

# Thermally Programmable pH Buffers

## Programmable Materials for Reversible CO<sub>2</sub> Sequestration

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# Targets for CO<sub>2</sub> Sequestration

*Prevent Global Warming associated with the burning fossil fuels.  
(Fuels introduce  $6 \times 10^9$  metric tons (6 GT) of CO<sub>2</sub> into the air each year.)*

**Remove CO<sub>2</sub> from air.**

**(Atmosphere =  $5.1 \times 10^{15}$  metric tons)**

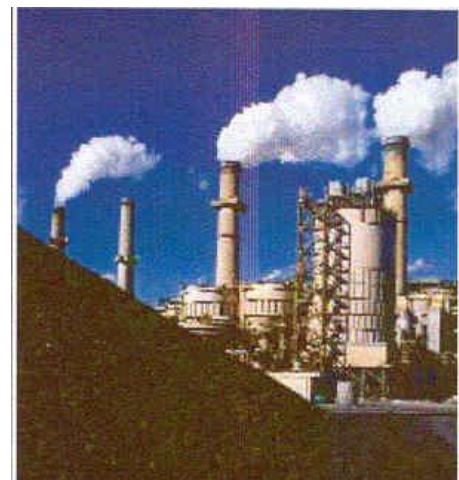
**Current CO<sub>2</sub>:** 377 ppm  
( $2 \times 10^{12}$  metric tons)

**Removal Goal:** 10<sup>9</sup> metric tons/yr  
(1 km<sup>3</sup> of liquid CO<sub>2</sub>)

**Disposal:** underground

**Desired Cost:** \$10/metric ton  
(4 kcal/mole)

**Alternate:** treat coal exhaust  
(10-15% CO<sub>2</sub>)



**Processes must be selective, reversible, cheap, and capable of handling billions of tons of CO<sub>2</sub>, preferably from air.**

# Nature Currently Mediates Atmospheric CO<sub>2</sub> Levels

*Natural processes for CO<sub>2</sub> capture/release all involve water.*

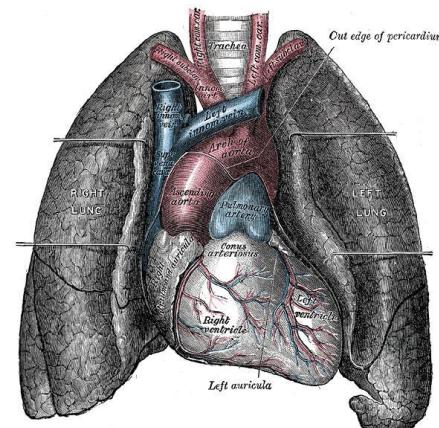
## Oceans (Capture/Release)



