_w c_p^{w,g} + \Delta \dot{n}_\text{CO2} c_p^{\text{CO2},g} + \Delta \dot{n}_w c_p^{w,l} + \Delta \dot{n}_\text{CO2} c_p^{A,l} - \Delta \dot{n}_\text{CO2} c_p^{B,l}](T_f - T_0)
\] (5.81)
\[
[\dot{n}_i^{w,g} c_p^{w,g} + \dot{n}_i^{\text{CO2},g} c_p^{\text{CO2},g}](T_i^g - T_f) + [\dot{n}_i^{A,l} c_p^{A,l} + \dot{n}_i^{B,l} c_p^{B,l}](T_i^l - T_f) \\
= [\Delta \dot{n}_w (c_p^{w,l} - c_p^{w,g}) - \Delta \dot{n}_\text{CO2} (c_p^{B,l} - c_p^{A,g} - c_p^{\text{CO2},g})](T_f - T_0)
\] (5.82)

The terms on the left hand side of this equation are the total heat capacities of the inlet streams, and they may be replaced by mean heat capacities (which may be more readily estimated from available data). Further, because the various solutions are ideal,
\[
\Delta h_{\text{w}}^{\text{vap}}(T) = \Delta h_{\text{w}}^{\text{vap}}(T_0) + (c_p^{w,l} - c_p^{w,g})(T - T_0)
\] (5.83)
The right hand side of Eq. (5.82) may then be combined with Eq. (5.75) and (5.78) to give \( \Delta h \) values at \( T = T_f \). Overall, then Eq. (5.72) may be simplified to the final enthalpy balance:

\[
c_{g,i}^{av} \dot{n}_g (T_g - T_f) + c_{l,i}^{av} \dot{n}_l (T_l - T_f) + \Delta \dot{n}_{CO2} \Delta h_{CO2}^{abs} (T_f) = \Delta \dot{n}_w (-\Delta h_{w}^{vap}(T_f)) \tag{5.85}
\]

where \( c_{p,av} \) refers to the molar-average heat capacity.

It is somewhat surprising that the enthalpy balance reduces to such a simple expression, even as matter is being transferred across the phase boundary. On intuitive grounds, one would expect that if, say, a large amount of water were added to the liquid stream, it should increase its overall thermal mass, and this ought to appear in the terms containing heat capacities on the left hand side of Eq. (5.85). However, these terms refer only to the initial molar flow rates and heat capacities, and this effect would instead appear within the \( \Delta h_{CO2}^{abs} \) term. This is not too unreasonable when it is considered that, in this system, the thermal mass of one phase cannot be increased without decreasing the thermal mass of the other; the line between thermal energy and energy of reaction is, in this case, blurry. In any case, the change in thermal mass due to mass transfer across the boundary is negligible compared to both enthalpies of absorption/vaporisation and the total thermal masses of the streams, and these effects are relatively minor within this system.

Note that (5.85) has 3 unknowns: \( T_f, \Delta \dot{n}_w \) and \( \Delta \dot{n}_{CO2} \). Two more equations are required to fully specify the system. These will be provided by the equilibrium conditions.

**Equilibrium Compositions**

The existence of phase and chemical equilibrium place several constraints on the chemical potentials of the species exiting the system (each of these refer to the
outlet stream, and so we will drop the ‘f’ subscript used above in what follows):

- **Water Equilibrium:** The chemical potential of the water in the gas and in the liquid are equal:

\[
\mu_{w,g}(T, p_{w,g}) = \mu_{w,l}(T)
\]

Expanding the expressions for an ideal gas and an ideal solution [153]:

\[
\mu_{w,g,0}(T) + RT \ln p_{w,g} = \mu_{w,l,0}(T, p) + RT \ln x_w
\]

Noting that the chemical potential of a liquid is insensitive to pressure:

\[
\mu_{w,g,0}(T) + RT \ln p_{w,g} \approx \mu_{w,l,0}(T, p_{\text{sat}}(T)) + RT \ln x_w
\]

Substituting in the expression for equality of the chemical potentials of the pure gas and pure liquid at the vapor pressure \(\mu_{w,g,0}(T) + RT \ln p_{\text{sat}} = \mu_{w,l,0}(T, p_{\text{sat}}(T))\) gives:

\[
\mu_{w,g,0}(T) + RT \ln p_{w,g} = \mu_{w,g,0}(T) + RT \ln p_{\text{sat}} x_w
\]

And finally, rearranging gives Raoult’s law:

\[
p_{w,g} = x_w p_{w,\text{sat}}(T)
\]

\[
y_w p = x_w p_{w,\text{sat}}(T)
\]

The mole fractions of water in the outlet liquid and gas, \(x_w\) and \(y_w\), themselves depend on the moles of water and CO\(_2\) transferred, \(\Delta n_w\) and \(\Delta n_{\text{CO2}}\). Therefore, Eq. (5.91) provides one extra equation, alongside Eq. (5.85), for the 3 unknowns, \(\Delta n_w\), \(\Delta n_{\text{CO2}}\) and \(T\) (or \(T_f\) before the subscript was dropped).

- **Reaction Equilibrium:** The chemical potentials of the various reactive
species are related by:

\[ \mu^{\text{CO}_2,g}(T, p) + \mu^A(T, p, y^A) = \mu^B(T, p, x^B) \] (5.92)

\[ \mu^{0,\text{CO}_2}(T) + RT \log p^{\text{CO}_2,g} + \mu^B(T, p) + RT \log x_A = \mu^B(T, p) + RT \log x_B \] (5.93)

\[ \frac{x_B}{x_{A\text{P}_{\text{CO}_2}}} = \frac{x_B}{x_{A_{\text{Y}_{\text{CO}_2}}}p} = K(T) \] (5.94)

These various mole fraction may be expressed in terms of \( \Delta \dot{n}_w \) and \( \Delta \dot{n}_{\text{CO}_2} \), which may be solved for (along with \( T \)) via Eqs (5.85), (5.91) and (5.94).

**Simplifications, and Equation to Solve**

It will be assumed that \( \Delta h_{\text{CO}_2}^{\text{abs}} \) and \( \Delta h_{w}^{\text{vap}} \) are both independent of temperature. This is reasonable, because the changes due to the difference in heat capacities of the liquid and gas are negligible (e.g. for water, we have \( c_p^l - c_p^g \approx 30 \frac{\text{J}}{\text{K} \cdot \text{mol}}, \) and \( \Delta h_{w}^{\text{vap}} \approx 40 \frac{\text{kJ}}{\text{mol}}, \) and so the variation is less than 10% over a 100 \( ^\circ \text{C} \) temperature swing.) Even in real systems, where non-idealities could lead to changes in \( \Delta h_{\text{CO}_2}^{\text{abs}} \), this is often reasonably constant over a range of temperature values (Mathias, 2013).

We summarise the above calculations in a simple system of equations:

- **Unknowns**: We will have two unknowns
  - Rate of CO2 Transfer to Gas: \( \Delta \dot{n}_{\text{CO}_2} \)
  - Rate of Water Transfer to Liquid: \( \Delta \dot{n}_w \)

We can avoid specifying \( T \) (or \( T_f \)) as a third unknown, because it may be explicitly calculated using enthalpy balance (see the next point.)

