Progress on Moisture Swing Sorbents

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Three Rules for Technological Fixes

D. Sarewitz and Richard Nelson:

Three rules for technological fixes, *Nature,* 2008*, 456*, 871-872

I. The technology must largely embody the cause-effect relationship connecting problem to solution.

II. The effects of the technological fix must be assessable using relatively unambiguous or uncontroversial criteria.

III. Research and development is most likely to contribute decisively to solving a social problem when it focuses on improving a standardized technical core that already exists.

"… direct removal of CO_2 from the atmosphere — air capture — satisfies the rules for technological fixes. Most importantly, air capture embodies the essential cause–effect relations — the basic go — of the climate change problem, by acting directly to reduce CO_2 concentrations, independent of the complexities of the global energy system (Rule I). There is a criterion of effectiveness that can be directly and unambiguously assessed: the amount of CO_2 removed (Rule II). And although air-capture technologies have been remarkably neglected in both R&D and policy discussions, they nevertheless seem technically feasible (Rule III)."

Make the air do your work

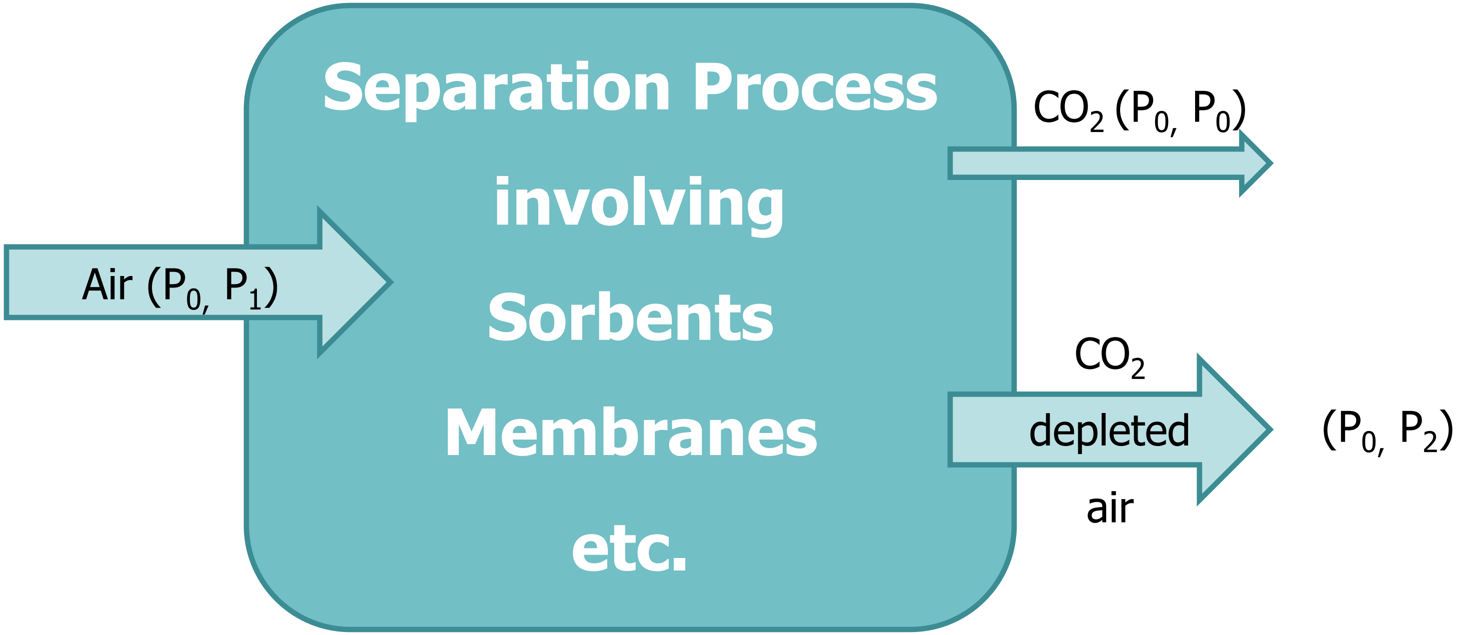
- **Air carries kinetic energy**
  - Plenty to move the air
- **Air carries thermal energy**
  - sufficient to evaporate water
- **Air carries chemical potential**
  - out of equilibrium with water
  - sufficient to compress CO_2 two hundredfold

Take advantage of the resource you have

Separation of a gas stream

Theoretical minimum free energy requirement for the regeneration is the free energy of mixing

