Sequestering Carbon Dioxide in Coalbeds

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ABSTRACT

The authors' long-term goal is to develop accurate prediction methods for describing the adsorption behavior of gas mixtures on solid adsorbents over complete ranges of temperature, pressure, and adsorbent types. The originally-stated, major objectives of the current project are to

- measure the adsorption behavior of pure CO₂, methane, nitrogen, and their binary and ternary mixtures *on several selected coals having different properties* at temperatures and pressures applicable to the particular coals being studied,
- generalize the adsorption results in terms of appropriate properties of the coals to facilitate estimation of adsorption behavior for coals other than those studied experimentally,
- delineate the sensitivity of the *competitive* adsorption of CO₂, methane, and nitrogen to the specific characteristics of the coal on which they are adsorbed; establish the major differences (if any) in the nature of this competitive adsorption on different coals, and
- test and/or develop theoretically-based mathematical models to represent accurately the adsorption behavior of mixtures of the type for which measurements are made.

As this project developed, an important additional objective was added to the above original list. Namely, we were encouraged to interact with industry and/or governmental agencies to utilize our expertise to advance the state of the art in coalbed adsorption science and technology. As a result of this additional objective, we participated with the Department of Energy and industry in the measurement and analysis of adsorption behavior as part of two distinct investigations. These include (a) Advanced Resources International (ARI) DOE Project DE-FC26-00NT40924, "Adsorption of Pure Methane, Nitrogen, and Carbon Dioxide and Their Mixtures on Wet Tiffany Coal", and (b) the DOE-NETL Project, "Round Robin: CO₂ Adsorption on Selected Coals". These activities, contributing directly to the DOE projects listed above, also provided direct synergism with the original goals of our work.

Specific accomplishments of this project are summarized below in three broad categories: experimentation, model development, and coal characterization.

Experimental Work: Pure-gas adsorption measurements were conducted for methane, nitrogen, ethane, and carbon dioxide on **ten** solid matrices: wet Fruitland coal (OSU #1 and OSU #2), wet Lower Basin Fruitland coal (OSU #3), wet / dry Illinois #6 coal, wet Tiffany coal, dry Beulah Zap coal, dry Wyodak coal, dry Upper Freeport coal, dry Pocahontas coal, and dry activated carbon.

Binary and ternary adsorption measurements were conducted for mixtures of methane, nitrogen and CO₂ at a series of compositions on **four** different matrices: Fruitland coal, Illinois #6 coal, Tiffany coal, and activated carbon. Ternary measurements were also

measured for methane/nitrogen/CO₂ mixtures on wet, mixed Tiffany coal and on dry activated carbon.

The expected experimental uncertainty of the pure-gas adsorption data is on average about 3%. However, the expected uncertainties in the amount adsorbed for the mixture data vary with pressure and composition. In general, average uncertainties are below 5% for total adsorption; while, the individual-component uncertainties vary from 0.02 to 0.4 mmol/g depending on the mixture composition. Moreover, the expected uncertainties (on a percent basis) in the amount of individual-component adsorption are significantly higher for the less-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20/80 nitrogen/CO₂ system).

As part of this project, an adsorption database was assembled (**OSU Adsorption Database**) which contains the pure, binary, and ternary mixture adsorption measurements conducted at Oklahoma State University. Included in the database are details regarding the adsorbates, the adsorbent, and the corresponding temperature and pressure ranges for each system. Also reported is the expected experimental uncertainty for each adsorption measurement.

The data are presented in terms of both Gibbs and absolute adsorption since absolute adsorption is the quantity most familiar to practitioners in coalbed methane (CBM) operations. Also for convenience, the data are reported both in SI and English engineering units.

Model Development: Our experimental data and similar data from the literature were used to evaluate and further develop the predictive capabilities of various adsorption models, including the Zhou-Gasem-Robinson (ZGR) two-dimensional equation of state (EOS), the 2-D analog of the Peng-Robinson (PR) EOS, the modified simplified local density model (SLD), and the Ono-Kondo (OK) lattice model. These models, selected because they are based on quite different physical premises, have been applied to our adsorption data to delineate each model's relative accuracy and utility. Model parameters have been obtained for the systems studied.

The model development efforts addressed two critical issues; namely, the ability of the selected models to (a) correlate the acquired adsorption data within their experimental uncertainties, and (b) provide a reliable *predictive* capability. Thus, beyond establishing models precision in summarizing existing data, we were also interested in evaluating the efficacy of such models in using pure and/or binary measurements to provide accurate predictions for ternary and other multicomponent mixtures.

The model development results indicate that (a) the selected frameworks provide models capable of precisely describing high-pressure adsorption, (b) the use of matrix-calibrated models will minimize the experimental effort required to obtain accurate adsorption predictions for a specific CBM site, and (c) a potential exists for developing a *priori* predictive models using fully-generalized parameters determined by accessible adsorbate and adsorbent characterizations. However, to realize the full benefits of

generalized predictions will require an accurate hard-sphere EOS, improved mixing rules, and a rigorous accounting for the water effects in the CBM adsorption systems.

Computational Algorithms: We have developed improved computational capabilities for high-pressure adsorption, including robust algorithms for solving adsorption equilibrium for a variety of models. For example, a new robust iteration function method (IFM) for mixture adsorption equilibrium calculations has been developed for 2-D EOS. Analysis of results involving many supercritical, CBM-type adsorption systems indicates that the new IFM algorithm is effective in performing equilibrium mixture adsorption calculations based on feed compositions. Further, excellent convergence characteristics are obtained using the new IFM, which employs the amount adsorbed as the iteration variable.

Compressibility Factor Predictions: We performed selected measurements of the gas-phase compressibility factor, Z , for binary and ternary mixtures of methane, nitrogen and CO_2 at 327.6 K (130 °F) and pressures to 13.8 MPa (2000 psia). These studies were necessitated by our need for accurate knowledge of gas-phase densities (or Z factors) for use in the data reduction procedure for our adsorption measurements. These Z data, along with literature results, were used to re-optimize parameters in the Benedict-Webb-Rubin (BWR) equation, which then predicted more accurate mixture Z factors. Use of the modified BWR equation reduced the uncertainties in our reported adsorption data.

Coal Characterization at Pennsylvania State University: Various characterization studies were conducted on a wide range of coals to discern the underlying physical and chemical properties of coal that determine their usefulness in enhanced coalbed methane and CO_2 sequestration operations,. Specifically, volumetric adsorption and microcalorimetry studies characterize the adsorption uptakes and enthalpies for coals ranging from lignite to low-volatile bituminous. To ascertain how specific adsorbate/adsorbent interactions are important in CO_2 adsorption, surface chemistry characterizations were conducted by measuring the point of zero charge (PZC) and the isoelectric point of the coals. No simple correlations were found between the CO_2 adsorption uptakes and the PZC values for the Argonne Premium coals, nor was a correlation found between the surface area of a coal and its adsorption capacity. Considering these findings, surface chemical effects (such as heteroatoms in the form of electron-donating or electron-withdrawing functional groups) should be further investigated to determine their relationship with CO_2 adsorption uptakes.

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A. Executive Summary

A summary of our major accomplishments in this project (1998-2002) appears below. Complementary tasks involving experimentation, model development, and coal characterization were undertaken to meet our project objectives.

Experimental Work

Facilities: Two experimental facilities have been dedicated to gas adsorption measurements at OSU. The first apparatus was developed in a prior project sponsored by the Amoco Corporation and the Oklahoma Center for the Advancement of Science and Technology. The second apparatus was assembled during the present project from an equipment donation from BP Amoco. The donation consisted of essentially the complete coalbed methane research equipment housed at BP Amoco's Tulsa Technology Center. In August 1999, the second apparatus was reassembled in OSU's new Advanced Technology Research Center, a \$35 million state-of-the-art complex dedicated to research and technology development. Essentially, the new facility allowed us to double our rate of data production.

Both experimental apparatuses were set up for pure-component and multicomponent adsorption measurements, and gas chromatograph calibrations were conducted to support the adsorption measurements. In addition, the two facilities were equipped with computerized data acquisition for gathering real-time data for the adsorption pressure and temperature. The acquired data are used to gauge with more certainty when the system reaches equilibrium. Data acquisition also serves as a useful tool for studying adsorption/desorption kinetics.

Pure-Component Adsorption Isotherms: After confirming the viability of our experimental apparatuses and procedures, we measured adsorption isotherms for CO₂, methane, ethane, and nitrogen on ~~ten~~ different coals and on activated carbon. Specifically, adsorption measurements were conducted for:

1. CO₂, methane, ethane, and nitrogen on wet Fruitland coal at 319.3 K (115 °F) and pressures to 12.4 MPa (1800 psia)
2. CO₂, methane, ethane, and nitrogen on dry activated carbon (Filtrisorb-400) at 318.5 K (113 °F); and CO₂, methane, and nitrogen at 327.6 K (130 °F) and pressures to 12.4 MPa (1800 psia)
3. CO₂, methane, and nitrogen on wet Illinois #6 coal at 319.3 K (115 °F) and pressures to 12.4 MPa (1800 psia)
4. CO₂, methane, and nitrogen on wet Lower Basin (LB) Fruitland coal at 319.3 K (115 °F) and pressures to 12.4 MPa (1800 psia).
5. CO₂, methane, and nitrogen on wet Tiffany coal at 327.6 K (130 °F) and pressures to 12.4 MPa (1800 psia)
6. CO₂, on dry Beulah-Zap, Illinois #6, Upper Freeport, Wyodak, and Pocahontas #3 coals at 328.2 K (131 °F) and pressures to 13.8 MPa (2000 psia)

7. CO₂ on wet activated carbon at 318.2 K and pressures to 12.4 MPa, with moisture contents of 35 and 42%.

These measurements are new additions to the existing database on coal adsorption. The expected uncertainty of these newly-acquired data is on average about 3%.

To support DOE project DE-FC26-00NT40924 at the request of project participant Advanced Resources International (ARI), a detailed adsorption study was made for the pure gases methane, nitrogen, and CO₂ and selected mixtures of these gases. These measurements were done to support field trials of gas injection in the Tiffany field. First, measurements were done for methane at 327.6 K (130°F) and pressures to 13.8 MPa (2000 psia) on two separate wet samples (Injection Wells No. 1 and 10) from the Tiffany field to assess the differences (if any) in the adsorption capacity of samples from the two wells. Results showed only minor differences (<5%), serving as a basis for further measurements on a mixed-well sample. The replicate runs for nitrogen and CO₂ show agreement within their experimental uncertainties. The measurements also agree with the previous coals in the *relative* amounts of nitrogen, methane, and CO₂ adsorbed, which are in the approximate ratio of 1:2.7:5 at 1000 psia.

At the invitation of DOE-NETL in Pittsburgh, we participated, along with five other laboratories, in a "Round-Robin" series of adsorption measurements designed to "(a) determine the reproducibility of CO₂ adsorption isotherms and (b) develop a standard method for measuring CO₂/coal adsorption isotherms." As part of this study, we have measured adsorption of pure CO₂ on dry Beulah-Zap, Illinois #6, Upper Freeport, Wyodak, and Pocahontas #3 coals at 328.2 K (131 °F) and pressures to 13.8 MPa (2000 psia). Data comparisons (conducted by DOE) among laboratories are incomplete at this time, but substantive differences exist. Speculative causes include differences in drying protocols (thus differences in coal sample moisture content) used among the labs and differences in experimental techniques utilized.

Binary Mixture Adsorption Isotherms: Adsorption from the three binary mixtures formed by methane, nitrogen, and CO₂ at a series of compositions was measured on **four** different matrices: Fruitland coal, Illinois #6 coal, Tiffany coal, and activated carbon.

- Adsorption isotherms were measured for methane/nitrogen, methane/CO₂, and nitrogen/CO₂ on wet Fruitland and Illinois #6 coals at 319.3 K (115 °F). The nominal molar feed compositions of these mixtures are 20%/80%, 40%/60%, 60%/40%, and 80%/20%. The experiments were conducted at pressures from 0.7 MPa (100 psia) to 12.4 MPa (1800 psia). The expected uncertainties for these binary mixture data vary from 2 to 10%.
- Adsorption isotherms were measured for methane/nitrogen, methane/CO₂, and nitrogen/CO₂ on wet, mixed Tiffany coal at 327.6 K (130 °F) and pressures to 13.7 MPa (2000 psia). The feed composition for the three binary system measured are 50%/50% methane/nitrogen, 40%/60% methane/CO₂, and

20%/80% nitrogen/CO₂. The expected uncertainties in the amount adsorbed for these binary mixtures vary with pressure and composition. In general, average uncertainties are below 5% (19 SCF/ton) for total adsorption; however, the expected uncertainties in the amount of individual-component adsorption are significantly higher for the less-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20%/80% nitrogen/CO₂ system).

- Binary adsorption of methane/nitrogen, nitrogen/CO₂, and methane/CO₂ on dry activated carbon were completed for the nominal molar feed compositions of about 20%/80%, 40%/60%, 60%/40%, and 80%/20%. These binary systems were studied at 318.2 K (113 °F) and pressures to 12.4 MPa (1800 psia). Error propagation analysis reveals expected average experimental uncertainties in the amount adsorbed of 2% for pure methane and nitrogen and 6% for CO₂. For the mixture measurements, uncertainties are estimated to be about 3% for the total adsorption, while the individual-component uncertainties vary from 0.02 to 0.4 mmol/g activated carbon, depending on the mixture composition.

Ternary Mixture Adsorption Isotherms: Adsorption for two ternary mixtures formed by methane, nitrogen and CO₂ at a single composition was measured on **two** different matrices: Tiffany coal and activated carbon.

- Ternary adsorption isotherms were measured for a single methane/nitrogen/CO₂ ternary mixture on wet, mixed Tiffany coal at 327.6 K (130 °F) and pressures to 13.8 MPa (2000 psia). The nominal molar feed composition was 10%/40%/50%. The average expected uncertainty for the total adsorption and for CO₂ adsorption is about 5% (16 SCF/ton). However, the low adsorption of nitrogen and methane in this ternary yield average experimental uncertainties of 14% (9 SCF/ton) and 27% (9 SCF/ton), respectively.
- Ternary adsorption isotherms were measured for a single methane/nitrogen/CO₂ ternary mixture on dry activated carbon at 318.2 K (113 °F) and pressures to 13.7 MPa (2000 psia). The nominal molar feed composition was 10%/40%/50%. The average expected uncertainty for the total adsorption is about 4%. However, the individual-component uncertainties vary from 0.02 to 0.2 mmol/g activated carbon, depending on the mixture composition.

Collectively, these ternary measurements are important (a) for direct use in engineering applications involving CO₂/methane/nitrogen CBM production and sequestration scenarios, (b) in model calibration and development, and (c) to confirm the viability of mixing rules used in adsorption models.

OSU Adsorption Database: As part of this project, an adsorption database was assembled which contains the pure, binary, and ternary mixture adsorption measurements conducted at Oklahoma State University. Included in the database are details regarding the adsorbates, the adsorbent, and the corresponding temperature

and pressure ranges for each system. Also, reported is the expected experimental uncertainty for each datum.

The data are presented in terms of both Gibbs and absolute adsorption since absolute adsorption is the quantity most familiar to practitioners in CBM operations. Also for convenience, the data are reported both in SI and English engineering units.

Model Development

Adsorption Models: We investigated five avenues for modeling adsorption equilibrium of systems encountered in CO₂ sequestration and coalbed methane production. These include (a) enhanced forms of the Langmuir-type isotherms, (b) two-dimensional equations of state (2-D EOS), (c) the simplified local density models (SLD), (d) use of the Ono-Kondo (OK) lattice theory, and (e) treating adsorption as a constrained form of vapor-liquid equilibrium. In doing so, our objective has been to develop reliable, simple analytic models capable of describing adsorption of near-critical and supercritical components on heterogeneous surfaces

Our experimental data and similar data from the literature were used to evaluate and further develop the predictive capabilities of 2-D EOS, SLD, and OK models. These models were selected because they originate from established theoretical frameworks and employ different physical bases for modeling adsorption. The models were developed and examined for their correlative and predictive capabilities as well as their utility in CBM operations.

The modeling developments can be illustrated by the following:

1. The SLD-PR model was modified to improve its description of repulsive interactions, which are especially important in the adsorbed phase. The results indicate that the modified SLD-PR model is capable of modeling the adsorption of pure methane, nitrogen, and CO₂ at coalbed conditions. In addition, accounting for the adsorption surface structure within the SLD-EOS framework is effective in improving modeling capability for high-pressure adsorption phenomena.
2. Mixing/combining rules were developed to extend the SLD and OK models to mixture modeling and improve the 2-D EOS mixture predictions. To do so, we have incorporated more contemporary rules (e.g., Wong-Sandler and excess Gibbs energy rules) to overcome inadequacies in the “one-fluid” mixing rules typically used to describe mixture interactions in adsorption models.
3. Model parameter generalizations were undertaken for the three models to provide for *a priori* predictive capability in terms of adsorbate and adsorbent physical properties. Although a generalized capability to predict CBM-type adsorption on wet coals has not been fully developed, the results obtained for the activated carbons demonstrate a realistic potential for achieving this goal once a rigorous accounting for the moisture effect is implemented.

Despite their different theoretical bases, in general, 2-D EOS, SLD, and OK models give comparable results in their correlative and predictive abilities based on the gas properties and the accessible characterization of the adsorbent. Specifically the models:

1. Correlate *pure* component adsorption within the experimental uncertainties (4% AAD).
2. Predict *pure* component adsorption within 10% AAD. This includes the prediction of a maximum exhibited in the pure component excess adsorption at high pressures.
3. Correlate the *total* and *individual* component adsorption in the *binary* systems within the expected experimental uncertainties.
4. Predict *total* adsorption for the *binary* and *ternary* systems studied within the expected experimental uncertainties.
5. Predict the *individual component* adsorption in the *binary* systems within twice the expected experimental uncertainties.
6. Predict the *individual component* adsorption in the *ternary* systems within the expected experimental uncertainties, if the information obtained from binary adsorption is included.

In addition, our results indicate that matrix-calibrated models provide reasonably accurate predictions (within twice the experimental uncertainties) for high-pressure adsorption at different temperatures based on low-pressure adsorption data for the same gas at a single temperature and, in addition, can predict the adsorption of other gases (at the same temperature).

To fully exploit the potential of the models in CBM recovery and CO₂ sequestration processes, we need to:

1. Develop a more rigorous approach to account for the effect of water on CBM adsorption systems.
2. Develop improved mixing/combining rules for the OK model, and apply an accurate equation of state to calculate the chemical potential of the gas phase.
3. Develop an accurate equation of state, which exhibits accurate hard-sphere limiting behavior, to improve modeling of high-pressure gas adsorption.

Computational Algorithms: We have developed improved computational capabilities for high-pressure adsorption, including robust algorithms for solving adsorption equilibrium for a variety of models. For example, our studies involving high-pressure mixture adsorption have indicated the inadequacy of the simultaneous solution calculation scheme, which requires the experimental gas-phase compositions. Therefore, a new iteration function method (IFM) for mixture adsorption equilibrium calculations was developed for 2-D EOS, and its robustness was evaluated. Analysis of results involving many supercritical, CBM-type adsorption systems indicate that the new IFM algorithm is effective in performing equilibrium mixture adsorption calculations based on feed compositions. Further, excellent convergence characteristics are

obtained using the new IFM, which employs the amount adsorbed as the iteration variable.

Compressibility Factor Predictions: Accurate compressibility factors are important input to our data-reduction procedure for gas mixture adsorption measurements. To facilitate accurate and reliable gas density predictions, the Benedict-Webb-Rubin (BWR) EOS pure-component and binary interaction parameters were re-optimized to improve compressibility factor predictions for coalbed gases (methane, nitrogen, carbon dioxide and their mixtures). A database of 1488 gaseous data points involving pure, binary, and ternary mixture PVT data was used in the parameter regressions, including some PVT measurements we made for selected compositions at 326.7 K and pressures to 13.9 MPa. Four separate parameter-optimization scenarios were evaluated to ensure the best quality fit for the data considered. The results indicate that, as expected, a simultaneous optimization of pure-component, binary, and ternary data leads to the best overall fit to the data (average absolute deviation of 0.1% and a maximum deviation of 1.4%).

In addition, a sensitivity analysis was conducted to demonstrate the effect of variability in compressibility factors on mixture adsorption calculations. Typical results for activated carbon indicate that a 0.5% error in the compressibility factor is multiplied six-fold (3.0% error) in total adsorption and almost seventeen-fold (8.5%) in the component adsorption.

Coal Characterization at Pennsylvania State University: In an attempt to provide support and meaningful input for the CO₂ sequestration modeling efforts of our colleagues at the Oklahoma State University, we investigated the physical and chemical properties of a wide range of coals. Both volumetric adsorption and microcalorimetry were used to characterize the adsorption uptakes and enthalpies of coals ranging from lignite to low-volatile bituminous. Methane adsorption showed evidence of the dominant effect of London dispersive adsorbate/adsorbent interactions. In contrast, carbon dioxide adsorption heats were significantly higher and rank-sensitive, suggesting that more specific adsorbate/adsorbent interactions are also important. Oxygen-rich lower-rank coal seams are suggested as being the more promising candidates for CO₂ sequestration. In view of these conclusions, a more detailed chemical surface characterization of the coals was undertaken. Huge differences were found between the measured values of the point of zero charge, which was mostly in the basic range (pH > 6-7) and the isoelectric point of the coals, which was very much in the acidic range (pH < 6). For some coals, depending on their mineral matter composition, these differences were due to the presence of mineral matter. For others, however, they were clearly due to nonuniform distribution of surface charge in the radial direction of the microporous coal particles. There was no simple correlation between CO₂ uptakes and PZC values for the Argonne Premium coals. Neither was there a clear correlation between the coal's surface area and its CO₂ adsorption capacity. This study has thus reinforced the conclusion that, for more reliable modeling of CO₂ adsorption on coal, the surface chemical effects (e.g., presence of heteroatoms in the form of electron-donating or electron-withdrawing functional groups) must be taken into account. In the present study we have not yet been successful in developing such a meaningful correlation.

B. Experimental Work

1. Experimental Facility

Currently, we have two experimental facilities dedicated to gas adsorption measurements. The first apparatus was developed in a prior project sponsored by Amoco Corporation and the Oklahoma Center for the Advancement of Science and Technology. As a precursor to the data acquisition, the apparatus was thoroughly re-tested and revised as necessary for operations in the present project. Details of the equipment design have been described previously [1,2]. A brief description of experimental methods and procedures is given in the following section.

The second apparatus was assembled from an equipment donation from BP Amoco. The donation consisted of essentially the complete coalbed methane research equipment housed at BP Amoco's Tulsa Technology Center. In August 1999, the second apparatus was reassembled in OSU's new Advanced Technology Research Center, a \$35 million state-of-the-art complex dedicated to research and technology development. Mr. Don Morgan, who formerly operated the equipment at BP Amoco, served as a consultant in reassembling and validating this apparatus. The new facility has allowed us to essentially double our rate of data production.

We have also enhanced our experimental capability to include measuring the adsorption kinetics of systems encountered in coalbed methane production and sequestration of CO₂. These measurements will help elucidate the pore structure of the coal matrices under study and improve our predictive capability when used in conjunction with equilibrium isotherms.

2. Experimental Methods and Procedures

Our two experimental facilities employ an identical mass balance method, utilizing volumetric accounting principles. The experimental apparatus, shown schematically in Figure 1, has been used successfully in previous measurements [1,2]. A brief description of the experimental apparatus and procedures follows.

The entire apparatus is maintained in a constant temperature air bath. The equilibrium cell (EC, Figure 1) is filled with the adsorbent to be studied, and the cell is placed under vacuum prior to gas injection. The void (gas) volume, V_{void} , in the equilibrium cell is then determined by injecting a known quantity of helium from a calibrated injection pump (Ruska). Since helium is not adsorbed, the void volume can be determined from measured values of the temperature, pressure and amount of helium injected into the cell. The equations are

$$V_{\text{void}} = n_{\text{He}} (Z_{\text{He}} RT / p)_{\text{cell}} \quad (1)$$

$$n_{\text{He}} = (pV / Z_{\text{He}} RT)_{\text{pump}} \quad (2)$$

In these equations, n_{He} is the number of moles of helium injected into the cell, V is the volume of gas injected from the pump, Z_{He} is the compressibility factor of helium, R is the universal gas constant, T is the temperature, p is the pressure, and the subscripts "cell" and "pump" refer to conditions in the cell and pump sections of the apparatus, respectively.

The amount of gas (methane, for example) adsorbed at a given pressure can be calculated based on the preliminary calibrations done above. First, a given quantity of methane, n_{inj} , is injected into the cell. This amount is determined by an equation analogous to Equation 2, above. A recirculating pump is used to circulate methane over the adsorbent until equilibrium is reached, where no further methane is adsorbed. The amount of unadsorbed methane, n_{unads} , is then determined based on the fact that any unadsorbed methane will remain in the void volume (determined from the helium calibration). The expression for this quantity is

$$n_{\text{unads}} = (pV_{\text{void}}/Z_{\text{methane}}RT)_{\text{cell}} \quad (3)$$

where the pressure p is measured after equilibrium is reached in the cell. The amount of adsorbed methane, n_{ads} , is then calculated by difference as

$$n_{\text{ads}} = n_{\text{inj}} - n_{\text{unads}} \quad (4)$$

These steps are repeated at sequentially higher pressures to yield a complete adsorption isotherm.

In mixture studies, the procedure is only slightly more complicated. The individual gases can be injected separately (or a gas mixture of known composition can be injected), so the total amount of each gas in the cell is known. The amount of unadsorbed gas at each pressure is calculated by Equation 3 with Z_{methane} replaced by Z_{mix} , the gas mixture compressibility factor. The composition of the gas mixture in the void volume is determined by chromatographic analysis of a microliter-size sample of the gas mixture captured in a sampling valve. This permits the total amount of unadsorbed gas to be apportioned among the various components according to their mole fractions in the gas. Then, Equation 4 can be applied to each component in the gas mixture. For methane, nitrogen, and CO_2 mixtures, the mixture Z factor is determined accurately from available experimental data and accurate equations of state.

Relationship between Gibbs and Absolute Adsorption

Adsorption data may also be reported in terms of *absolute* adsorption. Calculations for the Gibbs and absolute adsorption differ in the manner by which n_{unads} is calculated. The Gibbs adsorption calculation, described above, neglects the volume occupied by the adsorbed phase in calculating the amount of unadsorbed gas (i.e., in Equation 3, the entire void volume, V_{void} , is viewed as being available to the unadsorbed gas).

Following is a discussion to clarify the relationships between the Gibbs and absolute adsorption and to highlight the approximate nature of the calculated absolute adsorption. In addition, expressions are presented which facilitate calculation of the absolute component adsorption, $n_{ads(i)}^{Abs}$, and the adsorbed-phase mole fraction, x_i^{Abs} , in terms of the experimental Gibbs adsorption results.

Pure Component Adsorption: First, consider the various volumes that can be used to characterize the state existing in the equilibrium cell. Using a representation that envisions two distinct, homogeneous fluid phases (bulk gas and adsorbed phase), the total system volume V_{total} of the experimental apparatus is the sum of the volumes of solid adsorbent (V_{solid}), gas (V_{gas}), and adsorbed-phase (V_{ads}), as follows:

$$V_{total} = V_{solid} + V_{gas} + V_{ads} \quad (5)$$

The void volume, having been determined by helium injection, is related to these quantities as follows:

$$V_{void} = V_{gas} + V_{ads} = V_{total} - V_{solid} \quad (6)$$

Now, consider the amount of material adsorbed at equilibrium, which may be written in molar terms as follows:

$$n_{ads} = n_{total} - n_{unads} \quad (7)$$

The difference in the definitions of the Gibbs and total adsorption resides in the manner in which n_{unads} is related to the volume terms. As stated previously, in the Gibbs calculation, the volume occupied by the condensed phase is neglected in calculating n_{unads} , and the amount of unadsorbed gas is calculated using the entire void volume; thus, Equation 7 becomes, using Equation 6 for V_{void} ,

$$n_{ads}^{Gibbs} = n_{total} - V_{void} \rho_{gas} \quad (7a)$$

where ρ denotes density. In the calculation of the absolute adsorption, n_{unads} is determined using the volume actually available to the bulk gas phase (accounting for the reduction of volume accessible to the gas as a result of the volume occupied by the adsorbed phase):

$$n_{ads}^{Abs} = n_{total} - V_{gas} \rho_{gas} \quad (8)$$

By combining Equations 7a and 8 to eliminate n_{total} , the following relation between Gibbs and absolute adsorption is obtained:

$$n_{ads}^{Gibbs} = n_{ads}^{Abs} - V_{ads} \rho_{gas} \quad (7b)$$

The volume of the adsorbed phase may be expressed in terms of the amount adsorbed and the density of the adsorbed phase as

$$V_{\text{ads}} = n_{\text{ads}}^{\text{Abs}} / \rho_{\text{ads}} \quad (9)$$

Combining Equations 7b and 9 yields

$$n_{\text{ads}}^{\text{Gibbs}} = V_{\text{ads}} (\rho_{\text{ads}} - \rho_{\text{gas}}) \quad (7c)$$

Equation 7c clearly illustrates the physical interpretation of the Gibbs adsorption, namely, the amount adsorbed in excess of that which would be present if the adsorbed phase volume were filled with bulk gas. Combining Equations 9 and 7c leads to:

$$n_{\text{ads}}^{\text{Abs}} = n_{\text{ads}}^{\text{Gibbs}} \left(\frac{\rho_{\text{ads}}}{\rho_{\text{ads}} - \rho_{\text{gas}}} \right) \quad (10)$$

An important consideration in the calculation of the absolute adsorption is that it requires knowledge of the adsorbed phase density, ρ_{ads} , which is not readily accessible by experimental measurement. Thus, estimates of ρ_{ads} are usually employed. A commonly used approximation is the liquid density at the atmospheric pressure boiling point, as was done by Arri and Yee [3]. In this study, however, we used model-regressed estimates for the adsorbed-phase density.

Adsorption from Mixtures: For absolute adsorption, the component mole fractions in the adsorbed phase, x_i^{Abs} , may be calculated from the component Gibbs adsorptions; however, this requires some assumption regarding the density, ρ_{ads} , of the adsorbed phase *mixture*. In the following discussion, ρ_{ads} is approximated using the assumption of ideal mixing in the adsorbed phase, where the pure-component adsorbed-phase density estimates are used to calculate the mixture adsorbed-phase density. The component Gibbs adsorption (amount of component “i” in the adsorbed phase in excess of the amount that would be present if the bulk equilibrium gas mixture occupied the volume of the adsorbed phase) may be written using a component material balance as

$$n_{\text{ads}(i)}^{\text{Gibbs}} = n_{\text{ads}}^{\text{Abs}} x_i^{\text{Abs}} - V_{\text{ads}} \rho_{\text{gas}} y_i = V_{\text{ads}} (\rho_{\text{ads}} x_i^{\text{Abs}} - \rho_{\text{gas}} y_i) \quad (11)$$

For convenience, we define a fractional component Gibbs adsorption, θ_i^{Gibbs} , as

$$\theta_i^{\text{Gibbs}} \equiv \frac{n_{\text{ads}(i)}^{\text{Gibbs}}}{n_{\text{ads}}^{\text{Gibbs}}} \quad (12)$$

(Note that, although Equation 12 has the appearance of a mole fraction, the Gibbs adsorption is an excess quantity, not a total quantity for a specified phase; thus θ , rather than x , is used to denote the quantity.)

Inserting this definition into Equation 11, we obtain:

$$n_{ads}^{Gibbs} \theta_i^{Gibbs} = n_{ads}^{Abs} \left(x_i^{Abs} - y_i \frac{\rho_{gas}}{\rho_{ads}} \right) \quad (13)$$

Combining Equation 10 with Equation 13,

$$x_i^{Abs} = \theta_i^{Gibbs} \left(1 - \frac{\rho_{gas}}{\rho_{ads}} \right) + y_i \left(\frac{\rho_{gas}}{\rho_{ads}} \right) \quad (14)$$

Equation 14 reveals that x_i^{Abs} and q_i^{Gibbs} become identical in the limit of low pressure (where ρ_{gas} becomes small).

Inspection of Equation 14 reveals that all quantities on the right hand side can be obtained directly from experimental measurements except ρ_{ads} , for which some approximation must be made. If ideal mixing is used to represent ρ_{ads} in terms of the pure component adsorbed-phase densities, we have

$$\frac{1}{\rho_{ads}} = \frac{x_1^{Abs}}{\rho_{ads(1)}} + \frac{x_2^{Abs}}{\rho_{ads(2)}} \quad (15)$$

where the subscripts “1” and “2” refer to pure components. Then, Equation 14 may be written as

$$x_1^{Abs} = 1 - x_2^{Abs} = \frac{\theta_1^{Gibbs} \rho_{ads(2)} + \rho_{gas} (y_1 - \theta_1^{Gibbs})}{\rho_{ads(2)} + \rho_{gas} (y_1 - \theta_1^{Gibbs}) \left(1 - \frac{\rho_{ads(2)}}{\rho_{ads(1)}} \right)} \quad (16)$$

and the absolute component adsorption can be calculated as follows:

$$n_{ads(i)}^{Abs} = n_{abs}^{Abs} x_i^{Abs} \quad (17)$$

with Equation 10 used to calculate the *total* mixture adsorption, n_{ads}^{Abs} , where the densities, ρ_{ads} and ρ_{gas} , refer to mixtures of compositions x_i^{Abs} and y_i , respectively.

C. Model Development

We are pursuing five avenues for representing adsorption equilibrium. These include (a) enhanced forms of the Langmuir-type isotherms (see, e.g., [4]), (b) two-dimensional equations of state, (c) simplified local density models, (d) the Ono-Kondo (OK) lattice model [5], and (e) treating adsorption as a constrained form of vapor-liquid equilibrium [3]. In so doing, our objective is to develop reliable, simple analytic models capable of describing multilayer adsorption of near-critical and supercritical components on heterogeneous surfaces.

1. Adsorption Models

In the following, we briefly outline the first three methods and discuss the quality of their representation of the methane, nitrogen, ethane and CO₂ pure-fluid adsorption.

(a) Langmuir Models

Historically, simple models have been used to represent the behavior of pure and mixed gas adsorption on coal. The extended Langmuir model is used almost exclusively in literature studies [e.g., 4], although the Ideal Adsorbed Solution (IAS) model [6] has also been employed [7]. Both these models work well for essentially ideal adsorbed solutions, but neither is capable of handling nonidealities in the adsorbed phase with any accuracy. The extended Langmuir model is shown below as an illustration of the simple modeling approach used in most previous studies. For mixtures, it takes the form

$$\theta = \frac{\omega_i}{L_i} = \frac{B_i P y_i}{1 + \sum_j B_j P y_j} \quad (18)$$

where ω_i is the amount of component "i" adsorbed (moles of "i" adsorbed per unit mass of coal), L_i and B_i are Langmuir constants for "i", P is pressure, and y_i is the mole fraction of "i" in the gas phase. This relation allows mixture adsorption to be calculated from pure-component data, since values of L_i and B_i may be determined from the pure-component form of Equation 18.

The combined Langmuir-Freundlick adsorption isotherm, expressed in terms of ω_i , yields the loading ratio correlation (LRC) for mixtures

$$\theta = \frac{\omega_i}{L_i} = \frac{B_i (P y_i)^{\eta_i}}{1 + \sum_j B_j (P y_j)^{\eta_j}} \quad (19)$$

The additional parameter in the LRC (η_i) lends the Langmuir model more flexibility. Although the simplicity of Langmuir models is attractive, our data show that they are inadequate to represent the behavior of mixtures of the gases CO₂, methane, and nitrogen. In fact, previously we found errors greater than 100% when the extended Langmuir model was applied to our data on the adsorption of nitrogen from nitrogen + CO₂ mixtures [2].

(b) Equation-of-State Models

Simulations of coalbed gas recovery and CO₂ sequestering require reliable, yet simple analytic models beyond Langmuir-type correlations. Equation-of-state (EOS) frameworks offer an attractive potential for such requirements.

2-D EOS

A general form of the popular three-dimensional equation of state can be expressed by [8,9,33]:

$$\left[P + \frac{ap^2}{1 + Ub\rho + W(bp)^2} \right] [1 - b\rho] = \rho RT \quad (20)$$

where α and β are the traditional EOS parameters, and numerical values of U and W may be specified to give various forms of three-dimensional equations of state. An even more general two-dimensional analog can be written as follows (by introducing an additional coefficient, m):

$$\left[A\pi + \frac{\alpha\omega^2}{1 + U\beta\omega + W(\beta\omega)^2} \right] [1 - (\beta\omega)^m] = \omega RT \quad (21)$$

where A is the specific surface area, π is the spreading pressure, ω is the specific amount adsorbed, and α , β and m are model parameters. The model coefficients, U , W , and m must be specified to obtain a specific form of the 2-D EOS for application. For example, an analog of the van der Waals (VDW) EOS is obtained by setting $m = 1$ and $U = W = 0$, similarly for the Soave-Redlich-Kwong (SRK) ($m = U = 1$ and $W = 0$), the Peng-Robinson (PR) ($m = 1$, $U = 2$, and $W = -1$), and the Eyring ($m = 1/2$ and $U = W = 0$) EOS.

This general 2-D EOS can be used to investigate EOS behaviors by specifying various combinations of model coefficients. Selection of the model coefficient m is the most important among the EOS model coefficients, because it has a significant effect on the shape of the pure adsorption isotherm. If U and W are equal to zero, then by setting m to values of ∞ , 1 , and $1/2$, we obtain the 2-D ideal gas law, the VDW EOS, and the Eyring EOS, respectively. Actually, the pure gas isotherms vary considerably in shape and we have found that it is sometimes desirable to select an m value even smaller than $1/2$ to describe pure isotherms. We have determined that an equation with $m = 1/3$ and

$U = W = 0$ (the ZGR EOS) is promising [9]. The 2-D EOS can be applied to adsorbed phases containing mixtures by utilizing the traditional mixing rules (where x is the mole fraction in the adsorbed phase):

$$\alpha = \sum_i \sum_j x_i x_j \alpha_{ij} \quad (22)$$

$$\beta = \sum_i \sum_j x_i x_j \beta_{ij} \quad (23)$$

along with the non-traditional combination rules [9],

$$\begin{aligned} \alpha_{ij} &= (1 - C_{ij})(\alpha_i + \alpha_j) / 2 \\ \beta_{ij} &= (1 + D_{ij})\sqrt{\beta_i \beta_j} \end{aligned} \quad (24)$$

where C_{ij} and D_{ij} are the EOS binary interaction parameters.

2-D PR EOS

The 2-D PR EOS is specialization of Equation 21, which we have considered in our model development efforts, especially when dealing with mixtures. The 2-D PR EOS is given as:

$$\left[A\pi + \frac{\alpha\omega^2}{1 + 2\beta\omega - (\beta\omega)^2} \right] [1 - (\beta\omega)] = \omega RT \quad (25)$$

where α and β are defined in Equations 22-24.

2-D EOS Initialization

The initial guesses of α , β , and k are critical to the 2-D EOS parameters regression. Beyond the EOS parameters α , β , initial guesses are required for k , which represents the slope of the isotherm at the origin [9]. To improve the reliability of EOS calculations, an improved initialization technique was implemented in this study. Specifically, we recommend the following initial guesses for α , β and k , which are generated from the Langmuir model parameters of the same isotherm:

$$\begin{aligned} \alpha &= 200 \\ \beta &= 1/2 L \\ k &= 5 L B \end{aligned}$$

where L and B are the Langmuir model constants.

(c) The Simplified Local Density Model

Our experience to date indicates that the 2-D EOS approach is, in general, superior to the more widely-used theories such as the Ideal Adsorbed Solution (IAS) and the extended Langmuir isotherm. However, present applications of this approach are inherently deficient in representing multilayer adsorption, especially when it is applied to heterogeneous surfaces as in the case of coal.

Therefore, we are currently attempting to augment the EOS framework and render it useful for adsorption behavior beyond Type I isotherms by (a) using solid-fluid site characterization based on characteristic curves similar to those generated by the Polanyi potential theory (see, e. g., [10]), and (b) superimposing the fluid-solid potential on an improved EOS phase description to predict the near-critical adsorption behavior. The latter is well exemplified by the simplified local density (SLD) model (see, e.g., Lira and coworkers [11]). We believe such developments will facilitate the use of highly efficient EOS computational frameworks for representing adsorption behavior, as well as improving our understanding of the phenomenon.

The SLD model is a compromise between the traditional empirical / semi-empirical methods, which are computationally less demanding but are unable to account for the various adsorption isotherms seen near the critical region, and the computationally intensive molecular simulation methods. In applying the SLD adsorption model, the fluid-solid potential is superimposed on an equation of state (EOS) and the configurational energy integral in the inhomogeneous fluid phase is simplified with a local density approximation [11].

In this study, we evaluated the predictive capability of the SLD model for the supercritical adsorption systems encountered in CO₂ sequestering and coalbed methane recovery. Specifically, we correlated the experimental data on the adsorption of methane, nitrogen and carbon dioxide on wet coals and dry activated carbon using *flat-surface* and *slit* forms of the SLD. The SLD model predictions were then compared to predictions from the Langmuir, LRC, and the 2-D EOS models.

Flat-Surface SLD Model

The SLD model is formulated in terms of the surface excess adsorption (Γ^{ex}), defined as the excess number of moles per unit area of adsorbent, or

$$\Gamma^{ex} = \int_{z_0}^{\infty} (\rho(z) - \rho_{bulk}) dz \quad (26)$$

For a *flat surface geometry*, the lower limit of integration is the surface of the solid and is taken as the plane at $z_0 = \sigma_{ff}/2$, where σ_{ff} is the molecular distance between two solid molecules.

As indicated by Equation 26, the SLD theory predicts Gibbs excess, not absolute adsorption. To calculate the absolute adsorption, one must estimate a value for the adsorbed phase density.

In flat-surface adsorption, the SLD model asserts that the equilibrium chemical potential at any point z above the adsorbent surface is equal to the bulk phase chemical potential. Accordingly, the equilibrium chemical potential is calculated by contributions from fluid-fluid and fluid-solid interactions as

$$\mu = \mu_{\text{bulk}} = \mu_{\text{ff}}(z) + \mu_{\text{fs}}(z) \quad (27)$$

where the subscript bulk refers to the bulk fluid, ff refers to fluid-fluid interactions, and fs refers to the fluid-solid interactions.

The fluid-solid potential at a given point z is independent of temperature and the number of molecules in and around that point. The fluid-solid potential is given in terms of the molecular interactions potential $\psi(z)$ and N_A (Avogadro's Number) as

$$\mu_{\text{fs}} = N_A \Psi(z) \quad (28)$$

Lee's partially integrated 10-4 Lennard-Jones potential [12] is used to describe the adsorbate-adsorbent interactions

$$\Psi(z) = 4\pi\rho_{\text{atom}}\epsilon_{\text{fs}}\sigma_{\text{fs}}^6\left(\frac{\sigma_{\text{fs}}^6}{5x_i^{10}} - \frac{1}{2}\sum_{i=1}^4\frac{1}{x_i^4}\right) \quad (29)$$

where ϵ_{fs} is the fluid-solid interaction energy parameter, $\rho_{\text{atom}} = 0.382 \text{ \AA}^{-3}$, x_i is the intermolecular distance between fluid-molecule centers and the i th plane of solid molecules, σ_{fs} is taken as the arithmetic mean of the fluid and solid diameters. As indicated by Equation 29, the interactions are truncated at the fourth plane of solid atoms with an interplanar spacing of $3.35 \text{ \AA}$.

The fluid-fluid potential is then calculated as

$$\mu_{\text{ff}} = \mu_{\text{bulk}} - N_A \Psi(z) \quad (30)$$

where

$$\mu_{\text{bulk}} = \mu_{\circ} + RT \ln(f_{\text{bulk}}/f_{\circ})$$

$$\mu_{\text{ff}} = \mu_{\circ} + RT \ln(f_{\text{ff}}(z)/f_{\circ})$$

After rearrangement this leads to

$$f_{ff}(z) = f_{bulk} \exp[-\Psi(z)/(kT)] \quad (31)$$

In this study, we have used the PR equation of state to determine the fluid and the bulk fugacities. The fugacity expressions for the PR EOS are:

$$\ln f_b = \frac{bp_b}{1-bp_b} - \frac{a_b p_b}{RT(1+2bp_b-b^2p_b^2)} - \ln\left(\frac{1-bp_b}{RT p_b}\right) - \frac{a_b}{2\sqrt{2}bRT} \ln\left(\frac{1+b(1+\sqrt{2})p_b}{1+b(1+\sqrt{2})p_b}\right) \quad (32)$$

$$\ln f_{ff}(z) = \frac{bp(z)}{1-bp(z)} - \frac{a(z)p(z)}{RT(1+2bp(z)-b^2p^2(z))} - \ln\left(\frac{1-bp(z)}{RT p(z)}\right) - \frac{a(z)}{2\sqrt{2}bRT} \ln\left(\frac{1+b(1+\sqrt{2})p(z)}{1+b(1+\sqrt{2})p(z)}\right) \quad (33)$$

where a_b is the PR EOS constant, and $a(z)$ is evaluated as follows

$$a(z) = a_b \left(\frac{5}{16} + \frac{6}{16} \frac{z}{\sigma_{ff}} \right) \quad \text{for } 0.5 \leq \frac{z}{\sigma_{ff}} \leq 1.5 \quad (34)$$

$$a(z) = a_b \left[1 - \frac{1}{8 \left(\frac{z}{\sigma_{ff}} - \frac{1}{2} \right)^3} \right] \quad \text{for } 1.5 \leq \frac{z}{\sigma_{ff}} < \infty \quad (35)$$

Once the fugacity at the local point is determined, the EOS is used to calculate the corresponding local density $p(z)$. To apply the PR-SLD model, we have assumed that (a) the pure fluids are adsorbed on flat, homogenous coal surface, and (b) the coal has pseudo-crystalline structure. Details of our calculation procedure are given elsewhere [13].

Slit SLD Model

We also have evaluated a slit *form* of the SLD model, where the adsorbed fluid resides within a slit instead of residing near a flat surface. That is, in contrast to Equation 26, a slit width L is used to determine excess adsorption:

$$\Gamma^{ex} = \int_{\sigma_{ff}/2}^{L-\sigma_{ff}/2} [\rho(z) - \rho_b] dz \quad (36)$$

The value of slit width L is regressed from experimental data. Details for applying the slit theory are given elsewhere [14].

In this case, the adsorbed molecule has fluid-solid interactions with two surfaces, or

$$\mu_{fs}(z) = \mu_{fs1}(z) + \mu_{fs2}(L - z) \quad (37)$$

The fluid-solid potential, represented by $\rho(z)$, is defined on a molecular basis by

$$\Psi(z) = 4\pi\rho_{\text{atoms}}\varepsilon_{\text{fs}}\sigma_{\text{fs}}^2\left(\frac{\sigma_{\text{fs}}^{10}}{5(z')^{10}} - \frac{1}{2}\sum_{i=1}^4\frac{\sigma_{\text{fs}}^4}{(z' + (i-1)\cdot\sigma_{\text{ss}})}\right) \quad (38)$$

where ε_{fs} is the fluid-solid interaction energy parameter and $\rho_{\text{atom}} = 0.382 \text{ \AA}$. The molecular diameter of the adsorbate and the carbon interplanar distance are σ_{ff} and σ_{ss} , respectively. Molecular diameters were obtained from Reid [15]. Following Subramanian [16], the interplanar spacing is 0.335 nm.

Two other definitions are needed for convenience:

$$\sigma_{\text{fs}} = \frac{\sigma_{\text{ff}} + \sigma_{\text{ss}}}{2} \quad (39)$$

$$z' = z + \sigma_{\text{ss}}/2 \quad (40)$$

The potential energy is related to the fugacity, as

$$f_{\text{ff}}(z) = f_{\text{b}} \exp\left(-\frac{\Psi(z) + \Psi(L-z)}{kT}\right) \quad (41)$$

The fugacity expressions for the PR EOS are given by Equations 32 and 33. The parameter $a(z)$ in the PR EOS is a function of position within the slit when calculating the local phase density for that position. Chen and coworkers [16] provide equations that describe how 'a' changes with position; Table 1 provides these equations, which are necessarily case-dependent on the ratio of the slit length and the fluid molecular diameter σ_{ff} . To obtain these formulas, one integrates the sum of all the two body interactions between an arbitrarily selected central molecule and all the other molecules around it.

After the density profile along the slit is computed, the Gibbs adsorption Γ is numerically integrated, as expressed by Equation 36. Specifically, half of the slit was subdivided into 50 intervals and Equation 36 was solved for each interval. The amount adsorbed was calculated by numerically integrating with Simpson's rule.

