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Pure and Binary Adsorption Equilibrium of Nitrogen and Oxygen in Lilsx Zeolite

Himabindu Gandra
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PURE AND BINARY ADSORPTION EQUILIBRIUM OF NITROGEN AND OXYGEN IN LiLSX ZEOLITE

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Bachelor of Technology in Chemical Engineering
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Submitted in partial fulfillment of requirements towards the degree of
MASTER OF SCIENCE in Chemical Engineering
at
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May 2017
APPROVAL

We hereby approve this thesis

For

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For the Department of

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Date of Defense
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I appreciate my roommates’ patience in keeping calm with my odd hours. Their support and help in various forms made me feel as home in a new country and their help is greatly appreciated.
PURE AND BINARY ADSORPTION EQUILIBRIUM OF 
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HIMABINDU GANDRA 

ABSTRACT 

Chemical products are made by combination of processes that includes synthesis, separation and purification. Separation processes comprises a large portion in these industries and are considered to be critical as most of the applications in chemical industries involves mixtures. Traditional separation methods such as distillation, evaporation, drying etc., requires high energy. For example, air separation to produce nitrogen and oxygen was previously practiced by cryogenic distillation that involves high pressure units and large energy requirement. On other hand, adsorption processes utilize less energy resources and is unique among separation methods. The phase separation is achieved by the existence of a solid. Uniqueness of adsorption is the higher selectivity achievable by tailoring the adsorbents. Design and optimization of adsorption processes requires equilibrium information as models proofed by experimental data for understanding the conditions occurring in the process. This study is aimed at measuring, analyzing and reporting equilibrium data for pure component and binary mixture of N$_2$ and O$_2$ in LiLSX material. In addition, a model, Dual-Site Langmuir, is tested for its ability to represent the data in relevant range.
Volumetric measurement technique is one of the most commonly used method for measuring pure and binary adsorption which involves measuring pressure change in a known volume of gas. In this study, pure adsorption equilibria for N$_2$ and O$_2$ in LiLSX was measured at three temperatures (277.15K, 296.15K, 318.15K). Isotherms in this study were of Type-1 represented by Dual-Site Langmuir model which constitutes the primary source of information necessary to model on adsorption process. Dual-Site Langmuir model is also used in this work to predict binary adsorption data. It should be noted that no adjustable parameters are available hence, DSL model is completely predictive using only pure component isotherm information. Binary adsorption equilibria for N$_2$/O$_2$ mixture in LiLSX at constant pressure(241.15kPa), constant temperature(296.15K) with varying compositions was measured experimentally to compare to predictions. These measurements are tedious and the accuracy of results is proportional to the complexity of measurements in these experiments. In the present work, DSL model reasonably represents pure component isotherm data very well and predicts binary data within experimental accuracy.
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NOMENCLATURE

A  Area of molar adsorbate

$A_1, A_2$  Area of peak obtained for species 1 and 2 in GC analysis

$A_{12}$  Ratio of areas ($A_1/A_2$) of peaks obtained for species 1 and 2 in GC analysis

$B_{ii}$  Second virial coefficient, ccmol$^{-1}$

$B_{1-2}$  Cross second virial coefficient for species 1 and 2 in gas phase, ccmol$^{-1}$

$B_{mix}$  Second virial coefficient for the mixture in the gas phase, ccmol$^{-1}$

$b, d$  Langmuir affinity parameters on the first and second sites, kPa$^{-1}$

$b_i^0, d_i^0$  Langmuir affinity parameters of gas ‘i’ at a reference temperature and related to entropy of adsorption, kPa$^{-1}$

$b$  Langmuir parameter related to site energy

H  Henry’s Law constant

$H_{1i}, H_{2i}$  Heats of adsorption of gas ‘i’ on the two sites, cal/gmol

$k_1, k_2$  Constants in GC Calibration,

K  Calibration factor for GC analysis

$K_0, K_1, K_2$  Parameters for composition analysis

$m$  Mass of solid material, gm
m_b, m_d  Saturation capacities on first and second set of adsorption sites respectively, mol/kg

N_i  Number of moles of a component i adsorbed per unit mass of adsorbent

N  Number of moles adsorbed per gram of adsorbent

N^\infty, b  Langmuir parameters

N^\infty  Saturation limit of isotherm at infinitely high pressure representing monolayer capacity at the limit of \( \Theta = 1.0 \).

n_{ch}  Number of moles charged into the system in mmol (number of moles charged is same at the beginning and after expansion)

n^t  Total amount of gaseous species introduced into the system, mol

n^a  Amount adsorbed, mol/kg

n_i  Number of moles of component i in the gas mixture, mmol

n_t  Total number of moles of gas species, mmol

n^{ads}_{eq-1}  Moles of gas adsorbed at previous equilibrium, mmol

n^{bed}_{eq-1}  Moles of gas present in the void volume remaining unadsorbed in previous equilibrium step, mmol

n^{ch}_{eq}  Number of moles of gas charged to the tank, mmol

n^{bed}_{eq}  Final number of moles of gas present at equilibrium, mmol

n^{ads}_{eq}  Moles of gas adsorbed at equilibrium, mmol
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{\text{ch}} )</td>
<td>Pressure at charge conditions, kPa</td>
</tr>
<tr>
<td>( P_f )</td>
<td>Pressure at final conditions, kPa</td>
</tr>
<tr>
<td>( P_{\text{eq}} )</td>
<td>Total pressure at equilibrium, kPa</td>
</tr>
<tr>
<td>( P_i )</td>
<td>Equilibrium partial pressure of component ( i ), kPa</td>
</tr>
<tr>
<td>( R )</td>
<td>Universal gas constant, psi.cc/mmol/K</td>
</tr>
<tr>
<td>( S )</td>
<td>Entropy, JK(^{-1})g(^{-1})</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature, K</td>
</tr>
<tr>
<td>( U )</td>
<td>Molar internal energy, Jmol(^{-1})</td>
</tr>
<tr>
<td>( V_g )</td>
<td>Void volume up to Gibbs dividing surface, cc</td>
</tr>
<tr>
<td>( V_{\text{eq}} )</td>
<td>Volume accessible to gas phase at equilibrium, cc</td>
</tr>
<tr>
<td>( x_i )</td>
<td>Mole fraction of component “i” in adsorbed phase at equilibrium</td>
</tr>
<tr>
<td>( y_i )</td>
<td>Mole fraction of component ( i ) in gas phase</td>
</tr>
</tbody>
</table>

**GREEK LETTERS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_g )</td>
<td>Molar gas density, molcm(^{-3})</td>
</tr>
<tr>
<td>( \mu_i )</td>
<td>Chemical potential of a component “i”, Jmol(^{-1})</td>
</tr>
<tr>
<td>( \pi )</td>
<td>Spreading pressure at constant temperature for the adsorbed phase, Nm(^{-1})</td>
</tr>
<tr>
<td>( \psi )</td>
<td>Reduced spreading pressure, moles per mass of adsorbent</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>Fraction of surface covered</td>
</tr>
<tr>
<td>$\vartheta^{ch}$</td>
<td>Molar volume at charge conditions</td>
</tr>
<tr>
<td>$\vartheta^{bed}$</td>
<td>Molar volume at final equilibrium</td>
</tr>
<tr>
<td>$\vartheta_{eq}$</td>
<td>Molar volume for gas mixture at equilibrium</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

This chapter briefly explains adsorption definition, fundamental concepts in adsorption, components and types of isotherms involved in adsorption, adsorption in porous materials and brief description of zeolites.

Adsorption science first practical adoptions were noted in ancient times. The current adsorption theory and its applications that were initiated by Langmuir's fundamental work have been developed extensively during last 100 years (Dašbrowski 2001). In present scenario, this process comprises advanced approaches that includes wide range of knowledge in modern surface chemistry. The methods for separation of mixtures in laboratory as well as industrial scale are increasing based on considering the change in concentration of components at the interface. Innumerable physical and
chemical processes take place at the boundary between two phases while others are initiated at that interface. The change in concentration of a substance at interface as compared with neighboring phases is termed as adsorption. Practical applications of adsorption in industry and environmental protection are of paramount importance. These are based mainly on selective uptake of individual components from their mixtures by other substances.

Although distillation is assumed to have a dominant role in separation processes, adsorption ultimately becomes the more economic option as relative volatility decreases (D.M.Ruthven 1984). In the present technology, the cost of comparison is appreciative towards adsorption even when relative volatility is high in a scenario where cryogenic distillation is the only alternative (D.M.Ruthven 1984). In order to compensate for high energy expenses of traditional distillation processes this operation is combined with other separation technologies and utilized. Adsorption appears as one of the most attractive techniques. The economic evaluation indicates adsorption processes are competitive compared to traditional process and represent energy saving between 30% and 50% if they were introduced for separating propylene-propane mixtures in actual refineries (Kumar 1992).

Until late 1950's, industrial utilization of adsorption phenomena remained limited to purification of air and industrial vent gases besides water treatment (Dałbrowski 2001). The invention of synthetic zeolites and
development of new process cycles for product recovery and regenerating adsorbent has brought a revolutionary change in progress of adsorption process. Evolution of molecular sieve adsorbents, especially synthetic zeolites have enhanced the potential of adsorption as a separation process with adsorbent having high selectivity, capacity and life as a primary requirement (D.M.Ruthven 1984). The advantage in adsorption is higher selectivity that can be achieved by tailoring the adsorbents; better porous adsorbents increases importance of adsorption.

1.1 Adsorption

Adsorption is a surface phenomena in which it increases the concentration of the substance (gas or liquid) at the interface of a condensed phase(solid), creating a film of the adsorbate on the surface of the adsorbent. Here, adsorbate is termed as liquid or gas and adsorbent as a solid substance. Adsorption is classified as follows based on forces of attraction,

Physical adsorption or Physisorption is a phenomenon where the adsorbed molecules are held to the solid surface by means of weak physical or van der Waals forces such as polar interactions and dispersion. Chemical adsorption or Chemisorption is a phenomenon where the adsorbed molecules are held to the solid surface by means of chemical bonds. This thesis is focused on physical adsorption where the chemical nature of the gas in contact with the solid does not change.
The fundamental concept and an important tool in designing adsorption processes is measurement of adsorption isotherm. This is primary source of information on the adsorption process and is generally illustrated using these isotherms i.e., amount of adsorbate on adsorbent as a function of pressure or concentration at constant temperature. Broadly, experimental physical adsorption isotherms are classified in six types and they represent characteristics of adsorbents used.