## Plants (Capture)



## Animals (Release)



**Ocean Volume =**

$2 \times 10^9$  GT

$2 \times 10^9$  km<sup>3</sup>

**“Dissolved C”**  
**(solubility + biomass) =**  
**37,000 GT**

**Land Biomass =**

11,000 GT

$\beta$ -carbonic  
anhydrase

**100 kg/yr/liter blood**  
**(Humans exhale 6 GT/yr)**

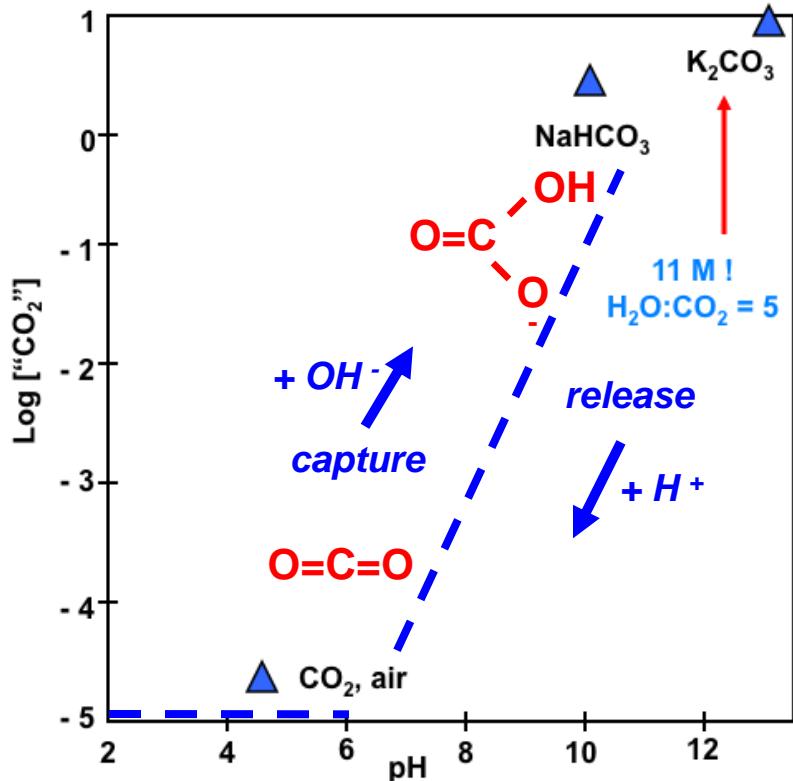
$\alpha$ -carbonic  
anhydrase

**Question: Can we adopt Nature’s processing schemes in artificial systems?**

# Reversible Sequestration of CO<sub>2</sub> Requires the Inter-conversion from “Insoluble” and Soluble

Carbonates for capture  $\leftrightarrow$  CO<sub>2</sub> for release

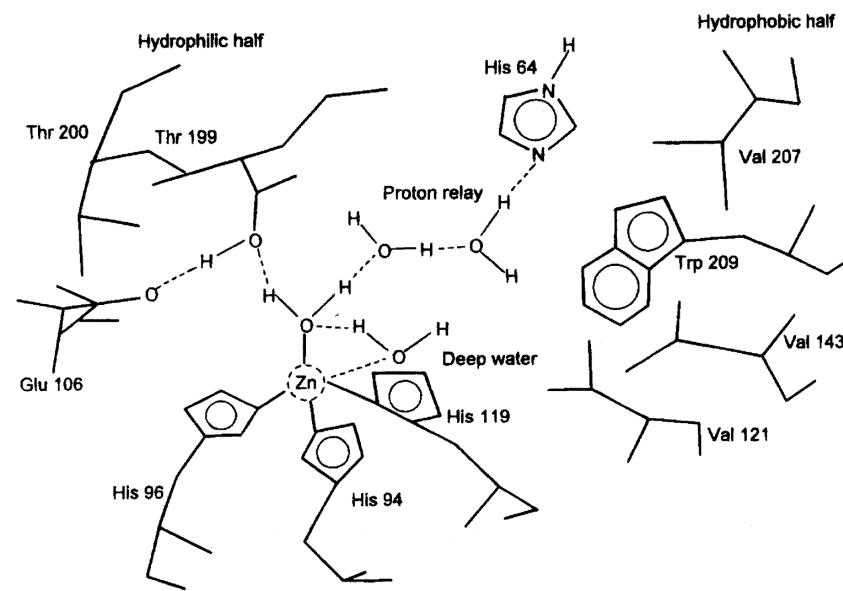
Solubility



$\Delta[“CO_2”]$  of 100,000 is possible.  
Requirement:  $\Delta“pH” = 4-5$ .

**Goal:** Develop programmable pH buffers that can be used to promote CO<sub>2</sub>:carbonate inter-conversions via pH control.

Catalytic Enzymes  
(carbonic anhydrase)



Same enzyme used for loading/unloading.  
Rapid, diffusion-controlled kinetics.  
Requirement:  $\Delta pH = 2$  (around pH 7).

# Chemical Equilibria

## Carbon Dioxide in Water



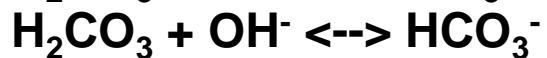
$$K_{\text{Henry}} = 0.033 \text{ M/atm}$$



