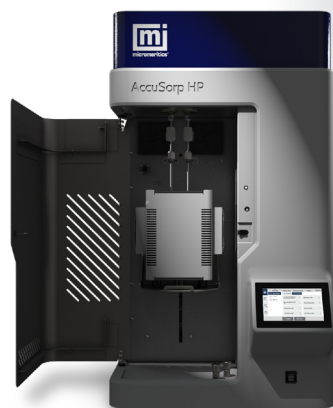


## Nitrogen Oxygen Separation in Lithium Exchanged Zeolite LiX



AccuSorp HP

### Introduction

Nitrogen and oxygen are among the most widely utilized industrial chemicals, with applications spanning healthcare, metallurgy, fertilizer synthesis, and food preservation. Despite their atmospheric abundance, isolating these gases in pure form presents a significant engineering challenge due to their similar kinetic diameters and boiling points. Nitrogen has a kinetic diameter of 3.64 Å compared to 3.46 Å for oxygen, therefore size-based separation will be challenging and highly inefficient. Furthermore, the molecules display similar boiling points, approximately 77K for nitrogen and 90K for oxygen. This renders traditional cryogenic distillation as an energy-intensive and costly operation. To circumvent these limitations, commercial separation technologies have researched and developed alternative, adsorption-based separations. Lithium-X zeolite (LiX) is a commercial lithium exchanged zeolite that exploits the strong quadrupole moment in the material to selectively adsorb nitrogen over oxygen. The separation can also be achieved at temperatures close to ambient, resulting in a cost-effective solution.

In this work, nitrogen and oxygen isotherms were collected on LiX using the new AccuSorp HP at 15, 25, and 35 °C up to a maximum pressure of 10 bar. The isotherms were then used to calculate heat of adsorption. Additionally, the selectivity between nitrogen and oxygen in the material was assessed using Ideal Adsorbed Solution Theory (IAST) predictions using the built-in feature within the MicroActive data processing software.

### Experimental

In this work, nitrogen and oxygen adsorption isotherms were collected on LiX zeolite using the AccuSorp HP. Measurements were collected up to a maximum pressure of 10 bar at three analysis temperatures, 15, 25, and 35 °C. A maximum pressure of 10 bar was selected due to safety concerns regarding the collection of oxygen isotherms above that pressure, stainless steel can become a fuel for combustion at high oxygen concentrations and pressures. However, there are no safety concerns regarding nitrogen, for which isotherms could be collected up to 200 bar at the chosen temperatures.

Prior to analysis, the LiX sample was degassed ex-situ using a VacPrep at 300 °C for 8 hours. The samples were then transferred to the AccuSorp HP for analysis. The sample holder consisted of a 2 mL stainless steel vessel. To maintain the analysis temperature, an iso controller was used and temperatures were set to 15, 25, or 35 °C for their respective analyses. To obtain the appropriate adsorbed quantity, blank corrections were used, as both nitrogen and oxygen deviate from ideal gas behavior at high pressures, like those used in the AccuSorp HP.

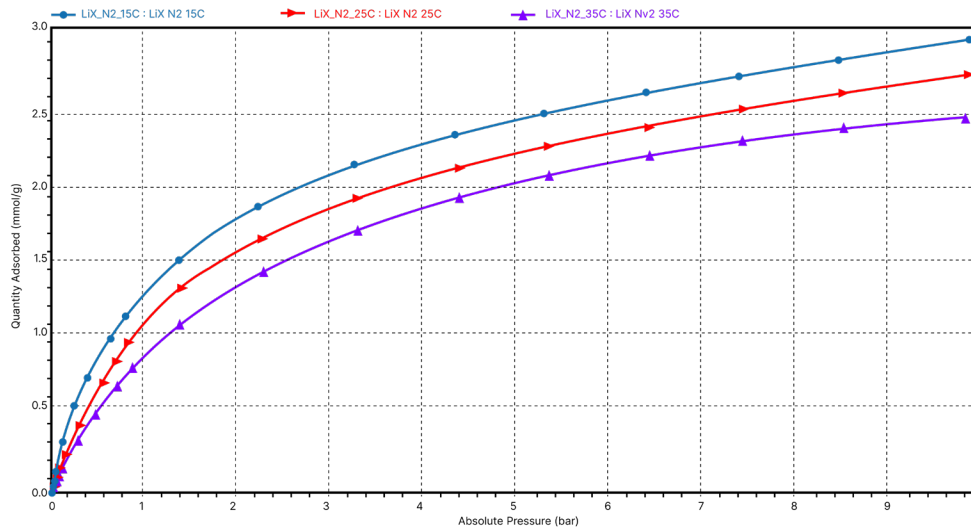
**Table 1:** Analysis Conditions for the Nitrogen and Oxygen Adsorption Analysis

