15AIChE
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Integration of High-Fidelity CO_2 Sorbent Models at the Process Scale Using Dynamic Discrepancy

Kuijun Li[*,†], David S Mebane[*,†] and Priyadarshi Mahapatra[*]

[*]National Energy Technology Laboratory
[†]Department of Mechanical and Aerospace Engineering
West Virginia University

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Overview

- Introduction: PEI adsorbents and reaction kinetics
- Motivation and new mechanism
- Dynamic discrepancy reduced model and Bayesian calibration
- Conclusions and future work

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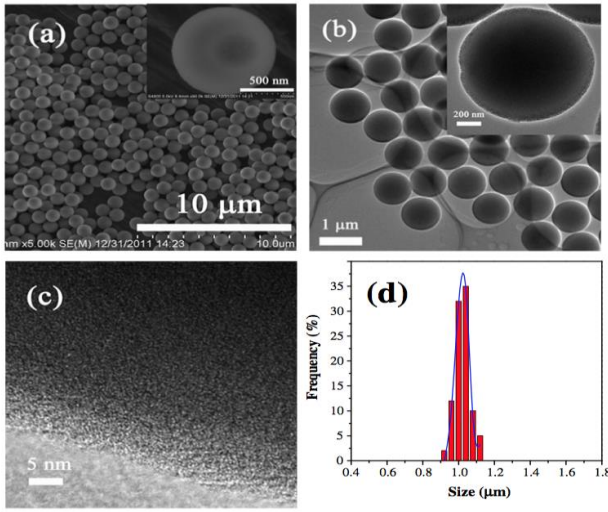
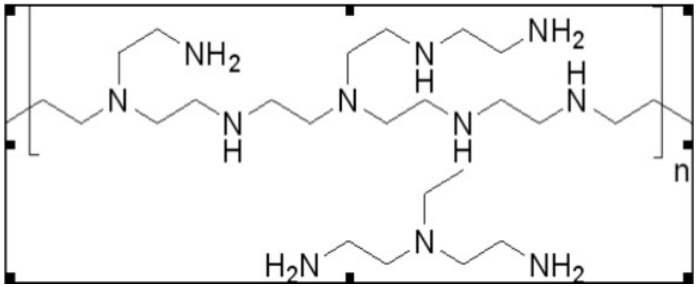
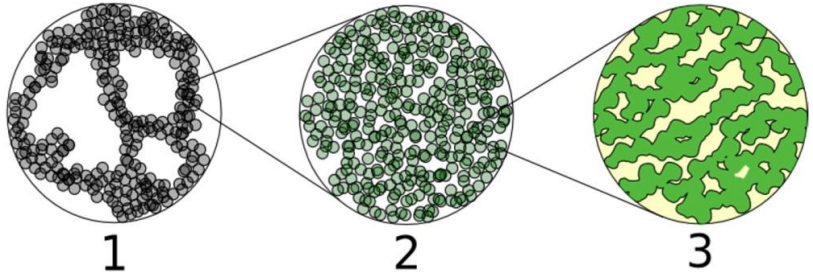
Introduction: Amine-based Adsorbents



SEM (a), TEM (b), HRTEM (c) images and particle-size distribution histogram (d) of the S600-10 sample



PEI structure



Length scale: (1) macroporosity
(2) meso-porous particles
(3) Silica-PEI composite

Mass transport:

Gas phase diffusion in mesopores;

Solid state diffusion in silica-PEI composites.

Yao, L., et al., Journal of colloid and interface science 408 (2013): 173-180
Mebane, D.S., et al., The Journal of Physical Chemistry C 117.50 (2013): 26617-26627.

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Introduction: Reaction Kinetics

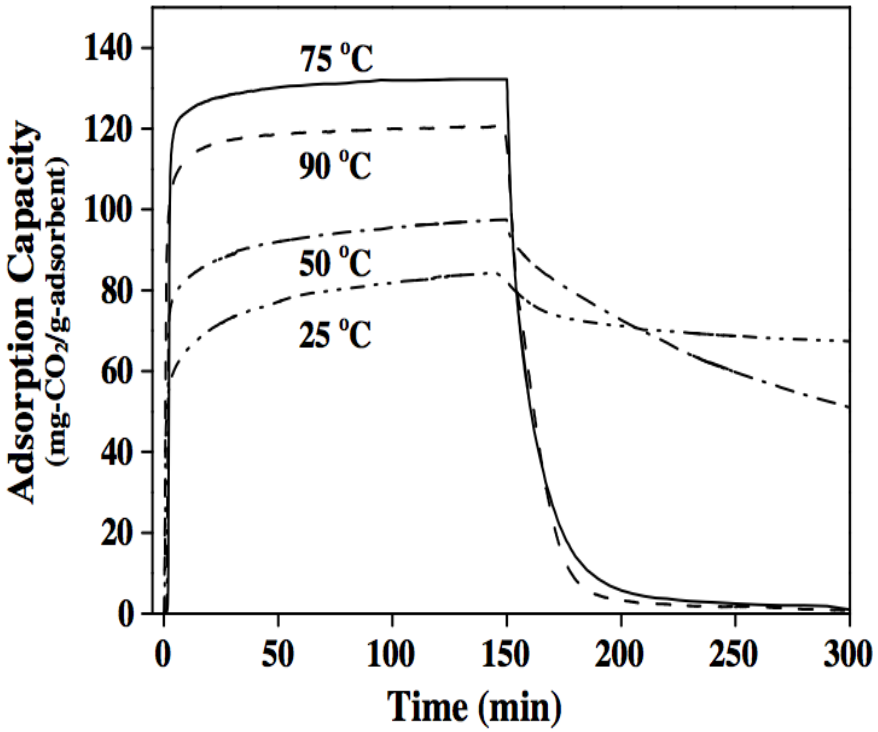
- Zwitterion Mechanism

$$R_2NH + CO_2(g) \rightleftharpoons R_2NH^+CO_2^-$$
$$R_2NH^+CO_2^- + B \rightleftharpoons R_2NCO_2^- + BH^+$$

