Revisiting the Volumetric Swing Frequency Response Method for the Determination of Limiting Mass Transfer Mechanisms of N\textsubscript{2} and O\textsubscript{2} in Carbon Molecular Sieve 3K172

Adam Marshall Burke

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Revisiting the Volumetric Swing Frequency Response Method for the Determination of Limiting Mass Transfer Mechanisms of N\textsubscript{2} and O\textsubscript{2} in Carbon Molecular Sieve 3K172

by

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Bachelor of Science
University of South Carolina, 2022

Submitted in Partial Fulfillment of the Requirements
For the Degree of Master of Science in
Chemical Engineering
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Abstract

Adsorption-based separations processes, along with the adsorbents that enable them, have benefited from a greater particular focus in recent years, following a desire to improve process energy efficiencies and cost economics. One such adsorbent, carbon molecular sieves (CMS), have likewise been a greater focus. CMS materials offer several key practical uses, such as the separation of nitrogen and oxygen, and the removal of carbon dioxide from methane process streams. In order to effectively design and implement an industrial scale process using a CMS material, the behavior of these gases on the chosen material must be known, including the limiting mass transfer regime. As frequency response methodology has proven useful in the individual determination of limiting mass transfer mechanisms, a volumetric swing frequency response (VSFR) apparatus built in-house at the University of South Carolina was used to collect experimental data, which was then modeled using COMSOL Multiphysics and MATLAB in an effort to identify the characteristic limiting mass transfer mechanisms of nitrogen and oxygen on one such CMS material.

The aforementioned VSFR method is relatively simple in approach: the volume of the system is sinusoidally perturbed, and the differential pressure between this system volume and a reference volume is measured as the response variable to the volume perturbation. The VSFR system constructed at the University of South Carolina is capable of operating at a wide range of frequencies, which allows mass transfer
mechanisms to be identified equally as effectively for different gases which may possess
a large range of diffusion rates. The frequency response variables, intensity and phase
lag, were determined from the data obtained using this VSFR apparatus, and several
variations of a micropore model were used to fit this experimental data in an effort to
identify the limiting mass transfer characteristics for nitrogen and oxygen on a sample of
Shirasagi CMS 3K172. Data was collected at a temperature of 25°C for pressures of 100
and 200 torr, and collected at a pressure of 750 torr at temperatures of 20, 30, 40, and
50°C for both nitrogen and oxygen on this material.

Multiple frequency regions in the experimental data observed for nitrogen and
oxygen indicated the presence of several important mechanisms. At low frequencies,
large plateau values of the intensity and near-zero values for the phase lag indicated the
absence of any limitations to mass transfer, and that the system was mainly governed by
local isothermal equilibrium conditions. At intermediate frequencies, a sharp decrease in
the experimental intensity curves and the growth of a peak in the phase lag curves
signified the emergence of micropore diffusion as the limiting mass transfer mechanism
for this frequency range. At high frequencies, the intensity curves leveled off to near-zero
values, and the phase lag peaks decreased to low/intermediate value plateaus, which
indicated the dominance of resistance at the micropore mouth, as well as some behavior
in the macropore that was not approximated by any micropore models.

The best-fit model results for nitrogen and oxygen on Shirasagi CMS 3K172
indicated that the most likely mass transfer model for nitrogen on this material was a
single site micropore diffusion limitation paired with a limitation at the micropore mouth,
and that both of these mass transfer coefficients followed a more complex loading
dependence than Darken’s original model. This behavior was described by an empirical Qinglin’s loading dependence approach. For oxygen, the most likely mass transfer model was observed to be a dual site micropore diffusion limitation paired with a single micropore mouth limitation. Likewise, each of these three mass transfer coefficients were observed to follow a loading dependence more complex than that which is predicted by Darken’s model.
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<td>K_{mo,r,2}</td>
<td>Input parameter for mouth resistance coefficient in loading 2, (s^{-1})</td>
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$K_{mo}^*$ Loading-adjusted mouth resistance coefficient for single site, s$^{-1}$

$K_{mo,1}^*$ Loading-adjusted mouth resistance coefficient in loading 1, s$^{-1}$

$K_{mo,2}^*$ Loading-adjusted mouth resistance coefficient in loading 2, s$^{-1}$

$K_s$ Overall mass transfer coefficient for diffusion in micropore, s$^{-1}$

$K_{s,1}$ Diffusion mass transfer coefficient in micropore in loading 1, s$^{-1}$

$K_{s,2}$ Diffusion mass transfer coefficient in micropore in loading 2, s$^{-1}$

$K_{s,r}$ Input parameter for diffusion in micropore for single site, s$^{-1}$

$K_{s,r,1}$ Input parameter for diffusion in micropore in loading 1, s$^{-1}$

$K_{s,r,2}$ Input parameter for diffusion in micropore in loading 2, s$^{-1}$

$K_s^*$ Loading-adjusted micropore diffusion coefficient for single site, s$^{-1}$

$K_{s,1}^*$ Loading-adjusted micropore diffusion coefficient in loading 1, s$^{-1}$

$K_{s,2}^*$ Loading-adjusted micropore diffusion coefficient in loading 2, s$^{-1}$

$m$ Mass of adsorbent, kg

$n$ Heterogeneity parameter for Toth isotherm, unitless

$n_i$ Value of Toth heterogeneity parameter at $T_o$, unitless

$n_o$ Base value of heterogeneity parameter, unitless

$n_r$ Value of Toth heterogeneity parameter at $T_r$, unitless

$n_t$ Temperature dependence term for heterogeneity Toth parameter, K

$n_{tot}$ Total moles of adsorbing gas species in working volume, mol

$\dot{n}$ Molar gas flow rate in the volume external to the sample, mol/s
\( P \)  
System pressure (absolute), kPa

\( P_b \)  
Bed pressure (absolute), kPa

\( P_{e,o} \)  
Equilibrium pressure (absolute) of empty system, kPa

\( P_{He,o} \)  
Equilibrium pressure (absolute) with helium, kPa

\( P_o \)  
Equilibrium (average) pressure in system with adsorbent, kPa

\( P_p \)  
Pressure (absolute) in macropore volume, kPa

\( \bar{P}_p \)  
Average pressure (absolute) in macropore volume, kPa

\( P_r \)  
Reference pressure at reference temperature \( T_r \), kPa

\( P_{ss,o} \)  
Equilibrium pressure (absolute) with stainless-steel beads, kPa

\( q \)  
Actual loading of adsorbate in micropore domain, mol/kg

\( \bar{q} \)  
Average loading in micropore domain, mol/kg

\( \bar{\bar{q}} \)  
Average loading in overall adsorbent pellet domain, mol/kg

\( q^* \)  
Overall loading determined by isotherm, mol/kg

\( q_1 \)  
Actual loading in the micropore at first site, mol/kg

\( q_2 \)  
Actual loading in the micropore at second site, mol/kg

\( q_1^* \)  
Loading determined by isotherm at first site, mol/kg

\( q_2^* \)  
Loading determined by isotherm at second site, mol/kg

\( q_o \)  
Overall equilibrium loading in the micropore, mol/kg

\( q_{o,1} \)  
Equilibrium loading in the micropore at first site, mol/kg

\( q_{o,2} \)  
Equilibrium loading in the micropore at second site, mol/kg
<table>
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<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$q_r$</td>
<td>Equilibrium loading at reference temperature $T_r$, mol/kg</td>
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<tr>
<td>$q_{r,1}$</td>
<td>Equilibrium loading at $T_r$ in first site, mol/kg</td>
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<td>$q_{r,2}$</td>
<td>Equilibrium loading at $T_r$ in second site, mol/kg</td>
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<tr>
<td>$q_s$</td>
<td>Saturation loading as determined by isotherm, mol/kg</td>
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<td>$q_{s,i}$</td>
<td>Initial saturation loading at equilibrium temperature $T_o$, mol/kg</td>
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<tr>
<td>$q_{s,o}$</td>
<td>Temperature-independent base value of saturation loading, mol/kg</td>
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<td>$q_{s,r}$</td>
<td>Saturation loading at reference temperature $T_r$, mol/kg</td>
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<td>$q_{s,t}$</td>
<td>Temperature dependence term for saturation loading, mol/kg/K</td>
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<tr>
<td>$R$</td>
<td>Ideal gas constant, 8.314 J/mol/K</td>
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<tr>
<td>$R_c$</td>
<td>Radius of micropore crystal, m</td>
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<td>$R_p$</td>
<td>Radius of adsorbent pellet, m</td>
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<tr>
<td>$r_c$</td>
<td>Radial coordinate within micropore crystal, m</td>
</tr>
<tr>
<td>$r_p$</td>
<td>Radial coordinate within adsorbent pellet, m</td>
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<td>$T$</td>
<td>Temperature in micropore domain, K</td>
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<td>$T^*$</td>
<td>Temperature at interface between sample and external volume, K</td>
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<td>$T_b$</td>
<td>Temperature in the sample bed, K</td>
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<tr>
<td>$T_{ext}$</td>
<td>Temperature in the volume external to adsorbent sample, K</td>
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<tr>
<td>$T_o$</td>
<td>Initial, equilibrium temperature of working volume, K</td>
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<tr>
<td>$T_r$</td>
<td>Reference temperature used in temperature dependencies, K</td>
</tr>
<tr>
<td>$t$</td>
<td>Time, s</td>
</tr>
</tbody>
</table>
\( \bar{U}_a \) Average internal energy of adsorbate, J/mol

\( U_{g,i} \) Internal energy of gas in interstitial volume, J/mol

\( U_{g,M} \) Internal energy of gas in macropore volume, J/mol

\( U_s \) Internal energy of adsorbent, J/kg

\( V_{acc} \) Accessible gas volume with helium, m³

\( V_{acc,adj} \) Non-helium gas accessible volume, m³

\( V_e \) Empty volume, m³

\( V_{ext} \) Volume completely external to sample chamber, m³

\( V_{ext,o} \) Exterior volume average, m³

\( V_{gb} \) Volume of glass beads, m³

\( V_{g,i} \) Interparticle volume, m³

\( V_{g,M} \) Macropore volume, m³

\( V_{g,m} \) Micropore volume, m³

\( V_{g,p} \) Total pore volume, m³

\( V_s \) Skeletal volume, m³

\( V_{ss} \) Volume of stainless-steel beads, m³

\( V_t \) Total working volume, m³

\( V_{t,o} \) Average total working volume, m³

\( Z_e \) Correction factor for empty volume determination, unitless

\( \alpha \) Parameter to define dual site split in the micropore, unitless
\( \beta_{mo} \) Pressure dependence parameter for \( K_{mo,p} \), unitless

\( \beta_{mo,1} \) Pressure dependence parameter for \( K_{mo,p,1} \), unitless

\( \beta_{mo,2} \) Pressure dependence parameter for \( K_{mo,p,2} \), unitless

\( \beta_{s} \) Pressure dependence parameter for \( K_{s,p} \), unitless

\( \beta_{s,1} \) Pressure dependence parameter for \( K_{s,p,1} \), unitless

\( \beta_{s,2} \) Pressure dependence parameter for \( K_{s,p,2} \), unitless

\( \Delta H^* \) Magnitude of change in enthalpy at sample boundary, J/mol

\( \Delta H_a \) Heat of adsorption, J/mol

\( \Delta P \) Magnitude of pressure change, kPa

\( \Delta P_e \) Magnitude of pressure change in empty system, kPa

\( \Delta P_{He} \) Magnitude of pressure change with helium, kPa

\( \Delta P_{ss} \) Magnitude of pressure change with stainless steel beads, kPa

\( \Delta t \) Magnitude of time interval, s

\( \Delta V \) Change in system volume, m\(^3\)

\( \Delta \delta \) Magnitude of shaft displacement, m

\( \delta \) Shaft position, m

\( \delta_{\text{max}} \) Maximum shaft position, m

\( \delta_{\text{min}} \) Minimum shaft position, m

\( \delta_{mp} \) Shaft midpoint position, m

\( \epsilon_b \) Bulk (interparticle) porosity, unitless
\( \epsilon_M \)  Macropore porosity, unitless

\( \epsilon_m \)  Micropore porosity, unitless

\( \epsilon_p \)  Total pore porosity, unitless

\( \theta \)  Overall fractional coverage of adsorbate, unitless

\( \theta_1 \)  Fractional coverage of adsorbate at first site, unitless

\( \theta_2 \)  Fractional coverage of adsorbate at second site, unitless

\( \theta_r \)  Overall initial, equilibrium fractional coverage at \( T_r \), unitless

\( \theta_{r,1} \)  Initial, equilibrium fractional coverage at \( T_r \) at first site, unitless

\( \theta_{r,2} \)  Initial, equilibrium fractional coverage at \( T_r \) at second site, unitless

\( \xi_c \)  Dimensionless radial position within micropore crystal, unitless

\( \pi \)  Pi, \(~3.14\) unitless

\( \rho_b \)  Bulk density (guess value), kg/m\(^3\)

\( \rho_p \)  Pellet density (guess value), kg/m\(^3\)

\( \rho_s \)  Skeletal density, kg/m\(^3\)

\( \phi \)  Phase “lag” of response curve, degrees

\( \phi_P \)  Phase angle of output variable, degrees

\( \phi_\delta \)  Phase angle of input variable, degrees
Chapter 1: Introduction

In any industrial-scale chemical process, the reaction step(s) to obtain the desired product(s) only accounts for one part of the process at hand; the product created must be purified or separated out from undesired side products or remaining feedstocks. As such, separation process design and its supporting research endeavors are immensely important to the fields of chemical engineering and industrial chemistry. Additionally, process economics justify the desire for continuous improvement of separations processes: separation steps may account for as much as 40-60% of the overall operating cost and the initial capital investment of a chemical process [1]. Although many separation process methods have had thorough research and investment, such as membrane separation or cryogenic distillation, adsorption processes have been considered as an alternative that does not require very low process temperatures or the high operating cost that often accompanies cryogenic operations.

Adsorption, a process in which a gas-phase molecule may preferentially adhere to the surface of a solid-phase “adsorbent”, may be used for the separation of two or more gas species at or near ambient temperatures. Although natural aluminosilicate formations, zeolites, have seen use in adsorptive separation of gases, there are numerous other materials that can achieve similar degrees of separation. One such material, carbon molecular sieves (CMS), have proven particularly useful in the separation of nitrogen and oxygen from an air feed. CMS materials may be formed from coal tar via high
temperature carbonization and oxidation followed by pelletizing, drying and treatment steps [2]. The separation between nitrogen and oxygen using a CMS material is facilitated by differences in adsorption kinetics between the two. While it may be noted that the equilibrium adsorption of oxygen and nitrogen are very close to one another, oxygen can achieve a higher rate of adsorption onto CMS materials, thus enabling separation between the two most prevalent components of air [3].