$$K_{\text{hyd}} = 2.6 \times 10^{-3}$$



$$K_{a1} = 1.7 \times 10^{-4} \text{ M}^{-1}$$



$$(K_{\text{app}} = 4.5 \times 10^{-7})$$

## Polymer Buffers in Water



$$K_p = \text{programmable}$$

$$pK_p = -\log K_p$$

## Programmable Buffer + CO<sub>2</sub>



loading →

← unloading

$$K_l = K_{\text{app}}/K_p \rightarrow pK_p > 8.5$$

$$K_u = 1/K_l \rightarrow pK_p < 5$$

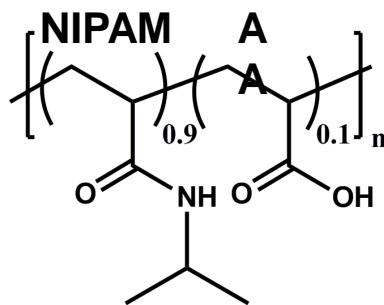
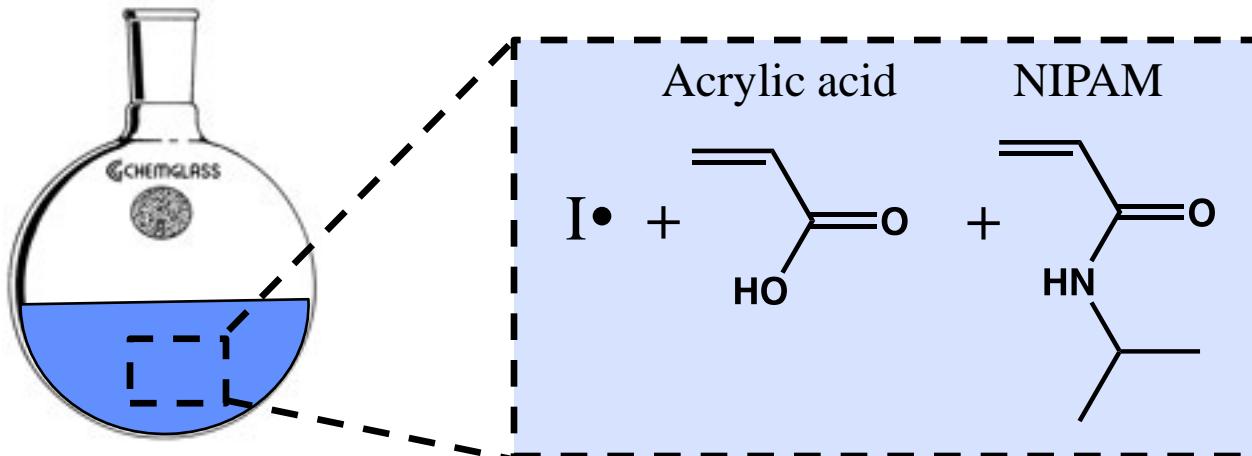
To reversibly load and unload CO<sub>2</sub> in water, a programmable pH buffer is required that can reversibly switch its acid dissociation constant by a factor of over 3000.

# Synthesis of Programmable Materials

**Switching mechanism: a reversible, thermally-activated swelling transition**

Below  $T_c$ : PNIPAM is swollen and hydrophilic.

Above  $T_c$ : PNIPAM is collapsed and hydrophobic.



**Synthesis: free radical polymerization (MW = 25,000 g/mole)**  
90% NIPAM (n-isopropylacrylamide)  $\rightarrow$  provides programming  
10% Acrylic acid  $\rightarrow$  provides acid-base activity

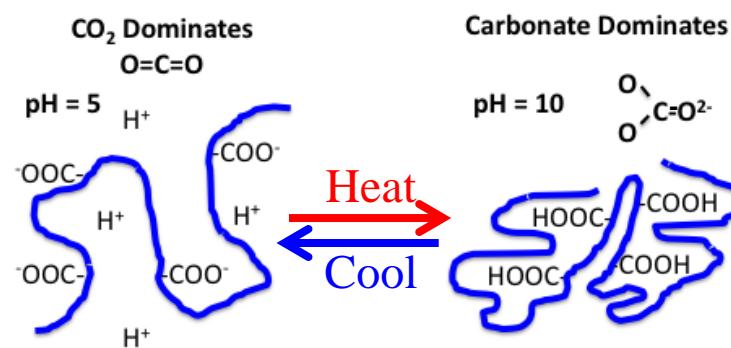
# Programmable pH Buffers: P(NIPAM-AA)

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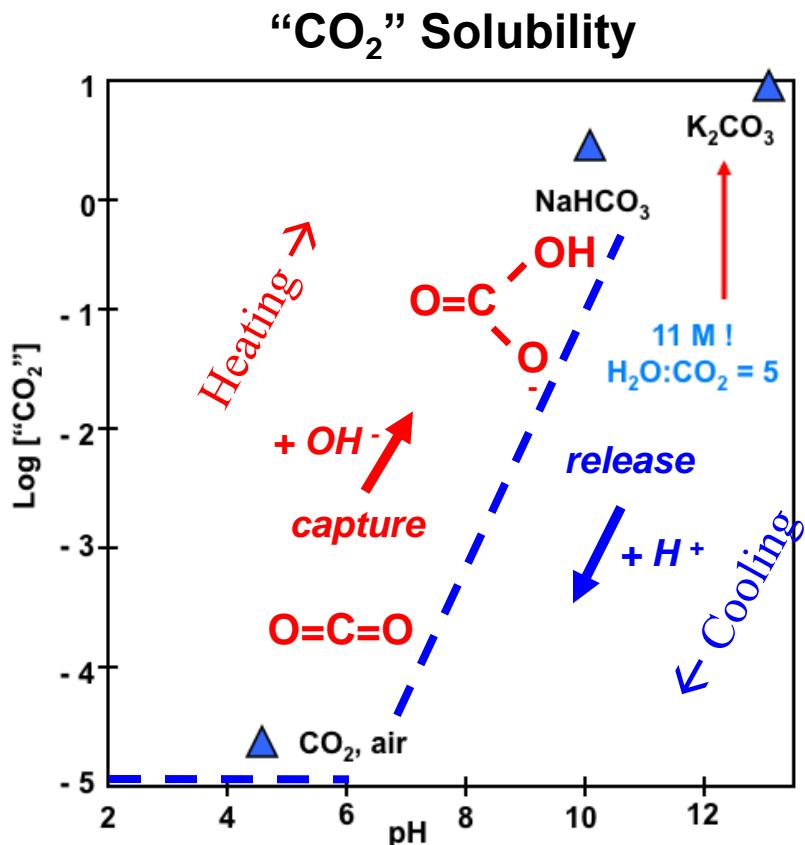
**Hydrophilic:**  
AA ionization promoted →  
Low  $pK_p$  for  $\text{CO}_2$  unloading  
 $\text{HA} \rightarrow \text{A}^-$   
 $\text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{CO}_2(\text{g})$