A key feature of SLD theory is that it predicts the Gibbs excess, not absolute adsorption. To calculate the absolute adsorption, one must assume the adsorbed phase density or volume. Past researchers have assumed that the phase density is close to the van der Waals co-volume. This assumption creates uncertainty in the absolute adsorption, especially at high pressure. In comparison, SLD uses only the Gibbs excess, which does not rely on phase density assumptions, to obtain model parameters. Furthermore, SLD may be used to predict an average adsorbed phase density as a function of pressure:

$$\bar{r} = \frac{\Gamma^{ex}}{L} + r_{bulk} \quad (42)$$

This average adsorbed phase density can be applied then to calculate the absolute adsorption:

$$n_{abs} = \frac{\Gamma^{ex}}{\left(1 - \frac{\rho_{bulk}}{\bar{\rho}_{ads}}\right)} \quad (43)$$

(d) The Ono-Kondo Model

We are also evaluating and further developing the Ono Kondo (OK) lattice model. In addition to its strong theoretical basis, the lattice theory offers several practical advantages that are potentially useful in the field of CO₂ sequestration and CBM production. Specifically the OK model:

1. Describes monolayer and multilayer adsorption
2. Represents both Gibbs and absolute adsorption
3. Has a potential to describe the adsorption behavior based on the physical properties of the adsorbates and the accessible characterization of the adsorbent
4. Is structured to incorporate accurate density calculations, which may reduce the correlative burden of the adsorption modeling

In the lattice model, the fluid system is assumed to be composed of layers of lattice cells that contain fluid molecules and vacancies. For the case of adsorption, more fluid molecules reside in the cells of the adsorbed-phase layers than in the cells of the bulk-phase layers. Molecular interactions are assumed to exist only between the nearest neighboring molecules. When equilibrium exists between the gas-phase and multilayer adsorbed phase, the expression for the thermodynamic equilibrium can be written as [5]:

$$\ln(x_i(1-x_b)/(x_b(1-x_i))) + z_0(x_i - x_b)\varepsilon/kT + z_2(x_{i+1} - 2x_i + x_{i-1})\varepsilon/kT = 0; \quad i = 2, 3, \dots \quad (44)$$

with the following boundary condition:

$$\ln(x_1(1-x_b)/(x_b(1-x_1))) + (z_1x_1 + z_2x_2 - z_0x_b)\varepsilon/kT + \varepsilon_s/kT = 0 \quad (45)$$

In these equations, x_i is the reduced density or fraction of sites occupied by adsorbed molecules in layer i , and x_b is the fraction of sites occupied by fluid molecules in the bulk. For a cubic lattice, the coordination numbers z_0 and z_1 are 6 and 4, respectively; and by definition, we set $z_2 = (z_0 - z_1)/2$. The adsorbate-adsorbate energy interaction parameter is expressed by ε/kT , and the adsorbate-adsorbent surface energy interaction parameter is expressed by ε_s/kT , where k is Boltzman's constant, and T is the absolute temperature.

The analytical expression for Gibbs excess adsorption for this model is:

$$G = C \sum_i^M (x_i - x_b) \quad (46)$$

where C is a prefactor related to the capacity of adsorbent for a specific gas, and M is the maximum number of layers that can be fit in an adsorption isotherm. The reduced densities x and x_b are expressed as $x = \rho_i / \rho_{mc}$ and $x_b = \rho_b / \rho_{mc}$, where ρ_i and ρ_b are the adsorbed and the bulk density of the adsorbate, respectively. The bulk density for pure methane, nitrogen, and CO_2 were determined from highly accurate equations of state. The maximum adsorbed-phase density ρ_{mc} may be estimated in various ways. Arri [3] used the saturated liquid density at atmospheric pressure and Hocker and Donohue [17] suggested a theoretical value from close-packed molecules. Application of these estimates, however, does not produce optimum fits of the Ono-Kondo model isotherms for pure methane, nitrogen, and CO_2 on activated carbon. Our recent study shows that better results are obtained when this maximum adsorbed-phase density is treated as a regressed parameter.

When the Ono-Kondo model is applied for the adsorption on activated carbon, a monolayer adsorption might be assumed [18]. In this case, the adsorbed molecules are directly mapped onto parallel graphite planes, where the spacing between adjacent graphite planes is only a few molecular diameters. Furthermore, we also choose the 2D-hexagonal configuration to match the graphite molecular structure. These assumptions simplify the thermodynamic equilibrium expression of Equations (44) and (45) to:

$$\ln[x_{\text{ads}}(1 - x_b) / x_b(1 - x_{\text{ads}})] + (7x_{\text{ads}} - 8x_b)\varepsilon / kT + \varepsilon_s / kT = 0 \quad (47)$$

Also, the Gibbs excess adsorption expression, Equation 46, simplifies to:

$$\Gamma = 2C (x_{\text{ads}} - x_b) = 2C \left(\frac{\rho_{\text{ads}}}{\rho_{mc}} - \frac{\rho_b}{\rho_{mc}} \right) \quad (48)$$

Extending OK Model to Mixtures

In our recent studies, we have established the viability of the OK model for correlating pure-component adsorption of the targeted gases on a variety of adsorbents over a wide range of pressure. Furthermore, the OK model is extended to mixture predictions. Specifically, we incorporate mixing rules into the OK model and evaluate its ability to correlate/predict the mixture total and component adsorptions.

For a binary mixed-gas containing components A and B, the equality of the chemical potential in the adsorbed and bulk phases for each component leads to the following equilibrium equations for monolayer, binary, and mixed-gas adsorption:

$$\ln \frac{x_A(1-x_{A,b}-x_{B,b})}{x_{A,b}(1-x_A-x_B)} + \frac{\varepsilon_{AA}}{kT}((z_1+1)x_A - z_0x_{A,b}) + \frac{\varepsilon_{AB}}{kT}((z_1+1)x_B - z_0x_{B,b}) + \frac{\varepsilon_{As}}{kT} = 0 \quad (49)$$

and

$$\ln \frac{x_B(1-x_{A,b}-x_{B,b})}{x_{B,b}(1-x_A-x_B)} + \frac{\varepsilon_{BB}}{kT}((z_1+1)x_B - z_0x_{B,b}) + \frac{\varepsilon_{AB}}{kT}((z_1+1)x_A - z_0x_{A,b}) + \frac{\varepsilon_{Bs}}{kT} = 0 \quad (50)$$

A linear combination rule is used to evaluate the interaction energy between molecule A and B; i.e.:

$$\varepsilon_{AB} = (1 + C_{AB})(\varepsilon_{AA} + \varepsilon_{BB})/2. \quad (51)$$

This combination rule is chosen in anticipation of different signs for ε_{AA} and ε_{BB} . Also, a regressed binary interaction parameter C_{AB} is introduced to account for unlike interactions.

For a binary mixture, the non-linear equations, Equations (49) and (50), are solved using the Newton-Raphson method to obtain x_A and x_B . A correction factor was introduced to calculate the Gibbs adsorption for each component, considering that the maximum capacity of a component might be different for pure and mixture adsorption. In this case, Equation 48 was modified as

$$\Gamma_i = 2C_i(x_i - x_{i,b})C_{\text{corr}} \quad (52)$$

The correction factor was evaluated through the following empirical expression:

$$C_{\text{corr}} = \sum_i^n \sum_j^n x_i^{\text{Abs}} x_j^{\text{Abs}} E_{ij} \quad (53)$$

Additional regressed binary interaction parameter, E_{ij} , is introduced in this expression, in which $E_{ii} = E_{jj} = 1$. The mixture bulk density is calculated separately using our recently-modified BWR equation of state.

2. Model Evaluations

In this section we present only model comparison results for the 2-D EOS, the SLD model, and OK lattice model for describing adsorption in systems encountered in CO₂ sequestration and coalbed methane recovery. Our detailed model-development analyses appear in a number of manuscripts as discussed in **Modeling Results** section on Page 31.

Pure-Gas Adsorption: Table 2 outlines the modeling case studies for pure-gas adsorption. Three cases were analyzed to evaluate (1) the correlative capability, (2) the

generalized-parameter *a priori* predictive capability, and (3) the matrix-calibrated predictions. In the correlative case, the model parameters were regressed to produce the best possible representations of the adsorption data. In the generalized-parameter predictive case, the model parameters were generalized based on physical properties of the adsorbates and accessible characterization information for the adsorbent. The matrix-calibrated predictive case shows the model capability to predict the adsorption of the gases of interests (on a given adsorbent) based solely on limited data for a single gas on the same adsorbent. Table 2 describes the model parameters used in the first two cases.

Mixture Adsorption: Similar to the pure-gas adsorption modeling, a correlative case and a predictive case were considered. In the predictive model, the parameters obtained from pure-gas adsorption were applied without the use of any binary interaction parameters; while in the correlative model binary interaction parameters (BIP) were regressed to produce the best representations of the binary mixture adsorption data. For the ternary adsorption, two predictive cases were evaluated; i.e. predictions based solely on the parameters obtained from pure adsorption data, and predictions based on the parameters obtained from pure adsorption and the BIP information from the binary mixture adsorption.

Most of our model evaluation results were conducted using Gibbs excess adsorption. However, some results are presented in terms of absolute adsorption since it is the quantity most familiar to practitioners in CBM operations.

3. Database and Data Reduction

To facilitate testing of the models described above, a database of adsorption on activated carbons was compiled consisting of 29 systems. In addition, a database of 17 systems was compiled for adsorption on coals, bringing the total to 46 systems. Each “system” consists at least of one gas isotherm on a specific adsorbent. Tables 3 and 4 list information for each of the 46 systems, including the adsorbent type, the adsorbate, the temperature and pressure ranges, and the original reference.

The objective function S_M , which minimizes the sum of the squared deviations in predicted adsorption, was used to correlate data:

$$S_M = \sqrt{\frac{\sum_{i=1}^{NPTS} \left[\frac{\omega_i^c - \omega_i^e}{\omega_i^e} \right]^2}{NPTS}} \quad (54)$$

Where ω^c and ω^e are the calculated and experimental adsorption amount, respectively. NPTS is the number of data points.

When estimated experimental uncertainties are available, the objective function $S_{M\sigma}$ was used. This function minimizes the sum of the squared weighted deviations in predicted adsorption:

$$S_{M\sigma} = \sqrt{\frac{\sum_{i=1}^{NPTS} \left[\frac{\omega_i^c - \omega_i^e}{\sigma_i^e} \right]^2}{NPTS}} \quad (55)$$

Here, σ^e is the expected experimental uncertainty.

For completeness, the percentage average absolute deviation (%AAD) and root-mean-square error (RMSE) are also reported:

$$\%AAD = \frac{100}{NPTS} \sum_{i=1}^{NPTS} \left| \frac{\omega_i^c - \omega_i^e}{\omega_i^e} \right| \quad (56)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{NPTS} (\omega_i^c - \omega_i^e)^2}{NPTS}} \quad (57)$$

The weighted average-absolute deviation (WAAD) is also reported when expected experimental uncertainties are available:

$$WAAD = \frac{1}{NPTS} \sum_{i=1}^{NPTS} \left| \frac{\omega_i^c - \omega_i^e}{\sigma_i^e} \right| \quad (58)$$

Since literature data in general do not provide the expected experimental uncertainties, the WAAD is not provided in some of the tables.

D. Results and Discussion

1. Experimental Data

In this section, we present the **OSU Adsorption Database** which contains the pure, binary, and ternary mixture adsorption measurements conducted at Oklahoma State University. Detailed analyses of our newly-acquired experimental measurements appear in several of the manuscripts listed in Section K on Page 172. Copies of the manuscripts are attached on the designated pages.

Table 5 documents the OSU CBM gas adsorption database. Listed are the adsorbates, the adsorbent, and the corresponding temperature and pressure ranges for each system.

Pure-gas adsorption measurements are reported for methane, nitrogen, ethane, and carbon dioxide on **ten** solid matrices comprised of wet Fruitland coal (OSU #1 and OSU #2), wet Lower Basin Fruitland coal (OSU #3), wet / dry Illinois #6 coal, wet Tiffany coal, dry Beulah Zap coal, dry Wyodak coal, dry Upper Freeport coal, dry Pocahontas coal, and dry activated carbon.

Binary adsorption measurements are presented for mixtures of methane, nitrogen and CO₂ at a series of compositions on **four** different matrices: Fruitland coal, Illinois #6 coal, Tiffany coal, and activated carbon. Ternary measurements are also presented for methane/nitrogen/CO₂ mixtures on wet, mixed Tiffany coal and on dry activated carbon.

Tables 6 through 8 present the compositional analyses for the various solid matrices considered. The activated carbon used was Filtrasorb 400, 12x40 mesh, from Calgon Carbon company. The activated carbon was dried under vacuum at 230°F for two days before the adsorption measurements. The nitrogen BET surface area at 77 K has been reported by Humayun and Tomasko (2000) to be 850 m²/g. The surface area value provided by the supplier, however, is 998 m²/g.

Four different wet coals were prepared for adsorption measurements. The Fruitland coal is from the San Juan Basin; it is a medium volatile bituminous coal. This recently prepared sample (OSU #2) has a slightly different composition from the one used in previous measurements (OSU #1). The Lower Basin (LB) Fruitland coal is from the same coalbed seam as Fruitland coal, but it was taken from a different location. The Illinois #6 coal is a high volatile bituminous coal. Other coal samples are from BP Amoco Tiffany Injection Wells #1 and #10. The coal samples were ground to 200µm particles and moistened with water. This made the sample moisture content vary from 4 to 15 percent (by weight), which is higher than the equilibrium moisture content. Equilibrium moisture content was determined gravimetrically by exposing dry coal to 303.1 K air at 96-99% saturation.

In addition, five types of coal samples prepared by Argonne National Laboratory were used to study CO₂ adsorption on dry coals. The coals were dried under vacuum in an equilibrium cell at 80°C for 36 hours before being used in the adsorption measurements.

Tables 5 through 100 of the **OSU Database** given in Section K on Page 172 present the gas-adsorption measurements conducted at OSU. The data are presented in terms of both Gibbs and absolute adsorption since absolute adsorption is the quantity most familiar to practitioners in CBM operations. Also for convenience, the data are reported both in SI and English engineering units.

The database includes the expected experimental uncertainties for the adsorption measurements. The expected experimental uncertainty of the pure-gas adsorption data is about 3%. However, the expected uncertainties in the amount adsorbed for the mixture data vary with pressure and composition. In general, average uncertainties are below 5% for total adsorption; while, the individual-component uncertainties vary from 0.02 to 0.4 mmol/g, depending on the mixture composition. Moreover, the expected uncertainties in the amount of individual-component adsorption are significantly higher for the less-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20/80 nitrogen/CO₂ system).

For purposes of illustration only, Figures 2-4 and 6-10 present typical pure-gas and mixture adsorption measurements acquired in this project. For detailed descriptions and analyses please refer to Section K on Page 172.

2. Modeling Results

In this section, we present model comparison results for two-dimensional equations of state (2-D EOSs), the simplified local density (SLD), and the Ono-Kondo (OK) lattice model for describing adsorption in systems encountered in CO₂ sequestration and coalbed methane recovery.

Our detailed model-development analyses appear in the manuscripts given in Section K on Page 172.

(a) Adsorption Model Comparisons

The 2-D EOS, SLD, and OK adsorption models considered in this project were judged by two main criteria. First, the model should correlate well the sorption data of interest. Second, the model should have predictive capability. Specifically, the model should correlate within the experimental uncertainties:

1. The adsorption of pure fluids, mixtures, and individual components in a given mixture on the adsorbents of interest
2. The adsorption behavior over the range of temperatures and pressures of interest

If the model is successful in correlating the data within the desired level of uncertainty, then it can be developed further to provide predictive ability. Ultimately, a generalized model should predict within the desired accuracy the sorption behavior of pure components and mixtures from the physical-chemical characteristics of the adsorbates and the adsorbent involved. However, limitations of the models and/or matrix characterization dictate, at times, the need for a matrix-calibrated model. In this case, the model is expected, for a specified matrix adsorbent, to provide accurate predictions for:

1. High-pressure adsorption from low-pressure sorption data
2. Adsorption at one temperature from data at another temperature
3. Adsorption of one gas from data on another gas on the same matrix
4. Multicomponent adsorption of several gases from their corresponding pure sorption data

Although the above capabilities are not fully *a priori* predictions, they would, when fully realized, minimize the experimental effort required for ECBM operations involving specific coal seams. Presently, some of these capabilities are developed and others require further refinement.

All correlation/predictive adsorption models requires physical or phenomenological parameters. Typically, the individual parameters reflect either to the properties of the adsorbing fluid or the adsorbent. For example, the surface area is a characteristic parameter of the adsorbent, and the gas density is a characteristic of the fluid. Models containing parameters which describe separately fluid-dependent or adsorbent-dependent interactions generally are better suited for model parameter generalizations. Moreover, existing knowledge on fluid-fluid interactions from volumetric (PVT) and/or vapor-liquid equilibrium (VLE) experiments may then be obtained, thus utilizing the adsorption data solely to account for fluid-solid interactions.

Each model considered (the 2-D EOS, SLD model, and the OK lattice model) offers practical advantages in modeling supercritical, high-pressure adsorption systems. Certain practical advantages are inherent in each model, namely, the physical validity of its theoretical development, ease of computation and applicability, and availability of model input data.

Advantages of the 2-D EOS include:

1. Ease of implementation of a well-developed framework; the 2-D EOS is an analog of the familiar 3-D EOS used for PVT behavior modeling
2. Availability of 2-D mixing rules for multi-component mixtures by direct analogy to 3-D mixing theories
3. Similarity of the adsorption algorithms to vapor-liquid equilibrium algorithms; thus the ability to facilitate CBM process simulations

Disadvantages of the 2-D EOS include its questionable theoretical premises, such as its applicability only to monolayer adsorption on flat surfaces, and its accounting only for the interactions among adsorbed molecules; i.e., there is no description of fluid-solid interactions, although the regressed 2-D EOS adsorption parameters indirectly reflect fluid-solid interactions.

The SLD framework has several theoretical attributes that suit the modeling demands incumbent of coalbed methane reservoirs. Specifically, the SLD model:

1. Provides a consistent theory which accounts separately adsorbate-adsorbate (fluid-fluid) and adsorbate-adsorbent (fluid-solid) molecular interactions
2. Delineates the adsorbent structural properties based on assumed physical geometries of the adsorbent
3. Predicts the adsorbed-phase density, which facilitates prediction of absolute gas adsorption

Relative to the 2-D EOS and the OK model, the SLD model requires additional computational effort associated with integrations across the adsorbed-phase density profile. This complexity, however, is far less than traditional local density models or Monte Carlo simulations [19].

In general, the OK model lies between the SLD and 2-D EOS models in the practicality of its theory and its ease of computation and applicability. Specifically, the OK model:

1. Is based on a well-developed lattice theory
2. Describes monolayer and multilayer adsorption
3. Describes adsorption behavior based on the physical properties of the adsorbates and the accessible characterization of the adsorbent

(b) Results and Discussion

Pure-Gas Adsorption: Detailed development and evaluations of pure-gas adsorption modeling using the 2-D EOS, OK, and SLD models appears in Section K of Page 172. Table 9 presents the correlative results for pure-gas adsorption on activated carbons. Despite their different theoretical bases, the three models give comparable results in fitting the data. Specifically, the 2-D EOS, the SLD and the OK models yield 2.6, 4.0 and 3.3% AAD, respectively. As shown in Table 9, the 2-D EOS model gives better results on activated carbon than the SLD and OK models.

Figure 2 shows the quality of representations obtained for the three models, as illustrated by results for the SLD model. As indicated by this figure for methane adsorption on wet coals, the models are capable of representing the data with their experimental uncertainties.

Parameters regressed per system are also presented for all three models in Table 2. In these results, the 2-D EOS parameters, β , α and k , and their temperature dependence

were related to the physical properties of the adsorbates and the accessible characterization of the adsorbent (surface area) by utilizing the generalized parameters relation developed in the OK lattice model and other theories. The slightly better representation of the 2-D EOS model than that of the OK model may be attributed to the manner in which the gas phase was described. For the OK model, the chemical potential in the gas was calculated (similar to the adsorbed phase) using the lattice model, while for the 2-D EOS, the Peng-Robinson (PR) EOS was employed to describe the gas phase. The SLD model gave the least satisfactory results, although it provides a more rigorous accounting for adsorbate-adsorbate (fluid-fluid) and adsorbate-adsorbent (fluid-solid) molecular interactions. This may be attributed to: the inadequate SLD parameter temperature dependence and the need for a more accurate EOS (than the PR EOS) to account for behaviors at high densities, near the hard-sphere limit.

For the 2-D EOS and OK models we used reported surface areas to represent the adsorption data, while the surface areas in the SLD model were regressed. In general, the regressed surface area obtained from the SLD model is within 50% of (and, on average, 15% lower than) the reported surface area. The regressed slit length (L) obtained from the SLD model appears to have some correlation with the fluid-solid (ϵ_{fs}/k) and solid-solid (ϵ_{ss}/k) interaction energy in the OK and 2-D EOS models, respectively: the larger the slit length, the smaller the fluid-solid interaction energy. For example, the wide slit length (1.5 nm) obtained for AC coconut shell [20] in the SLD model corresponds to the small values of ϵ_{fs}/k (1140 K) and ϵ_{ss}/k (23.7 K) obtained in the OK and 2-D EOS models, respectively.

Table 10 presents comparisons of the results of the three model representations for pure-gas adsorption on coals. For each model, 432 independent data points from the OSU experimental measurements of pure-gas adsorption on coals (Table 4) were employed. The same treatment was undertaken in applying the 2-D EOS and OK models for the gas adsorption on coals. In this case, only surface area and solid-solid (or fluid-solid) interaction are regressed, and the surface density and thermal expansion coefficient were fixed based on generalized correlation. The OK model shows better performance than the other two models. The less satisfactory results obtained by the 2-D EOS than those obtained by OK model may be because the thermal expansion coefficient used for CO₂ in the 2-D EOS is underestimated. The 2-D EOS used the same thermal expansion coefficient for all components (0.0024 K⁻¹), while the OK model used higher value for CO₂ (0.0039 K⁻¹) [see, Section K-IV on Page 172]. For the gas adsorption on coals, the regressed slit length (L) obtained from the SLD model also shows correlation to the fluid-solid (ϵ_{fs}/k) and solid-solid (ϵ_{ss}/k) interaction energy in the OK and 2-D EOS models. For example, the wide slit length (1.7 nm) obtained for CO₂ adsorption on dry Illinois #6 in the SLD model corresponds to the small value of ϵ_{fs}/k (1250 K) and ϵ_{ss}/k (25.9 K) in the OK and 2-D EOS models, respectively.

In general, all of the three models produce less precise results for CO₂ adsorption on coals at high pressure. For example, the SLD model underestimates the CO₂ sorption behavior at pressures greater than 10 MPa. Possible swelling, CO₂ solvation of coals or the effect of moisture may explain this behavior.

The parameters generated from the adsorption on wet coals were affected by the presence of water. In our experimental studies with wet coals, we assume that the water exists as a standing-phase and absorbs an amount of gas predicted from gas-water equilibrium. We subtract this gas-in-water amount from the sorption loading and present the difference as the amount of gas physically adsorbed on the wet coal. In reality, however, the water may be in a standing-phase form or adsorbed onto the coal itself; i.e., water is an adsorbed component. Four phases can exist when dealing with supercritical gas adsorption on wet coals: the gas-rich phase, the water-rich phase, the adsorbed phase (which may contain water), and the solid itself. Therefore, a more rigorous method to handle the water effect is needed for better representation of gas adsorption on wet coals. Such a model is currently under development.

Table 11 presents comparisons of the 2-D PR EOS and OK models predictions of pure-gas adsorptions on dry activated carbon. Generalized predictions for the SLD model are not included pending the development of a hard-sphere EOS. Both models show comparable capability in predicting pure-gas adsorptions on dry activated carbon based on the physical properties of the adsorbates and the accessible characterization of the adsorbent. On average, the models can predict pure-gas adsorption on activated carbon within 10% AAD.

Sample results to examine the predictive capabilities of matrix-calibrated models are included in Tables 12 and 13. In Table 12, our experimental data of pure-gas adsorption on dry activated carbon at 318.2 K (Systems 26-29) were employed. In this case, CO₂ adsorption data up to 800 psia (5.6 MPa) were regressed to obtain model parameters; using these parameters, we then predicted the higher-pressure adsorption of CO₂ and the adsorption of the other three gases. Table 12 presents the comparisons of these three models predictions. For the systems considered, on average, the OK model has the best ability to predict the other gas adsorptions based on the adsorption isotherm for one gas. The 2D-EOS model gives the worst predictions among the three models. This is because the thermal expansion coefficient used for CO₂ in the 2-D EOS is underestimated, as mentioned earlier. The Peng-Robinson (PR) SLD model shows better prediction than the other models for ethane adsorption; however, the SLD model produces poor prediction for methane and nitrogen adsorptions. Efforts have been initiated to develop a more accurate equation of state for the SLD model. Preliminary results using the SLD and an equation of state that accounts for the hard-sphere limit indicate that the SLD model gives not only better representation of the adsorption data but also better prediction of other gas adsorption based solely on one component isotherm [21].

For the predictive case, Table 12 also presents the parameters used in the models for systems 26-29. The surface area (A) obtained in the OK model ($= 954 \text{ m}^2/\text{g}$) is reasonable for Calgon F-400 activated carbon, compared to the $850 \text{ m}^2/\text{g}$ value reported by Humayun and Tomasko (2000) and $998 \text{ m}^2/\text{g}$ value provided by the company, based on nitrogen BET surface area at 77 K. The surface area obtained in the 2-D EOS model is significantly higher (about 30%) than the reported value. This is

in part due to thermal expansion coefficient used for the 2-D EOS was 0.0024 (1/K) whereas 0.0039 (1/K) was used in the OK model. The surface area obtained in the SLD model is significantly lower (about 25%) than the reported value. This is in part due to slit model used for the SLD whereas a flat surface was used in the 2-D EOS and OK models (or a multi-layer BET model). For the SLD model, a slit model and a flat surface model are equivalent for large values of the effective slit length L . For very small lengths, the surface area will be half that required for a flat surface to predict an equivalent amount of adsorption. Thus, the SLD model for slits has typically a surface area half that reported by the nitrogen BET surface area at 77K. The solid-solid interaction energy (ϵ_{ss}/k) obtained in the 2-D EOS and SLD models are relatively close; the solid-solid interaction energy (ϵ_{ss}/k) obtained in the OK model is significantly higher (about 30%).

Figure 3 illustrates the quality of the OK model predictions for pure-gas adsorption on dry activated carbon at 318.2 K using parameters given in Table 2. As shown in this figure, the model can predict the maximum gas adsorption behavior of CO₂ and ethane. In the figure, the solid line shows the region of data fitted, while the dashed lines are predictions from the fitted data.

Table 13 presents the comparisons of another aspect of the matrix-calibrated models. Here, we predict high-pressure CO₂ adsorptions on dry coals at 328.2 K based on low-pressure data. Specifically, CO₂ data up to 800 psia (5.6 MPa) were regressed to obtain model parameters; using this information, higher-pressure adsorptions were then *predicted*. For five coals considered (the Upper Freeport, Pocahontas, Illinois #6, Beulah Zap and Wyodak), the OK model gives better predictions than the 2-D EOS and the SLD models. As in the adsorption on activated carbon, the three models also predict the maximum gas adsorption as illustrated by the OK model in Figure 3.

The parameters presented in Table 13 shows similar trends for the three models. The surface areas of the coals increase in the following order: Upper Freeport, Pocahontas, Illinois #6, Beulah Zap and Wyodak. However, as expected, the surface areas obtained from the SLD model are about half of those obtained from the other models. The least solid-solid interaction energy was also obtained for Illinois #6 coal for all three models. Note that the fluid-solid interaction energy in the OK model presented in this table represents the potential energy and has a negative sign, while the fluid-solid interaction energy in the SLD model is the well depth energy parameter and the value is always positive.

A sample calculation is given to demonstrate the 2-D PR EOS matrix-calibrated predictions involving different isotherms. In this case, CH₄ adsorption data (System 16, 12 data points) up to 820 psia (5.7 MPa) at 233 K were regressed to obtain the EOS parameters, the surface area and fluid-solid interaction. Using this information, the model predicted, as shown in Figure 5, the higher-pressure adsorption of the same isotherm as well as the other adsorption isotherms over the full pressure range (System 16, 110 data points). The overall AAD and RMSE of 3.0% and 0.361 mmol/g, respectively, were obtained compared to 2.0% and 0.242 mmol/g, using parameters

regressed from all the data. These preliminary results indicate the effectiveness of (a) the newly-developed 2-D PR EOS temperature relations, and (b) the matrix-calibrated modeling.

Mixture Adsorption: Detailed development and evaluation of the mixture adsorption modeling using the 2-D EOS, OK, and SLD models appears in Section K of Page 172. Our experimental measurements of mixture adsorption on activated carbon and coals were used for model comparisons. The parameters obtained from pure-gas adsorption modeling were used to evaluate the three models for predicting and correlating mixture adsorption.

Table 14 presents the comparisons of the three models overall statistics in the modeling of binary mixture Gibbs adsorption. As shown in Table 14, the three models can predict the component adsorption in the binary systems on activated carbon within twice the experimental uncertainties, on average. The OK model appears to give worse predictions than the other models for nitrogen component of binary system adsorption on activated carbon. The WAAD of nitrogen is 2.6 for the OK model compared to 1.6 and 1.8 for the 2-D PR EOS and SLD models, respectively. As indicated, the %AAD is relatively large for some of the component adsorption. This is an artifact of calculating relative errors for near-zero Gibbs adsorption values. Identical calculations for the corresponding total Gibbs adsorption given in Table 15 leads to significant reduction in the %AAD.

Most importantly, all the three models can predict the component adsorption on coals within the experimental uncertainties, on average.

Table 15 presents the comparisons of the three models overall statistics for the total Gibbs adsorption. All the three models can predict total Gibbs adsorption on activated carbon and coals within the experimental uncertainties, on average. Better predictions for the total adsorption than the individual component adsorptions reveal that improved mixing rules are needed for better representations of the individual component adsorptions. These results for mixtures and the favorable results for pure-gas adsorption indicate that the 2-D EOS, the OK and the SLD modeling frameworks are effective in describing high-pressure adsorption, provided that satisfactory mixing and combining rules are employed.

Tables 18-24 present examples of detailed results for the model predictions and representations of mixture adsorptions. Tables 18 and 19 present the 2-D EOS model predictions and representations of the binary adsorption on activated carbon. As also shown in Figures 6-8 for the methane/CO₂ system, the model is capable in representing the data within the expected experimental uncertainties represented by the error bars in the figures.

Tables 20 and 21 present detail results of the OK model predictions and representations of the binary adsorption on wet Tiffany coal. As shown in Table 20, the worst prediction results were obtained for methane adsorption in the methane/CO₂ binary. About the

same results were also obtained for the other two models. The OK and the 2-D EOS models predict the methane adsorption of this system with 4.5 and 3.7 WAAD, respectively. Model representations of methane/nitrogen by the three models, as illustrated in Figure 9 by the OK model results, are within the expected experimental uncertainties when the binary interaction parameters were used. The size of the BIP (C_{ij}) for some binary interactions as shown in Table 21, however, are unrealistically large. This suggests that the mixing/combining rules applied in the OK model may not be appropriate to predict mixture adsorption. Other reasons for the large BIP values include inadequate accounting for fluid-fluid interactions by the OK model. Future work will address these matters.

Table 22 presents the results of the 2-D EOS model predictions for the ternary mixture adsorption on activated carbon, and Tables 23 and 24 present, respectively, the results of the OK and SLD model predictions for the ternary mixture adsorption on wet Tiffany coals. As shown in the tables and also elucidated by Figure 10 for the ternary adsorption on wet Tiffany coals, the model can predict the ternary data well within the expected experimental uncertainties when the binary interaction parameters are included in the predictions. Similar results were also obtained for the other models.

In summary, the model development results indicate that (a) the selected frameworks provide models capable of describing high-pressure adsorption, (b) using matrix-calibrated models will minimize the experimental efforts for obtaining accurate adsorption predictions for a specific CBM site, and (c) a potential exists for developing *an priori* predictive models using fully-generalized parameters determined by accessible adsorbate and adsorbent characterizations. To realize the full benefits of generalized predictions requires an accurate hard-sphere EOS, improved mixing rules, and a rigorous accounting for the water effects in the CBM adsorption systems.

(c) Modeling Conclusions

In this study, we investigated the efficacy of two-dimensional equations of state (2-D EOS), the simplified local density (SLD), and the Ono-Kondo (OK) lattice model to describe adsorption equilibrium for systems encountered in CO₂ sequestration and coalbed methane recovery. Despite their different theoretical bases, in general, the three models gave comparable results in their correlative and predictive abilities based on the gas properties and the accessible characterization of the adsorbent. Specifically the models:

1. Correlate *pure* component adsorption within the experimental uncertainties (4% AAD).
2. Predict *pure* component adsorption within 10% AAD. This includes the prediction of a maximum exhibited in the pure component excess adsorption at high pressures.
3. Correlate the *total* and *individual* component adsorption in the *binary* systems within the expected experimental uncertainties.

4. Predict *total* adsorption for the *binary* and *ternary* systems studied within the expected experimental uncertainties.
5. Predict the *individual component* adsorption in the *binary* systems within twice the expected experimental uncertainties.
6. Predict the *individual component* adsorption in the *ternary* systems within the expected experimental uncertainties, if the information obtained from binary adsorption is included.

In addition, our results indicate that matrix-calibrated models provide reasonably accurate predictions (within twice the experimental uncertainties) for high-pressure adsorption at different temperatures based on low-pressure adsorption data for the same gas at a single temperature and, in addition, can predict the adsorption of other gases (at the same temperature).

(d) Modeling Recommendations

To fully exploit the potential of the models studied, the following developments are needed:

1. Develop a more rigorous approach to account for the effect of water on CBM adsorption systems.
2. Develop improved mixing/combining rules for the OK model, and apply an accurate equation of state to calculate the chemical potential of the gas phase.
3. Develop an accurate equation of state, which exhibits accurate hard-sphere limiting behavior, to improve modeling of high-pressure gas adsorption.

E. Conclusions

Completion of this project has contributed the following knowledge to the field of adsorption of coalbed gases for CBM production and CO₂ sequestration:

- Significantly expanded database for adsorption, including valuable data on:
 - A variety of pure, binary, and ternary gas mixtures
 - Eight different coal matrices and activated carbon
 - Effects of moisture on adsorption behavior for selected systems
- An adsorption modeling capability based on theory, including development of:
 - Several state-of-the-art models for representing adsorption equilibrium of pure fluids and mixtures within their experimental uncertainties
 - Generalized and matrix-calibrated models to provide accurate predictions within one to three times the experimental uncertainties
- Improved models to estimate coal capacity for coalbed gases based solely on readily accessible coal characterizations parameters
- Improved computational capabilities, including robust algorithms for solving adsorption equilibrium for a variety of models
- An improved pure-fluid and mixture compressibility factor EOS model which is required for CBM adsorption measurements
- Dissemination of the above accomplishments to the scientific and engineering community through a series of technical reports, presentations, and journal publications.

F. Recommendations

Following are our recommendations based on our current assessment of equilibrium adsorption capabilities as they pertain to CBM production and CO₂ sequestration.

Experimental and modeling efforts should be focused on improving our predictive capability to describe accurately CBM mixture adsorption on wet coals. Specifically:

Experimental Work:

1. Systematically-selected measurements should be conducted to expand our database on mixtures adsorption. The studies should be performed on a variety of coals at temperatures from 90-140 °F and pressures to 2000 psia.
2. Experimental studies should be devoted to delineating the effects of moisture on pure, binary and ternary mixture gas adsorption on coals and on activated carbon. These measurements should be made in sufficient detail to provide meaningful input to the development and evaluation of models for mixture behavior.

Model Development:

1. Develop a more accurate EOS that obeys the hard-sphere limits; our results to date clearly demonstrate that this is required for accurate modeling of the high-density adsorbed phase.
2. Develop robust algorithms to rigorously account for the presence of moisture; this will require (a) EOS models capable of describing vapor-liquid equilibria of water-coalbed gases, and (b) generalized-parameter adsorption models capable of describing water-coalbed gases over a wide range of temperatures, pressures and compositions.
3. Develop improved mixing/combining rules to enhance the predictive capability of component adsorption in mixtures.

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Table 1. Equations for the Local Attractive Parameter $a(z)$

Region	Case 1: $\frac{L}{s_{ff}} \geq 3$
$0.5 \leq \frac{z}{s_{ff}} \leq 1.5$	$\frac{a(z)}{a_b} = \frac{3}{8} \left(\frac{z}{s_{ff}} + \frac{5}{6} - \frac{1}{3 \left(\frac{L-z}{s_{ff}} - 0.5 \right)^3} \right)$
$1.5 \leq \frac{z}{s_{ff}} \leq \frac{L}{s_{ff}} - 1.5$	$\frac{a(z)}{a_b} = \frac{3}{8} \left(\frac{8}{3} - \frac{1}{3 \left(\frac{z}{s_{ff}} - 0.5 \right)^3} - \frac{1}{3 \left(\frac{L-z}{s_{ff}} - 0.5 \right)^3} \right)$
$\frac{L}{s_{ff}} - 1.5 \leq \frac{z}{s_{ff}} \leq \frac{L}{s_{ff}} - 0.5$	$\frac{a(z)}{a_b} = \frac{3}{8} \left(\frac{L-z}{s_{ff}} + \frac{5}{6} - \frac{1}{3 \left(\frac{z}{s_{ff}} - 0.5 \right)^3} \right)$
	Case 2: $2 \leq \frac{L}{s_{ff}} \leq 3$
$0.5 \leq \frac{z}{s_{ff}} \leq \frac{L}{s_{ff}} - 1.5$	$\frac{a(z)}{a_b} = \frac{3}{8} \left(\frac{z}{s_{ff}} + \frac{5}{6} - \frac{1}{3 \left(\frac{L-z}{s_{ff}} - 0.5 \right)^3} \right)$
$\frac{L}{s_{ff}} - 1.5 \leq \frac{z}{s_{ff}} \leq 1.5$	$\frac{a(z)}{a_b} = \frac{3}{8} \left(\frac{L}{s_{ff}} - 1 \right)$
$1.5 \leq \frac{z}{s_{ff}} \leq \frac{L}{s_{ff}} - 0.5$	$\frac{a(z)}{a_b} = \frac{3}{8} \left(\frac{L-z}{s_{ff}} + \frac{5}{6} - \frac{1}{3 \left(\frac{z}{s_{ff}} - 0.5 \right)^3} \right)$
	Case 3: $1.5 \leq \frac{L}{s_{ff}} \leq 2$
Anywhere within slit	$\frac{a(z)}{a_b} = \frac{3}{8} \left(\frac{L}{s_{ff}} - 1 \right)$

Table 2. Description of the Parameters Used for Pure-Adsorption Modeling on Activated Carbon

Cases	Description
Correlative Ability	
2-D EOS	<p>Parameters used: A, e_{fs}, δ, $\sigma_{\mu,0}$, and e_{ff} and r_{mc}</p> <ul style="list-style-type: none"> - Based on N_2 BET surface area for each adsorbent - e_{fs}/k, δ, and $\sigma_{m,0}$, are regressed for each system - e_{ff}/k is estimated from a proportional relation to the well depth of the Lennard-Jones 12-6 potential: $e_{ff} = 0.432e_{ff}^*$ - r_{mc} is estimated from the reciprocal van der Waals co-volume: $r_{mc} = 1/b$
SLD	<p>Parameters used: A, L, ε_{fs}^*, and λ_i, k</p> <ul style="list-style-type: none"> - A and L are regressed for each adsorbent - ε_{fs}^* and λ_i are regressed for each system - k is regressed for each system having multiple isotherms
Ono-Kondo	<p>Parameters used: C, e_{fs}/k, e_{ff}/k and r_{mc}</p> <ul style="list-style-type: none"> - C is regressed for each adsorption isotherm. - e_{fs}/k is regressed for each system - e_{ff}/k is estimated from a proportional relation to the well depth of the Lennard-Jones 12-6 potential: $e_{ff} = 0.432e_{ff}^*$ - r_{mc} is estimated from the reciprocal van der Waals co-volume: $r_{mc} = 1/b$

Table 2. Description of the Parameters Used for Pure-Adsorption Modeling on Activated Carbon (Continued)

Cases	Description
Predictive Ability: Generalized Parameter Predictions	
2-D EOS	<p>Parameters used: A, e_{fs}, δ, $\sigma_{m,0}$, and e_{ff} and r_{mc}</p> <ul style="list-style-type: none"> - A based on N_2 BET surface area for each adsorbent - $\delta = 0.0024 \text{ (K}^{-1}\text{)}$ - e_{ff}/k is estimated from a proportional relation to the well depth of the Lennard-Jones 12-6 potential: $e_{ff} = 0.432 e_{ff}^*$ - r_{mc} is estimated from the reciprocal van der Waals co-volume: $r_{mc} = 1/b$
Ono-Kondo	<p>Parameters used: C, e_{fs}/k, e_{ff}/k and r_{mc}</p> <ul style="list-style-type: none"> - e_{ff}/k and r_{mc} are estimated as in correlative case - C and e_{fs}/k are generalized according to the equations: $\ln(1/C) = dT - [\ln C_{a,o} + dT_o + \ln(A/2)] \quad \text{and} \quad e_{fs} = -\frac{6}{5} p r_c e_{fs}^* s_{fs}^2$ <p>where: for CO_2; $C_{a,o} = 0.0142 \text{ mmol/m}^2$; $d = 0.0039 \text{ (K}^{-1}\text{)}$ for other component; $C_{a,o} = 0.102/\sigma^2 + 0.0034$; σ in $\text{\AA}$; $d = 0.0024 \text{ (K}^{-1}\text{)}$ T_o (K) is the normal boiling point of the adsorbate (triple point for CO_2) $r_c = 0.382 \text{ atom/\AA}^2$ $s_{fs} = \frac{1}{2}(s_{ff} + s_{cc})$; s_{ff} and s_{cc} are adsorbate and carbon diameter $e_{fs}^* = \sqrt{e_{ff}^* e_{ss}^*}$ Reported surface area was used for A, and $\epsilon_{ss}^*/k = 40 \text{ K}$.</p>

Table 3. Literature Data Used for Model Evaluations of Pure-Gas Adsorption on Activated Carbons

System No.	Adsorbent	Adsorbent Surf. Area (m ² /g)	Adsorbate	Temp. Range (K)	Pressure Range (MPa)	Reference
1	AC, Columbia Grade L	1152	N ₂	311 - 422	0.028 – 1.50	Ray (1950)
2	AC, Columbia Grade L	1152	CH ₄	311 - 422	0.026 – 1.48	Ray (1950)
3	AC, Columbia Grade L	1152	C ₂ H ₆	311 - 478	0.007 – 1.49	Ray (1950)
4	Charcoal	1157	CH ₄	283 - 323	0.5 – 13.8	Payne (1968)
5	Charcoal	1157	C ₃ H ₈	293 - 333	8x10 ⁻⁴ – 1.35	Payne (1968)
6	AC, BPL	988	CH ₄	213 - 301	0.012 – 3.83	Reich (1980)
7	AC, BPL	988	C ₂ H ₆	213 - 301	7x10 ⁻⁴ – 1.71	Reich (1980)
8	AC, BPL	988	C ₂ H ₄	213 - 301	7x10 ⁻⁴ – 1.70	Reich (1980)
9	AC, BPL	988	CO ₂	213 - 301	0.003 – 3.84	Reich (1980)
10	AC, PCB-Calgon Corp.	1150-1250	CH ₄	296 - 480	0.27 – 6.69	Ritter (1987)
11	AC, PCB-Calgon Corp.	1150-1250	CO ₂	296 - 480	0.11 – 3.67	Ritter (1987)
12	AC F30/470, Chemviron Carbon	993.5	CO ₂	278 - 328	0.05 – 3.35	Berlier (1997)
13	AC Norit R1 Extra	1450	N ₂	298	0.03 – 5.98	Dreisbach (1999)
14	AC Norit R1 Extra	1450	CH ₄	298	0.01 – 5.75	Dreisbach (1999)
15	AC Norit R1 Extra	1450	CO ₂	298	0.008 – 6.0	Dreisbach (1999)

Table 3. Literature Data Used for Model Evaluation of Pure-Gas Adsorption on Activated Carbons (Continued)

System No.	Adsorbent	Adsorbent Surf. Area (m²/g)	Adsorbate	Temp. Range (K)	Pressure Range (MPa)	Reference
16	AC from Coconut shell with KOH activation	3106 (CO ₂ ads.)	CH ₄	233 - 333	0.09 – 9.40	Zhou (2000)
17	AC -Calgon F-400	850	CO ₂	303 to 318	0.02 – 20.2	Humayun (2000)
18	AC-Norit RB1	1100	CH ₄	294 - 351	0.05 – 0.8	Vaart (2000)
19	AC-Norit RB1	1100	CO ₂	294 - 348	0.05 – 0.8	Vaart (2000)
20	AC from Coconut shell with KOH activation	3106 (CO ₂ ads.)	N ₂	178 - 298	0.44 – 9.19	Zhou (2001)
21	AC F30/470, Chemviron Carbon	993.5	N ₂	303 - 383	0.39 – 9.5	Frère (2002)
22	AC F30/470, Chemviron Carbon	993.5	CH ₄	303 - 383	0.44 – 8.98	Frère (2002)
23	AC F30/470, Chemviron Carbon	993.5	C ₃ H ₈	303 - 383	0.05 – 2.20	Frère (2002)
24	AC Norit R1	1262	N ₂	298	0.03 – 14.56	Beutekamp (2002)
25	AC Norit R1	1262	CO ₂	298	0.03 – 6.04	Beutekamp (2002)
26	AC –Calgon F-400	850	N ₂	298	0.67 – 12.9	OSU*
27	AC –Calgon F-400	850	CH ₄	298	0.67 – 12.9	OSU
28	AC –Calgon F-400	850	CO ₂	298	0.67 – 12.9	OSU
29	AC –Calgon F-400	850	C ₂ H ₆	298	0.67 – 12.9	OSU

*Data are given in the OSU Adsorption Database in Section K

Table 4. OSU Data Used for Model Evaluations of Pure-Gas Adsorption on Coals

System No.	Adsorbent	Adsorbent Surf. area (m²/g)	Adsorbate	Temp. (K)	Pressure Range (MPa)	Reference
30	Wet Fruitland Coal #2	--	N ₂	319.3	0.7 – 12.4	OSU
31	Wet Fruitland Coal #2	--	CH ₄	319.3	0.7 – 12.4	OSU
32	Wet Fruitland Coal #2	--	CO ₂	319.3	0.7 – 12.4	OSU
33	Wet Illinois #6 Coal	--	N ₂	319.3	0.7 – 12.4	OSU
34	Wet Illinois #6 Coal	--	CH ₄	319.3	0.7 – 12.4	OSU
35	Wet Illinois #6 Coal	--	CO ₂	319.3	0.7 – 12.5	OSU
36	Wet Tiffany Coal	--	N ₂	327.5	0.7 – 13.8	OSU
37	Wet Tiffany Coal	--	CH ₄	327.5	0.4 – 13.6	OSU
38	Wet Tiffany Coal	--	CO ₂	327.5	0.5 – 13.6	OSU
39	Wet LB Fruitland Coal	--	N ₂	319.3	1.5 – 12.4	OSU
40	Wet LB Fruitland Coal	--	CH ₄	319.3	1.4 – 12.5	OSU
41	Wet LB Fruitland Coal	--	CO ₂	319.3	0.7 – 12.4	OSU
42	Dry Illinois #6 Coal	--	CO ₂	328	0.7 – 13.8	OSU
43	Dry Beulah Zap Coal	--	CO ₂	328	0.6 – 13.8	OSU
44	Dry Wyodak Coal	--	CO ₂	328	0.7 – 13.8	OSU
45	Dry Upper Freeport Coal	--	CO ₂	328	0.7 – 13.8	OSU
46	Dry Pocahontas Coal	--	CO ₂	328	1.1 – 13.8	OSU

Table 5. OSU Adsorption Database

System No.	Adsorbent	Adsorbate	Temp. (K)	Pressure Range (MPa)
1	Dry AC – F 400	N ₂	318 & 328	0.7 – 13.7
2	Dry AC – F 400	CH ₄	318 & 328	0.7 – 13.7
3	Dry AC – F 400	CO ₂	318 & 328	0.7 – 13.7
4	Dry AC – F 400	C ₂ H ₆	318	0.7 – 13.7
5	Dry AC – F 400	N ₂ + CH ₄	318	0.7 – 12.4
6	Dry AC – F 400	CH ₄ + CO ₂	318	0.7 – 12.4
7	Dry AC – F 400	N ₂ + CO ₂	318	0.7 – 12.4
8	Dry AC – F 400	N ₂ + CH ₄ + CO ₂	318	0.7 – 12.4
9	Wet Fruitland Coal	N ₂	319	0.7 – 12.4
10	Wet Fruitland Coal	CH ₄	319	0.7 – 12.4
11	Wet Fruitland Coal	CO ₂	319	0.7 – 12.4
12	Wet Fruitland Coal	N ₂ + CH ₄	319	0.7 – 12.4
13	Wet Fruitland Coal	CH ₄ + CO ₂	319	0.7 – 12.4
14	Wet Fruitland Coal	N ₂ + CO ₂	319	0.7 – 12.4
15	Wet Illinois #6 Coal	N ₂	319	0.7 – 12.4
16	Wet Illinois #6 Coal	CH ₄	319	0.7 – 12.4
17	Wet Illinois #6 Coal	CO ₂	319	0.7 – 12.4
18	Wet Illinois #6 Coal	N ₂ + CH ₄	319	0.7 – 12.4
19	Wet Illinois #6 Coal	CH ₄ + CO ₂	319	0.7 – 12.4
20	Wet Illinois #6 Coal	N ₂ + CO ₂	319	0.7 – 12.4
21	Wet Tiffany Coal	N ₂	328	0.7 – 13.7
22	Wet Tiffany Coal	CH ₄	328	0.7 – 13.7
23	Wet Tiffany Coal	CO ₂	328	0.7 – 13.7
24	Wet Tiffany Coal	N ₂ + CH ₄	328	0.7 – 13.7
25	Wet Tiffany Coal	CH ₄ + CO ₂	328	0.7 – 13.7
26	Wet Tiffany Coal	N ₂ + CO ₂	328	0.7 – 13.7
27	Wet Tiffany Coal	N ₂ + CH ₄ + CO ₂	328	0.7 – 13.7
28	Wet LB Fruitland Coal	N ₂	319	0.7 – 12.4
29	Wet LB Fruitland Coal	CH ₄	319	0.7 – 12.4
30	Wet LB Fruitland Coal	CO ₂	319	0.7 – 12.4
31	Dry Illinois #6 Coal	CO ₂	328	0.7 – 13.7
32	Dry Beulah Zap Coal	CO ₂	328	0.7 – 13.7
33	Dry Wyodak Coal	CO ₂	328	0.7 – 13.7
34	Dry Upper Freeport Coal	CO ₂	328	0.7 – 13.7
35	Dry Pocahontas Coal	CO ₂	328	0.7 – 13.7

Table 6. Compositional Analysis of Solid Matrices Used in this Study

Analysis*	Activated Carbon	Fruitland Amoco	Fruitland OSU #1	Fruitland OSU #2	Illinois #6	Lower Basin Fruitland OSU #3a	Lower Basin Fruitland OSU #3b	Tiffany Well #1	Tiffany Well #10
<i>Ultimate</i>									
Carbon %	88.65	68.56	68.63	66.58	71.47	38.92	40.20	47.78	56.75
Hydrogen %	0.74	5.74	4.27	4.23	5.13	3.08	3.10	2.62	2.77
Oxygen %	3.01	7.19	0.89	5.08	9.85	3.75	2.87	6.19	5.16
Nitrogen %	0.40	1.40	1.57	1.47	1.46	0.87	0.89	0.92	1.02
Sulfur %	0.73	0.65	4.19	0.72	1.27	1.73	2.14	0.57	0.52
Ash %	6.46	16.45	20.45	21.92	10.81	51.66	50.81	49.71	47.74
<i>Proximate</i>									
Vol. Matter %	3.68	19.12	20.2	20.33	30.61	20.01	14.00	15.48	15.35
Fixed Carbon %	89.86	64.42	59.35	57.75	55.90	28.33	35.19	34.82	36.91

* Huffman Laboratories, Inc., Golden, Colorado.