Gas pressure P_0
CO_2 partial pressure P_x
Denoted as $(P_{0,}\ P_x)$

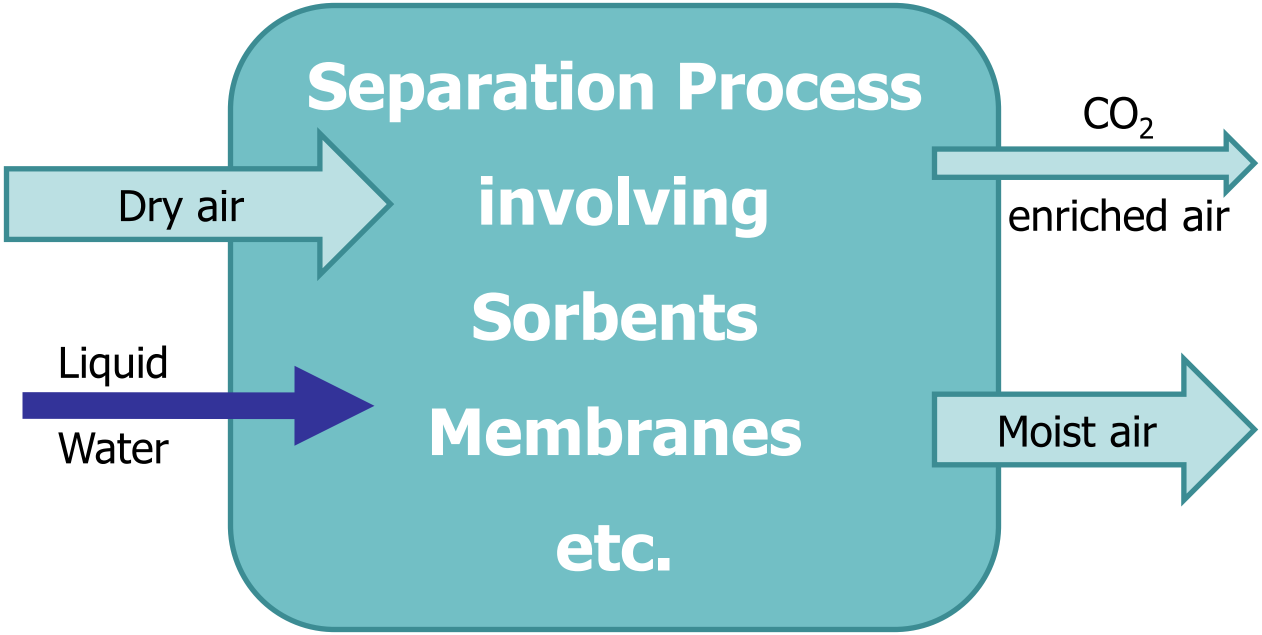


$$\Delta G = RT\left(\left(\frac{P_0 - P_2}{P_1 - P_2}\right)\frac{P_1}{P_0}\ln\frac{P_1}{P_0} - \left(\frac{P_0 - P_1}{P_1 - P_2}\right)\frac{P_2}{P_0}\ln\frac{P_2}{P_0} + \left(\frac{P_0 - P_1}{P_0}\right)\left(\frac{P_0 - P_2}{P_0}\right)\frac{P_0}{P_1 - P_2}\ln\frac{P_0 - P_1}{P_0 - P_2}\right)$$

