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## Thermodynamic parameters of cation exchange in MOF-5 and MFU-4l

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We present a method for approximating thermodynamic parameters  $\Delta G_{p,T}^\circ$ ,  $\Delta H$ , and  $\Delta S$  for the cation exchange process in metal-organic frameworks, as exemplified by  $\text{Ni}^{2+}$  exchange into  $\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})_3$  (MOF-5) and  $\text{Co}^{2+}$  exchange into MOF-5 and  $\text{Zn}_5\text{Cl}_4(\text{bis}(1H\text{-}1,2,3\text{-triazolo-}[4,5\text{-}b],[4',5'\text{-}i])\text{dibenzo-}[1,4]\text{-dioxin})_3$  (MFU-4l). For these examples, we find that the cation exchange process is endergonic and that parameters such as solvent and cation identity impact the thermodynamics.

Exchanging the native metal ions in the secondary building units (SBUs) of metal-organic frameworks (MOFs) is emerging as a powerful tool for synthesizing new materials.<sup>1–14</sup> Because the original metal sites in a MOF are often crystallographically determined, cation exchange is a predictive tool; the new metal sites should inherit the original ligand fields and coordination geometries. Spurred by the promise of this technique, cation exchange has been demonstrated with more than 30 distinct SBUs, uncovering interesting differences in the impact of cation identity, solvent, and MOF-type. Yet, few studies have explored the factors that govern the cation exchange process. Beyond reports of cation incorporation as a function of time,<sup>7,10</sup> the kinetics and thermodynamics have not been measured with precision. For cation exchange to become a rational synthetic tool, these fundamental studies must be performed. Therefore, we present a method to approximate the thermodynamic parameters of cation exchange in MOFs to explore the mechanistic role of factors such as solvent and cation identity.

As a test system, we reexamined the cation exchange of  $\text{Ni}^{2+}$  into the iconic material known as MOF-5.<sup>15</sup> Because we previously reported the effect of cation identity and solvent on the extent of cation exchange in pre-equilibrium conditions, we suspected they would influence the thermodynamics as well.<sup>3,9</sup> To measure the approximate thermodynamic parameters, we followed the

thermochemical analysis applied to cation exchange in zeolites.<sup>16–19</sup> In a manner analogous to the work of Sherry,<sup>18,19</sup> the free energy for the exchange of  $\text{Ni}^{2+}$  in MOF-5:  $\Delta G_{p,T}$ , of  $\text{Zn}_{\text{MOF}}^{2+} + \text{Ni}_{\text{solution}}^{2+} \rightarrow \text{Zn}_{\text{solution}}^{2+} + \text{Ni}_{\text{MOF}}^{2+}$  is given by the following relation:

Equation 1

$$\Delta G_{p,T} = -RT \ln K_{eq} + RT \ln \frac{f_{\text{Ni}}^2 Z_{\text{Ni}}^2 \gamma_{\text{Zn}}^2 m_{\text{Zn}}^2}{f_{\text{Zn}}^2 Z_{\text{Zn}}^2 \gamma_{\text{Ni}}^2 m_{\text{Ni}}^2}$$

Here,  $f$  and  $Z$  represent the activity coefficients and the molar fractions, respectively, of a given metal ion in MOF-5. Similarly,  $\gamma$  and  $m$  represent the mean activity coefficients and molalities, respectively, of the metal ions in solution. In all cases considered here, all terms are squared as a consequence of all ions involved being divalent.

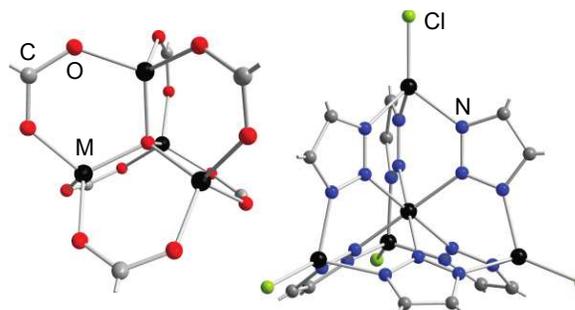


Figure 1. Secondary building units of MOF-5 (left) and MFU-4l (right). Metal, chlorine, oxygen, nitrogen, and carbon atoms are depicted as black, green, red, blue, and grey spheres, respectively.