- **Calculate Equilibrium Temperature**: We may calculate the outlet temperature from an overall energy balance:

\[
T = \frac{\Delta \dot{n}_{\text{CO}_2}(\Delta h_{\text{CO}_2}^{\text{abs}}) - \Delta \dot{n}_w(-\Delta h_w^{\text{vap}}) + \dot{n}_{\text{in},\text{liq}}c_p,\text{liq}T_{\text{liq}} + \dot{n}_{\text{in},\text{gas}}c_p,\text{gas}T_{\text{gas}}}{\dot{n}_{\text{in},\text{liq}}c_p,\text{liq} + \dot{n}_{\text{in},\text{gas}}c_p,\text{gas}}
\] (5.95)
where the molar flow rates of the liquid and gas, the heat capacities, and the gas and liquid temperatures all refer to the initial, average values. It may appear to be an oversimplification to only consider the initial flowrates, given that both energy and matter are being exchanged between the gas and the liquid, but this is the result of a rigorous mass and energy balance over the whole system. Somewhat surprisingly, changes in the heat content of the inlet and outlet streams due to mass transfer is implicitly accounted for in the temperature dependence of $\Delta h_{\text{abs}}^{\text{CO}_2}$ and $\Delta h_{\text{vap}}^{\text{w}}$.

- **Water Equilibrium:** Water will move between the phases until its chemical potential is equal in both phases. For an ideal gas above an ideal solution this reduces to:49

$$y_{\text{w}p} = x_{\text{w}}p_{\text{w}}^{\text{sat}}(T)$$

(5.96)

where $y_{\text{w}}$ is the mole fraction in the gas phase, $p$ is the total pressure (which must be specified), $x_{\text{w}}$ is the mole fraction of water in the liquid, and $p_{\text{w}}^{\text{sat}}(T)$ is an Antoine equation for the vapore pressure of water. The NIST chemistry WebBook [284] suggests the following parameters:

$$p_{\text{w}}^{\text{sat}}(\text{bar}) = 10^{5.08354 - 1663.125/(T(\text{K}) - 45.622)}; \quad 344 \text{ K} \leq T \leq 373 \text{ K}.$$  

(5.97)

While the temperature range only extends to 373 K, the predicted values are within 1% of those listed in the CRC Handbook of Chemistry and Physics [285] up to 150°C.

Expressions for the $x_{\text{w}}$ and $y_{\text{w}}$ in terms of $\Delta \dot{n}_{\text{CO}_2}$ and $\Delta \dot{n}_{\text{w}}$ are given below.

- **CO₂ Equilibrium:** For absorption accompanied by the simple reaction $A +$

---

49An ideal solution is Raoultian in the solvent (which is water in this case) even if it is only Henrian in the solutes. In fact, if a solution exhibits Henrian behaviour in all but one species (the solutes), thermodynamic consistency requires it must exhibit Raoultian behaviour in the final species (the solvent) - this is a fun little thermodynamic exercise.
CO₂ ⇌ B in an ideal solution, the equilibrium condition reduces to:

\[
\frac{x_B}{x_A y_{CO₂} p} = K(T) = \exp \left( -\frac{\Delta h^0}{RT} + \frac{\Delta s^0}{R} \right) \quad (5.98)
\]

This will be rearranged to

\[
y_{CO₂} p = \frac{x_B}{x_A K} \quad (5.99)
\]

In this form it is of the same magnitude as Eq. (5.96), which reduces the difficulty of the numerical solution.

- **Expressions for Mole Fractions:** The equilibrium mole fractions of the various species which appear in Eq. (5.96) and (5.99) are given by:

\[
y_w = \frac{\dot{n}^{in}_{w,\text{gas}} - \Delta \dot{n}_w}{\dot{n}^{in}_{w,\text{gas}} - \Delta \dot{n}_w + \dot{n}^{in}_{CO₂} + \Delta \dot{n}_{CO₂}} \quad (5.100)
\]

\[
y_{CO₂} = 1 - y_w \quad (5.101)
\]

\[
x_w = \frac{\dot{n}^{in}_{w,\text{liq}} + \Delta \dot{n}_w}{\dot{n}^{in}_{w,\text{liq}} + \Delta \dot{n}_w + \dot{n}^{in}_{A} + \dot{n}^{in}_{B}} \quad (5.102)
\]

\[
x_A = \frac{\dot{n}^{in}_{A} + \Delta \dot{n}_{CO₂}}{\dot{n}^{in}_{A} + \Delta \dot{n}_w + \dot{n}^{in}_{A} + \dot{n}^{in}_{B}} \quad (5.103)
\]

\[
x_B = 1 - x_A - x_w \quad (5.104)
\]

- **Solution methodology.** The solver takes an initial guess for values of \(\Delta \dot{n}_{CO₂}\) and \(\Delta \dot{n}_w\). From this value and the inlet conditions, it calculates the resulting equilibrium temperature, \(T\), via Eq. (5.95), and the resulting equilibrium mole fractions and water saturation pressure via Eq. (5.100) – (5.104) and Eq. (5.97). It then calculates and returns the difference between the left- and right-hand sides of Eq. (5.96) and (5.99) (i.e. the two residuals). The solver then iteratively searches for values of \(\Delta \dot{n}_{CO₂}\) and \(\Delta \dot{n}_w\) which make both of these residuals vanish. These equations were implemented in Julia v1.0 [283]. Both a local root finding algorithm from NLsolve.jl and a black box optimisation algorithm (set to minimise the absolute value of the residuals)
from BlackBoxOptim.jl in julia v1.0 consistently gave the same solution within 0.1 seconds.

\( N \) Theoretical Counter-Current Stages

We now extend the analysis to a system of \( N \) theoretical stages in counter-current operation. The known values are the inlet flow rates and conditions of the various gaseous and liquid species:

- **Inlet Liquid Stream:** \( \dot{n}^A_1, \dot{n}^B_1, \dot{n}^{w,\text{liq}}_1 \) and \( T^{\text{liq}}_1 \). In the model, the various molar flow rates (which were calculated on a basis of 1 mole of CO2 captured) were calculated from the rich solvent loading, \( \xi_{\text{rich}} \), and the water fraction in the solvent, \( x_w \), and the liquid was assumed to be preheated to \( T^{\text{liq}}_1 = T_{\text{steam}} \). When modelling the regeneration of SIPs or MECS, an extra flow term, \( \dot{n}^{\text{shell}}_1 \), must be included in \( \dot{n}^{\text{liq}}_1 \) in Eq. (5.95). In this work, the flow rate of the shell was calculated on the assumption that its mass fraction was 0.1, independent of the value of \( \beta \).

- **Inlet Gas Stream:** \( \dot{n}^{\text{CO2}}_{N+1}, \dot{n}^{w,\text{gas}}_{N+1} \) and \( T^{\text{gas}}_{N+1} \). In the model \( \dot{n}^{\text{CO2}}_{N+1} = 0, T^{\text{gas}}_{N+1} = T_{\text{steam}}, \) and \( \dot{n}^{w,\text{gas}}_{N+1} \) was set to \( \gamma \dot{n}^B_1 \), where \( \gamma \) was a parameter within the model.

The other parameters that were specified were:

- **Initial mean molar heat capacities:** \( c_{p,\text{liq}} \) and \( c_{p,\text{gas}} \). Ideal gas heat capacities were used for the gas phase. For pure liquid systems, \( c_{p,\text{liq}} \) was set equal to the heat capacity of water. However, as discussed above, for MECS/SIPs systems \( c_{p,\text{liq}} \) was a weighted average of water and the shell material, assuming a shell mass fraction of 0.1.