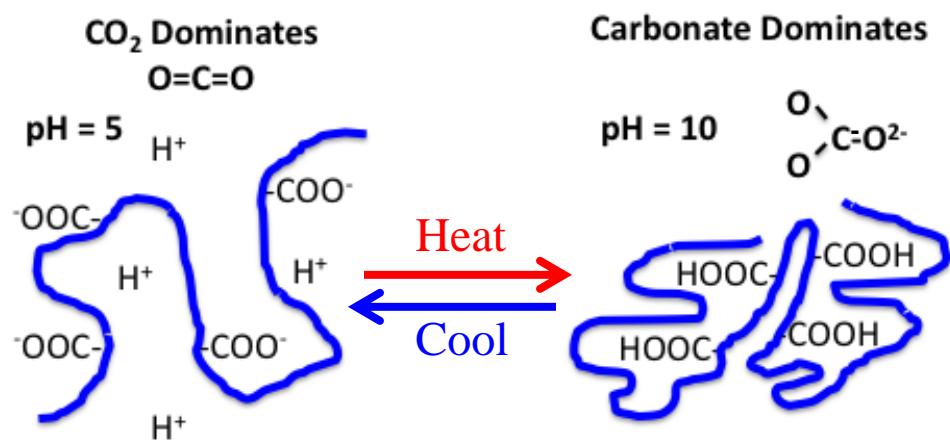
**Hydrophobic:**  
AA ionization suppressed →  
High  $pK_p$  for  $\text{CO}_2$  loading  
 $\text{A}^- \rightarrow \text{HA}$   
 $\text{CO}_2(\text{g}) \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^-$

*The dissociation constant for acrylic acid is sensitive to the local polymer environment, facilitating reversible programming of the pH buffer system.*