In order to properly select an adsorbent that will meet desired performance characteristics for a specific gas separation, the limiting mass transfer mechanisms for each adsorbate-adsorbent pair in a process should be known. Given that CMS materials are porous adsorbents, there are several mass transfer mechanisms that may be considered: Knudsen diffusion, viscous flow, surface diffusion, and mouth (or barrier) resistance. Knudsen diffusion is a form of gaseous diffusion that is governed by molecules of the diffusing species colliding with the walls of a pore of smaller diameter than the molecule’s mean free path, rather than by the collisions of gas molecules with one another [4]. Viscous flow is often described using Darcy’s Law to represent gas or fluid flow in a porous medium. Surface diffusion is characterized by a large surface gradient on high surface area pore walls, where molecules in essence “hop” from one adsorption site to another. Mouth resistance is the bottleneck effect created by a constriction at the passage from the macropore to the micropore. The word “sieve” in CMS materials is often in reference to this observed mouth resistance effect, which may facilitate size-specific separations of gases.

Frequency response experiments are a useful tool in identifying or ruling out these aforementioned limiting mass transfer mechanisms. As the name suggests, an input
variable is sinusoidally perturbed, and the output “response” variable may be measured across a range of frequencies for the perturbation waveform function. There are several established frequency response methods, each tied to a specific variable that may be perturbed: volume, pressure, or concentration.

The direct perturbation of system pressure is facilitated in a Pressure Swing Frequency Response (PSFR) method using a pressure flow controller. Flow rates of gas leaving the system are recorded as the corresponding response variable. This system offers greater control over sustained local isothermal conditions, as this apparatus is designed as an open flow system, rather than as a batch system. As such, the gas flowing through the system increases the average value of the heat capacity of the system, and so the heat of adsorption of a given adsorbent will have a smaller effect on the temperature change brought about by adsorption/desorption in this type of system. However, the useful data that can be obtained using PSFR methods does not extend past a frequency of around 0.5 Hz, as measurements become difficult to obtain at higher frequencies. As such, only mass transfer mechanisms that are prevalent at lower frequencies are able to be characterized by this method [5].

Concentration may also be sinusoidally perturbed, in the Concentration Swing Frequency Response (CSFR) method. This method is applicable to mixtures, where the variation in the concentration of one component is achieved through the use of a pair of mass flow controllers. The composition of the effluent leaving the test bed will vary in response to the input concentration perturbations for this method, and measurements are taken with a mass spectrometer. As is the case with the PSFR method, the CSFR method
is an open flow technique, and so it accordingly shares the same benefits and drawbacks as those associated with the PSFR method [6].

The final method is the Volumetric Swing Frequency Response (VSFR) method, in which system volume is sinusoidally perturbed, and the system pressure is measured as a response variable via a differential pressure transducer. Unlike PSFR and CSFR methods, the VSFR method can reliably take measurements at higher frequencies, allowing a broader range of mass transfer mechanisms to be studied. A VSFR system was previously constructed at the University of South Carolina, and was used to characterize the mass transfer mechanisms of nitrogen and carbon dioxide on 13X zeolite, as well as nitrogen, oxygen, carbon dioxide, and argon on Shirasagi CMS 3K172 from Takeda Chemicals. Several variations of macropore and micropore models have been developed to determine limiting mass transfer mechanisms of adsorbent-adsorbate pairs through fitting the experimental response data [7,8].

The principal objective of this thesis was to refine the work conducted by Smithson several years prior, and to determine the limiting mass transfer regimes of nitrogen and oxygen on Shirasagi CMS 3K172 adsorbent at 750 torr for temperatures of 20, 30, 40, and 50°C, and at 100 and 200 torr for a temperature of 25°C. Both the original Shirasagi CMS 3K172 adsorbent and the original experimental data were used for this purpose. The changes to the models will be highlighted throughout the body of this thesis, and best-fit results for several variations of the micropore model will be discussed.
Chapter 2: Experimental Apparatus and Procedure

Volumetric Swing Frequency Response (VSFR) Apparatus

A general schematic of the in-house designed volumetric swing frequency response system (VSFR) used in this experiment is included in Figure 2.1. This apparatus is capable of obtaining empirical data points between frequencies of $5 \times 10^{-5}$ and 10 Hz, and may operate at a pressure and temperature range of 100 to 760 torr and 0 to 80 °C, respectively. The sample chamber is large enough to accommodate samples up to a mass of approximately 100 grams.

Figure 2.1 A schematic of the volumetric swing frequency response system (VSFR) designed and built in-house at the University of South Carolina
As shown in Figure 2.1, there are several volumes contained within the system that are relevant to a volumetric swing frequency response experiment. The darker gray portion represents the working volume of the system, the section of volume that is sinusoidally perturbed through the expansion and contraction of a metal bellows included in the working volume. The bellows are controlled by an eccentric sheave connected to a motor drive (not shown). The working volume also contains a jacketed sample chamber, where an adsorbent sample is placed for the purpose of VSFR testing. The sample chamber contains a thermocouple placed along the centerline to record temperature measurements. The position of the metal bellows and shaft assembly are recorded using the linear variable differential transducer (LVDT) shown above. The exact change of the working volume may be subsequently calculated from the linear position measurement. The light gray portion represents the reference volume, which is held at constant temperature using the two-liter ballast and temperature bath shown in Figure 2.1. This volume is used as the reference for the pressure setpoint of the test gas at a given experimental temperature. A differential pressure transducer is placed between the working and reference volumes to record the pressure change in the working volume relative to the reference volume, which is the output variable tied to the volumetric perturbation of the working volume. Total pressure in the system is measured via an absolute pressure transducer contained within the reference volume. Both the reference and working volumes are thermally insulated in an effort to resist any effects from ambient temperature fluctuations in the laboratory. The last volumetric section is the exterior volume, shown in white in Figure 2.1. This section connects the working volume with feed gas or a vacuum pump.
The key components of the system are listed alongside their pertinent manufacturer information in Table 2.1.

Table 2.1 List of VSFR System Components and Manufacturer Information

<table>
<thead>
<tr>
<th>Component Name</th>
<th>Manufacturer</th>
<th>Model or Part Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Servo Drive Motor</td>
<td>Automation Direct</td>
<td>SVL-204B</td>
</tr>
<tr>
<td>9:1 Speed Reducer</td>
<td>Shimpo Driver Inc.</td>
<td>VRAFC09P0901902T</td>
</tr>
<tr>
<td>AC Servo Drive</td>
<td>Automation Direct</td>
<td>SVA-2040L</td>
</tr>
<tr>
<td>AC Servo Drive Interface</td>
<td>Automation Direct</td>
<td>ZL-RTB50</td>
</tr>
<tr>
<td>Linear Variable Differential Transducer</td>
<td>TE Connectivity</td>
<td>DC-EC-250</td>
</tr>
<tr>
<td>Linear Encoder</td>
<td>US Digital</td>
<td>PE-250-1-I-D-L</td>
</tr>
<tr>
<td>Differential Pressure Transducer (±2.5 kPa)</td>
<td>Omegadyne Inc.</td>
<td>MMDDDB-10WBIV10P2C0T2A2CEPS</td>
</tr>
<tr>
<td>Absolute Pressure Transducer (1000 torr)</td>
<td>MKS</td>
<td>628A13TEE</td>
</tr>
<tr>
<td>Absolute Encoder</td>
<td>US Digital</td>
<td>A2-A-B-E-M-D</td>
</tr>
<tr>
<td>Metal Bellows Assembly</td>
<td>Standard Bellows Company</td>
<td>103-55</td>
</tr>
<tr>
<td>Temperature Controller</td>
<td>Omega Engineering Inc.</td>
<td>CNi1643-C24</td>
</tr>
<tr>
<td>Refrigerated Circulating Bath (13L)</td>
<td>VWR North America</td>
<td>1157P</td>
</tr>
<tr>
<td>Turbo Molecular Drag Pump</td>
<td>Adixen Drytel</td>
<td>1025</td>
</tr>
<tr>
<td>Ionization Gauge Controller</td>
<td>Granville-Phillips</td>
<td>350</td>
</tr>
<tr>
<td>Bellows Valves (1/4” VCR)</td>
<td>Swagelok</td>
<td>SS-BNV51-C</td>
</tr>
<tr>
<td>Bellows Valves (1/2” VCR)</td>
<td>Swagelok</td>
<td>SS-BN8FR8-C</td>
</tr>
</tbody>
</table>
Piping and piping connections are not listed in Table 2.1, but each piping section is constructed from stainless-steel CF high vacuum pipe and fittings. Direct control of the VSFR system and data acquisition are facilitated through the use of National Instruments LabVIEW software. The specific LabVIEW program used in conjunction with this system was designed in-house. The servo drive motor used to perturb the working volume is operated by a control system contained within the LabVIEW program and follows a pre-set subroutine for facilitating testing at 32 predetermined frequencies. The connections between the different system volumes are manipulated through the control of air actuated valves V1, V2, V3, and V4 (Swagelok Bellows Valves listed in Table 2.1) within LabVIEW. Data measurements from the absolute and differential pressure transducers, thermocouple, and LVDT are cataloged and saved as .txt files through LabVIEW and may be exported to Excel for subsequent analysis.

Activation of Adsorbent Sample

The water jacket surrounding the sample chamber was removed, and the adsorbent sample was placed in the chamber. Valves V1, V2, and V4 were opened, and valve V3 was closed (see Figure 2.1). This allowed the vacuum pump to mostly evacuate the gas phase within the system. Aluminum concentric sleeves and electric band heaters were placed around the sample chamber. The heating bands were connected to a Variac, which allowed precise temperature control during the regeneration phase. Together, the low pressure facilitated by the vacuum pump and the high temperatures attained via the heater bands allowed moisture or adsorbed gas to be purged off of the adsorbent sample. This activation procedure was sustained for a period of several hours or days, until the pressure measured at the vacuum pump was a stable reading below $1.5 \times 10^{-5}$ torr for a
period of a few hours. Following pressure stabilization of the system, the Variac was switched off and the system was allowed to cool to safe working temperatures. The heating bands and aluminum concentric sleeves were removed from the exterior of the sample chamber, and the water jacket was replaced around the sample chamber. Through the LabVIEW software control window, the chiller was switched on and set to the desired experimental temperature to begin circulating water around the outside of the sample chamber.

**Equilibration of Adsorbent Sample**

After attaining the desired experimental temperature reading from the thermocouple located in the sample chamber, valve V4 was shut. The desired gas cylinder was connected to a pressure regulator that fed into the system. The experimental pressure setpoint was established in LabVIEW, and valve V3 was opened to allow the test gas to enter the system. Valve V3 was programmed to automatically close at the pressure setpoint so as to not allow backflow towards the gas cylinder, and for most experimental conditions needed to be reopened several times to ensure that the system absolute pressure remained steady at the desired value. Next, the shaft connected to the metal bellows was moved and set such that the bellows were at their midpoint. Valve V2 was shut, and the system was left to reach a steady equilibrium temperature and pressure for a period of several hours or days. Following this, valve V1 was shut, and the differential pressure between the reference and working volumes was ensured to be steady at a value of zero prior to beginning an experimental run. Once equilibrium was attained, as outlined above, an experimental run could begin.
VSFR Experimental Procedures

A total of three procedures were necessary to properly and effectively determine the limiting mass transfer mechanisms and corresponding rates for an adsorbent-adsorbate pair. The three procedures all consisted of a sweep between low and high frequencies with numerous discrete frequency values selected within this range. The first procedure was conducted with the adsorbent-adsorbate pair in the system and was used to directly provide experimental data to aid in determining limiting mass transfer mechanisms for the pair. During this series of runs at several pressures and temperatures, pure nitrogen and oxygen were used individually as the test gases. The second procedure was carried out with a volume of glass beads equal in volume to the adsorbent sample in lieu of the adsorbent. The data collected during this procedure was used to correct the experimental data for thermal effects. These thermal effects, often observed at high frequencies, are a result of the compression and expansion of gas in dead volumes within the system. Given that the rate of heat transfer with these regions is very poor, the target temperature would no longer be able to be maintained in these regions. This second procedure was repeated for each of the same pressures, temperatures, and test gases used in the first procedure. The final procedure used helium in an empty sample chamber, or with the sample chamber filled with various porous and non-porous solids. Data collected during this procedure were used for the purpose of experimentally determining several volume constants within the working volume of the system that were subsequently used in computer modeling of the system. For this final procedure, only one pressure and temperature were needed to effectively collect data. These three procedures are explained in greater detail during the next few sections.
Experimental Runs with Adsorbent Sample

After attaining equilibrium in the system, the adsorbent sample (CMS 3K172 from Shirasagi) was tested with nitrogen and oxygen (UHP Grade from Airgas). The frequency sweep across 32 predetermined frequencies was initiated from the LabVIEW window. The experimental frequencies are listed in Table 2.2.

Table 2.2 List of Experimental Test Frequencies

<table>
<thead>
<tr>
<th>Frequencies (Hz)</th>
<th>7.0x10^-5</th>
<th>1.5x10^-3</th>
<th>3.0x10^-2</th>
<th>7.0x10^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0x10^-4</td>
<td>2.0x10^-3</td>
<td>5.0x10^-2</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1.5x10^-4</td>
<td>3.0x10^-3</td>
<td>7.0x10^-2</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>2.0x10^-4</td>
<td>5.0x10^-3</td>
<td>1.0x10^-1</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>3.0x10^-4</td>
<td>7.0x10^-3</td>
<td>1.5x10^-1</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>5.0x10^-4</td>
<td>1.0x10^-2</td>
<td>2.0x10^-1</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>7.0x10^-4</td>
<td>1.5x10^-2</td>
<td>3.0x10^-1</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>1.0x10^-3</td>
<td>2.0x10^-2</td>
<td>5.0x10^-1</td>
<td>9.25</td>
</tr>
</tbody>
</table>

Ten cycles were run at each of these 32 frequencies during the experimental runs to ensure that periodic sinusoidal behavior could fully develop for each frequency. This entire frequency sweep was carried out by the LabVIEW software, which ran uninterrupted for around one week for each experimental run. To begin an additional run using the same test gas, the activation procedure did not need to be repeated. Instead, valves V1, V2, and V3 were opened, and a vacuum was pulled on the system for several
hours or days, this time without thermal regeneration. The adsorbent equilibration procedure was next repeated for the new desired pressure and/or temperature, after which the new experimental run could begin as detailed above.