- **Enthalpy of vaporisation and absorption:** \( \Delta h^{\text{abs}}_{\text{CO2}} \) and \( \Delta h^{\text{vap}}_w \)

- **Standard entropy of absorption:** \( \Delta s^{0,\text{abs}}_{\text{CO2}} \)

- **An Antoine equation:** \( p^{\text{sat}}_w(T) \).
For the simpler problem involving only a single stage, the root finding algorithm found the values of $\Delta \dot{n}_{CO2}$ and $\Delta \dot{n}_w$ which led to satisfaction of two constraints, Eq. (5.96) and Eq. (5.99), on the chemical potentials of the various species (i.e. which led to two residuals vanishing.) In the more generation problem, the transfer of CO2 and water in each of the $N$ stages, $\Delta \dot{n}_{CO2}^i$ and $\Delta \dot{n}_w^i$, where $i = 1 \ldots, N$, was allowed to vary, and the values of these which lead to satisfaction of $2N$ constraints on the chemical potential (i.e. 2 constraints of the form of Eq. (5.96) and Eq. (5.99) in each of the $N$ stages) were solved for using a root-finding algorithm. The liquid enters at stage $i = 1$, while the gas enters at stage $i = N$. A slightly unorthodox numbering system is used: the inlet liquid stream (to stage 1) is stream 1, followed by 2, 3, all the way to $N + 1$. The inlet gas stream (to stage $N$) is labelled $N + 1$, which is then followed by $N, N - 1$, all the way to the outlet gas stream 1.

We create a function that takes as input the $2N$ values of $\Delta \dot{n}_{CO2}^i$ and $\Delta \dot{n}_w^i$, and outputs the values of $2N$ residuals which will vanish when the equality constraints on the chemical potentials are satisfied. The function first calculates the flow of each species in the streams between each stage. For each of the $N$ stages, it calls the simple function developed for the single-stage analysis, in order to calculate the error in the constraints of the form of Eq. (5.96) and Eq. (5.99) in this stage. The function then returns these $2N$ residuals, and a root finding algorithm is used to determine the values of $\Delta \dot{n}_{CO2}^i$ and $\Delta \dot{n}_w^i$ which ensure thermodynamic equilibrium is attained within each stage of the column.

Before Eq. (5.96) and (5.99) can be evaluated, the temperature profile up the column must be calculated. While the inlet gas temperature, $T_g^{i=1}$, and the inlet liquid temperature, $T_l^{i=1}$, are known, the temperatures of each of the $N$ stages are not known. Let $T_i$ be the temperature of stage $i$. Then an energy balance around the $i$th stage (of identical form to that considered for the single stage) gives:

$$\dot{n}_{liq}^{i=1} c_{p,liq} (T_i - T_{i-1}) + \dot{n}_{gas}^{i+1} c_{p,gas} (T_i - T_{i+1}) = \Delta \dot{n}_{CO2}^i \Delta h_{CO2}^{vap} + \Delta \dot{n}_w^i \Delta h_w^{vap} \quad (5.105)$$
\[-\dot{n}_i^{\text{liq}} c_{p,i}^{\text{liq}} T_{i-1} + (\dot{n}_i^{\text{liq}} c_{p,i}^{\text{liq}} + \dot{n}_{i+1}^{\text{gas}} c_{p,i+1}^{\text{gas}}) T_i + (-\dot{n}_{i+1}^{\text{gas}} c_{p,i+1}^{\text{gas}}) T_{i+1} = \dot{n}_i^{\text{CO2}} \Delta h_{\text{vap}}^{\text{CO2}} + \dot{n}_i^{\text{w}} \Delta h_{\text{vap}}^{\text{w}} \]  

\hspace{1cm} (5.106)

This provides \( N \) equations: one for the temperature in each stage. In the first equation, \( T_0 \) is the inlet liquid temperature, while in the final equation \( T_{N+1} \) is the gas temperature. In matrix form, this system of equations is represented by a tridiagonal matrix, and so the system may be solved extremely efficiently by the Thomas algorithm [286].

Overall, for a given set of values of the inlet conditions and guesses for \( \Delta \dot{n}_i^{\text{w}} \) and \( \Delta \dot{n}_i^{\text{CO2}} \), the compositions and temperatures in each stage are first calculated, before the value of the \( 2N \) residuals given by Eq. (5.99) and (5.96) are calculated by repeatedly calling the simpler function developed for a single stage. Once again, the model was very robust, and a local root finding algorithm and a differential evolution optimisation algorithm gave identical results. The local root finding algorithm was quite fast - it typically converged in 0.1 – 1 seconds, depending on the value of \( N \). This was fast enough for the stripper model itself to be repeatedly called in the optimisation algorithms used to find optimal values of \( W_{\text{eq}} \).

**Regeneration Unit Behaviour**

The stripper itself behaved exactly as one would expect. The classical temperature bulge at the bottom of the stripper and the conversion profile are both shown in Figures 5.15 and 5.16, while in Figure 5.17 the conversion is shown as a function of the number of theoretical stages. The lean conversion typically asymptoted to a minimal value around \( N = 10 \), and this was the largest value analysed in this work (this asymptote may also be seen in Figure 5.9.) The larger temperatures near the bottom of the column (much greater than the steam temperature, and caused by spontaneous, exothermic condensation of the pure steam into the aqueous solution) increase the partial pressure at the bottom of the stripper, allowing for deeper regeneration. The temperature bulge is exacerbated at higher pressures, all else held constant, because of the greater driving force for steam condensation at the bottom.
Figure 5.15: Temperature profile inside 10-stage stripper from top (stage 1) to bottom (stage 10). Inlet gas and sorbent temperatures: 383 K; Pressure: 2 bar; $\Delta h_{CO_2} = -80 \text{ kJ mol}^{-1}$; $\gamma = 2.85$. Solvent has thermal properties of pure water.

of the column. Readers are referred to Chapter 13 of Smith’s *Design of Equilibrium Stage Processes* [287] for more details on the design of strippers containing non-ideal solutions, and guidance on developing computer algorithms substantially more efficient than those used here (the book is 56 years old, after all.)\(^{50}\)

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\(^{50}\)The author would like to put it on the record that it is truly remarkable how efficient even a naively-constructed stripper model is when combined with modern numerical solvers. In principle, the introduction of non-idealities would not significantly increase the computational complexity (it would lead to the simultaneous solution of $3N$ equations, rather than $2N$, as temperature could not be decoupled as was done here.) The pedagogical values of constructing such a model - in highlighting the physical causes of the temperature profile, and the way high temperatures near the bottom allow for deeper regeneration; or the role of steam in supplying energy while simultaneously reducing $p_{CO_2}$ - cannot be overstated.
Figure 5.16: Conversion profile inside 10-stage stripper from top (stage 1) to bottom (stage 10). Inlet gas and sorbent temperatures: 383 K; Pressure: 2 bar; $\Delta h_{\text{CO}_2} = -80 \text{ kJ mol}^{-1}$; $\gamma = 2.85$. Solvent has thermal properties of pure water.

