

LIQUID ABSORBENTS

Current Status

The connection between the amount of gas that is dissolved in a liquid and pressure is familiar to anyone who has ever opened a bottle or can of soda pop (Figure 1). At the relatively high pressure of the unopened bottle, carbon dioxide (CO₂) gas is mostly dissolved into the soda. Opening the bottle reduces the pressure, decreases the solubility, and produces the satisfying pop and fizz of escaping CO₂. Fortunately for soda drinkers, under normal conditions all the dissolved CO₂ doesn't escape instantly—bubbles continue to emerge slowly until the soda goes “flat.” The cooler the soda, the more gas that remains dissolved, and the more refreshing the soda!

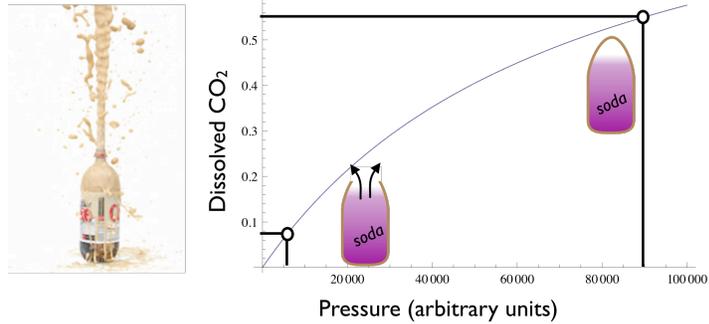


Figure 1. Releasing the pressure on a bottle of soda pop causes dissolved CO₂ to leave the liquid—slowly under normal conditions, or with spectacular rapidity if the transfer is promoted with an appropriate accelerating additive.⁴ This effect is due to the fundamental relation between pressure and dissolved gas, as captured in an isotherm (right).

Absorbent-based gas separations play on the same processes occurring in the soda bottle. The solubility of a gas in a liquid as a function pressure is described by an isotherm like that shown in Figure 1. “Opening the bottle” reduces the pressure and moves the mixture from a high to low solubility point. These isotherm shapes depend on other factors as well, such as temperature, and these differences can be exploited to separate a gas mixture. Figure 2 illustrates this process for a *temperature-swing* separation in which changes in solubility with temperature are used to effect separation of a target component from a mixture. In this example, CO₂ selectively dissolves to high concentration from a mixture of gases into the cool absorbent, separating it from the other gases (the “diluent”), which are rejected. The CO₂-saturated liquid absorbent is moved to a stripper and its temperature raised, lowering

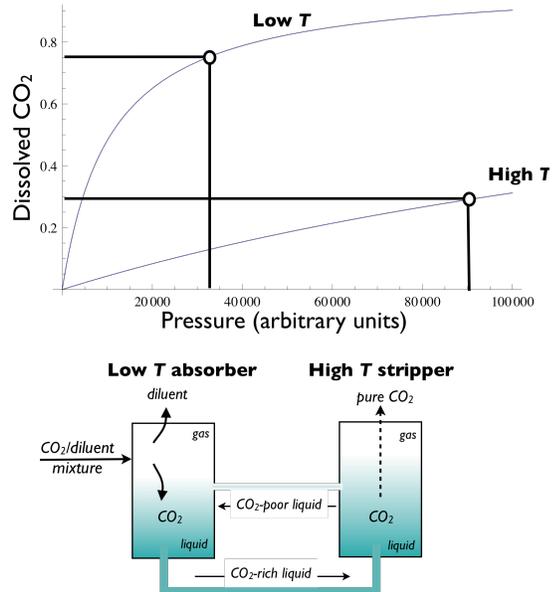


Figure 2. Absorption gas separation using temperature-swing gas separation takes advantage of high solubility of target gas at low temperature and lower solubility at high temperature.

the CO₂ solubility and releasing a gaseous stream of pure CO₂. The CO₂-depleted absorbent is then cooled to restart the cycle.

As suggested from this example, separating a mixture of gases into its constituents takes energy—in fact it is a fundamental consequence of thermodynamics that this energy cost can never be completely avoided. But the energy cost *can* be altered, by changing the boundaries or shapes of these isotherms, changing how they vary with temperature or other factors, and changing the selectively with which the liquid combines with the gas of interest. One of the fundamental scientific challenges of liquid adsorption is to control the solubility of the gas in the liquid in a way that minimizes the energy cost of a desired separation.

As described above, all the CO₂ does not instantly escape from the soda when the bottle is opened. Rather, it takes time for this transfer from liquid to gas to happen, and this time is another key factor in using absorbents for gas separation. The soda drinker is generally happy for the CO₂ to stay in the soda; the gas separations engineer generally is not. The time to transfer to and from liquid and gas phase is determined by the rates of mass transfer that ultimately depend on the microscopic processes that move molecules from one place to another. Slow rates imply slow processes that translate, ultimately, into larger, more costly separation systems. In the case of CO₂ in H₂O, the rates of these processes are intrinsically too slow to be practically useful for gas separations, and other materials, such as catalysts, must be used to speed the transfer. This is the effect illustrated so dramatically in Figure 1.⁴

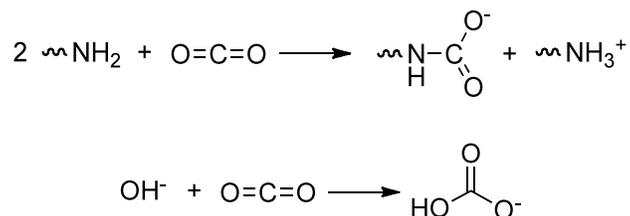
Liquid absorbents have many practical advantages for the large-scale gas separations necessary for practical carbon capture and sequestration: liquids are easy to handle and to pump around in large quantities; technologies are well-developed for heating and cooling liquids and for contacting liquids with gases in separations processes; and liquids can exhibit high gas solubility and selectivity. In addition, there is a wealth of experience in employing liquid absorbents in industrial processes.

Absorbents can exhibit a wide range of affinities for a gas molecule.

- Physical, non-reacting absorbents effect separations using weak interactions between the target gas and absorbent. This approach is most useful when separating gases across a large pressure difference or when the concentration of target gas is high.
- Reactive absorbents (chemical absorbents) effect separations using some type of chemical reaction between the target gas and the absorbent. This approach is useful for situations with smaller pressure differences, which requires larger binding energies.

Physical solvents are used in many “gas-sweetening” applications and take advantage of various types of organic solvents, such as glycols.⁷ They are also appropriate for pre-combustion CO₂ removal. CO₂ has been separated from natural gas for many years using

chemical absorption. As discussed in the **Aqueous Amines sidebar**, aqueous amines are commonly used to perform this separation: the amines combine strongly and selectively with CO₂, the solubilization process is relatively fast, and the amines themselves are inexpensive.⁸ Mechanisms depend on the particulars of the amine, but are generally thought to involve some combination of carbamate and bicarbonate formation, depending on the amine basicity and number of substituents:



While various classes of amines have been explored, including chilled ammonia (NH₃) itself, improvements in the ability to separate CO₂ by this approach have been incremental. Further, these separations are primarily driven by temperature swing (i.e., absorption at low temperature, desorption at high temperature), a reliable but not necessarily optimally efficient means. Nonetheless, these relatively mature methods are the ones most commonly discussed and most actively developed for use in post-combustion carbon capture.

These current CO₂ capture methods also have other limitations. Water and amines are themselves volatile, contributing to the energy costs of the separation and resulting in the loss of absorbent over time. Certain contaminants, like the sulfur oxides (SO_x), interfere with the amine-CO₂ reaction. The amine absorbents themselves are corrosive and also decompose over time. Most importantly, the energy required to drive these separations are high, representing a significant fraction of the energy produced by combusting coal.

Other industrial applications of liquid absorbents to separate other gases are far less common. The separation of oxygen (O₂) from air, needed to enable oxyfuel combustion, is, in fact, performed very effectively in the body. Blood is a complex, hierarchically structured liquid that builds on components (hemoglobin) tailored from the molecular level to selectively bind O₂ and transport it to cells. In these cells, the oxygen is used in the biological analog of oxyfuel combustion. We have not yet learned to master these approaches in the way nature has, but this powerful example illustrates the potential for expanding liquid absorption into broader domains that could revolutionize the ability to separate targeted gases from air.