**Type 1** isotherms depict monolayer adsorption and can be easily described using Langmuir adsorption isotherm. In the present work, this type of isotherm is of great importance. These are remarked for the adsorption of gases whose pore sizes are a few molecular diameters and they characterize microporous adsorbents (Findenegg 1984)

**Type 2** isotherms demonstrate multilayer formation and are generally found in adsorbents with a wide distribution of pore sizes. These describe macro porous adsorbents having strong interactions between adsorbate and adsorbent (Findenegg 1984).

**Type 3** isotherms are obtained when adsorbed species increases without limit (as saturation point approached) and in this type there is no monolayer formation; thus describing macro porous adsorbents having weak interactions between adsorbate and adsorbent (Findenegg 1984).
**Type 4** isotherm is a variety of Type 2 isotherms which explains the formation of monolayer followed by multilayer adsorption. These vapor adsorption isotherms display hysteresis loops (higher desorption branch).

**Type 5** isotherms are similar to Type 4 isotherms and these two types show capillary condensation phenomenon. They exhibit hysteresis loop associated with pore filling and discharging. Hysteresis loop here indicates that adsorption and desorption curves does not match and these isotherms are relatively rare.

**Type 6** isotherms are also relatively rare resulted in layer by layer adsorption in a highly uniform surface (Rouquerol, et al. 2013).

All isotherms involved in the study are Type-1, since O$_2$ and N$_2$ are gases around room temperature and the solid used is microporous zeolite LiLSX.
1.2 Defining adsorption in porous materials

An adsorption system typically consists of a gas phase and a solid phase and it is necessary to distinguish the molecules adsorbed from gas phase molecules (A.L.Myers 2002). For adsorbents, such as zeolites, adsorption mainly occurs in the pores of the adsorbent and it is difficult to define dividing surface within the micropores. Therefore, the exact location of dividing surface is not precise.
Gibbs (Gibbs 1928) defined the necessity of dividing surface between adsorbate and gas to treat adsorption thermodynamically. Hence, density profiles of the molecules are considered here. Gas density profile near a solid surface is depicted in Figure 2.

In the gas phase, density of adsorbate($\rho^g$) is constant and within the solid it is zero. There is an increase in density at the interface before it decreases to zero because of molecular interactions with the solid. The amount adsorbed($n^a$) is the area under that peak and its value depends on the integration limits. The actual interface in Figure 2a is mathematically replaced by definition of Gibbs dividing surface in Figure 2b. The difference between integral of 2a and 2b is attributed to the formation of a 2-dimensional “surface” adsorbed phase (no thickness) on the hyper-surface.

Mass balance for amount adsorbed ($n^a$) is as follows:

$$n^a = n^t - V_g \rho^g$$  \hspace{1cm} (1.2a)

$n^t$ is the total amount of gaseous species (mol), $V_g$ is void volume up to Gibbs dividing surface (cc), $\rho^g$ is gas density (mol/cm$^3$).

As the dividing surface moves away from the solid phase (i.e., decreasing $x_0$ value), the amount adsorbed($n^a$) changes from positive value to zero and finally becomes negative (A.L.Myers 2002). Commonly, the location of the dividing surface is fixed by using a reference gas for which the amount
adsorbed would be negligible such as helium around room temperature and at low pressure (A.L.Myers 2002).

\[ n^a = n^t - V^g \rho^g = 0 \]  \hspace{1cm} (1.2b)

\[ V^g = \frac{(n^f)}{\rho^g} \]  \hspace{1cm} (1.2c)

It is assumed that at room temperature and low pressure helium is not adsorbed. Equation 1.2b represents a method for measuring adsorption relative to helium by measuring the volume of the gas phase\((V^g)\), so called dead space or void volume (A.L.Myers 2002). Adsorption measured relative to helium is closest approximation of conceptual Gibbs excess adsorption.

Figure 2 Profile of Gas Density at Gas-Solid Interface

Source: (A. L. Myers 2002)
1.3 Zeolites

Practical adsorbents include silica gel, activated alumina, activated carbon, porous polymers as well as more recently developed crystalline aluminosilicates or zeolites, Metal-Organic Frameworks (MOFs), Carbon Nanotubes (D.M. Ruthven 1984). Zeolites are a large group of natural and synthetic hydrated crystalline alumino silicates which are porous (Zeolites 2004). Zeolite pore openings range from 0.2Å to about 10Å; consider O$_2$ and N$_2$ are both about 3.4Å in kinetic diameter. The atomic structure of zeolite is based on 3-dimensional network consisting of silicon and aluminum atoms bonded by oxygen bridges in a tetrahedral framework (Zeolites 2004). The structure built up from assemblages of secondary building units are themselves polyhedra made up of Si or Al tetrahedra. Different stacking of secondary building blocks result in different crystal structures with pores shown in Figure 3. A negative charge on the framework was introduced by each aluminum atom and it must be balanced by an extra crystalline cation. These cations are electrostatically bonded to the structure and are located at preferred sites which play an important role in determining adsorptive properties (D.M. Ruthven 1984).
Commercially important zeolites start with A-zeolite which has a small pore structure with 8 oxygen-ring openings made up of sodalite cages linked through double 4 oxygen-rings (Kim 2003). The X zeolite has a larger pore structure having 12 oxygen-ring openings made up of sodalite cages which are linked through double 6 oxygen-rings; thus, having more advantages than zeolite A (small pore structure) as adsorbents. In the present work, solid material used is LiLSX which is X type zeolite (discussed in detail in chapter 3).
CHAPTER II

THEORY

This chapter gives detail description of theory involved in adsorption. This includes phase rule definition, pure and binary adsorption, selectivity and its importance in adsorption, adsorption energy and importance of henry’s law constant.

2.1 Phase Rule

The bulk gas phase and adsorbed phase are the two phases which are in equilibrium with their own sets of intensive properties. Equilibrium is defined when thermal potential (or temperature), mechanical potential (or pressure) and mass potential (or chemical potential) are equal (Talu 1998). The equality of thermal potential of each species in the two phases at equilibrium assures no heat exchange; if temperature difference occurs, the system will not be in equilibrium. Similarly, equality of chemical potential
assures no net mass transfer. The challenge is in equating mechanical potentials leading to the work term; thermodynamically the adsorbed phase is two dimensional and pressure cannot be considered as an intensive variable. This two-dimensional phase does not have a volume; therefore, its extent can only be measured by area(A) per weight of solid adsorbent. The only way to increase the area of a system is by adding more solid. The corresponding canonical variable is the spreading pressure(Π). Consequently, pressure and extensive variable volume are not appropriate variables for the work term in two-dimensional phase and must be replaced by spreading pressure and area respectively. The fundamental property relation for a surface phase is therefore given by,

\[ dU = T \, dS - \Pi \, dA + \sum \mu_i \, dN_i \]  \hspace{1cm} (2.1a)

where \( \mu_i \) is chemical potential of a component “i” which is equal in all phases(Jmol\(^{-1}\)), \( N_i \) is the surface amount adsorbed of individual species.

There is an additional degree of freedom in the phase rule at equilibrium from the lack of mechanical equilibrium relation. The phase rule for adsorption is stated as follows,

\[ (# \, freedom) = (# \, components) - (# \, phases) + 3 \] \hspace{1cm} (2.1b)

In the above formulation following J.W.Gibb’s (Talu 1998), the solid is taken as inert and is not a component (as well as a phase) and equilibrium is established between a fluid(gas) and 2D adsorbed film in the solid.
2.2 Pure and Binary Gas Adsorption

Adsorption characteristics are illustrated using isotherms. At equilibrium, when pure gas (adsorbate) is in contact with adsorbent, adsorption isotherm is represented as follows:

\[ N = f(P) \quad \text{(Constant Temperature)} \quad (2.2a) \]

Thus, above functionality is described as the amount adsorbed (N) is a function of pressure of bulk gas phase (P) at a constant equilibrium temperature (T) (Gumma 2003), whereas mixture adsorption isotherm is represented as

\[ N_i = f(P, y_i) \quad \text{(Constant Temperature)} \quad (2.2b) \]

In contrast to pure component adsorption, for mixture adsorption, above functionality is described as the partial amount adsorbed (N_i) is a function of bulk gas phase pressure (P) as well as bulk gas phase composition (y_i) at constant equilibrium temperature (T) (Gumma 2003).

2.3 Spreading Pressure

The concept of the spreading pressure as an intensive variable accounting for surface adsorption was first introduced by Gibbs (Gumma 2003). Spreading pressure is not experimentally measurable quantity for microporous surfaces. It can be measured directly on a Langmuir thorough on flat liquid interfaces. Spreading pressure can be calculated using
macroscopically measured quantities by integrating Gibbs adsorption isotherm.

Gibbs adsorption isotherm derived from differential equilibrium relation is given as follows (Do 1998),

\[-A^*d\pi + \sum_i R \cdot T \cdot N_i \cdot d\ln P_i = 0 \quad \text{(constant T)} \quad (2.3a)\]

Follows,

\[\frac{A^*d\pi}{R \cdot T} = \sum_i N_i \cdot d\ln(P_i) \quad \text{(constant T)} \quad (2.3b)\]

where, \(N_i\) is the partial amount adsorbed of component \(i\) (mol/kg),

\(P_i\) is the equilibrium partial pressure of component \(i\) (kPa),

\(\pi\) is spreading pressure at constant temperature for the adsorbed phase (Nm\(^{-1}\)),

\(T\) is temperature (K).