Figure 5.17: Outlet conversion vs number of theoretical stages. Inlet gas and sorbent temperatures: 383 K; Pressure: 2 bar; $\Delta h_{\text{CO}_2} = -80 \text{ kJ mol}^{-1}$; $\gamma = 2.85$. Inlet sorbent conversion: 0.875. Solvent has thermal properties of pure water.
Appendix 5.III Derivation of Gibbs-Helmholtz Equation

The Gibbs-Helmholtz equation is a standard thermodynamic relation, whose derivation may be found in many texts [153, 247]. Nevertheless, it will be helpful to systematically derive this relationship in order to clearly highlight the physical meaning of the terms involved, and to justify several assumptions implicit in the analysis.

Consider a system consisting of two homogenous phases, a gas containing a mixture of CO$_2$ and N$_2$, and a non-volatile liquid solvent which chemically reacts with CO$_2$, held under isothermal, isobaric conditions. When the two phases are in chemical equilibrium, the entropy of the accessible universe will be maximised, and for an isothermal, isobaric system this will be achieved when the Gibbs free energy of the system, $G$, is minimised. Under these conditions, a necessary condition for the minimisation of $G$ is that, for each species $i$, the chemical potential of $i$, $\mu_i$, is the same in each phase ($\mu_i$ is analagous to the temperature, which must also be equal between phases at equilibrium.) Now suppose that the temperature and partial pressure of CO$_2$ undergo small changes, $dT$ and $dp_{CO2}$, such that the liquid composition, $x_i$, and total pressure remain unchanged (strictly speaking, the pressure should be adjusted by changing $p_{N2}$ in order to keep the solvent at its bubble point, however this adjustment has rarely been used in practice, leads to negligible error, and indeed was only noted by Mathias and O’Connel in 2012 [259].) Then the change in $\mu$ for each phase will be given by a modified form of the fundamental relation: [153, 247]

$$d\left(\frac{\mu_i}{RT}\right) = \frac{\bar{H}_i}{R}d\left(\frac{1}{T}\right) + \frac{\bar{V}_i}{RT}dP + \sum_{j=1}^{n-1} \left(\frac{\partial(\mu_i/RT)}{\partial x_j}\right)_{T,P,x_k} dx_j$$

(5.107)

where $\bar{H}_i$ and $\bar{V}_i$ are the partial molar enthalpy and partial molar volume of $i$ in each phase, respectively. In the liquid, the composition and pressure are unchanged,
and so, for CO$_2$

$$d \left( \frac{\mu_{\text{CO}_2}^{\text{liq}}}{RT} \right) = \frac{\bar{H}_{\text{CO}_2}^{\text{liq}}}{R} d \left( \frac{1}{T} \right)$$  \hspace{1cm} (5.108)

On the other hand, if the gas phase is ideal, the chemical potential is given by [153]:

$$\mu_{\text{CO}_2}^{\text{gas}}(T, p_{\text{CO}_2}) = \mu_{\text{CO}_2}^0(T) + RT \log p_{\text{CO}_2}$$ \hspace{1cm} (5.109)

where $\mu_{\text{CO}_2}^0(T)$ is the chemical potential of the gas at standard pressure. We then have:

$$d \left( \frac{\mu_{\text{CO}_2}^{\text{gas}}}{RT} \right) = \left( \frac{d(\mu_{\text{CO}_2}^0/RT)}{d (1/T)} \right)_{p_{\text{CO}_2}} d \left( \frac{1}{T} \right) + d \log p_{\text{CO}_2}.$$ \hspace{1cm} (5.110)

By Eq. (5.107), and noting that $\tilde{H}_i$ only depends on $T$ for an ideal gas,

$$\left( \frac{d(\mu_{\text{CO}_2}^0/RT)}{d (1/T)} \right)_{p_{\text{CO}_2}} = \left( \frac{d(\mu_{\text{CO}_2}^0/RT)}{d (1/T)} \right)_{p,y_{\text{CO}_2}} = \frac{\bar{H}_{\text{CO}_2}^{\text{gas}}}{R}$$ \hspace{1cm} (5.111)

which when combined with Eq. (5.110) gives

$$d \left( \frac{\mu_{\text{CO}_2}^{\text{gas}}}{RT} \right) = \frac{\bar{H}_{\text{CO}_2}^{\text{gas}}}{R} d \left( \frac{1}{T} \right) + d \log p_{\text{CO}_2}.$$ \hspace{1cm} (5.112)

At the new equilibrium condition we still have $\mu_{\text{CO}_2}^{\text{gas}} = \mu_{\text{CO}_2}^{\text{liq}}$, and so for the transition between equilibrium states, $d\mu_{\text{CO}_2}^{\text{gas}} = d\mu_{\text{CO}_2}^{\text{liq}}$. Equating Eq. (5.108) and Eq. (5.112) then gives

$$\frac{(\bar{H}_{\text{CO}_2}^{\text{liq}} - \bar{H}_{\text{CO}_2}^{\text{gas}})}{R} d \left( \frac{1}{T} \right) = d \log p_{\text{CO}_2}.$$ \hspace{1cm} (5.113)

And, defining

$$\Delta \bar{H}_{\text{abs,CO}_2} = \bar{H}_{\text{CO}_2}^{\text{liq}} - \bar{H}_{\text{CO}_2}^{\text{gas}},$$ \hspace{1cm} (5.114)

we get the Gibbs-Duhem equation:

$$\left( \frac{\partial \log p_{\text{CO}_2}}{\partial (1/T)} \right)_{p,y_i} \approx \frac{\Delta \bar{H}_{\text{abs,CO}_2}}{R}.$$ \hspace{1cm} (5.115)

In deriving this equation, it was assumed that the gas phase was ideal, and that N$_2$ is insoluble in the solvent (hence $p_{\text{N}_2}$ may be varied in order to keep the pressure
constant without changing the solvent composition.) Now consider $\Delta \bar{H}_{\text{abs,CO}_2} = \bar{H}_{\text{CO}_2}^{\text{liq}} - \bar{H}_{\text{CO}_2}^{\text{gas}}$. Physically, $\Delta \bar{H}_{\text{abs,CO}_2}$ represents the enthalpy released when an infinitesimal amount of CO$_2$ is transferred from the gas to the liquid phase, divided by the number of moles transferred. This ‘differential’ heat of absorption depends in principle on both the solvent loading and the temperature, however in this work, it will be assumed to be independent of both. This assumption is implicit in much of the discussion regarding chemical solvents, because the ‘heat of absorption’ of a solvent (a concept often cited when comparing prospective solvents [82]) is only meaningful and useful if $\Delta \bar{H}_{\text{abs,CO}_2}$ is independent of loading and relatively independent of temperature. Fortunately, this is often the case. For instance, Kim and Svendsen [263] found that for concentrated MEA $\Delta \bar{H}_{\text{abs,CO}_2}$ was roughly independent of loading (at least until chemical saturation was reached.) This implies that it is numerically equal to the ‘integral’ enthalpy of absorption, $\Delta h_{\text{abs,CO}_2}$, defined as the enthalpy released when a finite number of mols of CO$_2$ are absorbed into a solvent, divided by the number of moles absorbed. Kim and Svendsen [263] also investigated the temperature-dependence of $\Delta h_{\text{abs,CO}_2}$, and found that for concentrated MEA solutions $\Delta h_{\text{abs,CO}_2}$ varied by only $\sim$15% between 40°C and 120°C. Furthermore, Mathias et al [247] found that, for the same solvent, CO$_2$ absorption isotherms were better predicted by assuming a constant value for $\Delta h_{\text{abs,CO}_2}$ over the same temperature range.