Basic Science Challenges and Opportunities

The properties of an ideal gas-separating liquid absorbent are clear:

- It should have a high *selectivity* towards binding the gas of interest over all the other gases in the mixture to be separated.
- It should have a high *capacity* to bind the gas at one condition, and
- It should readily *release the gas on demand* with a minimal amount of input energy at another desired condition

- It should support *fast and reversible* transport and reaction between gas and absorbent phases
- It should be *thermally and chemically stable* in the environment of intended use
- It should have *physical properties* (heat capacity, density, viscosity, vapor pressure, enthalpy of vaporization,...) that are well matched to use
- It should be *readily synthesized* from abundant and accessible precursors

Today's inventory of liquid absorbents for carbon capture and other applications are far from this absorbent "paradise." Rather than having control over these properties and characteristics to affect selective separations, we are currently constrained to "make do" with the properties of known classes of materials and to design separation systems to accommodate the properties. Our toolkits for tuning the chemical and physical properties of absorbents are limited and largely empirical. And as a result, the pool of approaches available for driving separations is equally limited.

The enticing opportunity is to invert this practice, so that rather than fitting the separation process and conditions to the available absorbents, the absorbent properties are tailored to be optimally suited to the desired separation. There are several basic scientific challenges that must be overcome to realize the full potential of liquid absorbents for separation of targeted gases:

- The basic physical processes at work in the absorbent bulk and at the critical absorbent-gas interface must be understood and modeled in detail. Absorbents must be characterized in the working state, at spatial and temporal resolutions commensurate with separation processes. We need to answer basic questions about the liquid-gas system: What effect does dissolved gas have on the structure and properties of a liquid in the bulk and at the interface? What mechanisms, at the molecular level, are available to control selectivity towards one gas over another? What mechanisms govern the rates of gas transport and accommodation into (or out of) a liquid? How do we measure these properties, and how do we describe them in sufficient detail to guide the design of separation systems?
- Governing structure-property relations must be understood at a sufficient level of chemical and physical detail to enable rational absorbent material design. How do we go from basic molecular-level understanding to predictive models of physical and chemical absorbent properties? How do we design new absorbents based on this knowledge?
- The toolkit of approaches for driving separations must be radically expanded, to encompass new chemistries, new classes of materials, and new physical and chemical switches that go beyond the traditional thermal and pressure swings. How can chemistry (and biochemistry) be exploited to efficiently and selectively separate one gas from others? What sort of triggers can we use to turn the absorption of a gas either on or off? Can these triggers take advantage of otherwise waste energy, or alternative energy sources, like solar?

- Approaches must be developed to synthesize absorbent materials quickly at the lab scale and economically at the very large scales necessary for carbon capture. How can the discovery of new chemistries and preparation of new compounds be accelerated? How can highly selective, functional materials be prepared from abundant resources?
- New computational methods are needed to enable the rational design of new absorbents and to understand, at the molecular level, the physical and chemical processes that are critical to highly selective and efficient separations. How can computation at all levels be leveraged to accelerate discovery?

Real-world separations, such as the separations of CO₂ from combustion streams or O₂ from air, are invariably complex, multi-variate problems, and one absorbent will never be uniquely and universally optimal. Rather, an additional opportunity is to develop methods that produce virtual suites of absorbents, to fundamentally interconnect the optimization of material and application.

The need for new approaches to CO₂ separations separating compounds has been recognized in the last several years and has resulted in the discovery of several tantalizing new approaches, such as “task specific” ionic liquids,^{9,10} “switchable” solvents,¹ and “frustrated” acid-base pairs.⁵ These discoveries have been largely ad hoc and have yet to make a serious dent in the overall problem. They indicate, though, the potential for revolutionary new advances given resources and concerted scientific effort.

Conclusion

Liquids-based absorption separation is a proven approach that, with properly tailored absorbents, has the potential to achieve outstanding efficiencies for gas separations in general and post-combustion and oxyfuel separations in particular. The challenges to realizing breakthrough increases are substantial, but the scientific tools are today in place to advance the field from incremental improvements based on limited understanding to true knowledge and insight-driven discovery and optimization.

Priority Research Direction

Novel solvents and chemistries

Abstract

Gas separation *via* absorption is intimately connected with the physical and chemical properties of the gas-liquid system. The goal of this PRD is to develop the fundamental insights necessary to exercise exquisite control over this combination. Achieving this goal will require deep understanding of complex gas-liquid systems, especially the factors that govern selectivity and solubility, that determine non-ideal behavior, and that determine other important physical properties. It will require the ability to model, simulate, and predict these properties. It will require us to be able to discover liquid systems with chemistries carefully optimized to particular separations. And most importantly, it requires that we are able to close the loop, to combine experimental and theoretical insights to design and synthesize highly efficient and robust liquid separation systems.

Background and Motivation

The physical and chemical properties of a liquid absorbent are key to its performance in a gas separation. As shown in Figure 3, the absorbent, A, must be able to accommodate the targeted gases, in this case, CO₂, to the exclusion of others, typically due to differences in physical solubility. This physical solubility is controlled by the intermolecular interactions between absorbent molecules themselves and between absorbents and gases. These interactions are generally understood for simple fluids but not nearly as well for fluids as structurally and compositionally complex as those of interest for gas separations. It is further advantageous to have the absorbent chemically react with target gas, such as CO₂, to increase solubility. The isotherms that describe the absorption and desorption of gases, and the rates of transfer to and from the liquid phase, are ultimately controlled by these interactions and mechanisms.

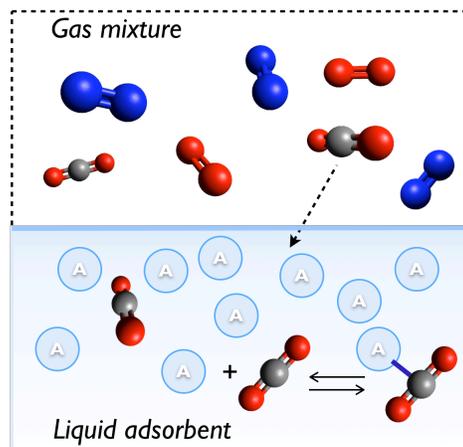


Figure 3. Schematic of CO₂ selectively isolated by dissolving in a liquid and its subsequent chemical reaction with absorbent A. CO₂, represented by the one atom of carbon (gray) and two atoms of oxygen (red), is initially in a mixture of O₂, represented by two red atoms; and N₂, represented by two blue atoms.

Liquid absorbents for CO₂ separations can be categorized into several classes, including water itself, chemically modified aqueous systems (including amines and non-aqueous organic solvents), and non-aqueous hybrids, like ionic liquids (see **Ionic Liquid sidebar**). Each class of absorbent presents its own challenges to understanding the thermodynamics and kinetics of gas separation. The current level of this understanding is far from what is needed to exploit known absorbents; further, other classes of absorbents remain to be discovered.

The overarching challenge and opportunity is to use understanding to drive discovery of radically new, better adsorbents that enable energy-efficient gas separations.

Research Directions

- **Fundamental understanding of intermolecular interactions of gases dissolved in liquids**

The liquid state exists because of the intrinsic intermolecular interactions between the molecules. These interactions can be of many types and ultimately control the physical characteristics of the liquid, like its density, viscosity (or resistance to flow), and boiling point. For single component, simple liquids characteristic of physical solvents these intermolecular interactions and their consequence are fairly well understood from both extensive experimentation and with classical molecular simulation. However, for liquids that have additional types of interactions, such as electrolytic liquids (e.g., aqueous, ionic liquids) or structured liquids (e.g., microemulsions) the connections between structure, composition, temperature, pressure, and physical properties are only now becoming understood.

Separation of gases via absorption introduces additional layers of complexity to understanding intermolecular interactions in liquids because of the myriad physical and chemical phenomena that occur in these complex mixtures. Simple physical dissolution of a gas into a liquid can dramatically alter important physical properties of the liquid. Models exist for describing how the properties of gas-liquid mixtures depend on the proportion of the two components in relatively simple liquids. For example, when the amount of gas in the liquid is small, the proportions can be described using Henry's Law, which states that the amount of dissolved gas is simply proportional to pressure. However, Henry's Law breaks down as the amount of dissolved gas gets large, and may have limited applicability in more complex liquids.

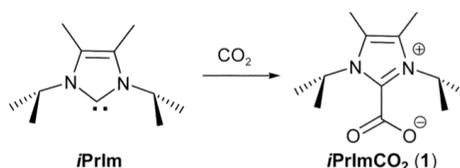
Because the key to separation by liquid adsorbents is the *selective* incorporation of one gas over many others, it is important to understand and control the intermolecular interactions that govern this physical selectivity. These interactions get even more complex when one considers adsorbents that undergo chemical reactions with a target gas molecule (e.g., CO₂) because both physically and chemically bound molecules are present in different proportions, which change depending upon solution conditions.

Understanding these many aspects of intermolecular interactions that contribute to gas separations in liquids requires characterization methods to elucidate key physical and chemical properties of these interactions, especially in complex mixtures and under reactive conditions. The insights gained by these measurements will serve as a foundation to develop new computational models to predict these interactions. Together, this understanding will catalyze the development of new adsorbent systems with precisely tailored properties to yield vastly improved separation selectivity and efficiency.