To reach equilibrium conditions, we left MOF-5 suspended in *N,N*-dimethylformamide (DMF) solutions of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  for 62 days (2 months) at constant temperatures of 238, 265, 296, and 313 K. During this time, the temperature was checked twice a day and was found to vary by less than 2 °C. Because determining accurate values for  $K_{eq}$  requires knowing all of the terms in Equation 1, we employed an approximation as follows. The moles of  $\text{Ni}^{2+}$  ions inserted into MOF-5 were calculated from relative Zn/Ni ratios determined by inductively coupled plasma atomic emission

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spectroscopy. The activity coefficients and mean activity coefficients were assumed to be the same, and were therefore cancelled out. Assuming each inserted  $\text{Ni}^{2+}$  displaces a  $\text{Zn}^{2+}$  from MOF-5 into solution, we employed the relation in Equation 2 to approximate  $K_{eq}$ .

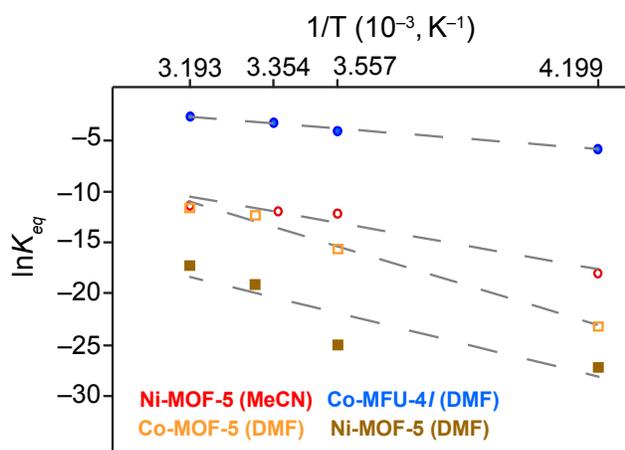


Figure 2.  $\ln K_{eq}$  versus  $1/T$  for the  $K_{eq}$  values that were measured from the four different cation exchange reactions, as denoted by colour. Dashed grey lines denote the best-fit lines used to extract thermodynamic parameters shown in Table 1.

Equation 2

$$K_{eq} = \frac{Z_{Ni}^2 S_{Zn}^2}{Z_{Zn}^2 S_{Ni}^2}$$

Here,  $Z_{Ni}$  and  $Z_{Zn}$  represent the molar fraction of Ni and Zn ions among all metal ions in MOF-5. Similarly,  $S_{Ni}$  and  $S_{Zn}$  represent the molar fraction of Ni and Zn ions among all metal ions in solution.

Assuming the system reached equilibrium, and using  $\Delta G_{p,T}^\circ = -RT \ln K_{eq} = \Delta H - T\Delta S$ , a plot of  $\ln K_{eq}$  vs.  $1/T$  yields approximate thermodynamic parameters. As shown in Figure 1, the data for  $\text{Ni}^{2+}$  exchange into MOF-5 yield  $\Delta G_{1\text{atm}, 238\text{K}}^\circ = 12.9$  kcal/mol,  $\Delta G_{1\text{atm}, 281\text{K}}^\circ = 13.9$  kcal/mol,  $\Delta G_{1\text{atm}, 296\text{K}}^\circ = 11.3$  kcal/mol, and  $\Delta G_{1\text{atm}, 313\text{K}}^\circ = 10.7$  kcal/mol. The slope and y intercept of the resulting line imply that  $\Delta H = 19.2$  kcal/mol and  $\Delta S = 24.7$  cal/mol·K. Hence, entropy increases in the replacement of  $\text{Zn}^{2+}$  by  $\text{Ni}^{2+}$ , but the exchange is endothermic to yield an overall endergonic process. One explanation for  $\Delta S > 0$  is that  $\text{Ni}^{2+}$  exchange into MOF-5 releases  $\text{Zn}^{2+}$  ions into solution, freeing them to perform cation exchange with either  $\text{Zn}^{2+}$  or  $\text{Ni}^{2+}$  in the material. Prior to  $\text{Zn}^{2+}$  displacement from the material, no  $\text{Zn}^{2+}$  ions exist in the solution to undergo cation exchange, creating a state with fewer degrees of freedom, and hence less entropy. For the process to be endothermic, the Ni-exchanged material or the solvated  $\text{Zn}^{2+}$  species must be enthalpically unfavorable compared to the initial species. Knowing that the hydration energy of  $\text{Zn}^{2+}$  is considerably less than that of  $\text{Ni}^{2+}$ , due to its ligand field stabilization energy of zero,<sup>20</sup> the solvation of  $\text{Zn}^{2+}$  is the likely culprit. The relatively low absolute free energy values suggest, however, that this exchange is essentially thermoneutral, such that large excess of inserting  $\text{Ni}^{2+}$  drives cation exchange in accordance with Le Chatelier's Principle.<sup>21</sup>