Under these assumptions, the enthalpy of absorption, $\Delta h_{\text{abs,CO}_2}$, may be taken as a physical property of a hypothetical solvent, which predicts both the heat required to desorb CO$_2$ from the hot, rich solvent, and also the temperature dependence of the absorption isotherms.
Appendix 5.IV: Standard Enthalpies and Entropies

In this Appendix, we calculate the standard entropy and enthalpy of formation for a number of chemical solvents.

**Potassium Carbonate**

We have the following values from Bishnoi and Rochelle [288]:

\[
\frac{a_{\text{CO}_2(aq)}a_{\text{H}_2\text{O}}}{a_{\text{HCO}_3^-}a_{\text{H}_3\text{O}^+}} = \exp \left( -231.4 + \frac{12092}{T} + 37.68 \log T \right) \tag{5.116}
\]

\[
\frac{a_{\text{H}_3\text{O}^+}a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}a_{\text{H}_2\text{O}}} = \exp \left( 216.0 - \frac{12432}{T} - 35.48 \right) \tag{5.117}
\]

\[
p_{\text{CO}_2}/\text{Pa} = \frac{H_{\text{CO}_2}}{a_{\text{CO}_2(aq)}} = \exp \left( 170.71 - \frac{8477.7}{T} - 21.95 \log T + 0.005781T \right) \tag{5.118}
\]

Multiplying these together gives

\[
\frac{a_{\text{CO}_3^{2-}}a_{\text{H}_2\text{O}}p_{\text{CO}_2} (\text{Pa})}{a_{\text{HCO}_3^-}^2} = \exp \left( 155.31 - \frac{8817}{T} - 19.75 \log T + 0.005781T \right) \tag{5.119}
\]

We also have:

\[
p_{\text{CO}_2}(\text{bar})/p_{\text{CO}_2}(\text{Pa}) = 10^{-5} = \exp(-11.51) \tag{5.120}
\]

Multiplying this in gives:

\[
\frac{a_{\text{CO}_3^{2-}}a_{\text{H}_2\text{O}}p_{\text{CO}_2}(\text{kPa})}{a_{\text{HCO}_3^-}^2} = \exp \left( 143.8 - \frac{8817}{T} - 19.75 \log T + 0.005781T \right) \tag{5.121}
\]

Inverting this gives the equilibrium constant:

\[
K(T) = \frac{a_{\text{HCO}_3^-}}{a_{\text{CO}_3^{2-}}a_{\text{H}_2\text{O}}p_{\text{CO}_2}(\text{kPa})} = \exp \left( -143.8 + \frac{8817}{T} + 19.75 \log T - 0.005781T \right) \tag{5.122}
\]
Standard enthalpies and entropies of formation may now be calculated from this at various temperatures. The standard enthalpy of absorption is given by:

\[
\Delta h^0 = RT^2 \frac{\partial \log K}{\partial T} = R(-8817 + 19.75T - 0.005781T^2)
\]

\[
= -73304 + 164.2T - 0.04806T^2
\]

Meanwhile, \(\Delta g^0 = -RT \log K\) is given by:

\[
\Delta g^0 = (143.8T - 8817 - 19.75T \log T + 0.005781T^2) R
\]

\[
= 1195.55T - 73304 - 164.2T \log T + 0.04806T^2
\]

And so

\[
\Delta s^0 = (\Delta h^0 - \Delta g^0)/T = -1195.55 + 164.2(\log T + 1) - 0.09612T
\]

At 313 K, we have \(\Delta h^0 = -26.6 \text{ kJ mol}^{-1}, \Delta s^0 = -117.9 \text{ J mol}^{-1} \text{ K}^{-1}\) and \(\Delta h^0/T\Delta s^0 = 0.72\). At 353 K, we have \(\Delta h^0 = -21.3 \text{ kJ mol}^{-1}, \Delta s^0 = -101.3 \text{ J mol}^{-1} \text{ K}^{-1}\) and \(\Delta h^0/T\Delta s^0 = 0.59\). At 383 K, we have \(\Delta h^0 = -17.5 \text{ kJ mol}^{-1}, \Delta s^0 = -91.5 \text{ J mol}^{-1} \text{ K}^{-1}\) and \(\Delta h^0/T\Delta s^0 = 0.50\).

**Piperazine**

The same calculation can be conducted for an aqueous piperazine solution; we will base our analysis on the paper of Cullinane and Rochelle [276]. From this paper,

\[
\frac{a_{PZH^+}a_{H_2O}}{a_{PZ}a_{H_3O^+}} = \exp \left(-241.5 + \frac{21918}{T} + 34.35 \log T \right)
\]

(5.126)

Here, both H\(_2\)O and PZ have activities based on the symmetric (i.e. Raoultian) convention, while all ions are based on the unsymmetric (i.e. Henrian) convention.

We also have:

\[
\frac{a_{PZCOO^-}a_{H_3O^+}}{a_{PZ}a_{CO_2}a_{H_2O}} = \exp \left(-10.15 + 21980 \left( \frac{1}{T} - \frac{1}{298.15} \right) + 44.42 \log \frac{T}{298.15} \right)
\]

(5.127)

\[
= \exp \left(-336.96 + \frac{21980}{T} + 44.42 \log T \right)
\]

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As above, we have

\[
\frac{a_{\text{CO}_2(\text{aq})}}{p_{\text{CO}_2}\,(\text{Pa})} = \exp\left(-170.71 + \frac{8477.7}{T} + 21.95 \log T - 0.005781T\right) \tag{5.128}
\]

and

\[
p_{\text{CO}_2}\,(\text{Pa}) = 10^5 = \exp(11.51) \tag{5.129}
\]

Multiplying these four expressions together gives

\[
\frac{a_{\text{PZ}^+}a_{\text{PZCOO}^-}}{a_{\text{PZ}}^2p_{\text{CO}_2}\,(\text{bar})} = \exp\left(-737.66 + \frac{52375}{T} + 100.72 \log T - 0.005781T\right) \tag{5.130}
\]

As mentioned above, this is based on a Raoultian standard state for the PZ. Cullinan and Rochelle [276] also provides a conversion factor, so \(a_{\text{PZ}}\) may be converted to a Henrian standard state, which is what has been assumed for all species except water throughout this analysis:

\[
\frac{a_{\text{PZ}}}{a_{\text{PZ}}^{\text{Henrian}}} = \exp\left(318.1 - \frac{19779}{T} - 44.42 \log T\right) \tag{5.131}
\]

Hence

\[
\frac{a_{\text{PZ}^+}a_{\text{PZCOO}^-}}{(a_{\text{PZ}}^{\text{Henrian}})^2p_{\text{CO}_2}\,(\text{bar})} = \frac{a_{\text{PZ}^+}a_{\text{PZCOO}^-}}{a_{\text{PZ}}^2p_{\text{CO}_2}\,(\text{bar})} \left[\exp\left(318.1 - \frac{19779}{T} - 44.42 \log T\right)\right]^2 \tag{5.132}
\]

\[
K(T) = \exp\left(-101.46 + \frac{12817}{T} + 11.88 \log T - 0.005781T\right) \tag{5.133}
\]