|  |                                   |                       |
|--|-----------------------------------|-----------------------|
| <b>Adsorptive Gas</b>                  | N <sub>2</sub> or O <sub>2</sub>  |                       |
| <b>Analysis Temperature</b>            | 298.15K                           |                       |
| <b>Free Space Type</b>                 | Measure Before                    |                       |
| <b>Temperature Control</b>             | Circulating Bath                  |                       |
| <b>Absolute Tolerance</b>              | 5 mbar                            |                       |
| <b>Relative Tolerance</b>              | 5%                                |                       |
| <b>Min Pressure Equilibration Time</b> | 60 s                              |                       |
| <b>Max Pressure Equilibration Time</b> | 99999 s                           |                       |
| <b>Pressure Increment (bar)</b>        | <b>Equilibration Interval (s)</b> | <b>Pressure (bar)</b> |
| 0.01                                   | 60                                | 0.02                  |
| 0.02                                   | 60                                | 0.04                  |
| 0.04                                   | 60                                | 0.08                  |
| 0.02                                   | 60                                | 0.1                   |
| 0.05                                   | 60                                | 0.2                   |
| 0.2                                    | 60                                | 1                     |
| 1                                      | 60                                | 10                    |

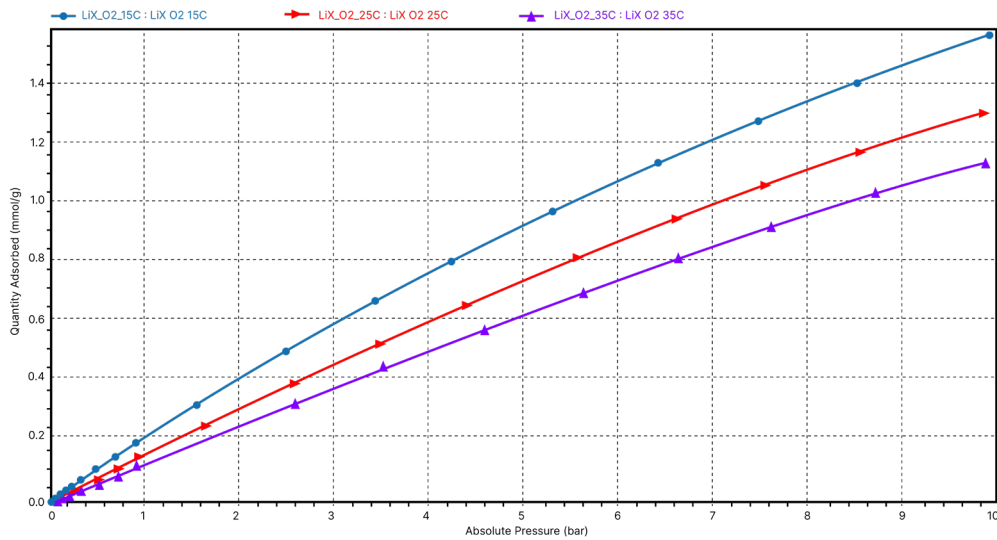
## Results and Discussion

### *Nitrogen and Oxygen Adsorption*

Nitrogen and oxygen isotherms were collected on LiX up to a maximum pressure of 10 bar using the AccuSorp HP, see figures 1 and 2 respectively. Isotherms were collected at temperatures of 15, 25, and 35 °C.