Table 7. Compositional Analysis of Coals Used in the DOE-NETL Round Robin Study

Analysis*	Beulah Zap	Wyodak	Illinois #6	Upper Freeport	Pocahontas
<i>Ultimate</i>					
Carbon %	72.9	75.0	77.7	85.5	91.1
Hydrogen %	4.83	5.35	5.00	4.70	4.44
Oxygen %	20.3	18.0	13.5	7.5	2.5
Sulfur %	0.80	0.63	4.83	2.32	0.66
Ash %	9.7	8.8	15.5	13.2	4.8
<i>Proximate</i>					
Moisture %	32.2	28.1	8.0	1.1	0.7
Vol. Matter %	30.5	32.2	36.9	27.1	18.5
Fixed Carbon %	30.7	33.0	40.9	58.7	76.1
Ash %	6.6	6.3	14.3	13.0	4.7

* Analyses were provided by the Argonne National Laboratory

Table 8. Analysis of BPL Activated Carbon Used in this Study

Analysis	Units	Value	Lower Limit	Upper Limit
Abrasion Number		87	75	-
Apparent Density	g/cc	0.53	0.44	-
Ash	%	7	-	9
Effective Size	mm	0.64	0.55	0.75
Iodine Number	mg/g	1046	1000	-
US Sieve Series on 12	%	1	-	5
US Sieve Series –40 Mesh	%	1	-	4
Fixed Carbon		1.7	-	1.9

Table 9. Summary Results for Model Representations of Pure-Gas Adsorption on Activated Carbons

System No.	NPTS	2-D PR EOS			Ono Kondo			SLD		
		%AAD	RMSE (mmol/g)	WAAD	%AAD	RMSE (mmol/g)	WAAD	%AAD	RMSE (mmol/g)	WAAD
1	36	3.7	0.029	—	3.1	0.015	—	3.6	0.030	—
2	45	3.1	0.057	—	2.6	0.049	—	3.6	0.068	—
3	58	4.5	0.152	—	4.4	0.145	—	6.6	0.240	—
4	55	0.9	0.053	—	1.2	0.051	—	3.0	0.201	—
5	52	3.8	0.133	—	6.7	0.200	—	6.3	0.257	—
6	72	2.5	0.115	—	3.1	0.112	—	3.7	0.210	—
7	49	4.4	0.207	—	6.3	0.318	—	6.7	0.360	—
8	52	4.3	0.218	—	4.5	0.234	—	7.9	0.460	—
9	60	3.7	0.336	—	4.9	0.325	—	6.5	0.420	—
10	22	1.8	0.059	—	3.2	0.066	—	4.3	0.156	—
11	12	1.8	0.187	—	4.6	0.230	—	6.8	0.344	—
12	164	2.6	0.241	—	1.2	0.138	—	2.6	0.187	—
13	10	0.7	0.016	—	3.3	0.021	—	2.6	0.074	—
14	12	1.7	0.036	—	3.3	0.124	—	3.6	0.058	—
15	12	2.1	0.086	—	9.5	0.267	—	7.5	0.405	—
16	122	2.0	0.242	—	3.0	0.237	—	2.1	0.247	—
17	116	6.7	0.315	—	8.8	0.306	—	7.8	0.400	—
18	64	1.3	0.026	—	1.5	0.030	—	2.4	0.059	—
19	64	1.0	0.033	—	1.7	0.060	—	4.4	0.193	—
20	71	2.1	0.267	—	1.5	0.162	—	3.2	0.377	—
21	116	2.2	0.065	—	2.0	0.044	—	2.3	0.063	—

**Table 9. Summary Results for Model Representations of Pure-Gas Adsorption on Activated Carbons
(Continued)**

System No.	NPTS	2-D PR EOS			Ono Kondo			SLD		
		%AAD	RMSE (mmol/g)	WAAD	%AAD	RMSE (mmol/g)	WAAD	%AAD	RMSE (mmol/g)	WAAD
22	122	1.9	0.104	—	2.2	0.094	—	2.8	0.134	—
23	102	1.5	0.106	—	2.3	0.173	—	2.8	0.158	—
24	31	1.1	0.064	—	1.5	0.035	—	2.4	0.055	—
25	29	1.1	0.121	—	3.6	0.269	—	4.0	0.229	—
26	22	0.4	0.018	—	0.4	0.012	—	0.8	0.036	—
27	22	0.5	0.025	—	0.8	0.037	—	1.4	0.044	—
28	52	1.4	0.144	—	4.4	0.222	—	4.6	0.237	—
29	21	5.5	0.394	—	6.4	0.153	—	4.2	0.135	—
Overall	1665	2.6	0.180	—	3.3	0.178	—	4.0	0.244	—

Table 10. Summary Results for Model Representations of Pure-Gas Adsorption on Coals

System No.	NPTS	2-D PR EOS			Ono Kondo			SLD		
		%AAD	RMSE (mmol/g)	WAAD	%AAD	RMSE (mmol/g)	WAAD	%AAD	RMSE (mmol/g)	WAAD
30	37	2.4	0.006	0.4	2.6	0.006	0.3	3.1	0.008	0.4
31	40	1.3	0.007	0.5	1.2	0.007	0.3	1.1	0.006	0.2
32	57	6.5	0.075	0.7	6.7	0.083	0.8	7.9	0.088	0.8
33	20	1.6	0.001	0.0	2.4	0.002	0.2	3.4	0.003	0.2
34	20	1.9	0.006	0.3	2.9	0.007	0.4	2.6	0.008	0.3
35	40	4.1	0.038	1.2	5.5	0.060	1.0	7.1	0.058	0.8
36	21	2.8	0.003	0.5	3.3	0.003	0.4	4.4	0.006	0.8
37	34	3.7	0.012	1.3	3.8	0.013	1.4	3.5	0.010	1.3
38	16	9.5	0.055	0.7	4.2	0.022	0.6	3.5	0.018	0.3
39	17	4.2	0.004	0.3	4.5	0.004	0.4	4.8	0.006	0.4
40	16	2.4	0.007	0.4	2.6	0.007	0.5	3.3	0.011	0.6
41	48	8.9	0.039	0.5	7.3	0.035	0.9	6.6	0.033	0.6
42	11	10.2	0.155	0.9	5.1	0.067	0.9	1.8	0.025	0.3
43	22	4.6	0.080	0.6	3.3	0.071	0.5	3.9	0.057	0.9
44	11	3.9	0.067	0.6	2.9	0.064	0.5	4.2	0.062	0.9
45	11	5.2	0.057	0.4	2.2	0.026	0.4	2.7	0.023	0.6
46	11	7.1	0.093	0.5	1.8	0.023	0.3	2.3	0.023	0.5
Overall	432	4.7	0.050	0.6	4.1	0.044	0.6	4.5	0.042	0.6

Table 11. Prediction Results for Pure-Gas Adsorption on Activated Carbons

System No.	NPTS	2-D PR EOS			Ono Kondo		
		%AAD	RMSE (mmol/g)	WAAD	%AAD	RMSE (mmol/g)	WAAD
1	36	17.8	0.106	—	16.5	0.085	—
2	45	8.0	0.074	—	4.3	0.052	—
3	58	14.7	0.292	—	7.7	0.174	—
4	55	6.5	0.501	—	11.9	0.773	—
5	52	4.5	0.154	—	5.6	0.196	—
6	72	9.6	0.346	—	10.1	0.285	—
7	49	11.6	0.546	—	5.8	0.258	—
8	52	13.9	0.572	—	5.9	0.294	—
9	60	16.9	1.092	—	17.8	0.730	—
10	22	6.9	0.296	—	5.0	0.091	—
11	12	12.7	0.550	—	14.4	0.367	—
12	164	10.8	0.945	—	4.6	0.259	—
13	10	8.3	0.318	—	7.3	0.128	—
14	12	11.4	0.639	—	5.3	0.180	—
15	12	14.8	0.553	—	22.0	0.464	—
16	122	4.2	0.428	—	3.7	0.353	—
17	116	7.4	0.739	—	8.7	0.545	—
18	64	8.5	0.122	—	5.1	0.158	—
19	64	5.3	0.216	—	21.7	0.652	—
20	71	7.4	0.971	—	8.9	1.050	—
21	116	6.2	0.153	—	4.6	0.115	—

Table 11. Prediction Results for Pure-Gas Adsorption on Activated Carbons (Continued)

System No.	NPTS	2-D PR EOS			Ono Kondo		
		%AAD	RMSE (mmol/g)	WAAD	%AAD	RMSE (mmol/g)	WAAD
22	122	4.4	0.194	—	5.1	0.242	—
23	102	4.9	0.262	—	2.7	0.184	—
24	31	12.3	0.250	—	6.7	0.094	—
25	29	16.1	1.861	—	13.5	0.620	—
26	22	7.2	0.189	—	12.4	0.315	—
27	22	1.1	0.061	—	12.0	0.491	—
28	52	18.6	0.500	—	7.2	0.531	—
29	21	11.5	0.707	—	8.8	0.314	—
Overall	1665	8.8	0.596	—	8.2	0.443	—

Table 12. Comparisons of the Matrix-Calibrated Model Predictions of Pure-Gas Adsorption on Dry Activated Carbon at 318.2 K ^a

Models	CO ₂	Ethane	Methane	Nitrogen
2-D EOS				
A (m ² /g)	1298	1298	1298	1298
ϵ_{ss}/k (K)	31.2	31.2	31.2	31.2
NPTS	52	21	40	22
% AAD	1.5	41.1	21.7	13.5
SLD				
A (m ² /g)	671	671	671	671
ϵ_{ss}/k (K)	26.3	26.3	26.3	26.3
L (nm)	1.01	1.01	1.01	1.01
NPTS	51	32	22	22
% AAD	5.2	6.0	24.3	30.1
Ono-Kondo				
A (m ² /g)	954	954	954	954
ϵ_{ss}/k (K)	39	39	39	39
NPTS	52	21	40	22
% AAD	4.7	11.3	2.3	4.0

^a CO₂ data up to 800 psia (5.6 MPa) were regressed to obtain model parameters; using these parameters, higher pressure adsorption of CO₂ and the complete isotherms of the other three gases were then *predicted*.

Table 13. Comparisons of the Matrix-Calibrated Models Predictions of the CO₂ Adsorptions on Dry Coals at 328.2 K ^a

Models	Wyodak	Beulah Zap	Illinois #6	Pocahontas	Upper Freeport
2-D EOS					
A (m ² /g)	404	363	353	213	174
ε_{ss}/k (K)	31.2	37.3	25.9	49.2	48.6
NPTS	11	22	11	11	11
% AAD	3.9	4.6	10.2	7.1	5.2
SLD					
A (m ² /g)	129	112	120	88	68
ε_{fs}/k (K)	79.8	97.3	64.6	85.5	88.5
L	1.36	1.40	1.31	1.18	1.24
NPTS	11	22	11	11	11
% AAD	6.0	5.2	2.7	3.4	4.5
Ono-Kondo					
A (m ² /g)	325	294	275	173	146
ε_{fs}/k (K)	-1270	-1370	-1200	-1540	-1480
NPTS	11	22	11	11	11
% AAD	2.9	3.3	5.6	1.8	2.2

^a CO₂ data up to 800 psia (5.6 MPa) were regressed to obtain model parameters; using this information, higher pressure adsorption behavior was then *predicted*.

Table 14. Model Comparison Results for Component Adsorption from Binary Mixtures

System	Methane				Nitrogen				CO ₂			
	NPTS	%AAD	RMSE mmol/g	WAAD	NPTS	%AAD	RMSE mmol/g	WAAD	NPTS	%AAD	RMSE mmol/g	WAAD
Predictive Ability												
Adsorption on AC												
2-D EOS	80	7.0	0.139	1.8	80	12.3	0.070	1.6	80	6.5	0.154	1.6
SLD	80	11.0	0.145	1.8	80	39.8*	0.112	1.8	80	4.8	0.161	1.3
OK	80	10.1	0.109	1.5	80	46.4	0.148	2.6	80	4.3	0.133	1.1
Adsorption on Coals												
2-D EOS	182	15.3	0.021	1.0	182	151.1	0.023	1.4	182	7.5	0.037	1.0
SLD	182	16.4	0.025	1.0	182	213.2	0.020	0.9	182	7.7	0.043	0.8
OK	182	12.4	0.020	1.0	182	75.2	0.017	0.8	182	8.5	0.051	1.2
Correlative Ability												
Adsorption on AC												
2-D EOS	80	5.1	0.081	1.2	80	8.4	0.037	0.7	80	4.2	0.130	1.1
SLD	80	5.0	0.117	1.3	80	4.6	0.046	0.7	80	5.9	0.170	1.6
OK	80	2.8	0.034	0.5	80	9.8	0.034	0.6	80	2.2	0.116	0.6
Adsorption on Coals												
2-D EOS	182	11.9	0.017	0.8	182	119.2	0.019	1.0	182	6.6	0.031	0.9
SLD	182	9.9	0.016	0.5	182	121.3	0.010	0.5	182	7.0	0.039	0.7
OK	182	6.5	0.012	0.4	182	54.9	0.009	0.5	182	4.2	0.026	0.5

*High %AAD are sensitively affected by relative errors for near-zero adsorption values.

Table 15. Model Comparison Results for Total Adsorption

System	NPTS	Total Adsorption		
		%AAD	RMSE, mmol/g	WAAD
Predictive Ability				
Adsorption on AC				
2-D EOS	120	2.9	0.126	1.0
SLD	120	1.6	0.172	0.7
OK	120	4.1	0.228	1.3
Adsorption on Coals				
2-D EOS	273	4.5	0.021	0.6
SLD	273	6.5	0.031	0.6
OK	273	8.1	0.046	1.0
Correlative Ability				
Adsorption on AC				
2-D EOS	120	2.4	0.117	0.8
SLD	120	2.5	0.243	0.8
OK	120	1.7	0.114	0.5
Adsorption on Coals				
2-D EOS	273	4.0	0.020	0.5
SLD	273	6.2	0.031	0.6
OK	273	3.1	0.021	0.4

Table 16. Model Comparison Results for Component Adsorption for both Gibbs and Absolute Adsorption Using 2-D PR EOS

System	Methane				Nitrogen				CO ₂			
	NPTS	%AAD	RMSE mmol/g	WAAD	NPTS	%AAD	RMSE mmol/g	WAAD	NPTS	%AAD	RMSE mmol/g	WAAD
Predictive Ability												
Adsorption on AC												
Gibbs	80	7.0	0.139	1.8	80	12.3	0.070	1.6	80	6.5	0.154	1.6
Absolute	80	5.4	0.156	1.8	80	5.6	0.068	1.2	80	6.2	0.154	1.5
Adsorption on Coals												
Gibbs	182	15.3	0.021	1.0	182	151.1	0.023	1.4	182	7.5	0.037	1.0
Absolute	182	11.0	0.021	0.8	182	27.8	0.023	0.9	182	8.3	0.045	0.8
Correlative Ability												
Adsorption on AC												
Gibbs	80	5.1	0.081	1.2	80	8.4	0.037	0.7	80	4.2	0.130	1.1
Absolute	80	3.6	0.081	1.1	80	2.7	0.035	0.5	80	3.9	0.128	1.0
Adsorption on Coals												
Gibbs	182	11.9	0.017	0.8	182	119.2	0.019	1.0	182	6.6	0.031	0.9
Absolute	182	9.0	0.018	0.6	182	20.2	0.018	0.5	182	7.7	0.043	0.7

Table 17. Model Comparison Results for Total Adsorption for both Gibbs and Absolute Adsorption Using 2-D PR EOS

System	NPTS	Total Adsorption		
		%AAD	RMSE mmol/g	WAAD
Predictive Ability				
Adsorption on AC				
Gibbs	120	2.9	0.126	1.0
Absolute	120	2.9	0.139	1.0
Adsorption on Coals				
Gibbs	273	4.5	0.021	0.6
Absolute	273	4.9	0.030	0.5
Correlative Ability				
Adsorption on AC				
Gibbs	120	2.4	0.117	0.8
Absolute	120	2.0	0.114	0.7
Adsorption on Coals				
Gibbs	273	4.0	0.020	0.5
Absolute	273	4.5	0.030	0.4

Table 18. 2-D EOS Model Predictions of the Binary Adsorption on Activated Carbon

Systems	NPTS	%AAD	RMSE mmol/g	WAAD
ZGR EOS				
CH₄-N₂				
Methane	40	5.4	0.169	2.1
Nitrogen	40	2.6	0.059	0.7
Total	40	4.2	0.179	1.8
CH₄-CO₂				
Methane	40	5.3	0.159	1.2
CO ₂	40	9.8	0.237	2.5
Total	40	1.5	0.097	0.4
N₂-CO₂				
Nitrogen	40	8.7	0.081	1.2
CO ₂	40	8.7	0.195	2.0
Total	40	2.9	0.123	0.8
2-D PR EOS				
CH₄-N₂				
Methane	40	6.4	0.186	2.5
Nitrogen	40	5.3	0.057	1.3
Total	40	3.7	0.156	1.6
CH₄-CO₂				
Methane	40	4.3	0.119	1.0
CO ₂	40	7.1	0.181	1.8
Total	40	1.3	0.085	0.4
N₂-CO₂				
Nitrogen	40	5.9	0.078	1.1
CO ₂	40	5.2	0.120	1.2
Total	40	3.6	0.162	1.1

Table 19. 2-D EOS Model Representations of the Binary Adsorption on Activated Carbon

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂ a ₁₂	t ₁₂ t ₂₁
ZGR EOS						
CH ₄ -N ₂					-0.2502 20.0	-0.1743 -0.2677
Methane	40	1.8	0.042	0.6		
Nitrogen	40	2.7	0.048	0.8		
Total	40	0.9	0.041	0.4		
CH ₄ -CO ₂					-0.4465 20.0	-0.0028 -0.3256
Methane	40	3.0	0.060	0.6		
CO ₂	40	4.0	0.092	1.0		
Total	40	2.1	0.134	0.6		
N ₂ -CO ₂					-0.1000 20.0	-0.0949 -0.1500
Nitrogen	40	5.0	0.052	0.8		
CO ₂	40	8.6	0.179	2.0		
Total	40	4.2	0.174	1.2		
2-D PR EOS						
CH ₄ -N ₂					-0.1206 20.0	-0.0988 -0.2643
Methane	40	4.2	0.091	1.5		
Nitrogen	40	1.9	0.027	0.5		
Total	40	2.0	0.081	0.8		
CH ₄ -CO ₂					-0.1405 20.0	-0.0947 -0.2448
Methane	40	3.0	0.069	0.6		
CO ₂	40	2.7	0.074	0.7		
Total	40	1.3	0.099	0.4		
N ₂ -CO ₂					-0.1194 20.0	-0.1314 -0.0056
Nitrogen	40	3.4	0.041	0.5		
CO ₂	40	5.1	0.165	1.3		
Total	40	2.8	0.151	0.9		

Table 20. OK Model Predictions of Binary Mixtures Adsorption on Wet Tiffany Coal at 327.6 K (OSU, 2002)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
CH₄-N₂				
Methane	11	6.9	0.018	1.0
Nitrogen	11	5.3	0.003	0.3
Total	11	6.5	0.020	1.0
CH₄-CO₂				
Methane	11	45.7	0.055	4.5
CO ₂	11	16.9	0.072	2.5
Total	11	3.5	0.020	0.6
N₂-CO₂				
Nitrogen	11	156	0.015	1.5
CO ₂	11	7.8	0.049	1.0
Total	11	5.9	0.036	0.9

Table 21. OK Model Representations of Binary Mixtures Adsorption on Wet Tiffany Coal at 327.6 K (OSU, 2002)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C_{ij}	E_{ij}
Based on One Regressed Parameter (C_{ij})						
CH4-N2					-0.364	1.0
Methane	11	7.0	0.019	1.0		
Nitrogen	11	8.1	0.004	0.4		
Total	11	5.0	0.016	0.8		
CH4-CO2					-0.692	1.0
Methane	11	12.5	0.021	1.0		
CO2	11	12.9	0.049	2.0		
Total	11	7.0	0.030	1.2		
N2-CO2					-1.239	1.0
Nitrogen	11	52.5	0.005	0.5		
CO2	11	6.0	0.036	0.8		
Total	11	5.1	0.031	0.7		
Based on Two Regressed Parameters						
CH4-N2					0.108	1.179
Methane	11	2.7	0.005	0.2		
Nitrogen	11	6.6	0.003	0.3		
Total	11	2.6	0.006	0.4		
CH4-CO2					-1.074	0.764
Methane	11	8.9	0.015	0.7		
CO2	11	4.4	0.017	0.7		
Total	11	1.8	0.007	0.4		
N2-CO2					-1.230	1.036
Nitrogen	11	53.1	0.005	0.5		
CO2	11	6.1	0.037	0.8		
Total	11	5.2	0.032	0.7		

Table 22. 2-D EOS Model Predictions for the Ternary Mixture Adsorption on Activated Carbon

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS Based on Pure Gas Parameters				
Methane	11	3.8	0.022	0.4
Nitrogen	11	28.2	0.468	5.4
CO ₂	11	13.4	0.676	3.4
Total	11	3.1	0.210	0.9
2-D PR EOS Based on Pure Gas Parameters				
Methane	11	3.8	0.023	0.4
Nitrogen	11	17.8	0.343	3.2
CO ₂	11	11.7	0.596	2.8
Total	11	3.7	0.252	1.1
ZGR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	11	5.9	0.037	0.6
Nitrogen	11	22.0	0.398	4.1
CO ₂	11	12.0	0.613	3.0
Total	11	3.0	0.197	0.9
2-D PR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	11	7.1	0.048	0.6
Nitrogen	11	21.5	0.396	4.0
CO ₂	11	13.6	0.688	3.3
Total	11	3.7	0.252	1.0

Table 23. OK Model Predictions of Ternary Mixtures Adsorption on Wet Tiffany Coal at 327.6 K

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
Based on Parameters from Pure-Adsorption Model				
Methane	11	34.0	0.010	0.7
Nitrogen	11	85.8	0.037	2.6
CO ₂	11	19.3	0.073	2.1
Total	11	5.1	0.028	0.6
Based on Pure and One Binary Interaction Parameters (C_{ij})				
Methane	11	7.0	0.002	0.1
Nitrogen	11	40.7	0.017	1.2
CO ₂	11	15.3	0.051	1.6
Total	11	8.5	0.034	1.0
Based on Pure and Two Binary Interaction Parameters				
Methane	11	29.2	0.010	0.6
Nitrogen	11	48.4	0.021	1.4
CO ₂	11	13.1	0.042	1.4
Total	11	7.5	0.030	0.9

Table 24. SLD Model Predictions of Ternary Mixtures Adsorption on Wet Tiffany Coal at 327.6 K

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
Based on Parameters from Pure-Adsorption Model				
Methane	11	49.5	0.014	1.2
Nitrogen	11	115.0	0.052	3.6
CO ₂	11	17.0	0.070	1.9
Total	11	3.0	0.013	0.4
Based on Pure and One Binary Interaction Parameters (C_{ij})				
Methane	11	6.6	0.002	0.1
Nitrogen	11	28.6	0.015	0.8
CO ₂	11	11.7	0.041	1.3
Total	11	6.8	0.028	0.9

Figure 1. Schematic Diagram of Experimental Apparatus

Figure 2. SLD-PR Model Representation of the Methane Adsorption on Various Wet Coals

Figure 3. Matrix-Calibrated OK Model Predictions of the Pure-Gas Adsorptions on Dry Activated Carbon at 318.2 K

Figure 4. Matrix-Calibrated OK Model Predictions of the CO₂ Adsorptions on Dry Coals at 328.2 K

Figure 5. Matrix-Calibrated 2-D PR EOS Prediction of the CH_4 Absolute Adsorption on Dry Activated Carbon

Figure 6. 2-D PR EOS Model Predictions and Representations of the *Total* Absolute Adsorption of Methane/CO₂ Binary Systems on Activated Carbon

Figure 7. 2-D PR EOS Model Predictions and Representations of the *Methane* Absolute Adsorption of Methane/CO₂ Binary Systems on Activated Carbon

Figure 8. 2-D PR EOS Model Predictions and Representations of the CO₂ Absolute Adsorption of Methane/CO₂ Binary Systems on Activated Carbon

Figure 9. Gibbs Adsorption of a 50/50 Mol % CH₄/N₂ Feed Mixture on Wet Tiffany Coal at 327.6 K (OSU Data)

Figure 10. Total and Individual Gibbs Adsorption of a 10/40/50 Mol % CH₄/N₂/CO₂ Feed Mixture on Wet Tiffany Coal at 327.6 K (OSU Data)

J. Penn State Collaboration

Sequestering Carbon Dioxide in Coalbeds

Final Technical Report

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A. Executive Summary

In an attempt to provide support and meaningful input for the CO₂ sequestration modeling efforts of our colleagues at the Oklahoma State University, we investigated the physical and chemical properties of a wide range of coals. Both volumetric adsorption and microcalorimetry were used to characterize the adsorption uptakes and enthalpies of coals ranging from lignite to low-volatile bituminous. Methane adsorption showed evidence of the dominant effect of London dispersive adsorbate/adsorbent interactions. In contrast, carbon dioxide adsorption heats were significantly higher and rank-sensitive, suggesting that more specific adsorbate/adsorbent interactions are also important.

Oxygen-rich lower-rank coal seams are suggested as being the more promising candidates for CO₂ sequestration. In view of these conclusions, a more detailed chemical surface characterization of the coals was undertaken. Huge differences were found between the measured values of the point of zero charge, which was mostly in the basic range (pH > 6-7) and the isoelectric point of the coals, which was very much in the acidic range (pH < 6). For some coals, depending on their mineral matter composition, these differences were due to the presence of mineral matter. For others, however, they were clearly due to nonuniform distribution of surface charge in the radial direction of the microporous coal particles. There was no simple correlation between CO₂ uptakes and PZC values for the Argonne Premium coals. Neither was there a clear correlation between the coal's surface area and its CO₂ adsorption capacity. This study has thus reinforced the conclusion that, for more reliable modeling of CO₂ adsorption on coal, the surface chemical effects (e.g., presence of heteroatoms in the form of electron-donating

or electron-withdrawing functional groups) must be taken into account. In the present study we have not yet been successful in developing such a meaningful correlation.

B. Experimental Work

1. Samples

Most of the coals used in this study were selected from the Argonne Premium sample bank (www.anl.gov/PCS/pcshome.html). Their particle size was <60 mesh. They cover the range from lignite to low-volatile bituminous coal. Tables 1 and 2 summarize their properties. Very different adsorption properties are indeed to be expected from such wide variations in physical and chemical properties, as has been documented in the voluminous literature on this subject [1, 2].

In ancillary experiments, samples of a commercially available and well characterized activated carbon (BPL, 12x30 mesh, Calgon Carbon Corp.) were also studied. Finally, two coal samples from the Fruitland formation in the San Juan basin (Colorado), where coalbed methane recovery and CO₂ sequestration may be of commercial interest, were analyzed as well.

For brevity and convenience, the following abbreviation code is occasionally used:

Beulah (lignite)	BE
Smith-Roland (subbituminous)	SM
Illinois #6 (high-volatile bituminous)	IL
Pittsburgh #8 (high-volatile bituminous)	PI
Stockton-Lewiston (medium-volatile bituminous)	ST
Pocahontas (low-volatile bituminous)	PO

Dry Fruitland (bituminous)

DF

BPL activated carbon

BPL

2. Equilibrium Adsorption and Microcalorimetry Experiments

The experimental apparatus consists of a Tian-Calvet type heat flow calorimeter, described in detail elsewhere [3]. It uses a cylindrical pyrex cell sandwiched between two thermopiles, which in turn are surrounded by heat sinks. The heat output is measured by integrating the voltage output from the thermopiles, and it is taken to be proportional to the adsorption heat. The output signal is amplified and collected using a Swan 386/25 PC equipped with a Labmaster data acquisition card. The amount of gas adsorbed is determined by measuring the pressure change in the dosing chamber. Two Baratron sensors monitor the pressure, one in the 10^{-4} -1 Torr range and the other in the 1-1000 torr range. The pressure measurements are also digitally recorded with the PC. The system is calibrated using a 491 ohm resistor and a constant power supply.

The powdered coal (or carbon) was heated for 4 h under vacuum, then it was transferred into the sample cell without exposure to air. The calorimeter was kept at constant temperature of about 298 K overnight, maintaining a dynamic vacuum (ca. 10^{-2} Torr) in the sample cell. Each measurement was taken when the equilibrium pressure was reached, and this was assumed to occur when the variation in pressure was less than 0.1 Torr in 10 min. The equilibration time for adsorption varied depending on the sample and the gas used. Therefore, the kinetics of CO₂ and CH₄ uptake were also studied. The approach to equilibrium was monitored during each dosing sequence by following the changes in pressure with time.

3. Surface Chemistry Characterization

The chemistry of the surface of the carbonaceous adsorbents was characterized using two complementary techniques, measurements of the point of zero charge (PZC) and the isoelectric point (IEP). The point of zero charge was determined by mass titration [4, 5], in an experiment that is quite similar to the determination of the pH of an aqueous suspension (see ASTM standards D3838-8 and D1512). Increasing amounts of powdered sample are added to a stirred suspension of distilled-deionized water, and the pH is measured as a function of carbon/water ratio. The penetration of the liquid into the pores is considered to be essentially complete and the method thus titrates the entire surface of the adsorbent. In contrast, the isoelectric point was determined by electrophoresis, from the electrophoretic mobility vs. pH curves. A Zeta-Meter 3.0+ apparatus was used, with 0.001 M KNO_3 as the supporting (indifferent) electrolyte. Motion of the particles suspended in the electric field was monitored as a function of pH using an optical microscope. The details of the procedure are provided by Leon y Leon [6].

4. Adsorption Breakthrough Experiments

A fixed amount of each coal or carbon sample (ca. 30 g) was loaded into a fixed-bed quartz reactor (22 mm ID). The feed gas contained 3% CO_2 (calibration grade, balance UHP Ar). The CO_2 concentration in the effluent from the reactor was measured by a non-dispersive infrared analyzer (Beckman, Model 864). The column was operated at room temperature (25-30 °C) at varying gas flow rates. Before each experimental run, the sample was thoroughly conditioned by flowing UHP N_2 , at room temperature for the low-rank coals (Beulah and Smith-Roland) and at ca. 100 °C for the other samples. Selected

samples were also used in a competitive adsorption study using the same apparatus. The feed gas contained a mixture of 3% CO₂ and 3% CH₄ (balance UHP Ar).

C. Results and Discussion

1. Surface Physical Properties of the Coals

Figures 1 and 2 summarize the calibration results for the experimental apparatus described in Section B1. As expected, the uptakes and the adsorption heats were higher for CO₂ than for CH₄. This is, of course, necessary for effective CO₂ sequestration in coalbeds. The heats are also in good agreement with the American Petroleum Institute data (see Table 15A1.12) which give values of ca. 16 kJ/mol for CH₄ and ca. 29 kJ/mol for CO₂. The results are moderately sensitive to the conditions of sample preparation: an increase in the outgassing temperature, from 80 to 150 °C, caused a small though inconsistent change in the uptake and very little change in the adsorption heats.

Figures 3 and 4 summarize the results obtained with the Illinois #6 coal. As expected, the uptakes are lower than those on the high-surface-area activated carbon, but the trends are the same: higher uptakes and higher adsorption heats for CO₂ than for CH₄. The effect of the outgassing temperature is important both from a fundamental and a practical point of view: most experimental data available in the literature, which were not obtained with CO₂ sequestration in mind, may have been obtained after inappropriate “sample preparation.” For our purposes, an *in situ* temperature of ca. 40 °C seems the most appropriate. This outgassing temperature was used consistently in the remainder of the study. Furthermore, each measurement was taken using always fresh samples. When coals are exposed to adsorbing species, they can swell to a greater or lesser extent [7-9]

and as a consequence their structure can relax and become weaker; in particular, upon water removal the pores can collapse and no longer be available for adsorbing gases.

The kinetics of adsorption were monitored by continuously measuring the pressure in the samples cell. In Figures 5 and 6 the pressure variations vs. time are shown. The parameter on the y-axis is the unaccomplished pressure change [10] and it is defined as $(P_t - P_f)/(P_0 - P_f)$, with P_0 being the initial pressure, P_f the final pressure and P_t the pressure at time t . The initial decrease is due to both expansion and adsorption. The pressure drop due to expansion is a constant contribution independent of the coal sample used. Thus the differences in pressure profiles are due only to differences in adsorption and diffusion properties of the samples.

In Figure 5 the kinetics of adsorption are reported for the Illinois #6 coal and the Beulah lignite at low pressure, with P_0 being ca. 25 Torr. For both coals it is seen that CH_4 is adsorbed faster than CO_2 . The CH_4 adsorption profile is very similar for both coals and the average ratio between the two profiles in the first 100 s is 0.99, while the same parameter for CO_2 is 0.60. Figure 6 shows the kinetics of adsorption at higher pressure, starting from ca. 300 Torr. Also in this case the adsorption of methane is faster. Moreover, the adsorption at higher pressure is generally faster than at lower pressure.

The adsorption isotherms of CO_2 and CH_4 for three coals are shown in Figures 7-9. The temperatures shown in these figures (313 and 383 K) represent the conditions of outgassing prior to adsorption measurements. Each adsorption isotherm was always recorder at ambient temperature. (In Figure 9 the CO_2 uptake shows a step at about 370 Torr. This is attributed to a temporary experimental error; in fact, previous measurements on the same coal did not show the same trend.) From these data we conclude that

adsorption of both CO₂ and methane on these coals does not depend on the outgassing temperature. One exception may be CO₂ adsorption on Illinois #6 coal, which seems to exhibit some dependence on outgassing temperature; this difference, however, may be within the limits of experimental error. Therefore, a comparison among the uptakes by different coals can be made by taking into account only one outgassing temperature. As mentioned previously, the choice of 313 K is better because this is closer to the temperature at which CO₂ sequestration is expected to occur in a coal mine.

Figure 10 compares the uptakes of CO₂ by the six coals. The lignite adsorbs more CO₂ than the other coals, followed by the subbituminous coal. Bituminous coals slightly increase their capacity for adsorbing CO₂ at increasing rank from high-volatile to low-volatile, even if this trend is not very evident. It is thus concluded that the CO₂ adsorption capacity is not very sensitive to variations in rank for higher-rank coals.

Figure 11 shows the adsorption isotherms of methane on the same six coals. In this case the gas uptake depends only slightly on rank. The Smith-Roland coal adsorbs the greatest amount, followed by the lignite. The bituminous coals adsorb less methane than the lower-rank coals.

A comparison between Figures 10 and 11 shows that all the coals investigated here have higher affinity for CO₂ than for CH₄ and the mean ratio between the CO₂ and CH₄ uptake is 6.3. Table 3 summarizes all these results. The ratio between the amounts of CO₂ and CH₄ adsorbed is calculated at 600 Torr. It is important to note the differences among the six coals; they are mainly due to different amounts of adsorbed CO₂. The ratio of uptakes does not exhibit, however, a clear dependence on coal rank. It is the highest for

the lignite, but in the case of higher-rank coals a clear trend does not exist for this data set.

Figures 12-14 shows the heats of adsorption vs. coverage for the Beulah lignite, the Smith-Roland and the Illinois #6 coal. The lignite shows a steep decrease in the adsorption heat for CO₂ at low coverage (up to 0.1 mmol/g), and then the heat of adsorption remains constant. It starts at ca. 50 kJ/mol in the first region and decreases to ca. 28 kJ/mol, values that are rather high for a purely 'physical' adsorption process. The adsorption heat for methane also shows a decrease at increasing coverage. This trend is not very evident, however, because in this case the measured absolute heats are quite small and almost of the same order as the experimental error. At low coverage the estimated heat is ca. 19 kJ/mol and it decreases to ca. 8 kJ/mol.

The Smith-Roland coal behaves differently, as shown in Figure 9. The heat of adsorption for CO₂ exhibits a gradual decrease in the entire coverage range investigated, starting from 40 kJ/mol to about 20 kJ/mol. The adsorption heat for methane appears to increase slightly with coverage, although a clear trend is not evident, and its value is ca. 20 kJ/mol.

The Illinois #6 coal (Figure 14) shows higher heats of adsorption of CO₂ at lower coverage, starting from ca. 35 kJ/mol to 30 kJ/mol. Also in this case a clear trend for methane adsorption cannot be seen and the average value of the adsorption heat is ca. 24 kJ/mol.

From the results presented above one sees that the outgassing temperature does not have any effect on the value of the adsorption heat, so that in the comparison of the

results for coal of different rank only the experiments performed with an outgassing temperature of 313 K are shown.

Figure 15 presents the comparison of the CO₂ adsorption heats for the six coals. At lower coverage the heat for Beulah lignite appears to be the highest. Above 0.12 mmol/g all the heats reach a value within the same range. In general, the adsorption heat appears to decrease with coverage for all the coals investigated, as expected for a heterogeneous surface. The Pocahontas low-volatile bituminous coal behaves differently, however, the adsorption heat for CO₂ appearing to increase somewhat at higher coverages.

Figure 16 shows that the heats of CH₄ adsorption for the Smith-Roland and Illinois #6 coals are very close in the entire coverage range investigated and these coals have the highest adsorption heat, whereas the lignite has the lowest. Table 4 summarizes the adsorption heats of CO₂ and CH₄ and their ratio for the six coals at 600 Torr.

In all cases it is seen that CO₂ uptake exceeds that of CH₄ by five-fold or more. This can be due to both adsorbate-adsorbate and adsorbate-adsorbent interactions. In an initial attempt to separate the two effects, the adsorption isotherms are reported on a normalized pressure scale. In Figure 17 isotherms for four coals are normalized using the vapor pressure of the adsorbate. For methane, which is at supercritical conditions, the extrapolated vapor pressure is used [11]. It is seen that CH₄ uptakes by all coals fall on the same curve, while the uptakes of CO₂ are much higher than those of CH₄ and also differ from sample to sample. In particular, the lower-rank coals, as expected from knowledge of their surface chemistry (see next section), exhibit higher normalized uptakes. Similar results are obtained in Figure 18, where data normalization is performed

using the critical pressure. It will be interesting to see how sensitive these conclusions are to the choice of the normalization parameter. In the studies of Kaneko and coworkers [12], it has been proposed that a modified version of the Dubinin-Radushkevich equation, involving the use of a quasi-saturated vapor pressure from a Langmuir plot, should be used for supercritical gases. An analysis of one aspect of use of the Dubinin-Radushkevich equation is provided in Section C4.

Another reason for the observed differences in uptake may be related to the size and shape of the two adsorbates. The CO₂ molecule is rod-like and its minimum dimension is 0.28 nm, whereas the CH₄ molecule is spherical with a slightly larger diameter. Therefore, coal can behave as a molecular sieve and methane may be excluded from pores accessible to CO₂. The results presented in Figures 5 and 6 are evidence that this factor should be taken into account.

It is also important to analyze the effect of pretreatment of the coal. As discussed above, the adsorption behavior of both CO₂ and CH₄ was found to be independent of the degassing temperature when fresh samples are used in each experiment. Our previous tests (unpublished results of J. Weigle) using the same coals have shown different results. The effect of degassing temperature was much more significant: less gas was adsorbed after high-temperature outgassing than after low-temperature outgassing. Also the heat released was lower in the second run. To avoid ambiguity, especially as relevant to *in situ* CO₂ sequestration in coal mines, each isotherm should be recorded using always fresh samples.

In the early experiments conducted by J. Weigle we had used the same coal samples for both degassing temperatures and the observed behavior (discussed above)

can be considered to be a combination of two different effects. It is well known that when coals are exposed to sorbates, they can swell to different extents. The geometry of the pores can change and even small differences in the porous structure may cause significant changes in uptakes and in interaction energies between gases and coal [13, 14]. Also a hysteresis phenomenon can occur. Once the gas enters the pores, it may interact strongly with some sites on the coal surface and may not be removed totally after the second degassing. An enhancement of irreversible CO₂ adsorption may be evidence of 'permanent' sequestration.

Among the six coals investigated no clear trend can be seen in the adsorption uptakes and heats with respect to coal rank. The lignite does seem to be the best candidate for CO₂ sequestration because, having the highest adsorption heat, it adsorbs the greatest amount of CO₂. Also, a larger amount of CO₂ can be adsorbed by displacing a given volume of methane; in fact, in this case the ratio of uptakes is the highest and its value is 8.4. Also the CH₄ adsorption heats and isotherms for the lignite show that this coal is well suited for methane recovery. However, it should be kept in mind that the greatest amount of methane in a coal mine is typically generated by medium- and low-volatile bituminous coals [15]. At the other extreme, the highest-rank coal investigated, Pocahontas, had the lowest ratio of uptakes. Moreover, if we consider the entire range of bituminous coals, it is seen that the methane adsorption capacity decreases from Illinois #6 to Stockton-Lewiston and then it increases again at higher rank. This is in agreement with what was found by earlier investigators [11]. It is intriguing to note that the coal surface area has a minimum in the same rank range [16]. The ST coal has a high ratio of

uptakes but the amounts of CO₂ and CH₄ adsorbed are the lowest when compared with the other coals, so this coal cannot be considered as best suited for CO₂ sequestration.

2. Surface Chemical Properties of the Coals

It was surmised from Section C1 that adsorbent surface chemical properties may be as important as, or more than, the surface physical properties in determining the uptake of CO₂. Much of the effort in this project was oriented, therefore, toward a search for the relevant quantifying parameters.

Figures 19-24 show the electrophoretic mobility vs. pH graphs for the six coals from the Argonne premium coal base. For the as-received coals they are seen to be very complex and in some cases extrapolation was necessary to estimate the isoelectric point. Figures 25-27 provide a comparison with a graphite, at one extreme, and with the BPL activated carbon as well as the Dry Fruitland coal at the other extreme. Figures 28-30 show the effect of demineralization of three coals on their electrophoretic mobility vs. pH curves; it is dramatic in the case of the Illinois #6 coal, indicating the importance of inorganics in determining the IEP. Figure 31 shows the results of the determination of the PZC of the coals using mass titration. Figures 32-34 show the effect of coal demineralization on the mass titration curves.

Table 5 summarizes the PZC and IEP parameters for all the samples. As documented in the activated carbon literature [4], there is a consistent discrepancy between the PZC and IEP values in all cases: PZC is larger than IEP, sometimes dramatically so. If the distribution of surface charge were uniform throughout a particle of the adsorbent, the two values should be identical. The fact that they are not tells us the

following: the charge carriers (predominantly the carboxyl groups, either inherently present in coal or created upon coal exposure to ambient air), which give rise to specific adsorbate/adsorbent interactions, are in all cases predominantly concentrated close to the external surface of the particles.

3. Adsorption Dynamics Characteristics of Coal Beds

The CO₂ breakthrough curves for the coals and the BPL carbon at different gas flow rates are shown in Figures 35 to 43 and summarized in Table 6. Generally, a breakthrough curve is defined by three characteristic features: geometric midpoint, steepness, and shape. The midpoint is determined by gas flow rate and concentration and by the capacity of the adsorbent for the gas at the relevant gas concentration and temperature. The steepness is related to the rate at which the gas is adsorbed from the main gas stream as it flows through the bed. If the adsorption rate coefficient is constant throughout this process, the shape of the breakthrough curve will be symmetrical. However, it has often been observed [17] that breakthrough curves are skewed, usually steeper at the beginning of breakthrough than at the end. It is seen that all measured breakthrough curves are not symmetrical, especially at the low flow rates (46.5 or 36.5 cm³/min).

The measured breakthrough times (in seconds), corresponding to the time when CO₂ is first detected at the outlet of the adsorbent bed, are listed in Table 7. A semi-empirical model originally developed by Rosen [18, 19] was used to analyze quantitatively the kinetics of CO₂ adsorption. The key assumptions in the Rosen model are: plug flow, isothermal adsorption, linear isotherm, constant flow velocity, and constant effective diffusivity. The results show that the Rosen model cannot give a good

prediction of the breakthrough curves at low flow rates. This is illustrated in Figures 44 and 45. Much better agreement between experimental and predicted curves was observed for the higher flow rates. The reason for this is thought to be the absence of plug flow at low gas velocities. Use of an alternative model will be necessary to extract meaningful equilibrium and kinetic parameters (adsorption affinity and effective diffusivity) that can be used with confidence in comprehensive CO₂ sequestration models.

Using the breakthrough curves for the Pittsburgh #8 coal as an example, we calculated the amount of adsorbed CO₂ at different flow rates. The results for single-component adsorption are listed in Table 8. In general, a lower flow rate resulted in a larger amount of adsorbed CO₂, which indicates that adsorption equilibrium was not reached under these conditions and that the approach to equilibrium is greater at lower flow rates. Based on the results shown in Table 8, we selected a flow rate of 46.5 cm³/min for comparison of coals' affinities for CO₂ vs. CH₄. When CO₂ was the more strongly adsorbing component in an activated carbon, and CH₄ the more weakly one, experiments showed that CH₄ broke through the carbon bed before CO₂ [20]. Our results for coals and BPL carbon are listed in Table 9. More detailed results for the BPL carbon are provided in Table 10 and Figure 43. It should be noted that the column length-to-diameter ratio (L/D) is a very important parameter. This is the reason why in two cases (Pocahontas and Dry Fruitland) the adsorbed CO₂ amount is even slightly larger in the presence of CH₄ than in the absence of CH₄.

4. On the Adsorption Affinity Coefficient of CO₂ in Microporous Carbons

The popularity and the flexibility of Polanyi's potential theory of adsorption and Dubinin's theory of volume filling of micropores (W , mol/g) stem from the convenient ambiguity regarding their physical significance. The postulated Gaussian (or simplified one-parameter Weibull) distribution function can be interpreted as describing the energetic heterogeneity of the adsorbent surface or reflecting the range of adsorbate/adsorbent interaction potentials (A , kJ/mol) which arises from a distribution of adsorbent's micropore sizes. In practical terms this ambiguity is reduced to variations in the adjustable parameter κ in the Dubinin-Radushkevich (DR) equation for microporous solids, $W = W_0 \exp(-\kappa A^2)$. Over the years, the analysis of this parameter has evolved into the following standard interpretation: $W = W_0 \exp[-(A/(\beta E_0))^2]$, with β (the so called "affinity coefficient" [21]), being taken as a property of the adsorbate and E_0 (the adsorption energy of the standard adsorbate) as a property of the adsorbent.

In an authoritative and thought-provoking study, Stoeckli and Morel [22] attempted to attach physical significance to these parameters. They concluded that the product βE_0 "represents an average excess of adsorption energy of the micropores, with respect to the open graphitic surface," and that β can be "identified, formally at least, with a ratio of adsorption potentials." Indeed, a linear relationship between β and this ratio for 12 adsorbates on a graphitized carbon black gives a correlation coefficient of 0.913, but the implications of these findings and of such analysis have yet to be explored. Furthermore, neither the absolute nor the relative values of the parameter β have been subjected to closer scrutiny in the literature. If it is indeed an "affinity" coefficient, it should be able, for example, to account for the published results [23-25] compiled in

Figure 46. While the high value for benzene ($\beta=1.0$, often taken as the ‘standard’ adsorbate) could be interpreted as a reflection of enhanced adsorbate/adsorbent interactions due to π - π overlap, the other β values remain puzzling. In particular, β_{CO_2} is of interest because adsorption of CO_2 – e.g., in abandoned or inaccessible coal mines [26] – is considered to be a potentially viable carbon sequestration technology [27]. How much greater the affinity of a given coal or carbon surface really is for CO_2 , vs. CH_4 or N_2 , is thus an important fundamental and practical issue. Figure 46 suggests that the often quoted β values – e.g., 0.35 for CO_2 [28], 0.33 for N_2 [29] and 0.35 for CH_4 [28] – lack physical significance. The purpose of this communication is to discuss the following two questions:

- (1) Can $\beta_{\text{CO}_2} = 0.35$ really be considered a “classical” value [28]?
- (2) What is the most ‘appropriate’ value for β_{CO_2} ?