As before, the standard enthalpies and entropies of formation may now be calculated from this at various temperatures. The standard enthalpy of absorption is given by:

\[
\Delta h^0 = RT^2 \frac{\partial \log K}{\partial T} = R(-12817 + 11.88T - 0.005781T^2) \tag{5.134}
\]

\[
= -106560 + 98.77T - 0.048067T^2
\]

Meanwhile, \(\Delta g^0\) is given by

\[
\Delta g^0 = R \left(101.46T - 12817 - 11.88T \log T + 0.005781T^2\right) \tag{5.135}
\]

\[
= 843.53T - 106560 - 98.77T \log T + 0.048067T^2
\]

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And
\[ \Delta s^0 = \frac{(\Delta h^0 - \Delta g^0)}{T} = -843.53 + 98.77(\log T + 1) - 0.09612T \]

At 313 K, we have \( \Delta h^0 = -80.35 \text{ kJ mol}^{-1}, \Delta s^0 = -207.29 \text{ J mol}^{-1} \text{ K}^{-1} \text{ and } \Delta h^0/T\Delta s^0 = 1.23, \) which corresponds to \( K = \exp(-\Delta g^0/RT) = 381.5. \) If a 1 kPa standard pressure were used, \( \Delta s^0 \) would be replaced by \( \Delta s^0 - R \log 100 = -245.5 \text{ J K}^{-1} \text{ mol, which gives } K = 3.81. \)

At 355 K, we have \( \Delta h^0 = -77.55 \text{ kJ mol}^{-1}, \Delta s^0 = -198.89 \text{ J mol}^{-1} \text{ K}^{-1} \text{ and } \Delta h^0/T\Delta s^0 = 1.10, \) which corresponds to \( K = \exp(-\Delta g^0/RT) = 10.5. \)

At 383 K, we have \( \Delta h^0 = -75.78 \text{ kJ mol}^{-1}, \Delta s^0 = -194.09 \text{ J mol}^{-1} \text{ K}^{-1} \text{ and } \Delta h^0/T\Delta s^0 = 1.02, \) which corresponds to \( K = \exp(-\Delta g^0/RT) = 1.57. \)

**MEA, DEA and MDEA**

The standard enthalpy and entropy of absorption for each of these common solvents were calculated from the model of Gabrielsen et al. [264] at infinite dilution. Their data was based on a standard CO\(_2\) pressure of 1 kPa, and this will be converted to 1 bar to maintain consistency with the rest of this analysis.

For MEA:
\[ K = \exp \left( -30.96 + \frac{10584}{T} \right) \]
\[ \Delta h^0 = RT^2 \frac{\partial \log K}{\partial T} = -10584 \times R = -88 \text{ kJ mol}^{-1} \]  \( (5.138) \)
\[ \Delta g^0 = (30.96T - 10584) \times R \]  \( (5.139) \)
\[ \Delta s^0 = \frac{\Delta h^0 - \Delta g^0}{T} = -30.96 \times R = -257 \text{ kJ mol}^{-1} \]  \( (5.140) \)

Converting to a 1 bar standard pressure,
\[ \Delta s^0 = -257 \text{ J mol}^{-1} \text{ K}^{-1} + R \log 100 = -219 \text{ J mol}^{-1} \text{ K}^{-1} \]  \( (5.141) \)

Overall, \( \Delta h^0/ (\Delta s^0 \times 355 \text{ K}) = 1.13 \) and \( \Delta h^0/ (\Delta s^0 \times 383 \text{ K}) = 1.05. \)
For DEA:

\[ K = \exp \left( -30.15 + \frac{8839}{T} \right) \]  

(5.142)

\[ \Delta h^0 = -73.5 \text{ kJ mol}^{-1}; \Delta s^0 = -250.67 \text{ J K}^{-1} \text{ mol}^{-1} \]  

(5.143)

Converting to a 1 bar standard state,

\[ \Delta s^0 = -250.67 \text{ J K}^{-1} \text{ mol}^{-1} + R \log 100 = -212.4 \text{ J K}^{-1} \text{ mol}^{-1} \]  

(5.144)

Giving \( \Delta h^0 / (\Delta s^0 \times 355 \text{ K}) = 0.98 \), and \( \Delta h^0 / (\Delta s^0 \times 383 \text{ K}) = 0.90 \).

For MDEA:

\[ K = \exp \left( -28.44 + \frac{5864}{T} \right) \]  

(5.145)

And again

\[ \Delta h^0 = 49 \text{ kJ mol}^{-1}; \Delta s^0 = -236 \text{ J K}^{-1} \text{ mol}^{-1} \]  

(5.146)

Converting to a 1 bar standard state,

\[ \Delta s^0 = -236 \text{ J K}^{-1} \text{ mol}^{-1} + R \log 100 = -197.7 \text{ J K}^{-1} \text{ mol}^{-1} \]  

(5.147)

Giving \( \Delta h^0 / (\Delta s^0 \times 355 \text{ K}) = 0.70 \) and \( \Delta h^0 / (\Delta s^0 \times 355 \text{ K}) = 0.64 \).
6 Conclusions and Recommendations for Future Work

Microencapsulated solvents (MECS) and the Solvent Impregnated Polymers (SIPs) presented in this work are promising approaches to carbon capture, which may enhance mass transfer rates and allow novel solvents to be used in a practical way. In this work, a large number of interrelated aspects of the MECS and SIP motifs were investigated. We begin this section by providing the key findings of this work, before briefly summarising the conclusions of each chapter in more detail. We then end with a list of recommendations for future work.

6.1 Key Findings

1. Microencapsulation is unlikely to affect the gas flux for concentrated chemical solvents, while for physical solvents it may increase the gas flux under some circumstances, as the reduction in spatial scales increases concentration gradients within the fluid. Overall, microencapsulation may increase the gas absorption rate by 1 order of magnitude for chemical solvents, and by 2 orders of magnitude for physical solvents.

2. A novel material for carbon capture, Solvent Impregnated Polymers (SIPs), is proposed. SIPs have many of the favourable properties of MECS, but are simpler and more scaleable to manufacture. SIPs were manufactured containing various solvents for CCS, including K2CO3 solutions, an ionic liquid, and a Nanoparticle Organic Hybrid Material.

3. A validated mass transfer model found that SIPs could increase the gas flux by a factor of 2 - 4 when immobilising solvents in the pseudo-first order reaction regime, and by 1 - 2 orders of magnitude for solvents in the instantaneous reaction regime. A 50-fold increase in flux was experimentally observed in a SIP containing a Nanoparticle Organic Hybrid Material. If such an increase in
flux were combined with an increase in surface area of 1 - 2 orders of magnitude, this could plausibly lead to a 3 - 4 order of magnitude increase in the specific gas absorption rate, which may enable slower solvents to be used in a practical way.

4. Modern amine processes for CCS are remarkably efficient, and even SIPS or MECS containing optimal solvents are unlikely to provide significant energy savings, especially if steam regeneration is used. On the other hand, it is possible that SIPS or MECS containing solvents which may be regenerated using low-grade waste- or electrically-generated heat could be used in novel processes at reduced cost.

5. An optimal solvent for CCS requires both a reasonably large enthalpy of absorption balanced by a sufficiently large entropy of absorption. In the development of novel solvents for CCS, the significance of the entropy of absorption has largely been ignored, and this should be considered more carefully into the future.