For a pure component isotherm, integrating above equation from zero pressure to pressure \(P\), the Gibbs adsorption isotherm for a pure component is as follows,

\[\psi = \frac{\pi^* A}{R \cdot T} = \int_0^P \frac{N}{P} \cdot dP \quad (2.3c)\]

“\(\psi\)” is called reduced spreading pressure and has units of moles per mass of adsorbent. Above equation is used to calculate spreading pressure (\(\Pi\)) from experimental isotherm adsorption data. Regardless of how it is actually calculated from experimental data, spreading pressure is an independent
intensive property of the 2D adsorbed phase; hence, it is a state function. Therefore, the following integration over a closed path must always be satisfied.

$$\oint d\left( \frac{nA}{RT} \right) = RT \oint \sum N_i d\ln P_i = 0$$  \hspace{1cm} (2.3d)

A typical 3D view of a binary gas adsorption system is shown below

![3D view of binary isotherm](image)

Figure 4 3D view of binary isotherm

Source: (Gumma 2003)

Experimental data for systems are carefully collected to facilitate integration of the above equation. For example, for a binary adsorption system referring to Figure 4, the curves OA, BC, DE represent the change in amount adsorbed with pressure at constant gas compositions and the curve ABE represent the change in amount adsorbed with gas composition at constant pressure. At any point, spreading pressure can be calculated by
following a proper integration path for equation 2.3a. Integration starts from selecting a known value of spreading pressure; generally chosen to be at zero pressure where spreading pressure is zero. For example, consider a point on the binary isotherm to calculate spreading pressure at that particular point, say E. As integration is started from a known value, here chosen to be zero pressure whence $\psi$ is zero, the numerous paths chosen to reach point E are DE, CBE, OAE. Regardless of the paths chosen spreading pressure has same value at that point E determined by $P, y_i, T$.

The equations used here gives the same value of $\psi$ as follows,

$$
\Psi_E = \Psi_D + \Delta\Psi_{DE} = \Psi_D + \Delta\Psi_{DC} + \Delta\Psi_{CB} + \Delta\Psi_{BE}
$$

$$
= \Psi_D + \Delta\Psi_{DO} + \Delta\Psi_{OA} + \Delta\Psi_{AE}
$$

(2.3e)

In the above equation, $\Delta$ denotes change over the path and single subscripts denote the value at that point.

Since pressure is zero follows,

$$
\Psi_D = \Delta\Psi_{DC} = \Delta\Psi_{DO} = 0
$$

(2.3f)

The other terms in the equation 2.3e can be calculated by integrating equation indicated below.

$$
d\Psi = N_i \ast d\ln(y_i, P)
$$

(2.3g)

$$
\Delta\Psi_{DE} = \int_0^P N_i d\ln P \text{ (constant } T, y_1=1) ;
$$

(2.3h)
\[ \Delta \Psi_{OA} = \int_0^P N_2^* \tilde{d} \ln P \quad \text{(constant } T, y_1 = 0) \]  
\[ (2.3i) \]

\[ \Delta \Psi_{BE} = \int_{y_1}^{1} \left( \frac{N_1}{y_1} - \frac{N_2}{y_2} \right) \, dy_1 \quad \text{(constant } T, P) \]  
\[ (2.3j) \]

where \( N_1, N_2, N_t \) are the amounts adsorbed from a binary mixture.

Constant pressure and composition planes are to be followed in order to evaluate change in spreading pressures as described above. All these calculations use numerical methods provided with the data meeting the requirements collected on a sufficiently constant \( P \) or \( y \).

### 2.4 Selectivity

Selectivity is one of the most important parameters for practical applications determining the efficiency of a separation (R. B. Rios 2013). Selectivity depends on a difference in either adsorption equilibrium or adsorption kinetics, but most of the adsorption processes depend on equilibrium selectivity (D.M.Ruthven 1984). In the present study, the efficiency of air separation was evaluated by the selectivity of the solid for \( N_2 \) over \( O_2 \) which was calculated from ratios of mole fractions in the gas phase and adsorbed phase. The selectivity of adsorbent for component i relative to component j is defined by (A. L. Myers 2004),

\[ S_{ij} = \frac{x_i / y_i}{x_j / y_j} \]  
\[ (2.4a) \]

where \( x_i \) and \( y_i \) are the mole fractions of component “i” in adsorbed and gas phases at equilibrium respectively.
2.5 Adsorption Energy: Isosteric heat

A description of energetics of gas adsorption requires an understanding of the binding nature of gas (pure and mixture forms) to the adsorbent. The isosteric heat of adsorption is central to an understanding of gaseous mixture separation methods and is an important parameter in the process of adsorption (Gerardo Domínguez 2010). This depends on the extent of surface coverage because adsorbate-adsorbate interactions can alter energetics of adsorption. As loading increases, lateral interactions between adsorbed molecules increases and on other hand vertical interactions between gas molecules decreases as it becomes more difficult for the gas molecules to access certain sites in the solid. The decrease in vertical interactions is higher than increase in lateral interactions that results in overall decrease in isosteric heat. This is typical behavior of isosteric heat with loading.

Isosteric heats denote the degree of adsorbent surface heterogeneity as these profiles reveal the type of heterogeneity in the solid adsorbent and degree of solid-gas interactions. The decrease in heat of adsorption with gas loading is characteristic of highly heterogenous adsorbents and vice-versa. A constant value indicates balance between strength of cooperative gas-gas interaction and the degree of heterogeneity of gas-solid interactions. The isosteric heat of adsorption of a pure gas does not depend on quantity of adsorbate on a homogeneous surface; However, it decreases with an increase in adsorbate loadings if the adsorbent surface is heterogeneous due to the
presence of several active sites. The isosteric heat can increase with increase in adsorbate loading when there are strong lateral interactions between adsorbed molecules.

Generally, it is difficult to experimentally measure the thermal properties of an adsorption process. Hence, isosteric heats are usually derived from adsorption isotherms using Clausius-Clapeyron equation. The isosteric heat equation derived using DSL model is given by,

$$Q_{st} = \frac{H_1 m_1 b (1 + dp)^2 + H_2 m_2 d (1 + bp)^2}{m_1 b (1 + dp)^2 + m_2 d (1 + bp)^2}$$  \hspace{1cm} (2.5a)

where \( m_{1i} \) and \( m_{2i} \) are saturation capacities on the two sites, \( H_{1i} \) and \( H_{2i} \) are heats of adsorption of gas ‘i’ on the two sites, \( b \) and \( d \) are affinity parameters of gas.

2.6 Henry’s Law (Adsorption at Low Coverage)

Henry’s law in gas adsorption describes the tendency between adsorbate molecules and adsorbent. For physical adsorption on a homogeneous surface at sufficiently low concentrations, the isotherm is linear and thus the limiting slope in the low concentration region is generally termed as Henry’s Law constant which is the thermodynamic equilibrium constant (D.M.Ruthven 1984). Henry’s law physically corresponds to the situation in which adsorbed phase is dilute that there is neither competition for active sites on the surface nor any significant interaction between adsorbed molecules. Hence, the system is completely described by “vertical” interactions between gas molecules and the solid. In the present work, the
plot of \( \ln(P/N_i) \) Vs \( N_i \) (obtained from pure component isotherm data) is used in evaluating henry's law constant; this plot should be linear at concentration below henry’s law limit. Thus, the simplest way of estimating henry’s law constant is by extrapolating this plot to zero adsorbed phase concentration. Equation can be expressed as follows,

\[
H = \lim_{P \to 0} \frac{N_i}{P} \quad (2.6a)
\]

2.7 Adsorption Models

Many models are available in the literature (Gumma 2003) which are developed empirically and also from the theory. The following section explains Langmuir model concept, Dual-Site Langmuir model which has been used to model isotherms in the present work. Numerous other models can be found in literature (D.M.Ruthven 1984).

2.7.1 Langmuir model

This is simplest theoretical model for monolayer adsorption and is based on some simple assumptions (D.M.Ruthven 1984). These assumptions are: 1) Molecules are adsorbed only at fixed number of defined localized sites, 2) Each site can hold one adsorbate molecule, 3) These sites are energetically equivalent and 4) There is no interaction between adsorbed molecules.

Langmuir using kinetic arguments for dynamic equilibrium has developed the following equilibrium relation between intensive properties.
Later, the equation was also shown by rigorous statistical mechanics derivations (Paul M. Mathias 1996),

\[
\theta = \frac{N}{N_\infty} = \frac{bP}{1+bP} \quad (2.7.1a)
\]

In the above equation, \(\theta\) is the fraction of surface covered, \(N\) is the number of moles adsorbed per gram of adsorbent, \(N_\infty\) and \(b\) are Langmuir parameters, \(P\) is the pressure.

Langmuir parameters have important significance; \(b\) is the slope of isotherm at low pressure representing affinity of gas molecules towards solid; “\(b\)” is related to site energy (Arrhenius relation), \(N_\infty\) is a saturation limit of isotherm at infinitely high pressure representing monolayer capacity at the limit of \(\theta = 1.0\).

2.7.2 Dual-Site Langmuir model (DSL)

Dual-Site Langmuir model is a modification for Langmuir model accounting for some level of heterogeneity. In this model, the total amount adsorbed is a result of adsorption contributed from two sites (or two physically mixed adsorbents) with different adsorption energies. The isotherm is represented as follows (Paul M. Mathias 1996),

\[
n = \frac{m_1bP}{1+bP} + \frac{m_2dP}{1+dP} \quad (2.7.2a)
\]
where $m_1$ and $b$ are the saturation capacity and the affinity parameter on first set of adsorption sites respectively, $m_2$ and $d$ are the similar parameters on the second set of series. Here, it is assumed that the first set of series has larger affinity compared to second set of series i.e., $b > d$.

This DSL model consists of four parameters $m_1$, $b$, $m_2$, $d$, which were regressed to provide a best least-squares fit of the data.