# CO<sub>2</sub> Behavior in Water

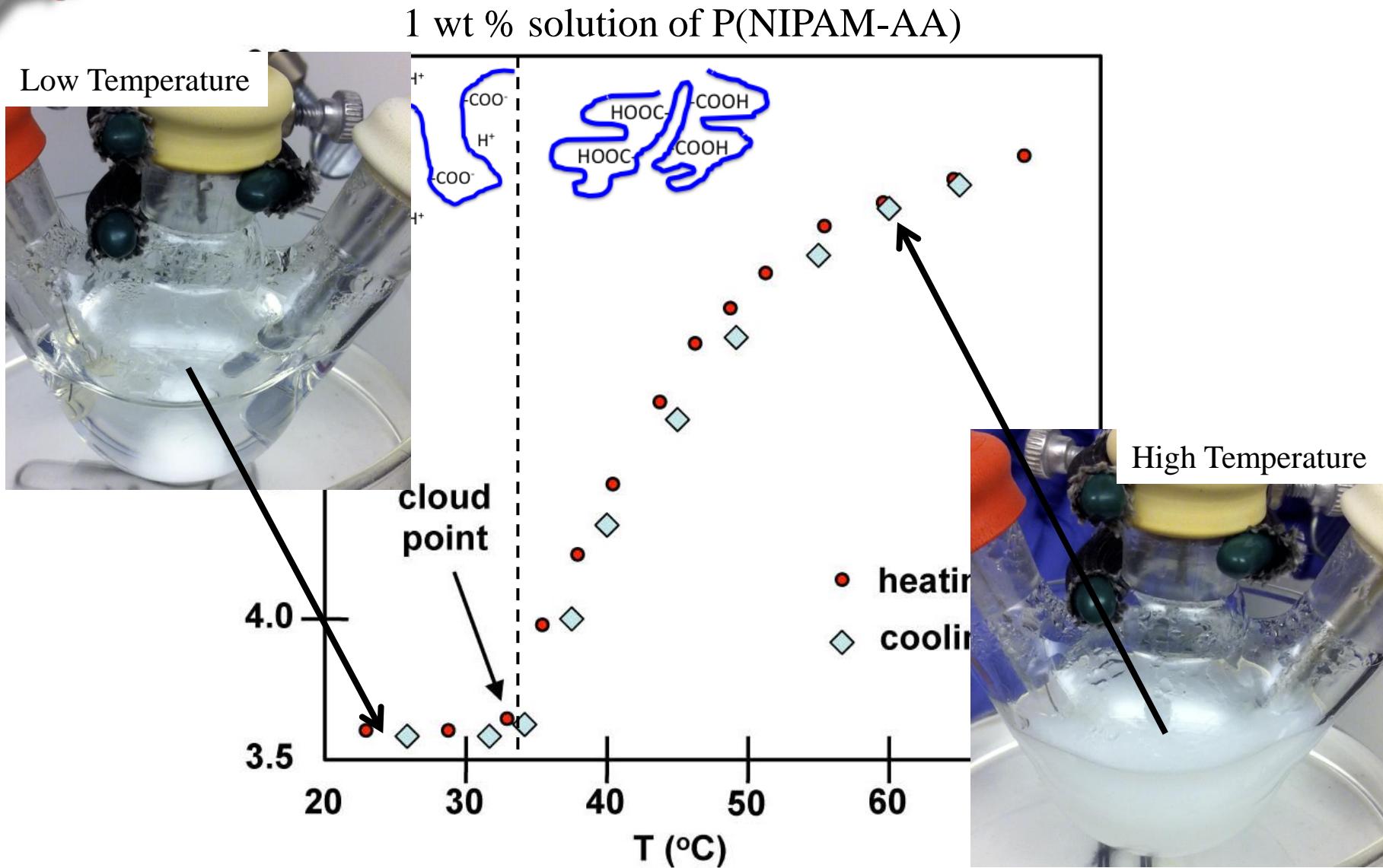


Low T: PNIPAM is swollen and hydrophilic  
High T: PNIPAM is collapsed and hydrophobic



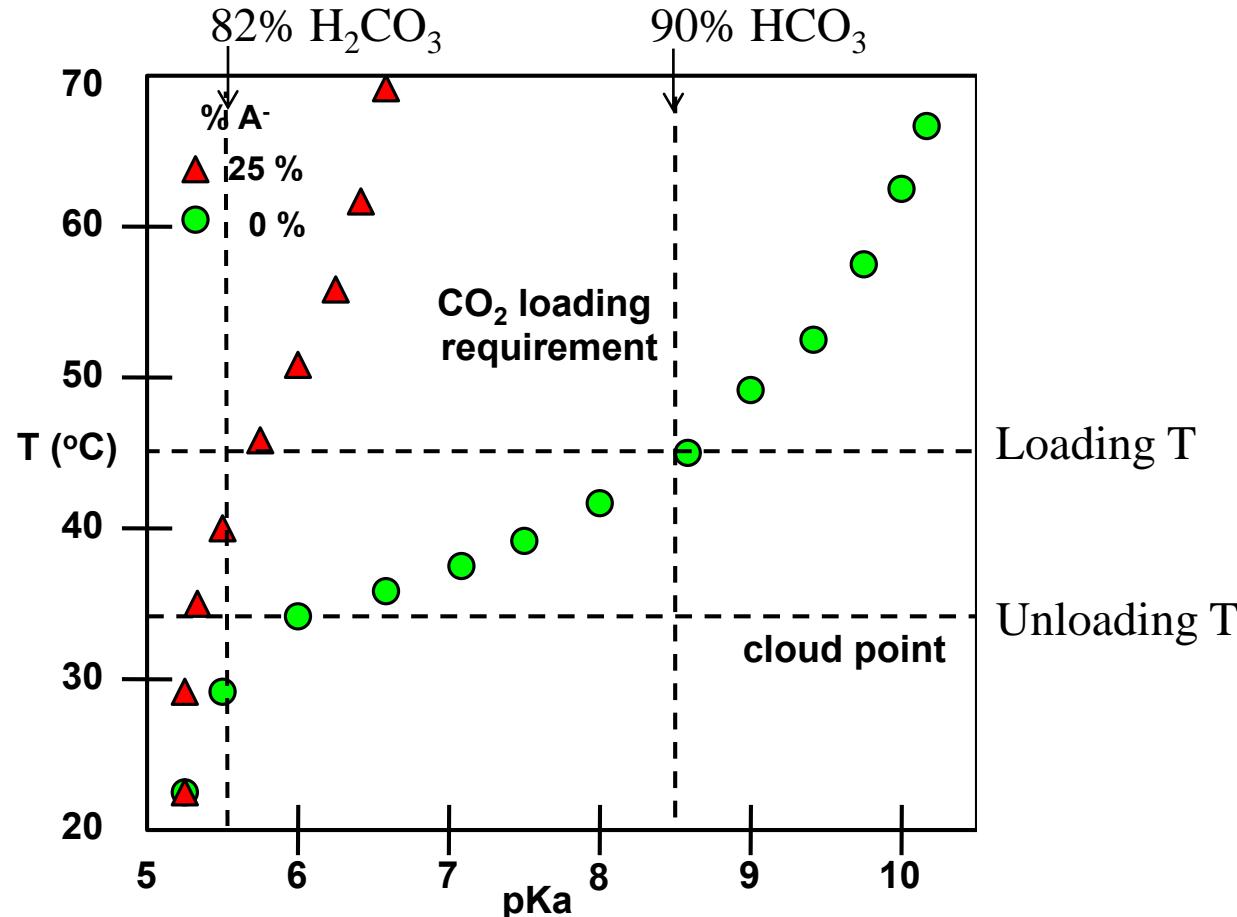
Carbonates for capture  $\leftrightarrow$  CO<sub>2</sub> for release