**Experimental Runs with Glass Beads**

To obtain the aforementioned measurements necessary to account for high frequency thermal effects, 3mm glass beads were placed into the sample chamber. The total volume of the glass beads used was carefully ensured to be equal in volume to the adsorbent sample. These remainder of the procedure was identical in approach to the procedure used for the adsorbent sample runs. A full detail on the enhancing factor function that was used to correct for thermal effects has been previously covered in Hossain’s similar work in 2014.

**Experimental Runs for Determining Displaced, Empty, and Helium-Accessible Volumes**

For the analysis discussed in Chapters 3 and 4, it was necessary to determine several volume constants pertinent to the experimental system. These first of these three volumes was the empty volume, $V_e$, which as the name describes was the volume of the system when it was void of any sample. Next, it was desired to find the helium accessible volume, $V_{acc}$, the volume of the system, including the adsorbent sample pore structure, that the helium gas phase could occupy. Lastly, it was necessary to measure the change in the working volume resulting from manipulation of the metal bellows, $\Delta V$, otherwise notated as the displaced volume.
Helium (UHP Grade from Airgas) was used as the test gas for all three of these volumetric term experimental runs. For the empty volume determination, one full frequency sweep was carried out with an empty sample chamber. To determine the helium gas accessible volume and the change in the working volume, two runs were carried out: one run was conducted while the sample chamber was filled with ¼” 528 stainless steel beads of known volume $V_{ss}$, and the other run was conducted with the 3K172 adsorbent sample in the sample chamber. For each of these three runs, the equilibration and frequency sweep procedures were followed.

**Experimental Conditions**

The experimental conditions used in each of the three distinct procedures are outlined in Table 2.3.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Gas(es)</th>
<th>Temperature(s) (°C)</th>
<th>Pressure(s) (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent Sample</td>
<td>O₂, N₂</td>
<td>20, 25, 30, 40, 50</td>
<td>100, 200, 750</td>
</tr>
<tr>
<td>Glass Beads</td>
<td>O₂, N₂</td>
<td>20, 25, 30, 40, 50</td>
<td>100, 200, 750</td>
</tr>
<tr>
<td>Volume Determinations</td>
<td>He</td>
<td>25</td>
<td>750</td>
</tr>
</tbody>
</table>

For the experimental runs conducted with the adsorbent sample, the 120 cm³ sample chamber was filled with 76.9 grams of CMS 3K172 adsorbent. For each regeneration step, the sample was regenerated under a vacuum of $1.5 \times 10^{-5}$ torr at 100°C. No runs were conducted with glass beads and adsorbent paired together.
Chapter 3: Theory and Numerical Analysis

**Volume and Frequency Response Variables**

To facilitate the analysis for this experiment, the primary response variable for this VSFR system, differential pressure, has been split into two response variables. The first response variable, intensity, is a comparison between the magnitudes of the input variable, the system volume, and the response variable, the pressure change in the system relative to the equilibrium system pressure. Equilibrium is assumed at the moment when valve V1 is shut and the working volume is isolated from the reference volume. The system volume average and the corresponding equilibrium pressure signify the case where the bellows and shaft are located at their midpoint. Any change in system volume and the resultant change in system pressure from these equilibrium values are notated as $\Delta V$ and $\Delta P$, respectively. A more robust interpretation of the intensity is that in this particular work, intensity is used to examine the extent to which adsorption occurs; in other words, the intensity serves as a measurement of the deviation of the VSFR system from ideal gas law behavior. In the case of a gas that does not adsorb appreciably, the pressure response should closely follow the relative magnitude of the volume perturbation, and the intensity should be at or near a value of zero regardless of frequency. The equation used to obtain and model the intensity response variable is shown below:

$$I = \left[ \frac{P_o}{V_{acc,adj}} \frac{\Delta V}{\Delta P(f)} - 1 \right]$$  \hspace{1cm} (1)
For equation 1, \( P_0 \) signifies the absolute pressure of the system at equilibrium, and \( V_{\text{acc,adj}} \) signifies the gas-accessible volume of the system adjusted for a test gas that is not helium. The accessible volume is dependent upon the model that is used: for the micropore model explored in this study, this parameter includes the volume of the macropore domain, and is optimized to a value that forces the intensity response variable to be approximately zero at the highest experimental frequency. The approach to determining \( V_{\text{acc,adj}} \) from other experimentally determined quantities will be explored in greater detail in subsequent paragraphs. It is important to consider that the term \( \Delta P \) is the only term in equation 1 that varies with the frequency of the input variable; every other term in equation 1 is constant across the experimental frequency range.

The second response variable for this analysis is the phase lag (or phase angle). The input variable, the system volume change, is a sinusoidal function with respect to time. In turn, the measured differential pressure response of the system is also sinusoidal. Phase lag is the difference between the angles at a point in time on the sinusoidal curves of the volume perturbation and the corresponding pressure change brought about in the system. It follows that the phase lag, \( \phi \), will have units of radians. The angle of a given point in the sinusoidal pressure curve, and the angle of that same point on the volume perturbation curve, both in units of radians, are represented by \( \phi_P \) and \( \phi_\delta \), respectively:

\[
\phi = \phi_P - \phi_\delta
\]  

(2)

As mentioned above, it is necessary to account for a test gas that is not helium in order to find the accessible volume for the test gas. The principal need for this correction stems from the assumption that helium does not adsorb to an appreciable extent on CMS materials. As such, any volume occupied by gas-phase helium in the micropore crystal
domain, where adsorption would typically occur, is accounted for in the helium-accessible volume measurement. For any other gas species, it may be assumed that only adsorbed-phase exists in the micropore domain, and that no gas-phase exists in the micropore. It then follows that using the helium-accessible volume as the true accessible volume would overestimate the volume that is accessible to the gas-phase of an adsorbing species; the volume occupied by the gas-phase of a strongly adsorbing component should be measurably less than the gas-phase volume accessible to helium. To correct this error, the volume of the micropore domain in the CMS adsorbent should be subtracted out from the helium-accessible volume:

$$V_{acc,adj} = V_{acc} - V_{g,m}$$  \hspace{1cm} (3)

where $V_{acc,adj}$ signifies the error-adjusted accessible volume, $V_{acc}$ is the experimentally-determined helium-accessible volume, and $V_{g,m}$ is the volume of the micropore.

Figure 3.1 serves to depict the individual portions of the working system volume that are critical in helping to form the basis of the model used in this work.
Figure 3.1 Illustration of the working volume, with identification of each of the pertinent volume components

The micropore volume may be found by subtracting the macropore volume, \( V_{g,M} \), from the total pore volume of the adsorbent \( V_{g,p} \) (see Figure 3.1):

\[
V_{g,m} = V_{g,p} - V_{g,M}
\]  

(4)

As such, it follows that the total pore volume, \( V_{g,p} \), shown in Figure 3.1 can be split into two separate volumes: the macropore volume and the micropore volume. In turn, the total pore volume of the adsorbent pellets may be found via the following equation:

\[
V_{g,p} = V \frac{\epsilon_p}{1-\epsilon_p}
\]  

(5)
where $V_s$ is the skeletal, solid volume of the pellet, as notated in Figure 3.1, and $\epsilon_p$ is the porosity of the adsorbent pellets.

The skeletal pellet volume may be approximated from several experimentally measured values:

$$V_s = V_e - V_{acc} - V_{gb} \quad (6)$$

where $V_e$ is the total volume of the working volume when it is completely empty and $V_{gb}$ is the volume of glass beads used in the experiment alongside the adsorbent sample, which was zero for this work.

The pellet porosity is obtained through relating the pellet density, $\rho_p$, and the skeletal density, $\rho_s$:

$$\epsilon_p = 1 - \frac{\rho_p}{\rho_s} \quad (7)$$

The skeletal density may be determined from the known experimental mass of adsorbent, $m$, and the skeletal volume:

$$\rho_s = \frac{m}{V_s} \quad (8)$$

It is worth noting that the pellet density is not a known value, rather, the specific value used, 900 kg/m$^3$, was selected as this value falls within the range of an expected value for the pellet density of a typical CMS adsorbent [8].

The macropore volume used to approximate the micropore volume within the adsorbent is given by:

$$V_{g,M} = V_s \frac{\epsilon_M}{1-\epsilon_M} \quad (9)$$
where $\epsilon_M$ is the porosity of the macropore.

In turn, the macropore porosity may be found from the pellet porosity and the micropore porosity, $\epsilon_m$:

$$\epsilon_M = \epsilon_p - \epsilon_m$$  \hspace{1cm} (10)

The value of the micropore porosity is not a known quantity; instead, this value was used as a fitting parameter, and the best-fit value of $\epsilon_m$ was selected to represent the micropore porosity. Equations 3 through 10 highlight the method by which the porosity of the micropore was utilized to correct the accessible volume used in the intensity response variable for species that adsorb appreciably on CMS materials, such as oxygen and nitrogen.

Additionally, the volume of the interstitial space between adsorbent particles is given by:

$$V_{g,i} = m \frac{1}{\rho_p} \frac{\epsilon_b}{1-\epsilon_b}$$  \hspace{1cm} (11)

where $\epsilon_b$ is the porosity of the bulk, which is given by equation 12.

$$\epsilon_b = 1 - \frac{\rho_b}{\rho_p}$$  \hspace{1cm} (12)

As with the pellet density, the bulk density, $\rho_b$, is not an experimentally determined value. Instead, this density was a guess value, and the value used, 710 kg/m$^3$, falls within expected values of bulk density for a CMS material [9].

The total volume at any given instant within the working volume of the system, $V_t$, is given by:
\[ V_t = V_{t,o} + \Delta V \sin(2\pi ft) \]  \hspace{1cm} (13)

where \( V_{t,o} \) is the average working volume of the system, which corresponds to the bellows at their midpoint. The frequency of the volume perturbation is given by \( f \), the instantaneous time is given by \( t \), and the period of the sinusoidal perturbation function corresponds to \( 1/f \). When time \( t \) is equal to \( n/2f \), and \( n \) is any integer value, the total volume of the system is equal to the average working volume, and the bellows and shaft are at their midpoint.

\( V_{ext,o} \), the average of the working volume external to the adsorbent sample, may be found from the experimentally determined helium-accessible volume and the approximated pore and interstitial volumes using equation 14.

\[ V_{ext,o} = V_{acc} - V_{g,i} - V_{g,p} \]  \hspace{1cm} (14)

The working volume of the system external to the pellet can also be related to the volume perturbation in a manner identical to equation 13:

\[ V_{ext} = V_{ext,o} + \Delta V \sin(2\pi ft) \]  \hspace{1cm} (15)

Equations 1 through 15 provide the basis for this volumetric swing frequency response experiment.

**Frequency Response Analysis**

For a VSFR system, the governing equations for the volumetric perturbation and the pressure output variable must be fit to input and output variable data in order to describe the intensity and phase lag response variables to be used in subsequent analysis. These governing equations are given by:
\[ \delta = \delta_{mp} + \Delta \delta \sin(2\pi ft + \phi) \quad (16) \]

\[ dP = dP_{mp} + \Delta P \sin(2\pi ft + \phi_P) \quad (17) \]

where \( \delta \) represents the linear position of the bellows shaft, and \( dP \) represents the differential pressure between the working and reference volumes. Additionally, \( \delta_{mp} \) represents the offset of the shaft position, which for this work is assumed to be identical to the midpoint of the bellows shaft. The offset for the differential pressure is represented by \( dP_{mp} \), the differential pressure when the bellows shaft is at its midpoint. Ideally, there should be no offset for the differential pressure in equation 17, as the system is assumed to be fully at equilibrium when an experimental run is initiated. Of course, this is an idealization, and the true value of the offset may be a nonzero value if the system is not fully at equilibrium, and so for this work \( dP_{mp} \) cannot be neglected. The amplitudes of the shaft position and differential pressure curves are given by \( \Delta \delta \) and \( \Delta P \), respectively. From fitting the experimental shaft position and differential pressure data to equations 16 and 17 at each experimental frequency, values of \( \Delta \delta \), \( \Delta P \), \( \phi \), \( \phi_P \), \( \delta_{mp} \), and \( dP_{mp} \) may be determined. The amplitude of the pressure response curve can be used in equation 1 to assist in determining the intensity at a given frequency, and the phase angles of the volume input and pressure output may be plugged directly into equation 2 to yield the phase lag for the given frequency.

**Experimental Determination of Displaced, Empty, and Helium-Accessible Volumes**

As outlined in Chapter 2’s procedures, several experiments were conducted in order to determine empirical values for \( \Delta V \), \( V_e \), and \( V_{acc} \) that are necessary to calculate the intensity response variable.
For the determination of the displaced volume or volume change caused by perturbation of the system with the metal bellows, $\Delta V$, a sample of stainless-steel beads was placed in the system, and equation 18 was used:

$$\Delta V = \frac{(V_e - V_{ss}) \Delta P_{ss}}{P_{ss,o}}$$  (18)

where $V_{ss}$ represents the volume of stainless-steel beads used in this procedure, $\Delta P_{ss}$ is the amplitude of the pressure change in the system containing stainless-steel beads in response to volume perturbation, and $P_{ss,o}$ is the average equilibrium absolute pressure of the system containing stainless-steel beads.

Equation 19 provides the expression used to experimentally determine the empty volume term used in equation 18:

$$V_e = \frac{V_{ss}}{1 - Z_e}$$  (19)

where $Z_e$ is a correction factor that is provided in equation 20.

This correction factor is as follows:

$$Z_e = \left(\frac{P_{ss,o}}{P_{e,o}}\right) \left(\frac{\Delta P_e}{\Delta P_{ss}}\right)$$  (20)

where $P_{e,o}$ signifies the equilibrium absolute pressure when the system is completely devoid of any adsorbent sample or stainless-steel beads, and $\Delta P_e$ is the magnitude of the pressure response to volume perturbation in this empty system.

As each of the necessary quantities used in equations 18-20 were either experimentally measured or fitted using the same governing equation outlined in equation
17, the empty volume and volume displacement of the system were empirically
determined from these results as outlined above.