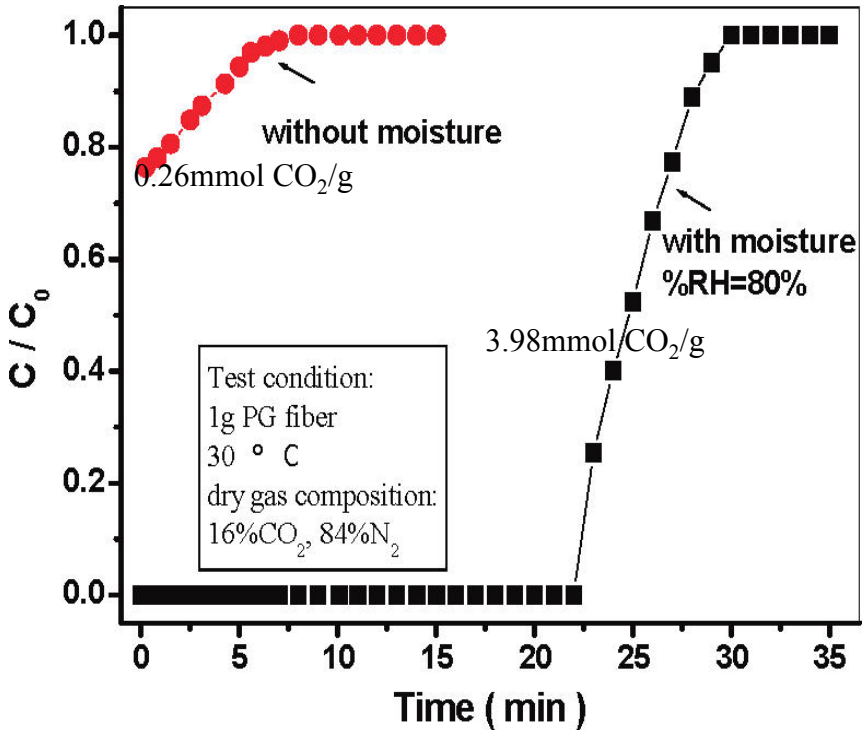
- Termolecular Mechanism

$$R_2NH\cdots B + CO_2(g) \rightleftharpoons R_2NCO_2^- + BH^+$$

Motivation



The effect of temperature on the CO_2 adsorption–desorption performance of KIT-6-PEI 50



Comparison of the adsorbed volume of CO2 from simulated dry and moist flue gas.

W.J. Son et al., Microporous and Mesoporous Materials 113 (2008) 31–40 Li, P., et al., Langmuir, 2008, 24 (13): 6567-6574

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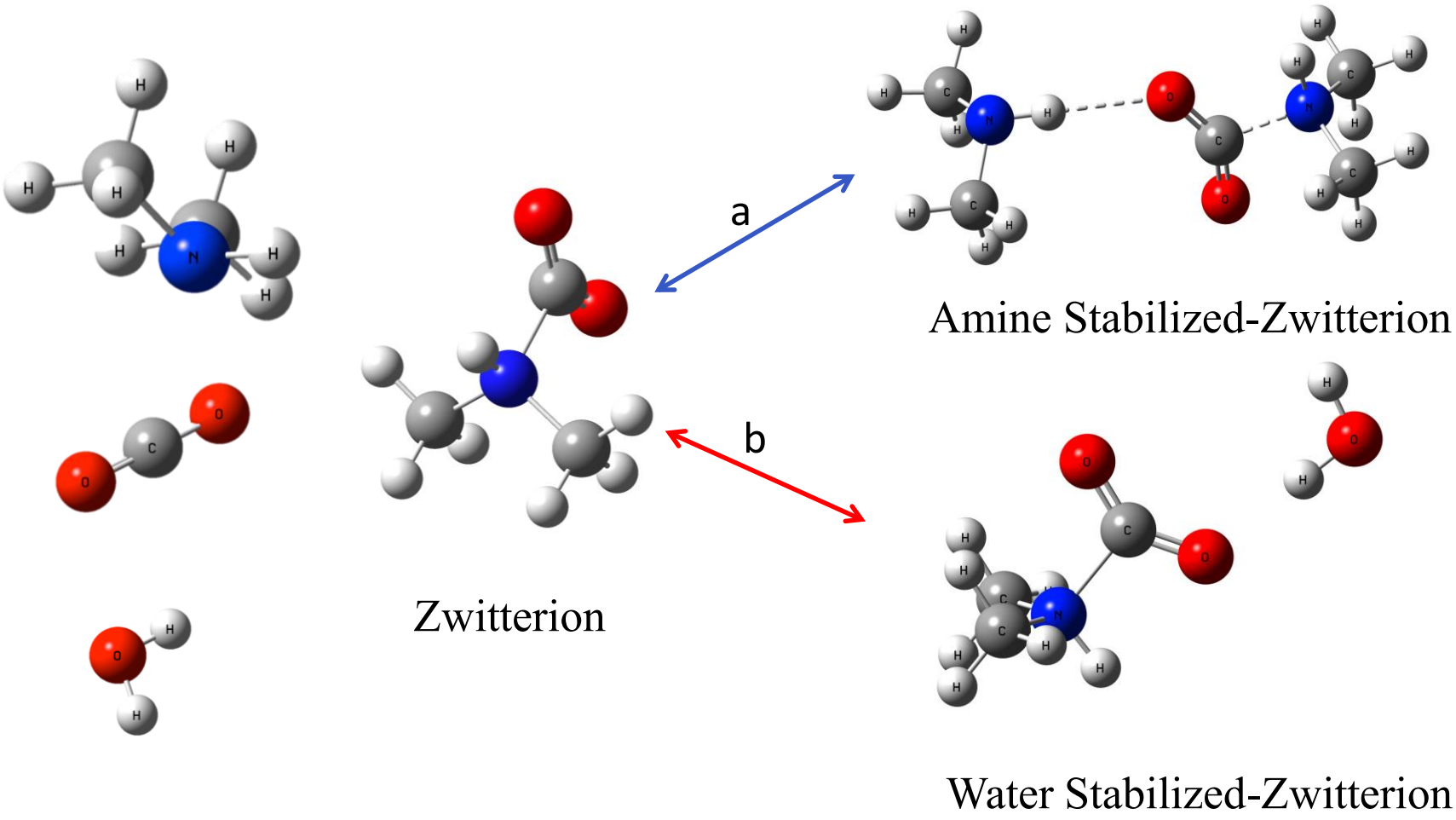
New Mechanism