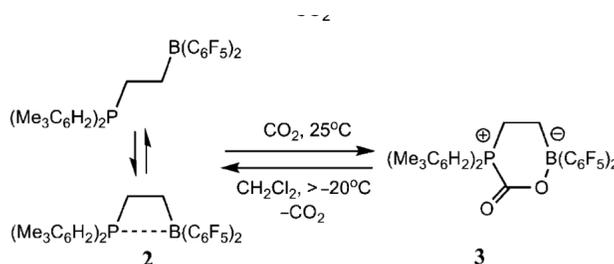
- **New chemistries, new absorbent systems**

A major challenge in large scale absorbent systems is to devise a means of lowering the energy required for separations, whether it is a change in temperature or pressure. As stated in the General Panel Report, oxygen is selectively isolated from air in blood with highly selective, cooperative, and reversible binding of O₂ to hemoglobin. Nature has an analogous system for isolating and transporting CO₂ in plants and animals using carbonic anhydrase. Using nature as inspiration, can new chemistries be devised to isolate targeted gases from a complex mixture selectively and efficiently? A potential advantage of such an approach is that the driving force of such reactions could lower the energy required for the separations. However, for applications in large-scale separation schemes, the molecules developed for these nature-inspired separations will need to be stable over many cycles of reuse. Thus the scientific challenge is to design highly specific and robust chemical systems with tailored physical and chemical properties for optimized separations.

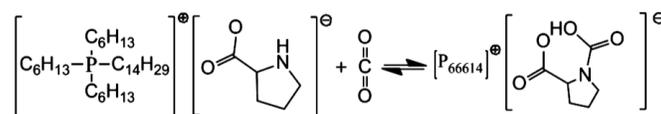
Is this vision possible—can molecules be designed to react stoichiometrically, reversibly, and in a controlled fashion with CO₂? Evidence suggests the answer is yes. Imidazolium carbenes were noted to have this ability in work reported first in 2004.¹¹



The heterocyclic carbenes can even catalyze the reduction of CO₂ to methanol through this carboxylate intermediate.¹² More recently, bifunctional “frustrated” Lewis acid-base pairs have been exploited to the same end (see **Getting a Grip on CO₂ sidebar**):⁵



Ionic liquids have been functionalized to have similarly selective reactions with CO₂, and the location of the tethered groups on either the cation or anion shown to provide an additional level of control on the reaction equilibria.^{9,10}



And solvents that reversibly form ionic liquids in the presence of CO₂ have been developed.¹ While challenges remain in translating any of these chemistries into a practical separation system, they give a good hint of the potential for designing new approaches to driving gas separations using chemical reactions.

Even within a given chemistry, the number of possible chemical permutations is enormous. Combinatorial synthetic methods could provide one way of developing chemical libraries, and can be combined with rapid screening to identify candidates. We need similarly efficient approaches to characterize the new absorbents for all the important properties (e.g., isotherms, viscosity, thermal stability, chemical stability, etc.) and how these properties change in response to external stimuli, down to the molecular scale, simultaneously, and *in situ*. Coupling to fully predictive computational models would revolutionize the ability to design candidates with optimized selectivity and efficiency. New computational tools would allow the same range of key properties to be predicted, and enable insightful computational “experiments” that would be difficult or even impossible to perform in the laboratory. Coupling computational simulation and experiment is obviously essential to validate models and to developing the physical and chemical insights that would form the basis for the development of new absorbents.

A further critical issue is the *rate of reaction* between absorbent and gas. Water itself can be used to separate CO₂ from flue gas through the formation of bicarbonate:



but the reaction rate is too low for practical use. Catalysts can be used to speed up this process, as happens in the body (see **Carbonic Anhydrase sidebar**). Translating this or other catalytic approaches to the challenging environment of a real gas separation will require major advances in chemistry.

The large scale of CO₂ separations implies the use of large quantities of absorbent, even for the best materials that can be identified. A modest-sized 500 MW power plant produces on the order of 22 kmol CO₂/s and would require on the order of 1000 metric tons of absorbent, based on simple order of magnitude estimates. To be practically useful, then, we need not only to discover new CO₂ chemistries, we need also to discover synthetic strategies for absorbents that have very high atom and energy efficiency from low-cost feedstocks. Can absorbents be prepared from CO₂ itself, for instance, or coupled somehow to the CO₂ separations? What inexpensive feedstocks can be used to make non-traditional absorbents?

- **Predict and exploit non-ideal absorption**

For thermodynamically driven separations, the equilibrium between gas and liquid phases, as embodied in absorption isotherms, ultimately determines the effectiveness of a material for a separation. To achieve energy efficient separations, control over chemistry must be accompanied by control over isotherms. These isotherms are determined both by the enthalpy *and* the entropy ΔS° of absorption, through $\Delta G^\circ(T) = \Delta H^\circ(T) - T\Delta S^\circ(T)$ (e.g.,

if the absorbent reacts with the gas $\ln K_{\text{eq}} = -\Delta G^\circ/RT$, where K_{eq} is the equilibrium constant).

In an ideal absorption system, the enthalpy of absorption is independent of the amount of absorbed material. Ideality gives the familiar Henry's Law behavior for physical absorption and Langmuir behavior for chemically reacting absorbents. Real absorbents always deviate to some extent from ideality: the absorption of one molecule of gas has some influence on the absorption of the next. The opportunity is to control these interactions. For instance, can we design absorbents that exhibit cooperativity, in which the absorption of one gas molecule *promotes* the absorption of the next? Cooperativity is accomplished in hemoglobin through the chemical linking of four porphyrin rings; can similar effects be achieved in molecules suitable for industrial gas separations?

For an efficient separation system, the adsorbent should have a high *capacity* and *selectivity* for the species being separated, which generally translates into a large exothermic heat of absorption, ΔH° . However, this enthalpy must be paid back during regeneration step, when the absorbate is separated from the absorbent, and thus easy regeneration demands low ΔH° . For thermodynamically based separations, then, these two objectives would appear to be at odds with one another. However, the absorption entropy provides a separate thermodynamic handle on separations. Can differences in sizes and shapes (entropy) of components to be separated be exploited as an alternative strategy to using differences in interaction energy (enthalpy)? Can strategies be developed to control absorption enthalpy and entropy in as independent a manner as possible? What are the limits on this independent control? These challenges would provide immense improvements in the cost and practicality of large-scale use of liquid absorbents for separation of CO_2 and O_2 from complex mixtures and would have broad impact on other applications of gas separation.

Scientific Questions

Absorbent-based gas separations essentially exploit the physical chemistry of gas-liquid equilibrium and reactions. The understanding of these interactions has advanced enormously over the years. CO_2 capture (and O_2 concentration) elevates these questions to a new level, however: Can they be described, understood, and modeled in the context of a gas mixture as complex as a flue gas, over the wide range of conditions that an absorbent will experience? Even more fundamentally, can they be controlled in such a way as to minimize the energy cost of separations? And lastly, can this control be realized in systems that meet all the other practical constraints of a real-world separation?

Potential Impact

This PRD touches on some of the most fundamental questions of intermolecular interactions and reactivity. This scientific knowledge is imperative if step change improvements in absorption-based separations are to be realized. Further, the evidence suggests that this step change is truly attainable, bringing practical, large-scale CCS much closer to reality. The basic questions addressed are not limited to this domain, however. Similar questions emerge in membrane- and adsorbent-based separations, of course. But gas-liquid interactions are also central to biology, to environmental and atmospheric

chemistry, to catalysis, to chemical processing, and even to sequestration. The knowledge and associated computational and experimental tools will advance fundamental scientific understanding and ultimately capability in all these domains.

Priority Research Direction

New uptake and release mechanisms

Abstract

The capture and release of CO₂ by solvents relies on changes in chemical potential that make capture favorable at one set of conditions and release favorable at another set of conditions. Most often these changes are accomplished by pressure or temperature swings, but there are other mechanisms for affecting chemical potential, such as the use of photons to excite molecules or electric fields to drive chemistry. Designing new capture and release processes that do not require thermal or pressure swings and that are more efficient and cost-effective than existing processes is the primary challenge in this priority research Direction. Progress in this direction will require new understanding of how energy is transferred and most importantly what are the sources of inefficiency in these alternative processes.

Background and Motivation

Historically pressure and temperature are the dominant external variables that control the chemical potential swings and gradients used in the capture and release of gases for separations applications. Both of these external variables allow energy to be directed into and out of capture systems. A key scientific challenge is to devise alternative mechanisms for driving the separation process that are more efficient or more targeted than today's temperature- and pressure-driven systems. For example, fuel cells are theoretically more efficient than heat engines because they are not limited by Carnot efficiencies. Are there analogous electrochemical capture processes that are more efficient than thermal or pressure swings? Can photons be used to selectively excite and rupture bonds to release gases or to change the configuration of molecules to modify how they interact with gases? Can hybrid systems be designed that efficiently use spatiotemporal pH swings or other concentration gradients to capture and release gases? Are there ways to modify the gas-liquid interface, e.g. by surfactants that facilitate the capture and release of gases? Can nature provide inspiration to these problems, for example enzymes or biomimetic approaches to accelerate absorption rates?