**Figure 1:** LiX N<sub>2</sub> adsorption isotherms at 15, 25, and 35 °C

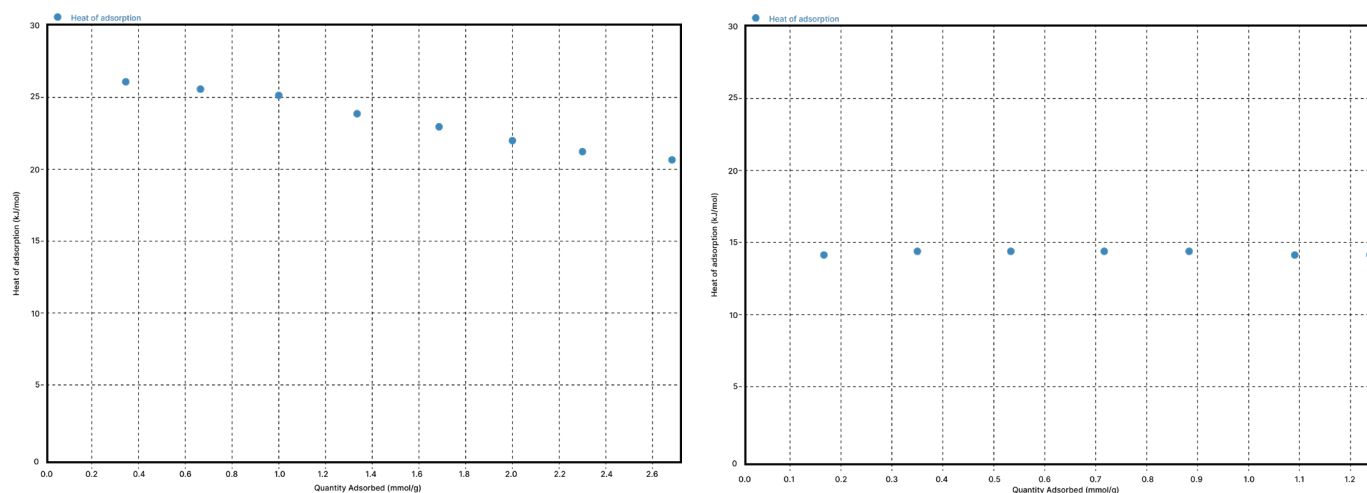


**Figure 2:** LiX O<sub>2</sub> Adsorption Isotherms at 15, 25, and 35 °C.

LiX displayed strong nitrogen adsorption even at ambient temperatures, resulting in an adsorption capacity of roughly 1 mmol/g at 1 bar and exceeding 2.5 mmol/g adsorbed at 10 bar. The adsorption of nitrogen is primarily driven by the interactions between the quadrupole moment of nitrogen with lithium that was exchanged in the zeolite. Comparatively, the oxygen adsorption was weak, reaching an adsorbed capacity of roughly 0.2 mmol/g at 1 bar and between 1.1 – 1.4 mmol/g at 10 bar across the three temperatures tested in this experiment.