Specific irreversible processes have higher free energy demands

Free energy from water evaporation

Water evaporation can drive CO_2 capture

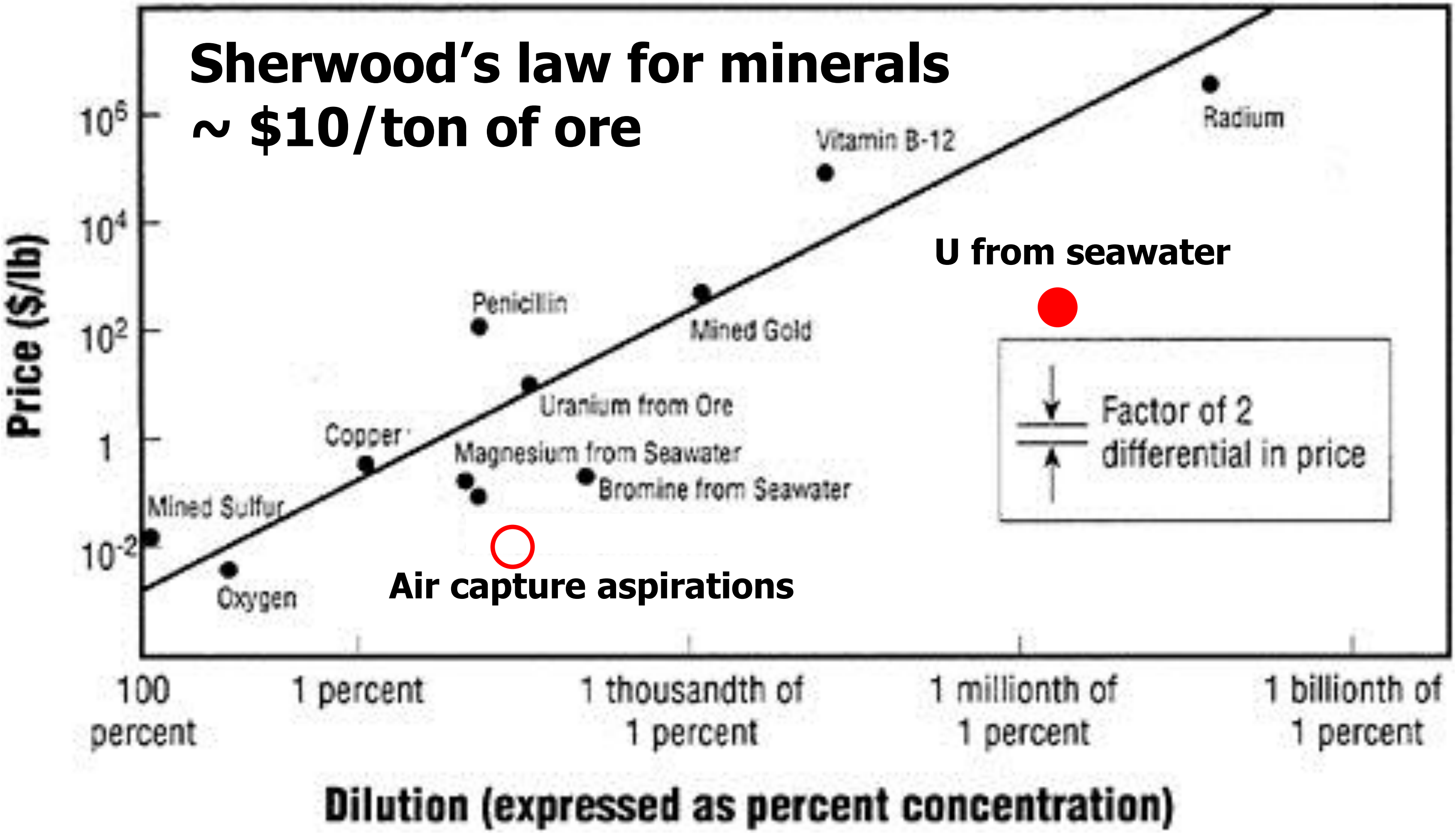


Free energy of water evaporation
at a relative humidity *RH:*
$\Delta G = RT \ln(P/P_{sat}) = RT\, ln(RH)$

Ball park estimate:	2.5 kJ/mol
	140 MJ/m^3
@ 20¢/m^3	0.5¢/kWh

Capture of CO_2 from ambient air

not your run-of-the-mill separation problem



Sherwood's law for minerals
~ $10/ton of ore

U from seawater

Air capture aspirations

SOURCE: National Research Council (1987)

Artificial kelp to absorb uranium from seawater

- **Passive, long term exposure to water**
  - Braids of sorbent covered buoyant plastic
  - Anchored to the floor
  - Replaced initially active systems
- **Low energy sorbent**
  - Laminar flow over sorbent
  - Uptake is limited by boundary layer transport
- **Regeneration**
  - After harvesting the strings
- **Gross violation of Sherwood's Law**
  - Cost estimates range from $200 to $1200/kg
  - Sherwood $3 million/kg

wikipedia

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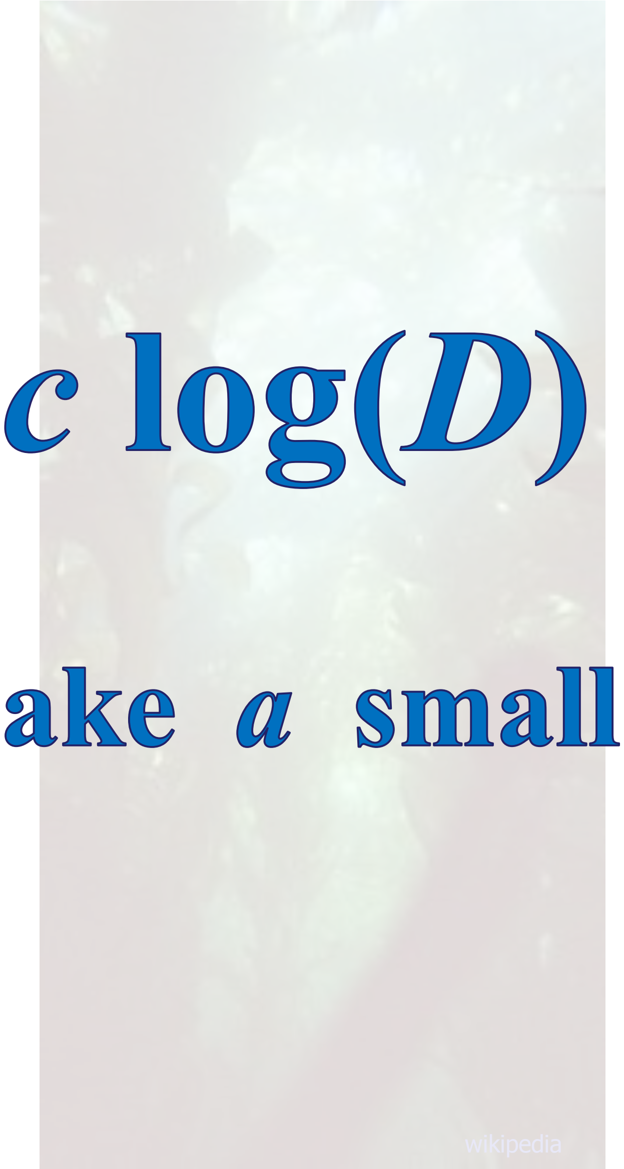
$$Cost = a\,D + b + c\,\log(D)$$

must make a small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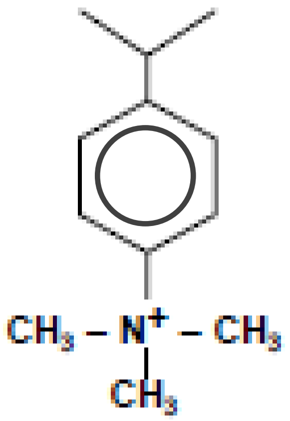
Anionic Exchange Resins