6.2 Summary of Results

- In chapter 3, the fundamentals of mass transfer into SIPS were analysed. It was found that the suppression of liquid mixing inside MECS is unlikely to reduce the gas flux (relative to an absorption column) for chemical solvents in the pseudo-first order regime. For physical solvents, an increase in the gas flux could be expected. Both of these conclusions are also relevant to the SIP motif, in which liquid mixing is also suppressed. However, the flux into SIPS is also affected by the permeability of the supporting polymer. Overall, the rate of absorption into MECS containing chemical solvents (in the pseudo-first order regime) and physical solvents can be expected 1 and 2 orders of magnitude greater than in a traditional absorber, respectively. Theoretical calculations for the sensitivity of liquid solvents to increased agitation suggested that sup-
pression of liquid mixing may reduce the gas flux if very fast solvents in the instantaneous reaction regime were encapsulated.

• In chapter 4, a novel material for carbon capture, SIPs, was described. SIPs are a gel material, in which droplets of liquid solvent are immobilised within a continuous polymer support. SIPs have comparable surface areas to MECS, and are manufactured via a simple and much more scaleable method. SIPs containing aqueous K₂CO₃ solutions, an ionic liquid, and a nanoparticle organic hybrid material (NOHM) were synthesised. Under a range of circumstances, the flux of gas into SIPs could be expected to be significantly greater than the flux into a MECS or stationary liquid. This is because the very large CO₂ permeability of the continuous phase accelerates the absorption of gas. Mass transfer mechanisms were investigated in detail. First, a complex PDE-based model was developed, and was shown to be in good agreement with uptake data into several SIPs containing K₂CO₃ solutions. Second, this model was non-dimensionalised, in order to compare mass transfer into SIPs with mass transfer into a neat liquid with the same surface area. It was found that, because of the high permeability of the polymer, SIPs could be expected to provide a 2 – 4 fold increase in the gas flux under a range of conditions, provided the liquid solvent absorbed gas in the pseudo-first order reaction regime. If the liquid solvent absorbed gas in the instantaneous reaction regime, much greater increases in the gas flux could be expected (though, as found in chapter 3, the reduction in liquid mixing may reduce the gas flux into such systems, and this tradeoff would need to be assessed.) After this the complex PDE-based model was shown to collapse to a much simpler, diffusion-limited model under a wide range of practical operating conditions. This diffusion-limited model was shown to give reasonable predictions for the rate of absorption into a SIP containing a NOHM, even though very little data was available on the chemistry of the NOHM. Furthermore, experimental measurements of the gas flux into the SIP containing the NOHM showed a remarkable 50-fold increase
in the gas flux, relative to a neat NOHM liquid. The very large increase was achievable because the NOHMs absorbed gas in the instantaneous reaction regime. This increase in flux could be complemented by the very large surface area of SIP materials, to produce sorbents which absorb gas many orders of magnitude faster than could be achieved using the neat liquid alone.

• In chapter 5, the energy requirements of a practical CCS process utilising SIPs and MECS was analysed. By idealising the process model in various ways which consistently favoured MECS or SIPs, and by optimising over both the process conditions and the thermodynamic properties of the immobilised solvent, lower bounds on the equivalent work requirements of a SIPs or MECS based process were established. For both aqueous and non-aqueous solvents, it was found that the use of SIPs and MECS is unlikely to lead to significant reductions in the parastic energy load of a CCS process, relative to a modern amine system. There were two principle reasons for this finding. First, sensible heat recovery is likely to be less efficient in a SIPs/MECS system, and the increase in the sensible heat capacity caused by the presence of the shell further compounds this problem. Second, modern amine processes have remarkable thermodynamic efficiencies, and leave little room for improvement. It is suggested that SIPs should focus on regeneration using waste or electrically-generated low grade heat, rather than directly attempting to compete with amine based processes regenerated using steam. Furthermore, non-aqueous solvents with large enthalpies of absorption balanced by appropriately large negative entropies of absorption should be sought, as these solvents will exhibit the necessary CO2 partial pressure change with the temperature swing while also absorbing CO2 reversibly under practical operating conditions.

6.3 Recommendations for Future Work.

There are many different directions in which research into SIPs or MECS could take. SIPs are probably the more promising of the two technologies, principally because
of the scalability of their manufacture and their superior mass transfer properties. On a purely practical level, it requires much less trial-and-error to manufacture a novel SIP system, and this could greatly accelerate R&D efforts. The enhanced mass transfer into SIPs is particularly relevant, as the kind of solvents which the SIP and MECS motifs are best suited for (viscous ionic liquids, NOHMs, CO$_2$-BOLS, etc.) are often severely diffusion limited, and, as was demonstrated with NOHMs, this can lead to very large increases in the gas flux. However, much will depend on the stability of SIPs in long-term use, which has not yet been established. A disadvantage of SIPs is the relatively low solvent fraction ($\sim 50\text{wt\%}$) compared with MECS (which exceed 70wt% solvent).

Focussing purely on SIPs, we provide a number of suggestions for future work. While the author believes all of these suggestions are worthwhile, the most urgent work probably relates to demonstrating the long-term durability of SIP systems (as it is plausible that these material may not be stable under industrially relevant conditions and timescales), and understanding the potential of SIPs for direct air capture and for CCS processes which utilise low-grade heat (as these appear to be the most promising applications for the technology.)

6.3.1 Material Development

- Further investigation into SIPs containing NOHMs is an obvious area for future research. Stability experiments should be conducted, and the development of finer particles and films (with length scales smaller than 1 mm) should be pursued. However, from a practical perspective, the potential of NOHMs as a sorbent for carbon capture is unclear at this point. Because of the high efficiency of modern amine processes, it seems unlikely NOHMs will be able to significantly reduce the energy requirements of a traditional CCS process. They are currently being developed with an emphasis on direct air capture,

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51 The author spent 12 months attempting to manufacture MECS inside microfluidic devices, and in that time succeeded on only two occasions. When developing SIPs containing a new solvent (NOHMs), two attempts were all that was required.
but most experiments involve much larger CO$_2$ partial pressures. Even if the NOHM have good capacity at low partial pressures, the gas fluxes (which are already quite slow) will be many orders of magnitude smaller.

• Material stability remains a major concern for SIPs. Leaching of the solvent, degradation of the internal structure over time, and the physical ‘squeezing’ of the solvent out of the material at high pressures are all serious concerns. Ultimately, SIPs rely on the intimate and high-surface-area contact of a very hydrophobic polymer with a hydrophilic or aqueous solvent, and there will always be a thermodynamic driving force for the solvent to leach out. The long-term stability of PDMS is itself unclear, especially in a process with continual temperature and pressure swings. Finally, the compression of SIPs (as would occur in a fluidised bed, at the bottom of a packed bed, or in a pressurised stripper) could physically squeeze the solvent out of the material over time. Both long-term thermal cycling and long-term pressure cycling would be required to demonstrate the material will be stable in practice.

• Water management issues will also need to be investigated, just as they have for MECS [117]. Even in a humid environment, it is possible that pressurised SIPs may lose water when compressed (the fluid may literally be ‘squeezed’ out of the material over time.) Such effects have not yet been investigated for SIPs, but it is possible they may limit the use of such materials in packed and fluidised beds. Whether such effects will be relevant for non-aqueous solvents largely depends on the permeability of the solvent inside the PDMS.