# Programming pH with Temperature



Sandia  
National  
Laboratories

# Programming pK<sub>a</sub> with Temperature



- 1) The initial polymer formulation (PNIPAM/PAA) has been synthesized.
- 2) Large concentrations of the polymer can be dissolved into water (> 5%).
- 3) The polymer transition temperature in water is 34°C.
- 4) The transition induces large, reversible changes in solution pH.
- 5) **Programming of the polymer should suffice for loading/unloading of  $\text{CO}_2$ .**

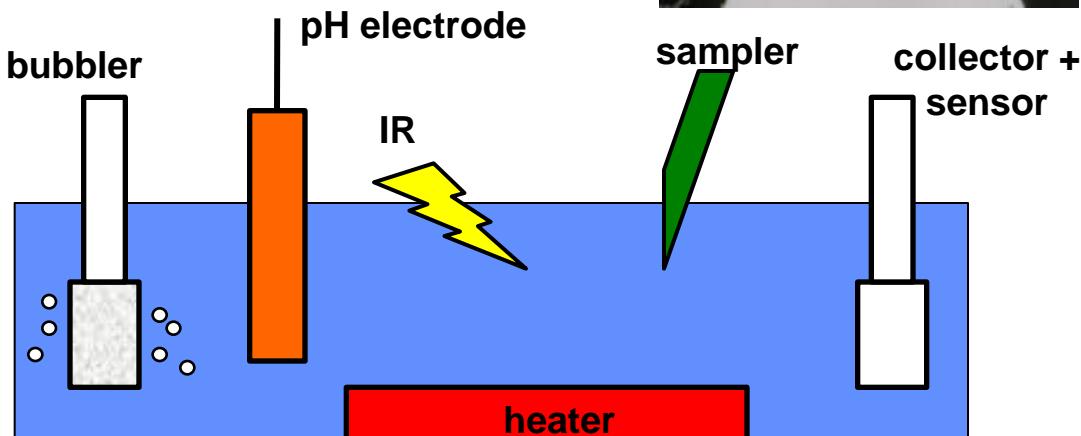
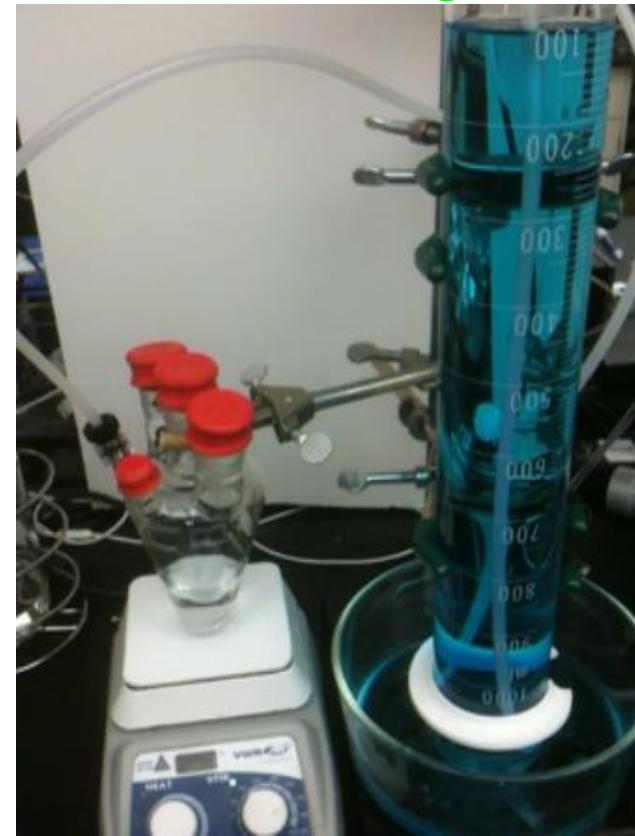
# Experimental Setup

## Loading

Components:  
Gas handling hardware  
CO<sub>2</sub> sensor  
Solution reaction vessel  
pH measurement/titration  
FTIR spectroscopy



## Unloading



**Goal:** Methodologies have been developed to introduce CO<sub>2</sub> gas, measure dissolved CO<sub>2</sub> and carbonates, collect and measure CO<sub>2</sub> gas, and determine the kinetics of CO<sub>2</sub> loading/unloading.