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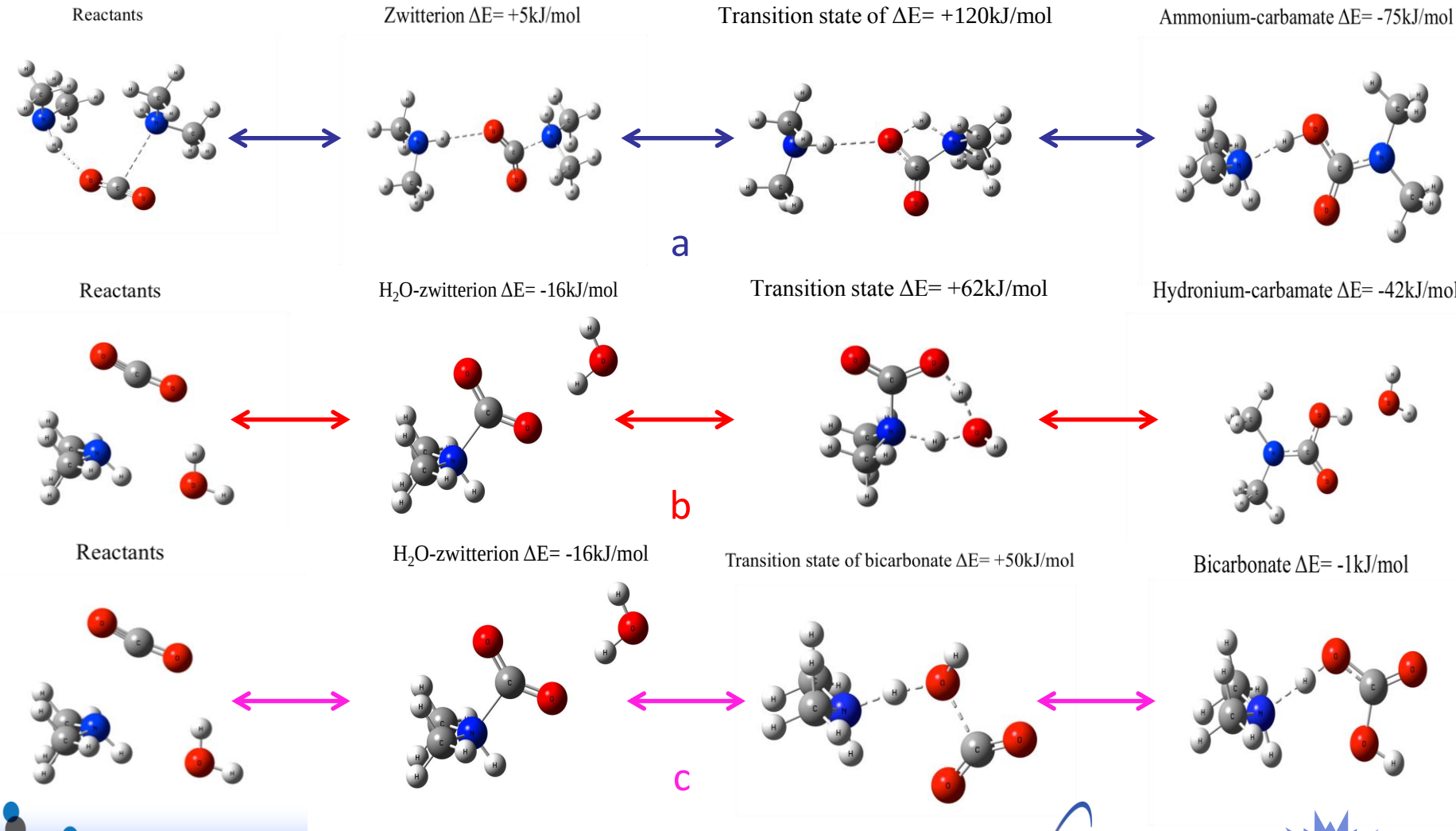
New Mechanism



New Mechanism

$$R_2NH\cdots NHR_2 + CO_2(g) \overset{\kappa_1}{\rightleftharpoons} R_2NH^+CO_2^- - R_2NH \quad (1)$$

$$R_2NH^+CO_2^- - R_2NH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2NCO_2^- : R_2NH_2^+ \quad (2)$$

$$R_2NH + H_2O(g) \overset{\kappa_3}{\rightleftharpoons} R_2NH - H_2O \quad (3)$$

$$R_2NH - H_2O + CO_2(g) \overset{\kappa_4}{\rightleftharpoons} R_2NH^+CO_2^- - H_2O \quad (4)$$

$$R_2NH^+CO_2^- - H_2O \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} R_2NCOO^- : H_3O^+ \quad (5)$$