The usefulness of carbon dioxide in characterizing the microporous structure of carbonaceous adsorbents, in conjunction with the DR equation, is by now very well established [30, 31]. It is thus surprising that there exists in the relevant literature some confusion, or at least quite a bit of inconsistency. In his pioneering studies, Dubinin [29, 32] has provided values of β for many adsorbates but not for CO_2 . In a widely cited study, Garrido et al. [30] used the values of 0.33 and 0.35 for N_2 and CO_2 , respectively, and implied that the justification is to be found in the earlier articles by Dubinin [32] and Rodríguez-Reinoso et al. [33]. However, these references do not contain any such information on β_{CO_2} . Dubinin has studied adsorption of CO_2 on the non-microporous silica gel and we have back-calculated values of β from his results. These are summarized in Table 11. It is seen that the value of β is very sensitive to the choice of the

characteristic energy; furthermore, for β to be 0.35 in this case requires that the adsorption energy be much lower than the adsorbate's heat of condensation, which is considered to be unrealistic.

More recently, Cazorla-Amorós and coworkers [34, 35] have also taken the affinity coefficient for CO₂ to be 0.35, “a value similar to that proposed by Dubinin,” again citing Ref. [32] which not only does not contain such a proposal, but does not even mention the adsorption of CO₂ on microporous carbons. In a very recent study, Guillot and Stoeckli [31] noted that the calculated β_{CO_2} for a graphitized carbon black turned out to be 0.46, “somewhat higher than the values of 0.35-0.41 found for microporous carbons.”

Table 12 summarizes much of the relevant information available from the recent literature, most of it from the slopes of DR plots at 273-298 K. The adsorption energies are seen to vary within a factor of two, presumably reflecting some differences in the nature of the adsorbents used. It is reassuring to note, though, that the expected inverse relationship between the average micropore size and E_0 has a reasonably high correlation coefficient ($R^2 > 0.90$). However, the table provides no clues regarding the most ‘appropriate’ value for β_{CO_2} . The range observed (0.33-0.58) translates into an uncertainty of ± 0.3 nm in the calculation of the micropore size from the slope of the DR plot. This may be significant if one keeps in mind that molecular sieving (e.g., for O₂/N₂ separation) often relies on pore size differences that are of the same order of magnitude as this uncertainty.

A value of β_{CO_2} can also be obtained from the very useful compilations and correlations provided by Wood [36]. This information is summarized in Table 3, along

with the results for CH₄ and N₂. Compared to the results in Table 12, here the range of β_{CO_2} values is even wider, from 0.69 when calculated using molar volumes (V_m) to 0.28 when calculated using polarizabilities (P); this corresponds to an uncertainty of ± 0.5 nm in the calculation of the micropore size. (For the often quoted enhanced adsorbed density of 1.04 g/cm³, due to compression effects close to the critical temperature [21], β_{CO_2} turns out to be 0.47.) In a recent analysis, Wu et al. [37] concluded that both the parachor and polarizability gives better β estimates than the molar volume, in agreement with Wood's findings [36]. It is interesting to note from Table 13, however, that the use of polarizability, but not the parachor, gives relative β values that are more consistent with the results shown in Figure 46; this is indeed what one would qualitatively expect if London dispersion forces were dominant in the adsorption process. In a pioneering study, Reucroft and coworkers [38, 39] had reached a similar conclusion in the case of adsorption of 15 organic vapors on BPL carbon, although Duisterwinkel's recommendation was that "the molecular parachor is to be preferred over the molar polarization" [40].

The above analysis highlights the uncertainties regarding the appropriate value of the affinity coefficient, the parameters that define it and the methods used to determine it. Whether or not β is indeed a true *affinity* coefficient or, as Dubinin himself has often called it, simply a "similarity coefficient" [29, 41], and thus essentially an adjustable parameter that depends also on adsorbent surface properties, remains an important issue. And, more generally, a potentially fruitful question is whether the Dubinin-Astakhov equation, $W = W_0 \exp[-(A/(\beta E_0))^n]$, can be reinterpreted as a three-parameter equation in which n and E_0 characterize the porous structure of the adsorbent, whereas β describes

the affinity of the adsorbate for the adsorbent surface and thus reflects the role of surface chemistry as well. In this regard, López-Ramón et al. [42] analyzed the effect of surface oxidation on β values for both alcohols and CO_2 . The latter did not change significantly (as shown in Table 12), but both $\beta_{\text{CH}_3\text{OH}}$ and $\beta_{\text{C}_2\text{H}_5\text{OH}}$ displayed a linear correlation with surface oxygen content, even though the range of values turned out to be significantly narrower than that shown for CO_2 in Tables 12 and 13. Additional evidence that the nature of the adsorbent is an important factor when determining affinity coefficients is available from the study of Oda et al. [43]. Until these issues are resolved, Duisterwinkel's recommendation [40] that there is “no need to perform experiments with benzene as long as an adsorption isotherm is determined for an adsorptive with a well known value of β ” will remain an overly optimistic one. Our analysis has shown that β_{CO_2} cannot be considered a “classical” value; to what extent the chemistry of the adsorbent surface has an influence on gas-or vapor-phase adsorption affinity [44] remains an unresolved question that deserves much more attention than its (too?) often analyzed ‘heterogeneity’ surrogate.

5. Implications for Carbon Dioxide Sequestration

The increasing presence of CO_2 in the atmosphere is now accepted to be one of the principal causes of the greenhouse effect. The CO_2 storage in a coal mine can be a way to solve this problem. In addition, coal mines provide a natural reservoir for atmospheric gases, predominantly methane. The three clear benefits of this elegant solution are that (a) the CO_2 concentration in the atmosphere will be reduced, (b) a valuable gaseous fuel will be recovered, and (c) the hazards of mine explosions will be reduced. The CH_4

extraction from a coalbed can be achieved by lowering the hydrostatic pressure on the coal seam, by displacing it with an inert gas, or injecting a higher-affinity gas such as CO₂ into the seam.

A true fundamental understanding of the phenomena that control these processes has been difficult to achieve, however. In principle, there are two basic types of interaction between an adsorbate such as CO₂ or CH₄ and an adsorbent such as coal: (a) dispersion interactions, due to temporarily induced dipoles (London forces), and (b) electrostatic or coulombic interactions, due to the presence of a permanent concentration of charge (dipoles, quadrupoles, etc.) on the adsorbate and/or the adsorbent. Both the theoretical and the experimental analysis of the former is at a much more advanced level of understanding than that of the latter. In an attempt to remedy this situation, and in an attempt to provide support to the modeling efforts of our colleagues at OSU, our studies were an attempt to provide some answers to the following key questions:

- (1) Why are the adsorption uptakes of different adsorbates (especially CO₂ and CH₄) different on the same adsorbent?
- (2) Why is the adsorption uptake of a given adsorbate (e.g., CO₂) different on different adsorbents?

Both equilibrium and dynamic adsorption experiments were completed for the suite of coals covering a wide range of rank. Significant differences in adsorption potential were documented, but they did not correlate with any of the parameters of the porous structure. Therefore, if CO₂ sequestration (and CH₄ storage in coalbeds) involves only adsorption on pore walls (rather than occlusion or trapping in multiple void spaces), then the inevitable conclusion is that quasi-equilibrated physical adsorption due to

dispersive van der Waals-type interactions does not appear to be the governing mechanism. Because of the differences in the chemistry of the surface among coals of different rank – and between coals, activated carbons and graphite – as well as between CO₂ and CH₄, we began to evaluate the importance of specific interactions. For some coals, the presence of mineral matter (which is not thought to contribute significantly to adsorption) was found to be a complicating factor. Removal of mineral matter by acid treatment led to much more consistent surface chemical parameters, but the characterization of demineralized (as opposed to as-received) coals may distort the effects of the porous structure and the diffusive characteristics of gases in coal.

In summary, we have documented how important some of the chemical properties of the coals are for CO₂ adsorption and that these must be the reason why CO₂ has a higher affinity for the carbon surface than CH₄. These properties vary from coal to coal, being the most prominent in lower-rank coals which showed the highest and most energetic CO₂ uptakes, and they are thought to be responsible for the different CO₂ uptakes on different coals. We have failed, however, in our attempt to identify a set of adsorbent characteristics that can quantify these effects. Further cross-fertilization between coal surface chemistry and adsorption modeling is needed to succeed in this challenging task. Now it is clear, though, that we must identify those adjustable parameters in adsorption models which have the best chance of revealing such correlations. For example, a promising avenue to explore within the framework of the potential theory of adsorption – and this we have begun to do in the final phase of this project – is the conversion of the ‘similarity’ coefficient β to a genuine *affinity* coefficient, which will reflect such specificity of adsorbate/adsorbent interactions.

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Table 1
The selected coal samples

Sample	Seam	ASTM rank	State
DECS-11	Beulah-Zap	Lignite A	ND
DECS-8	Smith-Roland	Subbituminous C	WY
DECS-12	Pittsburgh #8	High-volatile A bituminous	PA
DECS-16	Blind Canyon	High-volatile A bituminous	UT
DECS-24	Illinois #6	High-volatile C bituminous	IL
DECS-32	Stockton-Lewiston	High-volatile A bituminous	WV
DECS-19	Pocahontas	Low-volatile bituminous	VA
DF coal	Dry Fruitland	Bituminous	CO

Table 2a
Selected properties of coal samples

Sample	Ash (dry)	Sulfur (dry)	CV (BTU/lb)	C (dmmf)	H (dmmf)	VM (dmmf)	% Vitrinite	Vitrinite reflectance
Beulah	9.6	0.74	12350	74.1	4.5	61.6	74	0.35
Smith-Roland	13.8	0.73	13148	75.8	5.3	51.8	79	0.37
Pittsburgh #8	10.3	1.12	15259	84.7	5.8	39.4	83	0.87
Blind Canyon	13.9	0.47	14749	82.4	6.0	47.3	77	0.64
Illinois #6	13.4	5.53	14407	80.1	5.6	45.5	90	0.49
Stockton-Lewiston	20.3	0.73	15213	85.4	5.8	38.2	68	0.90
Pocahontas	4.6	0.74	15819	90.6	4.9	18.7	89	1.71

Table 2b
Selected properties of coal samples

Coal	BEU	SR	IL	PTT	SL	PO
Proximate Analysis						
% moisture (as received)	33.38	28.42	7.97	2.40	2.64	1.01
% ash, dry	9.56	13.8	15.5	10.3	20.3	4.60
% volatile matter, daf	62.01	52.49	47.39	40.13	39.61	19.19
% fixed carbon, daf	37.99	47.51	52.61	59.87	60.39	80.81
Ultimate Analysis						
% C, daf	73.14	74.43	77.67	83.32	83.25	89.87
% H, daf	4.46	5.23	5.00	5.69	5.65	4.09
% N, daf	1.00	1.00	1.37	1.37	1.38	1.14
% S, daf	0.82	0.85	5.72	1.25	0.92	0.78
% O, daf (by difference)	20.6	18.5	10.2	8.37	8.81	3.31
N₂ BET surface area, m²/g	1.85	6.20	23.5	2.38	N/A	2.8
CO₂ surface area, m²/g	206	229	132	N/A	N/A	N/A

Table 3

Amounts of CO₂ and CH₄ adsorbed at 600 Torr and their ratio for six coals

Coal	Adsorbed CO2 (mmol/g)	Adsorbed CH4 (mmol/g)	CO2/CH4 ratio (mol/mol)
Beulah	0.646	0.077	8.4
Smith-Roland	0.558	0.096	5.8
Illinois #6	0.348	0.068	5.1
Pittsburgh #8	0.303	0.049	6.2
Stockton-Lewiston	0.245	0.034	7.2
Pocahontas	0.336	0.068	4.9

Table 4

Heats of CO₂ and CH₄ adsorption at 600 Torr and their ratio for six coals

Coal	Adsorbed CO₂ (kJ/mol)	Adsorbed CH₄ (kJ/mol)	Ratio (kJ/kJ)
Beulah	28	8	3.5
Smith-Roland	26	24	1.1
Illinois #6	27	17	1.6
Pittsburgh #8	25	18	1.4
Stockton-Lewiston	13	14	0.9
Pocahontas	29	23	1.3

Table 5

Summary of isoelectric points (IEP) and the points of zero charge (PZC)
for selected samples

Sample	IEP	PZC
Beulah	1.8	6.4
Smith-Roland	1.0	5.4
Pittsburgh #8	3.7	7.7
Illinois #6	N/A	4.1
Blind Canyon	1.4	8.5
Stockton-Lewiston	1.8	8.4
Pocahontas	3.5	8.3
Dry Fruitland	4.9	9.4
Intermediate Fruitland	1.2	9.4
BPL activated carbon	5.0	7.8
Graphite	N/A	8.3

Table 6

Measured breakthrough times for CO₂ in coals and BPL activated carbon
(single-component adsorption)

Flow rate (cm³/min)	143	107	72.0	46.5	36.5
Sample	Breakthrough time (s)				
Beulah	45	82	130	226	291
Smith-Roland	74	111	174	273	372
Pittsburgh #8	130	234	388	782	960
Blind Canyon	135	216	417	663	892
Illinois #6	108	157	265	-	625
Stockton-Lewiston	122	212	370	601	912
Pocahontas	152	259	457	672	931
Dry Fruitland	406	-	-	1244	1486
BPL activated carbon	600	950	1300	-	-

Table 7
Measured breakthrough times for CO₂ in coals
(binary adsorption)

Flow rate (cm³/min)	143	107	72.0	46.5	36.5
Sample	Breakthrough time (s)				
Beulah	44	88	142	227	304
Smith-Roland	70	110	167	261	330
Pittsburgh #8	116	160	294	557	812
Blind Canyon	120	172	382	632	694
Illinois #6	80	128	204	360	490
Stockton-Lewiston	104	168	276	578	816
Pocahontas	157	-	430	870	1043
Dry Fruitland	612	-	1198	1620	2102

Table 8

Amounts of CO₂ adsorbed by Pittsburgh #8 coal at different flow rates

	Adsorbed CO ₂ (mg/g coal)					
Gas flow rate (cm ³ /min)	143	107	72.0	46.5	36.5	Mass (g)
3% CO ₂ + Ar	0.496	0.670	0.745	0.968	0.932	36.836
3% CO ₂ + 3% CH ₄ + Ar	0.442	0.458	0.564	0.690	0.789	36.421

Table 9Amounts of CO₂ adsorbed by the coals and BPL activated carbon(flow rate = 46.5 cm³/min)

Sample	3% CO₂	3% CO₂ + 3% CH₄
Beulah	0.288	0.285
Smith-Roland	0.328	0.302
Pittsburgh #8	0.970	0.698
Blind Canyon	0.934	0.813
Illinois #6	0.991	0.727
Stockton-Lewiston	0.729	0.685
Pocahontas	0.824	0.948
Dry Fruitland	2.100	2.369
BPL activated carbon	4.837	3.750

Table 10

Amount of CO₂ adsorbed by BPL activated carbon
(L/D = 4.95, 20.175 g; see Figure 43 for breakthrough curves)

Gas flow rate (cm ³ /min)	72.0	46.5
Gas composition	Adsorbed CO ₂ (mg/g)	
3% CO ₂	4.837	7.094
3% CO ₂ + 3% CH ₄	3.750	6.625

Table 11

Calculation of affinity coefficient for CO₂ (β_{CO_2}) from Dubinin (Ref. 21)^a using the characteristic equation for adsorbents “of the second structural type”

Comment	Characteristic energy E_0 (kJ/mol)	β_{CO_2}
Heat of condensation of benzene (298 K) ^b	33.9	0.13
E_0 for benzene on silica gel ^c	4.5	1.01
Characteristic energy for “classical” value ^d	13.0	0.35

^aThe calculated slope from Fig. 9 in Ref. 21 is ca. 4.1×10^{-4} mol/cal or 0.098 mol/kJ.

^bCalculated from heat of vaporization values in “Perry’s Chemical Engineers’ Handbook,” 7th Ed. (Table 2-193).

^cCalculated from Fig. 4 in Tamon et al., *J Chem Eng Jpn* 1997, 30, 735-741.

^dFrom Ref. 28.

Table 12
Experimental values of “affinity coefficient” β for CO₂

Adsorbent	E ₀ kJ/mol	β_{CO_2}	Micropore size, nm (experimental)	Micropore size, nm (calculated) ^c	Reference
MSC-5A carbon molecular sieve (Takeda Chem. Ind.)	28.9	0.39 ^a	0.5	0.90	T1
D-19 activated carbon	29.5 ^a	0.35		0.88	30
D-52	25.6 ^a	0.35		1.02	
D-80	22.9 ^a	0.35		1.14	
CMS	26.2	0.44	0.75	0.99	T2
U-03 activated carbon	17.2	0.44	1.8	1.51	
TB#5500 carbon black (Tokai Carbon)	18.3	0.47		1.42	T3
AC-720 activated carbon	22.8 ^a	0.48	0.98 ^a	1.14	T4
AC-735	22.4 ^a	0.48	1.04 ^a	1.16	
AC-750	21.8 ^a	0.48	1.06 ^a	1.19	
AC-770	21.3 ^a	0.48	1.14 ^a	1.22	
AC-780	20.5 ^a	0.48	1.16 ^a	1.27	
CFC14 activated carbon fibers	29.4	0.35		0.88	34
CFC40	23.0	0.35		1.13	
CFC50	24.3	0.35		0.83	
CAL activated carbon (Calgon Carbon Corp.)	18.2	0.58 ^b	0.8	1.43	T5
CMS II (Bergbau)	25.0	0.37	0.97	1.04	T6
F30-470	23.6	0.37	1.06	1.10	
Reactivated	18.0	0.37	1.44	1.44	
BPL 410	20.0	0.37	1.22	1.30	
WS 42	20.4	0.37	1.26	1.27	
Centaur HSV (Chemviron)	21.3	0.37	1.16	1.22	
CM activated carbon	26.2	0.35	0.75	0.99	28
KF-1500 activated carbon fibers	18.2	0.35	1.6	1.43	

Table 12
(continued)

AZ46-0 activated carbon	22.6	0.41		1.15	42
AZ46-3	23.5	0.40		1.11	
AZ46-5	23.9	0.38		1.09	
AZ46-24	24.7	0.38		1.05	
U-03	17.7	0.41		1.47	
XC-72 carbon black	22.4	0.38	0.96	1.16	31
U-103 activated carbon	20.7	0.37	1.15	1.26	
KF-1500 ACF	19.1	0.33	1.38	1.36	
CMS	28.0	0.33		0.93	
AGB activated carbon	14.3	0.40		1.82	
XC72-16 activated carbon black	21.3	0.35		1.22	T7
CAF-B activated carbon	28.3	0.36		0.92	
BPL activated carbon	28.2	0.35		0.92	This study
(Calgon Carbon Corp.)	35.4 ^d	0.28		0.73	
	14.4 ^d	0.69		1.81	

^aCalculated for this study from data provided in the references cited

^bCalculated using $k = (1/\beta E_0)^2$

^cCalculated as $2k/E_0$ ($k = 13$ kJ/mol), from Ref. T8

^dUsing the range of values suggested from analysis of Table 13

T1. Kawazoe et al., J Chem Eng Jpn 1974, 7, 158-162

T2. Stoeckli et al., Chimia 1993, 47, 213-214

T3. Ehrburger-Dolle, Langmuir 1994, 10, 2052-2055

T4. Parra et al., Carbon 1995, 33, 801-807

T5. Tamon et al., J Chem Eng Jpn 1997, 30, 735-741

T6. Frère et al., J Porous Mater 1998, 5, 275-287

T7. Stoeckli et al., Carbon 2002, 40, 211-215

T8. Dubinin and Stoeckli, J Colloid Interf Sci 1980, 75, 34-42

Table 13
Calculated values of affinity coefficient for CO₂, CH₄ and N₂

Equation	Relevant Data			
		β_{CO_2}	β_{CH_4}	β_{N_2}
$\beta = V_m/V_{m,\text{ref}}$	$V_{m,\text{CO}_2}(273 \text{ K}) = 47.5^{\text{a}}$	0.53	-- ^d	0.39
(V_m = molar volume)	$V_{m,\text{CO}_2}(298 \text{ K}) = 61.5^{\text{a}}$	0.69		
	$V_{m,\text{N}_2}(77 \text{ K}) = 34.6^{\text{a}}$			
	$V_{m,\text{benzene}}(298 \text{ K}) = 89.5^{\text{a}}$			
$\beta = P_e/P_{e,\text{ref}}$	$P_{e,\text{CO}_2} = 7.34^{\text{b}}$, $P_{e,\text{CH}_4} = 6.54^{\text{b}}$	0.28	0.25	0.17
(P_e = polarizability)	$P_{e,\text{N}_2} = 4.39^{\text{b}}$, $P_{e,\text{benz}} = 26.3^{\text{b}}$			
$\beta = \Omega/\Omega_{\text{ref}}$	$\Omega_{\text{CO}_2}(273 \text{ K}) = 68.6^{\text{c}}$, $\Omega_{\text{CH}_4} = 73.8^{\text{c}}$	0.33	0.36	0.29
(Ω = parachor)	$\Omega_{\text{N}_2} = 59.9^{\text{c}}$, $\Omega_{\text{benz}} = 206.2^{\text{c}}$	0.26		
	$\Omega_{\text{CO}_2}(298 \text{ K}) = 53.7^{\text{c}}$			
$\beta = aX^m$	$X = P_e$, $a=0.0381$, $m=1.0$	0.28	0.25	0.17
(see Ref. 36)	$X = P_e$, $a=0.0528$, $m=0.9$	0.32	0.29	0.20
	$X = P_e$, $a=0.0862$, $m=0.75$	0.38	0.35	0.26
	$X = \Omega$, $a=0.00485$, $m=1.00$	0.33	0.36	0.29
	$X = \Omega$, $a=0.00827$, $m=0.90$	0.37	0.40	0.33

^a From "Perry's Chemical Engineers' Handbook," 7th Ed. (Table 2-30), in m³/kmol

^b From Ref. 36

^c Using surface tension data from Jasper, *J. Phys. Chem. Ref. Data*, 1972, p. 1

^d Methane isotherms are typically obtained above the critical temperature

Figure 1
Gas adsorption on BPL activated carbon.

Figure 2
Heats of adsorption on BPL activated carbon.

Figure 3
Gas adsorption on Illinois #6 coal.

Figure 4
Heats of adsorption on Illinois #6 coal.

Figure 5
Pressure drop vs. time at ca. 25 Torr for Beulah lignite and Illinois #6 coal.

Figure 6
Pressure drop vs. time at ca. 300 Torr for Beulah lignite and Illinois #6 coal.

Figure 7
Adsorption isotherms of CO₂ and CH₄ for Beulah lignite.

Figure 8
Adsorption isotherms of CO₂ and CH₄ for Smith-Roland coal.

Figure 9
Adsorption isotherms of CO₂ and CH₄ for Illinois#6 coal.

Figure 10
Comparison of uptakes of CO₂ for the six Argonne Premium coals.

Figure 11
Comparison of uptakes of CH₄ for the six Argonne Premium coals.

Figure 12
Adsorption heats vs. coverage for Beulah lignite.

Figure 13
Adsorption heats vs. coverage for Smith-Roland coal.

Figure 14
Adsorption heats vs. coverage for Illinois #6 coal.

Figure 15
Comparison of CO₂ adsorption heats for the six Argonne Premium coals.

Figure 16
Comparison of CH₄ adsorption heats for the six Argonne Premium coals.

Figure 17

Normalized CO₂ and CH₄ adsorption isotherms for selected coals using vapor pressure.

Figure 18
Normalized CO₂ and CH₄ adsorption isotherms for selected coals using critical pressure.

Figure 19
Electrophoretic mobility vs. pH for the Beulah lignite.

Figure 20
Electrophoretic mobility vs. pH for the Smith-Roland coal.

Figure 21
Electrophoretic mobility vs. pH for the Illinois #6 coal.

Figure 22
Electrophoretic mobility vs. pH for the Pittsburgh #8 coal.

Figure 23
Electrophoretic mobility vs. pH for the Stockton-Lewiston coal.

Figure 24
Electrophoretic mobility vs. pH for the Pocahontas coal.

Figure 25
Electrophoretic mobility vs. pH for the Dry Fruitland coal.

Figure 26
Electrophoretic mobility vs. pH for the BPL activated carbon.

Figure 27
Electrophoretic mobility vs. pH for graphite.

Figure 28

Effect of removal of mineral matter on the electrophoretic mobility vs. pH curve for the Beulah lignite.

Figure 29

Effect of removal of mineral matter on the electrophoretic mobility vs. pH curve for the Illinois #6 coal.

Figure 30

Effect of removal of mineral matter on the electrophoretic mobility vs. pH curve for the Pocahontas coal.

Figure 31
 Summary of mass titration results for the coals and carbons (see Table 5).

Figure 32
Effect of mineral matter removal on the mass titration curve for the Beulah coal.

Figure 33
Effect of mineral matter removal on the mass titration curve for the Illinois #6 coal.

Figure 34
Effect of mineral matter removal on the mass titration curve for the Pocahontas coal.

Figure 35
CO₂ breakthrough curves for the Beulah lignite at different flow rates in cm³/min (L/D = 6.68, 36.361 g)
(a) 143 (b) 107 (c) 72.0 (d) 46.5 (e) 36.5

Figure 36
 CO₂ breakthrough curves for the Smith-Roland coal at different flow rates in cm³/min (L/D = 6.82, 39.419 g)
 (a) 143 (b) 107 (c) 72.0 (d) 46.5 (e) 36.5

Figure 37
CO₂ breakthrough curves for the Illinois \$6 coal at different flow rates in cm³/min (L/D = 3.82, 22.62 g)
(a) 143 (b) 107 (c) 72.0 (d) 46.5 (e) 36.5

Figure 38
 CO₂ breakthrough curves for the Pittsburgh \$8 coal at different flow rates in cm³/min (L/D = 6.00, 36.421 g)
 (a) 143 (b) 107 (c) 72.0 (d) 46.5 (e) 36.5

Figure 39
CO₂ breakthrough curves for the Blind Canyon high-volatile bituminous coal at different flow rates in
cm³/min (L/D = 5.68, 35.499 g)
(a) 143 (b) 107 (c) 72.0 (d) 46.5 (e) 36.5

Figure 40

CO₂ breakthrough curves for the Stockton-Lewiston coal at different flow rates in cm³/min (L/D = 6.20, 38.543 g)

(a) 143 (b) 107 (c) 72.0 (d) 46.5 (e) 36.5

Figure 41
CO₂ breakthrough curves for the Pocahontas coal at different flow rates in cm³/min (L/D = 7.27, 41.903 g)
(a) 143 (b) 107 (c) 72.0 (d) 46.5 (e) 36.5

Figure 42
CO₂ breakthrough curves for the Dry Fruitland coal at different flow rates in cm³/min
(L/D = 5.95, 31.234 g)
(a) 143 (b) 72.0 (c) 46.5 (d) 36.5

Figure 43

CO₂ breakthrough curves for BPL activated carbon at different flow rates in the presence and absence of CH₄

(3% CO₂, 3% CH₄, balance Ar; L/D = 4.95, 20.175 g)

(a) 72.0 cm³/min, 3% CO₂ + 3% CH₄ (b) 72.0 cm³/min, 3% CO₂

(c) 46.5 cm³/min, 3% CO₂ + 3% CH₄ (d) 46.5 cm³/min, 3% CO₂

Figure 44
CO₂ Breakthrough curves for the Pittsburgh #8 coal predicted by the Rosen model (3% CO₂)
(see Figure 38)

Figure 45
CO₂ Breakthrough curves for the Pittsburgh #8 coal predicted by the Rosen model (3% CO₂ + 3% CH₄)

Figure 46
Low relative pressure adsorption isotherms for several adsorbates on BPL activated carbon

K. Detailed Documentation of Results

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OSU Adsorption Database

Table 1 documents the OSU CBM gas adsorption database. The database contains the pure, binary, and ternary mixture adsorption measurements conducted at Oklahoma State University. Included in the database are details regarding the adsorbates, the adsorbent, and the corresponding temperature and pressure ranges for each system.

Pure-gas adsorption measurements are reported for methane, nitrogen, ethane, and carbon dioxide on **ten** solid matrices comprised of wet Fruitland coal (OSU #1 and OSU #2), wet Lower Basin Fruitland coal (OSU #3), wet / dry Illinois #6 coal, wet Tiffany coal, dry Beulah Zap coal, dry Wyodak coal, dry Upper Freeport coal, dry Pocahontas coal, and dry activated carbon.

Binary adsorption measurements are presented for mixtures of methane, nitrogen and CO₂ at a series of compositions on **four** different matrices: Fruitland coal, Illinois #6 coal, Tiffany coal, and activated carbon. Ternary measurements are also presented for methane/nitrogen/CO₂ mixtures on wet, mixed Tiffany coal and on dry activated carbon.

Tables 2 through 4 present the compositional analyses for the various solid matrices considered. The activated carbon used was Filtrasorb 400, 12x40 mesh, from Calgon Carbon company. The activated carbon was dried under vacuum at 431.5 K for two days before the adsorption measurements. The nitrogen BET surface area at 77 K has been reported by Humayun and Tomasko (2000) to be 850 m²/g. The surface area value provided by the supplier, however, is 998 m²/g.

Four different wet coals were prepared for adsorption measurements. The Fruitland coal is from the San Juan Basin; it is a medium volatile bituminous coal. This recently prepared sample (OSU #2) has a slightly different composition from the one used in previous measurements (OSU #1). The Lower Basin (LB) Fruitland coal is from the same coalbed seam as Fruitland coal, but it was taken from a different location. The Illinois #6 coal is a high volatile bituminous coal. Other coal samples are from BP Amoco Tiffany Injection Wells #1 and #10. The coal samples were ground to 200µm particles and moistened with water. This made the sample moisture content vary from 4 to 15% (by weight), which is higher than the equilibrium moisture content. Equilibrium moisture content was determined gravimetrically by exposing dry coal to 303.1 K air at 96-99% saturation.

In addition, five types of coal samples prepared by Argonne National Laboratory were used to study CO₂ adsorption on dry coals. The coals were dried under vacuum in an equilibrium cell at 353 K for 36 hours before being used in the adsorption measurements.

Tables 5 through 100 present the **OSU Database** for the gas adsorption measurements conducted at OSU. The data are presented in terms of both Gibbs

and absolute adsorption since absolute adsorption is the quantity most familiar to practitioners in CBM operations. Also for convenience, the data are reported both in SI and English engineering units.

The database includes the expected experimental uncertainties for the adsorption measurements. The expected experimental uncertainty of the pure-gas adsorption data is about 3%. However, the expected uncertainties in the amount adsorbed for the mixture data vary with pressure and composition. In general, average uncertainties are below 5% for total adsorption; while, the individual-component uncertainties vary from 0.02 to 0.4 mmol/g depending on the mixture composition. Moreover, the expected uncertainties in the amount of individual-component adsorption are significantly higher for the less-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20/80 nitrogen/CO₂ system).

Table 1. OSU Adsorption Database

System No.	Adsorbent	Adsorbate	Temp. (K)	Pressure Range (MPa)
1	Dry AC – F 400	N ₂	318 & 328	0.7 – 13.7
2	Dry AC – F 400	CH ₄	318 & 328	0.7 – 13.7
3	Dry AC – F 400	CO ₂	318 & 328	0.7 – 13.7
4	Dry AC – F 400	C ₂ H ₆	318	0.7 – 13.7
5	Dry AC – F 400	N ₂ +CH ₄	318	0.7 – 12.4
6	Dry AC – F 400	CH ₄ + CO ₂	318	0.7 – 12.4
7	Dry AC – F 400	N ₂ + CO ₂	318	0.7 – 12.4
8	Dry AC – F 400	N ₂ +CH ₄ + CO ₂	318	0.7 – 12.4
9	Wet Fruitland Coal	N ₂	319	0.7 – 12.4
10	Wet Fruitland Coal	CH ₄	319	0.7 – 12.4
11	Wet Fruitland Coal	CO ₂	319	0.7 – 12.4
12	Wet Fruitland Coal	N ₂ +CH ₄	319	0.7 – 12.4
13	Wet Fruitland Coal	CH ₄ + CO ₂	319	0.7 – 12.4
14	Wet Fruitland Coal	N ₂ + CO ₂	319	0.7 – 12.4
15	Wet Illinois #6 Coal	N ₂	319	0.7 – 12.4
16	Wet Illinois #6 Coal	CH ₄	319	0.7 – 12.4
17	Wet Illinois #6 Coal	CO ₂	319	0.7 – 12.4
18	Wet Illinois #6 Coal	N ₂ +CH ₄	319	0.7 – 12.4
19	Wet Illinois #6 Coal	CH ₄ + CO ₂	319	0.7 – 12.4
20	Wet Illinois #6 Coal	N ₂ + CO ₂	319	0.7 – 12.4
21	Wet Tiffany Coal	N ₂	328	0.7 – 13.7
22	Wet Tiffany Coal	CH ₄	328	0.7 – 13.7
23	Wet Tiffany Coal	CO ₂	328	0.7 – 13.7
24	Wet Tiffany Coal	N ₂ +CH ₄	328	0.7 – 13.7
25	Wet Tiffany Coal	CH ₄ + CO ₂	328	0.7 – 13.7
26	Wet Tiffany Coal	N ₂ + CO ₂	328	0.7 – 13.7
27	Wet Tiffany Coal	N ₂ +CH ₄ + CO ₂	328	0.7 – 13.7
28	Wet LB Fruitland Coal	N ₂	319	0.7 – 12.4
29	Wet LB Fruitland Coal	CH ₄	319	0.7 – 12.4
30	Wet LB Fruitland Coal	CO ₂	319	0.7 – 12.4
31	Dry Illinois #6 Coal	CO ₂	328	0.7 – 13.7
32	Dry Beulah Zap Coal	CO ₂	328	0.7 – 13.7
33	Dry Wyodak Coal	CO ₂	328	0.7 – 13.7
34	Dry Upper Freeport Coal	CO ₂	328	0.7 – 13.7
35	Dry Pocahontas Coal	CO ₂	328	0.7 – 13.7

Table 2. Compositional Analysis of Solid Matrices Used in This Study

Analysis*	Activated Carbon	Fruitland Amoco	Fruitland OSU #1	Fruitland OSU #2	Illinois-6	Lower Basin Fruitland OSU #3a	Lower Basin Fruitland OSU #3b	Tiffany Well #1	Tiffany Well #10
Ultimate									
Carbon %	88.65	68.56	68.63	66.58	71.47	38.92	40.20	47.78	56.75
Hydrogen %	0.74	5.74	4.27	4.23	5.13	3.08	3.10	2.62	2.77
Oxygen %	3.01	7.19	0.89	5.08	9.85	3.75	2.87	6.19	5.16
Nitrogen %	0.40	1.40	1.57	1.47	1.46	0.87	0.89	0.92	1.02
Sulfur %	0.73	0.65	4.19	0.72	1.27	1.73	2.14	0.57	0.52
Ash %	6.46	16.45	20.45	21.92	10.81	51.66	50.81	49.71	47.74
Proximate									
Vol. Matter %	3.68	19.12	20.2	20.33	30.61	20.01	14.00	15.48	15.35
Fixed Carbon %	89.86	64.42	59.35	57.75	55.90	28.33	35.19	34.82	36.91

* Huffman Laboratories, Inc., Golden, Colorado.

Table 3. Compositional Analysis of Coals Used in the DOE-NETL Round Robin Study

Analysis*	Beulah Zap	Wyodak	Illinois-6	Upper Freeport	Pocahontas
Ultimate					
Carbon %	72.9	75.0	77.7	85.5	91.1
Hydrogen %	4.83	5.35	5.00	4.70	4.44
Oxygen %	20.3	18.0	13.5	7.5	2.5
Sulfur %	0.80	0.63	4.83	2.32	0.66
Ash %	9.7	8.8	15.5	13.2	4.8
Proximate					
Moisture %	32.2	28.1	8.0	1.1	0.7
Vol. Matter %	30.5	32.2	36.9	27.1	18.5
Fixed Carbon %	30.7	33.0	40.9	58.7	76.1
Ash %	6.6	6.3	14.3	13.0	4.7

* Analyses were provided by the Argonne National Laboratory

Table 4. Analysis of BPL Activated Carbon Used in This Study

Analysis	Units	Value	Lower Limit	Upper Limit
Abrasion Number		87	75	-
Apparent Density	g/cc	0.53	0.44	-
Ash	%	7	-	9
Effective Size	mm	0.64	0.55	0.75
Iodine Number	mg/g	1046	1000	-
US Sieve Series on 12	%	1	-	5
US Sieve Series –40 Mesh	%	1	-	4
Fixed Carbon		1.7	-	1.9

Table 5. Nitrogen Adsorption on Dry Activated Carbon at 318.2 K (System 1, Run 1)**SI Units**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001003
Pump pressure (MPa)	6.9
Pump T (K)	307.8
Adsorbent mass (g)	47.1
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.69	0.996	1.006	0.056	0.057
1.73	1.741	1.786	0.055	0.057
2.86	2.225	2.322	0.055	0.057
4.10	2.566	2.729	0.054	0.058
5.53	2.823	3.070	0.054	0.059
6.97	2.990	3.326	0.054	0.060
8.31	3.086	3.508	0.055	0.062
9.66	3.155	3.664	0.055	0.064
11.10	3.199	3.804	0.056	0.067
12.46	3.199	3.889	0.057	0.069
13.66	3.197	3.965	0.058	0.072

English Engineering Units

Cell T (°F)	113.1
Moisture content (%)	0.0
Void volume (ft ³)	0.003542
Pump pressure (psia)	997.4
Pump T (°F)	94.4
Adsorbent mass (lb)	0.1038

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
100.7	755.7	763.5	42.7	43.2
250.9	1321.7	1355.9	42.0	43.1
415.4	1688.4	1762.1	41.5	43.3
594.9	1947.5	2071.3	41.2	43.8
801.9	2142.4	2329.9	41.0	44.6
1011.0	2269.3	2524.6	41.2	45.8
1204.6	2342.6	2662.4	41.5	47.1
1401.0	2394.4	2781.3	41.9	48.7
1609.6	2427.9	2886.9	42.6	50.6
1807.8	2427.8	2952.1	43.3	52.7
1981.2	2426.7	3009.2	44.1	54.7

Table 6. Nitrogen Adsorption on Dry Activated Carbon at 318.2 K (System 1, Run 2)**SI Units**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001003
Pump pressure (MPa)	6.9
Pump T (K)	307.8
Adsorbent mass (g)	47.1
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.89	1.190	1.206	0.022	0.022
1.81	1.796	1.844	0.022	0.022
2.80	2.217	2.311	0.022	0.023
4.19	2.600	2.769	0.023	0.024
5.56	2.841	3.091	0.024	0.026
6.96	3.005	3.343	0.026	0.029
8.29	3.105	3.528	0.028	0.032
9.70	3.173	3.689	0.030	0.035
11.19	3.214	3.828	0.033	0.039
12.45	3.229	3.925	0.035	0.043
13.65	3.235	4.011	0.037	0.046

English Engineering Units

Cell T (°F)	113.1
Moisture content (%)	0.0
Void volume (ft ³)	0.003542
Pump pressure (psia)	997.4
Pump T (°F)	94.4
Adsorbent mass (lb)	0.1038

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
129.7	903.0	915.0	16.5	16.7
262.5	1362.8	1399.8	16.4	16.8
405.8	1682.4	1754.0	16.6	17.3
607.3	1973.4	2101.7	17.3	18.4
806.7	2156.1	2345.9	18.3	19.9
1009.5	2280.8	2537.0	19.6	21.9
1202.4	2356.9	2678.0	21.1	24.0
1407.5	2408.4	2799.6	22.9	26.6
1623.4	2439.3	2905.1	24.8	29.6
1806.3	2450.6	2979.3	26.5	32.3
1979.7	2455.4	3044.4	28.2	35.0

Table 7. Nitrogen Adsorption on Dry Activated Carbon at 327.6 K (System 1)**SI Units**

Cell T (K)	327.6
Moisture content (%)	0.0
Void volume (m ³)	0.0000959
Pump pressure (MPa)	6.87
Pump T (K)	312.8
Adsorbent mass (g)	51.0
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.61	0.776	0.783	0.011	0.011
1.54	1.443	1.476	0.015	0.016
2.85	2.008	2.093	0.021	0.022
4.27	2.395	2.549	0.027	0.029
5.57	2.651	2.878	0.032	0.035
6.98	2.844	3.154	0.038	0.042
8.37	2.981	3.378	0.043	0.048
9.69	3.082	3.564	0.047	0.055
11.08	3.158	3.733	0.052	0.062
12.61	3.226	3.906	0.057	0.069

English Engineering Units

Cell T (°F)	130.0
Moisture content (%)	0.0
Void volume (ft ³)	0.003386
Pump pressure (psia)	996.4
Pump T (°F)	103.4
Adsorbent mass (lb)	0.1124

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
88.9	589.2	594.4	8.4	8.5
223.8	1095.4	1119.9	11.7	12.0
413.4	1524.4	1588.6	16.2	16.9
619.2	1817.9	1934.8	20.7	22.0
808.1	2012.2	2184.1	24.6	26.7
1012.5	2158.9	2394.3	28.6	31.7
1214.4	2262.9	2564.0	32.4	36.7
1404.8	2339.5	2705.4	35.9	41.6
1607.5	2397.1	2833.3	39.6	46.8
1828.8	2448.5	2964.3	43.6	52.7

Table 8. Methane Adsorption on Dry Activated Carbon at 318.2 K (System 2, Run 1)**SI Units**

Cell T (K)	318.1
Moisture content (%)	0.0
Void volume (m ³)	0.0001003
Pump pressure (MPa)	7.2
Pump T (K)	307.8
Adsorbent mass (g)	47.1
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.59	1.977	1.996	0.068	0.069
1.33	2.865	2.929	0.067	0.069
2.49	3.549	3.703	0.066	0.069
3.55	3.891	4.140	0.066	0.070
4.76	4.115	4.483	0.066	0.071
6.25	4.260	4.784	0.066	0.074
7.66	4.294	4.974	0.066	0.076
8.99	4.288	5.119	0.066	0.079
10.36	4.250	5.243	0.067	0.083
11.85	4.165	5.333	0.052	0.066
13.21	4.079	5.409	0.054	0.072

English Engineering Units

Cell T (°F)	113.0
Moisture content (%)	0.0
Void volume (ft ³)	0.003542
Pump pressure (psia)	1047.3
Pump T (°F)	94.4
Adsorbent mass (lb)	0.1038

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
85.0	1500.4	1514.9	51.9	52.4
192.9	2174.6	2223.2	51.1	52.3
361.4	2693.8	2810.9	50.5	52.6
514.7	2953.4	3142.5	50.1	53.3
689.7	3123.6	3402.2	49.8	54.3
906.2	3233.1	3631.0	49.8	55.9
1111.1	3259.4	3774.9	50.0	57.9
1303.6	3254.5	3885.4	50.4	60.1
1503.3	3225.5	3979.8	51.0	62.9
1718.6	3161.5	4047.8	39.4	50.5
1916.0	3096.1	4105.5	41.2	54.6

Table 9. Methane Adsorption on Dry Activated Carbon at 318.2 K (System 2, Run 2)**SI Units**

Cell T (K)	318.1
Moisture content (%)	0.0
Void volume (m ³)	0.0001003
Pump pressure (MPa)	7.2
Pump T (K)	307.8
Adsorbent mass (g)	47.1
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.55	1.872	1.889	0.068	0.068
1.23	2.764	2.822	0.067	0.068
2.55	3.589	3.749	0.066	0.069
3.48	3.894	4.138	0.065	0.069
4.80	4.149	4.523	0.065	0.071
6.18	4.286	4.807	0.065	0.073
7.64	4.343	5.027	0.065	0.075
9.03	4.341	5.187	0.066	0.078
10.37	4.289	5.293	0.066	0.082
11.76	4.213	5.382	0.068	0.086
13.25	4.110	5.456	0.069	0.092

English Engineering Units

Cell T (°F)	113.0
Moisture content (%)	0.0
Void volume (ft ³)	0.003542
Pump pressure (psia)	1047.3
Pump T (°F)	94.4
Adsorbent mass (lb)	0.1038

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
80.1	1421.0	1433.9	51.3	51.8
179.0	2098.1	2141.5	50.6	51.6
370.1	2724.3	2845.8	49.8	52.0
505.2	2955.6	3140.9	49.5	52.6
696.3	3148.7	3432.7	49.2	53.6
896.0	3253.4	3648.4	49.1	55.1
1107.5	3296.1	3815.3	49.4	57.1
1309.7	3294.5	3937.0	49.8	59.5
1504.3	3255.5	4017.4	50.5	62.3
1705.7	3197.8	4085.1	51.3	65.6
1921.7	3119.7	4141.0	52.5	69.7

Table 10. Methane Adsorption on Dry Activated Carbon at 327.6 K (System 2)**SI Units**

Cell T (K)	327.6
Moisture content (%)	0.0
Void volume (m ³)	0.0000959
Pump pressure (MPa)	6.87
Pump T (K)	313.2
Adsorbent mass (g)	51.0
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.59	1.361	1.373	0.012	0.012
1.26	2.052	2.094	0.017	0.018
2.59	2.753	2.874	0.025	0.026
4.26	3.198	3.440	0.032	0.035
5.67	3.361	3.715	0.038	0.042
6.92	3.446	3.907	0.043	0.049
8.29	3.528	4.117	0.049	0.057
9.74	3.546	4.271	0.055	0.066
11.05	3.548	4.404	0.061	0.075
13.49	3.556	4.680	0.071	0.094

English Engineering Units

Cell T (°F)	130.0
Moisture content (%)	0.0
Void volume (ft ³)	0.003386
Pump pressure (psia)	996.6
Pump T (°F)	104.0
Adsorbent mass (lb)	0.1124

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
85.5	1032.7	1042.5	9.2	9.3
182.9	1557.1	1589.2	13.2	13.4
375.9	2089.3	2181.0	18.8	19.6
618.1	2427.1	2611.2	24.6	26.4
821.8	2551.2	2819.7	28.9	32.0
1004.3	2615.8	2965.3	32.8	37.2
1202.6	2678.1	3124.6	37.2	43.4
1412.5	2691.3	3241.7	41.8	50.3
1603.0	2693.1	3342.9	46.0	57.1
1956.9	2699.4	3551.9	54.0	71.0

Table 11. Carbon Dioxide Adsorption on Dry Activated Carbon at 318.2 K (System 3, Run 1)**SI Units**

Cell T (K)	318.1
Moisture content (%)	0.0
Void volume (m ³)	0.0001011
Pump pressure (MPa)	6.9
Pump T (K)	307.8
Adsorbent mass (g)	44.4
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.50	3.531	3.561	0.325	0.328
1.11	5.016	5.112	0.321	0.327
1.93	5.960	6.170	0.317	0.328
2.72	6.436	6.774	0.314	0.330
3.99	6.912	7.504	0.310	0.336
5.47	7.005	7.962	0.305	0.347
6.85	6.849	8.269	0.301	0.363
8.30	6.332	8.521	0.296	0.399
9.11	5.371	8.195	0.299	0.456
10.30	3.808	7.992	0.342	0.718
11.58	2.995	7.901	0.331	0.874
13.01	2.547	7.849	0.332	1.022

English Engineering Units

Cell T (°F)	113.0
Moisture content (%)	0.0
Void volume (ft ³)	0.003570
Pump pressure (psia)	997.9
Pump T (°F)	94.4
Adsorbent mass (lb)	0.0979

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
72.9	2680.3	2702.8	246.9	248.9
160.4	3807.2	3880.0	243.3	248.0
279.5	4523.8	4682.8	240.3	248.8
394.1	4884.9	5141.2	238.2	250.7
579.3	5246.5	5695.8	235.0	255.1
793.7	5317.1	6043.1	231.6	263.2
993.8	5198.7	6276.2	228.3	275.6
1203.6	4806.3	6467.5	225.0	302.8
1321.9	4076.3	6219.9	227.0	346.4
1493.2	2890.1	6065.9	259.7	545.1
1678.9	2273.2	5996.5	251.6	663.7
1886.7	1933.2	5957.1	251.8	775.8

Table 12. Carbon Dioxide Adsorption on Dry Activated Carbon at 318.2 K (System 3, Run 2)**SI Units**

Cell T (K)	318.1
Moisture content (%)	0.0
Void volume (m ³)	0.0001003
Pump pressure (MPa)	6.9
Pump T (K)	307.8
Adsorbent mass (g)	47.1
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.59	3.841	3.879	0.305	0.308
1.15	5.054	5.155	0.301	0.307
1.89	5.880	6.083	0.298	0.308
2.63	6.346	6.666	0.295	0.310
3.47	6.678	7.153	0.293	0.313
4.94	6.895	7.695	0.288	0.322
5.94	6.882	7.963	0.286	0.330
6.84	6.757	8.151	0.283	0.341
7.96	6.404	8.334	0.280	0.364
8.64	5.996	8.425	0.279	0.391
9.17	5.438	8.391	0.281	0.434
10.02	4.167	8.141	0.324	0.634
11.11	3.339	8.233	0.326	0.804
12.90	2.710	8.267	0.326	0.993

English Engineering Units

Cell T (°F)	113.0
Moisture content (%)	0.0
Void volume (ft ³)	0.003542
Pump pressure (psia)	997.9
Pump T (°F)	94.4
Adsorbent mass (lb)	0.1038