Among the challenges in these approaches is identifying fundamental and practical efficiency limits for the capture and release of gases. The primary motivation for exploring these alternatives is the *possibility* that they can be more efficient than existing thermal and pressure swing systems. The fundamental limits of thermal cycles are fairly well understood, for example the Carnot cycles. While combined cycles improve these limits there is still substantial need for improvement. Our understanding of other types of energy transformation is much more limited. The upper bound for the efficiency (conversion of photons to electricity) of a sophisticated solar cell is estimated to be around 40%. Performance limits of hybrid or alternative processes are currently unknown or are poorly defined, and this limits our ability to prioritize research efforts and to identify new approaches to gas separations. A critical need in future research is to identify these limits, both the thermodynamic and practical limits.

Research Directions

Thermodynamics is often used to establish limits of a process in terms of capacities, minimal energy consumption, and so forth. All practical processes, however, operate away from equilibrium or involve transient changes between equilibrium states where there are gradients in temperature, composition and transport of molecules. Under these non-equilibrium conditions, the actual energy consumption of a process may be substantially higher than the thermodynamic minimum, because where there are gradients and transport, there is entropy generation and thus loss of efficiency. Each of the approaches described above has different types and magnitudes of gradients, and characteristic types of inefficiency. A key challenge to advancing these approaches for gas separations applications is a fundamental understanding of the approach—specific sources of inefficiency and the potential to reduce them.

This Priority Research Direction focuses on the development of novel mechanisms for creating driving forces for directing energy into and out of separation systems. Many examples of such concepts exist that can provide inspiration for the development of alternative approaches for driving chemical absorption processes. For example, in photosynthesis photochemical water oxidation is coupled with charge and ion separation membranes to develop pH gradients that facilitate CO₂ capture. An electrochemical analog of this can be developed by driving a reversible gas-ion redox reaction to generate gradients in pH that facilitate CO₂ and oxygen separation (Figure 4).¹³ A related concept uses electrochemistry to

create redox carriers that can selectively react with a gas, e.g. CO₂,¹⁴ and which can be electrochemically regenerated. These materials so far have selectivity and stability problems that need to be addressed. An alternative approach is the use of a chemical conversion cycle to capture CO₂ while producing valuable products.¹⁵ This chemical conversion cycle consumes lithium, and there has not yet been an approach with a fully closed materials balance. It is essential that these conversion cycles have fully closed materials balances (i.e. no accumulation of wastes or unused products) because the scale of CO₂ capture is so large.

As illustrated in the **Switchable Solvents sidebar**, there are already examples of solvents that take up or release CO₂ based on chemical, rather than physical, inputs.^{1,2} The reversible light-induced formation of micelles¹⁶ could provide inspiration for new materials that capture gases in one state and release it in the other state. The wettability

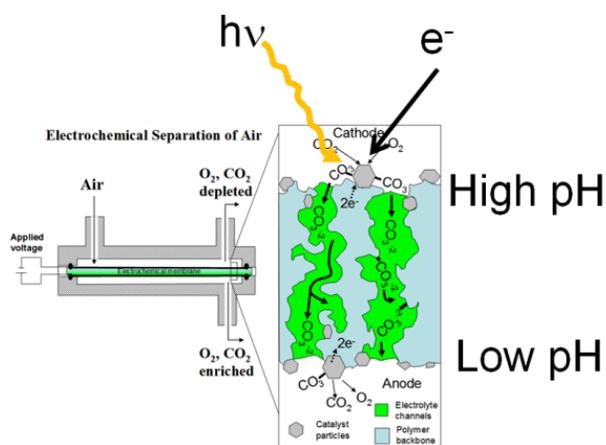


Figure 4. Prototype of a photoelectrochemical cell that utilizes a steady state pH gradient to separate CO₂ and oxygen from air. Combinations of photons and electrons are used to drive redox reactions that generate the pH gradient.

of surfaces can be controlled by electric fields,¹⁷ and one can imagine other surface or interfacial properties could also be tuned. Some block-copolymer brushes exhibit significant changes in structure upon mild temperature changes.¹⁸ Perhaps phase or structure transitions such as these could lead to new concepts in gas capture and release.

Finally, there are examples in nature and chemistry where many small bonds serve to stabilize species. For example CO₂ can react to form a bicarbonate ion that is multiply bonded in a polycyclic molecule.¹⁹ This kind of cooperative bonding might lead to lower enthalpies of interactions where only enough energy to break a few bonds is needed to result in release of the gas.

Scientific Questions

Current technologies based on thermal/pressure swings face thermodynamic limits on their ultimate efficiency that non-thermal/pressure swing technologies may not have. Fuel cells, for example, are potentially more efficient than an internal combustion engine because of the electrochemical energy conversion process. In practice, however, fuel cells are not much better than internal combustion engines unless run at very low current densities, and better electrocatalysts are required to improve this. The key scientific question for any alternative approach is whether it is theoretically more efficient (in a thermodynamic sense) than a thermal/pressure swing processes. Second, in practice (where kinetics are relevant) what is required to approach the theoretical efficiency?

Each alternative process will have its own set of key scientific questions. In a photochemically driven capture/release process some examples are: What molecular features control photon absorption and excitation to a reactive, excited state? What are the relative timescales of the relaxation of the excited states and that capture chemical reaction? What are the mechanisms for entropy production in photochemical reaction systems? Other processes have related questions. For a pH gradient, what is the work required to maintain the gradient, and under separation conditions what factors contribute to inefficiency? For mild temperature change driven polymer structure changes, is there enough of a free energy/chemical potential change to be useful for a CO₂ capture application? Or does absorbed CO₂ fundamentally alter the structure change?

Potential Impact

The impact of this PRD could be the development of new capture technologies that are substantially more efficient than existing CO₂ capture technologies. The core research effort in this PRD, however, is essentially how to efficiently put energy into and remove energy from systems to drive state changes. The more reversibly these changes can be made, the more efficient the process will be. Efficient energy transfer impacts innumerable technologies, including photovoltaics, fuel cells, catalysis, conversion of chemical energy to work in biology, and other separation applications.

Priority Research Direction

Interfacial processes and kinetics

Abstract

Mass transfer across the gas-liquid interface can be the rate-limiting step controlling the uptake and release of CO₂. A key barrier to the development of greatly improved liquid absorption separation processes is the lack of understanding of the nature of gas-liquid interfaces. Once understood, this information could be used to design specific modifications to those interfaces to enhance gas separation systems. Advancing knowledge in this area will require the strong coupling of theory and experiment with the assembly of interdisciplinary expertise in the structures of liquid, physics of interfaces, molecular spectroscopy and chemical kinetics. In addition, new approaches are needed to characterize dynamic and chemically complex interfaces—examining both the spatial and temporal distribution of solution components and reactants in the interface.

Background and Motivation

The gas-liquid interface is the gateway to bulk absorption. Transfer across this boundary is well-known to limit many CO₂ process rates. As such it plays a critical role in any carbon capture process utilizing a liquid. Liquids are intrinsically difficult to study since they are disordered and have a time-varying, dynamic structure. Even less is known about the chemical structure of liquid-gas interfaces. Surface composition is not a simple termination of the bulk structure but rather is dictated by minimization of surface free energy.