**The Mixed-Gas DSL Model** provides a powerful way to describe mixed gas adsorption and partial amounts adsorbed can be calculated as follows (Paul M. Mathias 1996),

$$n_i = \frac{m_{1i} \cdot b_i \cdot P \cdot y_i}{1 + \Sigma b_j \cdot P \cdot y_j} + \frac{m_{2i} \cdot d_i \cdot P \cdot y_i}{1 + \Sigma d_j \cdot P \cdot y_j} \tag{2.7.2b}$$

where $m_{1i}$ and $m_{2i}$ are saturation capacities on the two sites. Theoretically, these parameters must be same for all gases but often regressed experimental data does not obey the restriction. Hence, $m_1$ and $m_2$ in the above equation is also indexed by “$i$”. “$b_i$” and “$d_i$” are affinity parameters for gas ‘$i$’ on the two sites assumed to be depending on Arrhenius temperature relation as follows:

$$b_i = b_i^0 \cdot \exp\left(\frac{H_{1i}}{RT}\right) \tag{2.7.2c}$$
$$d_i = d_i^0 \cdot \exp\left(\frac{H_{2i}}{RT}\right) \tag{2.7.2d}$$

$H_{1i}$ and $H_{2i}$ are heats of adsorption of gas ‘$i$’ on the two sites, cal/gmol; $b_i^0$ and $d_i^0$ are affinity parameters of gas ‘$i$’ at a reference temperature and related to entropy of adsorption, atm$^{-1}$. 
In DSL model, the pure-gas isotherm offers a flexible mathematical form due to the high level of heterogeneity that it permits, whereas in mixed-gas adsorption the flexibility of allocation of the two sites allows the description of a relatively large variant of mixed-gas selectivity. For a binary system, the site order is matched through energy i.e., $H_{1i}$ is the higher energy site regressed from either pure component isotherm.
CHAPTER III

EXPERIMENTAL SECTION

This chapter provides details of materials used in the experiments and detailed description of property measurements and controls. Also, this section discusses the experimental procedures and their modeling for pure and binary adsorption. Later, summarizes the calculation procedures for estimating amounts adsorbed in pure and binary adsorption.

3.1 Materials used

3.1.1 Adsorbent details

The adsorbent used in the present study is Lithium low silica X (LiLSX), which is a member of X type zeolite. The X zeolite with a Si/Al ratio close to 1.0 is termed as low silica X(LSX) zeolite which is acknowledged as an outstanding nitrogen adsorbent and these X-structures becomes unstable
when Si/Al ratio drops below 1.0. Also, Li-exchanged X zeolite was suggested as a high-performance adsorbent for oxygen production (Kim 2003). In the structure, aluminum atom introduces negative charge on the framework balanced by exchangeable cation (Lithium in the present study). These lithium ions are at preferred sites within the framework that plays an important role in adsorptive properties. In the present work, 10.53 grams of LiLSX material (small spherical particles - \( \frac{1}{2} \) mm dimensions) was packed in a 7.5 cm column of 38 cc internal volume. The structure of zeolite X is shown in Figure 5.

![Figure 5 Structure of zeolite X [ Source (D.M.Ruthven 1984)]](image)

### 3.1.2 Adsorbates details

The gases used in the present study as adsorbates are nitrogen and oxygen: helium gas is used as a reference gas while measuring internal volumes in the system. Some of the physical properties of the adsorbates (nitrogen and oxygen) are listed below in Table 1.
Table 1. Physical properties of gases

<table>
<thead>
<tr>
<th>Property</th>
<th>Nitrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>N₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Molecular weight (gm/mol)</td>
<td>28.01</td>
<td>32.0</td>
</tr>
<tr>
<td>Critical Temperature (K)</td>
<td>126.2</td>
<td>154.37</td>
</tr>
<tr>
<td>Critical Pressure (atm)</td>
<td>33.49</td>
<td>49.61</td>
</tr>
<tr>
<td>Critical Volume (m³/gm)</td>
<td>0.198</td>
<td>2.50</td>
</tr>
<tr>
<td>Normal Boiling point (K)</td>
<td>77.3</td>
<td>90.20</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>63.2</td>
<td>54.31</td>
</tr>
</tbody>
</table>

Source: (Engineering Toolbox n.d.)

3.2 Apparatus

The volumetric experimental system designed for the present study is used to measure pure and binary component adsorption equilibria. The apparatus developed in our labs is shown in Figure 6. It consists of a closed volume with a recirculation loop charged with the gases to be adsorbed. The gases are then contacted with the solid and after equilibrium is established, a material balance is used with measured gas phase properties to calculate adsorbed phase properties. With this procedure, there is no direct control on either gas phase or adsorbed phase conditions at equilibrium, though they can be measured quite accurately. The closed volume system consists of
various sections such as Feed section, Adsorption/Desorption section, Bypass/Sampling section and Exit section (discussed in detail later in this section). The system is connected to a gas chromatography (GC) via a 6-way sampling valve. GC measures final gas phase composition at equilibrium for binary experiments. External water bath are used to keep temperature constant throughout the system. The adsorbent column temperature is controlled within ±0.1°C. The column temperature is measured internally with a thermocouple embedded in the adsorbent packing.

3.2.1 Property Measurements and Controls

3.2.1(a) Pressure Measurements

Pressure is one of the process variables that needs to be measured precisely. Since accuracy is an important factor and it is necessary to measure pressure over a wide range, two pressure transducers with different ranges is used. The two transducers from Sensotec Inc THE/713-10 ranging from 0-100 psi for high pressure measurements and THE/713-26 ranging from 0-15psi for low pressure measurements were used. These transducers are connected to individual indicators. The transducers ranges, accuracy etc., are listed in the Table 2 below.
Table 2. Pressure Transducer Units used and their Ranges

<table>
<thead>
<tr>
<th>Transducer</th>
<th>Range (in psia)</th>
<th>Accuracy (psia)</th>
<th>Overall Pressure Limit (psia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THE/713-10</td>
<td>0-100</td>
<td>±0.1</td>
<td>150</td>
</tr>
<tr>
<td>THE/713-26</td>
<td>0-15</td>
<td>±0.01</td>
<td>30</td>
</tr>
</tbody>
</table>

3.2.1(b) Temperature Measurements and Controls

Temperature is also an important process variable that needs to be controlled and measured accurately. Though the experiments were carried out at isothermal conditions, there will be some inevitable variations from ambient conditions and precise measurements are essential for calculations. J type thermocouples manufactured from Omega® Engineering Inc were used to measure temperature at different locations in the apparatus. Temperature measurements required for the system are 1) temperature of small and big tanks immersed in the same water bath (usually, water bath temperature), 2) temperature inside the column and 3) the ambient temperature. It is necessary to maintain the column temperature constant throughout the experiments and for this purpose, a controllable circulating water bath is used. Temperature inside the column must be accurate as the isotherms were measured at this temperature. One thermocouple is embedded inside at the center of the column. A thermocouple is placed in the
water bath around the tanks. Another thermocouple is used between heating element and the column to measure temperature during activation of the column as feedback for temperature controller. A temperature controller manufactured from Omega Eng Inc (Model: CN8241-RI-PVS V2) is used during activation of the column. It is set to ramp-soak mode which causes the controller to ‘ramp’ the heater temperature from starting point to the set point within a time specified.

3.2.1(c)   **Pump**

The pump is used for mixing and circulation of gas mixture during binary adsorption experiments to assure uniform gas composition throughout the system. It is a metal bellows pump (model: MB-158) driven by a motor. Bellows are of AM-350 made up of stainless steel and the pump has permanently lubricated ball bearings. Pump housing body is of cast aluminum and the operating speed @ 60Hz is 1725rpm gives free flow rate of 1.4(scfm). The maximum pressure pump can withstand is 45psig.

3.2.1(d)   **Cooling Water Circulation Pump and Controllable Isothermal Water Bath**

The cooling water circulation pump supplies water from the isothermal bath to the coil around the column with proper thermal contact. The water circulation pump is of type AC-2CP-MD manufactured by *March* can pump up to 260GPH at a head of 3ft. The isothermal bath made by Fisher Scientific
(model:9005) is used to maintain isothermal conditions around the column within ± 0.1°C.

3.2.1(e) Gas Chromatograph System

A gas chromatograph (GC) system is used in analysis of gas composition for binary adsorption experiments. The GC used in this study is Agilent model 7890A. The system is equipped with thermal conductivity detector and 3 feet long Supelco 5A molecular sieve to separate oxygen and nitrogen. GC requires extremely small samples, a few μg, of the mixture due to high sensitivity of the detector equipped in it.

There are different types of analysis techniques that can be used. An Elution Chromatography technique is used in the present thesis. In this technique, continuous constant flow of carrier gas (helium) is fed through the column. A Sampling valve with a sampling loop volume of 0.5cc is used to inject the sample of gas mixture to be analyzed in carrier gas stream flowing to a GC. This valve injects sample as pulse with 90° angle rotation. The sample along with the carrier gas is fed into GC and the individual components travel with different velocities through the column depending on the difference in sorption on the material in the column. Each component exits at a fixed time called retention time. Retention time is unique for each component for the same column and same flow rate of helium gas at a given temperature. The gas conductivity at the exit of the column is continuously monitored by the detector. The results are represented as two separate peaks.
(for two components) on the computer screen and the areas under these peaks are proportional to the amount of each species injected. The weakly adsorbed component travels for a shorter time; thus, hits detector first and the strongly adsorbed component travels for longer time exiting the column later.

3.2.2 Volumetric Experimental System Description

The flow sheet for volumetric setup shown in Figure.6 is divided into various sections described below:

Section A

**Feed** section consists of three gas lines connected to the lab-gas manifold. Gas manifold provides nitrogen (Grade 5.0, >99.999%), oxygen (Grade 4.4, >99.99%) and helium (Grade 4.7, >99.997%) from gas cylinders and were chosen by two three-way valve switching between them. The three-way valves used in the present work are Swagelok SS-41XSP. **Inlet** section includes small and big tanks with internal volumes 95cc and 162cc respectively, measured by helium expansion experiments (which are described in detail later). These tanks are equipped with water baths around them to maintain constant temperature around room temperature. **J-Type** thermocouples are used to measure temperature of the tanks. A2, A4 and A3, A5 are inlet and outlet valves for small and big tanks respectively. There is an interconnection valve (A13) between these tanks used for mixing gases for
mixture experiments. All these main valves used in the present study were B-type bellow valves, NUPRO SS-4BK.