# Initial Experiments on $\text{CO}_2$ Unloading/Loading

$T = 63^\circ\text{C}$ , 100%  $\text{HCO}_3^-$



$T = 50^\circ\text{C}$



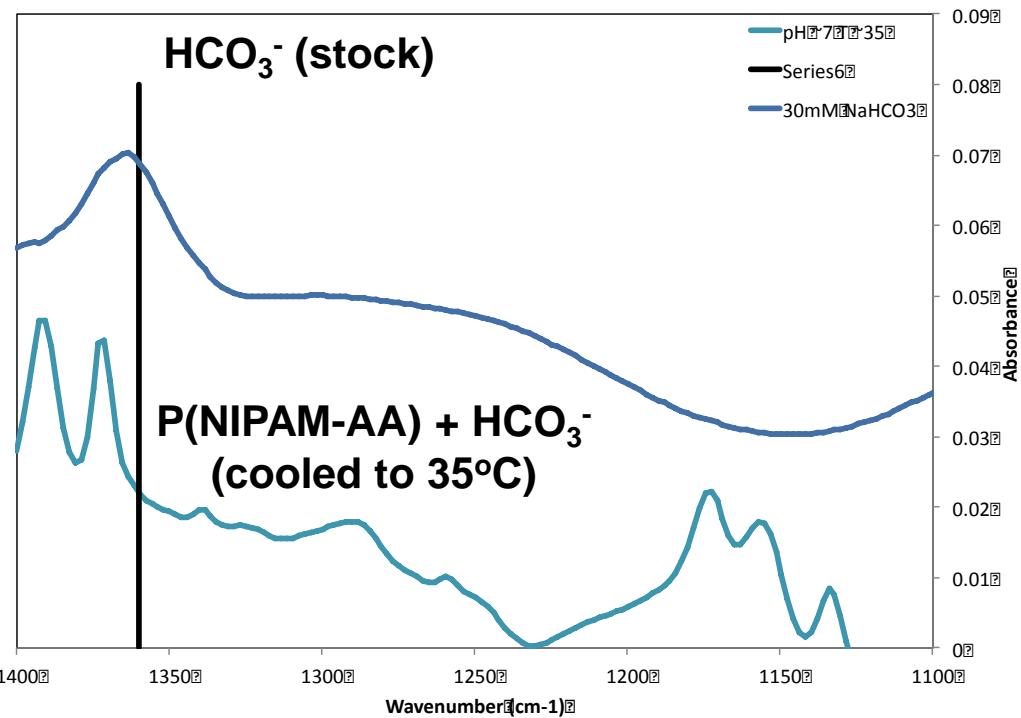
$T = 47^\circ\text{C}$ , 65%  $\text{HCO}_3^-$



$T = 45^\circ\text{C}$ , 0%  $\text{HCO}_3^-$



## Infrared Spectra for $\text{HCO}_3^-$ Unloading



**Good News** → Programmed  $\text{CO}_2$  unloading is successful.

$\text{HCO}_3^-$  is stable in contact with P(NIPAM-AA) above  $T_c$ .

$\text{HCO}_3^-$  completely decomposes to release  $\text{CO}_2(\text{g})$  as  $T$  drops below  $T_c$ .