Solid carbonate "solution"
Quaternary ammonium ions form strong-base resin



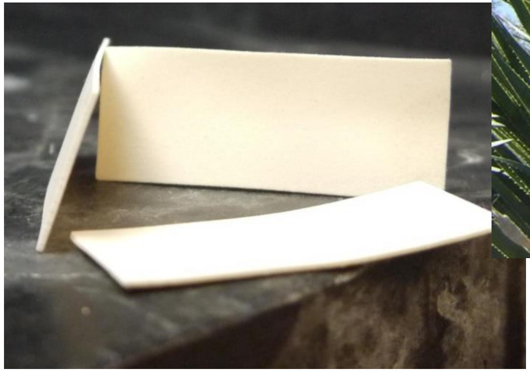
Type I Strong Base Resins

- Positive ions fixed to polymer matrix
  - Negative ions are free to move
  - Negative ions are hydroxides, OH^-
- Dry resin loads up to bicarbonate
  - $OH^- + CO_2 \rightarrow HCO_3^-$ (hydroxide → bicarbonate)
- Wet resin releases CO_2 to carbonate
  - $2HCO_3^- \rightarrow CO_3^{--} + CO_2 + H_2O$

Moisture driven CO_2 swing

Membrane material

thin sheets



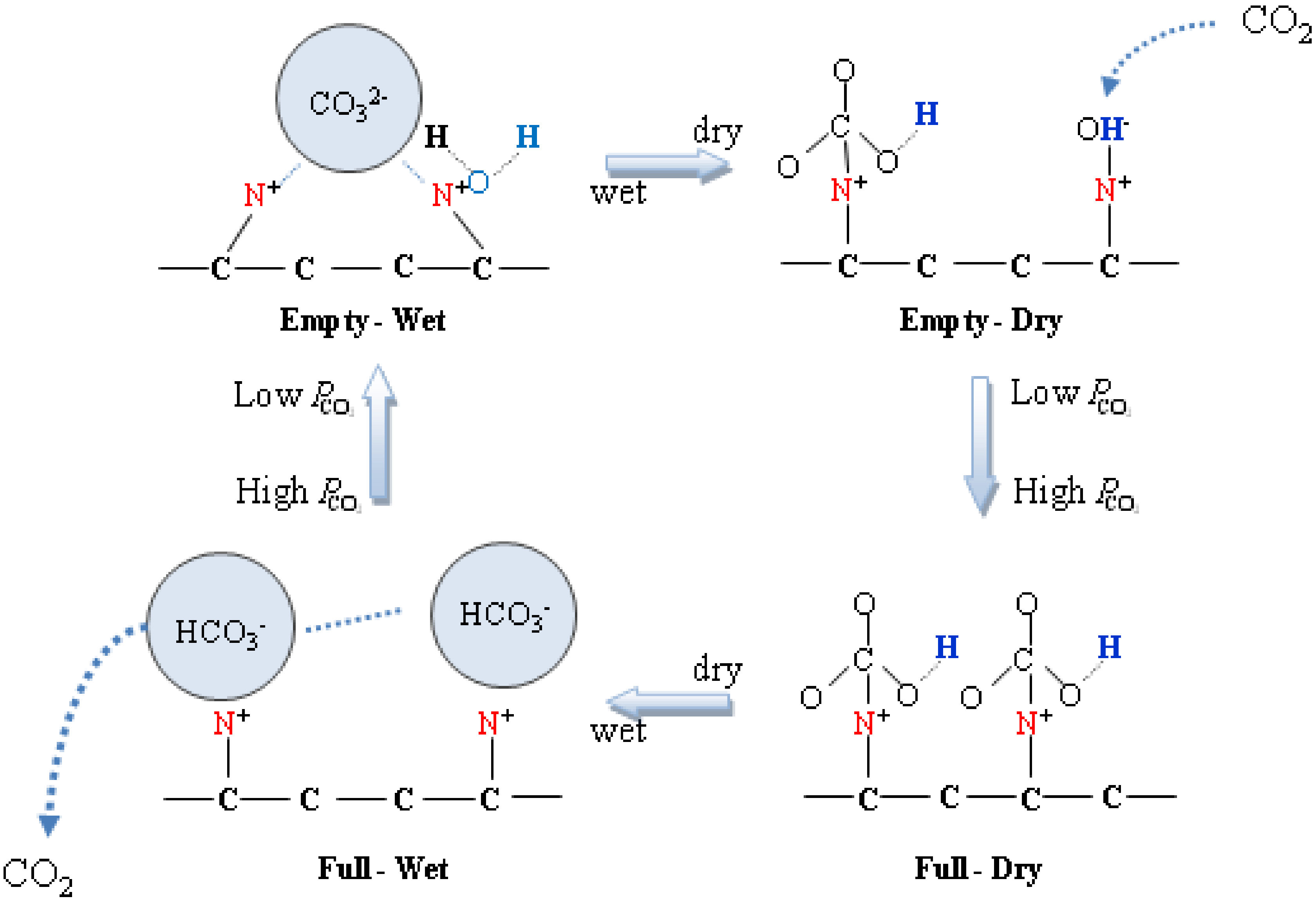
Snowpure electrochemical membrane (1mm thick)

Polypropylene matrix with embedded fine resin particles (25µm)