Variables: z_1 = Amine-Zw (1) x = Ammonium-Carbamate (2)

z_2 = Amine-H_2O (3) z_3 = H_2O-Zw (4)

y = Hydronium-Carbamate (5)

Solutions:

$$W_{CO_2} = M_{CO_2} n_v (x + y + z_1 + z_3)/\rho$$

$$W_{H_2O} = M_{H_2O} n_v (y + z_2 + z_3)/\rho$$

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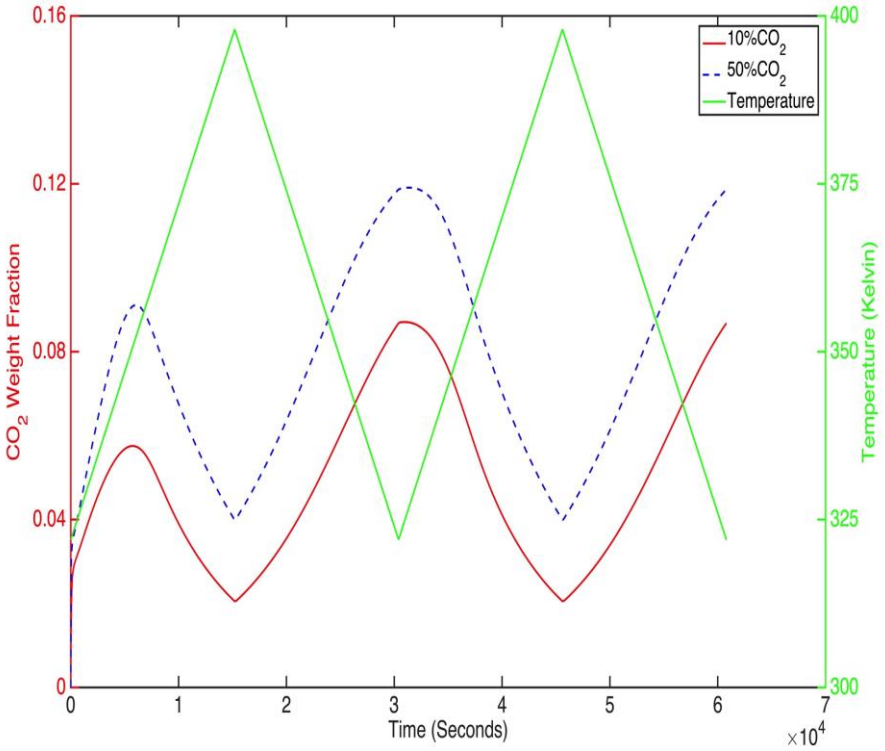
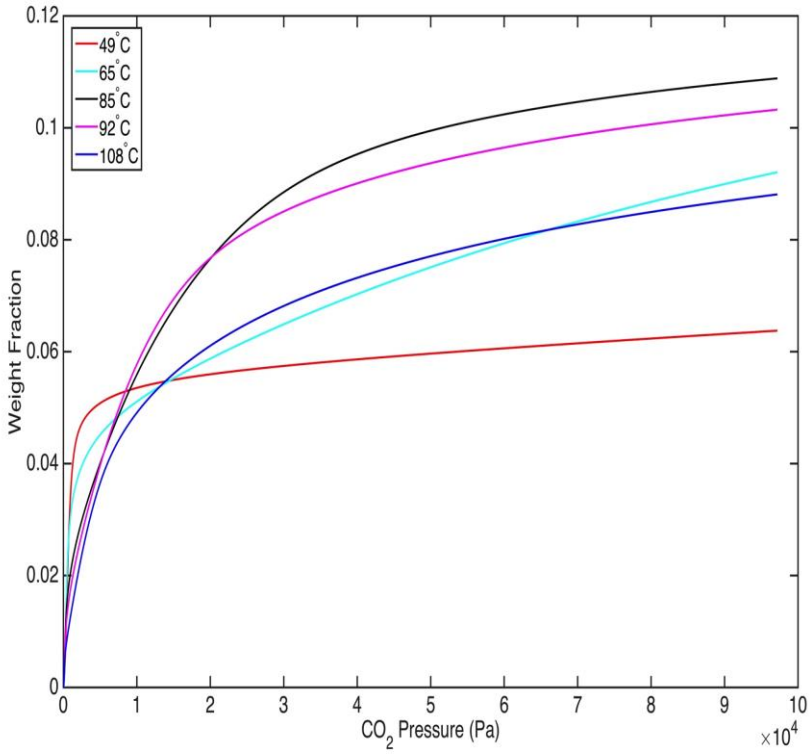
Simulation Results on Temperature Effect