## Heat of Adsorption

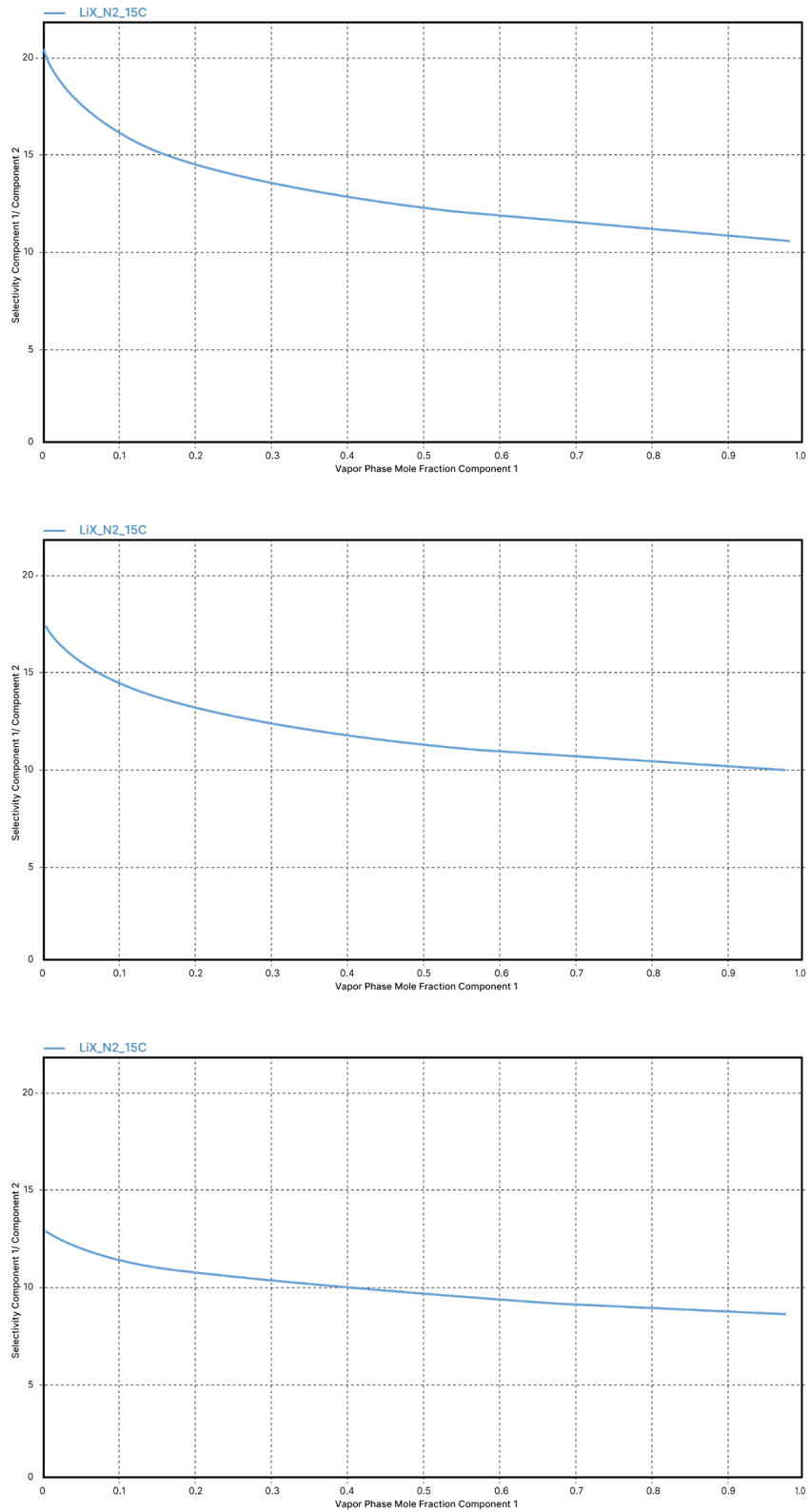
The collected isotherm data for LiX were analyzed using MicroActive data processing software to determine the heats of adsorption for both nitrogen and oxygen. Heat of adsorption is the amount of energy that is released upon adsorption of the adsorbing molecule onto the surface of a material. Higher numbers indicate a stronger interaction. As anticipated, LiX exhibited a significantly higher adsorption capacity for nitrogen compared to oxygen, which correlates directly with a greater heat of adsorption. Specifically, the heat of adsorption for nitrogen exceeded 25 kJ/mol at zero coverage and decreased steadily as coverage increased. In contrast, the heat of adsorption for oxygen remained relatively constant at approximately 14 kJ/mol across all measured coverage levels, see figure 3.



**Figure 3:** Heat of adsorption of nitrogen (left) and oxygen (right) on LiX

## IAST

Ideal Adsorbed Solution Theory (IAST), (A.L. Myers, J.M. Prausnitz, *AIChE Journal*, 1965) can be utilized in the MicroActive data processing software to predict multicomponent adsorption from single component adsorption data. This feature was utilized to predict the adsorption selectivity of nitrogen over oxygen in LiX using the obtained AccuSorp HP data. The calculated selectivity decreased with increasing temperature and with increasing nitrogen gas concentration in the mixture, see figure 4. At 15 °C and low nitrogen concentrations, the selectivity of nitrogen/oxygen adsorption was roughly 20 and decreased to a little over 10 at high nitrogen concentrations. A similar trend was observed across all temperatures tested, however, the highest selectivity values were observed in the 15 °C prediction.



**Figure 4:** Nitrogen/oxygen selectivity on LiX at 15 (top), 25 (middle), and 35 (bottom) °C. Nitrogen (component 1) / Oxygen (component 2)

## Conclusion

High-pressure nitrogen and oxygen adsorption isotherms were collected up to 10 bar on Lithium-X (LiX) zeolite using the AccuSorp HP. Measurements were performed at 15, 25, and 35 °C and subsequently analyzed utilizing advanced reports for isosteric heat of adsorption and Ideal Adsorption Solution Theory (IAST). The empirical data demonstrates the efficacy of LiX for selective nitrogen capture over oxygen at ambient conditions, achieving a maximum nitrogen adsorption capacity of 3 mmol/g at 15 °C and 10 bar. This application note highlights the capabilities of the AccuSorp HP for high-pressure adsorption characterization and illustrates how data can then be processed using the advanced reporting suite present within MicroActive software.