Quaternary ammonium cations Carbonate/bicarbonate form

1.7 mol/kg charge equivalent

The moisture swing – water driven

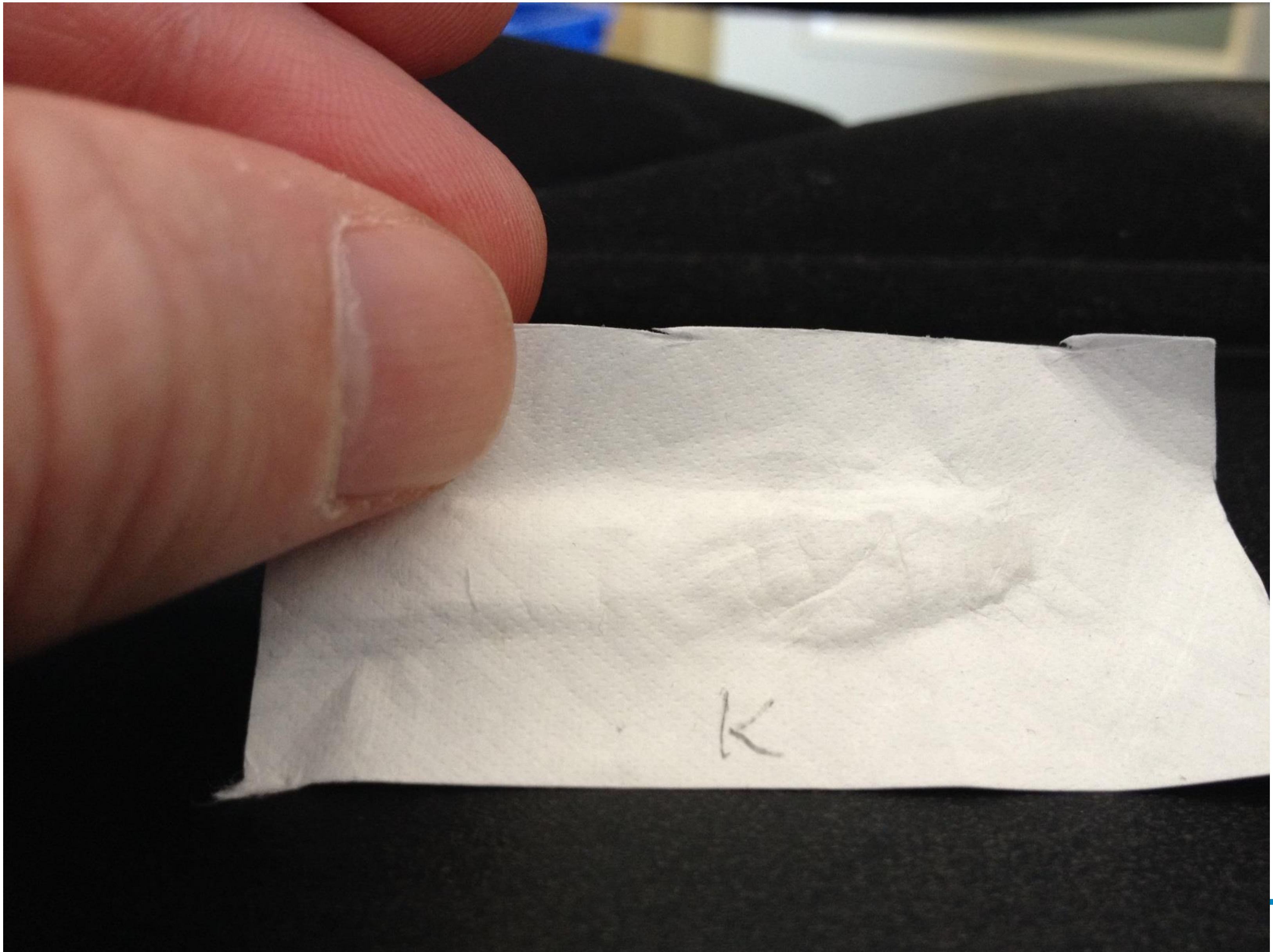


Progress on several fronts

- **Better form factors**
  - Embedded resin powder into paper matrix
- **Protection from liquids**
  - Tyvek and similar barriers
- **Alternative Sorbents**
  - Activated carbon impregnated with carbonate
- **Molecular dynamics results**
  - Humidity swing is calculable