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
86.1	2915.3	2944.3	231.5	233.8
167.4	3835.7	3912.5	228.6	233.1
274.6	4463.2	4617.0	226.0	233.8
381.1	4816.4	5059.2	224.0	235.3
503.7	5068.6	5429.4	222.0	237.8
716.2	5233.2	5840.6	218.9	244.3
861.6	5223.5	6044.0	216.7	250.8
992.1	5128.2	6186.9	214.7	259.0
1153.9	4860.6	6325.9	212.2	276.2
1253.8	4551.3	6394.3	211.4	297.0
1330.2	4127.2	6369.0	213.5	329.5
1452.7	3162.6	6179.0	246.2	481.0
1611.1	2534.5	6248.9	247.6	610.4
1870.8	2057.0	6274.3	247.2	754.0

Table 13. CO₂ Adsorption on Dry Activated Carbon at 327.6 K (System 3)**SI Units**

Cell T (K)	327.6
Moisture content (%)	0.0
Void volume (m ³)	0.0000959
Pump pressure (MPa)	6.18
Pump T (K)	313.3
Adsorbent mass (g)	51
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.60	2.895	2.924	0.071	0.072
1.26	4.052	4.138	0.078	0.080
2.36	5.015	5.229	0.089	0.093
3.82	5.783	6.226	0.102	0.110
5.37	6.260	7.027	0.118	0.132
6.78	6.407	7.557	0.133	0.157
8.16	6.333	7.990	0.152	0.192
8.93	6.216	8.261	0.166	0.221

English Engineering Units

Cell T (°F)	130.0
Moisture content (%)	0.0
Void volume (ft ³)	0.003386
Pump pressure (psia)	896.8
Pump T (°F)	104.3
Adsorbent mass (lb)	0.1124

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
87.5	2197.4	2218.9	53.9	54.4
182.6	3075.4	3140.9	59.5	60.7
342.2	3806.3	3968.5	67.4	70.2
554.7	4389.7	4725.7	77.7	83.7
778.4	4751.6	5333.3	89.4	100.4
983.2	4862.8	5735.8	101.3	119.4
1182.8	4806.8	6064.1	115.7	145.9
1294.5	4717.6	6269.9	126.2	167.8

Table 14. Ethane Adsorption on Dry Activated Carbon at 318.2 K (System 4, Run 1)**SI Units**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001003
Pump pressure (MPa)	8.62
Pump T (K)	307.8
Adsorbent mass (g)	47.1
Adsorbed phase density (g/cm ³)	0.463

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.50	3.819	3.868	0.104	0.106
1.25	4.457	4.611	0.105	0.109
2.28	4.694	5.026	0.106	0.113
3.54	4.740	5.371	0.107	0.121
4.84	4.473	5.584	0.108	0.135
6.25	3.000	5.491	0.118	0.217
7.57	1.905	5.150	0.130	0.351
9.04	1.545	5.049	0.134	0.440
10.73	1.311	4.990	0.138	0.525
13.26	1.055	4.798	0.141	0.643

English Engineering Units

Cell T (°F)	113.0
Moisture content (%)	0.0
Void volume (ft ³)	0.003542
Pump pressure (psia)	1250.5
Pump T (°F)	94.4
Adsorbent mass (lb)	0.1038

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
73.0	2898.4	2935.7	79.3	80.3
181.0	3383.1	3499.4	79.9	82.7
330.1	3563.1	3814.6	80.4	86.0
513.8	3597.6	4076.4	81.0	91.8
702.5	3395.0	4238.2	82.3	102.7
906.0	2277.3	4167.8	89.9	164.6
1097.3	1445.9	3909.0	98.4	266.0
1311.4	1172.4	3832.4	102.1	333.6
1556.6	995.2	3787.6	104.7	398.3
1922.6	800.7	3641.7	107.3	488.1

Table 15. Ethane Adsorption on Dry Activated Carbon at 318.2 K (System 4, Run 2)**SI Units**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001003
Pump pressure (MPa)	8.62
Pump T (K)	307.8
Adsorbent mass (g)	47.1
Adsorbed phase density (g/cm ³)	0.463

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.20	2.874	2.889	0.091	0.091
0.58	3.745	3.801	0.092	0.093
1.10	4.237	4.363	0.092	0.095
3.25	4.664	5.205	0.094	0.105
4.64	4.495	5.500	0.096	0.117
5.53	3.970	5.495	0.099	0.137
6.20	3.038	5.425	0.107	0.191
6.95	2.148	5.126	0.116	0.278
8.33	1.625	4.898	0.123	0.372
10.04	1.349	4.847	0.128	0.459
13.29	1.020	4.650	0.133	0.606

English Engineering Units

Cell T (°F)	113.0
Moisture content (%)	0.0
Void volume (ft ³)	0.003542
Pump pressure (psia)	1250.5
Pump T (°F)	94.4
Adsorbent mass (lb)	0.1038

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
28.8	2181.6	2192.4	68.8	69.2
84.2	2842.3	2884.9	69.5	70.6
159.0	3216.2	3311.8	70.1	72.1
471.7	3539.6	3950.8	71.4	79.6
673.3	3411.4	4174.3	72.8	89.1
802.5	3013.2	4170.8	75.1	103.9
899.3	2306.2	4117.5	81.2	145.1
1007.6	1630.4	3890.3	88.4	210.9
1207.9	1233.2	3717.8	93.5	282.0
1456.0	1024.0	3678.9	97.0	348.4
1927.2	774.5	3529.5	100.9	459.9

Table 16. Ethane Adsorption on Dry Activated Carbon at 318.2 K (System 4, Run 3)**SI Units**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001003
Pump pressure (MPa)	8.62
Pump T (K)	307.8
Adsorbent mass (g)	47.1
Adsorbed phase density (g/cm ³)	0.463

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.15	2.801	2.811	0.085	0.085
0.53	3.824	3.876	0.086	0.087
1.09	4.424	4.556	0.087	0.090
1.79	4.672	4.917	0.088	0.092
2.98	4.784	5.272	0.089	0.098
4.41	4.614	5.535	0.090	0.108
5.55	4.134	5.745	0.094	0.131
6.62	2.609	5.640	0.109	0.237
8.21	1.803	5.353	0.119	0.354
10.44	1.434	5.329	0.125	0.465
13.36	1.175	5.376	0.130	0.594

English Engineering Units

Cell T (°F)	113.0
Moisture content (%)	0.0
Void volume (ft ³)	0.003542
Pump pressure (psia)	1250.5
Pump T (°F)	94.4
Adsorbent mass (lb)	0.1038

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
22.1	2125.8	2133.8	64.5	64.7
76.6	2902.5	2941.9	65.3	66.2
158.7	3358.1	3457.7	66.1	68.0
259.5	3546.4	3731.9	66.6	70.0
432.0	3631.1	4001.2	67.3	74.1
640.2	3501.7	4201.2	68.6	82.3
805.2	3137.5	4360.3	71.7	99.6
959.5	1980.4	4281.0	83.1	179.6
1190.3	1368.7	4063.3	90.5	268.7
1513.9	1088.4	4044.7	95.0	353.2
1937.3	891.5	4080.6	98.6	451.2

Table 17. Adsorption of a 20/80 Mole % Methane/Nitrogen Feed Mixture on Dry Activated Carbon at 318.2 K (System 5)**SI Unit**

Cell T (K)	318.2	Feed Molar Composition	
Moisture content (%)	0.0	Methane	0.200
Void volume (m ³)	0.0001090	Nitrogen	0.800
AC mass (g)	42.4		
Pump T (K)	318.2		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.76	0.094	0.326	0.328	0.915	0.929	1.242	1.257	0.021	0.021	0.057	0.057	0.076	0.077
1.50	0.100	0.520	0.525	1.348	1.389	1.868	1.913	0.022	0.023	0.056	0.057	0.077	0.079
2.77	0.106	0.754	0.766	1.754	1.856	2.508	2.622	0.024	0.025	0.053	0.056	0.075	0.078
4.16	0.112	0.942	0.965	1.986	2.169	2.928	3.134	0.027	0.028	0.051	0.056	0.073	0.078
5.55	0.119	1.075	1.112	2.116	2.386	3.191	3.497	0.029	0.030	0.050	0.057	0.072	0.079
6.95	0.128	1.158	1.211	2.200	2.560	3.358	3.771	0.031	0.033	0.051	0.059	0.072	0.081
8.36	0.131	1.248	1.317	2.213	2.669	3.461	3.986	0.036	0.040	0.053	0.063	0.074	0.085
9.70	0.137	1.292	1.379	2.231	2.777	3.523	4.156	0.047	0.052	0.071	0.088	0.104	0.122
11.07	0.143	1.317	1.424	2.232	2.870	3.549	4.294	0.049	0.055	0.072	0.092	0.105	0.127
12.44	0.147	1.347	1.473	2.210	2.940	3.557	4.413	0.052	0.059	0.074	0.096	0.106	0.132

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003849
AC mass (lb)	0.0935
Pump T (°F)	113.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
109.6	0.094	247.7	248.8	694.8	705.0	942.5	953.7	15.7	15.8	42.9	43.5	58.0	58.7
217.8	0.100	394.8	398.2	1023.3	1054.1	1418.1	1452.3	17.0	17.2	42.4	43.6	58.3	59.7
401.8	0.106	572.4	581.6	1331.3	1408.8	1903.7	1990.4	18.6	19.0	40.4	42.8	56.8	59.4
603.6	0.112	714.9	732.4	1507.7	1646.2	2222.6	2378.6	20.2	20.9	38.8	42.3	55.3	59.2
805.5	0.119	816.0	843.7	1605.8	1810.6	2421.8	2654.3	21.9	23.1	38.2	42.9	54.7	59.9
1008.1	0.128	878.7	918.8	1669.8	1943.1	2548.5	2862.0	23.5	25.3	38.6	44.7	54.9	61.7
1212.1	0.131	947.3	999.6	1679.7	2025.5	2627.0	3025.1	27.4	30.1	40.3	48.1	56.0	64.5
1406.6	0.137	980.5	1046.6	1693.3	2107.9	2673.8	3154.4	35.4	39.1	53.9	66.6	78.7	92.9
1606.1	0.143	999.8	1080.7	1694.2	2178.4	2694.0	3259.1	37.1	41.8	54.8	69.7	79.5	96.2
1803.7	0.147	1022.7	1118.0	1677.2	2231.5	2700.0	3349.5	39.2	45.1	55.8	73.2	80.6	100.0

Table 18. Adsorption of a 40/60 Mole % Methane/Nitrogen Feed Mixture on Dry Activated Carbon at 318.1 K (System 5)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001092
AC mass (g)	42.2
Pump T (K)	318.2

Feed Molar Composition	
Methane	0.400
Nitrogen	0.600

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.77	0.204	0.735	0.739	0.731	0.745	1.466	1.484	0.031	0.031	0.031	0.032	0.061	0.061
1.60	0.230	1.155	1.169	1.058	1.104	2.213	2.273	0.033	0.033	0.030	0.032	0.061	0.063
2.85	0.240	1.593	1.627	1.261	1.366	2.854	2.993	0.035	0.036	0.029	0.031	0.059	0.062
4.16	0.251	1.917	1.977	1.343	1.521	3.260	3.499	0.037	0.039	0.028	0.031	0.058	0.062
5.53	0.271	2.115	2.210	1.404	1.660	3.518	3.870	0.041	0.043	0.031	0.036	0.058	0.064
6.98	0.284	2.278	2.414	1.408	1.750	3.686	4.164	0.056	0.060	0.039	0.047	0.081	0.092
8.29	0.291	2.415	2.589	1.368	1.792	3.783	4.382	0.059	0.064	0.040	0.050	0.081	0.094
9.62	0.298	2.514	2.729	1.322	1.829	3.836	4.558	0.064	0.071	0.044	0.056	0.083	0.099
11.01	0.305	2.574	2.835	1.277	1.869	3.852	4.704	0.076	0.086	0.050	0.067	0.099	0.121
12.44	0.315	2.593	2.903	1.254	1.931	3.847	4.834	0.083	0.095	0.054	0.074	0.106	0.134

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003855
AC mass (lb)	0.0930
Pump T (°F)	113.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
111.5	0.204	558.0	560.9	554.6	565.7	1112.6	1126.6	23.6	23.7	23.5	23.9	46.0	46.5
232.7	0.230	876.8	887.1	803.3	837.8	1680.0	1724.8	25.1	25.4	23.1	24.1	46.5	47.7
413.2	0.240	1209.3	1234.6	956.7	1036.9	2166.0	2271.4	26.7	27.3	21.8	23.5	45.1	47.3
603.5	0.251	1455.3	1500.7	1019.3	1154.7	2474.6	2655.4	28.3	29.3	21.4	23.9	44.1	47.3
802.4	0.271	1605.1	1677.5	1065.3	1259.7	2670.5	2937.2	31.0	32.8	23.7	27.2	44.3	48.7
1012.6	0.284	1728.8	1832.0	1068.6	1328.3	2797.4	3160.3	42.2	45.2	29.8	35.7	61.5	69.5
1202.6	0.291	1833.3	1965.3	1038.2	1360.4	2871.5	3325.7	44.7	48.7	30.6	37.9	61.8	71.6
1395.2	0.298	1908.4	2071.5	1003.1	1388.3	2911.5	3459.9	48.5	54.0	33.5	42.5	62.9	74.8
1596.3	0.305	1954.0	2151.5	969.5	1418.7	2923.5	3570.2	57.9	65.4	38.1	50.5	75.1	91.7
1803.6	0.315	1967.7	2203.2	952.1	1465.4	2919.9	3668.7	62.7	72.2	40.7	56.0	80.8	101.5

Table 19. Adsorption of a 60/40 Mole % Methane/Nitrogen Feed Mixture on Dry Activated Carbon at 318.1 K (System 5)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001092
AC mass (g)	42.2
Pump T (K)	318.2

Feed Molar Composition	
Methane	0.600
Nitrogen	0.400

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.75	0.370	1.156	1.164	0.491	0.504	1.647	1.668	0.054	0.054	0.024	0.025	0.075	0.076
1.43	0.394	1.692	1.714	0.647	0.682	2.339	2.396	0.056	0.057	0.023	0.024	0.076	0.078
2.70	0.424	2.318	2.380	0.763	0.848	3.081	3.227	0.057	0.059	0.023	0.025	0.074	0.078
4.20	0.451	2.756	2.878	0.802	0.951	3.557	3.829	0.058	0.061	0.023	0.026	0.072	0.078
5.52	0.468	3.006	3.190	0.793	1.002	3.798	4.192	0.060	0.064	0.024	0.028	0.071	0.079
6.97	0.482	3.193	3.451	0.763	1.040	3.956	4.491	0.063	0.068	0.027	0.032	0.072	0.082
8.36	0.491	3.342	3.675	0.702	1.047	4.044	4.722	0.067	0.074	0.029	0.036	0.074	0.086
9.71	0.501	3.405	3.814	0.659	1.067	4.065	4.881	0.072	0.082	0.036	0.045	0.077	0.092
11.07	0.508	3.459	3.948	0.611	1.083	4.070	5.031	0.096	0.110	0.040	0.053	0.104	0.128
12.43	0.513	3.520	4.089	0.541	1.081	4.062	5.170	0.100	0.118	0.043	0.059	0.106	0.134

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003855
AC mass (lb)	0.0930
Pump T (°F)	113.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
108.8	0.370	877.5	883.4	372.4	382.3	1249.9	1265.6	40.6	40.9	18.2	18.6	57.2	57.9
207.9	0.394	1283.9	1301.0	491.0	517.3	1774.9	1818.3	42.5	43.1	17.7	18.6	57.8	59.2
391.9	0.424	1759.0	1806.1	579.5	643.5	2338.5	2449.5	43.6	44.8	17.1	18.6	56.4	59.1
609.6	0.451	2091.7	2184.8	608.3	721.8	2700.0	2906.6	44.3	46.4	17.5	19.8	54.9	59.1
800.0	0.468	2281.3	2420.9	601.7	760.7	2883.1	3181.6	45.3	48.2	18.4	21.4	54.2	59.8
1010.6	0.482	2423.6	2619.6	579.1	789.5	3002.7	3409.0	47.5	51.6	20.1	24.1	54.9	62.3
1212.3	0.491	2536.6	2789.1	532.6	794.8	3069.2	3583.8	50.5	56.0	22.2	27.4	56.1	65.6
1408.5	0.501	2584.6	2895.0	500.5	809.9	3085.1	3704.9	54.9	62.4	27.2	34.0	58.1	69.8
1605.1	0.508	2625.7	2996.3	463.7	821.9	3089.3	3818.3	72.6	83.8	30.4	40.2	78.8	97.4
1802.7	0.513	2671.9	3103.7	410.8	820.5	3082.7	3924.2	76.0	89.6	32.7	44.5	80.1	102.0

Table 19. Adsorption of a 60/40 Mole % Methane/Nitrogen Feed Mixture on Dry Activated Carbon at 318.1 K (System 5)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001092
AC mass (g)	42.2
Pump T (K)	318.2

Feed Molar Composition	
Methane	0.600
Nitrogen	0.400

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.75	0.370	1.156	1.164	0.491	0.504	1.647	1.668	0.054	0.054	0.024	0.025	0.075	0.076
1.43	0.394	1.692	1.714	0.647	0.682	2.339	2.396	0.056	0.057	0.023	0.024	0.076	0.078
2.70	0.424	2.318	2.380	0.763	0.848	3.081	3.227	0.057	0.059	0.023	0.025	0.074	0.078
4.20	0.451	2.756	2.878	0.802	0.951	3.557	3.829	0.058	0.061	0.023	0.026	0.072	0.078
5.52	0.468	3.006	3.190	0.793	1.002	3.798	4.192	0.060	0.064	0.024	0.028	0.071	0.079
6.97	0.482	3.193	3.451	0.763	1.040	3.956	4.491	0.063	0.068	0.027	0.032	0.072	0.082
8.36	0.491	3.342	3.675	0.702	1.047	4.044	4.722	0.067	0.074	0.029	0.036	0.074	0.086
9.71	0.501	3.405	3.814	0.659	1.067	4.065	4.881	0.072	0.082	0.036	0.045	0.077	0.092
11.07	0.508	3.459	3.948	0.611	1.083	4.070	5.031	0.096	0.110	0.040	0.053	0.104	0.128
12.43	0.513	3.520	4.089	0.541	1.081	4.062	5.170	0.100	0.118	0.043	0.059	0.106	0.134

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003855
AC mass (lb)	0.0930
Pump T (°F)	113.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
108.8	0.370	877.5	883.4	372.4	382.3	1249.9	1265.6	40.6	40.9	18.2	18.6	57.2	57.9
207.9	0.394	1283.9	1301.0	491.0	517.3	1774.9	1818.3	42.5	43.1	17.7	18.6	57.8	59.2
391.9	0.424	1759.0	1806.1	579.5	643.5	2338.5	2449.5	43.6	44.8	17.1	18.6	56.4	59.1
609.6	0.451	2091.7	2184.8	608.3	721.8	2700.0	2906.6	44.3	46.4	17.5	19.8	54.9	59.1
800.0	0.468	2281.3	2420.9	601.7	760.7	2883.1	3181.6	45.3	48.2	18.4	21.4	54.2	59.8
1010.6	0.482	2423.6	2619.6	579.1	789.5	3002.7	3409.0	47.5	51.6	20.1	24.1	54.9	62.3
1212.3	0.491	2536.6	2789.1	532.6	794.8	3069.2	3583.8	50.5	56.0	22.2	27.4	56.1	65.6
1408.5	0.501	2584.6	2895.0	500.5	809.9	3085.1	3704.9	54.9	62.4	27.2	34.0	58.1	69.8
1605.1	0.508	2625.7	2996.3	463.7	821.9	3089.3	3818.3	72.6	83.8	30.4	40.2	78.8	97.4
1802.7	0.513	2671.9	3103.7	410.8	820.5	3082.7	3924.2	76.0	89.6	32.7	44.5	80.1	102.0

Table 20. Adsorption of a 80/20 Mole % Methane/Nitrogen Feed Mixture on Dry Activated Carbon at 318.1 K (System 5)**SI Unit**

Cell T (K)	318.2	Feed Molar Composition	
Moisture content (%)	0.0	Methane	0.817
Void volume (m ³)	0.0001089	Nitrogen	0.183
AC mass (g)	42.4		
Pump T (K)	318.2		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.65	0.649	1.600	1.613	0.227	0.234	1.827	1.847	0.068	0.068	0.011	0.011	0.077	0.078
1.39	0.674	2.372	2.416	0.293	0.314	2.665	2.730	0.070	0.071	0.011	0.011	0.078	0.080
2.76	0.702	3.193	3.317	0.330	0.382	3.523	3.699	0.070	0.072	0.012	0.013	0.076	0.080
4.21	0.721	3.598	3.822	0.309	0.395	3.907	4.218	0.069	0.073	0.014	0.015	0.074	0.080
5.65	0.732	3.877	4.214	0.267	0.390	4.143	4.604	0.070	0.077	0.016	0.019	0.073	0.081
6.94	0.744	3.994	4.441	0.257	0.411	4.250	4.852	0.072	0.080	0.020	0.023	0.074	0.084
8.35	0.752	4.082	4.657	0.224	0.414	4.306	5.070	0.086	0.098	0.023	0.027	0.087	0.103
9.74	0.759	4.123	4.828	0.195	0.419	4.318	5.247	0.088	0.104	0.027	0.034	0.088	0.107
11.05	0.763	4.145	4.975	0.156	0.414	4.301	5.390	0.109	0.131	0.030	0.039	0.109	0.136
12.44	0.768	4.132	5.099	0.130	0.423	4.261	5.522	0.113	0.140	0.034	0.045	0.111	0.144

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003847
AC mass (lb)	0.0935
Pump T (°F)	113.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
94.8	0.649	1214.2	1224.3	172.1	177.6	1386.3	1401.8	51.4	51.8	8.3	8.5	58.5	59.2
200.9	0.674	1800.5	1833.6	222.2	238.2	2022.8	2071.8	53.1	54.0	8.3	8.7	59.3	60.8
400.1	0.702	2423.4	2517.5	250.2	290.0	2673.6	2807.5	52.8	54.9	8.9	9.7	57.8	60.7
610.4	0.721	2730.9	2901.0	234.4	300.2	2965.3	3201.2	52.4	55.7	10.4	11.6	56.0	60.5
819.8	0.732	2942.3	3198.4	202.3	296.2	3144.6	3494.6	53.4	58.1	12.5	14.2	55.6	61.8
1006.2	0.744	3031.1	3371.1	194.9	311.8	3226.0	3682.9	54.6	60.9	14.9	17.4	56.0	64.0
1210.9	0.752	3098.4	3534.4	170.1	313.9	3268.5	3848.3	64.9	74.3	17.3	20.9	66.1	77.9
1412.5	0.759	3129.6	3664.4	147.6	317.9	3277.3	3982.3	67.1	78.9	20.6	25.5	67.0	81.4
1603.1	0.763	3146.0	3776.4	118.2	314.3	3264.2	4090.7	82.7	99.6	23.0	29.5	82.5	103.4
1804.5	0.768	3135.9	3870.2	98.4	320.8	3234.4	4191.0	85.6	106.1	25.6	33.9	84.3	109.3

Table 21. Adsorption of a 20/80 Mole % Methane/Carbon Dioxide Feed Mixture on Dry Activated Carbon at 318.1 K (System 6)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001090
AC mass (g)	42.4
Pump T (K)	318.2

Feed Molar Composition	
Methane	0.200
Carbon Dioxide	0.800

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.68	0.391	0.558	0.574	2.876	2.901	3.434	3.475	0.029	0.030	0.145	0.146	0.173	0.175
1.35	0.382	0.657	0.699	3.865	3.932	4.523	4.631	0.027	0.029	0.149	0.151	0.174	0.178
2.75	0.366	0.648	0.756	4.991	5.179	5.639	5.935	0.025	0.028	0.150	0.156	0.169	0.178
4.21	0.340	0.580	0.764	5.588	5.945	6.168	6.708	0.026	0.030	0.149	0.158	0.163	0.177
5.58	0.323	0.475	0.737	5.920	6.470	6.395	7.206	0.028	0.034	0.150	0.164	0.159	0.179
6.95	0.302	0.400	0.741	6.018	6.807	6.418	7.548	0.041	0.050	0.154	0.175	0.159	0.187
8.32	0.286	0.299	0.727	5.984	7.054	6.283	7.781	0.047	0.063	0.237	0.280	0.244	0.302
9.66	0.270	0.204	0.720	5.762	7.157	5.966	7.877	0.053	0.075	0.242	0.302	0.245	0.324
11.00	0.256	0.159	0.790	5.556	7.385	5.715	8.174	0.059	0.091	0.251	0.335	0.251	0.359
12.41	0.244	0.106	0.862	5.162	7.502	5.267	8.364	0.068	0.116	0.266	0.390	0.263	0.418

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003849
AC mass (lb)	0.0935
Pump T (°F)	113.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
98.9	0.391	423.6	435.6	2183.0	2201.7	2606.6	2637.3	22.0	22.6	109.9	110.8	131.0	132.6
195.3	0.382	498.9	530.4	2933.8	2984.7	3432.7	3515.1	20.7	21.9	112.9	114.8	131.7	134.9
398.9	0.366	491.8	574.0	3788.4	3931.0	4280.1	4505.0	19.1	21.5	114.1	118.4	128.1	134.9
611.2	0.340	440.2	579.6	4241.1	4512.0	4681.4	5091.6	19.6	23.0	113.0	120.3	123.5	134.3
809.1	0.323	360.2	559.1	4493.6	4910.5	4853.8	5469.7	21.5	26.1	113.6	124.3	120.8	136.2
1007.9	0.302	303.6	562.2	4567.8	5166.5	4871.4	5728.7	30.9	37.9	116.8	132.5	120.4	141.6
1206.3	0.286	227.0	551.9	4541.6	5354.1	4768.6	5906.0	35.6	47.8	179.7	212.4	185.2	229.5
1401.6	0.270	154.6	546.5	4373.5	5431.8	4528.1	5978.3	40.0	56.8	184.0	229.4	186.1	245.9
1595.3	0.256	120.9	599.3	4216.9	5605.0	4337.9	6204.3	44.9	69.0	190.3	254.4	190.3	272.6
1800.3	0.244	80.2	653.9	3917.7	5694.4	3997.9	6348.3	51.5	88.0	202.0	296.2	199.4	317.4

Table 22. Adsorption of a 40/60 Mole % Methane/Carbon Dioxide Feed Mixture on Dry Activated Carbon at 318.1 K (System 6)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001090
AC mass (g)	42.4
Pump T (K)	318.2

Feed Molar Composition	
Methane	0.401
Carbon Dioxide	0.599

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.68	0.618	1.044	1.066	1.922	1.935	2.966	3.001	0.052	0.053	0.094	0.095	0.145	0.147
1.44	0.610	1.328	1.391	2.737	2.777	4.064	4.169	0.049	0.051	0.099	0.100	0.145	0.149
2.75	0.602	1.436	1.591	3.567	3.670	5.003	5.261	0.044	0.048	0.102	0.105	0.141	0.148
4.18	0.582	1.403	1.671	4.107	4.300	5.510	5.971	0.042	0.048	0.104	0.109	0.136	0.147
5.54	0.560	1.330	1.713	4.426	4.726	5.756	6.439	0.043	0.052	0.107	0.114	0.133	0.149
6.90	0.548	1.189	1.700	4.680	5.102	5.869	6.802	0.051	0.065	0.127	0.140	0.151	0.175
8.29	0.529	1.077	1.718	4.769	5.341	5.846	7.059	0.056	0.076	0.152	0.172	0.178	0.214
9.69	0.513	0.940	1.723	4.805	5.547	5.745	7.270	0.065	0.091	0.160	0.187	0.178	0.225
11.01	0.499	0.820	1.741	4.754	5.677	5.575	7.417	0.075	0.113	0.193	0.234	0.211	0.281
12.43	0.486	0.699	1.774	4.641	5.776	5.340	7.550	0.082	0.133	0.217	0.275	0.233	0.330

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003849
AC mass (lb)	0.0935
Pump T (°F)	113.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
98.3	0.618	792.6	808.9	1458.6	1468.6	2251.2	2277.5	39.2	40.0	71.6	72.1	110.1	111.4
209.0	0.610	1007.7	1056.0	2077.2	2108.0	3084.9	3164.0	37.1	38.8	74.8	76.0	110.4	113.2
398.6	0.602	1089.6	1207.6	2707.5	2785.4	3797.2	3993.0	33.4	36.7	77.2	79.5	106.7	112.2
606.2	0.582	1065.0	1268.5	3117.1	3263.3	4182.1	4531.8	31.5	36.6	78.7	82.6	103.0	111.6
804.0	0.560	1009.8	1300.4	3359.0	3586.9	4368.7	4887.3	32.9	39.7	81.0	86.9	100.9	112.9
1001.1	0.548	902.6	1290.3	3552.1	3872.1	4454.7	5162.4	38.8	49.1	96.7	106.2	114.8	133.1
1202.8	0.529	817.4	1304.1	3619.8	4054.0	4437.3	5358.1	42.9	57.9	115.3	130.2	134.7	162.8
1405.7	0.513	713.6	1307.8	3646.8	4210.1	4360.4	5518.0	49.6	69.3	121.2	141.9	134.8	170.8
1596.6	0.499	622.7	1321.2	3608.5	4308.5	4231.3	5629.7	57.1	85.5	146.2	177.4	160.2	213.4
1802.9	0.486	530.8	1346.4	3522.3	4384.3	4053.2	5730.6	62.1	100.7	164.3	208.5	177.1	250.7

Table 23. Adsorption of a 60/40 Mole % Methane/Carbon Dioxide Feed Mixture on Dry Activated Carbon at 318.1 K (System 6)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001090
AC mass (g)	42.4
Pump T (K)	318.2

Feed Molar Composition	
Methane	0.600
Carbon Dioxide	0.400

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.68	0.777	1.475	1.500	1.182	1.189	2.657	2.689	0.083	0.085	0.067	0.067	0.150	0.151
1.42	0.775	1.938	2.009	1.705	1.726	3.642	3.735	0.080	0.083	0.071	0.072	0.150	0.154
2.77	0.766	2.240	2.418	2.275	2.329	4.515	4.748	0.074	0.080	0.075	0.077	0.145	0.153
4.17	0.755	2.306	2.614	2.667	2.766	4.972	5.380	0.069	0.077	0.078	0.082	0.140	0.152
5.56	0.744	2.267	2.717	2.949	3.103	5.216	5.820	0.066	0.078	0.082	0.087	0.137	0.153
6.95	0.727	2.215	2.810	3.099	3.323	5.315	6.132	0.065	0.081	0.086	0.093	0.136	0.157
8.30	0.720	2.063	2.810	3.252	3.543	5.315	6.353	0.072	0.093	0.097	0.108	0.137	0.164
9.66	0.707	1.946	2.848	3.310	3.683	5.256	6.531	0.091	0.126	0.135	0.154	0.197	0.245
11.04	0.700	1.788	2.859	3.377	3.838	5.165	6.697	0.091	0.135	0.143	0.167	0.198	0.257
12.41	0.688	1.674	2.908	3.344	3.903	5.017	6.811	0.093	0.146	0.149	0.180	0.200	0.272

English Engineering Unit

Void volume (ft ³)	0.0038493
AC mass (lb)	0.0935
Pump T (°F)	113.0
Cell T (°F)	113.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
99.2	0.777	1119.8	1138.4	897.0	902.4	2016.8	2040.7	63.3	64.3	50.8	51.1	113.5	114.9
206.6	0.775	1470.6	1524.8	1294.0	1309.7	2764.6	2834.6	61.0	63.3	53.8	54.5	113.7	116.6
401.2	0.766	1700.1	1835.6	1726.7	1768.0	3426.7	3603.6	56.1	60.5	56.9	58.4	110.2	115.9
604.8	0.755	1749.9	1984.0	2024.0	2099.8	3773.9	4083.7	52.1	58.8	59.4	61.9	106.3	115.1
806.5	0.744	1720.9	2062.3	2238.0	2355.2	3958.9	4417.5	49.8	59.0	62.5	66.2	104.2	116.3
1007.5	0.727	1681.4	2132.5	2352.5	2521.9	4033.9	4654.4	49.4	61.4	65.0	70.5	103.5	119.5
1204.2	0.720	1565.9	2133.1	2468.0	2689.0	4033.9	4822.1	54.4	70.3	73.4	82.0	104.1	124.5
1400.6	0.707	1477.4	2161.9	2512.0	2795.1	3989.3	4957.0	68.7	95.6	102.7	116.5	149.9	186.3
1601.4	0.700	1356.9	2170.3	2563.4	2912.7	3920.3	5082.9	69.3	102.3	108.5	126.6	150.5	195.2
1800.4	0.688	1270.4	2207.2	2537.8	2962.3	3808.2	5169.5	70.9	111.0	112.8	136.2	152.0	206.5

Table 24. Adsorption of a 80/20 Mole % Methane/Carbon Dioxide Feed Mixture on Dry Activated Carbon at 318.1 K (System 6)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001090
AC mass (g)	42.4
Pump T (K)	318.2

Feed Molar Composition	
Methane	0.800
Carbon Dioxide	0.200

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.77	0.890	1.930	1.960	0.567	0.571	2.497	2.531	0.109	0.111	0.032	0.033	0.141	0.143
1.46	0.886	2.515	2.591	0.784	0.794	3.299	3.385	0.109	0.112	0.034	0.035	0.142	0.146
2.81	0.884	3.035	3.225	1.057	1.082	4.092	4.307	0.103	0.110	0.037	0.038	0.138	0.146
4.12	0.883	3.237	3.556	1.249	1.291	4.486	4.847	0.097	0.107	0.040	0.041	0.133	0.144
5.55	0.877	3.317	3.789	1.396	1.462	4.713	5.251	0.094	0.108	0.044	0.046	0.131	0.146
6.92	0.871	3.322	3.951	1.495	1.588	4.817	5.540	0.108	0.128	0.054	0.058	0.151	0.174
8.30	0.866	3.252	4.042	1.561	1.684	4.813	5.726	0.122	0.151	0.064	0.071	0.175	0.208
9.67	0.861	3.166	4.127	1.616	1.771	4.782	5.898	0.121	0.158	0.070	0.080	0.174	0.215
11.04	0.856	3.060	4.194	1.649	1.839	4.708	6.033	0.143	0.195	0.085	0.099	0.209	0.268
12.41	0.852	2.943	4.253	1.664	1.892	4.608	6.146	0.152	0.218	0.095	0.113	0.225	0.301

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003849
AC mass (lb)	0.0935
Pump T (°F)	113.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
111.7	0.890	1464.6	1487.3	430.6	433.4	1895.2	1920.7	82.7	84.0	24.5	24.7	106.9	108.4
211.5	0.886	1908.8	1966.5	594.9	602.4	2503.7	2568.9	82.4	84.9	26.1	26.5	107.9	110.7
407.3	0.884	2303.6	2447.6	802.4	821.3	3106.0	3268.8	78.3	83.2	28.3	29.0	105.0	110.5
597.7	0.883	2457.0	2699.1	947.8	980.0	3404.8	3679.1	73.9	81.1	30.2	31.4	101.2	109.4
805.0	0.877	2517.3	2876.0	1059.5	1109.6	3576.9	3985.6	71.6	81.7	33.1	35.2	99.5	110.8
1003.5	0.871	2521.3	2999.1	1135.0	1205.5	3656.2	4204.6	81.6	96.9	40.7	44.1	114.9	132.2
1203.3	0.866	2468.2	3068.1	1185.2	1278.2	3653.3	4346.3	92.6	114.9	48.7	53.8	132.9	158.2
1402.4	0.861	2403.3	3132.4	1226.3	1344.1	3629.6	4476.5	92.2	119.6	53.1	60.4	132.3	163.3
1601.7	0.856	2322.2	3183.2	1251.5	1396.0	3573.7	4579.2	108.3	147.7	64.8	75.3	158.6	203.4
1800.4	0.852	2233.9	3228.3	1263.3	1436.1	3497.2	4664.4	115.3	165.4	71.9	85.8	171.0	228.2

Table 25. Adsorption of a 20/80 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Dry Activated Carbon at 318.2 K (System 7)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001045
AC mass (g)	51.1
Pump T (K)	318.2

Feed Molar Composition	
Nitrogen	0.200
Carbon Dioxide	0.800

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.66	0.582	0.316	0.333	2.243	2.255	2.559	2.587	0.019	0.019	0.110	0.110	0.125	0.126
1.46	0.567	0.359	0.414	3.540	3.583	3.899	3.997	0.018	0.020	0.117	0.119	0.128	0.132
2.79	0.521	0.289	0.423	4.776	4.900	5.065	5.323	0.020	0.022	0.117	0.120	0.123	0.129
4.13	0.471	0.207	0.420	5.478	5.718	5.686	6.138	0.021	0.024	0.115	0.120	0.118	0.127
5.53	0.432	0.103	0.401	5.941	6.333	6.044	6.734	0.024	0.028	0.116	0.123	0.115	0.128
6.98	0.394	0.019	0.401	6.183	6.771	6.202	7.172	0.036	0.042	0.120	0.132	0.114	0.133
8.35	0.366	-0.068	0.397	6.278	7.083	6.210	7.480	0.039	0.048	0.176	0.199	0.169	0.204
9.73	0.341	-0.146	0.402	6.245	7.305	6.098	7.707	0.042	0.054	0.178	0.210	0.169	0.214
11.12	0.320	-0.232	0.405	6.122	7.475	5.890	7.880	0.046	0.062	0.184	0.226	0.171	0.229
12.52	0.299	-0.290	0.429	5.826	7.510	5.536	7.939	0.051	0.072	0.191	0.249	0.175	0.252

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003689
AC mass (lb)	0.1127
Pump T (°F)	113.0

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
95.3	0.582	240.1	252.6	1702.2	1711.2	1942.3	1963.8	14.1	14.6	83.4	83.8	94.7	95.7
211.3	0.567	272.2	314.4	2686.9	2719.2	2959.1	3033.7	13.9	15.0	89.1	90.2	97.4	99.9
405.2	0.521	219.3	321.1	3625.4	3718.8	3844.6	4039.9	14.8	16.5	89.0	91.3	93.2	97.9
599.0	0.471	157.4	319.1	4157.9	4339.8	4315.4	4658.9	16.3	18.4	87.4	91.3	89.2	96.3
802.2	0.432	78.5	304.7	4508.9	4806.6	4587.5	5111.3	18.2	21.0	87.7	93.7	87.3	97.3
1012.3	0.394	14.2	304.5	4692.9	5139.3	4707.2	5443.8	27.3	31.9	90.8	100.0	86.9	100.6
1211.0	0.366	-51.4	301.3	4765.1	5376.3	4713.7	5677.6	29.5	36.3	133.2	150.9	128.5	154.9
1411.4	0.341	-111.0	305.1	4739.6	5544.8	4628.7	5849.9	31.9	40.8	135.4	159.2	128.5	162.6
1612.8	0.320	-176.3	307.1	4646.6	5673.5	4470.3	5980.6	35.1	46.9	139.4	171.5	129.9	174.1
1816.5	0.299	-220.2	325.5	4422.0	5699.9	4201.9	6025.3	38.7	55.0	145.1	188.8	133.1	191.3

Table 26. Adsorption of a 40/60 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Dry Activated Carbon at 318.2 K (System 7)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001045
AC mass (g)	51.1
Pump T (K)	318.2

Feed Molar Composition	
Nitrogen	0.400
Carbon Dioxide	0.600

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.78	0.794	0.585	0.606	1.472	1.477	2.057	2.084	0.038	0.039	0.089	0.089	0.122	0.124
1.43	0.779	0.742	0.796	2.166	2.181	2.908	2.978	0.036	0.039	0.094	0.095	0.124	0.127
2.72	0.767	0.791	0.934	3.149	3.192	3.940	4.126	0.034	0.038	0.099	0.101	0.120	0.126
4.15	0.749	0.697	0.957	3.922	4.009	4.618	4.965	0.035	0.041	0.103	0.105	0.115	0.124
5.53	0.724	0.574	0.953	4.456	4.600	5.029	5.553	0.038	0.045	0.106	0.110	0.112	0.124
6.97	0.693	0.449	0.953	4.839	5.062	5.288	6.016	0.042	0.050	0.109	0.116	0.111	0.126
8.26	0.673	0.310	0.934	5.129	5.432	5.439	6.366	0.061	0.073	0.121	0.131	0.111	0.130
9.87	0.637	0.213	0.970	5.267	5.699	5.481	6.669	0.065	0.083	0.168	0.185	0.162	0.197
11.23	0.619	0.073	0.953	5.400	5.942	5.474	6.896	0.071	0.092	0.174	0.196	0.161	0.203
12.66	0.604	-0.080	0.936	5.521	6.187	5.441	7.124	0.076	0.102	0.181	0.209	0.162	0.212

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003689
AC mass (lb)	0.1127
Pump T (°F)	113.0

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
112.7	0.794	444.3	460.2	1117.3	1121.4	1561.6	1581.6	28.7	29.6	67.4	67.6	92.8	94.0
206.7	0.779	563.3	604.5	1644.1	1655.8	2207.4	2260.3	27.7	29.3	71.4	72.0	94.1	96.3
394.7	0.767	600.1	708.7	2390.1	2423.0	2990.2	3131.8	26.1	29.1	75.3	76.4	91.2	95.6
602.0	0.749	528.8	726.2	2976.5	3042.6	3505.3	3768.7	26.8	30.9	77.9	79.9	87.5	94.0
801.6	0.724	435.5	723.5	3381.8	3491.6	3817.2	4215.1	29.0	34.0	80.1	83.4	85.0	93.9
1010.3	0.693	340.7	723.7	3672.9	3842.3	4013.6	4566.0	31.8	38.1	83.0	87.8	84.1	95.8
1198.4	0.673	235.4	709.0	3892.7	4122.8	4128.1	4831.8	46.2	55.3	91.6	99.5	84.0	98.4
1432.0	0.637	162.0	736.2	3997.9	4325.3	4159.9	5061.6	49.5	63.2	127.7	140.7	122.6	149.3
1629.3	0.619	55.8	723.7	4098.9	4510.0	4154.6	5233.7	53.7	70.1	131.9	148.6	122.2	154.0
1835.8	0.604	-60.4	710.8	4190.4	4696.1	4129.9	5406.8	57.7	77.5	137.5	158.6	123.0	161.2

Table 27. Adsorption of a 60/40 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Dry Activated Carbon at 318.2 K (System 7)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001044
AC mass (g)	51.1
Pump T (K)	318.2

Feed Molar Composition	
Nitrogen	0.581
Carbon Dioxide	0.419

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.90	0.888	0.808	0.831	0.949	0.952	1.757	1.783	0.055	0.056	0.064	0.064	0.115	0.116
1.54	0.880	1.042	1.095	1.365	1.373	2.407	2.468	0.053	0.056	0.068	0.068	0.116	0.119
2.74	0.872	1.234	1.363	1.957	1.976	3.191	3.339	0.049	0.053	0.073	0.073	0.112	0.118
4.26	0.866	1.265	1.511	2.543	2.581	3.808	4.092	0.046	0.053	0.078	0.080	0.109	0.117
5.56	0.853	1.222	1.578	2.926	2.987	4.148	4.564	0.046	0.054	0.081	0.084	0.105	0.116
6.96	0.843	1.121	1.603	3.278	3.368	4.399	4.970	0.047	0.058	0.087	0.091	0.104	0.118
8.31	0.831	1.011	1.618	3.552	3.675	4.563	5.293	0.066	0.080	0.103	0.111	0.106	0.123
9.67	0.817	0.897	1.631	3.766	3.930	4.663	5.562	0.073	0.096	0.143	0.154	0.157	0.187
11.12	0.808	0.740	1.616	3.988	4.197	4.728	5.813	0.077	0.104	0.151	0.165	0.156	0.192
12.54	0.795	0.603	1.615	4.137	4.397	4.740	6.012	0.080	0.111	0.157	0.175	0.156	0.198

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003688
AC mass (lb)	0.1127
Pump T (°F)	113.0

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
130.2	0.888	613.2	630.5	720.3	722.5	1333.5	1352.9	41.5	42.6	48.3	48.5	87.1	88.4
223.4	0.880	790.6	831.4	1036.2	1041.8	1826.8	1873.2	40.2	42.1	51.5	51.8	87.7	90.0
397.0	0.872	936.4	1034.3	1485.6	1499.9	2422.0	2534.2	37.1	40.5	55.1	55.8	85.4	89.3
617.2	0.866	960.3	1146.9	1930.0	1958.9	2890.3	3105.7	35.0	40.2	59.2	60.5	82.4	88.6
806.7	0.853	927.6	1197.4	2220.5	2266.9	3148.1	3464.3	34.7	41.2	61.8	63.9	79.9	87.9
1010.1	0.843	851.0	1216.6	2487.7	2556.0	3338.7	3772.5	35.9	44.0	66.0	69.1	79.1	89.4
1205.1	0.831	767.3	1227.9	2695.7	2789.6	3463.0	4017.4	50.2	61.1	78.1	84.2	80.2	93.1
1402.2	0.817	681.2	1238.2	2858.2	2983.0	3539.4	4221.2	55.4	72.7	108.5	116.7	119.0	142.0
1612.6	0.808	561.3	1226.5	3027.0	3185.5	3588.3	4412.0	58.5	78.7	114.3	125.0	118.4	145.7
1818.2	0.795	457.8	1225.6	3140.0	3337.5	3597.8	4563.1	61.0	84.3	119.1	132.5	118.5	150.4

Table 28. Adsorption of a 80/20 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Dry Activated Carbon at 318.2 K (System 7)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001044
AC mass (g)	51.1
Pump T (K)	318.2

Feed Molar Composition	
Nitrogen	0.800
Carbon Dioxide	0.200

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.80	0.954	0.959	0.975	0.357	0.358	1.316	1.333	0.081	0.082	0.031	0.031	0.110	0.112
1.53	0.945	1.398	1.443	0.563	0.566	1.961	2.009	0.080	0.082	0.033	0.034	0.111	0.113
2.74	0.944	1.792	1.902	0.827	0.833	2.618	2.736	0.075	0.079	0.036	0.037	0.107	0.112
4.18	0.946	2.015	2.221	1.090	1.101	3.105	3.322	0.070	0.077	0.040	0.041	0.104	0.111
5.57	0.947	2.099	2.408	1.312	1.330	3.411	3.738	0.066	0.075	0.045	0.046	0.101	0.111
6.95	0.946	2.117	2.537	1.503	1.527	3.621	4.065	0.064	0.076	0.049	0.051	0.100	0.112
8.34	0.942	2.102	2.637	1.663	1.696	3.764	4.332	0.068	0.083	0.059	0.063	0.100	0.115
9.70	0.937	2.061	2.711	1.792	1.835	3.853	4.546	0.088	0.113	0.080	0.085	0.144	0.170
11.12	0.934	1.994	2.766	1.919	1.974	3.913	4.740	0.087	0.117	0.085	0.093	0.144	0.174
12.65	0.929	1.909	2.813	2.032	2.101	3.941	4.914	0.087	0.122	0.091	0.101	0.144	0.180

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003688
AC mass (lb)	0.1127
Pump T (°F)	113.0

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
115.3	0.954	727.8	739.7	271.1	271.7	998.9	1011.4	61.3	62.3	23.6	23.6	83.7	84.8
222.3	0.945	1061.0	1095.4	427.6	429.6	1488.6	1525.0	60.4	62.3	25.3	25.5	84.0	86.1
397.9	0.944	1359.9	1443.9	627.5	632.5	1987.3	2076.4	56.7	60.1	27.6	28.0	81.5	85.1
606.0	0.946	1529.5	1685.7	827.0	835.9	2356.5	2521.7	52.8	58.1	30.6	31.3	78.7	84.2
807.4	0.947	1593.1	1827.9	996.0	1009.2	2589.1	2837.0	49.9	57.0	33.8	34.9	76.6	84.0
1007.8	0.946	1607.2	1925.7	1141.0	1159.3	2748.2	3085.0	48.4	57.4	37.1	38.8	75.7	85.0
1209.8	0.942	1595.2	2001.1	1261.9	1286.9	2857.1	3288.1	51.6	62.9	44.6	48.0	75.6	87.1
1407.5	0.937	1564.4	2057.3	1360.0	1393.0	2924.3	3450.3	67.0	85.9	60.5	64.7	109.2	128.9
1612.6	0.934	1513.3	2099.2	1456.6	1498.3	2969.9	3597.5	66.4	88.6	64.7	70.3	109.0	132.1
1834.8	0.929	1449.0	2135.4	1542.1	1594.7	2991.1	3730.1	66.4	92.5	69.2	76.5	109.5	136.6

Table 29. Adsorption of a 10/50/40 Mole % Methane/Carbon Dioxide/Nitrogen Feed Mixture on Dry Activated Carbon at 318.1 K (System 8)**SI Unit**

Cell T (K)	318.2
Moisture content (%)	0.0
Void volume (m ³)	0.0001055
AC mass (g)	50.2
Pump T (K)	318.2

Feed Molar Composition	
Nitrogen	0.400
Carbon Dioxide	0.499
Methane	0.101

Pressure (MPa)	N ₂ Gas mole fraction	CO ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		CH ₄ Ads. (mmol/g)		Total Ads. (mmol/g)	
			Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute
0.76	0.777	0.144	0.592	0.612	1.244	1.246	0.222	0.224	2.058	2.081
1.51	0.750	0.163	0.761	0.815	1.885	1.892	0.317	0.323	2.963	3.030
2.78	0.720	0.184	0.825	0.955	2.640	2.661	0.404	0.420	3.870	4.036
4.19	0.696	0.201	0.768	0.995	3.244	3.286	0.445	0.476	4.457	4.758
5.62	0.676	0.216	0.654	0.989	3.724	3.794	0.456	0.506	4.833	5.289
7.03	0.653	0.236	0.540	0.983	4.064	4.174	0.455	0.525	5.060	5.682
8.50	0.632	0.255	0.410	0.968	4.343	4.501	0.444	0.538	5.197	6.007
9.83	0.615	0.272	0.297	0.958	4.526	4.736	0.430	0.545	5.253	6.240
11.22	0.597	0.289	0.188	0.956	4.663	4.936	0.407	0.546	5.258	6.438
12.63	0.583	0.303	0.062	0.943	4.770	5.108	0.392	0.554	5.224	6.605
13.99	0.565	0.322	-0.005	0.966	4.744	5.159	0.376	0.559	5.115	6.683

