

Homework 8 Advanced Thermodynamics Due Monday November 1, 2021

Novendra Novendra Energetics of Substitution Effects on the Stability of Metal-Organic Frameworks, PhD Dissertation University of California, Davis 2021 recently completed a PhD dealing with various metal organic framework materials (MOFs). This is an active area of research involving a wide range of materials for hydrogen and methane storage, gas separation, and absorption of solar radiation as described in the dissertation's abstract (<https://www.proquest.com/openview/634e3b8c2b5897d6fbee2d79d238be17/1?pq-origsite=gscholar&cbl=18750&diss=y>).

- a) Give a description of MOFs with a few examples particularly in hydrogen storage and production of perovskite structures for solar harvesting. You might want to look at the Wikipedia page, though this focuses on synthetic schemes with applications at the end. (https://en.wikipedia.org/wiki/Metal-organic_framework). There is also a book on the webpage "MOF Synthesis, Structure and a few Applications 2018". Limit this to one paragraph.
- b) Novendra was involved in a study of MOF-74 family of materials that show promise for CO₂ capture from power-plants but are sensitive to exposure to water, Voskanyan AA, Goncharov VG, Novendra N, Guo X, Navrotsky A *Thermodynamics Drives the Stability of the MOF-74 Family in Water* ACS OMEGA **5** 13158-13163 (2020). Table 1 shows the cycle used to calculate the enthalpy of reaction between the organic ligand and the metallic oxide that forms the MOF framework and releases water, equation 1. The reverse reaction is exothermic and drives water sensitivity of the MOFs. Explain the logic behind the calculation in Table 1. What role does the lattice enthalpy play in this logic? What role does entropy play?
- c) Novendra lead a study of orthorhombic cesium lead iodide which is a perovskite solar absorber because the alpha crystal form has a band gap of 1.73 eV (black) close to the peak of the solar spectrum at around 1.6 eV. (Silicon has a band gap of 1.1 eV.) The delta polymorph which is stable at room temperature has a band gap of 2.82 eV (yellow). Wang B, Novendra N, Navrotsky A *Energetics, Structures, and Phase Transitions of Cubic and Orthorhombic Cesium Lead Iodide (CsPbI₃) Polymorphs* J. Am. Chem. Soc. **141** 14501-14504 (2019). Table 2 shows the thermodynamic cycle used to calculate the formation of the alpha and delta polymorphs at 25° C. Explain the logic of the cycle and the source of the values that are used. Is lattice enthalpy considered in this study? If yes, where.
- d) Wilmer CE, Leaf M, Lee CY, Farha OK, Hauser BG, Hupp JT, Snurr RQ *Large-scale screening of hypothetical metal-organic frameworks* Nature Chem. **4** 83-89 (2011) consider the number of possible MOFs that could be constructed from 102 building blocks which can lead to 137,953 hypothetical MOFs with some potential for methane storage. Wilmer uses a Lego approach, using molecular sizes for the groups and structure from existing MOFs to find units that can fit together from the possibilities. No energy calculations are made. Wilmer claims that allowing the structures to relax by energy minimization using a computer simulation (Universal Force Field) the structures basically do not change. They then calculate the methane adsorption isotherms from their model structures and compare with experimental data on similar existing structures to

their satisfaction in figure 2. This is an ad hoc approach that proposes that calculation of the enthalpy of formation is useless and crystal structure relies only on geometry. From the studies of Novendra and what was discussed in class point out a few pitfalls in Wilmer's proposition.

- e) Novendra's advisor, Alexandra Navrotsky, is involved in prebiotic chemistry and is interested in how templated formation of metal-organic-ceramic nanomaterials was involved in the formation of life. In Navrotsky A, Hervig R, Lyons J, Seo D-K, Shock E, Voskanyan A, *Cooperative formation of porous silica and peptides on the prebiotic Earth* PNAS **118** e2021117118 (2021) she states:

The difference in enthalpy and free energy between different zeolite polymorphs is less than about 15 kJ/mol (only 2 to 3 times the thermal energy available at synthesis conditions), with more open frameworks being energetically metastable relative to silica glass and less open frameworks somewhat more stable. This means that the role of the SDA is not to energetically stabilize an initially grossly metastable structure but to select among possible structures in a dense landscape of similar energies, enhancing the formation of a structure that is a good fit to the SDA (2). The interaction of the SDA and zeolite is also relatively weak (13). Thus, the structure selection may rely more on enhancing nucleation kinetics than on major differences in thermodynamic driving forces. This energy landscape is good news in the prebiotic context in that with a silica source and organic molecules present, the early Earth system is likely to sample many configurations and products, with some relevant to the origin of life.

Comment on how this might impact your assessment of Wilmer's paper from part d. What factors beyond the enthalpy of formation are important in the formation of nano-structured materials and complex biotic and prebiotic materials?