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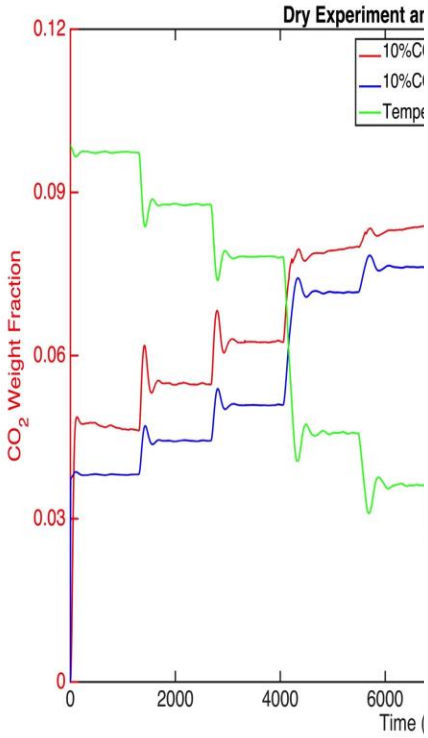
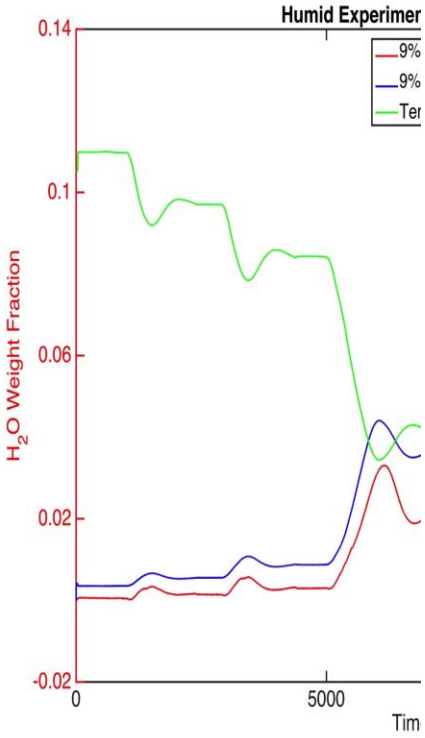
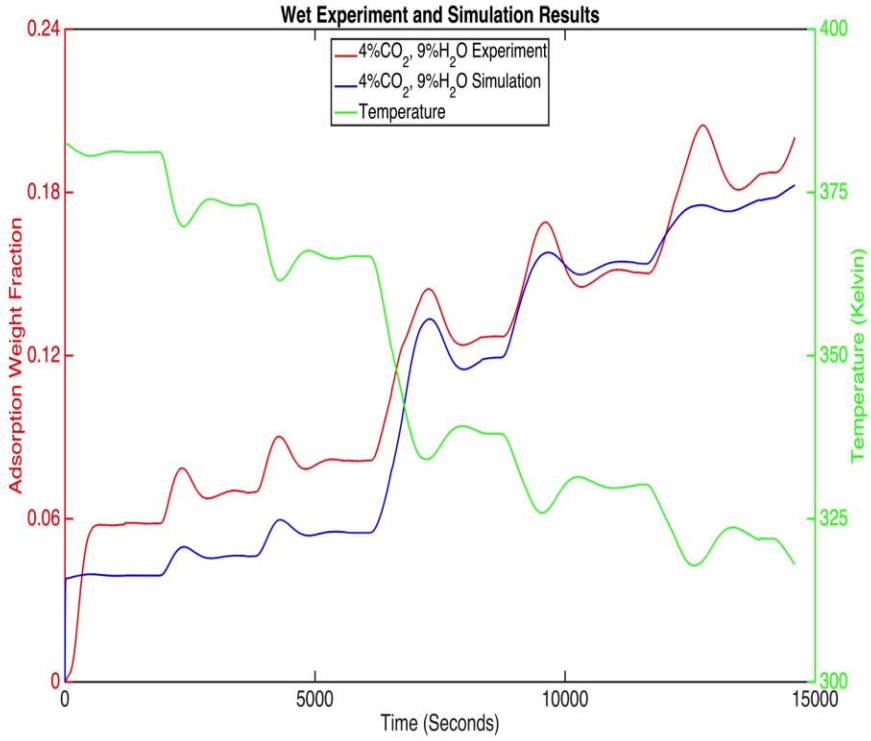
Experiment and Simulation Results







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Methods: Bayesian Calibration and Dynamic Discrepancy

Bayesian Calibration:

$$\mathcal{P}(A|B) = \frac{\mathcal{P}(B|A)\mathcal{P}(A)}{\int_{A'} \mathcal{P}(B|A')dA'}$$

$$\mathcal{Z} = Y(\theta) + \delta(\xi) + \epsilon(\psi)$$

$$\Omega(\theta, \xi, \psi|Z) \propto \mathcal{L}(Z|\theta, \xi, \psi)\pi(\theta, \xi, \psi)$$

Dynamic Discrepancy:

Discrepancy on Kinetic non-ideality :

$$u^*_{b_i} = \zeta_b \exp\left(\frac{-\Delta H^{\ddagger}_b}{RT}\right)$$

$$u^*_{bi,new} = \zeta_b \exp\left(\frac{-\Delta H^{\ddagger}_b}{RT}\right) \exp[\delta(z_{i-1}, z_i, z_{i+1}, \frac{1}{T})]/T$$

$$= u^*_{b_i} \exp[\delta(z_{i-1}, z_i, z_{i+1}, \frac{1}{T})]$$

Discrepancy on Thermodynamic Equilibrium :