Lastly, the helium-accessible volume was determined when the adsorbent sample
was in the system using the following:

\[ V_{acc} = \left( \frac{P_{He,o}}{P_{e,o}} \right) \left( \frac{\Delta P_e}{\Delta P_{He}} \right) V_e \]  

where \( P_{He,o} \) is the equilibrium absolute pressure of the system using helium as the
working gas with the adsorbent sample present, and \( \Delta P_{He} \) is the resultant magnitude of
the pressure change of this system when the volume is sinusoidally perturbed. Equation
20 allowed for the empirical approximation of the volume that helium is able to access
across a given sample in the gas phase. Of course, it was necessary to adjust this value for
use in the intensity response variable equation, as discussed previously.

**Mass and Energy Balances**

The starting point of the mass balance is the assumption that as the system is a
closed system, the total number of moles of adsorbate in the system, \( n_{tot} \), will remain
constant:

\[ n_{tot} = (m)(\bar{q}) + (\bar{C}_{g,M})(V_{g,M}) + (C_{g,i})(V_{g,i}) + (C_{g,ext})(V_{ext}) \]  

\[ \frac{\partial n_{tot}}{\partial t} = 0 \]  

where \( \bar{q} \) is the average loading of the adsorbed phase across the entire adsorbent pellet,
\( \bar{C}_{g,M} \) is the average concentration of gas within the volume of the macropore domain, \( C_{g,i} \)
is the concentration of gas in the interstitial adsorbent particle volume, and \( C_{g,ext} \) is the
concentration of gas in the portion of the working volume completely external to the
adsorbent sample.

By applying equation 23 to equation 22, the overall mass balance was derived,
and the form of the mass balance used in the model for this VSFR system is provided
below:

\[ m \frac{\partial q}{\partial t} + \frac{V_{g,M}}{RT} \left( \frac{\partial p}{\partial t} - \frac{p \partial T}{T \partial t} \right) + \frac{V_{g,i}}{RT} \left( \frac{\partial p}{\partial t} - \frac{p \partial T}{T \partial t} \right) + \dot{n} = 0 \]  

(24)

where \( \dot{n} \) is the molar rate of mass transfer from the exterior volume to the sample
chamber; the full form of \( \dot{n} \) is derived from the product \( C_{g,\text{ext}} V_{\text{ext}} \), and is given in
equations A.6 and A.7. Additionally, the ideal gas law was assumed for each gas phase
concentration to describe the mass balance in terms of pressure and temperature. This
assumption is explored in greater detail in Appendix A, specifically in equations A.1-A.5.

The energy balance that applies to this VSFR system is provided in equation 25:

\[ V_{g,M} \left[ (C_{pg} - R)C_{g,M} \frac{\partial T}{\partial t} - RT \frac{\partial C_{g,M}}{\partial t} \right] + V_{g,i} \left[ C_{pg} \frac{p}{RT} \frac{\partial T}{\partial t} - \frac{\partial p}{\partial t} \right] + \\
m \ddot{q} \left[ C_{pg} + \frac{\partial \Delta H_a}{\partial T} \right] \frac{\partial T}{\partial t} + m C_{pp} \frac{\partial T}{\partial t} + m \left[ \Delta H_a + \ddot{q} \frac{\partial \Delta H_a}{\partial \ddot{q}} \right] \frac{\partial \ddot{q}}{\partial t} = \\
hA(T_{\text{bath}} - T) + \dot{n} \Delta H^* \]  

(25)

where \( C_{pp} \) is the heat capacity of the adsorbent, \( C_{pg} \) is the heat capacity of the test gas,
\( \Delta H_a \) is the heat of adsorption, \( h \)A is the coefficient for heat transfer between the sample
chamber and the water jacket, \( \Delta H^* \) is the change in enthalpy of the test gas between the
exterior volume and the sample volume, and \( T_{\text{bath}} \) is the temperature of the water bath
circulating through the sample chamber jacket.
While the mass balance provided in equation 24 is applied across the entire working volume, the energy balance in equation 25 is only applied to the volumes directly related to the sample volume: \(V_{g,m}, V_{g,M}, V_{g,i},\) and \(V_s.\) As with the mass balance, a more in-depth derivation of the energy balance is provided in Appendix A.

Equations 24 and 25 summarize the mass and energy balances that describe this VSFR system, which may be simultaneously solved alongside the micropore model equation(s) in order to properly describe the behavior of the system, and to be able to model the experimental values of intensity and phase lag that were found using equations 1 and 2.

Several other equations are important to consider regarding the mass and energy balances. First, the expression is given for the average adsorbed phase, \(\bar{q},\) is given by:

\[
\bar{q} \equiv \frac{3}{R_p^2} \int_0^{R_p} \bar{q} r_p^2 dr_p
\]

where \(R_p\) is the radius of the spherical adsorbsent pellets, \(r_p\) is the radial coordinate within the overall pellet domain, and \(\bar{q}\) is the average adsorbed phase loading across the micropore crystal at a given location within the pellet, as the existence of loading outside of the micropore domain was assumed to be negligible in this analysis. For equation 26, \(\bar{q}\) is equal to \(\bar{q}\) when a micropore model is used, as there is thereby assumed to be no mass transfer resistance in the macropore domain.

As such, a simplification may be made to the mass balance in equation 24:

\[
\frac{\partial \bar{q}}{\partial t} = \frac{\partial \bar{q}}{\partial t}
\]
which is used to simplify the computational complexity of simultaneously solving the mass, energy, and micropore model equations.

Assuming a spherical micropore domain, the expression for $\bar{q}$ becomes:

$$\bar{q} \equiv \frac{3}{R_c^2} \int_0^{R_c} q r_c^2 dr_c$$

(28)

where $R_c$ is the radius of the micropore crystal domain, $r_c$ is the radial coordinate within the micropore domain, and $q$ is the loading of adsorbed phase at a given point within the micropore crystal. It is worth noting that $q$ is a function of $r_c$, and so $\bar{q}$ is not equal in value to $q$.

Additionally, there is a simplification that was made to the form of $C_{g,M}$ that appears in equation 24, which is justified by:

$$\bar{C}_{g,M} \equiv \frac{3}{R_p^2} \int_0^{R_p} C_{g,M} r_p^2 dr_p = \frac{3}{R_p} \frac{1}{RT} \int_0^{R_p} P_p r_p^2 dr_p = \frac{\bar{P}_p}{RT}$$

(29)

which is paired with the assumption made for the micropore model that there is no macropore resistance. As such, $\bar{P}_p$ is assumed to be equal to $P_p$, and the result of equation 29 matches the result used in the mass balance.

Several other assumptions are important to consider for the mass and energy balances. Primarily, the existence of any spatial gradients within the sample volume was neglected, with the exception of the micropore volume. As mentioned above, the sample volume, the portion of the working volume containing adsorbent including interstitial volume, was selected as the control volume for the energy balance. Heat transfer into and out of the sample chamber is driven by the temperature difference between the sample
volume and the jacket surrounding the sample chamber, as reflected in equation 25. The
temperature of the circulating water bath, $T_{\text{bath}}$, was assumed to be equal to both the
initial, equilibrium system temperature, $T_o$, and the temperature of the external volume,
$T_{\text{ext}}$.

In order to be able to solve the system mass and energy balances given in
equations 24 and 25, respectively, the value of the average micropore crystal loading, $\bar{q}$,
and its first order time derivative must be individually solved for. As shown in equation
28, this value may be found from the local value of the loading within the micropore
crystal, $q$. As such, a third differential equation is necessary to fully solve for each degree
of freedom within this VSFR system model. In the case of a dual-site model, a third and
fourth differential equation are needed to adequately describe the system. These
additional differential equations are defined such that the output variable is the local
value of the loading, $q$, such that the value $\bar{q}$ may then be found using equation 28. The
general basis of the single-site and dual-site models, as well as specific applications of
these models, will be discussed in subsequent sections.

**The Basis of the Single-Site Micropore Mass Transfer Model**

The basis of the micropore models used in this analysis, the single-site and the
dual-site models, remains identical throughout several different model variations that will
be examined subsequently in greater detail. The primary basis of the micropore mass
transfer model used in this analysis is the assumption that the Darken relationship fully
describes the dependency of the loading of the adsorbed phase on the micropore diffusion
coefficient, which is in accordance with work done by Yang in 1987 [10].
First, the radial coordinate at any location $r_c$ within the micropore domain from a radius of zero to $R_c$ was defined as a dimensionless quantity $\xi_c$:

$$\xi_c = \frac{r_c}{R_c}$$  \hspace{1cm} (30)

For the basis of the single-site micropore model, the instantaneous rate of change of the loading with respect to time may be related to the micropore diffusion coefficient:

$$\frac{\partial q}{\partial t} = \frac{1}{\xi_c^2} \frac{\partial}{\partial \xi_c} (\xi_c^2 K_s) \frac{\partial q}{\partial \xi_c}$$  \hspace{1cm} (31)

where $K_s$ is the micropore diffusion coefficient. Equation 31 is the base equation from which single-site models may be further specified.

Several initial and boundary conditions are necessary to include alongside equation 31 in order to fully describe mass transfer within this system according to the single-site micropore model:

$$q = q_o \quad \text{at } t = 0$$  \hspace{1cm} (32)

$$\frac{\partial q}{\partial t} = 0 \quad \text{at } t = 0$$  \hspace{1cm} (33)

$$\frac{\partial q}{\partial \xi_c} = 0 \quad \text{at } \xi_c = 0$$  \hspace{1cm} (34)

$$K_s \frac{\partial q}{\partial \xi_c} = \frac{K_m}{3} (q^* - q) \quad \text{at } \xi_c = 1$$  \hspace{1cm} (35)

where $q_o$ is the equilibrium value of the loading at the initial equilibrium conditions, $q^*$ is the instantaneous value of the loading at the local value of T and P as determined by the isotherm model, and $K_m$ is the mass transfer coefficient that describes the resistance at the mouth of the micropore, referred to as the mouth resistance. In this analysis, both $q_o$
and $q^*$ are evaluated using the Toth isotherm model with previously determined empirical isotherm parameters, which will be discussed in greater detail following the introduction of the several model variations. These boundary conditions apply to all of the subsequent single-site model variations.

Several other important quantities appear in the model variations. First, a simplified quantity was defined to relate the local value of loading with the saturation loading as determined by the isotherm for the adsorbing species:

$$\theta = \frac{q}{q_s}$$  \hfill (36)

where $\theta$ is the unitless fractional coverage of the adsorbent surface in the micropore domain, and $q_s$ is the saturation loading of the adsorbent-adsorbate pair.

A similar quantity may be defined for the loading at the reference temperature:

$$\theta_r = \frac{q_r}{q_{s,r}}$$  \hfill (37)

where $\theta_r$ is the fractional surface coverage at the reference temperature. The saturation loading at the reference temperature is provided by $q_{s,r}$.

The rate of change of pressure relative to a change in loading is also pertinent to subsequent application of the micropore model, and may be defined at any time $t$ in addition to at the initial equilibrium state:

$$\frac{d \ln(p)}{d \ln(q)} = \frac{1}{1-\theta^n}$$  \hfill (38)

$$\frac{d \ln(p_r)}{d \ln(q_r)} = \frac{1}{1-\theta_r^{n_r}}$$  \hfill (39)
where $P_r$ is the reference pressure and $n, n_r$ are the heterogeneity parameters for the isotherm at temperatures $T$ and $T_r$, respectively.

**Single Site Micropore-Only (SSMI) Model**

For the SSMI model, it is assumed that the only limiting mass transfer mechanism is diffusion in the micropore. As such, the mass transfer coefficient for the mouth resistance is very large relative to the value of the micropore mass transfer coefficient. Under this condition, the exterior boundary condition for equation 31 becomes:

$$ q \equiv q^* \quad \text{at } \xi_c = 1$$

such that there is no decrease in loading from the instantaneous equilibrium loading value across the micropore mouth. All other boundary and initial conditions remain unchanged for the SSMI model.

Aside from this change to a boundary condition, equation 31 may still be used to describe the behavior of adsorbates in this system. Accordingly, the value of the micropore mass transfer coefficient is related to the input parameter value, $K_{s,r}$, by the following:

$$ K_s = K_{s,r} * \frac{\text{dln}(P)}{\text{dln}(q)} * \exp \left[ -E_s \left( \frac{1}{T} - \frac{1}{T_r} \right) \right]$$

where $E_s$ is the energy parameter used to describe the temperature dependency of the micropore mass transfer coefficient, and $T_r$ is the reference temperature used to establish the temperature dependence for the micropore mass transfer coefficient. For simplicity, the energy term for the micropore mass transfer coefficient includes the ideal gas constant as a factor of $R^{-1}$ within the value as used in equation 41.
Single Site Mouth-Resistance-Only (SSMR) Model

In the SSMR model, the assumption is made that the only limiting mass transfer mechanism in this system is linked to the mouth of the micropore. For this case, the value of the micropore mass transfer coefficient is much larger than the value of the mouth resistance mass transfer coefficient. Accordingly, the boundary conditions at both edges of the micropore must be adjusted:

\[
\frac{\partial q}{\partial \xi_c} = \frac{K_{mo}}{3K_s} (q^* - q) \quad \text{at} \quad \xi_c = 0
\]  

(42)

Alternatively:

\[
\frac{\partial q}{\partial \xi_c} = 0 \quad \text{at} \quad 0 \leq \xi_c \leq 1
\]  

(43)

which signifies that as there is no mass transfer in the micropore, the value of the loading in the micropore should be equal at all radial coordinates \( r_c \). Initial conditions remain unchanged for this model.

For this case, the micropore balance expressed in equation 31 is not necessary; instead, the system may be described with:

\[
\frac{\partial q}{\partial t} = K_{mo}(q^* - q)
\]  

(44)

which is consistent with the assumption for the SSMR model that only the mouth resistance mass transfer coefficient has any impact on the loading of adsorbate in the micropore.

The expression used to obtain \( K_{mo} \) from the input parameter, \( K_{mo,r} \), is given by:
\[ K_{mo} = K_{mo,r} \ast \exp \left[ -E_{mo} \left( \frac{1}{T} - \frac{1}{T_r} \right) \right] \]  \hspace{1cm} (45)

where \( E_{mo} \) is the energy parameter used to relate \( K_{mo} \) to temperature, and \( T_r \) is the reference temperature for this temperature dependence for the mouth resistance mass transfer coefficient. The reference temperature is identical to the reference point selected for \( K_s \). As with energy term for the micropore in the SSMI model, the energy term for the mouth resistance mass transfer coefficient includes the inverse of the ideal gas constant, \( R^{-1} \), within the value as used in equation 41.

