**Motivation**

- With the world continuing to rely on a significant use of fossil fuels for electricity generation and other large-scale industrial processes, the capture and subsequent storage of atmospheric CO₂ emissions will likely be a necessary part of future climate change abatement strategies.
- Many technologies have been and are being proposed to effectively separate and capture CO₂ emitted from these processes. This leads to two key questions: How do these varied technologies compare against each other? How does each compare to its thermodynamic limits of operation (how well is it performing)?

**Method Development: Exergy of the Adsorbed Phase**

**Background: Thermodynamic Properties of Adsorbed Phases**

- The boundaries of the adsorbed phase (as separate from gas or solid) were originally defined by Gibbs. Although in reality the particle number density transitions smoothly between phases, he defined a sharp interface between gas and solid phases, where all properties of the adsorbed phase would exist as a delta function on that interface. This allowed clear definitions with no loss of thermodynamic information.
- Often, the additional free energy that a surface phase has (as a result of having an additional energy storage mode) is referred to in terms of a spreading pressure if and area. Myers 2002 argues that for porous sorbents, A is undefined, so this free energy term is better represented by a surface potential, Φ.

**Derivation: Exergy of Adsorbed Phases**

- We start with a system at $T_a$ and $P_{sat}$ that is composed of a mass $M$ of sorbent, moles $N_{i,sys}$ of all species $i$ in the gas phase, in equilibrium with moles $N_{i,a}$ of species $i$ adsorbed on the sorbent.
- By allowing transfers of heat (Q), boundary work ($W_{b}$), and species $i$ ($W_{i}$), the system comes into equilibrium with an environment at $T_e$ and $P_e$, the system can effectively separate and capture CO₂ (as separate from gas or solid) were originally defined by Gibbs. Although in reality the particle number density transitions smoothly between phases, he defined a sharp interface between gas and solid phases, where all properties of the adsorbed phase would exist as a delta function on that interface. This allowed clear definitions with no loss of thermodynamic information.
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**Method Application: Exergy of CO₂ Adsorbed on Zeolite-13X**

**Problem Statement**

- In order to perform an exergy analysis, we need to be able to account for the accumulation of exergy in system devices or process steps.
- In batch-cycle adsorption processes in particular, accounting for accumulation of an adsorbed phase in the column is critical.

**Approach**

- By directly applying the exergy analysis from Myers 2002, we can substitute the Euler equation for each of the gas and the adsorbed phases at the dead state:

$$U_i = P_{sys}V_i - T_iS_i - \sum \mu_i N_{i,sys} - \Phi_i M_i$$

- This is the exergy of the combined system, with gas, sorbent, and adsorbed phases. We can expand each extensive quantity (where $Z$ represents any extensive quantity):

$$Z = Z_g + Z_a + Z_s$$

- We can also substitute the Euler equation for each of the gas and the adsorbed phases at the dead state:

$$X_{sys} = X_t - T_aS_a - \sum \mu_i N_{i,sys} - M_i\Phi_i$$

- After assuming an incompressible, non-reactive solid (same assumptions as Myers), we arrive at a general form for the total system exergy:

$$X_t = [U_t + U_{a,t}] - T_a[S_a + S_{a,t}] - [\sum \mu_i N_{i,sys} + M_i\Phi_i]$$

- But we wanted the exergy of the adsorbed phase alone, so we need to subtract the exergy of the gas and of the solid sorbent, defined as:

$$X_{a} = X_t - T_aS_a - \sum \mu_i N_{i,sys}$$

- Subtracting these from the total system exergy, we arrive at a general expression for the exergy of an adsorbed phase on a sorbent mass $M$:

$$X_{a} = U_{a,t} - T_aS_{a,t} - \sum \mu_i N_{i,sys} - M_i\Phi_i$$

- Up to this point, we have assumed that the species $i$ are only species present in the fully equilibrated environment. We can extend the exergy expression to include chemical species $j$ that are not present in the environment, but would react to form environmental species (derivation not shown here):

$$X_{a} = U_{a,t} - T_aS_{a,t} - \sum \mu_i N_{i,sys} - \sum \mu_j N_{j,sys} - M_i\Phi_i$$

- Where $v$'s are stoichiometric coefficients for the chemical reaction $A_i + \sum v_i A_j$, which is the generalized form of a chemical reaction that forms environmental species $j$ from non-environmental species $i$, e.g.:

$$aaA \rightarrow hbB + cC + ddD$$

- Where B, C, D are env't 1, A is not.

**Conclusions**

- We have developed a general expression for the exergy of the adsorbed phase, based on known thermodynamic properties.
- This expression is the basis for performing an energy analysis of adsorption-based carbon capture systems. Analyzing the energy destroyed in these processes will tell us how well these systems are performing relative to absolute thermodynamic limits.
- Although it was developed for the analysis of carbon capture systems, the expression for the exergy of the adsorbed phase can be used to perform energy analyses of any adsorption-based system (air separation, hydrogen purification, gas dehumidification, etc.). This generality could therefore be useful across a wide range of applications.
- As an example, we have applied this general expression to the specific case of CO₂ adsorbed on zeolite 13X, using a dual-site Langmuir adsorption isotherm.

**Next Steps**

- Currently, we are using our derived exergy expression to perform the exergy analysis of a pressure-swing adsorption CO₂ capture cycle (thanks to Reza Haghpanah).
- An eventual goal would be to use exergy efficiency as the objective for the optimization of adsorption systems for carbon capture.