Section B

This section includes changeable 7.5cm stainless steel adsorption column (1/2 inch tubing) with 10.53 grams of LiLSX adsorbent in ½ mm small spherical particles packed in it. The column has an embedded J type thermocouple and temperature in the column (whenever needed) is kept constant using thermostat water bath around the column. The water bath is connected to water circulator to maintain isothermal conditions and stabilizing the column temperature within ± 0.1°C accuracy throughout the experiments. A6 and A7 valves represented in the Figure.7 are the inlet and outlet valves for the column. A10 valve shown in the Figure 6 bypasses the column to exit section.

Section C

Bypass/Sampling section is mainly used for binary gas adsorption experiments and during column activation. This section includes 1) The recirculating bellows pump, 2) a mass flow controller, and 3) a sampling valve for GC analysis. The pump is used to mix gases and to circulate the gas mixture throughout the system including the column to maintain uniform composition while running binary gas experiments. Helium gas flow during activation of the column is controlled with the mass flow controller (model:
FMA123) ranging between 0-100 sccm. The sampling valve is connected to Hewlett Packard gas chromatograph system to analyze the gas composition. The gas mixture that needs to be analyzed is injected into GC as a pulse through sampling valve. The GC is calibrated by injecting known gas mixtures prepared in the system.

Section D

**Exit** section includes two pressure transducers to measure pressure in various sections of the system at different times. One pressure transducer ranging from 0-100 psi is used for high pressure measurements and the other pressure transducer ranging from 0-15 psi is used for low pressure measurements (more accurately). These pressure transducers are enclosed by four pressure gauge valves (P1, P2, P3, P4) which are H-type compact rugged bellow valves, NUPRO SS-2H. The only exit from the system is through valve A11 which is connected to either 1) a laboratory size vacuum pump (Welch duo-seal model:1400) or 2) atmospheric exhaust, both located in a fume hood. The vacuum pump can lower system pressure to less than 0.01 psi.
3.3 Experimental Measurement Techniques

3.3.1 Pure Component Isotherm Measurements

The amount of gas adsorbed per specific amount of adsorbent (N) is a function of pressure (P) at constant temperature (T) for pure components and is represented as follows:

\[ N = f(P) \]  
(Constant Temperature)  \hspace{1cm} (3.3.1)
Pure component measurements are relatively easier and there are several methods used for the measurement of pure component isotherms. These include 1) Volumetric, 2) Gravimetric, and 3) Dynamic (Talu 1998). The closed volumetric method is used in the present study.

3.3.2 Volumetric Analysis

In volumetric analysis, the amount adsorbed is determined based on difference in moles of substance in gas phase in a closed system before and after contact with the adsorbent solid.

Closed systems

The closed system apparatus used in the present work is shown in Figure 6. The volumes for various sections of the apparatus are accurately measured using helium expansion experiments (assuming helium to be non-adsorbing gas) (Talu 1998). The main advantage using closed systems is their accuracy. In these systems, pressure, temperature and gas compositions need to be measured for multi component experiments. The gas phase properties at final equilibrium cannot be controlled since they depend on the amount adsorbed, but equilibrium conditions can be measured accurately. The equilibrium conditions are set by estimating charge conditions using predictive methods. Dual-Site Langmuir model is used in the present work to estimate the charge conditions for binary adsorption measurements.
3.4 Preliminary Measurements

Prior to actual experiments, preliminary measurements need to be performed. These include helium expansions to determine internal volumes and gas chromatograph calibration.

3.4.1 Void Volume Measurements

Helium expansion techniques are used to measure internal volumes in the stainless system. These experiments were performed at sub-atmospheric pressure i.e., 0-15psia assuming helium is not adsorbed at low pressures and ambient temperature while calculating volume of the column (Talu 1998). In the system, volume of reference section was previously measured using mercury displacement technique. A known amount of helium gas ($P_{ch}$) is charged into reference section and expanded into completely evacuated unknown volume section in the system. Once pressure ($P_t$) is stabilized, its value is recorded. From known volume section, unknown volume are calculated using ideal gas law as experiments were performed at sub atmospheric conditions with helium at low pressures and ambient temperatures. Material balances for calculating unknown volume is given as follows:

$$n_{ch} = \frac{P_{ch}V_{known}}{RT_{ch}} = \frac{P_f(V_{known}+V_{unknown})}{RT_{final}}$$

...... 3.4.1(a)

$n_{ch} =$ Number of moles charged into the system in mmol (number of moles charged is same at the beginning and after expansion);
\( P_{ch} = \text{Pressure at charge conditions (psia)}; \ P_f = \text{Pressure at final conditions (psia)} \)

\( R = \text{Universal gas constant (psi.cc/mmol/K)}; \ T = \text{Temperature (K)} \).

The measured volumes are tabulated as below:
<table>
<thead>
<tr>
<th>Section</th>
<th>Valves enclosed</th>
<th>Volume (cc)</th>
<th>Standard deviation</th>
<th>CV%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>A1+A2+A4+A9+A12</td>
<td>20.05</td>
<td>0.24</td>
<td>1.18</td>
</tr>
<tr>
<td>Bypass</td>
<td>A6+A8+A9+A10</td>
<td>9.96</td>
<td>0.15</td>
<td>1.53</td>
</tr>
<tr>
<td>Exit</td>
<td>A3+A5+A10+A7+A11+P1+P2</td>
<td>14.48</td>
<td>0.28</td>
<td>1.96</td>
</tr>
<tr>
<td>Pump</td>
<td>A12+A18</td>
<td>70.45</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td>Big Tank</td>
<td>A2+A3+A13</td>
<td>162.22</td>
<td>2.51</td>
<td>1.54</td>
</tr>
<tr>
<td>Small Tank</td>
<td>A4+A5+A13</td>
<td>95.60</td>
<td>1.46</td>
<td>1.53</td>
</tr>
<tr>
<td>Bed(full)</td>
<td>A6+A7</td>
<td>33.55</td>
<td>0.19</td>
<td>0.58</td>
</tr>
<tr>
<td>Bed(empty)</td>
<td>A6+A7</td>
<td>38.00</td>
<td>0.68</td>
<td>1.81</td>
</tr>
<tr>
<td>Low P</td>
<td>P1+P3</td>
<td>6.57</td>
<td>0.13</td>
<td>2.03</td>
</tr>
<tr>
<td>High P</td>
<td>P2+P4</td>
<td>6.44</td>
<td>0.09</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Table 3. Internal Volumes in the System Measured Using Helium Expansion Techniques
3.4.2 *Gas Chromatograph (GC) Calibration*

Gas Chromatography is used to separate/analyze the different components of a gas mixture to determine their relative compositions. In the present work, gas chromatography is used in binary adsorption experiments to measure the final gas phase composition at equilibrium. It is necessary to calibrate GC for the gases of interest before performing binary adsorption experiments for the calculations. In our volumetric system, any composition gas mixture can be prepared. These known samples are injected into GC for analysis and a calibration is generated. The calibration method is explained next.

The mole fraction of component $i$ in gas phase is given by:

$$y_i = \frac{n_i}{n_t} \quad \text{(3.4.2a)}$$

where, $y_i$ = mole fraction of component $i$ in gas phase,

$n_i$ = number of moles of component $i$ in the gas mixture (mmol),

$n_t$ = total number of moles of gas species (mmol) = $n_1 + n_2$ (for 2 components).

The results from GC gives two separate peaks representing one for each of the species in the gas mixture and areas under these peaks are
calculated by the GC. The GC areas are proportional to the amount of each species injected. This dependency can be written as follows:

\[ A_i \propto n_i \]  \hspace{1cm} (3.4.2b)

\[ A_1 = k_1 \cdot n_1 \quad ; \quad A_2 = k_2 \cdot n_2 \]

or

\[ A_1 = k_1 \cdot n_t \cdot y_1 \quad ; \quad A_2 = k_2 \cdot n_t \cdot y_2 \]  \hspace{1cm} (3.4.2c)

\[ k_1 \text{ and } k_2 \text{ are constants, } A_1 \text{ and } A_2 \text{ are areas under the peaks given by GC.} \]

The proportionality constants in the above relations can be combined as \( K = \frac{k_1}{k_2} \). This K-factor relates area fractions and mole fractions by the following equations.

\[ K = \frac{(A_1/y_1)}{(A_2/y_2)} \]  \hspace{1cm} (3.4.2d)

\[ y_1 = \frac{A_1}{A_1 + KA_2} \]  \hspace{1cm} (3.4.2e)

\( K \) = Calibration factor; \( y_1 \) and \( y_2 \) = mole fractions of individual components in the gas mixture.

The system was used to mix oxygen and nitrogen for 7 different compositions. These mixtures were injected to the GC and analysis was performed 4-6 times to average. Each mixture yields are calculated for K from equation (3.4.2d). Then these K values are plotted/regressed against %A as shown in Figure 7. The functionality is given by,
\[ K = K_0 + K_1 A_{12} \quad \cdots \cdots \quad (3.4.2f) \]

The regressed equation is

\[ K = 0.2759 \times \%AO2 + 0.9688 \quad \cdots \cdots \quad (3.4.2g) \]

Then in the binary experiments the area fraction of an unknown gas mixture can be used to calculate \( K \) from equation (3.4.2.g) and subsequently the mole fraction, \( y \) from equation (3.4.2.e).