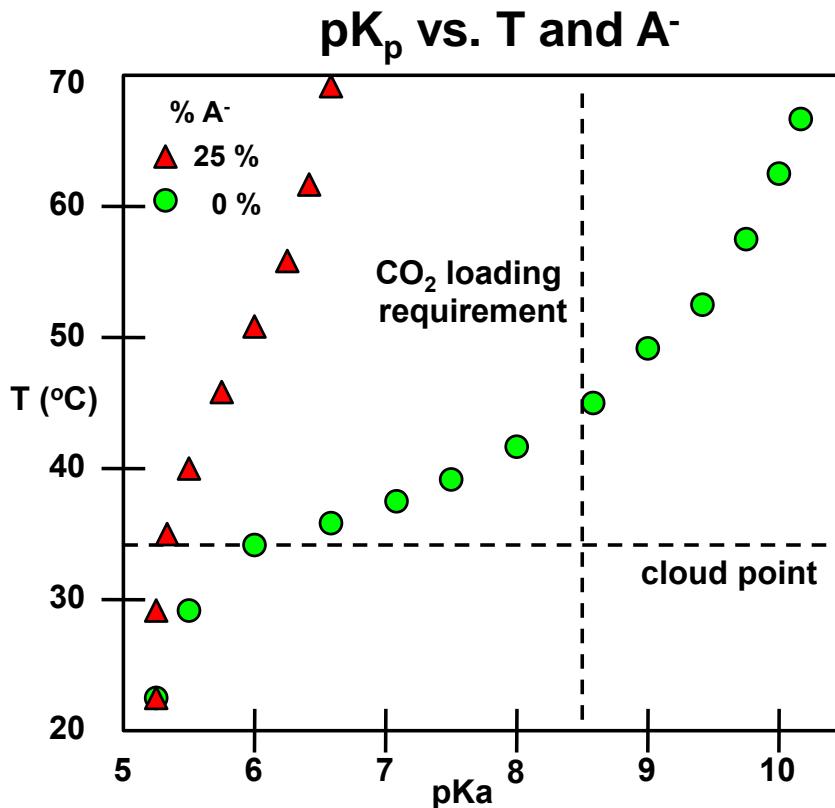
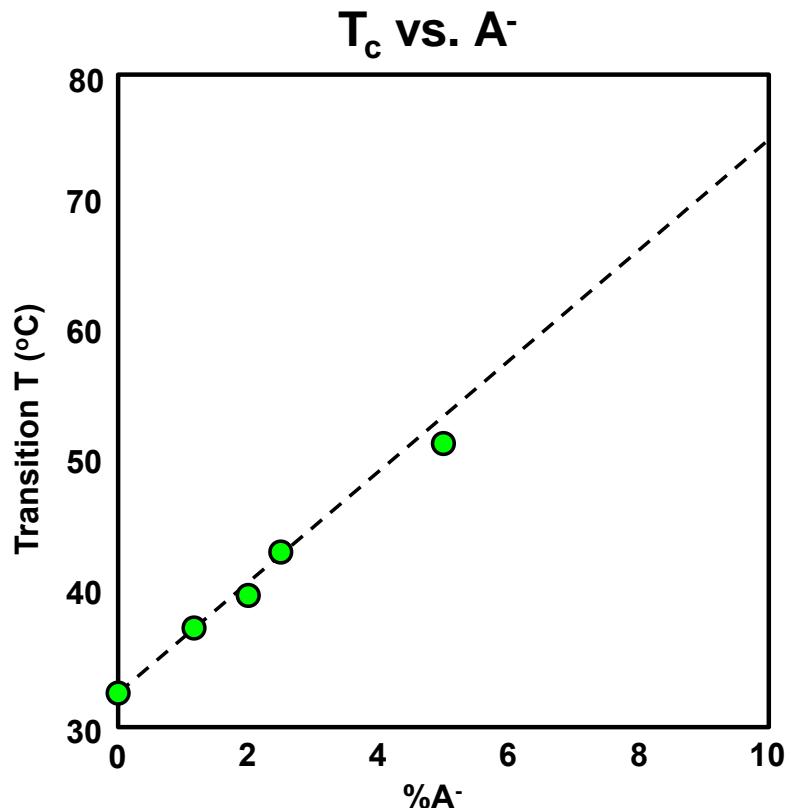
**Bad News** → Extensive reloading with  $\text{CO}_2$  does not occur.

After complete unloading, P(NIPAM-AA) does not exhibit a phase transition.

Reheating “used” P(NIPAM-AA) does not result in significant pH or  $\text{pK}_a$  increases.

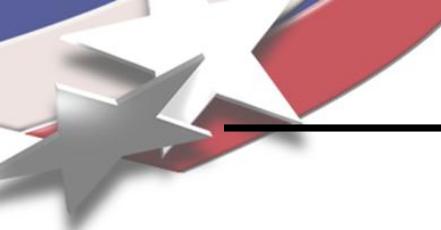
# The Mechanism for Irreversible Polymer Behavior: Buffer Ionization Impacts Hydrophobic:Hydrophilic Switching

Introduction of  $A^-$  into the polymer makes the environment more hydrophilic. Hydrophilic groups suppress the phase transition and  $pK_p$  changes.



Loading/unloading is reversible if only a fraction of the buffer capacity is used. The maximum  $\text{HCO}_3^-$  attainable on loading scales with usable buffer capacity ( $A^-$ ).





## Summary

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- Polymer-based programmable pH buffers have the potential for promoting the reversible loading and unloading of  $\text{CO}_2$  from water.
- Our initial P(NIPAM-AA) provides complete unloading of  $\text{HCO}_3^-$  to  $\text{CO}_2$ .
- $\text{CO}_2$  loading is limited by the maximum anion content the buffer can maintain and still support the required thermal phase transition.
- The current buffer will require modifications to achieve a buffer capacity that is sufficient to deploy in a practical process for the reversible capture and release of  $\text{CO}_2$  from air.

### Ongoing Work

- Varying polymer properties through composition
- Exploring properties of grafted copolymers

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