Mass transfer considerations suggest that kinetic modifications of CO₂ absorption processes are best targeted very near the surface to maximize flux into the bulk. Understanding the structure and dynamics of this interface is key to tailoring uptake and release kinetics and will allow

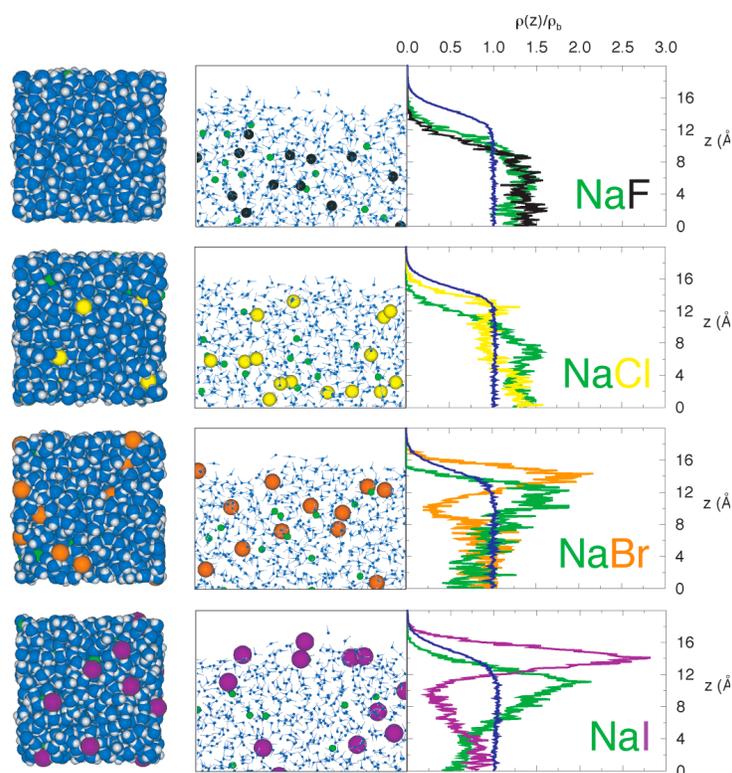


Figure 5. Snapshots (top and side views) of the solution /air interface of 1.2 M aqueous sodium halides from molecular dynamics simulations and number density profiles of water oxygen atoms and ion plotted vs distance from the center of the slabs in the direction normal to the interface, normalized by the bulk water density. Notice the preferential segregation of the more polarizable anions Br and I to the interface.⁶

controlled design of future sorption materials.

Interfaces warrant study in order to avoid potential kinetic bottlenecks, understand structure and dynamics of complex liquid-gas interfaces, and understand the linkage between composition, structure and chemistry of the interface. Liquids potentially useful for carbon capture, oxygen purification, or other gas separation approaches are likely to be complex systems such as highly concentrated basic solutions, ionic liquids, or exotic multiphase fluids – but we don't really understand simple fluids yet. For example, even relatively low concentration aqueous salt solutions have been predicted to have an asymmetric distribution of anions and cations at the vapor-liquid interface (Figure 5), a result confirmed by recent experiments.²⁰

Research Directions

A key barrier to the development of greatly improved liquid absorption separation processes is the lack of understanding of the nature of gas-liquid interfaces. Once understood, this information could be used to design specific modifications to those interfaces to enhance gas separation systems. Advancing knowledge in this area will require the assembly of interdisciplinary expertise in the structures of liquid, physics of interfaces, molecular spectroscopy and chemical kinetics. In addition, new approaches are needed to characterize dynamic and chemically complex interfaces—examining both the spatial and temporal distribution of solution components and reactants in the interface. Current experimental tools have shown that the surface composition can be strongly segregated and further knowledge needed to understand dynamic separation processes will also require temporal resolution. Experimental approaches are needed to enable liquid interfaces to be probed *in situ*, capturing the molecular processes that occur during active transfer of gas across the interface. Understanding the distribution of absorption phenomena that are primarily molecular, versus those that are reactive, and the interplay between the two, will be required to both predict and design better interfacial properties for enhanced gas separation systems. By varying the chemical nature and composition of the liquid it may be possible to tailor and control the gas/liquid interface in such a manner as to improve the overall reversibility and switchability of the sorption reactions. These goals will require strong coupling of experiment and theory, including experimental probing and computer simulations of liquids with greatly improved spatio-temporal resolution. Ideally one would like to chemically image these dynamic interfaces with atomic scale spatial resolution on time scales ranging from femtoseconds to minutes.

Reactions at solid surfaces are routinely studied today—for example catalysis on solids is a mainstay of surface science. That level of understanding is not available for liquid-gas interfaces, but reactive processes in these gas capture systems is also a critical phenomenon. For most CO₂ capture processes the rate of chemical reaction can be the most important determinant of the transfer rate across the interface. Rational design of improved processes can be expected to locate catalytic functions in the interface, both to improve chemical reaction rates and to improve the physical characteristics of the surface through functions like surfactants. Chemically tailored structures that self-organize these functions at the correct interface locations will be required to optimize interface function

in capture systems. These tailored systems can become the foundations of facilitated transport mechanisms similar to those prevalent in biological systems.

Scientific Questions and Opportunities

A key scientific question is to understand the concentration and chemical state of targeted gases and associated materials at liquid interfaces. For CO₂, such materials at the interface may include molecular CO₂, carbonate/bicarbonate, and stronger complexes such as the carbamates that occur in amine solutions. Further, it is important to understand how this chemistry changes as materials transfer from the surface into the bulk. While such distance dependent composition changes will exist in static systems they will be crucial to understanding and predicting mass flux across the interface of an active gas capture system. Addressing these issues will require surface-specific spectroscopies to avoid interference from the bulk. Depth profiling at the very small scale—perhaps as small as a few molecular diameters—is required. Tools are becoming available to probe time-averaged structure and composition (vibrational sum frequency generation, photoemission from liquids, x-ray and neutron scattering). Ideally one would like to use spectroscopic tools and techniques with sufficient temporal resolution to study the kinetics and dynamics of absorption/desorption phenomena. This will require the development of new experimental methods and instrumentation that are capable of working in coexisting gas-liquid environments (moving from high vacuum to high pressure.) At the solid/liquid and solid/vapor interfaces, probe microscopes like STM and AFM have provided a wealth of information about dynamics and reactivity. The liquid-vapor interface is far more dynamic, so that extracting this type of information is presently unfeasible. New approaches are needed to extract comparable information.

The combination of both theory and experiment has led to an unprecedented understanding of how ions are distributed at the aqueous/air interface of salt solutions. Owing to the more complex nature of the liquids envisioned for capture processes the combination of theory and experiment that will be available with exascale computing suggests that major improvement in theory will be possible within the next decade. Challenges are to describe liquid-vapor interfaces of more complex fluids incorporating explicit interactions with the vapor phase. Capturing static and dynamic features and especially capturing reactions at the interface. First-principles simulation based on density functional theory (DFT) has proved invaluable for studying reactions at the solid-gas interface and only today are methods becoming available for the solid-gas. The liquid-gas interface, because it is disordered on both sides, becomes much more difficult.

Exascale computing and new experimental methods will permit development of fundamental understanding necessary to allow rational design of novel liquid interfaces for CO₂ capture and other separation processes (*e.g.* O₂). With enhanced understanding of the details of interface structure and chemistry, it will be possible to design interface properties that enhance capture rates and eliminate transfer resistances that currently constrain large-scale capture systems. This rational design of interfaces will incorporate modification of surface physical properties, catalysis of key chemical reactions responsible for enhancing transport across the interface, and improve the handling and environmental characteristics of fluids where a very large surface area in industrial

practice is both an operational requirement and a major limitation due to evaporation, oxidation, and other deleterious side reactions.

Potential Impact

Advances in this area can be expected to increase understanding of liquid-gas interfaces and complex solutions. This will be the foundational underpinning of rational design of new materials and processes with enhanced capture capacity and reduced energy demand for regeneration of CO₂ and other purified gases potentially allowing capture device performance near the thermodynamic limit. Understanding gained in these studies could also find practical application in such diverse areas as catalysis, atmospheric science, and ocean/atmosphere interface questions.

Priority Research Direction

Process Concepts Discovery

Abstract

Current methods for carbon capture, based primarily on the use of liquid solvents such as amines to scrub CO₂ from post-combustion flue gas, have cost estimates in the range of \$20/t CO₂ to nearly \$100/t CO₂.^{21,22} These are low-end estimates, since they represent operating costs only. Such costs are not acceptable economically, since they would potentially double the cost of electricity reflecting the power lost to carbon capture and sequestration activities, and thus put US industry in an even less competitive position than it currently is. Thus, fundamentally new, low-cost, low-energy methods for carbon capture must be identified with more acceptable economics. This requires the development of the fundamental understanding and the methodologies needed to enable exploration of novel process concepts—that is, designing separations from a systems perspective. One of the fundamental limitations to process concept exploration and discovery is the lack of robust, accurate theoretical methods to predict the physical, chemical and kinetic properties needed as input to process calculations. Thus, we require the development of these methods by combining first principles and molecular approaches, through the derivation of new theory, and by their implementation on state of the art computing platforms.