Pressure (MPa)	Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in CH ₄ Ads.		Error in Total Ads.	
	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.8	0.037	0.038	0.074	0.074	0.019	0.019	0.120	0.121
1.5	0.034	0.036	0.075	0.076	0.021	0.022	0.115	0.118
2.8	0.032	0.036	0.078	0.079	0.025	0.026	0.110	0.115
4.2	0.033	0.038	0.082	0.084	0.029	0.031	0.107	0.114
5.6	0.040	0.047	0.101	0.104	0.038	0.042	0.122	0.133
7.0	0.043	0.052	0.106	0.110	0.043	0.048	0.122	0.137
8.5	0.053	0.065	0.129	0.137	0.054	0.062	0.142	0.164
9.8	0.067	0.084	0.163	0.174	0.068	0.080	0.173	0.205
11.2	0.075	0.097	0.180	0.196	0.076	0.093	0.185	0.226
12.6	0.081	0.107	0.188	0.208	0.082	0.103	0.186	0.235
14.0	0.085	0.114	0.188	0.216	0.086	0.111	0.185	0.242

Table 29. Adsorption of a 10/50/40 Mole % Methane/Carbon Dioxide/Nitrogen Feed Mixture on Dry Activated Carbon at 318.1 K (Continued)

English Engineering Unit

Cell T (°F)	113.0
Void volume (ft ³)	0.003726
AC mass (lb)	0.1107
Pump T (°F)	113.0

Pressure (psia)	N ₂ Gas mole fraction	CO ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		CH ₄ Ads. (SCF/ton)		Total Ads. (SCF/ton)	
			Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute
110.9	0.777	0.144	449.6	464.3	944.3	945.8	168.4	169.7	1562.3	1579.9
218.8	0.750	0.163	577.3	618.5	1430.7	1436.0	241.0	245.3	2249.0	2299.7
403.8	0.720	0.184	626.3	725.2	2004.1	2019.7	306.6	318.6	2937.0	3063.4
607.9	0.696	0.201	582.7	755.5	2462.6	2494.3	337.8	361.4	3383.1	3611.2
815.0	0.676	0.216	496.1	750.5	2826.3	2879.7	346.1	384.2	3668.6	4014.4
1019.8	0.653	0.236	410.2	746.1	3084.8	3168.0	345.2	398.8	3840.2	4313.0
1233.5	0.632	0.255	311.4	734.7	3296.1	3416.4	337.2	408.3	3944.8	4559.4
1425.5	0.615	0.272	225.6	727.4	3435.3	3594.9	326.5	413.8	3987.4	4736.1
1627.2	0.597	0.289	142.6	726.0	3539.4	3746.2	309.0	414.5	3991.0	4886.7
1832.0	0.583	0.303	47.2	715.5	3620.5	3877.1	297.5	420.6	3965.3	5013.2
2028.7	0.565	0.322	-3.6	732.8	3600.4	3915.3	285.3	424.0	3882.1	5072.2

Pressure (psia)	Error in N ₂ Adsorp.		Error in CO ₂ Ads.		Error in CH ₄ Ads.		Error in Total Ads.	
	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
110.9	28.2	29.0	55.9	56.0	14.4	14.5	90.8	91.8
218.8	26.0	27.5	57.1	57.4	16.1	16.4	87.3	89.3
403.8	24.6	27.1	59.5	60.1	19.1	19.8	83.6	87.2
607.9	25.1	28.6	62.6	63.8	22.4	23.8	81.1	86.5
815.0	30.4	35.6	76.4	78.6	29.0	31.7	92.4	101.2
1019.8	33.0	39.4	80.5	83.8	32.5	36.4	92.3	103.7
1233.5	40.5	49.6	98.3	103.7	40.6	46.7	107.7	124.5
1425.5	50.7	63.7	123.6	132.2	51.3	60.6	131.1	155.8
1627.2	57.1	73.5	136.7	148.6	57.9	70.4	140.2	171.7
1832.0	61.5	80.9	142.5	157.7	62.4	78.2	140.8	178.2
2028.7	64.2	86.9	142.5	164.2	65.0	84.1	140.5	183.8

Table 30. Nitrogen Adsorption on Wet Fruitland Coal at 319.3 K (System 9 OSU #1, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	9.7
Void volume (m ³)	0.0000733
Pump pressure (MPa)	6.87
Pump T (K)	309.1
Adsorbent mass (g)	68.6
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.80	0.068	0.069	0.009	0.009
1.43	0.109	0.111	0.009	0.010
2.79	0.183	0.191	0.012	0.012
4.15	0.242	0.257	0.015	0.016
5.52	0.287	0.312	0.018	0.020
6.90	0.325	0.361	0.022	0.024
8.27	0.355	0.404	0.026	0.029
9.65	0.383	0.444	0.029	0.034
11.03	0.406	0.482	0.033	0.039
12.38	0.424	0.514	0.037	0.044

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	9.7
Void volume (ft ³)	0.002589
Pump pressure (psia)	996.3
Pump T (°F)	96.7
Adsorbent mass (lb)	0.1511

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
115.5	51.8	52.4	6.6	6.7
207.7	82.8	84.5	7.2	7.3
405.1	139.0	144.9	9.0	9.4
601.2	183.5	195.3	11.3	12.1
801.2	217.6	236.5	14.0	15.2
1000.4	246.6	273.9	16.7	18.6
1199.6	269.8	306.3	19.5	22.2
1400.0	290.6	337.3	22.3	25.9
1599.1	308.3	365.9	25.1	29.8
1795.4	321.9	390.5	27.8	33.8

Table 31. Nitrogen Adsorption on Wet Fruitland Coal at 319.3 K (System 9 OSU #1, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	7.7
Void volume (m ³)	0.0000750
Pump pressure (MPa)	6.87
Pump T (K)	309.1
Adsorbent mass (g)	67.1
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.80	0.069	0.070	0.008	0.008
1.51	0.120	0.123	0.009	0.009
2.79	0.191	0.199	0.012	0.012
4.17	0.244	0.260	0.015	0.016
5.58	0.292	0.318	0.018	0.020
6.91	0.322	0.357	0.022	0.024
8.28	0.350	0.397	0.026	0.029
9.67	0.374	0.434	0.030	0.034
11.03	0.398	0.472	0.033	0.039
12.40	0.415	0.504	0.037	0.045

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	7.7
Void volume (ft ³)	0.002649
Pump pressure (psia)	996.3
Pump T (°F)	96.7
Adsorbent mass (lb)	0.1479

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
116.7	52.2	52.9	6.4	6.4
218.3	91.1	93.2	7.0	7.2
404.7	145.2	151.3	8.8	9.2
604.9	185.1	197.1	11.3	12.0
808.7	221.6	241.1	14.0	15.3
1001.8	244.1	271.2	16.7	18.6
1201.2	265.6	301.6	19.6	22.2
1402.3	283.7	329.4	22.4	26.0
1600.0	302.1	358.5	25.2	29.9
1798.7	315.3	382.7	28.0	34.0

Table 32. Nitrogen Adsorption on Wet Fruitland Coal at 319.3 K (System 9 OSU#2, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	10.2
Void volume (m ³)	0.0000777
Pump pressure (MPa)	6.88
Pump T (K)	309.0
Adsorbent mass (g)	60.5
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.74	0.049	0.049	0.009	0.009
1.45	0.093	0.095	0.010	0.010
2.78	0.144	0.150	0.013	0.013
4.15	0.189	0.201	0.016	0.017
5.56	0.232	0.252	0.021	0.022
6.95	0.256	0.285	0.025	0.028
8.33	0.283	0.321	0.029	0.033
9.69	0.301	0.350	0.034	0.039
11.08	0.316	0.375	0.038	0.045
12.45	0.336	0.408	0.042	0.051

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	10.2
Void volume (ft ³)	0.002744
Pump pressure (psia)	998.5
Pump T (°F)	96.6
Adsorbent mass (lb)	0.1335

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
107.8	37.1	37.5	6.6	6.7
210.6	70.3	71.8	7.3	7.5
403.7	109.0	113.6	9.6	10.0
602.5	143.7	152.9	12.4	13.2
805.9	176.1	191.5	15.7	17.0
1007.9	194.6	216.3	18.9	21.1
1207.9	214.5	243.7	22.2	25.3
1405.9	228.6	265.5	25.5	29.6
1607.6	239.6	284.6	28.8	34.2
1805.0	255.2	310.0	31.9	38.8

Table 33. Nitrogen Adsorption on Wet Fruitland Coal at 319.3 K (System 9 OSU #2, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	10.2
Void volume (m ³)	0.0000779
Pump pressure (MPa)	6.88
Pump T (K)	309.0
Adsorbent mass (g)	60.5
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.73	0.052	0.052	0.009	0.009
1.43	0.088	0.090	0.010	0.010
2.77	0.146	0.152	0.013	0.013
4.25	0.193	0.206	0.017	0.018
5.55	0.227	0.247	0.021	0.022
6.95	0.259	0.288	0.025	0.028
8.30	0.283	0.321	0.029	0.033
9.70	0.302	0.351	0.034	0.039
11.09	0.325	0.386	0.038	0.045
12.42	0.341	0.414	0.042	0.051

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	10.2
Void volume (ft ³)	0.002751
Pump pressure (psia)	998.5
Pump T (°F)	96.6
Adsorbent mass (lb)	0.1335

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
105.6	39.2	39.6	6.6	6.6
206.7	67.2	68.6	7.3	7.4
402.5	110.5	115.1	9.5	9.9
616.5	146.8	156.4	12.7	13.5
804.9	172.2	187.2	15.6	17.0
1008.5	196.5	218.5	19.0	21.1
1204.4	214.4	243.6	22.2	25.2
1406.8	229.2	266.2	25.5	29.6
1607.8	246.4	292.7	28.8	34.2
1801.8	258.6	314.0	31.9	38.8

Table 34. Nitrogen Adsorption on Wet Fruitland Coal at 319.3 K (System 9 OSU #2, Run 3)**SI Units**

Cell T (K)	319.3
Moisture content (%)	10.2
Void volume (m ³)	0.0000712
Pump pressure (MPa)	6.91
Pump T (K)	319.3
Adsorbent mass (g)	79.5
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
1.42	0.096	0.098	0.004	0.004
2.90	0.162	0.169	0.008	0.008
4.18	0.203	0.217	0.011	0.012
5.61	0.242	0.264	0.015	0.016
6.90	0.269	0.299	0.018	0.020
8.32	0.294	0.334	0.021	0.024
9.75	0.319	0.371	0.025	0.029
10.96	0.335	0.397	0.027	0.033

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	10.2
Void volume (ft ³)	0.002515
Pump pressure (psia)	1002.1
Pump T (°F)	115.0
Adsorbent mass (lb)	0.1753

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
205.8	72.9	74.5	3.3	3.4
420.6	122.7	128.1	6.0	6.2
605.7	154.4	164.4	8.3	8.9
813.1	183.9	200.1	11.0	12.0
1000.2	204.4	227.0	13.4	14.9
1206.0	223.3	253.7	16.1	18.2
1413.5	242.0	281.3	18.7	21.7
1590.2	254.2	301.4	20.9	24.7

Table 35. Nitrogen Adsorption on Wet Fruitland Coal at 319.3 K (System 9 OSU #2, Run 4)**SI Units**

Cell T (K)	319.3
Moisture content (%)	14.0
Void volume (m ³)	0.0000676
Pump pressure (MPa)	6.89
Pump T (K)	308.3
Adsorbent mass (g)	83.1
Adsorbed phase density (g/cm ³)	0.808

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
1.49	0.092	0.093	0.005	5.743
2.74	0.144	0.149	0.008	5.475
4.13	0.194	0.206	0.011	5.698
5.52	0.230	0.248	0.014	6.241
6.90	0.264	0.290	0.018	6.689
8.30	0.290	0.325	0.021	7.241
9.65	0.315	0.360	0.024	7.678
11.03	0.335	0.390	0.027	8.189
12.41	0.352	0.418	0.031	8.688

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	14.0
Void volume (ft ³)	0.002387
Pump pressure (psia)	999.2
Pump T (°F)	95.4
Adsorbent mass (lb)	0.1831

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
215.7	69.5	70.9	4.0	4358.6
397.8	109.1	113.1	6.0	4155.5
598.9	147.6	156.0	8.4	4324.7
800.4	174.9	188.4	10.9	4736.6
1000.3	200.6	220.3	13.4	5077.2
1203.6	220.3	246.8	16.0	5495.7
1400.2	239.4	273.4	18.4	5827.5
1599.8	254.2	296.0	20.8	6215.3
1799.4	267.1	317.2	23.2	6594.2

Table 36. Methane Adsorption on Wet Fruitland Coal at 319.3 K (System 10 OSU #1, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	11.4
Void volume (m ³)	0.0000727
Pump pressure (MPa)	6.87
Pump T (K)	309.1
Adsorbent mass (g)	69.9
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.66	0.191	0.193	0.006	0.006
1.40	0.312	0.320	0.008	0.008
2.77	0.459	0.481	0.011	0.012
4.17	0.548	0.590	0.015	0.017
5.53	0.603	0.667	0.020	0.022
6.90	0.642	0.731	0.024	0.028
8.28	0.663	0.778	0.029	0.034
9.67	0.677	0.820	0.034	0.041
11.02	0.690	0.864	0.039	0.048
12.40	0.695	0.900	0.044	0.057

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	11.4
Void volume (ft ³)	0.002567
Pump pressure (psia)	996.3
Pump T (°F)	96.7
Adsorbent mass (lb)	0.1541

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
95.4	145.3	146.9	4.8	4.8
203.0	237.0	242.6	5.8	6.0
401.1	348.2	365.1	8.6	9.0
604.4	416.2	448.0	11.8	12.7
802.6	457.9	506.4	15.1	16.7
1000.2	487.4	554.7	18.5	21.1
1201.4	503.3	590.6	22.1	25.9
1401.8	513.8	622.6	25.7	31.2
1598.3	523.6	655.6	29.4	36.8
1798.9	527.1	683.3	33.1	42.9

Table 37. Methane Adsorption on Wet Fruitland Coal at 319.3 K (System 10 OSU #1, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	5.9
Void volume (m ³)	0.0000768
Pump pressure (MPa)	6.87
Pump T (K)	309.1
Adsorbent mass (g)	65.8
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.76	0.218	0.221	0.006	0.006
1.43	0.323	0.331	0.007	0.008
2.69	0.460	0.481	0.011	0.011
4.27	0.553	0.596	0.016	0.017
5.57	0.603	0.668	0.020	0.022
6.92	0.638	0.727	0.025	0.028
8.33	0.665	0.781	0.030	0.035
9.67	0.677	0.820	0.034	0.042
11.03	0.689	0.863	0.039	0.049
12.35	0.695	0.899	0.044	0.057

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	5.9
Void volume (ft ³)	0.002712
Pump pressure (psia)	996.5
Pump T (°F)	96.7
Adsorbent mass (lb)	0.1451

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
110.5	165.7	167.8	4.5	4.6
207.1	245.4	251.2	5.6	5.8
390.5	349.0	365.5	8.3	8.7
618.6	419.4	452.2	12.0	13.0
807.9	457.8	506.7	15.3	16.9
1004.3	484.3	551.5	18.8	21.4
1208.6	504.5	592.7	22.5	26.5
1402.9	513.8	622.7	26.1	31.7
1599.3	522.9	654.8	29.8	37.4
1790.7	527.2	682.4	33.5	43.3

Table 38. Methane Adsorption on Wet Fruitland Coal at 319.3 K (System 10 OSU #2, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	10.1
Void volume (m ³)	0.0000785
Pump pressure (MPa)	6.88
Pump T (K)	309.0
Adsorbent mass (g)	60.7
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.71	0.193	0.196	0.008	0.008
1.43	0.312	0.320	0.009	0.009
2.75	0.449	0.470	0.013	0.014
4.19	0.543	0.585	0.018	0.019
5.57	0.601	0.665	0.023	0.026
6.93	0.640	0.729	0.028	0.032
8.32	0.658	0.772	0.034	0.040
9.70	0.671	0.814	0.039	0.048
11.07	0.683	0.856	0.045	0.056
12.43	0.690	0.895	0.051	0.066

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	10.1
Void volume (ft ³)	0.002773
Pump pressure (psia)	998.5
Pump T (°F)	96.6
Adsorbent mass (lb)	0.1339

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
102.6	146.8	148.5	5.9	5.9
208.1	236.8	242.5	7.0	7.2
398.9	340.4	356.8	9.9	10.4
608.0	412.4	444.1	13.7	14.7
808.0	456.4	505.1	17.5	19.4
1004.8	486.0	553.5	21.5	24.5
1207.0	499.2	586.3	25.7	30.1
1407.3	509.4	617.8	29.9	36.3
1605.7	518.4	649.9	34.2	42.8
1802.3	524.0	679.7	38.4	49.8

Table 39. Methane Adsorption on Wet Fruitland Coal at 319.3 K (System 10 OSU #2, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	9.4
Void volume (m ³)	0.0000790
Pump pressure (MPa)	6.88
Pump T (K)	309.0
Adsorbent mass (g)	60.3
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.74	0.201	0.203	0.008	0.008
1.44	0.316	0.324	0.009	0.010
2.78	0.448	0.470	0.013	0.014
4.15	0.535	0.575	0.018	0.019
5.54	0.594	0.657	0.023	0.025
6.94	0.634	0.722	0.028	0.032
8.33	0.652	0.766	0.034	0.040
9.69	0.672	0.815	0.039	0.048
11.04	0.680	0.852	0.045	0.056
12.41	0.691	0.895	0.051	0.066

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	9.4
Void volume (ft ³)	0.002788
Pump pressure (psia)	998.5
Pump T (°F)	96.6
Adsorbent mass (lb)	0.1329

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
106.9	152.5	154.4	5.9	6.0
209.1	240.0	245.9	7.1	7.2
403.7	339.9	356.5	10.0	10.5
602.0	405.8	436.7	13.6	14.6
804.1	450.7	498.6	17.5	19.3
1006.4	480.9	547.8	21.5	24.5
1207.9	494.7	581.1	25.7	30.2
1405.9	509.9	618.3	29.9	36.3
1601.8	516.0	646.5	34.1	42.8
1800.4	524.1	679.6	38.4	49.8

Table 40. CO₂ Adsorption on Wet Fruitland Coal at 319.3 K (System 11 OSU #1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	5.2
Void volume (m ³)	0.0000774
Pump pressure (MPa)	6.18
Pump T (K)	309.1
Adsorbent mass (g)	65.27
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.70	0.509	0.515	0.043	0.044
1.44	0.719	0.737	0.044	0.045
2.25	0.842	0.878	0.045	0.047
2.93	0.910	0.962	0.047	0.049
3.60	0.965	1.037	0.049	0.052
4.35	1.010	1.106	0.051	0.056
5.06	1.036	1.160	0.054	0.061
5.62	1.048	1.196	0.057	0.065
6.29	1.064	1.246	0.061	0.072
7.33	1.091	1.349	0.070	0.087
8.31	1.052	1.404	0.083	0.110
9.46	1.197	1.905	0.105	0.167
10.55	0.976	2.056	0.177	0.373
11.66	0.772	1.973	0.331	0.846

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	5.2
Void volume (ft ³)	0.002733
Pump pressure (psia)	896.7
Pump T (°F)	96.7
Adsorbent mass (lb)	0.1439

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
101.7	386.4	391.0	32.9	33.3
208.9	545.8	559.6	33.4	34.3
326.5	639.4	666.1	34.4	35.8
425.1	690.6	730.1	35.5	37.5
522.5	732.4	786.8	36.9	39.6
630.4	766.4	839.6	38.8	42.5
733.5	786.4	880.2	41.0	45.9
814.8	795.2	907.4	43.2	49.3
911.6	807.2	945.9	46.4	54.4
1063.6	827.8	1023.8	53.2	65.8
1205.3	798.3	1065.3	62.8	83.8
1371.5	908.2	1446.2	79.8	127.0
1529.5	741.2	1560.8	134.4	283.1
1691.5	585.6	1497.6	250.9	641.8

Table 41. CO₂ Adsorption on Wet Fruitland Coal at 319.3 K (System 11 OSU #2, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	9.1
Void volume (m ³)	0.0000781
Pump pressure (MPa)	6.87
Pump T (K)	309.0
Adsorbent mass (g)	59.4
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.72	0.508	0.514	0.093	0.094
1.44	0.691	0.709	0.094	0.096
2.77	0.898	0.946	0.096	0.101
4.21	0.999	1.091	0.099	0.108
5.49	1.031	1.171	0.105	0.119
6.93	1.024	1.238	0.115	0.139
8.30	0.963	1.283	0.133	0.178
9.55	0.891	1.451	0.173	0.281
10.26	0.906	1.781	0.207	0.406
12.33	0.737	2.046	0.256	0.710

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	9.1
Void volume (ft ³)	0.002758
Pump pressure (psia)	996.3
Pump T (°F)	96.6
Adsorbent mass (lb)	0.1310

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
104.7	385.7	390.4	70.9	71.7
209.4	524.7	538.0	71.1	72.9
401.2	681.7	718.1	72.5	76.4
611.3	758.6	828.0	75.3	82.2
796.6	782.7	889.1	79.4	90.2
1005.1	777.2	939.3	87.2	105.3
1203.6	730.8	974.1	101.1	134.8
1385.2	676.5	1101.6	130.9	213.2
1487.8	687.9	1351.7	156.9	308.2
1789.0	559.1	1552.6	194.2	539.3

Table 42. CO₂ Adsorption on Wet Fruitland Coal at 319.3 K (System 11 OSU #2, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	6.4
Void volume (m ³)	0.0000798
Pump pressure (MPa)	6.87
Pump T (K)	309.0
Adsorbent mass (g)	57.7
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.72	0.503	0.509	0.093	0.094
1.38	0.665	0.681	0.094	0.096
2.75	0.888	0.935	0.095	0.101
4.15	1.000	1.089	0.099	0.108
5.53	1.047	1.190	0.105	0.120
6.93	1.056	1.276	0.115	0.140
8.27	1.055	1.402	0.134	0.178
9.52	1.043	1.687	0.174	0.282
10.66	0.961	2.074	0.225	0.485
12.20	0.855	2.338	0.258	0.707

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	6.4
Void volume (ft ³)	0.002818
Pump pressure (psia)	996.3
Pump T (°F)	96.6
Adsorbent mass (lb)	0.1272

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
104.8	381.4	386.1	70.9	71.7
200.0	504.6	516.8	71.1	72.8
398.3	673.9	709.5	72.5	76.3
601.8	758.9	826.9	75.2	81.9
802.1	794.3	903.5	79.8	90.7
1005.4	801.2	968.4	87.6	105.9
1199.7	800.5	1064.2	101.8	135.4
1381.3	791.3	1280.1	132.2	213.8
1545.4	729.6	1573.8	170.8	368.4
1769.5	648.9	1774.8	196.1	536.3

Table 43. CO₂ Adsorption on Wet Fruitland Coal at 319.3 K (System 11 OSU #2, Run 3)**SI Units**

Cell T (K)	319.3
Moisture content (%)	9.0
Void volume (m ³)	0.0000723
Pump pressure (MPa)	6.56
Pump T (K)	319.3
Adsorbent mass (g)	78.51
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
1.31	0.603	0.617	0.015	0.015
3.06	0.843	0.894	0.020	0.022
4.21	0.916	1.000	0.025	0.028
5.69	0.968	1.107	0.033	0.038
6.95	0.989	1.196	0.042	0.051
8.24	0.993	1.317	0.056	0.074
9.20	1.002	1.513	0.074	0.112
10.45	0.957	1.971	0.074	0.152
12.36	0.726	2.021	0.085	0.237

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	9.0
Void volume (ft ³)	0.002553
Pump pressure (psia)	951.6
Pump T (°F)	115.0
Adsorbent mass (lb)	0.1731

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
189.4	457.8	468.3	11.2	11.4
443.3	640.2	678.7	15.5	16.5
610.4	695.6	759.2	19.2	20.9
825.7	734.3	840.3	25.1	28.7
1007.9	750.4	907.8	31.9	38.5
1195.8	753.9	999.6	42.4	56.2
1335.0	760.4	1148.5	56.1	84.7
1515.9	726.1	1496.4	56.1	115.6
1792.3	551.0	1533.7	64.5	179.6

Table 44. CO₂ Adsorption on Wet Fruitland Coal at 319.3 K (System 11 OSU #2, Run 3)**SI Units**

Cell T (K)	319.3
Moisture content (%)	7.5
Void volume (m ³)	0.0000736
Pump pressure (MPa)	7.25
Pump T (K)	308.4
Adsorbent mass (g)	77.24
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
1.52	0.647	0.664	0.047	0.048
2.94	0.820	0.868	0.052	0.055
4.36	0.918	1.006	0.059	0.065
5.66	0.959	1.097	0.069	0.079
7.09	0.961	1.171	0.084	0.103
8.32	0.953	1.273	0.106	0.142
9.74	0.867	1.480	0.137	0.234
11.06	0.660	1.537	0.167	0.390
12.34	0.478	1.328	0.183	0.509

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	7.5
Void volume (ft ³)	0.002599
Pump pressure (psia)	1051.6
Pump T (°F)	95.4
Adsorbent mass (lb)	0.1703

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
221.0	490.7	503.9	35.6	36.5
426.0	622.8	658.5	39.3	41.5
632.9	696.8	763.7	45.1	49.4
821.6	728.2	832.3	52.4	59.9
1027.7	729.0	888.6	64.1	78.1
1206.9	723.1	966.0	80.7	107.8
1412.2	657.8	1123.4	103.9	177.4
1603.4	500.8	1166.7	126.9	295.6
1790.4	362.6	1007.9	138.9	386.1

Table 45. Adsorption of a 20/80 Mole % Methane/Nitrogen Feed Mixture on Wet Fruitland Coal at 319.3 K (System 12 OSU #1)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	9.7	Methane	0.200
Void volume (m ³)	0.0000751	Nitrogen	0.800
Coal mass (g)	66		
Pump T (K)	309.1		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.86	0.139	0.045	0.045	0.053	0.054	0.098	0.099	0.016	0.016	0.019	0.019	0.031	0.032
1.48	0.144	0.069	0.070	0.080	0.083	0.149	0.153	0.017	0.017	0.019	0.020	0.032	0.032
2.74	0.152	0.109	0.111	0.121	0.130	0.230	0.241	0.018	0.018	0.019	0.020	0.032	0.033
4.13	0.157	0.145	0.148	0.155	0.172	0.300	0.320	0.019	0.019	0.019	0.021	0.032	0.034
5.56	0.161	0.170	0.175	0.170	0.197	0.340	0.372	0.020	0.021	0.020	0.023	0.033	0.036
6.97	0.165	0.191	0.198	0.184	0.222	0.375	0.420	0.022	0.023	0.021	0.025	0.034	0.039
8.32	0.167	0.210	0.220	0.193	0.242	0.403	0.462	0.024	0.026	0.023	0.027	0.036	0.041
9.70	0.170	0.222	0.234	0.200	0.260	0.421	0.495	0.026	0.028	0.024	0.030	0.038	0.044
11.04	0.172	0.234	0.249	0.207	0.281	0.441	0.530	0.027	0.031	0.026	0.033	0.040	0.048
12.42	0.173	0.250	0.269	0.225	0.315	0.474	0.584	0.029	0.033	0.027	0.036	0.042	0.052

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002652
Coal mass (lb)	0.1455
Pump T (°F)	96.7

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
125.2	0.139	33.8	33.9	40.4	41.2	74.2	75.1	12.4	12.5	14.3	14.5	23.6	24.0
214.1	0.144	52.6	53.0	60.8	63.0	113.4	116.0	12.8	13.0	14.3	14.8	24.0	24.5
397.9	0.152	82.9	84.1	92.0	98.5	174.9	182.5	13.3	13.6	14.4	15.3	24.0	25.1
599.1	0.157	110.1	112.5	117.4	130.4	227.5	242.9	14.1	14.5	14.7	16.2	24.4	26.1
807.0	0.161	129.2	133.1	129.2	149.4	258.4	282.5	15.3	16.1	15.3	17.4	25.1	27.5
1010.8	0.165	144.9	150.5	139.9	168.4	284.8	318.9	16.5	17.6	16.1	18.9	26.1	29.3
1207.1	0.167	159.4	166.8	146.4	183.6	305.8	350.5	18.0	19.5	17.1	20.7	27.3	31.3
1406.4	0.170	168.3	177.7	151.5	197.6	319.7	375.3	19.4	21.3	18.2	22.7	28.7	33.7
1601.8	0.172	177.4	189.0	157.1	213.0	334.4	402.0	20.8	23.3	19.4	25.0	30.3	36.4
1801.0	0.173	189.6	204.0	170.5	239.1	360.0	443.1	22.1	25.1	20.8	27.5	31.9	39.3

Table 46. Adsorption of a 40/60 Mole % Methane/Nitrogen Feed Mixture on Wet Fruitland Coal at 319.3 K (System 12 OSU #1)**SI Unit**

Cell T (K)	319.3
Moisture content (%)	9.7
Void volume (m ³)	0.0000751
Coal mass (g)	66
Pump T (K)	309.1

Feed Molar Composition	
Methane	0.400
Nitrogen	0.600

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
1.05	0.312	0.103	0.104	0.045	0.046	0.148	0.150	0.024	0.024	0.013	0.014	0.031	0.031
1.71	0.320	0.150	0.152	0.062	0.066	0.212	0.218	0.024	0.025	0.013	0.014	0.032	0.032
2.79	0.331	0.205	0.210	0.079	0.088	0.284	0.297	0.025	0.026	0.014	0.015	0.032	0.033
3.48	0.336	0.237	0.244	0.088	0.101	0.326	0.344	0.026	0.027	0.014	0.015	0.032	0.034
4.16	0.342	0.262	0.271	0.104	0.121	0.366	0.392	0.026	0.027	0.014	0.016	0.032	0.034
5.53	0.349	0.302	0.316	0.111	0.137	0.413	0.453	0.027	0.029	0.015	0.018	0.033	0.036
6.90	0.354	0.335	0.355	0.119	0.155	0.455	0.511	0.029	0.031	0.017	0.019	0.034	0.039
8.30	0.358	0.363	0.389	0.120	0.168	0.483	0.557	0.031	0.034	0.018	0.022	0.036	0.042
9.62	0.361	0.381	0.414	0.125	0.184	0.507	0.598	0.033	0.037	0.019	0.024	0.038	0.045
11.04	0.364	0.399	0.439	0.125	0.196	0.524	0.635	0.036	0.041	0.021	0.027	0.040	0.049
12.38	0.367	0.410	0.459	0.129	0.212	0.539	0.671	0.038	0.044	0.023	0.030	0.043	0.053

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002652
Coal mass (lb)	0.1455
Pump T (°F)	96.7

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
152.1	0.312	78.3	78.9	33.9	35.1	112.2	114.0	17.9	18.0	10.1	10.3	23.4	23.8
248.7	0.320	113.8	115.3	47.3	50.3	161.1	165.6	18.5	18.7	10.2	10.7	23.9	24.6
404.0	0.331	155.7	159.0	60.1	66.7	215.8	225.7	19.1	19.6	10.5	11.2	24.0	25.1
504.1	0.336	180.1	184.9	67.0	76.6	247.1	261.5	19.5	20.2	10.7	11.6	24.2	25.6
603.3	0.342	199.0	205.7	78.7	91.6	277.8	297.3	19.4	20.2	10.9	12.1	24.4	26.1
802.0	0.349	229.1	239.6	84.5	104.2	313.6	343.8	20.6	21.8	11.6	13.3	25.1	27.5
1001.0	0.354	254.4	269.5	90.5	118.0	345.0	387.5	21.9	23.5	12.5	14.8	26.1	29.3
1203.7	0.358	275.3	295.2	91.3	127.2	366.6	422.4	23.7	25.9	13.7	16.6	27.4	31.6
1394.7	0.361	289.3	314.4	95.2	139.6	384.6	454.0	25.2	28.0	14.7	18.4	28.8	34.0
1601.6	0.364	302.6	333.4	94.9	148.7	397.6	482.1	27.3	30.9	16.1	20.7	30.5	37.0
1795.0	0.367	311.6	348.2	97.8	161.0	409.4	509.2	29.2	33.6	17.3	23.0	32.5	40.4

Table 47. Adsorption of a 60/40 Mole % Methane/Nitrogen Feed Mixture on Wet Fruitland Coal at 319.3 K (System 12 OSU #1)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	9.7	Methane	0.600
Void volume (m ³)	0.0000751	Nitrogen	0.400
Coal mass (g)	66		
Pump T (K)	309.1		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.71	0.524	0.109	0.110	0.030	0.031	0.139	0.140	0.025	0.025	0.009	0.009	0.030	0.031
1.47	0.530	0.192	0.195	0.046	0.049	0.238	0.244	0.026	0.026	0.009	0.009	0.031	0.032
2.76	0.543	0.286	0.295	0.064	0.072	0.351	0.367	0.027	0.027	0.009	0.010	0.031	0.033
4.14	0.551	0.357	0.375	0.075	0.089	0.432	0.463	0.028	0.029	0.010	0.011	0.032	0.034
5.54	0.557	0.412	0.440	0.083	0.105	0.495	0.544	0.029	0.031	0.011	0.013	0.033	0.036
6.91	0.563	0.448	0.487	0.090	0.120	0.538	0.607	0.031	0.033	0.012	0.014	0.034	0.039
8.28	0.567	0.478	0.529	0.091	0.130	0.569	0.659	0.033	0.036	0.014	0.017	0.036	0.042
9.65	0.569	0.498	0.562	0.091	0.139	0.589	0.700	0.035	0.040	0.015	0.019	0.038	0.045
11.04	0.572	0.520	0.598	0.089	0.148	0.609	0.745	0.038	0.044	0.017	0.022	0.041	0.050
12.38	0.574	0.535	0.627	0.089	0.158	0.624	0.784	0.041	0.048	0.018	0.024	0.043	0.054

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002652
Coal mass (lb)	0.1455
Pump T (°F)	96.7

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
102.7	0.524	82.7	83.3	22.7	23.2	105.4	106.6	18.6	18.8	6.6	6.8	23.1	23.3
213.9	0.530	145.7	148.0	35.2	37.2	180.8	185.2	19.8	20.1	6.8	7.0	23.7	24.3
400.5	0.543	217.3	224.0	48.8	54.4	266.1	278.4	20.2	20.8	7.1	7.6	23.8	24.9
600.8	0.551	271.3	284.3	56.6	67.2	327.9	351.5	21.0	22.1	7.7	8.5	24.2	25.9
802.8	0.557	312.8	333.6	63.0	79.5	375.8	413.1	22.0	23.6	8.5	9.6	24.9	27.4
1002.0	0.563	340.0	369.3	68.4	91.1	408.3	460.4	23.2	25.3	9.4	11.0	26.0	29.3
1201.3	0.567	362.7	401.2	69.3	98.8	432.0	500.0	24.8	27.6	10.4	12.6	27.4	31.7
1399.0	0.569	378.3	426.5	68.8	105.2	447.1	531.6	26.7	30.3	11.5	14.3	28.9	34.4
1601.8	0.572	394.7	453.6	67.8	112.0	462.5	565.6	28.8	33.5	12.8	16.3	30.8	37.6
1796.0	0.574	405.7	475.5	67.8	119.7	473.5	595.2	30.9	36.7	14.0	18.4	32.6	41.0

Table 48. Adsorption of a 80/20 Mole % Methane/Nitrogen Feed Mixture on Wet Fruitland Coal at 319.3 K (System 12 OSU #1)**SI Unit**

Cell T (K)	319.3
Moisture content (%)	9.1
Void volume (m ³)	0.0000756
Coal mass (g)	65.5
Pump T (K)	309.1

Feed Molar Composition	
Methane	0.800
Nitrogen	0.200

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.72	0.747	0.158	0.159	0.017	0.017	0.174	0.176	0.028	0.028	0.005	0.005	0.031	0.031
1.37	0.757	0.247	0.251	0.026	0.027	0.273	0.279	0.029	0.030	0.005	0.005	0.032	0.033
2.78	0.764	0.375	0.390	0.033	0.038	0.408	0.427	0.030	0.031	0.005	0.006	0.032	0.034
4.12	0.770	0.454	0.482	0.037	0.045	0.491	0.527	0.031	0.033	0.006	0.007	0.033	0.035
5.56	0.774	0.509	0.553	0.037	0.050	0.547	0.603	0.032	0.035	0.008	0.009	0.034	0.037
6.95	0.779	0.537	0.597	0.041	0.058	0.578	0.655	0.034	0.038	0.009	0.010	0.035	0.040
8.29	0.781	0.563	0.640	0.043	0.065	0.605	0.705	0.036	0.041	0.010	0.012	0.037	0.043
9.67	0.783	0.582	0.679	0.040	0.067	0.623	0.747	0.039	0.045	0.012	0.015	0.039	0.047
11.04	0.784	0.598	0.715	0.037	0.070	0.635	0.785	0.042	0.050	0.014	0.017	0.042	0.052
12.41	0.785	0.613	0.753	0.035	0.074	0.648	0.826	0.045	0.055	0.015	0.020	0.045	0.057

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002670
Coal mass (lb)	0.1444
Pump T (°F)	96.7

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
104.2	0.747	119.6	120.8	12.6	13.0	132.2	133.7	21.4	21.6	3.4	3.5	23.4	23.7
199.4	0.757	187.3	190.9	19.6	20.7	206.9	211.6	22.3	22.7	3.6	3.7	24.4	25.0
403.0	0.764	284.6	295.9	25.0	28.5	309.6	324.4	22.8	23.7	4.1	4.4	24.4	25.6
597.7	0.770	345.0	366.0	27.8	34.1	372.7	400.1	23.4	24.9	4.9	5.4	24.8	26.6
806.8	0.774	386.7	419.7	28.4	38.0	415.0	457.7	24.5	26.6	5.9	6.6	25.6	28.3
1007.3	0.779	407.6	453.1	31.4	44.3	439.0	497.4	25.7	28.6	6.9	8.0	26.7	30.3
1201.7	0.781	427.0	486.1	32.5	49.1	459.5	535.2	27.3	31.1	8.0	9.4	28.1	32.8
1402.3	0.783	441.9	515.6	30.6	51.0	472.5	566.6	29.3	34.3	9.1	11.2	29.8	35.8
1601.6	0.784	453.8	543.0	28.3	52.8	482.1	595.8	31.6	37.9	10.3	13.0	31.8	39.3
1800.0	0.785	465.3	571.3	26.8	55.8	492.1	627.2	34.0	41.9	11.6	15.0	33.8	43.1

Table 49. Adsorption of a 20/80 Mole % Methane/Carbon Dioxide Feed Mixture on Wet Fruitland Coal at 319.3 K (System 13 OSU #1)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	8.2	Methane	0.200
Void volume (m ³)	0.0000760	Carbon Dioxide	0.800
Coal mass (g)	64.9		
Pump T (K)	309.0		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.66	0.334	0.038	0.040	0.364	0.367	0.403	0.407	0.005	0.005	0.026	0.026	0.028	0.028
1.38	0.301	0.054	0.058	0.547	0.557	0.600	0.615	0.006	0.006	0.036	0.037	0.039	0.040
2.78	0.271	0.063	0.074	0.735	0.765	0.798	0.839	0.007	0.007	0.036	0.038	0.039	0.041
4.12	0.256	0.060	0.079	0.833	0.888	0.892	0.966	0.008	0.009	0.037	0.040	0.039	0.042
5.50	0.244	0.057	0.085	0.889	0.976	0.946	1.061	0.010	0.011	0.039	0.043	0.040	0.045
6.92	0.236	0.053	0.092	0.926	1.054	0.979	1.146	0.012	0.014	0.042	0.048	0.043	0.050
8.27	0.231	0.040	0.094	0.957	1.134	0.997	1.228	0.015	0.019	0.047	0.056	0.046	0.057
9.66	0.226	0.036	0.108	0.977	1.223	1.013	1.331	0.021	0.028	0.066	0.083	0.065	0.085
10.86	0.222	0.034	0.127	0.983	1.307	1.017	1.434	0.029	0.042	0.103	0.138	0.102	0.144
11.91	0.217	0.029	0.135	0.911	1.293	0.940	1.428	0.032	0.052	0.119	0.169	0.118	0.179

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002684
Coal mass (lb)	0.1431
Pump T (°F)	96.6

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
96.1	0.334	29.2	30.3	276.5	278.8	305.7	309.1	3.8	3.9	19.4	19.6	21.1	21.4
199.7	0.301	40.6	43.9	415.2	422.7	455.8	466.6	4.5	4.7	27.4	27.9	29.8	30.5
403.0	0.271	47.6	56.1	557.9	580.6	605.5	636.7	5.1	5.5	27.6	28.7	29.5	31.1
597.7	0.256	45.4	59.7	632.0	673.7	677.3	733.4	6.0	6.7	28.3	30.2	29.7	32.2
798.2	0.244	43.3	64.7	674.9	741.0	718.2	805.7	7.3	8.4	29.6	32.5	30.6	34.3
1003.2	0.236	40.0	70.0	702.8	799.9	742.7	869.9	9.0	10.8	31.8	36.3	32.3	37.8
1199.6	0.231	30.7	71.2	726.1	860.9	756.8	932.1	11.3	14.2	35.6	42.4	35.2	43.4
1400.7	0.226	27.5	81.9	741.5	928.4	769.0	1010.4	16.0	21.5	49.9	62.9	49.1	64.5
1575.3	0.222	26.0	96.1	745.8	992.0	771.8	1088.1	21.8	32.0	78.2	104.5	77.8	109.7
1728.1	0.217	22.1	102.6	691.4	981.5	713.5	1084.1	24.6	39.3	90.0	128.4	89.4	135.8

Table 50. Adsorption of a 40/60 Mole % Methane/Carbon Dioxide Feed Mixture on Wet Fruitland Coal at 319.3 K (System 13 OSU #1)**SI Unit**

Cell T (K)	319.3
Moisture content (%)	7.9
Void volume (m ³)	0.0000762
Coal mass (g)	64.7
Pump T (K)	309.0

Feed Molar Composition	
Methane	0.400
Carbon Dioxide	0.600

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.74	0.568	0.087	0.089	0.278	0.280	0.365	0.369	0.016	0.016	0.039	0.040	0.050	0.051
1.36	0.537	0.103	0.109	0.376	0.382	0.479	0.490	0.018	0.018	0.049	0.050	0.061	0.062
2.73	0.508	0.133	0.151	0.559	0.576	0.692	0.726	0.018	0.019	0.050	0.052	0.060	0.063
4.16	0.480	0.152	0.183	0.643	0.676	0.795	0.858	0.018	0.021	0.051	0.053	0.060	0.065
5.54	0.469	0.150	0.197	0.714	0.767	0.864	0.964	0.019	0.023	0.052	0.057	0.060	0.067
6.92	0.459	0.145	0.210	0.759	0.836	0.905	1.046	0.021	0.026	0.055	0.060	0.061	0.071
8.32	0.451	0.132	0.217	0.782	0.885	0.915	1.101	0.023	0.029	0.058	0.066	0.063	0.076
9.63	0.445	0.128	0.236	0.809	0.944	0.938	1.179	0.025	0.034	0.061	0.072	0.065	0.082
11.00	0.440	0.124	0.261	0.837	1.011	0.961	1.272	0.028	0.039	0.065	0.079	0.068	0.090
12.35	0.435	0.110	0.276	0.843	1.059	0.953	1.335	0.031	0.047	0.070	0.090	0.072	0.101

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002691
Coal mass (lb)	0.1426
Pump T (°F)	96.6

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
107.5	0.568	65.9	67.8	211.0	212.5	276.9	280.3	11.9	12.2	30.0	30.2	38.0	38.4
197.8	0.537	77.8	82.4	285.7	289.6	363.5	372.0	13.3	13.9	37.3	37.8	46.0	47.1
396.4	0.508	101.1	114.3	424.2	437.0	525.3	551.3	13.5	14.6	38.3	39.5	45.7	47.9
603.0	0.480	115.2	138.6	487.8	513.0	603.0	651.6	14.0	15.8	38.5	40.5	45.6	49.3
803.8	0.469	114.2	149.6	541.7	581.9	655.8	731.5	14.7	17.3	39.8	43.0	45.8	51.1
1003.6	0.459	110.4	159.5	576.4	634.3	686.8	793.8	15.8	19.4	41.4	45.8	46.5	53.7
1206.9	0.451	100.5	164.4	593.7	671.5	694.1	835.9	17.4	22.3	43.7	49.9	47.6	57.3
1397.4	0.445	97.4	179.0	614.3	716.2	711.7	895.2	19.0	25.5	46.1	54.3	49.2	61.9
1595.6	0.440	94.5	198.3	635.0	767.4	729.5	965.6	21.0	29.8	49.1	60.3	51.6	68.3
1791.3	0.435	83.4	209.5	640.0	803.6	723.4	1013.1	23.6	35.6	53.5	68.6	54.7	76.6

Table 51. Adsorption of a 60/40 Mole % Methane/Carbon Dioxide Feed Mixture on Wet Fruitland Coal at 319.3 K (System 13 OSU #1)**SI Unit**

Cell T (K)	319.3
Moisture content (%)	7.9
Void volume (m ³)	0.0000762
Coal mass (g)	64.7
Pump T (K)	309.0

Feed Molar Composition	
Methane	0.600
Carbon Dioxide	0.400

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.72	0.757	0.124	0.127	0.172	0.173	0.296	0.299	0.020	0.021	0.027	0.027	0.043	0.044
1.40	0.733	0.180	0.188	0.267	0.270	0.447	0.458	0.022	0.023	0.031	0.031	0.049	0.050
2.76	0.709	0.230	0.252	0.395	0.404	0.625	0.656	0.022	0.023	0.033	0.034	0.048	0.051
4.13	0.688	0.258	0.297	0.469	0.487	0.728	0.784	0.022	0.025	0.034	0.036	0.048	0.052
5.55	0.678	0.261	0.320	0.533	0.561	0.794	0.882	0.023	0.027	0.037	0.039	0.049	0.054
6.93	0.665	0.263	0.343	0.554	0.595	0.817	0.938	0.024	0.029	0.038	0.042	0.050	0.057
8.29	0.657	0.246	0.347	0.576	0.628	0.821	0.976	0.025	0.033	0.042	0.046	0.052	0.061
9.65	0.655	0.231	0.361	0.621	0.690	0.852	1.051	0.028	0.037	0.046	0.052	0.054	0.066
11.02	0.648	0.234	0.395	0.637	0.725	0.871	1.119	0.030	0.042	0.049	0.058	0.057	0.073
12.41	0.643	0.220	0.411	0.642	0.747	0.862	1.158	0.033	0.048	0.053	0.065	0.060	0.080

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002691
Coal mass (lb)	0.1426
Pump T (°F)	96.6

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
104.1	0.757	94.1	96.1	130.4	131.0	224.4	227.1	15.4	15.7	20.3	20.4	32.9	33.3
202.7	0.733	136.8	142.7	202.7	204.8	339.5	347.6	16.7	17.3	23.3	23.6	36.9	37.8
400.7	0.709	174.7	191.2	300.0	306.8	474.7	498.0	16.4	17.7	25.0	25.6	36.7	38.5
599.4	0.688	195.9	225.5	356.3	369.7	552.2	595.2	16.6	18.7	25.9	27.0	36.8	39.6
804.6	0.678	198.0	243.2	404.6	426.1	602.5	669.3	17.2	20.1	27.7	29.5	37.2	41.3
1005.1	0.665	199.5	260.3	420.6	451.3	620.2	711.6	18.1	22.1	29.0	31.6	38.0	43.6
1202.9	0.657	186.5	263.6	436.9	477.0	623.4	740.6	19.4	24.7	31.5	35.1	39.2	46.6
1399.6	0.655	175.4	274.1	471.5	523.6	646.9	797.7	21.0	28.0	34.7	39.7	40.8	50.4
1598.1	0.648	177.6	299.7	483.7	550.0	661.3	849.7	22.7	31.8	37.0	43.7	42.9	55.1
1800.3	0.643	167.0	311.7	487.0	567.2	654.0	879.0	25.0	36.8	40.4	49.4	45.4	61.0

Table 52. Adsorption of a 80/20 Mole % Methane/Carbon Dioxide Feed Mixture on Wet Fruitland Coal at 319.3 K (System 13 OSU #1)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	7.9	Methane	0.800
Void volume (m ³)	0.0000762	Carbon Dioxide	0.200
Coal mass (g)	64.7		
Pump T (K)	309.1		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.74	0.904	0.161	0.164	0.086	0.086	0.247	0.250	0.027	0.027	0.015	0.015	0.040	0.040
1.42	0.886	0.246	0.254	0.134	0.135	0.380	0.389	0.029	0.030	0.017	0.017	0.043	0.044
2.76	0.868	0.342	0.365	0.197	0.201	0.540	0.566	0.028	0.030	0.018	0.018	0.043	0.045
4.24	0.856	0.403	0.446	0.243	0.250	0.646	0.697	0.028	0.031	0.019	0.020	0.043	0.046
5.52	0.847	0.441	0.505	0.265	0.277	0.706	0.782	0.029	0.033	0.019	0.021	0.044	0.048
6.91	0.845	0.449	0.540	0.304	0.320	0.753	0.860	0.030	0.035	0.022	0.024	0.045	0.051
8.28	0.840	0.450	0.566	0.320	0.342	0.770	0.907	0.031	0.038	0.024	0.027	0.047	0.055
9.69	0.836	0.451	0.596	0.334	0.362	0.785	0.958	0.033	0.042	0.027	0.031	0.049	0.059
11.01	0.834	0.447	0.623	0.352	0.387	0.800	1.010	0.035	0.047	0.030	0.035	0.051	0.065
12.41	0.831	0.441	0.648	0.354	0.396	0.795	1.044	0.037	0.053	0.032	0.039	0.054	0.071