Paper Air Filters

A Tyvek® Pouch



Alternative sorbent options

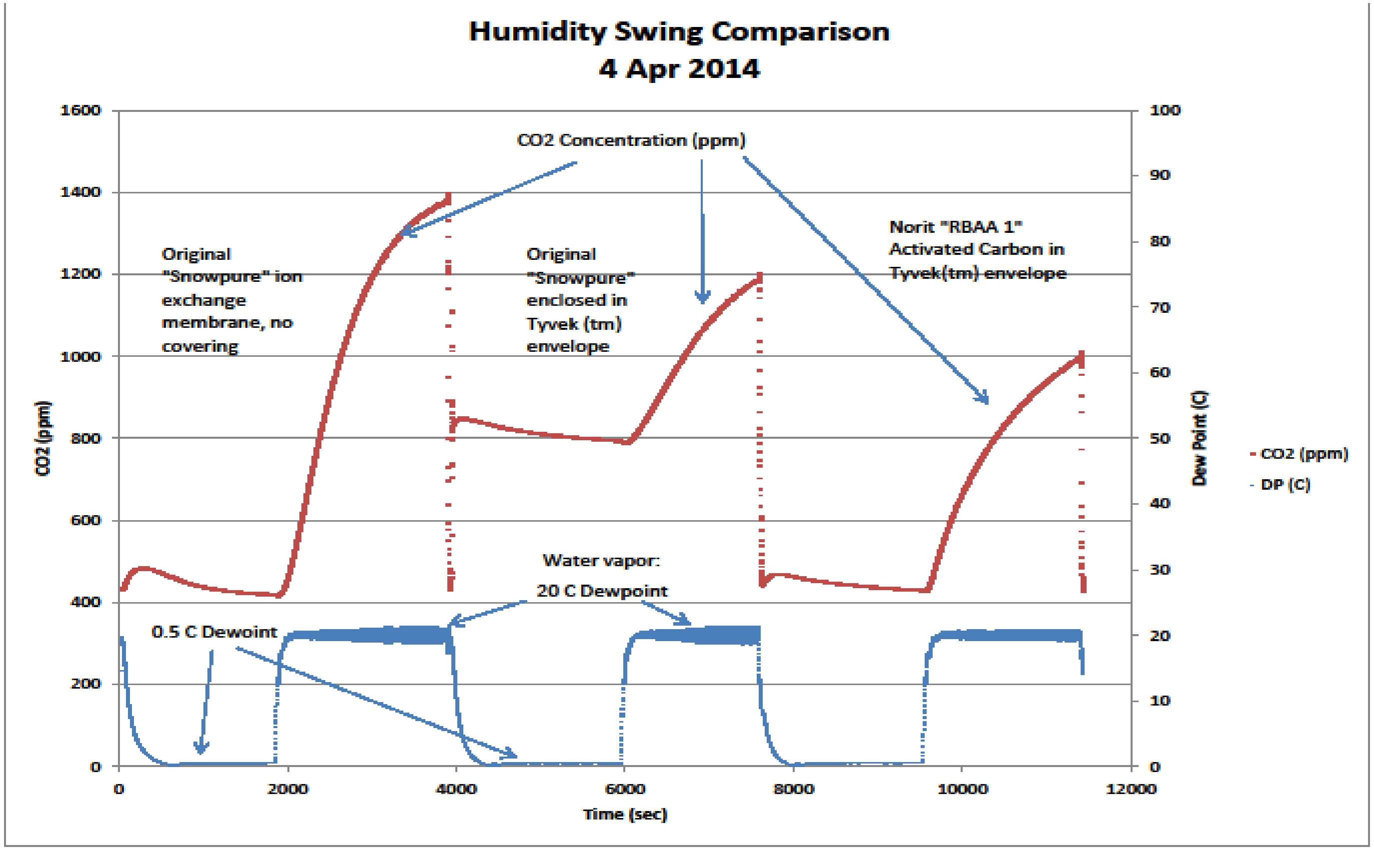
- **Activated carbon**
  - No discernable moisture swing
- **Carbonate brines**
  - No discernable moisture swing
- **Carbon impregnated with carbonate**
  - Strong moisture swing
  - Moisture induced pressure change is small

Different materials for sorption

- Different samples tested for moisture swing

Tyvek® barrier for sample comparison

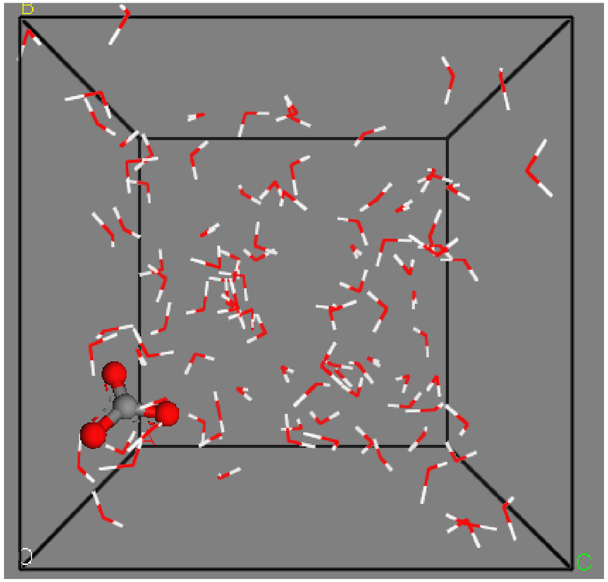
Membrane without Tyvek®, with Tyvek®, and Carbonate impregnated activated carbon