Background and Motivation

The development of a new solvent process in the processing industry—particularly the chemical industry, is a relatively mature process, as illustrated by the methodology in

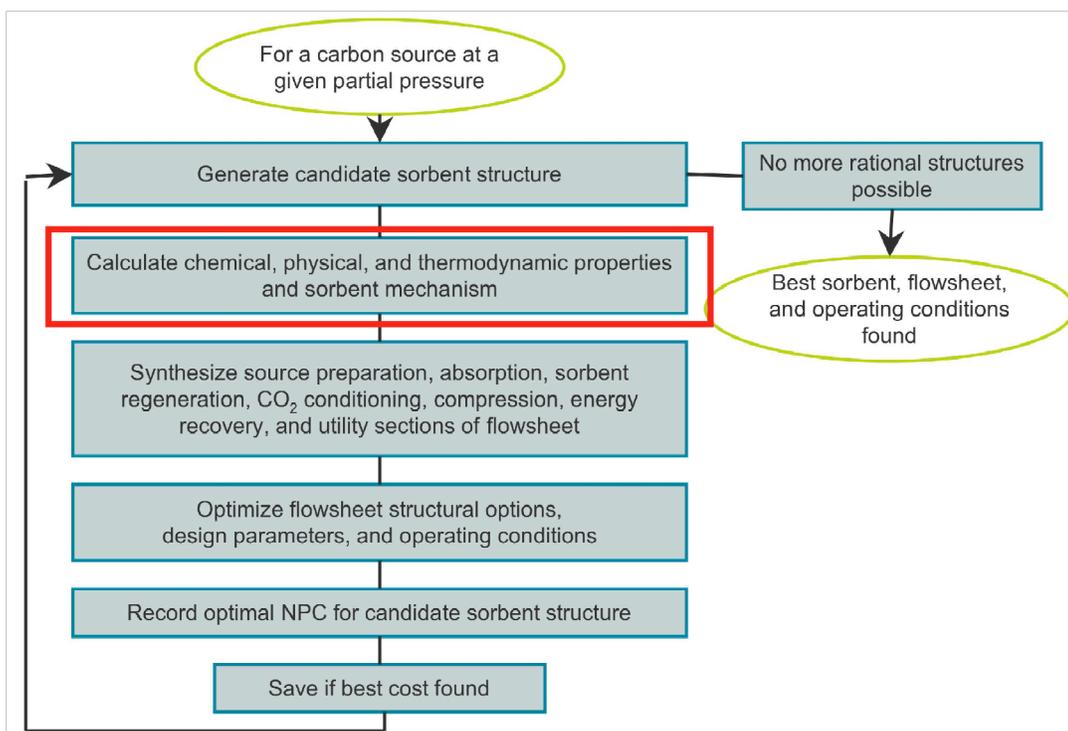


Figure 6. Systematic methodology for developing optimal liquid-solvent separation processes. This includes the “structure” of the process – represented by a “flowsheet” – that lays out how inputs to the process inputs, intermediate streams, and process outputs are connected to and by “unit operations,” such as separation columns, pumps, and compressors. An optimized process is one in which the cost-optimal structure is identified, as well as optimal values of all stream properties and unit operation conditions. The key scientific impediment to routine application of this methodology, particularly to invent new processes, is the absence of methods to predict robustly and accurately the physical, chemical and kinetic properties of fluids and materials under the conditions of process operation (see ref. 23). Courtesy of J. Simons, Eastman

Figure 6 used by process developers to develop liquid-solvent-based separations processes. While methods are well established for designing standard temperature or pressure swing absorption separation processes when the physical and chemical properties of the absorbent are well known, its application to novel carbon capture processes is essentially impossible for lack of a robust theoretical capability to predict the physical, chemical, and kinetic properties of absorbents under realistic separation conditions. Engineering models of new absorbents and new separation methods require knowledge of a myriad of physical, chemical, and kinetic properties over the enormous range of operating temperature, pressure, composition, and other conditions. To accelerate both the evaluation and the application of new absorbents, we require robust, accurate, atom/molecule-specific theoretical methodologies for representing and predicting physical, chemical, and kinetic properties. process

The traditional chemical engineering approaches for estimating such properties are based on the concept of group contributions – i.e., that a mixture of molecules can be regarded as a mixture of the molecular groups within the molecules, when due account is taken of connectivity of individual molecules (i.e., which molecular groups belong to which molecules). This concept also underlies molecular simulation: molecular dynamics (MD) and Monte Carlo (MC) simulations are performed using models for the interactions between atoms. These models are described by forcefields, which are expressions for the energy of a system of molecules that includes terms for repulsive, attractive, electrostatic, bond-stretch, bond-angle-bending and torsional interactions. More sophisticated models also include polarizability. The concept of transferable forcefields, which underpins all the biological, and the majority of physical and chemical MD and MC simulations performed today, is that once the interaction between, for example, a methyl group and a hydroxyl group is determined, it can be used (transferred) for use in simulations of other mixtures. General forcefields based on this concept include CHARMM, AMBER, OPLS, TRAPPE-UA, TRAPPE-AA, and OPLS. Forcefields are developed by fitting to *ab initio* (first principles quantum) calculations and to experiment; however, as the sophistication and accuracy of first principles methods increases over time, along with the availability of the required large computational resources, forcefields are increasingly determined exclusively by fitting to *ab initio* methods. The problem with engineering correlations for thermodynamic properties (such as UNIQUAC/UNIFAC for activity coefficients) is that the group contribution concept, which as we see is equivalent to the assumption of transferability in forcefields, is applied using a model for activity coefficients that is too simplistic. UNIQUAC/UNIFAC and similar properties correlations revolutionized the chemical industries ability to conceptualize new processes in which the chemical natures of the fluids became variables; however, UNIQUAC/UNIFAC is based on regressing group-group contributions from *experimental* data, which over limited ranges of conditions compensates for the simplistic nature of the underlying activity coefficient model. Conceptualizing new carbon capture processes needs a completely new approach in which properties prediction is based on modern molecular theory and simulation methods, since the experimental data for the vast majority of candidate solvent systems is not going to be available, either for direct use or for regression of parameters.

The urgency of conceptualizing new carbon capture processes is illustrated in the **Engineering Design sidebar**: the more concepts for carbon capture we can explore early, the higher the probability that more cost-effective carbon capture processes will be discovered, and that the eventual cost of carbon capture can be significantly reduced. The discovery process is strongly impacted by and interleaved with experiment, since many of the innovations in new solvents originate from insights originating in experimental studies.

Research Directions

- **New computational tools for modeling intermolecular interactions in complex environments**

The rise of molecular simulation and first principles methods in recent decades has benefited from two trends. First, the exponential increase in computing driven by Moore's law, which at the high end (the top 500 supercomputers in the world, updated twice yearly at top500.org) has resulted in an increase of three orders of magnitude in speed per decade. The result is that the first scientific calculations to achieve 1 petaflop (PF = 10^{15} floating point operations per second, or FLOPS) have been reported in the past two years. There is every indication that this trend will continue, with exaflop computing (10^{18} FLOPS) expected around 2018, although achieving high levels of computational efficiency will be challenged by the emergence of multi-core chips. We have entered the era when Moore's law is achieved by doubling the number of cores in each microprocessor chip, rather than increasing clock speed, thus adding another level of complexity to the programming model for scientific computing. Second, the community of materials simulations scholars is constantly innovating, with the result that new algorithms can often result in multiple orders of magnitude increase in speed without any change in hardware. Examples abound, particularly in Monte Carlo methods for classical simulation (such as multi-spin methods for Ising systems and continuum configuration bias methods for complex molecules). There are new $O(N)$ methods for first principles calculations in which the cost of the computation scales linearly with the number of electrons, N , rather than the non-linear $N^3 - N^7$ scaling of current methods. The combination of algorithmic and hardware advances will result in first principles and molecular simulation computations becoming far more routine. *De novo* predictions of the properties of a proposed new solvent requires first principles methods (such as quantum chemistry methods, density functional theory, or DFT, and *ab initio* molecular dynamics, in which the classical equations of motion for atoms are solved using forces calculated on the fly from quantum chemistry or DFT methods) to obtain gas phase properties, calibrate classical force fields, and model chemical reactions, and classical molecular simulations to obtain condensed-phase properties. Several methods exist for automated fitting of classical force fields to first principles calculations, but today are not widely practiced. To develop the capability of providing the key physical and chemical properties needed for novel carbon capture process design, a suite of molecular modeling tools based on state-of-the-art first principles and molecular simulation tools will be required. A partnership between end-users of the predicted properties (process design researchers) and the molecular modeling community will be needed to identify the

properties required, and a mechanism established for ensuring computed properties are made available in standards-compliant properties databases used by process designers.

- **New Molecular Theory for Novel Solvent Design**

Continuing improvements in theory, algorithms and computing hardware speed are resulting in computationally intensive methods, such as quantum chemistry and molecular simulation, that increasingly provide routes to key physical and chemical properties that are considered equal in accuracy and precision to experimental measurements. For example, in gas phase thermochemistry, more than a decade ago many companies moved away from experiment to computational quantum chemistry methods to obtain free energies of formation and reaction²³ due to the equivalent or higher accuracy from quantum chemistry methods combined with much lower cost. The development of the computational molecular-based approach to properties prediction described in the previous paragraph will result in a large properties database for novel solvent system, plus the capability of adding to this in ways that directly provide data for group contribution approaches. Thus, the opportunity exists to create a new, molecular-based *theoretical* approach to properties prediction to replace the current engineering group-contribution methods, whose limitations are described above. The idea of using modern molecular-theory-based equations of state (such as variants of the statistical associating fluid theory, and other statistical-mechanics-based approaches) in a group contribution context is in its infancy; such approaches, because they are based on molecular models for the molecules involved that parallel intermolecular forcefields, are the only potential route to analytic formulae for condensed-phase thermo-physical and chemical properties that accurately reflect the chemistry and structure of the constituents of mixtures. Analytic formulae are crucial for repeated calculation of properties needed in process *optimization*; additionally, because analytic formulae can be evaluated many orders of magnitude faster than molecular computational approaches, they make molecular design feasible. That is, rather than beginning with a candidate system and calculating properties, one can begin with the desired properties, and find the system(s) that will give them, yielding a molecular design capability for new solvents.