To utilize the SSMR model, the result from equation 45 may be plugged directly into equation 44 and solved simultaneously along with the mass and energy balances according to the initial conditions and the boundary condition established in equation 43.

**Single Site Combined Micropore and Mouth Resistance (SSC) Model**

For the SSC model, the contributions of both the micropore and mouth resistance mass transfer coefficients to the loading in the micropore are considered. No changes to the boundary conditions are necessary in this case, as the conditions at the interior and exterior edges of the micropore domain established in equations 34 and 35 both hold true for this model. This model assumes that the loading both decreases across the mouth of the micropore as well as when the adsorbate penetrates further into the micropore crystal. As discussed individually for the SSMI and SSMR models, the same temperature-dependent relationships for the micropore and mouth resistance mass transfer coefficients were used:

\[ K_s = K_{s,r} \ast \frac{\frac{dln(P)}{dln(q_r)}}{\frac{dln(P)}{dln(q_r)}} \ast \exp \left[ -E_s \left( \frac{1}{T} - \frac{1}{T_r} \right) \right] \]  \hspace{1cm} (46)
\[ K_{mo} = K_{m,o,r} \exp \left[ -E_{mo} \left( \frac{1}{r} - \frac{1}{T_r} \right) \right] \quad (47) \]

The outputs of equations 46 and 47 may then be used with equation 31 and solved per the initial and boundary conditions in equations 32-35 directly.

**Single Site Combined with Loading Dependence (SSCLD) Model**

As will be discussed in the subsequent chapter containing results, it was noted that the micropore mass transfer coefficient, \( K_s \), varied more strongly with loading than predicted by Darken’s model. Similarly, the mouth resistance mass transfer coefficient, \( K_{mo} \), exhibited loading-dependent behavior that could not be sufficiently described using Darken’s model. Similar results to those observed were noted in Yang et.al, who used a form of the following relationships, notated as the Qinglin loading dependence to describe the behavior of the mass transfer coefficients [11]:

\[ K_s^* = K_{s,r} \frac{[1 + \beta_s (\frac{\theta}{1-\theta})]}{[1 + \beta_s (\frac{\theta_r}{1-\theta_r})]} \quad (48) \]

\[ K_{mo}^* = K_{m,o,r} \frac{[1 + \beta_{mo} (\frac{\theta}{1-\theta})]}{[1 + \beta_{mo} (\frac{\theta_r}{1-\theta_r})]} \quad (49) \]

where \( K_s^* \) and \( K_{mo}^* \) represent the corrected loading-dependent values of the micropore and mouth resistance mass transfer coefficients, respectively. The terms \( \beta_s \) and \( \beta_{mo} \) represent unitless fitting parameters that are used to adjust the output values of the mass transfer coefficients based upon the observed loadings in each experimental run.

The outputs from equations 48 and 49 are then adjusted to account for the temperature-dependence of the mass transfer coefficients in a similar manner to previous model variations:
\[ K_s = K_s^* \exp \left( \frac{d \ln (p)}{d \ln (P_r)} \right) \exp \left[-E_s \left( \frac{1}{T} - \frac{1}{T_r} \right) \right] \] (50)

\[ K_{mo} = K_{mo}^* \exp \left[-E_{mo} \left( \frac{1}{T} - \frac{1}{T_{mo}} \right) \right] \] (51)

The mass transfer coefficients obtained from equations 50 and 51 may then be used in accordance with the micropore balance in equation 31 and its initial and boundary conditions to obtain results with the SSCLD model. As such, this combined model differs from the SSC model only in terms of the additional loading dependence that was added.

**The Basis of the Dual-Site Micropore Mass Transfer Model**

In order to better approximate the behavior of oxygen on the CMS sample, it was necessary to add another layer of complexity to the micropore model, in the form of the dual site micropore model. Here, it is assumed that the adsorbate interacts with two different adsorbent site geometries, which represents a departure from the sole value of loading expressed in equation 31. This in turn allows the micropore model to capture the inflection points observed for the experimental data of oxygen on CMS. As such, the overall loading, \( q \), may be split into two parts:

\[ q = q_1 + q_2 \] (52)

where \( q_1 \) and \( q_2 \) represent the individual portions of loading in the micropore domain.

With this assumption of two discrete site geometries, it is also assumed that each split of the mass of adsorbed phase is subject to different mass transfer coefficients for the micropore and mouth resistance. The single site micropore balance in equation 31 may be adjusted to reflect the assumption made by equation 52:

\[ \frac{\partial q_1}{\partial t} = \frac{1}{\xi_c^2} \frac{\partial}{\partial \xi_c} \left( \xi_c \right) \frac{\partial q_1}{\partial \xi_c} K_{s,1} \frac{\partial q_1}{\partial \xi_c} \] (53)
\[ \frac{\partial q_2}{\partial t} = \frac{1}{\xi_c} \frac{\partial}{\partial \xi_c} (\xi_c^2 K_{s,2}) \frac{\partial q_2}{\partial \xi_c} \]  

(54)

where \( K_{s,1} \) and \( K_{s,2} \) are the micropore mass transfer coefficients relevant to the first and second sites, respectively.

Similar to the assumed split of \( K_s \) for this dual site model basis, the mouth resistance mass transfer coefficient at the external boundary condition may also be split:

\[ K_{s,1} \frac{\partial q_1}{\partial \xi_c} = \frac{K_{mo,1}}{3} (q_1^* - q_1) \quad \text{at } \xi_c = 1 \]  

(55)

\[ K_{s,2} \frac{\partial q_2}{\partial \xi_c} = \frac{K_{mo,2}}{3} (q_2^* - q_2) \quad \text{at } \xi_c = 1 \]  

(56)

where \( K_{mo,1} \) and \( K_{mo,2} \) are the mouth resistance mass transfer coefficients that describe the first and second sites. Although specified individually, these values of \( K_{mo,1} \) and \( K_{mo,2} \) were substituted with a single value, \( K_{mo} \), for modeling work using this dual-site model, as this was sufficient to achieve a good model fit. The values \( q_1^* \) and \( q_2^* \) describe the equilibrium loading values of the first and second loadings on these sites, respectively. For the dual site micropore model, all other boundary and initial conditions discussed in the single-site model basis section remain unchanged, but should be updated to reflect \( q_1 \) and \( q_2 \).

The equilibrium values for the loadings may be related to the original equilibrium value used in each of the other model variations:

\[ q^* = q_1^* + q_2^* = \alpha q^* + (1 - \alpha)q \]  

(57)

where \( \alpha \) is a fitting parameter between zero and one that describes the fractional split in loadings.
Other quantities describing the loadings may be split similarly:

\[ q_o = q_{o,1} + q_{o,2} = \alpha q_o + (1 - \alpha) q_o \]  
(58)

\[ q_r = q_{r,1} + q_{r,2} = \alpha q_r + (1 - \alpha) q_r \]  
(59)

\[ \theta = \theta_1 + \theta_2 = \frac{q_1}{q_s} + \frac{q_2}{q_s} \]  
(60)

\[ \theta_r = \theta_{r,1} + \theta_{r,2} = \frac{q_{r,1}}{q_{r,s}} + \frac{q_{r,2}}{q_{r,s}} \]  
(61)

Additionally, the slope values of the natural log of pressure relative to the natural log of the loading may be individually defined:

\[ \frac{d \ln(P)}{d \ln(q_1)} = \frac{1}{1 - \theta_1^n} \]  
(62)

\[ \frac{d \ln(P)}{d \ln(q_2)} = \frac{1}{1 - \theta_2^n} \]  
(63)

\[ \frac{d \ln(P_r)}{d \ln(q_{r,1})} = \frac{1}{1 - \theta_{r,1}^{n_r}} \]  
(64)

\[ \frac{d \ln(P_r)}{d \ln(q_{r,2})} = \frac{1}{1 - \theta_{r,2}^{n_r}} \]  
(65)

**Dual Site Combined with Loading Dependence (DSCLD) Model**

For this work, the single application of the dual site model presented in equations 53 and 54 is the DSCLD model, which accounts for a loading dependence in a manner identical to the previously discussed SSCLD model, with the caveat that this particular loading dependence is built from the basis of the dual site micropore model, as opposed to the basis of the single site micropore model. As such, for the DSCLD model,
and temperature dependencies identical to those used for the SSCLD model may be defined individually for \( K_{s,1} \), \( K_{s,2} \), \( K_{mo,1} \), and \( K_{mo,2} \):

\[
K_{s,1}^* = K_{s,r,1} * \frac{[1+\beta_{s,1}(\frac{\theta_1}{\alpha-\theta_1})]}{[1+\beta_{s,1}(\frac{\theta_{r,1}}{\alpha-\theta_{r,1}})]}
\]

\[
K_{s,2}^* = K_{s,r,2} * \frac{[1+\beta_{s,2}(\frac{\theta_2}{\alpha-\theta_2})]}{[1+\beta_{s,2}(\frac{\theta_{r,2}}{\alpha-\theta_{r,2}})]}
\]

\[
K_{s,1} = K_{s,1}^* \frac{dln(P)}{dln(q_1)} \frac{dln(P)}{dln(q_{r,1})} \exp \left[ -E_{s,1} \left( \frac{1}{T} - \frac{1}{T_{r,1}} \right) \right]
\]

\[
K_{s,2} = K_{s,2}^* \frac{dln(P)}{dln(q_2)} \frac{dln(P)}{dln(q_{r,2})} \exp \left[ -E_{s,2} \left( \frac{1}{T} - \frac{1}{T_{r,2}} \right) \right]
\]

\[
K_{mo,1}^* = K_{mo,r,1} * \frac{[1+\beta_{mo,1}(\frac{\theta_1}{\alpha-\theta_1})]}{[1+\beta_{mo,1}(\frac{\theta_{r,1}}{\alpha-\theta_{r,1}})]}
\]

\[
K_{mo,2}^* = K_{mo,r,2} * \frac{[1+\beta_{mo,2}(\frac{\theta_2}{\alpha-\theta_2})]}{[1+\beta_{mo,2}(\frac{\theta_{r,2}}{\alpha-\theta_{r,2}})]}
\]

\[
K_{mo,1} = K_{mo,1}^* \exp \left[ -E_{mo,1} \left( \frac{1}{T} - \frac{1}{T_{r,1}} \right) \right]
\]

\[
K_{mo,2} = K_{mo,2}^* \exp \left[ -E_{mo,2} \left( \frac{1}{T} - \frac{1}{T_{r,2}} \right) \right]
\]

where \( \beta_{s,1}, \beta_{s,2}, \beta_{mo,1}, \) and \( \beta_{mo,2} \) are the loading dependency parameters, and where \( E_{s,1}, E_{s,2}, E_{mo,1}, \) and \( E_{mo,2} \) are the temperature dependency parameters. The results from equations 68, 69, 72, and 73 may be plugged into the balances in equations 53 and 54 and solved accordingly with the boundary conditions in equations 55 and 56 to solve the DSCLD model. Alternatively, following the assumption that there is only a singular
mouth resistance mass transfer coefficient, only one of each of the loading and
temperature dependency equations for $K_{mo}$ needs to be solved, with the alpha expression
term in the loading correction set to a value of one in equation 70, or set to zero in
equation 71. No other models of further complexity were deemed necessary to adequately
model and describe the experimental frequency response curves.

**Adsorption Isotherm**

The Toth isotherm model was selected to describe the instantaneous, equilibrium,
and reference values of the loading, $q^*$, $q_o$, and $q_r$, used in the micropore model. The Toth
isotherm expression is given by:

$$q^*(T, P) = \frac{bPq_s}{(1+(bP)^n)^{\frac{1}{n}}} \tag{74}$$

$$q_o(T_o, P_o) = \frac{bPq_s}{(1+(bP)^n)^{\frac{1}{n}}} \tag{75}$$

$$q_r(T_r, P_r) = \frac{bPq_s}{(1+(bP)^n)^{\frac{1}{n}}} \tag{76}$$

where $b$ represents the affinity parameter, $q_s$ represents the saturation loading for the
specific adsorbent-adsorbate pair, and $n$ represents the heterogeneity parameter.

Additionally, $b_i$, $q_{s,i}$, and $n_i$ represent these same parameters at the initial, equilibrium
temperature for an experimental run. These parameters at the reference temperature are
represented by $b_r$, $q_{s,r}$, and $n_r$.

Several equations that define the temperature dependencies of these isotherm
fitting parameters are provided by:
\[ b = b_o \exp \left( \frac{B}{T} \right) \] 

(77)

\[ q_s = q_{s,o} + \frac{q_{s,t}}{T} \] 

(78)

\[ n = n_o + \frac{n_t}{T} \] 

(79)

\[ b_i = b_o \exp \left( \frac{B}{T_o} \right) \] 

(80)

\[ q_{s,i} = q_{s,o} + \frac{q_{s,t}}{T_o} \] 

(81)

\[ n_i = n_o + \frac{n_t}{T_o} \] 

(82)

\[ b_r = b_o \exp \left( \frac{B}{T_r} \right) \] 

(83)

\[ q_{s,r} = q_{s,o} + \frac{q_{s,t}}{T_r} \] 

(84)

\[ n_r = n_o + \frac{n_t}{T_r} \] 

(85)

where \( b_o, B, q_{s,o}, q_{s,t}, n_o, \) and \( n_t \) are all fitting parameters determined through isotherm measurements made at several temperatures.

**COMSOL Model**

A one-dimensional geometry with a dimensionless length is used in COMSOL Multiphysics to model behavior along the radius of the micropore crystal. The general form partial differential equations representing the mass and energy balances are solved alongside the micropore model equation(s) in order to generate model data regarding the time-dependent values of pressure, temperature, and loading across the geometrical representation of the micropore domain.
The mesh used to select the nodes at which to solve these PDEs is split into several components: a coarse mesh is used at the interior of the micropore, a normal mesh is used for the middle, and an extra-fine mesh is selected for the outer region of the representative geometry. The optimization of model accuracy against computational time in order to arrive at this mesh selection was carried out by Smithson in 2020 [12]. A further change was made to the mesh sizing in an effort to reduce the computational complexity of this COMSOL model: a fourth and final mesh region is defined to consist of a single point at the outer edge of the micropore domain. The mass and energy balances are solved only at this outer edge, and the resulting pressure and temperature values are applied to the entire micropore geometry. This is following the assumption that there is no resistance to gas-phase diffusion or heat transfer in the micropore, which signifies that the pressure and temperature values obtained at the outer edge of the micropore crystal should remain constant for any change in the radial coordinate, \( r_c \).