![Figure 7 GC Calibration Curve](attachment:image.png)
3.5 Experimental Operating Procedure

3.5.1 Column Activation

First, the adsorbent needs to be activated to desorb any gases or moisture content or impurities in the material. During activation of zeolite, helium gas is allowed to flow through the column for about 8 hours (typically overnight) under vacuum. This is done by opening the valves $A_1, A_{12}, A_8, A_6, A_7, A_{11}$ in Figure 6 so that all the helium gas flows through the column. The flow rate of helium gas is set to 20sccm on the flow controller. The temperature controller is activated and was set to ramp-soak mode. The column is now heated at the rate of 1°C/min to 120°C, holds at 120°C for 1 hour, continues to heat the column at 1°C/min to 350°C and holds until morning. The activations were performed overnight. After activation, the helium flow is stopped and the column is fully vacuumed and valves A6, A7 closed to isolate it. The temperature controller is stopped to allow the column cool down eventually the water bath is started to control experiment temperature.

3.5.2 Pure Component Adsorption Equilibria Measurement Experimental Procedure

Pressure-Volume-Temperature (PVT) measurements are performed to calculate number of moles in the system at different times. For pure component adsorption equilibria measurements, an amount of gas is charged in either of the tanks and initial moles of gas charged is calculated from PVT measurements. Now, the gas is allowed to expand into the column.
Adsorption occurs on to the solid. Adsorption bed temperature rises a few degrees as adsorption process is exothermic. The column temperature eventually decreases to external bath temperature. Once pressure and temperature are stabilized, equilibrium is established and the final equilibrium PVT conditions are recorded. Equilibrium is assumed to be established when difference in pressure was less than 0.01psia for 30 minutes. From the final equilibrium pressure recordings, using appropriate equations final number of moles can be calculated. The difference between initial and final number of moles is the amount adsorbed at that step.

Calculations

The material balance for calculating amount adsorbed in the column is given as follows:

\[ n_{ads}^{eq} \cdot m + n_{bed}^{eq} \cdot m + n_{ch}^{eq} \cdot m = n_{bed}^{eq} \cdot m + n_{ads}^{eq} \cdot m \]  
(3.5.2a)

\[ n_{ads}^{eq} \cdot m + \frac{V_{bed}}{\vartheta_{bed}} \cdot m + \frac{V_{ch}}{\vartheta_{ch}} \cdot m = \frac{V_{bed}}{\vartheta_{bed}} \cdot m + n_{ads}^{eq} \cdot m \]  
(3.5.2b)

\[ \vartheta = \frac{RT}{2} \left( 1 + \sqrt{1 + \frac{4B_{mix}P}{RT}} \right) \ldots \text{(3.5.2.c)} \]

where, \( \vartheta \) is molar volume of a gas species.

(H.C. 1969), \( B_{mix} = \Sigma \Sigma y_i y_j B_{ij} \ldots \ldots \text{(3.5.2d)} \)  
\( B_{ij} = \left( \frac{B_{ij}}{2} + \frac{B_{ji}}{2} \right)^3 \ldots \ldots \text{(3.5.2e)} \) and second virial coefficient is given by \( B_{ii} = a_i + \frac{b_i}{T} + \frac{c_i}{T^3} + \frac{d_i}{T^5} + \frac{e_i}{T^7} \ldots \ldots \text{(3.5.2f)} \) ;
$\vartheta^{ch}$ and $\vartheta^{bed}$ are molar volumes at charge conditions and final equilibrium respectively;

$$n^{ads}|_{eq-1} = \text{moles of gas adsorbed at previous equilibrium (mmol)};\ n^{bed}|_{eq-1}=\ \text{moles of gas present in the void volume remaining unadsorbed in previous equilibrium step(mmol)};\ n^{ch}|_{eq} = \text{number of moles of gas charged to the tank (mmol)};\ n^{bed}|_{eq} = \text{final number of moles of gas present at equilibrium (mmol)};\ n^{ads}|_{eq} = \text{moles of gas adsorbed at equilibrium (mmol)} ;\ m = \text{mass of solid material(kg)}.$$

From above equations, the pure component amounts adsorbed are calculated. When the column is activated $n^{ads}|_{eq-1}$ and $n^{bed}|_{eq-1}$ are equal to zero by definition. Hence, the isotherm is stepped up in pressure. Pure component isotherms at 3 different temperatures ($4^\circ C, 23^\circ C, 45^\circ C$) were measured. For each isotherm at each temperature, approximately 6-7 points were measured to minimize measurement errors and also with the stepwise calculation procedure this will cause accumulation in uncertainty.

3.5.3 Binary Gas Adsorption Equilibria Measurement Experimental Procedure

In binary experiments, different compositions of the gas mixtures are made using volumetric system. Firstly, known amounts of gases predicted using DSL model are charged into two tanks. These gases are mixed using pump and are allowed to circulate throughout the system including the
column; thus, maintaining uniform composition in the system. The circulation path followed by the gases is shown in Figure 8. Gases are mixed well for about 5 hours for adsorption to occur and establish equilibrium. Once pressure is stabilized (equilibrium is achieved), the final equilibrium value is noted. A small sample is now sent to GC using sampling valve for analysis. These experiments were performed at constant pressure 35psi and constant temperature 23°C at different gas compositions. Binary adsorption experiments are difficult to measure and only one point on phase diagram is measured per day.

Calculations

By the above procedure, the experimental data PVT, \( y_i \) by GC measured is used to calculate the partial amounts adsorbed. Only one equilibrium point can be measured after each activation.

Let two species whose binary adsorption is being measured is denoted by subscripts 1 and 2 respectively. For instance, species 1 be charged to a pressure \( P_1 \) into a known volume \( V_1 \) in the system and similarly, species 2 charged to a pressure \( P_2 \) into a known volume \( V_2 \) of the system. The moles of each individual species \( n_1 \) and \( n_2 \) charged is given by

\[
\begin{align*}
n_1 &= \frac{V_1}{\vartheta_1} \\
n_2 &= \frac{V_2}{\vartheta_2}
\end{align*}
\]  

(3.5.3a)

\( \vartheta_1 \) and \( \vartheta_2 \) are molar volumes obtained as in pure component case given by equation (3.5.2 c ). The gas mixture is equilibrated with the adsorbent. \( V_{eq} \)

45
and $P_{eq}$ are volume accessible to gas phase at equilibrium and total pressure at equilibrium respectively. The gas composition was analyzed by GC. The area fractions $A_{1,eq}$ and $A_{2,eq}$ at equilibrium are obtained and if $A_{12,eq}$ is their ratio ($\frac{A_{1,eq}}{A_{2,eq}}$) then using the parameters from GC calibration experiments, K-factor can be calculated by using equations discussed in section 3.4.2.

The mole fraction determined from equation 3.4.2 is then used to calculate the total number of moles of gas mixture at equilibrium. This can be calculated using equation (3.5.3b).

$$n_{eq} = \frac{v_{eq}}{\vartheta_{eq}}$$  \hspace{1cm} (3.5.3.b)

$\vartheta_{eq}$ is molar volume for gas mixture at equilibrium (ccm/mmol) and is determined using equation (3.5.2.c). Second virial coefficients for pure components are determined using equation (3.5.2.f) and for the mixture is determined using equation (3.5.2.d).

The cross coefficient ($B_{12}$) given by equation (3.5.2e) is approximated by hard sphere model.

Using all these equations, total number of moles of gas mixture at equilibrium can be estimated and the partial number of moles of individual components are then determined from these values. Therefore, the partial amounts adsorbed ($n_{1,ads}^1$, $n_{2,ads}^2$) for individual components can be calculated using following equations,
\[ n_1 = n_1^{\text{ads}} \cdot m + n_{\text{eq}} \cdot y_{1,\text{eq}} \]  
(3.5.3.c)

\[ n_2 = n_2^{\text{ads}} \cdot m + n_{\text{eq}} \cdot y_{2,\text{eq}} \]  
(3.5.3.d)
Figure 8 Circulation Path for Gas Mixture in Binary Gas Adsorption Experiments
CHAPTER IV

RESULTS AND DISCUSSION

This chapter gives detail description of the pure and binary component experimental results and their modeling. Pure component isotherms were represented in the graphs and this experimental data uses Dual-Site Langmuir model to predict and to compare with experimental binary isotherm data.

The equilibrium data for pure component (Nitrogen and Oxygen in LiLSX) at three different temperatures i.e., 4°C, 23°C, 45°C and binary adsorption (Nitrogen/Oxygen mixture in LiLSX) at 23°C temperature and 241.6kPa pressure at various compositions were collected using the closed volumetric system described earlier. This data is necessary for designing adsorption separation processes and provides information on selectivity of a particular solid material for the gases of interest.
4.1 Pure Component Isotherm Data Measurement Analysis

Before measuring actual isotherm data, it is necessary to measure internal volumes in the system. These are obtained from helium expansion measurements. Apart from these volume measurements, the only measurable quantities for pure component isotherms are temperature and pressure before and after equilibrium respectively. From Pressure-Volume-Temperature measurements explained in section 3.5.2, the amounts adsorbed at different pressures and constant temperature are calculated using material balances. All these pure component isotherms and virial plots in their domains i.e., N vs P and ln(P/N) vs N respectively are represented in Figures.9 to 12.
Figure 9 Nitrogen Adsorption Isotherms on LiLSX
Figure 10 Nitrogen Virial plots on LiLSX
Figure 11 Oxygen Isotherms on LiLSX
Figure 12 Oxygen Virial Plots on LiLSX
The uncertainties in the system needs to be considered while performing experiments and are calculated using propagation of error analysis (detailed in Appendix A). With successive charges and equilibrations while performing experiments, each isotherm is plotted by measuring only six isotherm points after each activation to limit accumulation of cumulative uncertainty. Uncertainty of measurement is additive for a set of valves taken after column activation. Total cumulative error at the highest point for nitrogen isotherm is about 1.7 percent and for oxygen it is about 2.4 percent at 23°C. Therefore, largest uncertainty is for the last few data points on the isotherms. Table 4 provides uncertainties in the isotherms which are obtained from volumetric system.