• The immobilisation of solvents which can be regenerated at lower temperatures, including biphasic solvents [133, 134] and protic ionic liquids [132] should be investigated further. A literature review of the solvents which may be regenerated at low temperatures would be helpful in identifying the most promising solvents. Non-aqueous solvents would probably be preferred in these applications, as water loss is always going to be an issue for immobilised, aque-
ous solvent systems (see [117]).

- The results of chapter 5 suggest that the immobilisation of aqueous solvents which could be used in a traditional absorption process is unlikely to beneficial, especially if researchers are hoping to improve the kinetics of a slow system in order to thermodynamically outperform an advanced amine process. The sensible heat losses in the SIPs process will probably be too great, and modern processes leave little room for further energy savings.

- SIPs may of course be applied to other gas separations beyond CCS. In many ways, such applications are much more promising in the medium term, as they may be more likely to find funding. An obvious application is the immobilisation of Selexol for CO2/CH4 separations. As was shown in Chapter 3, immobilisation of physical solvents can be expected to increase both the surface area and the gas flux (technically, this was only shown for MECS, but the same arguments can be made for SIPs provided the CO2 permeability in the PDMS is not substantially smaller than in the physical solvent.) Furthermore, there is significant interest in designing compact separation units for off-shore applications, and the very large flux into SIPs containing Selexol may allow for the use of a relatively small packed or fluidised bed, or a small monolith with walls coated with the SIP. The scale of such a process should be within the range of what is possible to manufacture. The fact that the solvent is non-aqueous may allow for further increases in the absorption rate using some of the ideas discussed in section 4.7.5 when considering NOHMs.

- Immobilisation of solvents, like NOHMs, in the instantaneous reaction regime is likely to give the biggest increase in the gas flux, and it may be worthwhile identifying promising systems which exist in this absorption regime.

- Prof. Qiao at The University of Melbourne has recently shown that adding ~ 1 wt% of metal organic framework (MOF) sheets or rods to PDMS is able to increase the CO2 permeability of the material by several times [235]. It
may be possible to create SIPs with MOF sheets embedded in the PDMS, and this may improve mass transfer into the material.

6.3.2 Process Development and Modelling

- A major unanswered question relates to the sensible heat recovery that is achievable in SIPs-based systems. As shown in Chapter 5, efficient sensible heat recovery is essential if a process is to be competitive. Only rough estimates from the literature were used in the work, but simulations of the various sensible heat recovery methods described in section 5.4 may allow for more accurate estimates for achievable recovery efficiencies.

- It was suggested in section 5.4 that research into SIPs should focus on non-aqueous solvents which can be regenerated using waste heat or electrically generated heat, rather than using steam (if steam is used, it will be hard to outperform a traditional amine process.) However, regeneration in pure CO2 may be difficult without a very large temperature swing (or a solvent with very large enthalpy of absorption) and alternative processing schemes should be considered. Vacuum assisted regeneration, vacuum assisted steam stripping, and stripping using a non-aqueous stripping gas such as pentane should all be considered. For stripping with a non-aqueous, condensable stripping gas, it is plausible that clever heat integration could be used to assist in the continual evaporation of the stripping gas. For example, part of the sensible heat of the hot, lean sorbent could be recovered by using it to boil the stripping gas. The design and simulation of processes utilising SIPs containing solvents that can be regenerated at low temperatures is an interesting avenue for future research.

- An article on the CFD simulation of a fluidised bed containing MECS was recently published [118]. Similar work on a fluidised bed containing SIPs would be worthwhile. However, care should be taken to ensure the simulation properly accounts for the stickiness of the material, as otherwise it may incorrectly predict the fluidisation behaviour.
• Simulation of SIPs in a packed bed process also deserves further research. Directly placing SIPs/MECS in a packed bed will lead to implausible pressure drops, but the use of a monolith or SIPs supported on structured packings could mitigate this. A major question relates to the time-scales required to heat up and cool down a packed bed. If these time-scales are much larger than the time-scales required for breakthrough of the moving absorption front, many beds will need to be run in parallel, increasing capital costs. The recovery of sensible heat from packed beds may be achieved by passing an intermediate fluid through the bed in plug flow, however the axial dispersion of the moving thermal front will limit the heat recovery efficiency, and these effects could certainly be estimated. Any researchers interested in modelling packed bed absorption should also be aware of the complex interplay between mass transfer fronts and thermal fronts (a good reference is [165]). A simple constant pattern calculation developed from an isothermal analysis may be inaccurate for an adiabatic system.52

• Absorption of CO2 is an exothermic process, and it is possible that this could lead to unwanted temperature increases in the absorber, especially if a packed bed process is used. These effects should be investigated further.

• If the reader is theoretically-inclined, they may be interested in a more fundamental analysis on volume utilisation within a packed bed system containing MECS and a traditional liquid absorption column. In a packed bed, only a fraction (typically less than 10%) of the volume of the bed is actively involved in mass transfer (this is referred to as the mass transfer zone (MTZ)) while the rest of the bed remains unused. However, in a traditional absorption column, the entire volume of the column is used for gas absorption, and indeed, with an appropriate change of coordinates, it is not difficult to show that the concen-

52Several simple constant-pattern, isothermal models were developed for monoliths containing SIPs. It was not possible to include a description of these models in this work, but they can be obtained from the author at request. However, the fact they don’t account for non-isothermal effects leads the author to believe that they may not be accurate in a practical process.
tration profile within an absorption column may be thought of as a stationary MTZ.\textsuperscript{53} Because of the relatively poor utilisation of the bed volume, even a 10-fold increase in the specific absorption rate into SIPs may ultimately lead to a packed bed absorber of exactly the same dimensions, and it will likely have greater pressure drop too! There is scope for expressing this tradeoff in a more rigorous way, and finding criterion for exactly when placing a solvent into a SIP will reduce unit operation volumes or overall pressure drops in a packed bed.

- The possibility of utilising moving bed absorbers of simulated moving bed absorbers containing SIPs should be considered in more depth, as each of these technologies could increase the utilisation of the volume of the absorber.

- Bench-scale demonstrations of SIPs absorbing gas in a fluidised or packed bed would be quite worthwhile. A demonstration that fluidisation is possible at gas velocities not too much greater than the minimum fluidisation velocity would be particularly interesting. SIPs which aren’t too sticky, such as those used to encapsulate NOHMs, should be used for such a body of work.

- The development of a rigorous process simulation of a CCS process utilising SIPs would also be worthwhile. However, a great deal of care must be taken when developing such a simulation, as, at every scale (from the individual SIP sorption kinetics, to the fluidisation of sticky particles, to the recovery of heat between two solid streams) non-standard processes are occurring.

- Direct air capture is a particularly promising area for application of the SIP motif. One simple reason for this is that DAC processes often have relatively poor sorption kinetics (because of the very low CO\textsubscript{2} partial pressure), and so the possibility of increasing the gas flux using SIPs is enticing. SIPs may also be shaped into high surface area materials which may act as efficient passive absorbers. Beyond the immobilisation of NOHMs, a literature review

\textsuperscript{53}Please contact the author for further details.
to identify other liquid solvents for direct air capture would be worthwhile. Recently, Puxty et al. [277] have demonstrated that various aromatic amines have very large and negative entropies and enthalpies of absorption, and such materials may be a good candidate for direct air capture applications; it may be worth contacting these authors. However, the fact that such solvents are typically used in an aqueous form may be problematic, as evaporation of water may hinder their performance.
References


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