Scientific Questions and Opportunities

The drive toward the successful development of the computational and theoretical molecular-based approaches to properties prediction described above will have significant impact on several scientific fields. It will require the development of new theory (e.g., new density functional theories that will accurately describe the particular systems of relevance in carbon capture, new methods for connecting the electronic and atomistic scales, new statistical mechanics theory for computing condensed phase properties analytically) as well as new algorithms leading to efficient computation on exascale computing platforms, multicore chips, and novel architectures such as graphic processing units (GPUs). We are at just the beginning of the GPU and multicore revolution, but already speed-ups by factors of 20-80 are being reported for quantum chemistry and molecular simulation codes on GPUs. GPUs and multicore chips are creating the potential for a truly revolutionary change in the level of computing available to the research community, and hence the utility and ubiquity of computational approaches, but researchers must learn how to use them effectively. Today, the majority

of the best minds engaged in computational chemistry are focused on biology; refocusing the efforts of the best computational and theoretical researchers on chemical systems will have a dramatic impact on the field of chemistry in general, and energy-relevant chemistry in particular.

Potential Impact

Successful development of the computational and theoretical molecular-based approaches to properties prediction described above will revolutionize our ability to conceive of novel solvent-based separations for carbon capture; indeed, the frameworks proposed will result in the creation of true integrated product-process design for carbon capture. The extension of this approach to other chemistries and processes will revolutionize all of the processing industries at a time when many processes need reinvention to take into account the rapid changes taking place in industry, such as future likely mandates to reduce or eliminate greenhouse gas emissions, increasing environmental regulation on waste, and changes in feedstock from petroleum to coal, biomass, natural gas or even carbon dioxide. Providing the scientific tools to enable U.S. industry to meet all of these changes is crucial to protecting the environment and making these industrial processes more efficient to keep jobs in the U.S.

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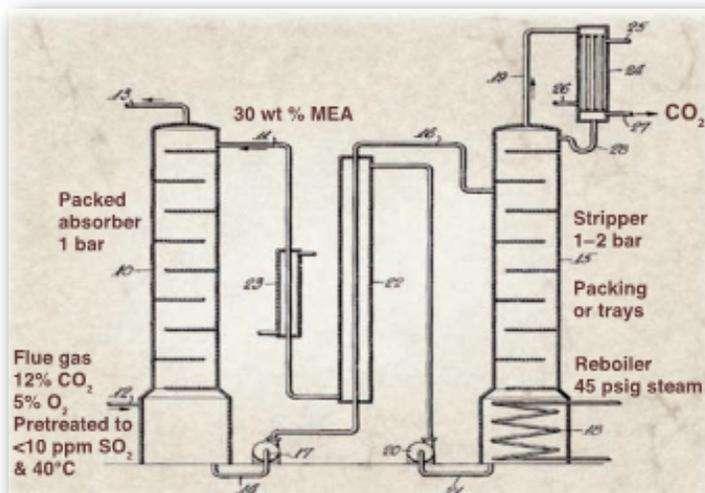
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Aqueous amines for CO₂ separations

The capture of CO₂ by aqueous amines has been practiced for over 80 years² in the removal of CO₂ from natural gas and hydrogen, and to produce beverage grade CO₂. In a typical process, CO₂ containing flue gas is contacted with an aqueous amine solvent in an absorber column at a relatively low temperature where it is absorbed. The loaded solvent is pumped to a stripping column where it is heated up to regenerate the solvent and release the CO₂. The hot regenerated solvent is then returned to the absorber column through a heat exchanger, which cools the hot solvent and preheats the rich solvent going to the stripper. The majority of the energy required to capture CO₂ is consumed in heating the rich solvent up in the stripper column.

It is essential to consider the entire CO₂ capture process when evaluating the efficiency and energy cost of capture. For example, developing a solvent with a low absorption energy for a thermal swing regeneration may not result in an energy savings due to the need for additional heat to maintain pressure, or the need for additional compressors downstream of the absorber to obtain sequestration pipeline pressures.⁴ Alternatively, the low absorption energy solvent may work more efficiently in a vacuum desorption process.⁶



The original patented process for aqueous amine solvent scrubbing process²

Ionic Liquids: Non-volatile solvents for CO₂ capture

Ionic liquids are a new class of salts that are liquid in their pure state near or below ambient temperatures. This sets them apart from common salts such as their familiar cousin sodium chloride (table salt), which melts at around 800°C. The oppositely charged ions in table salt are small (Na⁺ and Cl⁻) and pack neatly into an ordered, stable crystal. In contrast, large inorganic or organic ions are found to pack more loosely and thus to form low-melting ionic liquids.

Ionic liquids are being investigated for CO₂ capture because they have many unique and highly desirable properties. They have a high intrinsic physical solubility for CO₂, and even higher CO₂ capacities can be achieved by adding functional groups that chemically react with CO₂. They have high thermal stabilities, making them attractive for use in pre- and post-combustion CO₂ capture. They have essentially no vapor pressure, meaning they will not evaporate during use and novel regeneration strategies may be possible. Most importantly, by altering the cation, anion, and functional groups, an almost limitless number of ionic liquids can be prepared, suggesting a rich area for future research.

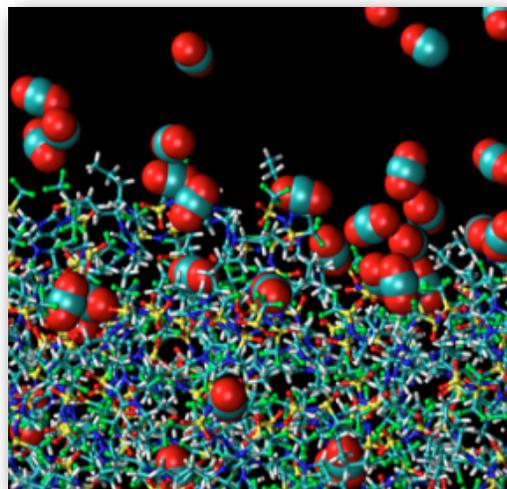
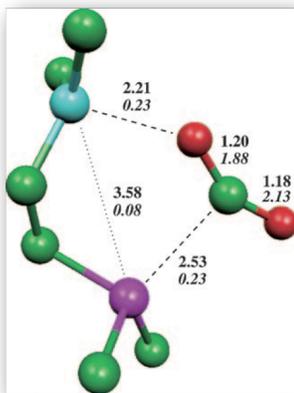


Image from a molecular simulation showing CO₂(depicted by two red oxygen atoms and gray carbon atom) absorbing into the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Graphic courtesy of E. Maginn

Getting a “grip” on CO₂

Acids and bases are the *yin yang* of chemistry—opposite yet interconnected forces behind chemical bonding and reactions. In the Lewis definition, an *acid* is an electron pair acceptor and a *base* an electron pair donor. When brought together, the female acid and male base tend to combine to form an acid-base pair, neutralizing each other. Most common molecules are thus either Lewis acidic or basic, but not both.