$$\kappa = \exp\left(\frac{-\Delta H + T\Delta S}{RT}\right)/P$$

$$\kappa_{new} = \kappa * \exp[\delta^E(P, T)]$$

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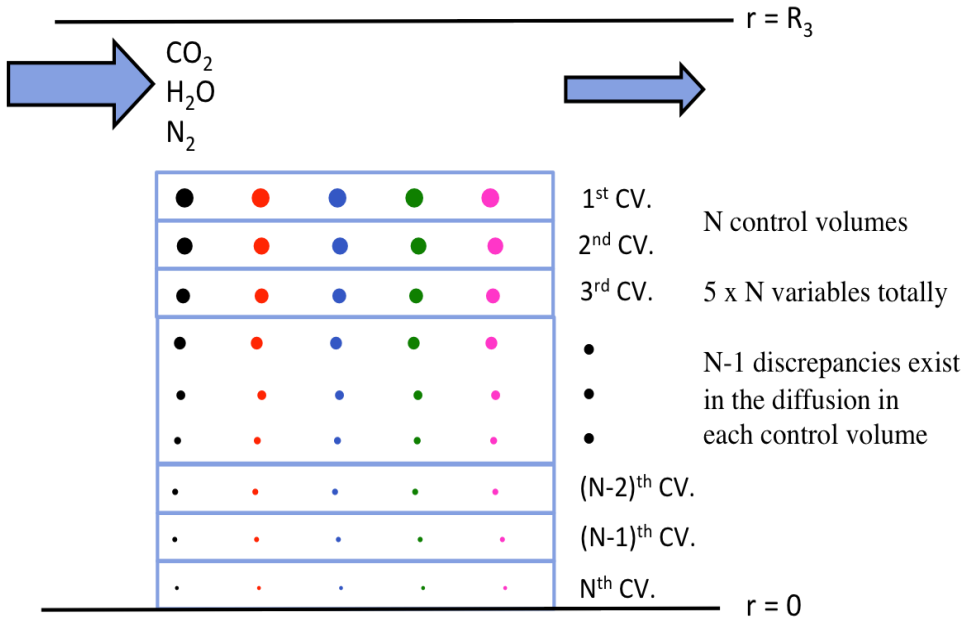
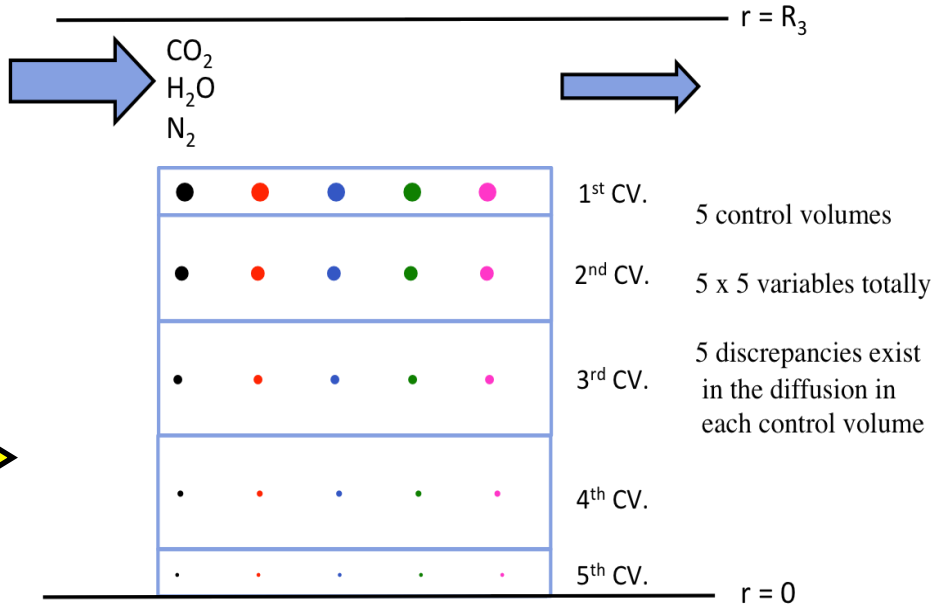
Reduced Model



Normal Model

Increase the calculation speed by reducing the control volumes and add discrepancy to diffusivity coefficients

Reduced Model



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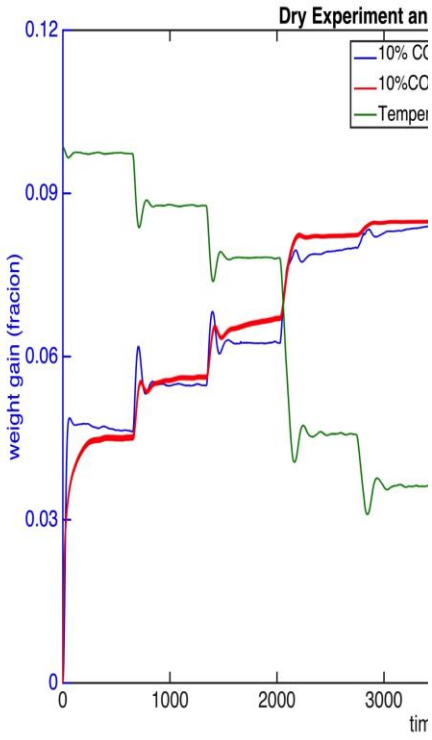
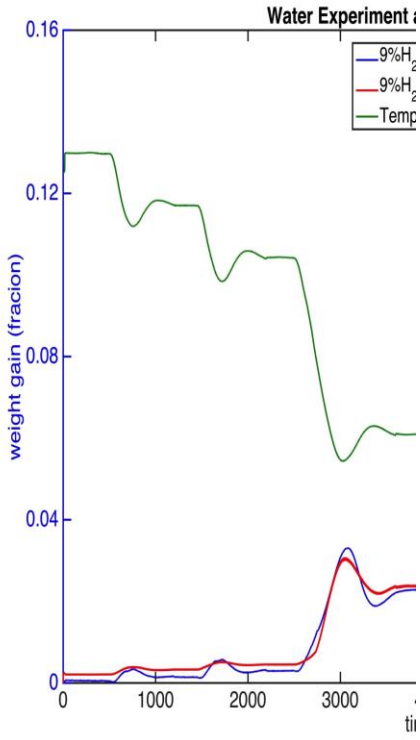
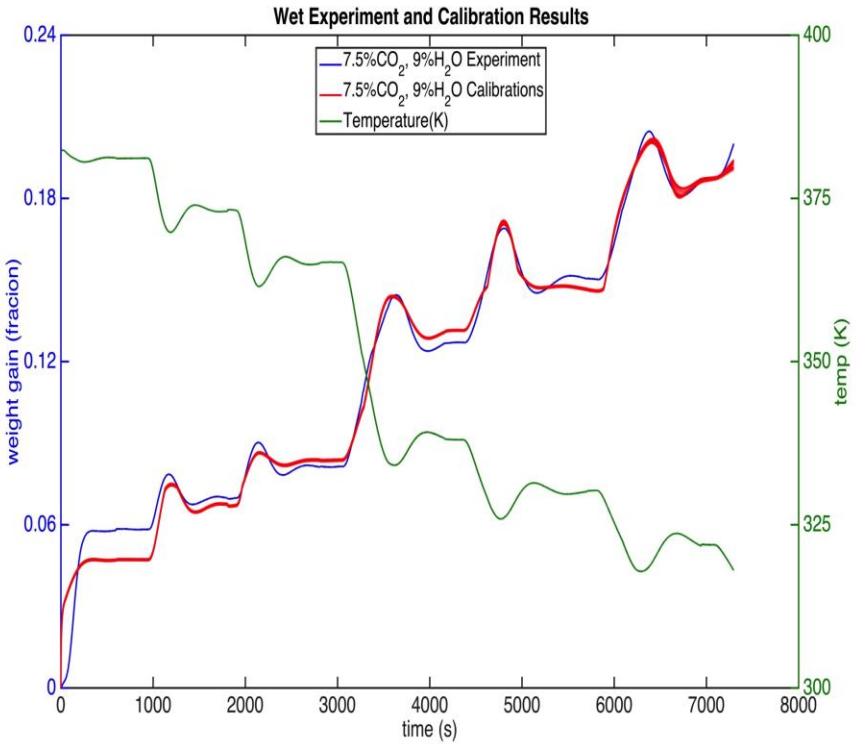
Calibration Results