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002691
Coal mass (lb)	0.1426
Pump T (°F)	96.7

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
107.8	0.904	122.2	124.3	65.3	65.5	187.5	189.8	20.3	20.7	11.7	11.7	30.3	30.6
206.6	0.886	186.3	192.5	101.8	102.6	288.2	295.1	21.7	22.5	12.7	12.8	32.6	33.4
400.5	0.868	259.9	277.2	149.8	152.4	409.7	429.7	21.5	22.9	13.3	13.7	32.5	34.1
615.3	0.856	305.8	338.9	184.4	190.0	490.2	528.9	21.6	23.9	14.2	14.8	32.7	35.3
800.8	0.847	334.5	383.3	201.5	210.3	536.0	593.6	22.2	25.3	14.8	15.7	33.2	36.8
1002.4	0.845	341.2	409.6	230.5	243.1	571.7	652.7	22.5	26.8	16.8	18.3	34.1	38.9
1200.7	0.840	341.6	429.3	242.7	259.4	584.3	688.7	23.5	29.1	18.5	20.5	35.3	41.6
1404.8	0.836	342.4	452.3	253.5	275.0	595.8	727.3	24.8	32.2	20.3	23.2	36.9	45.1
1596.3	0.834	339.4	472.9	267.5	294.0	606.9	766.9	26.2	35.5	22.6	26.4	38.8	49.0
1800.5	0.831	334.9	492.2	268.5	300.5	603.3	792.7	28.1	39.9	24.6	29.8	41.0	53.9

Table 53. Adsorption of a 20/80 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Wet Fruitland Coal at 319.3 K (System 14 OSU #1)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	7.1	Nitrogen	0.200
Void volume (m ³)	0.0000768	Carbon Dioxide	0.800
Coal mass (g)	64.1		
Pump T (K)	309.0		

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.84	0.393	0.004	0.006	0.407	0.411	0.411	0.417	0.012	0.012	0.047	0.047	0.046	0.047
1.43	0.351	0.007	0.011	0.552	0.561	0.559	0.572	0.012	0.012	0.063	0.064	0.062	0.064
2.71	0.306	0.004	0.015	0.739	0.764	0.742	0.779	0.013	0.013	0.063	0.065	0.062	0.065
4.15	0.276	0.007	0.025	0.840	0.890	0.847	0.915	0.013	0.014	0.062	0.066	0.061	0.066
5.58	0.260	0.000	0.028	0.913	0.993	0.913	1.022	0.015	0.017	0.063	0.069	0.062	0.069
6.91	0.247	0.003	0.040	0.938	1.052	0.941	1.092	0.016	0.019	0.064	0.072	0.063	0.073
8.32	0.242	-0.017	0.033	0.974	1.129	0.957	1.162	0.019	0.023	0.068	0.079	0.064	0.078
9.61	0.235	-0.018	0.044	0.978	1.180	0.960	1.224	0.021	0.027	0.072	0.087	0.068	0.086
10.99	0.227	-0.017	0.059	0.947	1.204	0.931	1.263	0.024	0.033	0.078	0.100	0.073	0.099
12.36	0.226	-0.042	0.057	0.996	1.333	0.954	1.390	0.030	0.043	0.089	0.121	0.081	0.118

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002712
Coal mass (lb)	0.1413
Pump T (°F)	96.5

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
121.4	0.393	2.9	4.6	309.0	311.6	311.9	316.2	9.2	9.3	35.7	36.0	34.9	35.3
207.0	0.351	5.0	8.7	419.0	425.7	424.1	434.4	9.1	9.3	47.5	48.3	47.2	48.3
393.4	0.306	2.9	11.4	560.6	579.8	563.5	591.1	9.7	10.2	47.5	49.2	46.8	49.1
601.2	0.276	5.0	19.3	637.9	675.5	642.9	694.9	10.1	11.0	47.3	50.2	46.6	50.4
809.3	0.260	0.2	21.6	693.1	753.8	693.3	775.4	11.2	12.6	48.1	52.4	46.8	52.4
1002.2	0.247	2.1	30.4	712.1	798.3	714.3	828.7	12.1	14.2	48.9	54.9	47.5	55.1
1206.7	0.242	-12.9	24.7	739.0	856.9	726.1	881.6	14.4	17.5	51.9	60.3	48.9	59.4
1393.6	0.235	-13.9	33.0	742.4	895.7	728.4	928.8	16.2	20.6	54.8	66.4	51.3	65.5
1594.5	0.227	-12.7	44.8	719.0	914.2	706.3	959.0	18.6	25.3	59.6	76.2	55.6	75.5
1792.1	0.226	-31.7	43.2	755.7	1011.8	724.0	1055.0	22.8	32.9	67.8	91.6	61.2	89.3

Table 54. Adsorption of a 40/60 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Wet Fruitland Coal at 319.3 K (System 14 OSU #1)**SI Unit**

Cell T (K)	319.3
Moisture content (%)	13.8
Void volume (m ³)	0.0000727
Coal mass (g)	68.7
Pump T (K)	309.0

Feed Molar Composition	
Nitrogen	0.400
Carbon Dioxide	0.600

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.72	0.671	0.016	0.019	0.246	0.247	0.263	0.266	0.017	0.018	0.044	0.044	0.043	0.043
1.38	0.627	0.025	0.031	0.389	0.392	0.414	0.423	0.018	0.018	0.049	0.050	0.049	0.050
2.71	0.576	0.027	0.044	0.577	0.589	0.605	0.633	0.019	0.020	0.050	0.051	0.049	0.051
4.14	0.542	0.025	0.055	0.704	0.729	0.729	0.784	0.020	0.022	0.051	0.053	0.049	0.053
5.55	0.519	0.019	0.063	0.781	0.822	0.800	0.885	0.022	0.024	0.053	0.056	0.049	0.055
6.95	0.501	0.013	0.073	0.831	0.891	0.844	0.963	0.024	0.027	0.055	0.060	0.050	0.058
8.32	0.488	-0.001	0.074	0.860	0.939	0.859	1.013	0.026	0.031	0.058	0.065	0.052	0.061
9.70	0.477	-0.008	0.085	0.885	0.988	0.877	1.072	0.029	0.035	0.062	0.070	0.054	0.066
11.06	0.469	-0.024	0.086	0.888	1.012	0.864	1.098	0.032	0.041	0.066	0.078	0.057	0.072
12.40	0.462	-0.034	0.094	0.892	1.041	0.858	1.135	0.036	0.047	0.072	0.086	0.060	0.079

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002567
Coal mass (lb)	0.1515
Pump T (°F)	96.5

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
105.1	0.671	12.5	14.1	187.1	187.8	199.6	201.9	13.1	13.3	33.1	33.3	32.5	32.9
199.5	0.627	18.7	23.2	295.2	297.8	313.9	321.1	13.3	13.7	37.4	37.8	37.3	38.1
393.4	0.576	20.7	33.2	438.2	447.3	458.9	480.5	14.2	15.0	38.1	39.0	37.0	38.8
600.9	0.542	19.0	41.7	534.3	553.5	553.4	595.2	15.2	16.5	38.9	40.5	37.1	39.9
805.6	0.519	14.2	47.9	592.8	624.0	607.0	671.9	16.5	18.4	40.1	42.6	37.5	41.5
1008.1	0.501	9.8	55.2	630.7	676.0	640.5	731.2	17.9	20.6	41.7	45.2	38.3	43.7
1207.2	0.488	-0.9	56.4	652.6	712.7	651.7	769.1	19.9	23.5	44.2	49.0	39.4	46.5
1406.6	0.477	-6.4	64.4	672.0	749.6	665.6	814.0	21.8	26.7	46.7	53.2	41.0	50.1
1604.6	0.469	-18.2	65.1	673.9	768.3	655.7	833.4	24.4	30.9	50.5	59.0	43.0	54.7
1798.7	0.462	-25.6	71.5	676.7	790.0	651.1	861.5	27.1	35.7	54.4	65.5	45.4	60.1

Table 55. Adsorption of a 60/40 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Wet Fruitland Coal at 319.3 K (System 14 OSU #1)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	13.4	Nitrogen	0.600
Void volume (m ³)	0.0000730	Carbon Dioxide	0.400
Coal mass (g)	68.4		
Pump T (K)	308.9		

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.73	0.852	0.022	0.024	0.154	0.155	0.177	0.179	0.018	0.018	0.035	0.035	0.034	0.035
1.40	0.818	0.038	0.044	0.256	0.257	0.294	0.301	0.018	0.019	0.036	0.037	0.037	0.037
2.72	0.781	0.056	0.072	0.407	0.412	0.463	0.484	0.019	0.020	0.037	0.038	0.036	0.038
4.12	0.756	0.057	0.088	0.519	0.529	0.576	0.617	0.021	0.022	0.039	0.040	0.037	0.040
5.53	0.736	0.055	0.103	0.597	0.615	0.652	0.718	0.022	0.025	0.041	0.043	0.038	0.041
6.92	0.721	0.046	0.112	0.656	0.681	0.702	0.794	0.025	0.028	0.044	0.047	0.039	0.044
8.30	0.708	0.039	0.123	0.693	0.728	0.732	0.851	0.027	0.032	0.047	0.051	0.041	0.047
9.66	0.698	0.027	0.130	0.723	0.768	0.751	0.898	0.030	0.036	0.051	0.056	0.043	0.051
11.03	0.690	0.015	0.138	0.746	0.802	0.761	0.939	0.033	0.041	0.055	0.062	0.045	0.056
12.40	0.682	0.009	0.153	0.764	0.831	0.773	0.984	0.037	0.047	0.060	0.069	0.048	0.061

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002578
Coal mass (lb)	0.1508
Pump T (°F)	96.4

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
105.9	0.852	16.9	18.3	117.2	117.5	134.2	135.8	13.8	14.0	26.4	26.5	26.0	26.3
203.0	0.818	29.1	33.3	194.0	194.9	223.1	228.2	13.8	14.2	27.6	27.8	27.8	28.4
394.7	0.781	42.2	54.8	309.0	312.5	351.2	367.3	14.5	15.3	28.1	28.7	27.7	29.0
598.2	0.756	43.0	66.8	393.8	401.5	436.8	468.3	15.7	17.0	29.6	30.5	28.0	30.0
801.7	0.736	41.7	78.2	453.3	466.4	495.0	544.7	17.0	19.0	31.1	32.6	28.6	31.4
1003.4	0.721	35.3	85.4	497.7	517.1	533.0	602.5	18.8	21.5	33.3	35.5	29.5	33.4
1203.8	0.708	29.7	93.7	526.1	552.5	555.8	646.2	20.6	24.3	35.7	38.7	30.8	35.8
1401.5	0.698	20.7	98.9	549.1	583.0	569.8	681.8	22.9	27.6	38.6	42.7	32.3	38.7
1600.4	0.690	11.4	104.4	566.5	608.4	577.9	712.8	25.3	31.4	42.0	47.4	34.2	42.1
1798.3	0.682	6.7	115.7	580.1	630.9	586.8	746.7	27.8	35.6	45.3	52.3	36.2	46.1

Table 56. Adsorption of a 80/20 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Wet Fruitland Coal at 319.3 K (System 14 OSU #1)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	14.1	Nitrogen	0.799
Void volume (m ³)	0.0000725	Carbon Dioxide	0.201
Coal mass (g)	68.9		
Pump T (K)	309.0		

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.72	0.948	0.036	0.037	0.070	0.070	0.106	0.107	0.018	0.019	0.026	0.026	0.031	0.032
1.43	0.934	0.066	0.070	0.125	0.126	0.191	0.195	0.019	0.019	0.026	0.026	0.032	0.033
2.79	0.917	0.104	0.117	0.211	0.212	0.314	0.329	0.019	0.021	0.027	0.028	0.032	0.034
4.14	0.905	0.126	0.151	0.276	0.278	0.401	0.429	0.020	0.022	0.029	0.029	0.033	0.035
5.55	0.896	0.137	0.177	0.330	0.334	0.467	0.512	0.022	0.025	0.031	0.032	0.034	0.037
6.93	0.888	0.143	0.199	0.373	0.380	0.516	0.579	0.024	0.027	0.033	0.035	0.035	0.039
8.31	0.882	0.140	0.213	0.409	0.419	0.549	0.633	0.026	0.031	0.036	0.039	0.037	0.042
9.67	0.877	0.137	0.229	0.442	0.455	0.579	0.684	0.029	0.036	0.040	0.044	0.039	0.046
11.05	0.872	0.131	0.241	0.463	0.479	0.594	0.720	0.032	0.040	0.045	0.050	0.043	0.052
12.40	0.868	0.125	0.254	0.486	0.505	0.610	0.759	0.035	0.045	0.049	0.055	0.045	0.056

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002560
Coal mass (lb)	0.1519
Pump T (°F)	96.5

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
104.7	0.948	27.1	27.9	53.2	53.2	80.2	81.2	14.0	14.3	19.5	19.6	23.8	24.0
207.3	0.934	49.8	52.9	95.1	95.4	144.9	148.2	14.2	14.7	19.8	19.9	24.6	25.1
405.1	0.917	78.6	88.6	160.0	160.9	238.6	249.5	14.6	15.6	20.5	20.9	24.6	25.7
600.6	0.905	95.4	114.5	209.1	211.1	304.5	325.6	15.4	16.9	21.6	22.3	25.0	26.7
804.9	0.896	104.1	134.5	250.3	253.8	354.4	388.3	16.5	18.7	23.3	24.4	25.7	28.1
1004.8	0.888	108.3	150.9	283.1	288.4	391.3	439.4	17.9	20.9	25.2	26.8	26.7	29.9
1205.2	0.882	106.4	162.0	310.7	318.1	417.0	480.1	19.6	23.5	27.7	29.8	27.9	32.1
1402.6	0.877	104.2	173.9	335.5	345.2	439.7	519.1	22.1	27.1	30.7	33.6	29.4	34.7
1601.9	0.872	99.7	183.0	351.2	363.4	450.9	546.4	24.2	30.6	34.1	38.0	32.3	39.1
1797.9	0.868	94.8	192.9	368.6	383.5	463.4	576.3	26.4	34.3	37.1	42.0	34.0	42.3

Table 57. Nitrogen Adsorption on Wet Illinois #6 Coal at 319.3 K (System 15, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	15.5
Void volume (m ³)	0.0000743
Pump pressure (MPa)	6.87
Pump T (K)	310.8
Adsorbent mass (g)	64.4
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.79	0.021	0.021	0.010	0.010
1.40	0.035	0.036	0.011	0.011
2.77	0.067	0.069	0.013	0.014
4.16	0.091	0.097	0.017	0.018
5.59	0.111	0.120	0.021	0.023
6.92	0.127	0.141	0.025	0.028
8.30	0.139	0.158	0.029	0.033
9.69	0.152	0.177	0.033	0.039
11.04	0.163	0.193	0.037	0.044
12.42	0.175	0.212	0.041	0.050

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	15.5
Void volume (ft ³)	0.002624
Pump pressure (psia)	996.3
Pump T (°F)	99.8
Adsorbent mass (lb)	0.1420

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
114.5	15.9	16.1	7.6	7.7
203.8	26.5	27.0	8.2	8.3
401.5	50.6	52.7	10.1	10.5
603.9	68.9	73.3	12.8	13.6
810.8	83.9	91.3	15.8	17.2
1003.7	96.3	107.1	18.8	20.9
1204.4	105.7	120.0	22.0	25.0
1405.5	115.4	134.0	25.2	29.2
1600.5	123.6	146.7	28.3	33.5
1801.1	132.8	161.2	31.4	38.1

Table 58. Nitrogen Adsorption on Wet Illinois#6 Coal at 319.3 K (System 15, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	14.6
Void volume (m ³)	0.0000745
Pump pressure (MPa)	6.87
Pump T (K)	309.0
Adsorbent mass (g)	63.7
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.69	0.020	0.020	0.010	0.010
1.40	0.037	0.038	0.011	0.011
2.78	0.068	0.071	0.013	0.014
4.31	0.094	0.100	0.017	0.018
5.54	0.111	0.120	0.021	0.023
6.87	0.127	0.141	0.025	0.027
8.27	0.138	0.156	0.029	0.033
9.69	0.153	0.178	0.033	0.039
11.03	0.163	0.193	0.037	0.044
12.40	0.172	0.209	0.041	0.050

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	14.6
Void volume (ft ³)	0.002631
Pump pressure (psia)	996.3
Pump T (°F)	96.6
Adsorbent mass (lb)	0.1404

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
99.9	15.4	15.5	7.7	7.7
202.9	28.3	28.8	8.2	8.4
403.5	51.6	53.8	10.2	10.6
625.5	71.4	76.2	13.1	14.0
803.6	83.9	91.2	15.8	17.1
996.3	96.5	107.2	18.7	20.8
1199.7	104.4	118.5	21.9	24.9
1405.7	116.1	134.8	25.2	29.3
1600.1	123.7	146.9	28.3	33.6
1799.0	130.7	158.6	31.4	38.1

Table 59. Methane Adsorption on Wet Illinois #6 Coal at 319.3 K (System 16, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	13.5
Void volume (m ³)	0.0000747
Pump pressure (MPa)	6.87
Pump T (K)	309.1
Adsorbent mass (g)	62.9
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.69	0.086	0.087	0.008	0.008
1.41	0.146	0.150	0.009	0.009
2.73	0.221	0.232	0.012	0.013
4.17	0.278	0.299	0.017	0.018
5.53	0.317	0.351	0.022	0.024
6.91	0.343	0.391	0.027	0.031
8.31	0.359	0.422	0.033	0.038
9.46	0.379	0.457	0.037	0.045
11.04	0.396	0.496	0.044	0.055
12.47	0.413	0.536	0.049	0.064

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	13.5
Void volume (ft ³)	0.002639
Pump pressure (psia)	996.3
Pump T (°F)	96.7
Adsorbent mass (lb)	0.1387

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
99.8	65.3	66.0	5.8	5.8
204.4	110.9	113.5	6.7	6.8
395.8	167.9	175.9	9.3	9.8
604.5	210.8	226.9	12.9	13.9
801.8	240.8	266.3	16.6	18.4
1001.8	260.7	296.7	20.6	23.4
1206.0	272.7	320.3	24.7	29.0
1371.5	287.4	346.5	28.2	34.0
1600.9	300.3	376.1	33.1	41.4
1807.9	313.1	406.5	37.5	48.7

Table 60. Methane Adsorption on Wet Illinois #6 Coal at 319.3 K (System 16, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	12.6
Void volume (m ³)	0.0000751
Pump pressure (MPa)	6.87
Pump T (K)	309.1
Adsorbent mass (g)	62.2
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.68	0.098	0.099	0.008	0.008
1.40	0.141	0.145	0.009	0.009
2.75	0.219	0.229	0.012	0.013
4.17	0.283	0.304	0.017	0.018
5.56	0.310	0.343	0.022	0.024
6.92	0.337	0.384	0.027	0.031
8.32	0.362	0.425	0.033	0.038
9.67	0.377	0.456	0.038	0.046
11.04	0.388	0.487	0.044	0.055
12.40	0.399	0.517	0.049	0.064

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	12.6
Void volume (ft ³)	0.002653
Pump pressure (psia)	996.3
Pump T (°F)	96.7
Adsorbent mass (lb)	0.1372

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
98.3	74.2	75.0	5.8	5.8
202.6	107.4	109.9	6.7	6.8
398.8	166.0	174.0	9.4	9.8
604.2	214.6	231.0	12.9	13.9
806.5	235.1	260.2	16.7	18.5
1004.0	256.1	291.6	20.6	23.5
1207.2	274.6	322.5	24.8	29.1
1401.9	285.8	346.3	28.9	35.0
1601.7	294.8	369.3	33.1	41.5
1798.7	302.7	392.3	37.3	48.4

Table 61. CO₂ Adsorption on Wet Illinois #6 Coal at 319.3 K (System 17, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	15.8
Void volume (m ³)	0.0000753
Pump pressure (MPa)	6.15
Pump T (K)	309.1
Adsorbent mass (g)	63.86
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.68	0.291	0.294	0.068	0.069
1.46	0.454	0.465	0.068	0.070
2.84	0.616	0.650	0.070	0.074
4.18	0.726	0.791	0.074	0.081
5.56	0.745	0.848	0.080	0.092
6.93	0.819	0.990	0.091	0.110
8.26	0.789	1.048	0.109	0.145
8.74	0.845	1.184	0.120	0.169
9.81	0.841	1.463	0.161	0.281
11.75	0.715	1.850	0.223	0.578

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	15.8
Void volume (ft ³)	0.002659
Pump pressure (psia)	892.7
Pump T (°F)	96.7
Adsorbent mass (lb)	0.1408

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
98.9	220.8	223.3	51.7	52.2
211.2	344.5	353.3	51.9	53.3
412.0	467.8	493.6	53.4	56.4
606.7	550.8	600.7	56.3	61.4
806.4	565.3	643.7	61.0	69.5
1004.8	621.7	751.3	69.2	83.6
1198.5	598.9	795.6	83.0	110.2
1267.1	641.2	898.6	91.4	128.1
1422.4	638.1	1110.6	122.4	213.0
1704.9	542.3	1404.2	169.5	439.0

Table 62. CO₂ Adsorption on Wet Illinois #6 Coal at 319.3 K (System 17, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	15.8
Void volume (m ³)	0.0000754
Pump pressure (MPa)	7.21
Pump T (K)	309.1
Adsorbent mass (g)	63.86
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.67	0.320	0.324	0.112	0.114
1.46	0.434	0.445	0.113	0.115
2.75	0.630	0.664	0.114	0.120
4.17	0.741	0.808	0.117	0.127
5.54	0.746	0.849	0.121	0.138
6.86	0.802	0.965	0.130	0.156
8.30	0.761	1.015	0.147	0.196
9.47	0.782	1.250	0.181	0.290
10.74	0.667	1.464	0.235	0.515
12.54	0.673	1.910	0.270	0.766

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	15.8
Void volume (ft ³)	0.002663
Pump pressure (psia)	1046.1
Pump T (°F)	96.7
Adsorbent mass (lb)	0.1408

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
97.7	243.1	245.9	85.4	86.3
211.3	329.2	337.6	85.5	87.7
398.8	478.5	503.8	86.3	90.9
604.5	562.3	612.9	88.5	96.4
803.4	566.2	644.3	92.1	104.8
995.0	608.5	732.7	98.4	118.5
1203.9	577.6	770.1	111.6	148.8
1373.4	593.9	948.5	137.6	219.8
1557.1	506.5	1111.0	178.1	390.8
1818.2	510.9	1449.6	205.0	581.6

Table 63. CO₂ Adsorption on Wet Illinois #6 Coal at 319.3 K (System 17, Run 3)**SI Units**

Cell T (K)	319.3
Moisture content (%)	4.9
Void volume (m ³)	0.0000725
Pump pressure (MPa)	6.18
Pump T (K)	313.4
Adsorbent mass (g)	69.5
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.61	0.258	0.261	0.050	0.051
1.38	0.415	0.425	0.051	0.052
2.73	0.572	0.602	0.052	0.055
4.16	0.693	0.756	0.056	0.061
5.48	0.751	0.853	0.061	0.069
6.90	0.805	0.972	0.069	0.084
8.29	0.795	1.060	0.085	0.113
9.28	0.752	1.152	0.106	0.163
10.35	0.674	1.354	0.091	0.183
12.04	0.586	1.573	0.104	0.280

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	4.9
Void volume (ft ³)	0.002561
Pump pressure (psia)	896.6
Pump T (°F)	104.4
Adsorbent mass (lb)	0.1532

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
88.7	195.9	197.9	38.3	38.7
200.4	314.8	322.4	38.6	39.5
396.4	434.3	457.1	39.7	41.8
604.0	526.1	573.5	42.3	46.1
795.4	569.8	647.1	46.1	52.3
1000.9	611.1	737.4	52.7	63.6
1202.6	603.7	804.2	64.3	85.7
1345.9	570.6	874.5	80.7	123.7
1500.6	511.4	1027.8	69.2	139.1
1746.5	444.7	1194.1	79.3	212.8

Table 64. Adsorption of a 20/80 Mole % Methane/Nitrogen Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 18)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	22.9	Methane	0.194
Void volume (m ³)	0.0000764	Nitrogen	0.806
Coal mass (g)	58.7		
Pump T (K)	308.8		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.70	0.178	0.013	0.013	0.020	0.020	0.033	0.034	0.019	0.019	0.026	0.027	0.041	0.042
1.38	0.179	0.022	0.022	0.026	0.027	0.048	0.049	0.022	0.023	0.025	0.026	0.042	0.043
2.75	0.181	0.039	0.039	0.048	0.051	0.086	0.090	0.022	0.022	0.026	0.027	0.042	0.044
4.32	0.182	0.055	0.057	0.063	0.069	0.118	0.126	0.024	0.025	0.026	0.029	0.043	0.046
5.58	0.183	0.066	0.068	0.069	0.080	0.135	0.148	0.026	0.028	0.027	0.031	0.044	0.048
6.89	0.184	0.076	0.079	0.079	0.094	0.154	0.173	0.028	0.030	0.028	0.033	0.045	0.051
8.26	0.184	0.084	0.088	0.084	0.104	0.168	0.192	0.030	0.033	0.030	0.036	0.048	0.054
9.66	0.184	0.095	0.101	0.085	0.110	0.180	0.211	0.034	0.038	0.032	0.040	0.050	0.059
11.01	0.184	0.106	0.113	0.089	0.121	0.195	0.234	0.037	0.042	0.034	0.043	0.053	0.063
12.45	0.185	0.109	0.118	0.095	0.134	0.204	0.252	0.039	0.045	0.037	0.048	0.056	0.069

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002699
Coal mass (lb)	0.1294
Pump T (°F)	96.2

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
101.4	0.178	10.1	10.2	15.0	15.3	25.2	25.4	14.3	14.4	19.8	20.1	31.2	31.6
199.5	0.179	16.8	16.9	19.5	20.2	36.3	37.1	17.0	17.2	19.1	19.7	31.7	32.4
398.7	0.181	29.3	29.8	36.1	38.4	65.4	68.3	16.6	17.1	19.5	20.7	31.8	33.2
627.1	0.182	41.8	43.0	47.5	52.7	89.3	95.6	18.2	18.9	19.9	21.9	32.4	34.7
809.0	0.183	49.9	51.6	52.6	60.4	102.5	112.1	19.8	20.9	20.5	23.3	33.3	36.4
999.3	0.184	57.3	59.9	59.9	71.2	117.2	131.1	21.0	22.5	21.6	25.2	34.5	38.6
1197.6	0.184	63.7	67.1	63.7	78.7	127.4	145.8	22.9	24.9	22.9	27.5	36.1	41.3
1401.6	0.184	72.0	76.3	64.5	83.8	136.5	160.2	25.8	28.5	24.2	30.1	37.9	44.5
1596.5	0.184	80.5	86.0	67.3	91.7	147.8	177.6	28.4	31.9	25.8	33.0	40.0	48.0
1806.2	0.185	83.0	89.7	72.0	101.5	155.0	191.1	29.9	34.3	27.7	36.6	42.3	52.1

Table 65. Adsorption of a 40/60 Mole % Methane/Nitrogen Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 18)**SI Unit**

Cell T (K)	319.3
Moisture content (%)	22.9
Void volume (m ³)	0.0000764
Coal mass (g)	58.7
Pump T (K)	308.4

Feed Molar Composition	
Methane	0.398
Nitrogen	0.602

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.71	0.372	0.027	0.027	0.011	0.012	0.038	0.039	0.028	0.028	0.016	0.016	0.036	0.037
1.42	0.374	0.050	0.051	0.021	0.022	0.071	0.072	0.028	0.029	0.016	0.016	0.037	0.038
2.79	0.379	0.082	0.084	0.037	0.040	0.119	0.124	0.028	0.029	0.016	0.017	0.037	0.039
4.17	0.380	0.106	0.110	0.044	0.051	0.151	0.161	0.030	0.031	0.017	0.019	0.038	0.041
5.54	0.381	0.129	0.136	0.045	0.055	0.174	0.191	0.033	0.035	0.019	0.021	0.040	0.043
6.90	0.382	0.148	0.157	0.046	0.060	0.193	0.217	0.037	0.039	0.021	0.024	0.042	0.047
8.30	0.382	0.165	0.177	0.044	0.064	0.209	0.241	0.041	0.045	0.023	0.028	0.044	0.051
9.67	0.383	0.177	0.192	0.042	0.067	0.219	0.259	0.045	0.050	0.025	0.031	0.047	0.056
11.04	0.385	0.185	0.205	0.048	0.078	0.233	0.283	0.047	0.054	0.028	0.035	0.050	0.061
12.52	0.385	0.200	0.224	0.050	0.089	0.251	0.313	0.051	0.059	0.030	0.040	0.054	0.067

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002699
Coal mass (lb)	0.1294
Pump T (°F)	95.4

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
102.5	0.372	20.4	20.5	8.7	8.9	29.1	29.4	21.1	21.2	11.9	12.1	27.4	27.7
206.0	0.374	38.0	38.4	15.8	16.6	53.8	55.0	21.6	21.9	12.0	12.4	28.0	28.7
405.3	0.379	61.9	63.5	28.1	30.7	90.0	94.2	21.3	21.9	12.4	13.3	28.2	29.5
605.2	0.380	80.5	83.6	33.8	38.8	114.3	122.4	22.7	23.7	13.1	14.5	28.9	30.9
803.7	0.381	98.1	103.0	34.2	42.1	132.3	145.1	25.3	26.8	14.3	16.2	30.0	32.9
1001.2	0.382	112.1	119.1	34.6	45.8	146.7	164.9	27.8	29.9	15.7	18.3	31.5	35.4
1204.1	0.382	125.2	134.5	33.2	48.2	158.4	182.8	30.9	33.8	17.5	21.0	33.4	38.6
1403.0	0.383	134.1	145.8	32.1	50.9	166.2	196.7	33.9	37.8	19.3	23.9	35.6	42.1
1600.5	0.385	140.7	155.3	36.2	59.5	176.8	214.8	35.9	40.7	20.9	26.6	37.9	46.1
1815.7	0.385	152.1	170.3	38.3	67.4	190.3	237.8	38.9	45.1	22.9	30.2	40.7	50.9

Table 66. Adsorption of a 60/40 Mole % Methane/Nitrogen Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 18)**SI Unit**

Cell T (K)	319.2	Feed Molar Composition	
Moisture content (%)	22.9	Methane	0.599
Void volume (m ³)	0.0000766	Nitrogen	0.401
Coal mass (g)	58.7		
Pump T (K)	309.1		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.70	0.574	0.047	0.048	0.014	0.014	0.061	0.062	0.028	0.028	0.010	0.010	0.035	0.035
1.40	0.573	0.083	0.085	0.017	0.018	0.101	0.103	0.031	0.032	0.010	0.011	0.036	0.037
2.81	0.579	0.131	0.135	0.027	0.030	0.158	0.165	0.032	0.033	0.011	0.012	0.036	0.038
4.15	0.581	0.163	0.171	0.029	0.035	0.192	0.206	0.033	0.035	0.012	0.014	0.037	0.040
5.64	0.582	0.196	0.210	0.025	0.035	0.222	0.244	0.037	0.040	0.015	0.016	0.039	0.043
6.93	0.583	0.217	0.235	0.024	0.037	0.241	0.272	0.040	0.044	0.016	0.019	0.041	0.046
8.30	0.584	0.240	0.264	0.021	0.038	0.260	0.302	0.044	0.049	0.019	0.022	0.044	0.051
9.66	0.584	0.255	0.285	0.013	0.034	0.268	0.320	0.050	0.056	0.022	0.026	0.047	0.056
11.10	0.585	0.269	0.307	0.011	0.038	0.280	0.344	0.054	0.063	0.024	0.031	0.050	0.062
12.53	0.586	0.282	0.327	0.009	0.041	0.291	0.368	0.059	0.070	0.027	0.035	0.054	0.069

English Engineering Unit

Cell T (°F)	114.9
Void volume (ft ³)	0.002706
Coal mass (lb)	0.1294
Pump T (°F)	96.8

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
101.0	0.574	36.0	36.3	10.3	10.6	46.4	46.9	21.2	21.4	7.7	7.9	26.5	26.8
202.5	0.573	63.2	64.2	13.1	13.9	76.3	78.0	23.5	23.9	8.0	8.2	27.3	28.0
407.2	0.579	99.5	102.7	20.1	22.5	119.6	125.2	24.0	24.8	8.5	9.0	27.5	28.9
601.5	0.581	123.9	130.0	22.0	26.4	145.9	156.5	25.4	26.7	9.4	10.3	28.2	30.3
817.5	0.582	149.1	159.1	19.2	26.3	168.3	185.4	28.2	30.2	11.0	12.4	29.6	32.6
1004.9	0.583	164.7	178.5	18.3	28.1	182.9	206.6	30.5	33.3	12.5	14.4	31.1	35.2
1204.1	0.584	181.8	200.3	15.7	28.9	197.6	229.2	33.6	37.4	14.3	16.9	33.2	38.5
1401.3	0.584	193.5	216.4	9.9	26.1	203.4	242.5	37.6	42.5	16.6	20.1	35.5	42.3
1609.4	0.585	204.3	232.7	8.5	28.6	212.8	261.3	41.1	47.5	18.6	23.2	38.2	46.9
1818.0	0.586	213.8	248.1	7.1	31.3	220.8	279.4	44.9	53.0	20.7	26.6	41.1	52.0

Table 67. Adsorption of a 80/20 Mole % Methane/Nitrogen Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 18)**SI Unit**

Cell T (K)	319.3
Moisture content (%)	22.9
Void volume (m ³)	0.0000766
Coal mass (g)	58.7
Pump T (K)	309.0

Feed Molar Composition	
Methane	0.792
Nitrogen	0.208

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.68	0.773	0.065	0.066	0.007	0.007	0.072	0.073	0.035	0.035	0.006	0.006	0.038	0.038
1.40	0.776	0.117	0.120	0.013	0.014	0.131	0.134	0.036	0.037	0.006	0.006	0.040	0.041
2.79	0.778	0.176	0.183	0.015	0.017	0.190	0.200	0.037	0.039	0.007	0.008	0.040	0.042
4.21	0.780	0.214	0.228	0.015	0.019	0.229	0.246	0.039	0.041	0.009	0.010	0.041	0.044
5.53	0.781	0.249	0.270	0.017	0.023	0.266	0.293	0.041	0.044	0.010	0.011	0.042	0.046
6.89	0.782	0.273	0.303	0.013	0.021	0.286	0.324	0.044	0.049	0.012	0.014	0.044	0.050
8.27	0.782	0.299	0.338	0.008	0.019	0.307	0.358	0.048	0.054	0.015	0.017	0.047	0.055
9.66	0.782	0.314	0.363	0.002	0.016	0.316	0.379	0.053	0.061	0.017	0.021	0.050	0.060
11.04	0.783	0.327	0.388	0.003	0.020	0.330	0.408	0.056	0.067	0.019	0.024	0.053	0.066
12.48	0.784	0.323	0.393	-0.003	0.017	0.321	0.410	0.062	0.076	0.022	0.028	0.057	0.073

English Engineering Unit

Cell T (°F)	115.1
Void volume (ft ³)	0.002706
Coal mass (lb)	0.1294
Pump T (°F)	96.5

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
99.3	0.773	49.5	49.9	5.2	5.3	54.6	55.2	26.4	26.6	4.5	4.5	28.9	29.2
203.7	0.776	89.1	90.9	10.1	10.7	99.2	101.5	27.2	27.8	4.7	4.8	30.1	30.8
405.3	0.778	133.5	138.9	11.0	12.6	144.5	151.4	28.3	29.5	5.5	5.8	30.2	31.7
610.3	0.780	162.5	172.7	11.2	14.1	173.7	186.8	29.6	31.4	6.6	7.2	30.9	33.2
802.1	0.781	189.0	205.1	12.6	17.1	201.6	222.3	30.9	33.5	7.8	8.7	31.9	35.2
998.6	0.782	207.2	229.7	10.0	16.3	217.2	246.0	33.3	36.9	9.3	10.7	33.5	37.9
1199.2	0.782	226.6	256.8	6.4	14.8	233.0	271.5	36.3	41.2	11.1	13.1	35.5	41.4
1400.7	0.782	238.3	275.9	1.5	12.0	239.8	287.9	39.9	46.3	13.1	15.8	37.9	45.5
1601.6	0.783	248.0	294.6	2.2	15.1	250.2	309.7	42.8	51.0	14.6	18.2	40.6	50.2
1810.1	0.784	245.4	298.5	-2.0	12.7	243.4	311.2	47.0	57.6	16.8	21.5	43.6	55.7

Table 68. Adsorption of a 20/80 Mole % Methane/Carbon Dioxide Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 19)**SI Unit**

Cell T (K)	319.4	Feed Molar Composition	
Moisture content (%)	21.0	Methane	0.233
Void volume (m ³)	0.0000634	Carbon Dioxide	0.767
Coal mass (g)	75.4		
Pump T (K)	313.8		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.72	0.375	0.020	0.021	0.222	0.224	0.242	0.245	0.011	0.012	0.043	0.043	0.045	0.046
1.40	0.346	0.031	0.034	0.341	0.347	0.372	0.381	0.012	0.013	0.059	0.060	0.063	0.065
2.90	0.326	0.027	0.036	0.511	0.530	0.538	0.567	0.014	0.015	0.061	0.064	0.063	0.066
4.20	0.302	0.035	0.050	0.558	0.593	0.593	0.643	0.015	0.017	0.061	0.065	0.063	0.068
5.54	0.293	0.028	0.051	0.629	0.686	0.657	0.737	0.017	0.019	0.063	0.068	0.063	0.071
6.94	0.282	0.027	0.059	0.650	0.732	0.677	0.791	0.019	0.022	0.064	0.072	0.064	0.075
8.35	0.271	0.025	0.065	0.622	0.730	0.647	0.796	0.021	0.027	0.067	0.079	0.066	0.081
9.74	0.262	0.030	0.082	0.605	0.750	0.635	0.832	0.023	0.031	0.069	0.087	0.069	0.090
11.09	0.257	0.020	0.081	0.548	0.722	0.568	0.803	0.028	0.041	0.076	0.101	0.073	0.103
12.51	0.252	0.018	0.092	0.514	0.734	0.532	0.826	0.032	0.051	0.083	0.120	0.079	0.123

English Engineering Unit

Cell T (°F)	115.2
Void volume (ft ³)	0.002239
Coal mass (lb)	0.1662
Pump T (°F)	105.2

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
103.8	0.375	15.0	15.8	168.5	169.9	183.5	185.7	8.7	8.8	32.6	32.8	34.3	34.7
203.0	0.346	23.3	25.6	259.1	263.6	282.4	289.2	9.3	9.7	44.8	45.6	48.0	49.1
420.9	0.326	20.5	27.7	387.5	402.3	408.0	430.0	11.0	11.7	46.4	48.3	47.6	50.1
609.5	0.302	26.7	38.1	423.6	450.2	450.3	488.3	11.5	12.7	46.1	49.0	47.5	51.5
804.0	0.293	21.2	39.0	477.6	520.4	498.8	559.4	12.9	14.7	47.5	51.8	47.8	53.6
1005.9	0.282	20.5	45.0	493.3	555.6	513.8	600.6	14.2	16.9	48.6	54.9	48.5	56.7
1211.7	0.271	19.0	49.7	471.8	554.4	490.7	604.1	15.9	20.1	50.5	59.6	49.9	61.4
1412.8	0.262	23.0	62.4	458.9	569.5	482.0	631.9	17.6	23.8	52.6	65.7	52.1	68.4
1607.9	0.257	15.4	61.2	415.9	548.3	431.3	609.5	21.2	30.9	57.4	76.5	55.4	78.3
1814.3	0.252	13.8	70.0	390.0	557.1	403.8	627.1	24.3	39.1	62.7	90.8	59.9	93.0

Table 69. Adsorption of a 40/60 Mole % Methane/Carbon Dioxide Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 19)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	21.0	Methane	0.398
Void volume (m ³)	0.0000634	Carbon Dioxide	0.602
Coal mass (g)	75.4		
Pump T (K)	314.3		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.71	0.579	0.033	0.034	0.167	0.168	0.200	0.202	0.013	0.014	0.034	0.034	0.037	0.038
1.45	0.542	0.049	0.053	0.260	0.264	0.309	0.316	0.015	0.015	0.040	0.041	0.045	0.046
2.81	0.513	0.060	0.072	0.376	0.387	0.437	0.459	0.016	0.017	0.041	0.043	0.045	0.047
4.23	0.500	0.051	0.072	0.467	0.488	0.518	0.560	0.018	0.020	0.044	0.047	0.045	0.049
5.68	0.480	0.058	0.090	0.502	0.536	0.560	0.626	0.020	0.023	0.046	0.049	0.046	0.052
6.97	0.465	0.065	0.108	0.514	0.563	0.580	0.671	0.021	0.025	0.047	0.052	0.048	0.055
8.35	0.454	0.077	0.133	0.528	0.596	0.605	0.729	0.023	0.029	0.049	0.056	0.050	0.060
9.86	0.445	0.078	0.152	0.540	0.632	0.618	0.785	0.026	0.035	0.053	0.063	0.053	0.068
11.08	0.441	0.063	0.150	0.534	0.645	0.598	0.795	0.030	0.042	0.059	0.073	0.057	0.076
12.70	0.436	0.057	0.170	0.550	0.696	0.607	0.866	0.035	0.053	0.067	0.088	0.063	0.090

English Engineering Unit

Cell T (°F)	115.1
Void volume (ft ³)	0.002239
Coal mass (lb)	0.1662
Pump T (°F)	106.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
103.1	0.579	24.7	25.7	126.7	127.5	151.4	153.2	10.1	10.3	25.4	25.6	28.4	28.7
210.6	0.542	36.8	40.0	197.5	200.2	234.3	240.2	11.0	11.4	30.4	30.9	34.3	35.1
407.0	0.513	45.8	54.5	285.6	293.8	331.5	348.3	12.0	12.9	31.4	32.4	34.1	35.9
612.9	0.500	38.8	55.0	354.1	370.2	393.0	425.2	13.7	15.2	33.7	35.4	34.3	37.2
823.2	0.480	44.2	68.4	380.7	407.0	424.8	475.4	14.9	17.2	34.6	37.2	35.0	39.2
1011.5	0.465	49.5	81.8	390.4	427.5	439.9	509.3	16.2	19.3	35.6	39.5	36.1	41.8
1211.3	0.454	58.1	101.0	400.8	452.5	458.9	553.5	17.6	22.0	37.1	42.5	37.8	45.6
1430.1	0.445	59.3	115.7	409.7	479.9	469.0	595.6	19.9	26.4	40.2	48.1	40.4	51.4
1607.2	0.441	48.0	114.0	405.6	489.5	453.5	603.6	22.9	31.8	44.7	55.4	43.3	57.6
1842.7	0.436	43.6	129.2	417.2	528.1	460.8	657.3	26.8	40.0	50.7	66.5	47.8	68.2

Table 70. Adsorption of a 60/40 Mole % Methane/Carbon Dioxide Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System19)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	21.0	Methane	0.597
Void volume (m ³)	0.0000634	Carbon Dioxide	0.403
Coal mass (g)	75.4		
Pump T (K)	314.7		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.74	0.779	0.045	0.046	0.115	0.115	0.160	0.162	0.017	0.017	0.029	0.029	0.036	0.036
1.40	0.760	0.067	0.071	0.187	0.189	0.254	0.260	0.018	0.019	0.033	0.033	0.040	0.041
2.73	0.738	0.077	0.090	0.290	0.295	0.367	0.385	0.020	0.021	0.036	0.037	0.040	0.042
4.28	0.710	0.092	0.117	0.355	0.366	0.447	0.483	0.021	0.024	0.038	0.039	0.041	0.044
5.62	0.696	0.097	0.136	0.404	0.421	0.501	0.557	0.023	0.027	0.040	0.042	0.041	0.046
6.95	0.683	0.106	0.160	0.435	0.460	0.541	0.621	0.025	0.030	0.042	0.046	0.043	0.049
8.29	0.670	0.111	0.180	0.436	0.469	0.547	0.649	0.028	0.034	0.044	0.049	0.045	0.053
9.69	0.661	0.111	0.196	0.440	0.484	0.551	0.680	0.031	0.040	0.048	0.055	0.047	0.059
11.02	0.653	0.114	0.215	0.431	0.485	0.544	0.700	0.034	0.046	0.051	0.061	0.051	0.065
12.49	0.643	0.127	0.245	0.401	0.467	0.528	0.712	0.038	0.054	0.054	0.068	0.055	0.073

English Engineering Unit

Cell T (°F)	115.1
Void volume (ft ³)	0.002239
Coal mass (lb)	0.1662
Pump T (°F)	106.8

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
108.0	0.779	33.9	35.0	87.3	87.6	121.2	122.7	13.0	13.3	22.2	22.4	27.2	27.5
203.6	0.760	50.7	54.2	142.2	143.3	192.9	197.5	13.8	14.4	25.1	25.4	30.5	31.2
395.5	0.738	58.5	68.5	220.3	223.8	278.8	292.3	15.0	16.0	27.6	28.3	30.4	31.9
621.3	0.710	69.6	89.0	269.7	277.7	339.3	366.7	16.2	18.1	28.7	29.9	30.8	33.3
815.3	0.696	73.3	103.1	306.6	319.6	380.0	422.7	17.6	20.3	30.3	32.2	31.4	35.0
1008.6	0.683	80.2	121.6	330.2	349.4	410.4	471.0	19.1	22.8	31.8	34.5	32.5	37.3
1202.9	0.670	84.3	136.5	330.6	356.3	415.0	492.7	20.9	26.0	33.5	37.5	34.0	40.4
1405.2	0.661	84.3	149.0	334.0	367.2	418.3	516.2	23.3	30.2	36.3	41.8	36.0	44.5
1598.2	0.653	86.3	163.1	327.0	367.9	413.3	530.9	25.8	35.0	39.0	46.5	38.4	49.3
1810.8	0.643	96.3	185.9	304.5	354.2	400.8	540.1	28.6	40.9	41.3	51.4	41.4	55.8

Table 71. Adsorption of a 80/20 Mole % Methane/Carbon Dioxide Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 19)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	21.0	Methane	0.766
Void volume (m ³)	0.0000634	Carbon Dioxide	0.234
Coal mass (g)	75.4		
Pump T (K)	314.5		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.91	0.875	0.080	0.082	0.072	0.072	0.152	0.154	0.024	0.025	0.022	0.022	0.040	0.041
1.54	0.875	0.103	0.108	0.112	0.113	0.215	0.221	0.025	0.026	0.026	0.027	0.043	0.044
2.76	0.869	0.123	0.136	0.175	0.177	0.299	0.313	0.025	0.027	0.031	0.031	0.043	0.045
4.22	0.840	0.167	0.191	0.192	0.197	0.360	0.388	0.026	0.029	0.029	0.030	0.043	0.047
5.58	0.838	0.167	0.204	0.237	0.244	0.404	0.448	0.027	0.032	0.033	0.035	0.044	0.049
6.91	0.825	0.186	0.235	0.237	0.247	0.422	0.482	0.029	0.035	0.033	0.036	0.045	0.052
8.15	0.819	0.196	0.259	0.243	0.257	0.439	0.516	0.031	0.038	0.034	0.038	0.047	0.055
9.66	0.819	0.184	0.268	0.282	0.301	0.466	0.569	0.034	0.044	0.040	0.046	0.049	0.060
11.02	0.809	0.202	0.300	0.254	0.277	0.456	0.577	0.036	0.049	0.040	0.048	0.052	0.065
12.43	0.803	0.210	0.325	0.243	0.272	0.453	0.597	0.040	0.057	0.043	0.052	0.055	0.072

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002239
Coal mass (lb)	0.1662
Pump T (°F)	106.5

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
131.6	0.875	60.8	62.4	54.3	54.5	115.2	116.9	18.2	18.6	16.7	16.9	30.3	30.8
223.7	0.875	78.3	82.0	85.2	85.8	163.5	167.8	18.9	19.6	20.0	20.3	32.8	33.6
400.8	0.869	93.7	103.3	133.0	134.5	226.7	237.8	18.8	20.3	23.2	23.8	32.7	34.3
612.2	0.840	126.8	144.8	146.1	149.5	272.9	294.3	19.9	22.2	21.7	22.6	33.0	35.6
809.5	0.838	126.9	154.9	179.6	185.0	306.4	339.8	20.7	24.0	24.9	26.4	33.6	37.2
1001.9	0.825	141.1	178.7	179.6	187.5	320.6	366.2	22.0	26.5	25.0	27.2	34.5	39.4
1182.4	0.819	148.8	196.8	184.4	195.0	333.2	391.8	23.4	29.2	26.2	29.0	35.6	41.9
1400.9	0.819	139.5	203.4	213.9	228.1	353.4	431.5	25.5	33.3	30.7	35.0	37.3	45.5
1597.7	0.809	153.4	227.9	192.7	210.4	346.2	438.3	27.7	37.5	30.7	36.2	39.2	49.7
1803.4	0.803	159.1	246.8	184.7	206.1	343.7	453.0	30.3	42.9	32.4	39.7	41.5	54.7

Table 72. Adsorption of a 20/80 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 20)**SI Unit**