Frustrated Lewis pairs are cleverly designed molecules that break this rule.³ These molecules contain acidic and basic elements linked together in a way that prevents the two from internally neutralizing one another. These frustrated systems can promote normally difficult reactions, such as the heterolytic splitting of H₂. CO₂ as a molecule is Lewis acidic—the C center is electron deficient and likes to behave as an electron pair donor, as in its reactions with amines described in the previous Sidebar. The O centers are weakly Lewis basic, becoming more so when CO₂ combines with a base. This internal *yin yang* can be exploited in reactions with frustrated Lewis pairs. As shown in the picture below, a properly designed frustrated pair (purple, basic phosphorus and light blue, acidic boron) can put a pincer grip on CO₂, grabbing both the more acidic carbon (green) and somewhat basic oxygen (red).⁵ Because both the shape of the pincer and the strengths of the acidic and basic ends can be tuned, frustrated pairs hold promise for reversible CO₂ capture



CO₂ binds to both ends of a frustrated Lewis pair in this calculated reaction transition state⁵

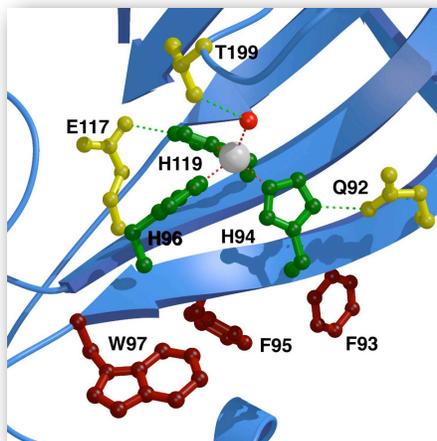
Biomolecules that reversibly catalyze CO₂ hydration: Carbonic Anhydrase

Carbonic anhydrases are enzymes that catalyze the hydration of carbon dioxide and the dehydration of bicarbonate:



This reversible reaction can be exploited to separate CO₂ from other gases. These carbonic anhydrase-driven reactions are of great importance in a number of human tissues where it is important for facilitated diffusion and transport of CO₂, secretion of bicarbonate and protons and maintaining acid-base and fluid balance. In particular, carbon dioxide generated by metabolism in all cells diffuses to red cells in the blood where carbonic anhydrase catalyzes the formation of bicarbonate for transport to the lungs. In the lungs, carbonic anhydrase catalyzes the formation of carbon dioxide for exhalation.

Carbonic anhydrases in humans consist of a single polypeptide chain with a zinc atom complexed by three histine ligands. These enzymes are among the fastest catalysts known; at low concentrations of CO₂ and HCO₃⁻ the reaction is limited by diffusion and at high concentrations the turnover rate is 10⁶ reactions per second per mole enzyme. Catalysis of this reaction is reversible. CO₂ hydration is catalyzed by the enzyme bound zinc-hydroxide while bicarbonate reacts with the zinc-water form of the enzyme (pK_a ~ 7).

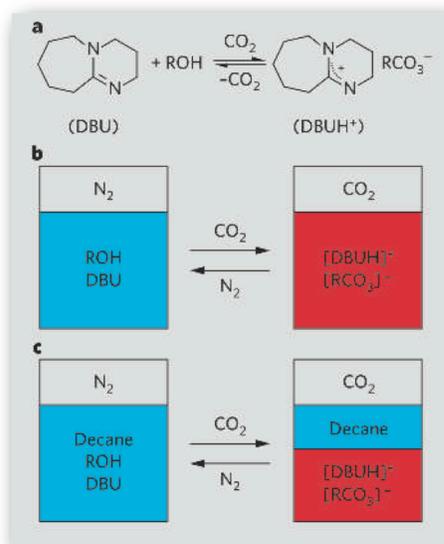


*Active site of carbonic anhydrase isozyme II
Graphic courtesy of XXX?*

“Switchable” solvents

Many types of solvents are available to the chemist—polar or non-polar, aqueous, protic or aprotic, conventional or ionic. Choosing a solvent is often a compromise amongst the many jobs the solvent must do. But what if the properties of a solvent could be switched from one type to another? Such a switch could be used, for instance, to facilitate the separation of one compound from another. Such switchable solvents have in fact been demonstrated. As shown in the example below, an organic solvent mixture of an amine (DBU) and an alcohol (ROH) can actually be “switched” to an ionic liquid with completely different physical and chemical properties simply by adding CO₂ to the mixture.^{1,2} Removing the CO₂ “switches” the solvent back to its original state. In the example shown, this switch is used to separate another organic compound, decane, from the solvent—decane is completely soluble in the unswitched state but insoluble in the switched, ionic liquid state.

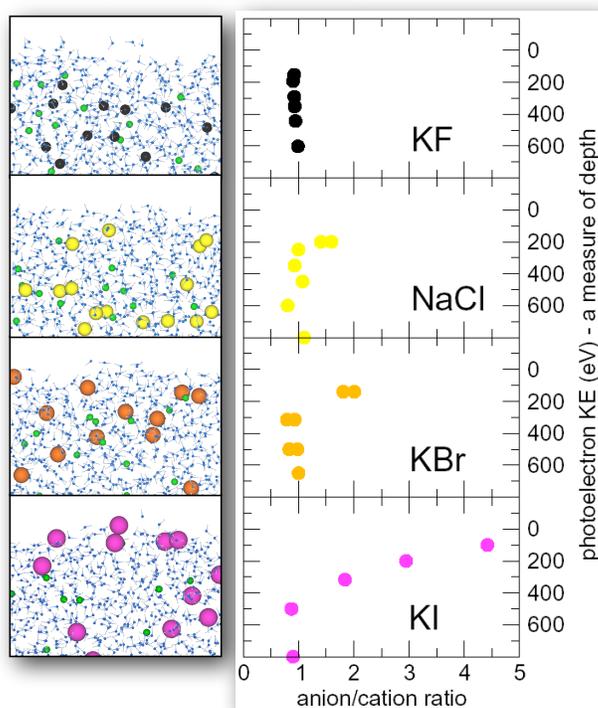
The fact that that CO₂ is the chemical switch in this example suggests that this system itself may be useful for CO₂ separations [ref]. Even more exciting, though, are the prospects for discovering other solvents and switches designed specifically for CO₂ capture or air separation.



CO₂ switches a solvent between non-ionic and ionic states²

Sidebar on interfacial reactions

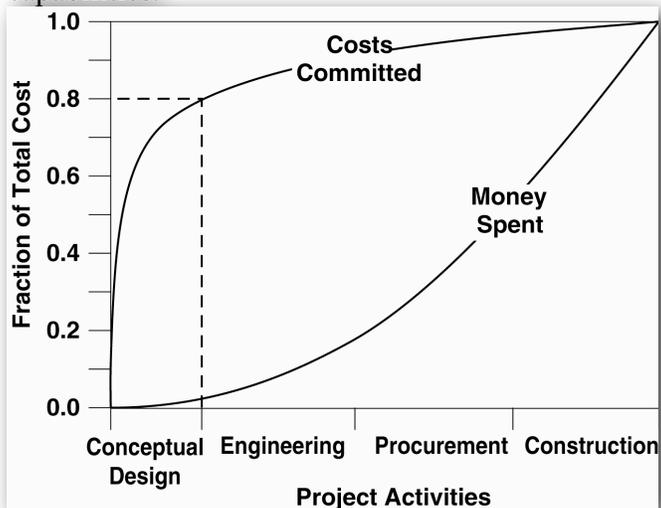
Gas-liquid interfaces are tumultuous places with molecules in the interfacial region involved in a tug-of-war between attractive solvation forces that pull them into the liquid and entropic forces that drive them out. This results in ceaseless, rapid excursions of individual molecules back and forth across the imaginary line separating the two phases. Understanding these complex, dynamic interfaces requires new analytical techniques with the ability to discriminate between molecules in the interfacial region, typically just a few molecules thick at most, and those in the vastly larger bulk liquid region. New non-linear spectroscopies (second harmonic generation and sum frequency generation) are capable of identifying particular species in the interfacial region, but they do not provide depth resolution. Photoelectron spectroscopy, especially with synchrotron light sources, has allowed species-selective depth-profiling of a wide range of atomic and molecular species at gas-liquid interfaces. Complementing experimental techniques, molecular dynamics simulations, based on either empirical force fields or *ab initio* potentials, can provide a dynamic, molecular scale view of gas-liquid interfaces. Computational methods assist in the interpretation of experimental data and also inspires the development of new experimental capabilities. In turn, modern experiments are providing a wealth of data that can be used to scrutinize and refine theoretical models.



Left panel: Snapshots from molecular dynamics simulations depicting air-solution interfaces of aqueous alkali halide solutions. Right panel: Depth-profiles of the anion/cation ratios from photoelectron spectroscopy experiments on deliquesced potassium halide crystals. The prediction of the presence of ions at the air-water interface defies conventional wisdom and stimulated the development of new experiments. The increasing enhancement of the population of the anion over the cation with increasing halide mass predicted by the simulations is verified by the experiments.

The Lessons from Engineering Design

The accumulated experience of decades of engineering project management shows that early consideration of the widest possible range of designs is crucial to minimizing costs in the long term. As illustrated below, in any major engineering project – such as designing a chemical plant, a building, a bridge, an aircraft or a car – the conceptual design stage is the one at which costs are committed and locked in. Once a conceptual design is determined, it is optimized (engineering), and the procurement and construction stages begin; during these latter stages is when the great majority of money is expended. Changing the conceptual design at this late stage is extraordinarily costly, and the engineering literature is filled with examples of order-of-magnitude or more cost overruns when conceptual designs are changed later in the process. The lesson for carbon capture is that we must consider the different possible scenarios for carbon capture as early as possible, and this in turn requires unprecedented predictive capabilities.



Graphic courtesy of M. Malone, UMass