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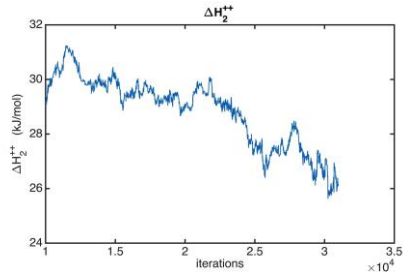
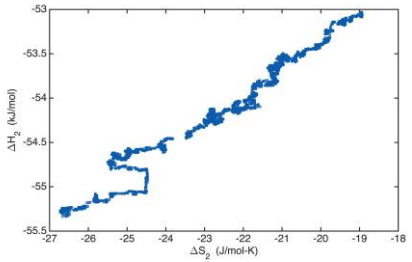
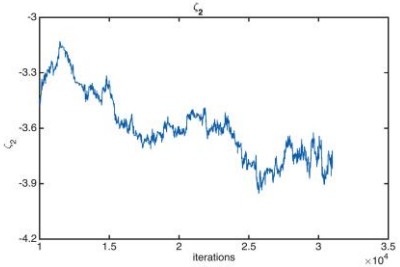
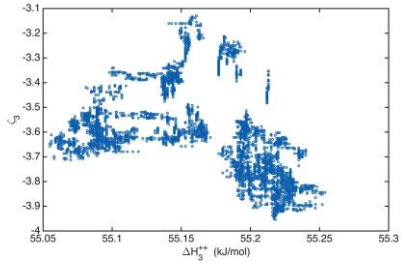
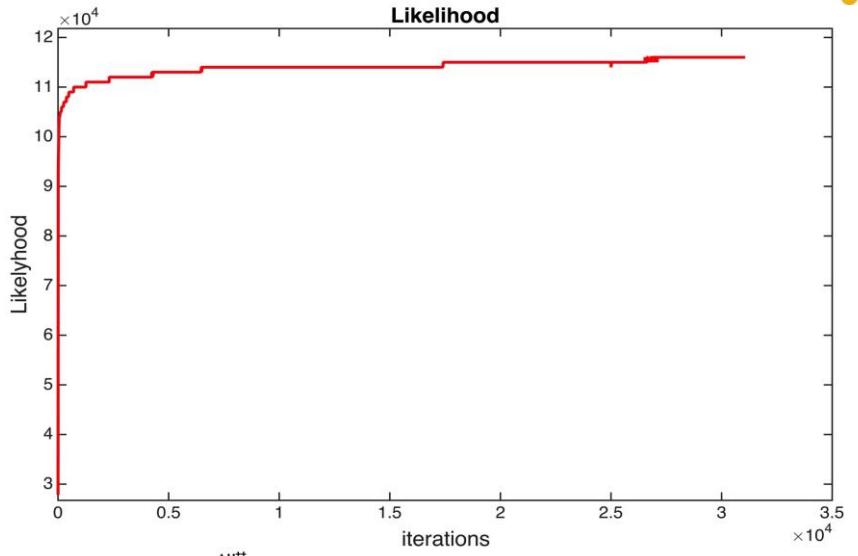
Calibration Results