Table 4 Uncertainty in Pure Component Adsorption Isotherms Obtained from Volumetric System

<table>
<thead>
<tr>
<th>Gas</th>
<th>Minimum Error</th>
<th>Maximum Error</th>
<th>Average Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absolute (mol/kg)</td>
<td>%</td>
<td>Absolute (mol/kg)</td>
</tr>
<tr>
<td>N₂</td>
<td>± 0.002</td>
<td>± 0.15</td>
<td>± 0.022</td>
</tr>
<tr>
<td>O₂</td>
<td>± 0.001</td>
<td>± 0.30</td>
<td>± 0.011</td>
</tr>
</tbody>
</table>
4.2 Pure Component Isotherm Data Modeling

The model used in the present work for pure isotherms is Dual-Site Langmuir model. The model parameters were obtained by a least squares method that minimizes differences between experimental and calculated data using non-linear regression. These parameters are listed in Table 5. DSL model represents pure component isotherm data as can be observed in isotherm and virial plots.

Table 5. Dual-Site Langmuir Parameters for N2/O2 Adsorption on LiLSX Zeolite

<table>
<thead>
<tr>
<th>DSL Parameters</th>
<th>Nitrogen</th>
<th>Standard Error</th>
<th>Oxygen</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_1$(mmol/g)</td>
<td>1.77</td>
<td>± 0.204</td>
<td>1.24</td>
<td>± 0.403</td>
</tr>
<tr>
<td>$b^0 \times 10^{-7}$(kPa$^{-1}$)</td>
<td>1.24</td>
<td>± 0.346</td>
<td>1.58</td>
<td>± 0.467</td>
</tr>
<tr>
<td>H1/R(K)</td>
<td>3365</td>
<td>± 120.5</td>
<td>2373</td>
<td>± 438.1</td>
</tr>
<tr>
<td>$m_2$(mmol/g)</td>
<td>2.10</td>
<td>± 0.109</td>
<td>5.40</td>
<td>± 1.23</td>
</tr>
<tr>
<td>$d^0 \times 10^{-6}$(kPa$^{-1}$)</td>
<td>5.13</td>
<td>± 0.921</td>
<td>3.39</td>
<td>± 0.508</td>
</tr>
<tr>
<td>H2/R(K)</td>
<td>2263</td>
<td>± 99.44</td>
<td>1221</td>
<td>± 139</td>
</tr>
</tbody>
</table>
4.3 Binary Adsorption Equilibrium Results

4.3.1 Binary Adsorption Isotherms Measurement Results

Binary adsorption measurements, compared to pure component measurements, is time consuming because of additional degree of freedom i.e., there are three degrees of freedom for a binary system. Typically, two out of the three are held constant as temperature, pressure and gas composition is varied. The accuracy of results is proportional to the complexity of measurements. The partial amounts are calculated as differences in material balances for the system before and after gases are contacted on activated sample. The results from these experiments are compared to predictions from Dual-Site Langmuir model. Resulting phase diagram are for the model and data are shown in Figures 13. The results are also tabulated in Table 6.

4.3.2 Analysis of Binary Adsorption Data

4.3.2 a) Variation of Partial and Total Amounts Adsorbed with Gas Composition

The partial amounts adsorbed and total amounts adsorbed from the gas mixture varying with composition at constant temperature (296.15K) and constant pressure (241.6kPa) are represented in Figure 13. As expected the partial amount adsorbed for nitrogen increases as the mole fraction of nitrogen increases while the partial amount adsorbed for oxygen decreases. The oxygen and nitrogen pure component limits on graphs related to pure
component isotherm values at same temperature and pressure. This provides a simple check for accuracy of binary adsorption data (Talu 1998). This is the only thermodynamic requirement for the plot. It can been seen that the DSL predictions are within the accuracy of experimental data.
Figure 13 Amounts Adsorbed Vs Gas Composition

(N$_2$ and O$_2$ on LiLSX at 296.15K and 241.6kPa)
Table 6 Binary Equilibrium Data for N2 and O2 in LiLSX at 296.15K

<table>
<thead>
<tr>
<th>$y_{N_2}$ (mol/kg)</th>
<th>$N_{N_2}$ (mol/kg)</th>
<th>Standard Error ($\pm$)</th>
<th>$N_{O_2}$ (mol/kg)</th>
<th>Standard Error ($\pm$)</th>
<th>N (mol/kg)</th>
<th>Standard Error ($\pm$)</th>
<th>Equilibrium Pressure (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.21</td>
<td>0.0212</td>
<td>0.32</td>
<td>0.0486</td>
<td>0.52</td>
<td>0.0439</td>
<td>35.85</td>
</tr>
<tr>
<td>0.10</td>
<td>0.39</td>
<td>0.0234</td>
<td>0.28</td>
<td>0.0468</td>
<td>0.67</td>
<td>0.0420</td>
<td>35.95</td>
</tr>
<tr>
<td>0.80</td>
<td>1.48</td>
<td>0.0513</td>
<td>0.06</td>
<td>0.0240</td>
<td>1.54</td>
<td>0.0472</td>
<td>35.9</td>
</tr>
<tr>
<td>0.4</td>
<td>1.04</td>
<td>0.0340</td>
<td>0.16</td>
<td>0.0392</td>
<td>1.20</td>
<td>0.0403</td>
<td>35.85</td>
</tr>
<tr>
<td>0.6</td>
<td>1.28</td>
<td>0.0428</td>
<td>0.12</td>
<td>0.0330</td>
<td>1.40</td>
<td>0.0422</td>
<td>36</td>
</tr>
<tr>
<td>0.2</td>
<td>0.68</td>
<td>0.0255</td>
<td>0.23</td>
<td>0.0490</td>
<td>0.90</td>
<td>0.0453</td>
<td>35.85</td>
</tr>
<tr>
<td>0.95</td>
<td>1.62</td>
<td>0.0579</td>
<td>0.02</td>
<td>0.0205</td>
<td>1.64</td>
<td>0.0543</td>
<td>35.85</td>
</tr>
<tr>
<td>0.90</td>
<td>1.57</td>
<td>0.0558</td>
<td>0.04</td>
<td>0.0213</td>
<td>1.61</td>
<td>0.0518</td>
<td>35.95</td>
</tr>
</tbody>
</table>
4.3.2 b) Binary Equilibrium Measurements Uncertainties

The uncertainties in binary adsorption measurements are higher compared to pure component experiments. These include:

1) **Dependency on Compositions Measured by GC:** The material balances in these experiments are dependent on compositions and
these are measured by GC which have higher standard deviation
(±0.5% for composition).

2) The partial amounts adsorbed for lighter component is lowered
because of the presence of heavy component. The material balances
resulting in smaller values are thus associated with large errors.
Therefore, the uncertainties in binary experiments using closed
volumetric system increases with increase in selectivity of heavily
adsorbed component.

Table 7 gives percentage of uncertainties in binary adsorption
experiments calculated using propagation of error analysis.

<table>
<thead>
<tr>
<th>Gas 1</th>
<th>Gas 2</th>
<th>Error % in total amount adsorbed (N)</th>
<th>Error % in Selectivity</th>
<th>Error % in x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>Oxygen</td>
<td>3.87</td>
<td>23.27</td>
<td>2.85</td>
</tr>
</tbody>
</table>

4.3.2 c) The X-Y plot

The x-y plot is function of temperature and pressure as there is an extra
degree of freedom. Figure.14 shows x-y plot for nitrogen and oxygen in LiLSX
at constant temperature(296.15) and constant pressure (241.6kPa). This
gives overview of adsorption for this gas mixture. Figure 14 shows that the solid adsorbent LiLSX is heavily selective towards nitrogen in nitrogen-oxygen mixture. Since, none of the curves in the x-y plot does not cross each other azeotrope does not occur for this system with considered conditions. These plots do not completely characterize binary adsorption as total amount adsorbed data is required for complete characterization.
4.3.2 d) Variation of Selectivity with Gas Phase Composition

The variation of selectivity with gas composition at constant temperature (296.15K) and constant pressure (261.6kPa) is shown in Figure.15. Selectivity is one of the most important parameters in adsorption processes. For practical applications, selectivity determines the efficiency of a separation process. The effectiveness of separation depends crucially on the selection of adsorbent with large differences in adsorption of individual components. For all thermodynamically consistent data/model at constant temperature and pressure must cross each other at least once since the standard states (at two ends of the diagram) are the same. This is a result of integral thermodynamic consistency test. The requirement for this plot is that the experimental data curve and the curve obtained from DSL model must cross each other only once throughout the composition. The selectivity curve shown in Figure.15 conforms to the trend and as explained, these two curves cross each other only once.

At constant pressure, selectivity decreases with increase in composition of heavily adsorbed component. Thus, decrease of selectivity with increasing solid loading is a typical behavior for binary adsorption occurring in a heterogenous system. In addition, selectivity at any finite loading can never be greater than surface selectivity at infinite dilution (on completely clean surface). From this Figure.15, it can been seen that it does not conform
to the trend as explained in the last statement because it shows a slight increase in selectivity exceeding limiting value at low values. This may be a result of some molecular packing issues as N$_2$ replaces O$_2$. It is also noted that there are no thermodynamic restrictions for the behavior of selectivity with composition in checking the data.

In Figure.15, the intercept is the ratio of pure Henry’s law constants. All the trajectories must approach that value and it is evident from the graph that all the curves i.e., experimental selectivity plot, DSL model selectivity and limiting selectivity approach the same value. If the experiments are not performed accurately, the uncertainties in the results will reach to unacceptable levels specially for variables such as selectivity. The uncertainty in measured selectivity goes to infinity as composition approaches zero (Orhan Talu 1996).
Figure 15 Selectivity of N2/O2 on LiLSX Varying with Composition
4.3.3 Evaluation of Binary Adsorption Data

There are simple checks to be considered while evaluating the accuracy of binary adsorption data. These include:

1) The total amount adsorbed from a binary mixture must approach the respective pure component isotherm values as the mole fraction approaches unity. From Figure 13, it is evident that at considered temperature (23°C) and pressure (241.6 kPa), the limits on the plot gives respective pure component isotherm values.