Molecular dynamics calculations

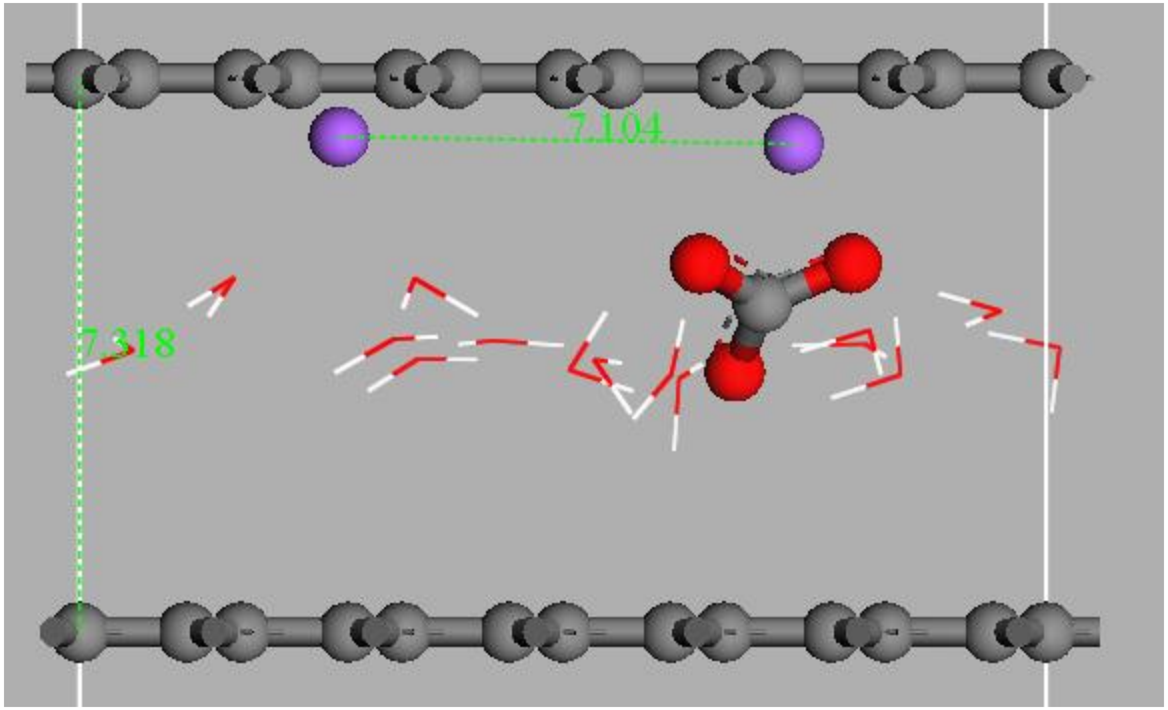
Xiaoyang Shi

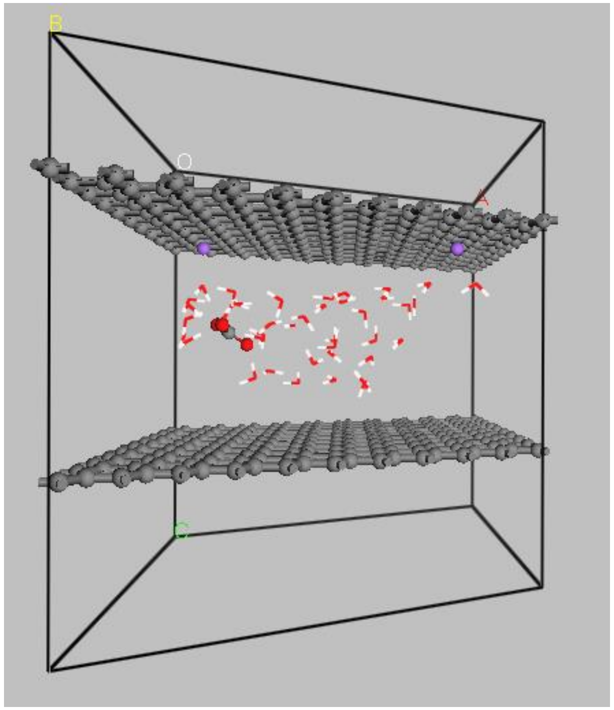
- Learned how to set up models
- Learned how to run test examples
- Using mainly public domain software
    - ○ Affordability
    - ○ Flexibility