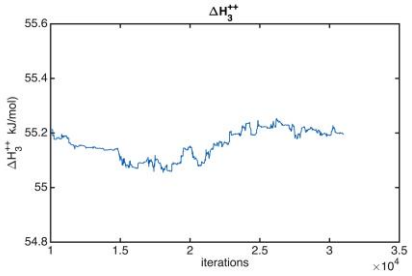


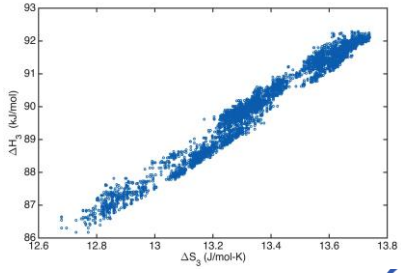


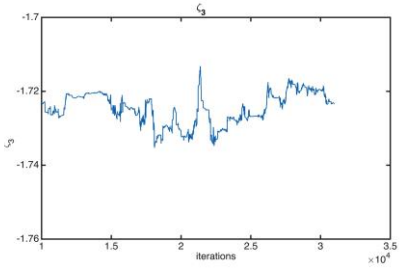












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Conclusion

- A new mechanism using amine and water stabilized zwitterions as diffusive intermediates has been proposed
- Model simulation replicated the experiment results qualitatively
- Bayesian calibration and dynamic discrepancy implemented in the model to get quantitatively matched results
- Reduced model is used to improve the calculation speed

Future Work

- Apply this model to bubbling fluidized bed model
- Quantify the uncertainty from model reduction and model upscaling

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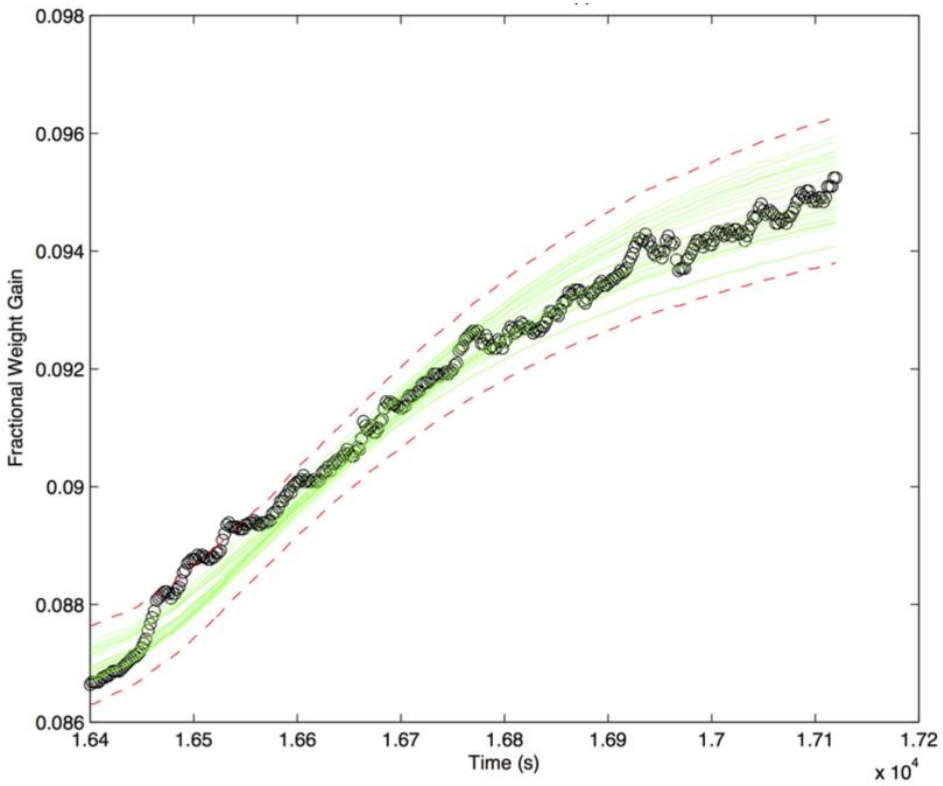
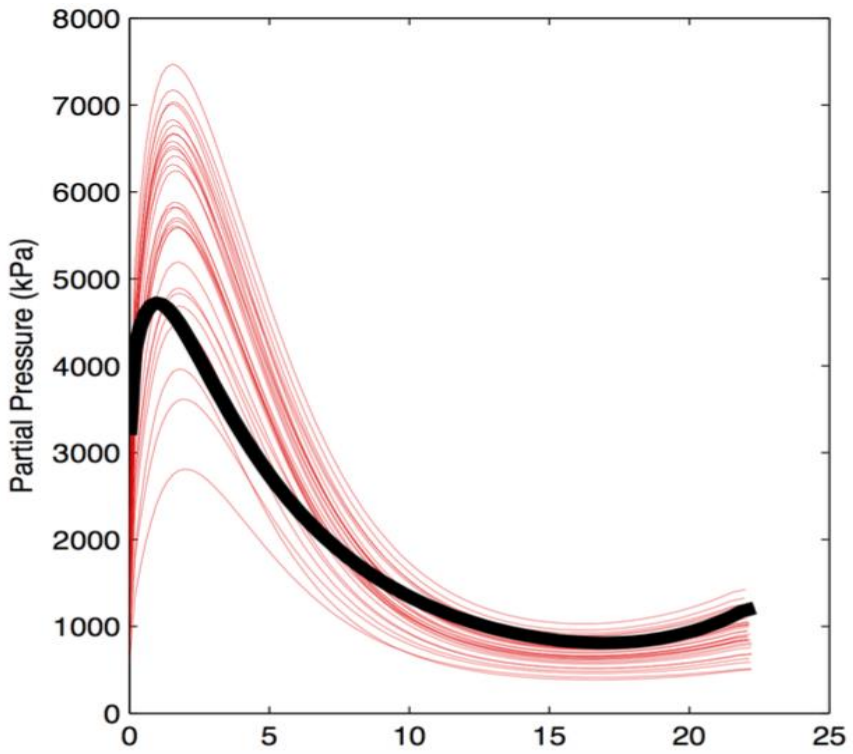
Upscaling Results





Bhat, K.S., et al., arXiv preprint arXiv:1411.2578 (2014).

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