Unchanged from the previous iteration, however, the micropore model equation(s) must be solved across the entire representative micropore geometry. Even so, as a result of this simplifying assumption, the number of unknowns that are required to be solved for in this COMSOL model is reduced nearly threefold; as such, the computational complexity of the COMSOL model is able to be reduced to an even greater degree.

As mentioned previously, the dependent variables of the PDEs solved by COMSOL are the pressure in the sample bed, \( P_b \), the temperature of the bed, \( T_b \), and the loading in the micropore, \( q \) (or \( q_1 \) and \( q_2 \)). The model used to solve these PDEs is a time-dependent model, set such that 256 time steps are made per cycle, and 10 cycles are conducted for each experimental frequency value.
**MATLAB Model**

To develop and obtain modeling results, a code routine was set up in MATLAB, such that the COMSOL model could be iteratively run across the entire set of 32 frequencies, or across the frequency range for a given set of experimental conditions. The experimental temperatures, pressures, and frequencies are read within the MATLAB file, such that one full iteration of the MATLAB code may develop model results for all six experimental runs of a test gas at one time. The code is also set up to prompt the user to input mass transfer coefficients, the heat transfer coefficient, energies for the temperature dependencies of the MTCs, and the micropore porosity. These input values serve as the fitting parameters for a given micropore model fit. Additionally, while not prompted as input parameters, the pressure dependency beta values could be adjusted within the MATLAB code in between runs. As with the input parameters, these beta values also serve as fitting parameters for micropore models that account for the impact of pressure on the mass transfer coefficients. Lastly, the alpha value used to determine the partition between sites may be adjusted within the code for the dual site model.

Plots of the model fits based on a set of parameter values are generated once the code finishes its full iterative routine. Alongside these plots, which may be used as a quick visual inspection of the quality of the model fits, an Excel file is generated, which contains the model-predicted intensity and phase lag at each frequency for each set of conditions that is fed into the code. Although this MATLAB code is capable of optimizing these input parameters through the use of a Davidon-Fletcher-Powell optimization subroutine, as previously discussed in Smithson’s earlier work, this optimization technique was not used for the purpose of this modeling work [12]. As will
be observed in the following chapter, when a current model is too simple to adequately
describe the observed experimental data, the global minimum found by the optimization
subroutine may not coincide with an accurate approximation of the data, and as a result
will often inadequately predict the behavior of the frequency response variables in favor
of minimizing the sum squared error across the set of experimental runs. Given that the
scope of this work is to improve upon the depth and quality of these model fittings, the
optimizer code is omitted in favor of manually seeking accurate model fits.
Chapter 4: Results and Conclusions

Overall Modeling Results

For each of the micropore model variations, several parameters and experimental conditions remained constant across each of these individual models. These values will be explored in this section, in addition to the summarized best-fit parameters for each model variation, which will then be analyzed individually in their respective model sections. First, Table 4.1 shows the experimental conditions and model conditions that were used for each model for both nitrogen and oxygen. These conditions were established such that the effects of temperature and pressure could be observed for each test gas.

Table 4.1 Detailed conditions for each frequency response run and its corresponding model fitting

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temperature (°C)</th>
<th>Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>O₂</td>
<td>25</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>750</td>
</tr>
<tr>
<td>N₂</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>750</td>
</tr>
</tbody>
</table>
Additionally, many parameters used in the COMSOL and MATLAB models were not varied, and only a select few were manipulated in an effort to approximate the observed experimental data. These constant parameter values, which did not vary across any of the subsequently examined model variations, are contained in Table 4.2. Many of these parameters reflect the isotherm fittings for oxygen and nitrogen, and others reflect the heat capacity temperature correlations for these gases. The remainder of the parameters in Table 4.2 describe the adsorbent characteristics, which are constant between the two test gases, experimental measurements of volume constants, model reference points, and several well-known constant values.

Table 4.2 Constant parameters in COMSOL and MATLAB codes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value in N₂ Model</th>
<th>Value in O₂ Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_c) [J/mol/K]</td>
<td>3.115x10¹</td>
<td>2.811x10¹</td>
</tr>
<tr>
<td>(B) [K]</td>
<td>2.315x10³</td>
<td>2.260x10³</td>
</tr>
<tr>
<td>(b_{cp}) [J/mol/K²]</td>
<td>-1.357x10⁻²</td>
<td>-3.680x10⁻⁶</td>
</tr>
<tr>
<td>(b_o) [1/kPa]</td>
<td>1.054x10⁻⁶</td>
<td>1.154x10⁻⁶</td>
</tr>
<tr>
<td>(C_{pp}) [J/kg/K]</td>
<td>8.800x10²</td>
<td>8.800x10²</td>
</tr>
<tr>
<td>(c_{cp}) [J/mol/K²]</td>
<td>2.680x10⁻⁵</td>
<td>1.746x10⁻⁵</td>
</tr>
<tr>
<td>(d_{cp}) [J/mol/K²]</td>
<td>1.168x10⁻⁴</td>
<td>-1.065x10⁻⁸</td>
</tr>
<tr>
<td>(m) [kg]</td>
<td>7.69x10⁻²</td>
<td>7.69x10⁻²</td>
</tr>
<tr>
<td>(n_o) [unitless]</td>
<td>7.711x10⁻¹</td>
<td>8.232x10⁻¹</td>
</tr>
<tr>
<td>(n) [K]</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(P_f) [kPa]</td>
<td>9.999x10¹</td>
<td>9.999x10¹</td>
</tr>
<tr>
<td>(q_{s,o}) [mol/kg]</td>
<td>2.014x10⁰</td>
<td>2.014x10⁰</td>
</tr>
<tr>
<td>(q_{s,t}) [mol/kg/K]</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(R) [J/mol/K]</td>
<td>8.314</td>
<td>8.314</td>
</tr>
<tr>
<td>(T_r) [K]</td>
<td>3.032x10²</td>
<td>3.032x10²</td>
</tr>
<tr>
<td>(V_{ac}) [m³]</td>
<td>1.88x10⁻⁴</td>
<td>1.883x10⁻⁴</td>
</tr>
<tr>
<td>(V_c) [m³]</td>
<td>2.37x10⁻⁴</td>
<td>2.367x10⁻⁴</td>
</tr>
<tr>
<td>(V_{gb}) [m³]</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\Delta H_a) [J/mol]</td>
<td>-1.925x10⁴</td>
<td>-1.879x10⁴</td>
</tr>
<tr>
<td>(\Delta V) [m³]</td>
<td>1.10x10⁻⁶</td>
<td>1.10x10⁻⁶</td>
</tr>
<tr>
<td>(\varepsilon_o) [unitless]</td>
<td>0.120</td>
<td>0.120</td>
</tr>
<tr>
<td>(\pi) [unitless]</td>
<td>3.14</td>
<td>3.14</td>
</tr>
<tr>
<td>(\rho_a) [kg/m³]</td>
<td>7.10x10²</td>
<td>7.10x10²</td>
</tr>
<tr>
<td>(\rho_p) [kg/m³]</td>
<td>9.00x10²</td>
<td>9.00x10²</td>
</tr>
</tbody>
</table>
The best-fit parameters for each model are compiled in Table 4.3 for nitrogen, and in Table 4.4 for oxygen. Note that in Table 4.4, the parameters with the first site subscript are taken to signify the first and only site for every model other than the dual site model. The results that correspond to the models deemed to provide the most adequate representation of the empirical data are highlighted. Additionally, the objective function for each model’s approximation of the empirical data, the sum squared error for the intensity curve fits, is tabulated under each model.

Table 4.3 Best-fit model parameters for each model variation for nitrogen on Shirasagi CMS 3K172 and value of the objective function (SSE) for each model fitting

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SSMI</th>
<th>SSMR</th>
<th>SSC</th>
<th>SSCLD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{s,r}$ (1/s)</td>
<td>6.00x10^{-4}</td>
<td>1.00x10^{4}</td>
<td>1.20x10^{-3}</td>
<td>1.50x10^{-3}</td>
</tr>
<tr>
<td>$K_{mo,r}$ (1/s)</td>
<td>1.00x10^{4}</td>
<td>1.00x10^{-2}</td>
<td>1.37x10^{-2}</td>
<td>1.09x10^{-2}</td>
</tr>
<tr>
<td>$hA$ (W/K)</td>
<td>0.500</td>
<td>0.500</td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>$E_s$ (K)</td>
<td>1600</td>
<td>0</td>
<td>1600</td>
<td>2000</td>
</tr>
<tr>
<td>$E_{mo}$ (K)</td>
<td>0</td>
<td>3000</td>
<td>3000</td>
<td>3600</td>
</tr>
<tr>
<td>$\beta_s$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.5</td>
</tr>
<tr>
<td>(unitless)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{mo}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.50</td>
</tr>
<tr>
<td>(unitless)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSE</td>
<td>24.311</td>
<td>19.916</td>
<td>8.716</td>
<td>0.932</td>
</tr>
</tbody>
</table>
Table 4.4 Best-fit model parameters for each model variation for oxygen on Shirasagi CMS 3K172

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SSMI</th>
<th>SSMR</th>
<th>SSC</th>
<th>SSCLD</th>
<th>DSCLD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ (unitless)</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>0.800</td>
</tr>
<tr>
<td>$K_{s,r,1}$ (1/s)</td>
<td>1.40x10^{-2}</td>
<td>1.00x10^{4}</td>
<td>2.33x10^{-2}</td>
<td>2.33x10^{-2}</td>
<td>1.73x10^{-2}</td>
</tr>
<tr>
<td>$K_{s,r,2}$ (1/s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.63x10^{0}</td>
</tr>
<tr>
<td>$K_{m0,r}$ (1/s)</td>
<td>1.00x10^{4}</td>
<td>2.75x10^{-1}</td>
<td>5.47x10^{-1}</td>
<td>4.32x10^{-1}</td>
<td>4.32x10^{-1}</td>
</tr>
<tr>
<td>$hA$ (W/K)</td>
<td>0.500</td>
<td>0.500</td>
<td>0.500</td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>$E_{s,1}$ (K)</td>
<td>2200</td>
<td>0</td>
<td>2200</td>
<td>3625</td>
<td>3625</td>
</tr>
<tr>
<td>$E_{s,2}$ (K)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$E_{m0}$ (K)</td>
<td>0</td>
<td>2500</td>
<td>2500</td>
<td>3000</td>
<td>3000</td>
</tr>
<tr>
<td>$\beta_{s,1}$ (unitless)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>255</td>
<td>205</td>
</tr>
<tr>
<td>$\beta_{s,2}$ (unitless)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>22.0</td>
</tr>
<tr>
<td>$\beta_{m0}$ (unitless)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.50</td>
<td>2.50</td>
</tr>
<tr>
<td>SSE</td>
<td>27.968</td>
<td>35.421</td>
<td>22.333</td>
<td>2.404</td>
<td>1.512</td>
</tr>
</tbody>
</table>

Next, each model variation shown in Tables 4.3 and 4.4 will be individually expanded upon in greater detail, and the model plots corresponding to these best-fit parameters will be discussed. The problem-solving methodology and pathway to arriving at the best-fit models will be reflected upon as well.

**Single Site Micropore-Only (SSMI) Model**

As explored in Chapter 3, the first modeling approach was conducted using one of the most simplified versions of a micropore model. In this case, it is assumed that there is no resistance to mass transfer at the mouth of the micropore, and that the only barrier to
mass transfer is diffusion in the micropore. Figure 4.1 shows the intensity and phase lag plots of the SSMI model fits for both nitrogen and oxygen on the CMS sample. Table 4.5 contains the parameters that were used to obtain these fits. As observed in the intensity plots in 4.1a and 4.1c, the SSMI model is accurate at very low frequencies, where the frequency is small enough such that there is no resistance to mass transfer in either case. These initial plateaus describe the VSFR system under conditions of local isothermal equilibrium, where parameters related to heat transfer and the isotherm model are the primary factor in model fits. As such, it may be seen in Figure 4.1 that the isotherm fits, heat transfer and heat capacity parameters, and the micropore porosity parameter are all within acceptable values. Given this accurate modeling of low frequency behavior, these aforementioned parameters were used in subsequent model fittings. As the frequency increases towards intermediate values, the intensity begins to drop off in 4.1a and 4.1c, which is characteristic of limitations to the rate of diffusion within the micropore. Given that the SSMI model emphasizes this limitation, the quality of the model fits at the initial intensity drop-off is acceptable. However, the SSMI model results indicate that it is incapable of adequately describing the behavior of the intensity curves at high frequencies, where the intensity levels off at near-zero values. This feature occurs around 0.02 Hz for nitrogen, and 0.9 Hz for oxygen. Additionally, the magnitude and location of the phase lag curve peaks, as predicted by the model, are not satisfactory. As the phase lag peaks correlate with the steepest point of decrease in intensity, it is logical that as the SSMI model cannot fully predict the intensity drop-off, the phase lag fits will be of poor quality as well.
Figure 4.1 Plot for frequency response variables of nitrogen and oxygen on CMS with SSMI model: (a) nitrogen intensity (b) nitrogen phase lag (c) oxygen intensity (d) oxygen phase lag

Table 4.5 Fitting parameters used for SSMI model in Figure 4.1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nitrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{s,r}$ (1/s)</td>
<td>6.00x10^{-4}</td>
<td>1.40x10^{-2}</td>
</tr>
<tr>
<td>$K_{mo,r}$ (1/s)</td>
<td>1.00x10^{4}</td>
<td>1.00x10^{4}</td>
</tr>
<tr>
<td>$hA$ (W/K)</td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>$E_s$ (K)</td>
<td>1600</td>
<td>1200</td>
</tr>
<tr>
<td>$E_{mo}$ (K)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Single Site Mouth-Resistance-Only (SSMR) Model

