Langmuir Competitive Adsorption Model Applied to Real Example

In the 1st CheKiPEUQ paper, the CO adsorption on Fe3O4 was shown to have several adsorption states.

The supporting information of one of the studies (<https://pubs.acs.org/doi/full/10.1021/acs.jpcb.7b04228> ) shows that the CO adsorption state that we are referring to as “State 1” has a competitive adsorption with H2O.

Experiments have shown that water adsorption has a coverage dependent adsorption enthalpy and activation energy for desorption.

<https://onlinelibrary.wiley.com/doi/10.1002/anie.201711890#anie201711890-fig-0001>

<https://onlinelibrary.wiley.com/doi/10.1002/anie.201506439>

However, based on the references above, it is the most strongly bound water that is in competitive adsorption with the particular CO adsorption that we are referring to.

From our 1st paper, we have an estimate of the Hads° adsorption for the State 1 CO as -66.3 +/- 4.8 kJ/mol. Note that the the posterior of that example becomes the prior distribution of this example.

Since we are interested in the water from the supporting information of <https://pubs.acs.org/doi/full/10.1021/acs.jpcb.7b04228> , we perform a BPE for the Hads° adsorption of that state. We note that the Tp for desorption can be described by 320 +/- 30. We take an initial estimate of the strongly bound state Hads° as 80+/- 20 kJ mol. Example runfile\_Example14\_StateH2O\_mcmc.py then yields 82.8 +/- 12.1 kJ/mol for the posterior. Again, we take that posterior as our “new best guess” and use it as our prior to feed into the equilibrium example.

For Sads°, we use the approximation of the loss of all translational degrees of freedom. For simplicity, we approximate that Sads° and Hads° (and individual standard entropies and enthalpies) are independent of temperature. From the NIST webbook, S°gas, H2O = 188.84 J/(mol\*K) and S°gas, CO =197.66 J/(mol\*K). We take the Sackur-Tetrode sheet from the following reference supporting info. <https://pubs.acs.org/doi/10.1021/acs.jpcc.7b05171>

We are only interested in the “Full Sackur Tetrode Equation for 3D” from cell A60. For CO, the value is 150.42 J/(mol\*K), and for H2O it is 144.91 J/(mol\*K). We will take these values for Sads° adsorption and We will assume a standard uncertainty of 20 J/mol for the Sads° adsorption of each of these molecules.

Sads°,H2O ≈ -144.91 +/- 20

Sads°,CO ≈ -150.42 +/- 20

And from above,

Hads°,CO = -66.3 +/- 4.8 kJ/mol.

Hads°,H2O = -82.8 +/- 12.1 kJ/mol.

Then, Gads°= Hads°-TSads°. Note that for any given temperature, the standard uncertainty in the prior distribution for uGads° can then be calculated from that of the other two terms, reducing to a single prior: uGads°=( (uHads°)2 +(T\*uSads°)2 ) 0.5

In this specific case, by running some test simulations, we were able to assess that we have conditions that can be described by a Langmuir Replacement reaction. The extent of empty vacancy sites is nearly zero at all times, so the reaction is approximately either CO replacing water as an adsorbate or vice versa.

If we write the reaction as CO replacing water,

CO(g) + H2O(ads) 🡪 CO(ads) + H2O(g)

then the Langmuir Replacement reaction will have thermodynamics and an equilibrium coverage of CO as follows:

Hrxn°=Hads°,CO - Hads°,H2O

Srxn°=Sads°,CO - Sads°,H2O

Propagating the uncertainties as orthogonal we arrive at the following expressions, indicating that the uncertainty in Grxn° is temperature dependent.  
Grxn°= Hrxn°-TSrxn°

Hrxn°= 16.5

Srxn°= 5.41

uGads°=( (13.01729619 / (kJ/mol/K) )2 +(T\*28.28427125 / (J/mol) )2 ) 0.5

The design of experiments is ultimately run in the below two files which do sampling of 3 temperatures.

We use the log of coverage and set the uncertainty of the coverage for experimental measurement under synthetic data conditions as being log(1.5) which means a 50% uncertainty.

runfile\_Example13\_CO\_H2O\_four\_parameters\_replacement\_log\_doe\_neg\_1std\_offset.py

runfile\_Example13\_CO\_H2O\_four\_parameters\_replacement\_log\_doe\_pos\_1std\_offset.py

Output is in:

ipython\_neglog10\_200000.html

ipython\_poslog10\_200000.html