Carbonate ion hydration

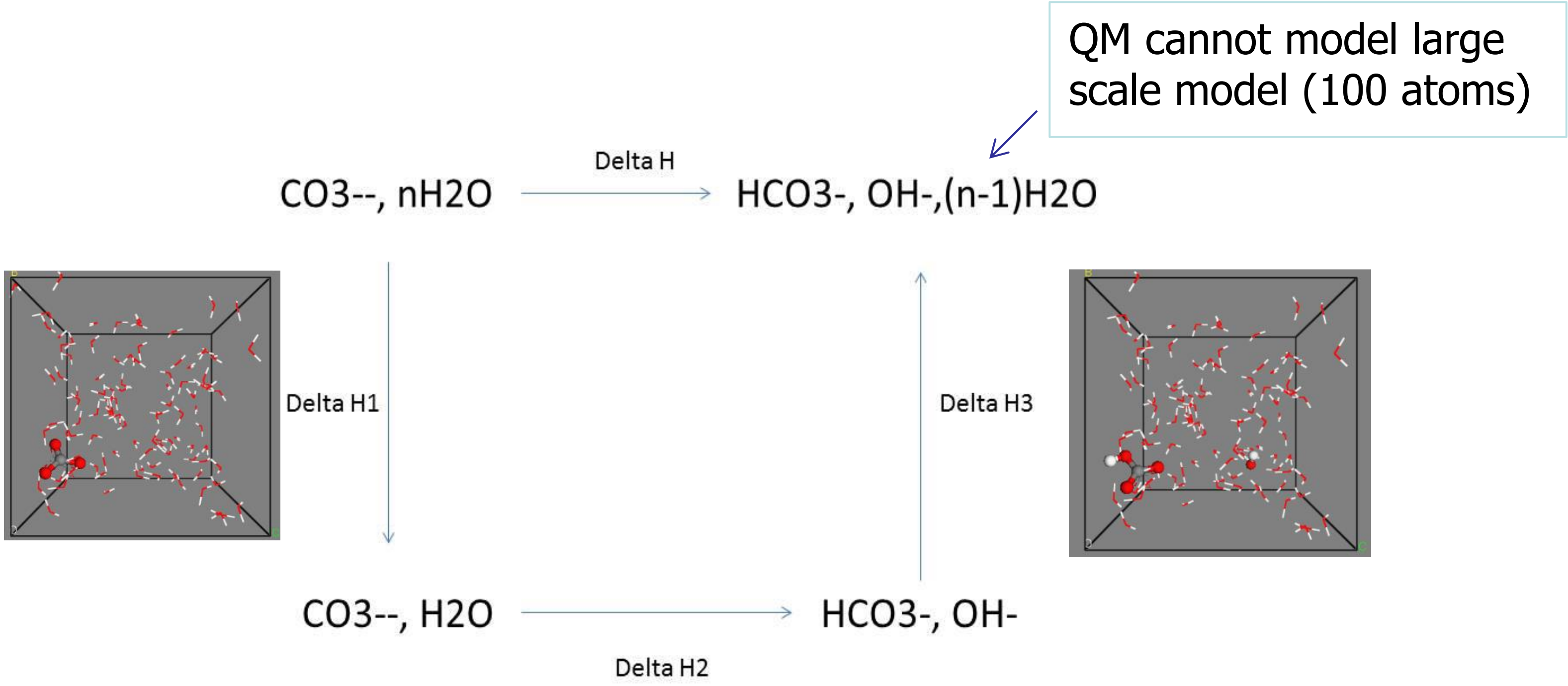
Geometry Configurations of Models





Purple atoms are fixed cations (fashioned after sodium), grey atoms are graphene as confined layers, and carbonate ions with water molecules are in the confined region.

Methodology



QM cannot model large scale model (100 atoms)

Delta H= Delta H1 + Delta H2 + Delta H3

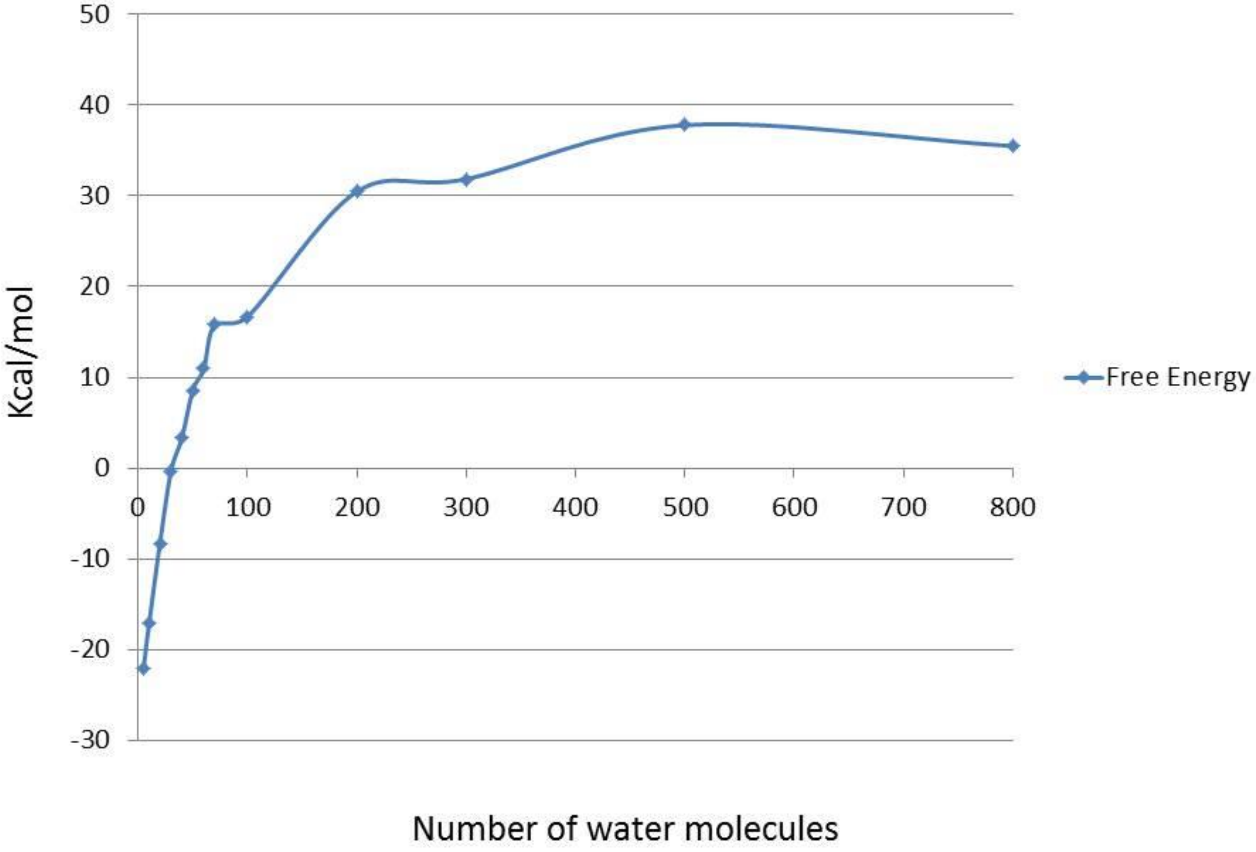
$$CO_3^{--} \cdot nH_2O \Leftrightarrow HCO_3^- \cdot m_1H_2O + OH^- \cdot m_2H_2O + (n-1-m_1-m_2)H_2O$$

$$CO_3^{--} + H_2O \Leftrightarrow HCO_3^- + OH^-$$

reaction energy is -48.3255 kcal/mol based on QM calculation

Free Energy Change with Humidity

CO_3^{--} (aq) + $H_2O \leftrightarrow HCO_3^-$ (aq)+ OH^-(aq)   ΔF



Carbonate ion and bicarbonate with hydroxide ions free energy changes with the number of water molecules in the calculational volume