In order to attempt to correct the shortcomings of the SSMI model at high frequencies, the next fittings were conducted using the SSMR model. Whereas the SSMI model is built from the assumption that the only limitation to mass transfer is diffusion in the micropore, the SSMR model is centered around the assumption that the only limiting mass transfer mechanism is resistance at the mouth of the micropore. As seen in Figure 4.2, the quality of the model fits using the SSMR model is greatly improved at high frequency values. However, the behavior at intermediate frequencies, as seen in 4.2a and 4.2c, is not adequately predicted. Likewise, while the shapes of the phase lag curves in 4.2b and 4.2d appear to be a more adequate representation of the experimental data than obtained with the SSMI model, the magnitudes and peak locations are still not within acceptable tolerances. As such, it was recognized from the results of the SSMI/SSMR models that a combination of micropore diffusion and mouth resistance limitations is necessary to begin to describe the frequency response behavior of nitrogen and oxygen on Shirasagi CMS 3K172. The best-fit parameters obtained using the SSMR model are included in Table 4.6.
Figure 4.2 Plot for frequency response variables of nitrogen and oxygen on CMS with SSMR model: (a) nitrogen intensity (b) nitrogen phase lag (c) oxygen intensity (d) oxygen phase lag

Table 4.6 Fitting parameters used for SSMR model in Figure 4.2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nitrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_s,r$ (1/s)</td>
<td>$1.00 \times 10^4$</td>
<td>$1.00 \times 10^4$</td>
</tr>
<tr>
<td>$K_{mo,r}$ (1/s)</td>
<td>$1.00 \times 10^{-2}$</td>
<td>$2.75 \times 10^{-1}$</td>
</tr>
<tr>
<td>$hA$ (W/K)</td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>$E_s$ (K)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_{mo}$ (K)</td>
<td>3000</td>
<td>2500</td>
</tr>
</tbody>
</table>

**Single Site Combined Micropore and Mouth Resistance (SSC) Model**

Following the identification that it is necessary to account for both micropore diffusion and mouth resistance as sources of limitation to mass transfer for these data
sets, the SSC model was explored in greater detail. As the name suggests, the SSC model adds an additional layer of complication to the micropore model, as both $K_{s,o}$ and $K_{mo,o}$ are used as fitting parameters to describe the behavior of these adsorbent-adsorbate pairs. The best-fit results obtained using the SSC model are shown in Figure 4.3, and the corresponding parameters are included in Table 4.7. As seen in 4.3a and 4.3c, the intensity behavior for the experimental runs near atmospheric pressure was able to be predicted with a fair degree of accuracy. Correspondingly, the model fittings for the phase lag behavior of these same sets of conditions in 4.3b and 4.3d greatly improved as well. However, it is clear that the runs at lower pressures, and thus lower loadings were not closely modeled. From 4.3a and 4.3c, it appears that the values of $K_{s,o}$ and $K_{mo,o}$ should have been decreased if good quality fits were desired for pressures of 100 and 200 torr. As expected, however, doing so would sacrifice the quality of the fits at 750 torr. Furthermore, it was noted that the best-fit values of the mass transfer coefficients at each pressure condition possessed a stronger dependence upon loading than that predicted by Darken’s model. In light of this observation, it was recognized that in order to model all three pressures simultaneously, a more complex loading dependence should be added into the micropore model for both the micropore diffusion and mouth resistance mass transfer coefficients.
Figure 4.3 Plot for frequency response variables of nitrogen and oxygen on CMS with SSC model: (a) nitrogen intensity (b) nitrogen phase lag (c) oxygen intensity (d) oxygen phase lag

Table 4.7 Fitting parameters used for SSC model in Figure 4.3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nitrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_s, r$ (1/s)</td>
<td>1.20x10^{-3}</td>
<td>2.33x10^{-2}</td>
</tr>
<tr>
<td>$K_{mo}, r$ (1/s)</td>
<td>1.37x10^{-2}</td>
<td>5.47x10^{-1}</td>
</tr>
<tr>
<td>$hA$ (W/K)</td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>$E_s$ (K)</td>
<td>1600</td>
<td>2200</td>
</tr>
<tr>
<td>$E_{mo}$ (K)</td>
<td>3000</td>
<td>2500</td>
</tr>
</tbody>
</table>

**Single Site Combined with Loading Dependence (SSCLD) Model**

As discussed for the SSC model results, it was recognized that the addition of a more complex loading dependence for $K_s$ and $K_{mo}$ would be crucial in obtaining better
fits to the intensity and phase lag curves. In the corresponding section in Chapter 3, one such correlation was identified in the literature. Although this correlation is not derived from any existing theory and is instead an empirical model arbitrarily set up to describe observed results, preliminary work indicated that this same model would be effective in improving these modeling results. These results and their corresponding parameters are shown in Figure 4.4 and Table 4.8, respectively. As shown in 4.4a and 4.4c, the intensity curves for pressures of 100 and 200 torr match the experimental data more closely than achieved with any simpler model. Additionally, the quality of the fittings at 750 torr were not sacrificed in order to make this improvement, as a direct result of integrating the loading dependence model equations into the overall micropore model.

For nitrogen on Shirasagi CMS 3K172, the fits shown in 4.4a and 4.4c appeared to be an adequate representation of the observed experimental data, and no further modeling work was deemed necessary for nitrogen. The intensity curve for nitrogen is almost a direct match between the model and the empirical data, and while the peak locations at 100 and 200 torr for the phase lag model curves are at lower frequencies than observed in the experiments, their respective magnitudes are almost exactly predicted by the model. While improvement could be made to the phase lag model curve magnitudes at 750 torr, the foci of the predicted peaks appear to fully match the empirical data. The increase, or “tails”, observed in the phase lag data at high frequencies were presumed to be beyond the scope of this modeling work. A likely cause for these tails is some small gas capacity carried in the macropore domain at high frequency, which would explain a discrepancy in phase angle of the output differential pressure relative to the phase angle of the volumetric perturbation. This could be a particular area of focus of future work,
which would require the transition between a micropore model to a macropore model at high frequencies. Despite this limitation of the current model, it was concluded from 4.4a and 4.4c that the most likely mass transfer mechanism of nitrogen on this particular CMS is a combination of micropore diffusion and mouth resistance at the micropore entrance.

While the SSCLD model was deemed a proper endpoint for the behavior of nitrogen on CMS, there is an inflection point, or “shoulder”, that may be observed for the phase lag peaks of oxygen at 100 and 200 torr in 4.4d. As such, an additional complication to the model was made in order to describe this phenomenon.

Figure 4.4 Plot for frequency response variables of nitrogen and oxygen on CMS with SSCLD model: (a) nitrogen intensity (b) nitrogen phase lag (c) oxygen intensity (d) oxygen phase lag
Table 4.8 Fitting parameters used for SSCLD model in Figure 4.4

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nitrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{s,r}$ (1/s)</td>
<td>1.50x10^{-3}</td>
<td>2.33x10^{-2}</td>
</tr>
<tr>
<td>$K_{mo,r}$ (1/s)</td>
<td>1.09x10^{-2}</td>
<td>4.32x10^{-1}</td>
</tr>
<tr>
<td>hA (W/K)</td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>$E_s$ (K)</td>
<td>2000</td>
<td>3625</td>
</tr>
<tr>
<td>$E_{mo}$ (K)</td>
<td>3600</td>
<td>3000</td>
</tr>
<tr>
<td>$\beta_s$ (unitless)</td>
<td>12.5</td>
<td>255</td>
</tr>
<tr>
<td>$\beta_{mo}$ (unitless)</td>
<td>2.50</td>
<td>2.50</td>
</tr>
</tbody>
</table>

**Dual Site Combined with Loading Dependence (DSCLD) Model**

From the quality of the model fits for oxygen obtained using the SSCLD model, it was decided that another layer of complication must be made to the model in order to fully capture the behavior of oxygen on Shirasagi CMS 3K172. As discussed in Chapter 3, this additional complication is built from the assumption that oxygen, which has a slightly smaller kinetic diameter than nitrogen, is able to interact with two different site geometries. Since nitrogen is larger, it is assumed that there is no effective difference between these sites for nitrogen, and so it interacts with either as if there was a single site geometry. However, oxygen’s kinetic diameter is assumed to be small enough such that the interaction is different from one site geometry to another. This model assumes that the limitation to the mass transfer of oxygen in the micropore is much greater across only one of these site geometries and is much less limited by the other. While this model has the capability of making this same partition for the micropore mouth, it was not deemed necessary for this modeling work, as a single value for the mouth resistance mass transfer coefficient was able to effectively capture oxygen’s behavior. As such, two values were
established for the micropore mass transfer coefficients, as well as their respective loading and temperature dependencies. Additionally, an additional parameter, alpha, was established in order to define the partition between the relative quantities of adsorbed phase on these two site geometries.

The results and parameters for the DSCLD model are shown in Figure 4.5 and Table 4.9. As observed in Figure 4.5a, the intensity model curves at 100 and 200 torr are slightly closer to the experimental data than the best attempt made with the SSCLD model, and the fits at 750 torr are mostly unchanged. For the phase lag plot in 4.5b, the “shoulder” phenomenon observed at 100 and 200 torr was able to be predicted, and the peak locations and magnitudes of the two lower pressure phase lag model curves are much closer to approximating the experimental data. Interestingly, this inflection point observed at 100 and 200 torr disappeared at 750 torr, both for the model and the data. As such, it may be concluded that the phenomenon captured by this dual site model only begins to appear at pressures that are below atmospheric pressure. Similar to the SSCLD model, the increase in phase lag at high frequency was not effectively predicted by the DSCLD model, and was deemed to be outside of the scope of this modeling work.

Given the good quality of the intensity and phase lag model fits, it may be presumed that the most likely source of mass transfer limitations for oxygen on Shirasagi CMS 3K172 is a two site limitation to micropore diffusion paired with a singular mouth resistance.
Figure 4.5 Plot for frequency response variable of oxygen on CMS with DSCLD model:
(a) oxygen intensity (b) oxygen phase lag
Table 4.9 Fitting parameters used for DSCLD model in Figure 4.5

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ (unitless)</td>
<td>0.800</td>
</tr>
<tr>
<td>$K_{s,r,1}$ (1/s)</td>
<td>$1.73 \times 10^{-2}$</td>
</tr>
<tr>
<td>$K_{s,r,2}$ (1/s)</td>
<td>$1.63 \times 10^{0}$</td>
</tr>
<tr>
<td>$K_{m,o,r}$ (1/s)</td>
<td>$4.32 \times 10^{-1}$</td>
</tr>
<tr>
<td>$hA$ (W/K)</td>
<td>0.500</td>
</tr>
<tr>
<td>$E_{s,1}$ (K)</td>
<td>3625</td>
</tr>
<tr>
<td>$E_{s,2}$ (K)</td>
<td>3625</td>
</tr>
<tr>
<td>$E_{m,o}$ (K)</td>
<td>3000</td>
</tr>
<tr>
<td>$\beta_{s,1}$ (unitless)</td>
<td>205</td>
</tr>
<tr>
<td>$\beta_{s,2}$ (unitless)</td>
<td>22.0</td>
</tr>
<tr>
<td>$\beta_{m,o}$ (unitless)</td>
<td>2.50</td>
</tr>
</tbody>
</table>

**Best Fit Results**

For clarity, the best fit parameters for the corresponding best fit models for nitrogen and oxygen are included in Table 4.10. As discussed previously, the SSCLD model was effective at describing the behavior of nitrogen on CMS, whereas the additional complication added by the use of the DSCLD model was necessary to approximate the behavior of oxygen on the same CMS material.
Table 4.10 Best fit parameters obtained for nitrogen (SSCLD model) and oxygen (DSCLD model) on Shirasagi CMS 3K172

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nitrogen (SSCLD)</th>
<th>Oxygen (DSCLD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α (unitless)</td>
<td>-</td>
<td>0.800</td>
</tr>
<tr>
<td>$K_{s,r,1}$ (1/s)</td>
<td>1.50x10³</td>
<td>1.73x10⁻²</td>
</tr>
<tr>
<td>$K_{s,r,2}$ (1/s)</td>
<td>1.63x10¹</td>
<td>1.63x10⁰</td>
</tr>
<tr>
<td>$K_{mo,r}$ (1/s)</td>
<td>1.09x10⁻²</td>
<td>4.32x10⁻¹</td>
</tr>
<tr>
<td>$h_A$ (W/K)</td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>$E_{s,1}$ (K)</td>
<td>2000</td>
<td>3625</td>
</tr>
<tr>
<td>$E_{s,2}$ (K)</td>
<td>3600</td>
<td>3000</td>
</tr>
<tr>
<td>$E_{mo}$ (K)</td>
<td>3600</td>
<td>3000</td>
</tr>
<tr>
<td>$\beta_{s,1}$ (unitless)</td>
<td>12.5</td>
<td>205</td>
</tr>
<tr>
<td>$\beta_{s,2}$ (unitless)</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>$\beta_{mo}$ (unitless)</td>
<td>2.50</td>
<td>2.50</td>
</tr>
<tr>
<td>SSE</td>
<td>0.932</td>
<td>1.512</td>
</tr>
</tbody>
</table>

As shown in Table 4.10, for the oxygen modeling results, the second site micropore diffusion term is several orders of magnitude larger than the micropore diffusion mass transfer coefficient at the first site, which matches the assumption made in the DSCLD model discussion. The value for the micropore diffusion term at the first site geometry for oxygen appears to each be around an order of magnitude larger than the corresponding single site micropore diffusion term for nitrogen. For the mouth resistance term, the value for oxygen appears to be around an order of magnitude larger than the value observed for nitrogen. As such, it may be concluded that the effective separation of nitrogen and oxygen across this CMS material is enabled by a two-fold kinetic limitation.

As suggested by Table 4.10, oxygen is able to diffuse through the micropore mouth at a faster rate than nitrogen, and is also able to diffuse faster than nitrogen through the
micropore domain itself, especially at the second site, where around 20% of the oxygen is able to diffuse through the micropore at a rate many times faster than that predicted for nitrogen.

**Conclusions**

As discussed in Chapter 1, the primary objective of this modeling work was to determine the limiting mass transfer mechanisms for the adsorption of nitrogen and oxygen on Shirasagi CMS 3K172. This was achieved through the use of frequency response techniques reflected upon in Chapter 2, and subsequent modeling of the frequency response variables using COMSOL Multiphysics and MATLAB, as discussed in Chapter 3. As such, experimental data was gathered for nitrogen and oxygen on Shirasagi CMS 3K172 at 100 and 200 torr at 25°C, and at 750 torr and 20, 30, 40, and 50°C using the in-house built VSFR system, and best-fit model results were obtained for five different micropore models in an effort to approximate the observed experimental data trends.