To explore the dependence of the thermodynamic parameters on the nature of the solvent, we repeated the procedure above for  $\text{Ni}^{2+}$  exchange in MOF-5 using acetonitrile (MeCN) under otherwise identical conditions. Using similar approximations and data analysis as before revealed enthalpy and entropy values of  $\Delta H = 13.8$  kcal/mol and  $\Delta S = 23.0$  cal/mol·K, respectively. These suggest that in acetonitrile the exchange is less endothermic and makes available fewer degrees of freedom with respect to the same cation exchange performed in DMF. The small difference in  $\Delta S$  might be caused by the inherent uncertainty of the measurements, but the large difference in  $\Delta H$  might be explained by the relative stability of the solvated  $\text{Ni}^{2+}$  precursors. Based on calculations we reported previously,<sup>3</sup> the Ni–MeCN interaction is weaker than that for Ni–DMF so that the resulting  $\Delta H$  for the exchange performed in MeCN is expected to be smaller than when performed in DMF. Meanwhile, the difference in energy between  $\text{Zn}(\text{MeCN})_6^{2+}$  and  $\text{Zn}(\text{DMF})_6^{2+}$  is likely less significant due to the negligible ligand field stabilization energy of  $\text{Zn}^{2+}$ .

Driven by these interesting results, we extended our method to study  $\text{Co}^{2+}$  exchange in MOF-5 and MFU-4l to examine the effect of cation and MOF identity. Using  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as the precursor for exchange, we obtained thermodynamic parameters of  $\Delta H = 23.8$  kcal/mol and  $\Delta S = 54.2$  cal/mol·K for MOF-5 and  $\Delta H = 6.28$  kcal/mol,  $\Delta S = 14.6$  cal/mol·K for MFU-4l. The thermodynamic parameters of all systems discussed here are summarized in Table 1. Although the enthalpies of exchange for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  substituting  $\text{Zn}^{2+}$  into MOF-5 are similar, the exchange entropy is significantly more positive for  $\text{Co}^{2+}$  when compared to  $\text{Ni}^{2+}$ . A possible explanation is that the resulting  $\text{Co}^{2+}$  center in MOF-5 is capable of releasing its bound DMF ligands into solution, whereas  $\text{Ni}^{2+}$  is more likely to remain in pseudo- $O_h$  symmetry. The  $\text{Zn}^{2+}$  sites of the starting material may also bind and release DMF molecules, but, as proposed above, only in the final state are both  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  available in solution to exchange with metal sites in the material, leading to greater entropy. Altering the MOF system offers interesting comparisons as well. The more covalent bonding provided by the nitrogen environment of MFU-4l may explain why  $\text{Co}^{2+}$  insertion is less endothermic in this material than in MOF-5. In other words, the favorable formation of the  $\text{Co}^{2+}$ -doped material may counterbalance the less favorable solvation of  $\text{Zn}^{2+}$ . The smaller  $\Delta S$  is more puzzling. One possibility is that the coordination sphere around  $\text{Co}^{2+}$  is less disordered when in MFU-4l compared to the disorder imposed by  $\text{Co}^{2+}$  inserting into MOF-5.

Table 1. The enthalpy and entropy parameters extracted from the best-fit lines shown in Figure 1. The cation exchange systems are labelled according to the solvent involved, shown in parentheses.

	$\Delta H$ (kcal/mol)	$\Delta S$ (cal/mol·T)
Ni-MOF-5 (DMF)	19.2	24.7
Ni-MOF-5 (MeCN)	13.8	23.0
Co-MOF-5 (DMF)	23.8	54.2
Co-MFU-4l (DMF)	6.28	14.6

Although the values listed in Table 1 are approximations of the thermodynamic parameters, comparing their relative magnitudes offers useful mechanistic insight. We glean from these data that solvent and cation identity do influence the equilibrium conditions of cation exchange in a given MOF-system and that the thermodynamics alter considerably

between MOFs. Despite these differences, all data suggest that the processes are endergonic, requiring a large excess of inserting cation to drive the cation exchange. Prior to this report, qualitative observations intimated these findings. With this simple method, we have a quantitative measure of systematic differences between cation exchange in MOFs.

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