2) The selectivity must approach the ratio of pure component Henry’s law constants as pressure approaches zero regardless of gas composition in the mixture. It should be noted that data presented in Figure 15 for selectivity is at constant pressure and temperature and there are no thermodynamic limitations to exclude the observed data.
5.1 Pure Component Equilibrium Measurements using Volumetric System

“Adsorption equilibrium data are the ultimate characterization of a porous adsorbent from an application perspective. (Talu 1998). Pure component equilibrium data are the most basic measurements. A closed volumetric system is used to measure pure component adsorption equilibria of nitrogen and oxygen in LiLSX at temperatures 4°C, 23°C, 45°C. Nitrogen has higher quadrupole moment compared to oxygen and thus, interacts stronger with cation sites in LiLSX. This results in larger adsorption of nitrogen in LiLSX. The adsorption capacity on the adsorbent increases with decreasing temperature for adsorbates, since physical adsorption is always an exothermic process. The pure component isotherms were modeled using
Dual-Site Langmuir model. Predicting mixture behavior from pure component adsorption data is very sensitive to Henry’s law constants. Therefore, it is extremely important 1) to determine Henry’s law constants in experiments and 2) to assure that models used conform to Henry’s law.

5.2 Binary Adsorption Equilibrium Measurements using Volumetric System

Direct measurement of mixture equilibria is complicated and time consuming even for a binary system due to extra degree of thermodynamic freedom in adsorption. Binary adsorption isotherms for nitrogen and oxygen were measured at various compositions at constant temperature (23°C) and constant pressure (241.6kPa). These were predicted by Dual-Site Langmuir model and the data measured is compared with the model. DSL prediction closely matched experimentally measured total amount adsorbed results for the complete range of composition. The reason is the total amount adsorbed is controlled by heavily adsorbed component.

Adsorption selectivity is extremely an important property in adsorption, analogous to relative volatility of vapor-liquid equilibria. Selectivity varies between 12 to 5 as loading increases at 23°C and 241.6kPa. One of the primary objectives of this work was to determine adsorption selectivity in equilibrium measurements with minimal amount of experimental input. Measuring this thermodynamic variable is a challenging task as small errors in the measurements are greatly magnified. This
difficulty is due to the fact that surface phase properties are only measurable as changes in gas phase unlike directly measurable quantities. And, for the lighter component the amount adsorbed is so small compared to the total amount of that component in the apparatus. From the results of experimental measurements, it is obvious that the percent error in selectivity is large compared to total amount adsorbed. Further, the uncertainties in selectivity goes to infinity as the composition approaches unity for either species in a binary mixture.

Therefore, from pure component and binary mixture isotherm data of Nitrogen-Oxygen in LiLSX zeolite, it can be concluded that LiLSX is a good adsorbent for air separation due to its high selectivity for nitrogen over oxygen.

**Recommendations**

- More binary adsorption experiments can be performed at different pressures and constant composition cross section.

- Different models can be used and compare them against Dual-Site Langmuir model thus, models can be scrutinized as molecular simulations become important tools.
REFERENCES


APPENDIX
Appendix A. Propagation of Error Analysis in Primary Measurements

Estimating the impact of uncertainties in experimental measurements on thermodynamic properties is necessary as some of the quantities measured depend on accuracy of the measurement of others. The pure and binary component adsorption experimental data was collected using closed volumetric system. The measurements involved in the closed system that appear in equations used to calculate total and partial amounts adsorbed are:

a.) Pressure measured by a transducer at different times.

b.) Volumes that are measured in the different parts of the apparatus using helium expansion techniques.

c.) Temperature measured by a thermocouple in the column and controlled by an external bath.

d.) Gas composition at equilibrium measured using gas chromatograph(GC) and

e.) Mass of porous solid in the column which was measured using balance.

Indeed, all these measurements are related to only three measurements: a.) Pressure, b.) Mass, and c.) Temperature.

There are numerous ways to estimate the uncertainties in measurements that have impact on final calculated results. One technique used in the present work is propagation of error analysis, which calculates the most
probable errors on the final results. If a quantity $X$ is calculated by a mathematical expression,

$$X = f(Y,Z,...) \quad \text{A.1}$$

where $Y, Z,...$ measurements are subjected to uncertainty of $\Delta Y, \Delta Z,...$, then the uncertainty in $X$ i.e., $\Delta X$ can be estimated as (Freund 1977)

$$\Delta X = \left( \sqrt{\left( \frac{\partial y}{\partial x} \cdot \Delta Y \right)^2 + \left( \frac{\partial y}{\partial x} \cdot \Delta Y \right)^2 + ...} \right) \quad \text{A.2}$$
Appendix B. Gas Chromatograph Calibration

This section summarizes the results of GC calibration. In binary adsorption experiments, the gas phase composition at equilibrium is analyzed using gas chromatograph. The K-factor is given by equation (3.4.2g) which is related to gas phase composition of the mixture being analyzed through equation (3.4.2e).

Table B.1 lists the results of GC calibration performed for binary mixture of Nitrogen-Oxygen at different gas phase compositions. The column $y_{O2}$ represents actual mole fraction of oxygen in calibration gas mixture. The column $\%A_{O2}$ indicates the area that counts under peak for oxygen. The values in the columns $y_{pred}$ and $d(y)$ corresponds to predictions for mole fraction of $O_2$ using parameters obtained from calibration experiments and standard deviation for mole fraction of $O_2$ respectively. The last column $\%CV$ gives values of percentage difference between the predicted and calibrated values.
Table B.1 Results of GC Calibration for Nitrogen-Oxygen Mixture

<table>
<thead>
<tr>
<th>yo₂</th>
<th>%AO₂</th>
<th>K-GC</th>
<th>K-pred</th>
<th>y_pred</th>
<th>d(y)</th>
<th>%CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.056</td>
<td>5.54%</td>
<td>1.006</td>
<td>0.984</td>
<td>0.055</td>
<td>-0.00104</td>
<td>-1.909</td>
</tr>
<tr>
<td>0.206</td>
<td>20.05%</td>
<td>1.0317</td>
<td>1.024</td>
<td>0.204</td>
<td>-0.0012</td>
<td>-0.585</td>
</tr>
<tr>
<td>0.401</td>
<td>38.49%</td>
<td>1.069</td>
<td>1.075</td>
<td>0.402</td>
<td>0.00117</td>
<td>0.291</td>
</tr>
<tr>
<td>0.501</td>
<td>48.11%</td>
<td>1.082</td>
<td>1.102</td>
<td>0.505</td>
<td>0.00433</td>
<td>0.857</td>
</tr>
<tr>
<td>0.604</td>
<td>57.61%</td>
<td>1.120</td>
<td>1.128</td>
<td>0.605</td>
<td>0.00159</td>
<td>0.264</td>
</tr>
<tr>
<td>0.798</td>
<td>77.61%</td>
<td>1.144</td>
<td>1.183</td>
<td>0.804</td>
<td>0.00539</td>
<td>0.671</td>
</tr>
<tr>
<td>0.944</td>
<td>93.04%</td>
<td>1.272</td>
<td>1.225</td>
<td>0.942</td>
<td>-0.00199</td>
<td>-0.212</td>
</tr>
</tbody>
</table>
Appendix C. Pure Adsorption Equilibrium Data for Nitrogen-Oxygen in LiLSX Zeolite

The data for all the pure component isotherms and virial plots in their domains i.e., N vs P and ln(P/N) vs N respectively represented in Figures 9 to 12 are shown in Tables below.

Table C.1 Pure Component Experimental Isotherm Data for Nitrogen on LiLSX

<table>
<thead>
<tr>
<th>N2 isotherm data 23°C</th>
<th>P(kPa)</th>
<th>N(mol/kg)</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.24</td>
<td>0.13</td>
<td>± 0.001</td>
</tr>
<tr>
<td></td>
<td>28.62</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>81.36</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>190.99</td>
<td>1.52</td>
<td>± 0.013</td>
</tr>
<tr>
<td></td>
<td>367.17</td>
<td>1.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>562.99</td>
<td>2.28</td>
<td>± 0.029</td>
</tr>
<tr>
<td></td>
<td>1.59</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.41</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.17</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.37</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>61.023</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>107.57</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>175.83</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>32.06</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>61.02</td>
<td>0.81</td>
<td></td>
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<tr>
<td></td>
<td>107.22</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>176.17</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>P(kPa)</td>
<td>N(mol/kg)</td>
<td>Standard Error</td>
<td>P(kPa)</td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
<td>----------------</td>
<td>--------</td>
</tr>
<tr>
<td>10.69</td>
<td>0.10</td>
<td>+0.0017</td>
<td>3.31</td>
</tr>
<tr>
<td>42.33</td>
<td>0.35</td>
<td></td>
<td>16.16</td>
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<tr>
<td>106.87</td>
<td>0.73</td>
<td></td>
<td>55.85</td>
</tr>
<tr>
<td>221.34</td>
<td>1.16</td>
<td>+0.0112</td>
<td>162.03</td>
</tr>
<tr>
<td>387.51</td>
<td>1.55</td>
<td></td>
<td>350.62</td>
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<tr>
<td>570.92</td>
<td>1.84</td>
<td>+0.0156</td>
<td>556.44</td>
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</tbody>
</table>
Table C.2 Pure Component Experimental Isotherm Data for Oxygen on LiLSX

<table>
<thead>
<tr>
<th>O2 isotherm 23°C</th>
<th>O2 isotherm 45°C</th>
<th>O2 isotherm 4°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(kPa)</td>
<td>N(mol/kg)</td>
<td>Standard Error</td>
</tr>
<tr>
<td>21.09</td>
<td>0.03</td>
<td>± 0.0013</td>
</tr>
<tr>
<td>71.98</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>154.79</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>272.01</td>
<td>0.43</td>
<td>± 0.0078</td>
</tr>
<tr>
<td>425.43</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>590.57</td>
<td>0.86</td>
<td>± 0.010</td>
</tr>
</tbody>
</table>