For the empirical results for nitrogen and oxygen, both exhibited similar behavior: at low frequencies, the intensity curves for each had a plateau at a state of isothermal local equilibrium that was governed by the isotherm fittings and heat transfer effects, at intermediate frequencies, the intensity began to drop as a direct result of limits to the rate of diffusion in the micropore, and at high frequencies, the intensity dropped further until leveling off at a near-zero value, as a function of limits to diffusion across the micropore mouth. Correspondingly, the phase lag curves started off at zero at low frequencies, and began to increase as the micropore diffusion limitation was encountered. Once the mouth resistance began to impact intensity, the phase lag curves began to decrease towards zero.
as the mouth of the micropore began to function as an impermeable barrier at high
frequencies. The peaks of the phase lag curves were observed at intermediate frequency
values, likely in the region of transition from micropore diffusion to mouth resistance as
the principal limitation to mass transfer. Lastly, at very high frequencies, the phase lag
curves did not converge to zero. This is theorized to be a result of some small,
measurable capacity of gas being retained in the macropore domain and should be a
greater area of focus in future modeling endeavors.

Several modeling results indicate agreement with the observed experimental data.
For nitrogen on Shirasagi CMS 3K172, the good-quality fits obtained using the SSCLD
model indicate that the most likely mass transfer mechanism for nitrogen on this CMS
material is a combined limitation to diffusion in the micropore and resistance at the
micropore mouth. Additionally, the SSCLD model fit suggests that the mass transfer
coefficients for the micropore and the mouth both exhibit a strong dependence upon the
loading in the micropore crystal domain. For oxygen on Shirasagi CMS 3K172, the best
model fits were observed for the DSCLD model, which suggests that the mass transfer
regime for oxygen on this CMS material is likewise a combined limitation of micropore
diffusion and mouth resistance, but also that oxygen diffuses in two separate partitions,
such that there are two micropore diffusion terms, where one is much more limiting than
the other. The DSCLD model was the only model examined that was able to effectively
mirror the behavior of the empirical phase lag curves at 100 and 200 torr for oxygen and
predict the same “shoulder” observed in the experimental data. Similar to the results for
nitrogen, the DSCLD model’s good approximation of the experimental data for oxygen
suggests that both micropore diffusion terms as well as the mouth resistance term are all
more strongly dependent upon loading than predicted by Darken’s model. Overall, these modeling results suggest that the most likely mass transfer regimes are the SSCLD model for nitrogen on Shirasagi CMS 3K172, and the DSCLD model for oxygen on Shirasagi CMS 3K172.
References


Appendix A: Derivations of Mass and Energy Balances

Given that the VSFR system is a closed system, the total number of moles of adsorbate in the system, \( n_{tot} \), will remain constant at all values of time \( t \):

\[
\frac{\partial n_{tot}}{\partial t} = 0
\]  

where \( \bar{q} \) is the average loading of the adsorbed phase in the overall domain of the adsorbent, \( \bar{C}_{g,M} \) is the average concentration of gas within the volume of the macropore domain, \( C_{g,i} \) is the concentration of gas in the interstitial adsorbent particle volume, and \( C_{g,ext} \) is the concentration of gas in the portion of the working volume completely external to the adsorbent sample.

This mass balance can be further simplified by making the assumption that the entire working volume is at the same absolute pressure. The time derivative of each component on the right-hand side of equation 22 may be evaluated to set their summation equal to zero in correspondence with equation 23, which is valid across all values of time \( t \). Another key assumption was made in order to describe the concentration values in terms of other more easily accessible quantities: the adsorbate gas was assumed to behave ideally under the experimental conditions used, and so the ideal gas law was applied for each:
\[ \overline{C_{g,M}} = \frac{\overline{P}_p}{RT} = \frac{P_p}{RT} = \frac{P}{RT} \]  
(A.1)

\[ C_{g,i} = \frac{P}{RT} \]  
(A.2)

\[ C_{g,ext} = \frac{P}{RT_{ext}} \]  
(A.3)

where R is the ideal gas constant, \( \overline{P}_p \) is the average pressure of gas within the pellet macropore volume, and \( P_p \) is the local pressure of gas within the macropore volume, assumed to be equal to the pressure outside the pellet as the diffusion of oxygen and nitrogen should not be strongly limited across the macropore domain. It is worth noting that the temperature in the interstitial volume is assumed to be identical to the temperature in the pores of the adsorbent pellets, while the temperature in the volume external to the sample volume is considered individually.

The time derivatives of equations A.1-A.3 are necessary to be calculated in order to substitute the terms of equation 22 into equation 23:

\[ \frac{\partial \overline{C_{g,M}}}{\partial t} = \frac{\partial C_{g,i}}{\partial t} = \frac{1}{RT} \frac{\partial P}{\partial t} - \frac{P}{RT^2} \frac{\partial T}{\partial t} \]  
(A.4)

\[ \frac{\partial C_{g,ext}}{\partial t} = \frac{1}{RT_{ext}} \frac{\partial P}{\partial t} - \frac{P}{RT_{ext}^2} \frac{\partial T_{ext}}{\partial t} \]  
(A.5)

While the macropore and interstitial volumes are constant with respect to time and can be used directly in equation 23, the volume external to the sample volume changes relative to the position of the metal bellows. As such, the time derivative of this volume must be taken to account for the time-dependence of this volume, which is expressed as \( \dot{n} \), the molar rate of change of gas species external to the sample volume, in subsequent equations:
\[ \frac{\partial (C_{g,ext}V_{ext})}{\partial t} = V_{ext} \left( \frac{1}{RT_{ext}} \frac{\partial P}{\partial t} - \frac{P}{RT_{ext}} \frac{\partial T_{ext}}{\partial t} \right) + \frac{P}{RT_{ext}} \frac{\partial V_{ext}}{\partial t} = \dot{n} \]  
(A.6)

The time-derivative of the external volume is provided in equation A.7:

\[ \frac{\partial V_{ext}}{\partial t} = 2\pi f \Delta V \cos(2\pi f t) \]  
(A.7)

Each of the terms expressed in equations A.4-A.6, in addition to the time-derivative of the average loading across the micropore domain, may be substituted into equation 23:

\[ m \frac{\partial \bar{q}}{\partial t} + \frac{V_{g,M}}{RT} \left( \frac{\partial P}{\partial t} - \frac{P}{T} \frac{\partial T}{\partial t} \right) + \frac{V_{g,i}}{RT} \left( \frac{\partial P}{\partial t} - \frac{P}{T} \frac{\partial T}{\partial t} \right) + \dot{n} = 0 \]  
(24)

Equation 24, as previously mentioned in Chapter 3, summarizes the mass balance that describes this VSFR system, and may be simultaneously solved with the energy balance and the micropore model equation(s) in order to model this system.

While the mass balance provided in equation 24 is applied across the entire working volume, the energy balance is only applied to the volumes directly related to the sample volume: \( V_{g,m} \), \( V_{g,M} \), \( V_{g,i} \), and \( V_s \). The starting point for the determination of the energy balance is provided by the following relationship, which relates the difference between the final and initial internal energy values to the net result of the energy gained and lost from the sample volume:

\[ \int_0^{V_{g,M}} U_{g,M} C_{g,M} dV|_{t+\Delta t} + U_{g,i} C_{g,i} V_{g,i}|_{t+\Delta t} + U_s m|_{t+\Delta t} + \int_0^{V_s} U_a q \, dV|_{t+\Delta t} - \]

\[ \int_0^{V_{g,M}} U_{g,M} C_{g,M} dV|_t + U_{g,i} C_{g,i} V_{g,i}|_t + U_s m|_t + \int_0^{V_s} U_a q \, dV|_t = hA(T_{bath} - T) \Delta t - \dot{n} H_g^* \Delta t \]  
(A.9)
where $\Delta t$ signifies a change in time $t$, and $U_{g,M}$, $U_{g,i}$, $U_s$, and $\bar{U}_a$ are the internal energy values for the macropore, interstitial volume, solid adsorbent, and adsorbed phase average, respectively. The average loading evaluated across the micropore domain is symbolized by $\bar{q}$, the temperature of the circulating water jacket is $T_{bath}$, $H_g^*$ is the enthalpy of the gas at the boundary between the sample bed and the exterior volume, and $C_{g,M}$ is the local value for the concentration of gas in the macropore.

A simplification may be made to equation A.9 by dividing both sides by $\Delta t$, and evaluating the expression at the limit as $\Delta t$ approaches zero:

$$
\int_0^{V_g,M} \frac{\partial (U_{g,M}C_{g,M})}{\partial t} dV + V_{g,i} \frac{\partial (U_{g,i}C_{g,i})}{\partial t} + m \frac{\partial (U_s)}{\partial t} + \int_0^{V_s} \frac{\partial (\bar{U}_a\bar{q})}{\partial t} dV = \\
\int_0^{V_g,M} \frac{\partial (U_{g,M}C_{g,M})}{\partial t} dV + V_{g,i} \frac{\partial (U_{g,i}C_{g,i})}{\partial t} + m \frac{\partial (U_s)}{\partial t} + \int_0^{V_s} \frac{\partial (\bar{U}_a\bar{q})}{\partial t} dV = \\
hA(T_{bath} - T) - \dot{n}H_g^* 
$$

(A.10)

Following the ideal gas assumption that was made during simplifications to the mass balance, the internal energies of the macropore and interstitial volumes are not a function of pressure, and are instead related to only temperature and enthalpy:

$$
U_{g,M} = H_{g,M} - RT 
$$

(A.11)

$$
U_{g,i} = H_{g,i} - RT 
$$

(A.12)

where $H_{g,M}$ and $H_{g,i}$ are the enthalpies of the gas occupying the macropore and interstitial volumes, respectively.

The simplifications made in equations A.11 and A.12 may be plugged into their related time-derivatives in equation A.10:

$$
\frac{\partial (U_{g,M}C_{g,M})}{\partial t} = C_{g,M} \left( \frac{\partial H_{g,M}}{\partial t} - R \frac{\partial T}{\partial t} \right) + \frac{\partial C_{g,M}}{\partial t} \left( H_{g,M} - RT \right) 
$$

(A.13)
\[
\frac{\partial (u_{g,l}c_{g,l})}{\partial t} = C_{g,l} \left( \frac{\partial H_{g,l}}{\partial t} - R \frac{\partial T}{\partial t} \right) + \frac{\partial c_{g,l}}{\partial t} (H_{g,l} - RT) \tag{A.14}
\]

Additionally:

\[
\frac{\partial H_{g,M}}{\partial t} = \frac{\partial H_{g,M}}{\partial T} \frac{\partial T}{\partial t} = C_{pg} \frac{\partial T}{\partial t} = \frac{\partial H_{g,l}}{\partial t} = \frac{\partial H_{g}}{\partial t} \tag{A.15}
\]

\[
\int_0^{V_{g,M}} C_{g,M} dV = \bar{c}_{g,M} V_{g,M} \tag{A.16}
\]

where \(C_{pg}\) is the heat capacity of the test gas, and \(H_g\) is the enthalpy of the gas, which should be identical in value between the macropore and interstitial volumes following the assumption that their temperatures are equal to one another.

Given the simplifications made in equations A.15 and A.16, equations A.13 and A.14 as listed in equation A.10 become:

\[
\int_0^{V_{g,M}} \frac{\partial (u_{g,M}c_{g,M})}{\partial t} dV = \left( C_{pg} - R \right) \bar{c}_{g,M} V_{g,M} \frac{\partial T}{\partial t} + (H_g - RT) V_{g,M} \frac{\partial c_{g,M}}{\partial t} \tag{A.17}
\]

\[
V_{g,l} \frac{\partial (u_{g,l}c_{g,l})}{\partial t} = \left( C_{pg} - R \right) C_{g,l} V_{g,l} \frac{\partial T}{\partial t} + (H_g - RT) V_{g,l} \frac{\partial c_{g,l}}{\partial t} \tag{A.18}
\]

Next, the expression for the solid adsorbent may be simplified, using the assumption that the internal energy of the adsorbent is directly equivalent to its enthalpy:

\[
m \frac{\partial u_s}{\partial t} = m \frac{\partial H_s}{\partial t} = m C_{pp} \frac{\partial T}{\partial t} \tag{A.19}
\]

where \(C_{pp}\) is the heat capacity of the solid-phase adsorbent material.

Lastly, the adsorbed-phase term may be simplified using the following relationship:

\[
\bar{U}_a = H_g + \Delta H_a \tag{A.20}
\]
where $\Delta H_a$ is the heat of adsorption, the change in energy correlated to the loss of degrees of freedom associated with adsorption onto a surface.

As such, the adsorbed-phase term becomes:

$$
\int_0^{V_g} \frac{\partial (\overline{u_a q})}{\partial t} \, dV = \overline{q} \left( c_{pg} + \frac{\partial \Delta H_a}{\partial T} \right) \frac{\partial T}{\partial t} + (H_g + \Delta H_a + \overline{q} \frac{\partial \Delta H_a}{\partial \overline{q}}) \frac{\partial \overline{q}}{\partial t}
$$

(A.21)

Plugging these simplifications into equation A.10 and simplifying further yields the energy balance for the sample volume:

$$
V_{g,M} \left( \left( c_{pg} - R \overline{C_{g,M}} \right) \frac{\partial T}{\partial t} - RT \left( \frac{\partial \overline{C_{g,M}}}{\partial t} \right) \right) + V_{g,i} \left[ c_{pg} \left( \frac{P}{RT} \frac{\partial T}{\partial t} - \frac{\partial P}{\partial t} \right) \right] +

m \overline{q} \left[ c_{pg} + \frac{\partial \Delta H_a}{\partial T} \right] \frac{\partial T}{\partial t} + m c_{pp} \frac{\partial T}{\partial t} + m \left[ \Delta H_a + \overline{q} \frac{\partial \Delta H_a}{\partial \overline{q}} \right] \frac{\partial \overline{q}}{\partial t} =

hA(T_{bat\h} - T) + \dot{n} \Delta H^*
$$

(25)

where:

$$
\Delta H^* = H_g(T) - H_g^*(T^*) = \int_{T^*}^T c_{pg} \, dT
$$

(A.22)

$$
T^* = \frac{T + T_{ext}}{2}
$$

(A.23)

and where $H_g^*(T^*)$ is the enthalpy of the gas at the interfacial boundary between the sample and exterior volumes, while $T^*$ is the temperature at the interface.