Cell T (K)	319.3	Feed Molar Composition	
Moisture content (%)	4.9	Nitrogen	0.198
Void volume (m ³)	0.0000689	Carbon Dioxide	0.802
Coal mass (g)	72.85		
Pump T (K)	315.6		

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.73	0.353	0.002	0.003	0.219	0.221	0.221	0.224	0.008	0.008	0.030	0.030	0.029	0.029
1.41	0.317	0.004	0.007	0.335	0.340	0.339	0.347	0.007	0.008	0.039	0.040	0.039	0.040
2.91	0.286	-0.001	0.007	0.497	0.516	0.497	0.523	0.008	0.009	0.040	0.041	0.039	0.041
4.28	0.268	-0.004	0.009	0.592	0.629	0.588	0.638	0.009	0.010	0.040	0.043	0.039	0.042
5.56	0.257	-0.009	0.011	0.652	0.709	0.643	0.720	0.010	0.012	0.041	0.045	0.039	0.044
6.87	0.247	-0.013	0.014	0.696	0.779	0.684	0.793	0.012	0.014	0.043	0.048	0.041	0.047
8.29	0.236	-0.007	0.029	0.707	0.823	0.700	0.851	0.013	0.016	0.046	0.053	0.043	0.053
9.57	0.229	-0.004	0.041	0.712	0.864	0.708	0.905	0.015	0.019	0.050	0.060	0.047	0.060
10.95	0.222	0.000	0.056	0.685	0.878	0.685	0.934	0.018	0.025	0.056	0.072	0.053	0.072
12.40	0.217	0.001	0.068	0.643	0.884	0.644	0.951	0.022	0.032	0.067	0.092	0.063	0.093

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002433
Coal mass (lb)	0.1606
Pump T (°F)	108.5

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
106.1	0.353	1.4	2.1	166.4	167.8	167.8	169.8	5.7	5.8	22.6	22.8	22.0	22.3
203.9	0.317	3.4	5.4	254.1	258.3	257.5	263.7	5.6	5.8	29.6	30.1	29.5	30.2
422.6	0.286	-0.4	5.3	377.5	391.9	377.0	397.2	6.4	6.7	30.0	31.2	29.3	30.8
621.2	0.268	-3.3	6.8	449.5	477.2	446.2	484.0	7.0	7.6	30.5	32.4	29.4	31.9
806.6	0.257	-6.7	8.1	495.1	538.2	488.3	546.3	7.9	8.8	31.3	34.1	29.9	33.5
996.0	0.247	-9.6	10.9	528.5	591.1	518.9	601.9	8.9	10.3	32.7	36.7	30.9	35.9
1202.3	0.236	-5.2	21.8	536.8	624.4	531.6	646.2	10.1	12.2	34.7	40.5	32.9	39.9
1388.4	0.229	-3.2	31.1	540.8	656.1	537.6	687.2	11.5	14.8	37.7	45.9	35.7	45.6
1588.3	0.222	0.3	42.3	519.6	666.7	520.0	709.0	13.6	18.7	42.5	54.8	40.3	54.9
1799.0	0.217	0.7	51.3	487.9	670.8	488.7	722.1	16.3	24.5	50.5	69.9	47.8	70.7

Table 73. Adsorption of a 40/60 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 20)**SI Unit**

Cell T (K)	319.2	Feed Molar Composition	
Moisture content (%)	4.9	Nitrogen	0.417
Void volume (m ³)	0.0000689	Carbon Dioxide	0.583
Coal mass (g)	72.85		
Pump T (K)	314.2		

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.83	0.639	0.002	0.004	0.168	0.169	0.170	0.172	0.014	0.015	0.034	0.034	0.031	0.031
1.48	0.608	0.002	0.006	0.254	0.257	0.256	0.262	0.015	0.015	0.038	0.038	0.035	0.036
2.70	0.568	0.001	0.011	0.371	0.378	0.371	0.389	0.015	0.016	0.038	0.039	0.035	0.037
4.24	0.543	-0.007	0.013	0.480	0.497	0.472	0.509	0.016	0.018	0.039	0.041	0.035	0.038
5.59	0.520	-0.005	0.025	0.535	0.563	0.531	0.588	0.017	0.019	0.040	0.043	0.036	0.040
6.90	0.508	-0.012	0.029	0.585	0.625	0.573	0.654	0.019	0.021	0.042	0.046	0.037	0.042
8.32	0.495	-0.012	0.042	0.615	0.670	0.603	0.712	0.020	0.024	0.044	0.049	0.039	0.046
9.63	0.483	-0.005	0.061	0.627	0.698	0.622	0.759	0.021	0.026	0.046	0.052	0.041	0.050
11.06	0.471	0.006	0.085	0.612	0.700	0.618	0.785	0.023	0.029	0.049	0.057	0.043	0.055
12.57	0.467	-0.004	0.094	0.645	0.757	0.641	0.851	0.026	0.034	0.054	0.065	0.047	0.062

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002433
Coal mass (lb)	0.1606
Pump T (°F)	106.0

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
120.9	0.639	1.5	2.7	127.5	128.1	129.0	130.8	11.0	11.1	25.5	25.7	23.3	23.6
214.3	0.608	1.3	4.2	193.1	195.0	194.4	199.2	11.1	11.4	28.7	29.1	26.7	27.3
392.3	0.568	0.6	8.1	281.3	287.0	281.8	295.2	11.4	12.0	28.9	29.6	26.6	27.9
614.4	0.543	-5.7	9.5	364.2	377.1	358.6	386.6	12.5	13.4	29.9	31.2	26.8	28.9
810.7	0.520	-3.7	19.0	406.4	427.3	402.7	446.3	13.0	14.4	30.5	32.3	27.3	30.3
1001.3	0.508	-9.4	21.8	444.3	474.4	434.9	496.2	14.2	16.1	32.0	34.6	28.1	32.1
1206.3	0.495	-8.9	31.9	466.6	508.2	457.7	540.1	15.2	17.9	33.6	37.2	29.4	34.7
1396.8	0.483	-4.1	46.2	475.8	529.6	471.7	575.9	16.2	19.8	35.1	39.8	30.9	37.7
1603.8	0.471	4.7	64.4	464.3	531.4	469.0	595.8	17.1	22.0	36.9	43.2	33.0	41.9
1823.6	0.467	-3.0	71.6	489.5	574.6	486.4	646.2	19.5	26.2	40.8	49.2	35.6	47.3

Table 74. Adsorption of a 60/40 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 20)**SI Unit**

Cell T (K)	319.2	Feed Molar Composition	
Moisture content (%)	4.9	Nitrogen	0.600
Void volume (m ³)	0.0000689	Carbon Dioxide	0.400
Coal mass (g)	72.85		
Pump T (K)	314.5		

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.83	0.799	0.007	0.008	0.106	0.106	0.113	0.115	0.018	0.018	0.034	0.034	0.031	0.031
1.42	0.771	0.012	0.015	0.158	0.159	0.170	0.174	0.018	0.018	0.036	0.036	0.033	0.034
2.74	0.745	0.017	0.027	0.258	0.261	0.275	0.288	0.019	0.019	0.036	0.037	0.033	0.035
4.12	0.728	0.013	0.032	0.337	0.344	0.351	0.376	0.020	0.021	0.038	0.039	0.033	0.036
5.63	0.707	0.016	0.046	0.389	0.402	0.406	0.448	0.021	0.023	0.039	0.041	0.034	0.038
6.88	0.697	0.017	0.058	0.433	0.451	0.450	0.509	0.022	0.025	0.040	0.043	0.035	0.040
8.29	0.681	0.030	0.083	0.447	0.472	0.477	0.555	0.023	0.027	0.041	0.044	0.036	0.042
9.59	0.673	0.029	0.094	0.465	0.497	0.494	0.591	0.024	0.030	0.043	0.048	0.038	0.046
11.02	0.664	0.041	0.121	0.474	0.514	0.514	0.635	0.025	0.032	0.045	0.051	0.040	0.050
12.40	0.659	0.035	0.131	0.493	0.543	0.528	0.673	0.028	0.037	0.048	0.056	0.042	0.054

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002433
Coal mass (lb)	0.1606
Pump T (°F)	106.5

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
119.7	0.799	5.5	6.4	80.6	80.8	86.1	87.2	13.8	14.0	25.9	26.1	23.5	23.8
206.2	0.771	9.0	11.3	120.2	120.9	129.2	132.2	13.6	14.0	27.1	27.3	25.2	25.8
398.1	0.745	12.8	20.1	195.9	198.4	208.8	218.6	14.0	14.8	27.4	28.0	25.2	26.3
597.2	0.728	10.2	24.3	255.9	261.2	266.1	285.5	15.0	16.2	28.6	29.6	25.4	27.2
816.2	0.707	12.4	35.0	295.4	304.7	307.8	339.7	15.8	17.5	29.5	31.0	25.9	28.6
998.4	0.697	13.0	44.2	328.6	342.2	341.6	386.4	16.7	19.0	30.5	32.6	26.6	30.1
1202.8	0.681	22.8	63.2	339.1	358.0	361.8	421.1	17.2	20.3	31.1	33.8	27.7	32.2
1390.6	0.673	21.7	71.3	353.2	377.2	374.9	448.6	18.4	22.4	32.8	36.3	28.9	34.6
1597.7	0.664	30.9	91.8	359.5	390.3	390.4	482.0	19.3	24.5	34.0	38.4	30.5	37.6
1798.8	0.659	26.6	99.2	374.2	411.8	400.8	511.0	21.2	27.7	36.7	42.4	32.2	41.0

Table 75. Adsorption of a 80/20 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Wet Illinois #6 Coal at 319.3 K (System 20)**SI Unit**

Cell T (K)	319.2	Feed Molar Composition	
Moisture content (%)	4.9	Nitrogen	0.817
Void volume (m ³)	0.0000689	Carbon Dioxide	0.183
Coal mass (g)	72.85		
Pump T (K)	314.6		

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.96	0.939	0.012	0.013	0.056	0.056	0.068	0.069	0.021	0.021	0.032	0.032	0.030	0.030
1.41	0.931	0.015	0.017	0.076	0.076	0.091	0.093	0.021	0.021	0.033	0.033	0.031	0.032
3.02	0.918	0.027	0.035	0.144	0.145	0.171	0.180	0.021	0.023	0.033	0.034	0.031	0.033
4.15	0.909	0.031	0.044	0.179	0.181	0.210	0.225	0.022	0.024	0.034	0.035	0.031	0.033
5.55	0.902	0.034	0.056	0.221	0.223	0.255	0.279	0.023	0.026	0.036	0.038	0.032	0.035
6.84	0.885	0.067	0.098	0.222	0.226	0.288	0.324	0.022	0.026	0.033	0.035	0.033	0.037
8.34	0.881	0.065	0.108	0.254	0.260	0.319	0.368	0.024	0.029	0.036	0.039	0.034	0.039
9.64	0.878	0.065	0.119	0.275	0.282	0.340	0.401	0.026	0.032	0.038	0.042	0.036	0.042
10.97	0.871	0.076	0.141	0.280	0.290	0.356	0.430	0.027	0.034	0.039	0.043	0.037	0.045
12.43	0.867	0.083	0.162	0.290	0.303	0.373	0.464	0.029	0.038	0.041	0.046	0.039	0.049

English Engineering Unit

Cell T (°F)	115.0
Void volume (ft ³)	0.002433
Coal mass (lb)	0.1606
Pump T (°F)	106.6

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
139.0	0.939	9.1	9.8	42.2	42.3	51.3	52.1	15.7	16.0	24.0	24.2	22.6	23.0
204.4	0.931	11.4	12.9	57.8	57.9	69.2	70.8	15.8	16.2	24.9	25.1	23.5	24.0
438.5	0.918	20.7	26.8	109.3	109.8	130.0	136.6	16.2	17.2	25.3	25.8	23.5	24.7
601.3	0.909	23.3	33.5	136.1	137.1	159.4	170.7	16.8	18.2	26.1	26.9	23.7	25.4
804.7	0.902	25.7	42.6	167.6	169.4	193.2	212.0	17.8	19.8	27.3	28.5	24.3	26.6
992.0	0.885	50.7	74.3	168.2	171.3	219.0	245.6	16.9	19.6	24.9	26.4	24.9	28.0
1209.6	0.881	49.3	81.9	192.8	197.2	242.1	279.1	18.5	22.0	27.2	29.3	26.0	29.9
1398.7	0.878	49.4	90.4	208.5	214.2	257.9	304.6	19.7	24.2	29.0	31.6	27.1	31.9
1590.4	0.871	57.3	106.7	212.7	220.0	270.0	326.7	20.6	26.1	29.7	33.0	28.3	34.2
1802.9	0.867	62.9	122.9	220.4	229.6	283.4	352.5	21.9	28.7	31.2	35.3	29.8	37.1

Table 76. Nitrogen Adsorption on Wet Tiffany Coal at 327.6 K (System 21, Run 1)**SI Units**

Cell T (K)	327.6
Moisture content (%)	11.7
Void volume (m ³)	0.0000727
Pump pressure (MPa)	7.0
Pump T (K)	327.6
Adsorbent mass (g)	94.2
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.74	0.024	0.024	0.006	0.006
1.40	0.039	0.039	0.006	0.007
2.80	0.067	0.070	0.007	0.007
4.16	0.087	0.092	0.008	0.009
5.49	0.108	0.117	0.009	0.010
6.90	0.123	0.136	0.011	0.012
8.29	0.134	0.152	0.012	0.013
9.73	0.147	0.170	0.014	0.016
11.07	0.157	0.185	0.015	0.018
12.45	0.164	0.198	0.017	0.020

English Engineering Units

Cell T (°F)	130.0
Moisture content (%)	11.7
Void volume (ft ³)	0.002567
Pump pressure (psia)	1016.5
Pump T (°F)	130.0
Adsorbent mass (lb)	0.2077

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
106.6	18.0	18.2	4.7	4.8
202.9	29.4	30.0	4.8	4.9
406.0	51.0	53.1	5.3	5.6
602.7	66.0	70.1	6.1	6.5
795.6	82.0	88.8	7.0	7.6
1000.2	93.4	103.5	8.1	9.0
1202.5	102.1	115.5	9.0	10.2
1410.9	111.2	128.7	10.3	11.9
1604.9	119.0	140.5	11.5	13.5
1806.2	124.5	150.3	12.7	15.3

Table 77. Nitrogen Adsorption on Wet Tiffany Coal at 327.6 K (System 21, Run 2)**SI Units**

Cell T (K)	327.6
Moisture content (%)	11.7
Void volume (m ³)	0.0000659
Pump pressure (MPa)	6.9
Pump T (K)	313.5
Adsorbent mass (g)	93.9
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.87	0.040	0.041	0.006	0.006
1.54	0.056	0.057	0.006	0.006
2.88	0.081	0.084	0.007	0.007
4.24	0.099	0.105	0.008	0.008
5.58	0.117	0.127	0.009	0.010
6.96	0.131	0.145	0.011	0.012
8.35	0.141	0.160	0.012	0.014
9.68	0.152	0.176	0.014	0.016
11.14	0.166	0.197	0.015	0.018
12.53	0.175	0.212	0.017	0.020
13.75	0.184	0.227	0.018	0.023

English Engineering Units

Cell T (°F)	130.0
Moisture content (%)	11.7
Void volume (ft ³)	0.002326
Pump pressure (psia)	996.4
Pump T (°F)	104.7
Adsorbent mass (lb)	0.2070

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
126.8	30.6	31.0	4.6	4.6
222.7	42.4	43.3	4.7	4.8
418.3	61.5	64.1	5.3	5.5
615.7	75.0	79.8	6.1	6.4
808.7	88.9	96.5	7.0	7.6
1008.9	99.1	109.9	8.1	9.0
1211.4	107.0	121.2	9.1	10.3
1404.6	115.6	133.7	10.3	11.9
1615.8	126.1	149.2	11.5	13.7
1817.6	133.0	160.8	12.8	15.5
1994.8	139.6	172.2	13.9	17.1

Table 78. Methane Adsorption on Wet Tiffany Coal at 319.3 K (System 22, Well 1)**SI Units**

Cell T (K)	327.6
Moisture content (%)	5.6
Void volume (m ³)	7.391E-05
Pump pressure (MPa)	6.87
Pump T (K)	313.7
Adsorbent mass (g)	83.2
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.43	0.066	0.066	0.011	0.012
0.96	0.114	0.116	0.011	0.012
2.06	0.192	0.198	0.012	0.012
3.34	0.242	0.256	0.012	0.013
4.52	0.280	0.303	0.013	0.014
6.19	0.318	0.355	0.014	0.016
7.29	0.333	0.381	0.015	0.018
8.52	0.345	0.404	0.017	0.020
9.97	0.352	0.427	0.019	0.023
11.92	0.357	0.453	0.021	0.027
13.52	0.362	0.477	0.024	0.031

English Engineering Units

Cell T (°F)	130.0
Moisture content (%)	5.6
Void volume (ft ³)	0.0026101
Pump pressure (psia)	996.6
Pump T (°F)	104.9
Adsorbent mass (lb)	0.1834

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
62.0	50.107	50.448	8.702	8.761
139.3	86.607	87.953	8.688	8.823
298.3	145.500	150.493	8.795	9.097
485.0	183.837	194.490	9.161	9.691
655.5	212.803	230.066	9.704	10.491
898.3	240.989	269.178	10.788	12.050
1057.1	253.022	289.034	11.662	13.322
1235.1	261.626	306.791	12.766	14.969
1446.4	267.483	323.976	14.207	17.207
1728.1	271.171	343.618	16.285	20.635
1960.3	274.804	361.970	18.077	23.811

Table 79. Methane Adsorption on Wet Tiffany Coal at 319.3 K (System 22, Well 10)**SI Units**

Cell T (K)	327.6
Moisture content (%)	16.5
Void volume (m ³)	6.39E-05
Pump pressure (MPa)	6.87
Pump T (K)	313.2
Adsorbent mass (g)	91
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.56	0.071	0.072	0.011	0.011
1.32	0.131	0.134	0.011	0.011
2.59	0.199	0.207	0.011	0.012
4.08	0.257	0.276	0.012	0.013
5.58	0.296	0.327	0.013	0.015
7.02	0.310	0.352	0.015	0.017
8.24	0.321	0.374	0.016	0.018
9.61	0.325	0.391	0.018	0.021
11.03	0.327	0.406	0.020	0.025
12.46	0.332	0.426	0.022	0.028
13.62	0.337	0.444	0.024	0.032

English Engineering Units

Cell T (°F)	130.0
Moisture content (%)	16.5
Void volume (ft ³)	0.002257
Pump pressure (psia)	996.6
Pump T (°F)	104.05
Adsorbent mass (lb)	0.2006

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
81.2	54.162	54.647	8.110	8.183
191.1	99.557	101.699	8.142	8.317
375.5	150.870	157.488	8.419	8.788
591.6	195.214	209.318	9.083	9.739
809.1	224.668	247.899	10.077	11.118
1018.2	235.494	267.516	11.282	12.816
1194.5	243.813	284.170	11.962	13.943
1393.2	247.028	296.733	13.447	16.152
1599.8	248.542	308.450	15.080	18.715
1807.4	251.861	323.350	16.779	21.541
1975.9	255.446	337.363	18.183	24.014

Table 80. CO₂ Adsorption on Wet Tiffany Coal at 327.6 K (System 23, Run 1)**SI Units**

Cell T (K)	327.6
Moisture content (%)	11.7
Void volume (m ³)	0.0000725
Pump pressure (MPa)	6.1
Pump T (K)	327.6
Adsorbent mass (g)	94.2
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.48	0.197	0.199	0.016	0.016
1.41	0.360	0.368	0.016	0.017
2.76	0.536	0.502	0.017	0.018
4.30	0.536	0.584	0.018	0.020
5.61	0.555	0.627	0.020	0.023
6.96	0.555	0.660	0.024	0.029
8.34	0.529	0.674	0.029	0.037
9.67	0.486	0.690	0.038	0.053
10.97	0.436	0.737	0.051	0.086
12.30	0.392	0.820	0.063	0.132
13.63	0.225	0.553	0.073	0.179

English Engineering Units

Cell T (°F)	130.0
Moisture content (%)	11.7
Void volume (ft ³)	0.002560
Pump pressure (psia)	886.5
Pump T (°F)	130.0
Adsorbent mass (lb)	0.2077

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
69.5	149.5	150.7	12.4	12.5
204.5	272.9	279.4	12.3	12.6
400.7	407.2	380.8	12.7	13.4
624.3	407.2	443.5	13.8	15.1
813.3	421.1	476.1	15.5	17.5
1010.0	421.3	500.6	18.5	22.0
1209.1	401.4	511.6	22.0	28.1
1402.1	369.1	524.0	28.5	40.5
1590.5	330.9	559.5	38.8	65.5
1784.6	297.9	622.7	48.1	100.5
1976.5	170.8	419.7	55.4	136.1

Table 81. CO₂ Adsorption on Wet Tiffany Coal at 327.6 K (System 23, Run 2)**SI Units**

Cell T (K)	327.6
Moisture content (%)	11.7
Void volume (m ³)	0.0000726
Pump pressure (MPa)	6.1
Pump T (K)	327.6
Adsorbent mass (g)	94.2
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.67	0.231	0.233	0.016	0.016
3.63	0.505	0.541	0.017	0.019
7.09	0.471	0.657	0.024	0.029
10.37	0.471	0.727	0.044	0.067
13.49	0.371	0.898	0.073	0.176

English Engineering Units

Cell T (°F)	130.0
Moisture content (%)	11.7
Void volume (ft ³)	0.002562
Pump pressure (psia)	886.5
Pump T (°F)	130.0
Adsorbent mass (lb)	0.2077

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
97.3	175.1	177.0	12.3	12.5
526.8	383.0	410.4	13.2	14.2
1028.3	357.1	498.3	18.2	21.7
1504.0	357.1	551.9	33.1	51.2
1956.1	281.5	681.6	55.3	133.9

Table 82. Adsorption of a 50/50 Mole % Methane/Nitrogen Feed Mixture on Wet Tiffany Coal at 327.6 K (System 24)**SI Unit**

Cell T (K)	327.6	Feed Molar Composition	
Moisture content (%)	10.5	Methane	0.500
Void volume (m ³)	0.0000738	Nitrogen	0.500
Coal mass (g)	93.0		
Pump T (K)	327.6		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		N ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.82	0.432	0.049	0.049	0.011	0.012	0.060	0.061	0.005	0.005	0.002	0.002	0.006	0.006
1.52	0.436	0.085	0.086	0.019	0.021	0.104	0.107	0.006	0.006	0.003	0.003	0.007	0.007
2.76	0.444	0.131	0.134	0.027	0.030	0.158	0.164	0.007	0.008	0.003	0.004	0.008	0.008
4.22	0.454	0.169	0.175	0.036	0.043	0.205	0.218	0.009	0.009	0.004	0.005	0.010	0.010
5.61	0.456	0.203	0.213	0.034	0.045	0.238	0.258	0.012	0.012	0.006	0.006	0.012	0.013
6.94	0.461	0.224	0.237	0.038	0.053	0.262	0.290	0.014	0.015	0.007	0.008	0.015	0.016
8.33	0.464	0.246	0.263	0.034	0.054	0.280	0.317	0.017	0.018	0.008	0.009	0.017	0.019
9.72	0.467	0.260	0.282	0.035	0.060	0.295	0.341	0.019	0.021	0.010	0.011	0.019	0.022
11.10	0.469	0.274	0.301	0.034	0.064	0.308	0.365	0.022	0.025	0.011	0.013	0.022	0.026
12.50	0.473	0.280	0.312	0.038	0.074	0.318	0.386	0.024	0.028	0.012	0.015	0.025	0.030
13.86	0.474	0.292	0.330	0.039	0.081	0.331	0.411	0.027	0.031	0.013	0.017	0.027	0.033

English Engineering Unit

Cell T (°F)	130.0
Void volume (ft ³)	0.002606
Coal mass (lb)	0.2050
Pump T (°F)	130.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		N ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in N ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
118.5	0.432	37.2	37.4	8.7	9.0	45.9	46.4	4.1	4.2	1.8	1.9	4.7	4.7
220.1	0.436	64.4	65.2	14.8	15.7	79.2	80.9	4.8	4.8	2.1	2.1	5.4	5.5
400.0	0.444	99.5	101.7	20.4	23.1	120.0	124.7	5.6	5.8	2.6	2.7	6.2	6.4
611.6	0.454	128.3	132.7	27.2	32.5	155.5	165.2	6.9	7.1	3.3	3.6	7.5	7.9
813.8	0.456	154.4	161.4	26.1	34.5	180.5	195.8	8.7	9.2	4.4	4.9	9.0	9.7
1005.9	0.461	170.1	179.9	29.0	40.6	199.1	220.5	10.7	11.4	5.2	5.9	11.2	12.4
1208.5	0.464	186.5	199.5	26.2	41.3	212.6	240.8	12.7	13.7	6.2	7.2	12.8	14.5
1409.7	0.467	197.2	213.7	26.6	45.5	223.8	259.2	14.6	16.0	7.2	8.6	14.5	16.8
1609.6	0.469	207.9	228.1	25.8	48.6	233.7	276.7	17.0	18.9	8.2	10.0	16.8	20.0
1812.8	0.473	212.6	236.7	29.0	55.9	241.5	292.7	18.5	21.0	8.9	11.3	18.6	22.6
2010.8	0.474	221.6	250.1	29.9	61.5	251.5	311.7	20.2	23.2	9.7	12.6	20.2	25.1

Table 83. Adsorption of a 40/60 Mole % Methane/Carbon Dioxide Feed Mixture on Wet Tiffany Coal at 327.6 K (System 25)**SI Unit**

Cell T (K)	327.6	Feed Molar Composition	
Moisture content (%)	11.4	Methane	0.414
Void volume (m ³)	0.0000728	Carbon Dioxide	0.586
Coal mass (g)	93.91		
Pump T (K)	327.6		

Pressure (MPa)	CH ₄ Gas mole fraction	CH ₄ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.73	0.541	0.048	0.049	0.132	0.133	0.179	0.182	0.004	0.004	0.010	0.010	0.013	0.014
1.45	0.530	0.066	0.070	0.210	0.213	0.276	0.283	0.004	0.005	0.011	0.011	0.014	0.014
2.77	0.500	0.091	0.101	0.290	0.299	0.381	0.400	0.005	0.005	0.012	0.012	0.014	0.015
4.15	0.488	0.096	0.113	0.345	0.363	0.441	0.476	0.006	0.006	0.013	0.014	0.015	0.017
5.66	0.473	0.104	0.130	0.373	0.403	0.477	0.533	0.007	0.008	0.015	0.016	0.017	0.019
6.96	0.465	0.103	0.139	0.390	0.431	0.493	0.570	0.009	0.011	0.019	0.021	0.021	0.025
8.37	0.455	0.109	0.155	0.391	0.446	0.500	0.601	0.010	0.013	0.021	0.024	0.024	0.029
9.72	0.448	0.111	0.168	0.385	0.455	0.497	0.623	0.013	0.017	0.024	0.029	0.028	0.035
11.10	0.443	0.115	0.183	0.373	0.460	0.488	0.643	0.015	0.020	0.028	0.035	0.033	0.044
12.46	0.438	0.119	0.200	0.357	0.462	0.476	0.662	0.017	0.025	0.031	0.041	0.037	0.051
14.03	0.432	0.126	0.221	0.327	0.452	0.453	0.673	0.019	0.030	0.034	0.047	0.042	0.062

English Engineering Unit

Cell T (°F)	130.0
Void volume (ft ³)	0.002570
Coal mass (lb)	0.2070
Pump T (°F)	130.0

Pressure (psia)	CH ₄ Gas mole fraction	CH ₄ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in CH ₄ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
105.3	0.541	36.3	37.2	99.8	100.6	136.1	137.8	3.2	3.3	7.6	7.7	10.1	10.2
210.0	0.530	50.4	53.2	159.3	161.7	209.7	214.9	3.4	3.5	8.3	8.5	10.6	10.8
402.4	0.500	69.1	76.4	219.8	227.1	288.9	303.5	3.7	4.0	8.7	9.0	10.9	11.5
601.4	0.488	72.7	85.8	262.0	275.7	334.7	361.5	4.3	4.8	9.8	10.3	11.6	12.6
820.7	0.473	78.6	98.7	283.2	305.7	361.8	404.4	5.6	6.4	11.2	12.2	13.0	14.5
1010.0	0.465	78.4	105.4	296.0	327.1	374.4	432.6	6.7	8.1	14.1	15.7	16.3	18.8
1214.0	0.455	82.7	117.6	296.4	338.2	379.2	455.8	7.9	10.0	15.8	18.2	18.2	21.9
1409.3	0.448	84.6	127.6	292.3	345.2	376.8	472.8	9.5	12.6	18.3	21.9	21.1	26.4
1609.3	0.443	87.0	139.0	283.4	348.8	370.4	487.8	11.1	15.5	21.4	26.7	25.1	33.0
1806.7	0.438	90.2	151.7	271.3	350.4	361.5	502.1	12.6	18.7	23.5	30.8	28.1	39.0
2034.8	0.432	95.5	167.7	248.4	343.3	344.0	511.0	14.4	22.9	25.5	35.7	31.6	46.9

Table 84. Adsorption of a 20/80 Mole % Nitrogen/Carbon Dioxide Feed Mixture on Wet Tiffany Coal at 327.6 K (System 26)**SI Unit**

Cell T (K)	327.6
Moisture content (%)	10.4
Void volume (m ³)	0.0000737
Coal mass (g)	92.9
Pump T (K)	327.6

Feed Molar Composition	
Nitrogen	0.201
Carbon Dioxide	0.799

Pressure (MPa)	N ₂ Gas mole fraction	N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		Total Ads. (mmol/g)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.63	0.363	0.006	0.006	0.183	0.184	0.189	0.190	0.003	0.003	0.016	0.016	0.016	0.016
1.35	0.325	0.009	0.011	0.295	0.299	0.304	0.310	0.003	0.003	0.017	0.017	0.017	0.017
2.78	0.289	0.009	0.014	0.419	0.432	0.428	0.446	0.004	0.004	0.017	0.018	0.017	0.018
4.16	0.268	0.010	0.019	0.479	0.504	0.489	0.522	0.005	0.005	0.018	0.019	0.018	0.019
5.68	0.253	0.008	0.021	0.517	0.556	0.525	0.577	0.006	0.007	0.020	0.022	0.019	0.021
6.97	0.241	0.014	0.031	0.520	0.573	0.534	0.604	0.007	0.008	0.025	0.028	0.025	0.028
8.37	0.233	0.012	0.034	0.519	0.589	0.532	0.623	0.008	0.010	0.028	0.032	0.027	0.032
9.71	0.227	0.013	0.039	0.508	0.596	0.521	0.634	0.010	0.013	0.031	0.037	0.030	0.037
11.06	0.223	0.010	0.040	0.485	0.591	0.495	0.631	0.012	0.016	0.038	0.047	0.037	0.047
12.45	0.219	0.009	0.044	0.456	0.580	0.465	0.624	0.014	0.019	0.043	0.055	0.041	0.056
13.82	0.216	0.007	0.048	0.436	0.583	0.444	0.631	0.016	0.023	0.048	0.064	0.046	0.065

English Engineering Unit

Cell T (°F)	130.0
Void volume (ft ³)	0.002601
Coal mass (lb)	0.2048
Pump T (°F)	130.0

Pressure (psia)	N ₂ Gas mole fraction	N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		Total Ads. (SCF/ton)		Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in Total Ads.	
		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
91.9	0.363	4.5	4.9	138.7	139.5	143.1	144.4	2.3	2.4	12.1	12.2	12.2	12.3
196.4	0.325	6.8	8.2	223.9	226.9	230.7	235.1	2.5	2.5	12.6	12.8	12.7	13.0
402.7	0.289	6.9	10.8	317.8	327.5	324.7	338.4	2.9	3.1	13.1	13.5	13.0	13.6
602.9	0.268	7.5	14.2	363.9	382.2	371.4	396.4	3.5	3.7	13.7	14.4	13.5	14.4
824.4	0.253	6.2	16.2	392.3	421.9	398.4	438.1	4.7	5.2	15.3	16.4	14.7	16.2
1011.5	0.241	10.7	23.5	394.7	435.2	405.4	458.7	5.3	6.1	19.0	21.0	18.7	21.2
1213.7	0.233	9.4	25.6	394.0	447.2	403.4	472.9	6.3	7.5	21.1	24.0	20.6	24.1
1407.7	0.227	9.7	29.4	385.4	452.1	395.2	481.5	7.8	9.6	23.6	27.8	22.9	27.9
1604.3	0.223	7.7	30.7	368.3	448.6	376.0	479.3	9.1	11.8	29.0	35.4	28.1	35.8
1805.2	0.219	6.7	33.1	346.0	440.5	352.7	473.6	10.6	14.4	32.6	41.8	31.5	42.3
2004.2	0.216	5.7	36.3	331.2	442.3	336.9	478.6	12.1	17.4	36.2	48.7	34.7	49.3

Table 85. Adsorption of a 40/50/10 Mole % Methane/Carbon Dioxide/Nitrogen Feed Mixture on Wet Tiffany Coal at 327.6 K (System 27)

SI Unit

Cell T (K)	327.6
Moisture content (%)	10.4
Void volume (m ³)	0.0000737
Coal mass (g)	92.9
Pump T (K)	327.6

Feed Molar Composition	
Nitrogen	0.400
Carbon Dioxide	0.499
Methane	0.101

Pressure (MPa)	N ₂ Gas		CO ₂ Gas		N ₂ Ads. (mmol/g)		CO ₂ Ads. (mmol/g)		CH ₄ Ads. (mmol/g)		Total Ads. (mmol/g)	
	mole fraction		mole fraction		Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute
0.7	0.543		0.350		0.019	0.020	0.094	0.095	0.012	0.012	0.126	0.127
1.4	0.537		0.351		0.026	0.028	0.166	0.167	0.017	0.018	0.209	0.213
2.7	0.514		0.374		0.031	0.037	0.261	0.265	0.024	0.025	0.315	0.327
4.2	0.491		0.398		0.035	0.047	0.321	0.329	0.027	0.030	0.384	0.407
5.6	0.475		0.414		0.040	0.057	0.353	0.365	0.029	0.033	0.421	0.455
7.0	0.464		0.426		0.040	0.064	0.375	0.394	0.029	0.034	0.444	0.491
8.3	0.455		0.436		0.041	0.070	0.384	0.408	0.029	0.036	0.455	0.515
9.7	0.448		0.443		0.041	0.076	0.393	0.424	0.027	0.036	0.461	0.535
11.1	0.442		0.451		0.043	0.083	0.386	0.423	0.029	0.038	0.457	0.544
12.5	0.436		0.457		0.045	0.091	0.379	0.421	0.030	0.041	0.453	0.554
13.8	0.432		0.463		0.047	0.100	0.371	0.420	0.033	0.046	0.451	0.566

Pressure (MPa)	Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in CH ₄ Ads.		Error in Total Ads.	
	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
0.7	0.006	0.006	0.016	0.016	0.006	0.006	0.021	0.021
1.4	0.007	0.007	0.017	0.017	0.006	0.007	0.020	0.021
2.7	0.007	0.008	0.018	0.018	0.007	0.007	0.020	0.021
4.2	0.008	0.009	0.019	0.019	0.008	0.008	0.020	0.022
5.6	0.010	0.011	0.024	0.025	0.010	0.011	0.026	0.028
7.0	0.011	0.013	0.025	0.027	0.011	0.012	0.027	0.030
8.3	0.013	0.015	0.027	0.030	0.012	0.014	0.029	0.033
9.7	0.015	0.018	0.034	0.037	0.015	0.018	0.035	0.041
11.1	0.017	0.021	0.036	0.040	0.017	0.020	0.038	0.045
12.5	0.018	0.023	0.037	0.042	0.018	0.022	0.040	0.048
13.8	0.019	0.025	0.037	0.045	0.019	0.023	0.041	0.052

Table 85. Adsorption of a 40/50/10 Mole % Methane/Carbon Dioxide/Nitrogen Feed Mixture on Wet Tiffany Coal at 327.6 K (Continued)

English Engineering Unit

Void volume (ft ³)	0.002601
Coal mass (lb)	0.205
Pump T (°F)	130.0
Cell T (°F)	130.0

Pressure (psia)	N ₂ Gas		CO ₂ Gas		N ₂ Ads. (SCF/ton)		CO ₂ Ads. (SCF/ton)		CH ₄ Ads. (SCF/ton)		Total Ads. (SCF/ton)	
	mole fraction	mole fraction	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute
102.3	0.543	0.350	14.6	15.1	71.7	71.9	9.1	9.2	95.4	96.2		
199.4	0.537	0.351	19.4	21.0	126.2	127.0	13.3	13.6	158.9	161.7		
393.1	0.514	0.374	23.4	28.2	197.9	200.8	18.1	19.1	239.4	248.1		
612.6	0.491	0.398	26.9	36.0	243.9	250.1	20.8	22.7	291.6	308.8		
807.2	0.475	0.414	30.1	43.2	267.6	277.4	21.9	24.8	319.5	345.4		
1008.8	0.464	0.426	30.7	48.2	284.8	298.8	21.7	25.7	337.1	372.7		
1206.4	0.455	0.436	31.5	53.4	291.7	310.0	22.0	27.1	345.1	390.5		
1410.7	0.448	0.443	30.9	57.6	298.2	321.5	20.7	27.0	349.8	406.1		
1607.6	0.442	0.451	32.3	63.2	293.0	320.8	21.6	29.0	347.0	413.0		
1808.7	0.436	0.457	34.0	69.4	287.3	319.8	22.8	31.2	344.2	420.4		
2005.4	0.432	0.463	35.6	75.7	281.9	319.2	25.2	34.5	342.7	429.4		

Pressure (psia)	Error in N ₂ Ads.		Error in CO ₂ Ads.		Error in CH ₄ Ads.		Error in Tot. Adsorp.	
	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.	σ Gibbs	σ Abs.
102.3	4.8	4.9	12.4	12.5	4.4	4.5	15.6	15.7
199.4	5.0	5.2	13.1	13.2	4.9	4.9	15.4	15.7
393.1	5.5	5.8	13.7	13.9	5.4	5.6	15.3	15.8
612.6	6.0	6.5	14.3	14.7	6.0	6.3	15.5	16.5
807.2	7.8	8.6	18.1	18.9	7.7	8.3	19.6	21.2
1008.8	8.5	9.6	19.0	20.2	8.4	9.2	20.3	22.5
1206.4	9.6	11.1	20.8	22.4	9.5	10.7	22.0	24.9
1410.7	11.7	14.0	25.6	28.1	11.6	13.4	26.9	31.2
1607.6	12.7	15.6	27.2	30.3	12.5	14.9	28.6	34.0
1808.7	13.6	17.2	28.3	32.2	13.4	16.3	30.0	36.6
2005.4	14.4	18.8	28.3	33.9	14.2	17.8	31.2	39.1

Table 86. Nitrogen Adsorption on Wet Lower Basin Fruitland Coal at 328.1 K (System 28, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	7.7
Void volume (m ³)	0.0000607
Pump pressure (MPa)	6.95
Pump T (K)	319.5
Adsorbent mass (g)	100.3
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
1.45	0.035	0.035	0.006	0.006
2.99	0.061	0.064	0.007	0.007
4.28	0.070	0.075	0.007	0.008
5.70	0.082	0.090	0.009	0.009
7.06	0.095	0.106	0.010	0.011
8.52	0.108	0.123	0.012	0.013
9.81	0.118	0.137	0.013	0.015
11.25	0.128	0.153	0.014	0.017
12.55	0.139	0.169	0.016	0.019

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	7.7
Void volume (ft ³)	0.002144
Pump pressure (psia)	1008.3
Pump T (°F)	115.4
Adsorbent mass (lb)	0.2211

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
210.2	26.4	26.9	4.4	4.5
433.0	46.6	48.7	5.0	5.2
620.2	53.0	56.6	5.7	6.0
826.4	62.6	68.2	6.6	7.2
1023.5	72.2	80.4	7.6	8.5
1236.2	82.0	93.5	8.7	10.0
1422.3	89.5	104.2	9.6	11.1
1631.0	97.4	116.0	10.7	12.8
1820.1	105.3	128.1	11.8	14.3

Table 87. Nitrogen Adsorption on Wet Lower Basin Fruitland Coal at 328.1 K (System 28, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	7.5
Void volume (m ³)	0.0000609
Pump pressure (MPa)	6.95
Pump T (K)	319.5
Adsorbent mass (g)	100.1
Adsorbed phase density (g/cm ³)	0.725

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
1.59	0.040	0.041	0.008	0.008
3.82	0.074	0.079	0.009	0.010
5.55	0.086	0.094	0.010	0.011
6.99	0.099	0.110	0.011	0.013
8.53	0.111	0.126	0.013	0.014
9.80	0.115	0.134	0.014	0.016
11.11	0.126	0.149	0.015	0.017
12.46	0.137	0.166	0.016	0.019

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	7.5
Void volume (ft ³)	0.002151
Pump pressure (psia)	1008.3
Pump T (°F)	115.4
Adsorbent mass (lb)	0.2207

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
231.1	30.3	31.1	6.3	6.4
553.8	56.3	59.6	6.9	7.3
805.4	65.6	71.4	7.8	8.4
1014.2	74.9	83.3	8.6	9.6
1237.6	84.1	95.9	9.7	11.0
1421.9	87.4	101.7	10.6	12.3
1611.3	95.3	113.3	11.1	13.2
1806.5	103.7	126.0	12.2	14.8

Table 88. Methane Adsorption on Wet Lower Basin Fruitland Coal at 319.3 K (System 29, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	8.0
Void volume (m ³)	0.0000604
Pump pressure (MPa)	6.95
Pump T (K)	319.5
Adsorbent mass (g)	100.6
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
1.54	0.125	0.128	0.008	0.008
3.80	0.197	0.211	0.009	0.009
4.95	0.222	0.243	0.010	0.011
6.41	0.246	0.278	0.011	0.013
7.77	0.262	0.303	0.013	0.015
9.37	0.278	0.334	0.015	0.018
11.25	0.296	0.373	0.017	0.022
12.64	0.300	0.392	0.019	0.025
13.69	0.311	0.417	0.020	0.027

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	8.0
Void volume (ft ³)	0.002133
Pump pressure (psia)	1008.3
Pump T (°F)	115.4
Adsorbent mass (lb)	0.2218

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
222.8	95.037	97.500	5.922	6.076
551.6	149.625	159.928	6.703	7.164
717.3	168.738	184.413	7.370	8.055
930.0	187.041	210.672	8.436	9.502
1127.5	198.545	230.340	9.586	11.121
1359.3	210.694	253.550	11.079	13.332
1631.8	224.973	283.308	12.961	16.322
1832.7	227.956	297.269	14.402	18.781
1985.6	236.220	316.558	15.511	20.786

Table 89. Methane Adsorption on Wet Lower Basin Fruitland Coal at 319.3 K (System 29, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	7.9
Void volume (m ³)	0.0000605
Pump pressure (MPa)	6.95
Pump T (K)	319.5
Adsorbent mass (g)	100.5
Adsorbed phase density (g/cm ³)	0.374

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
2.13	0.159	0.164	0.008	0.008
4.69	0.216	0.235	0.010	0.010
6.34	0.240	0.270	0.011	0.012
7.92	0.257	0.299	0.013	0.015
9.17	0.268	0.321	0.014	0.017
10.81	0.286	0.356	0.017	0.021
12.38	0.299	0.387	0.018	0.024

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	7.9
Void volume (ft ³)	0.002137
Pump pressure (psia)	1008.3
Pump T (°F)	115.4
Adsorbent mass (lb)	0.2216

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
308.8	120.321	124.722	6.112	6.335
680.8	164.103	178.453	7.262	7.897
919.6	182.453	205.193	8.424	9.474
1148.9	194.775	226.713	9.756	11.355
1329.5	203.288	243.459	10.913	13.069
1568.4	216.720	269.990	12.541	15.623
1795.8	226.742	293.769	13.816	17.900

Table 90. CO₂ Adsorption on Wet Lower Basin Fruitland Coal at 319.3 K (System 30, Run 1)**SI Units**

Cell T (K)	319.3
Moisture content (%)	7.3
Void volume (m ³)	0.0000612
Pump pressure (MPa)	6.51
Pump T (K)	319.5
Adsorbent mass (g)	99.8
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
1.61	0.321	0.330	0.039	0.040
3.00	0.415	0.439	0.038	0.040
4.22	0.433	0.472	0.038	0.041
5.83	0.443	0.510	0.038	0.043
7.17	0.415	0.509	0.038	0.047
8.26	0.400	0.532	0.041	0.054
9.56	0.396	0.647	0.059	0.097
10.74	0.294	0.647	0.072	0.158
12.34	0.249	0.696	0.079	0.219

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	7.3
Void volume (ft ³)	0.002161
Pump pressure (psia)	944.3
Pump T (°F)	115.4
Adsorbent mass (lb)	0.2200

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
233.3	243.4	250.3	29.4	30.2
434.4	314.7	333.2	28.9	30.6
612.6	328.3	358.5	28.7	31.3
844.9	336.5	387.0	28.6	32.9
1039.7	315.2	386.1	29.1	35.6
1197.5	303.8	403.5	30.9	41.1
1385.9	300.3	490.8	44.8	73.3
1558.2	222.8	491.0	54.5	120.1
1789.3	189.3	528.0	59.7	166.6

Table 91. CO₂ Adsorption on Wet Lower Basin Fruitland Coal at 319.3 K (System 30, Run 2)**SI Units**

Cell T (K)	319.3
Moisture content (%)	7.2
Void volume (m ³)	0.0000613
Pump pressure (MPa)	6.95
Pump T (K)	319.5
Adsorbent mass (g)	99.7
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
1.34	0.308	0.315	0.045	0.046
3.72	0.460	0.495	0.044	0.047
4.33	0.440	0.482	0.044	0.048
5.62	0.444	0.507	0.044	0.050
6.98	0.434	0.526	0.044	0.053
8.28	0.411	0.547	0.046	0.061
9.51	0.408	0.658	0.061	0.099
9.84	0.435	0.767	0.068	0.120
10.90	0.344	0.781	0.080	0.181
12.26	0.223	0.617	0.073	0.202

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	7.2
Void volume (ft ³)	0.002165
Pump pressure (psia)	1008.3
Pump T (°F)	115.4
Adsorbent mass (lb)	0.2198

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
193.7	234.0	239.4	34.3	35.1
538.9	349.0	376.0	33.5	36.0
627.9	333.7	365.5	33.3	36.5
815.8	337.3	385.0	33.1	37.8
1012.1	329.2	398.9	33.3	40.3
1200.8	312.1	415.5	34.9	46.4
1378.8	309.3	499.5	46.4	75.0
1427.5	330.5	582.1	51.6	90.8
1580.3	260.9	592.5	60.4	137.1
1778.3	169.3	468.0	55.4	153.1

Table 92. CO₂ Adsorption on Wet Lower Basin Fruitland Coal at 319.3 K (System 30, Run 3)**SI Units**

Cell T (K)	319.3
Moisture content (%)	7.1
Void volume (m ³)	0.0000614
Pump pressure (MPa)	6.95
Pump T (K)	319.5
Adsorbent mass (g)	99.6
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.79	0.215	0.218	0.046	0.046
1.47	0.304	0.312	0.045	0.047
2.85	0.397	0.419	0.045	0.047
4.22	0.442	0.482	0.044	0.048
5.51	0.434	0.493	0.044	0.050
6.98	0.414	0.502	0.044	0.053
8.29	0.393	0.524	0.041	0.054
9.55	0.389	0.634	0.059	0.095
10.55	0.399	0.844	0.064	0.136

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	7.1
Void volume (ft ³)	0.002168
Pump pressure (psia)	1008.3
Pump T (°F)	115.4
Adsorbent mass (lb)	0.2196

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
115.2	163.5	165.7	34.7	35.2
213.8	230.9	236.9	34.4	35.3
413.1	301.0	317.7	33.9	35.7
611.6	335.3	366.0	33.5	36.5
798.8	329.4	374.4	33.3	37.8
1011.7	314.2	380.7	33.4	40.5
1202.0	298.4	397.5	31.0	41.3
1384.9	294.9	481.2	44.4	72.5
1530.2	303.1	640.9	48.9	103.4

Table 93. CO₂ Adsorption on Wet Lower Basin Fruitland Coal at 319.3 K (System 30, Run 4)**SI Units**

Cell T (K)	319.3
Moisture content (%)	8.0
Void volume (m ³)	0.0000613
Pump pressure (MPa)	6.95
Pump T (K)	319.3
Adsorbent mass (g)	100.6
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.70	0.188	0.191	0.044	0.045
1.46	0.290	0.298	0.044	0.045
2.82	0.381	0.402	0.043	0.045
4.21	0.410	0.447	0.043	0.046
5.54	0.408	0.465	0.042	0.048
6.99	0.414	0.503	0.043	0.052
8.29	0.409	0.544	0.045	0.060
9.58	0.362	0.593	0.066	0.108
10.83	0.296	0.661	0.068	0.153
12.28	0.224	0.617	0.065	0.179

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	8.0
Void volume (ft ³)	0.002165
Pump pressure (psia)	1008.3
Pump T (°F)	115.0
Adsorbent mass (lb)	0.2218

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
101.8	143.0	144.7	33.6	34.0
211.1	220.3	225.9	33.2	34.0
409.1	289.3	305.1	32.7	34.4
610.5	311.1	339.6	32.3	35.2
804.2	310.0	352.8	32.1	36.5
1014.5	314.6	381.5	32.3	39.2
1201.6	310.2	413.0	34.0	45.2
1389.1	274.4	449.8	50.1	82.2
1570.6	224.5	501.7	51.9	115.9
1781.3	169.8	468.6	49.2	135.8

Table 94. CO₂ Adsorption on Wet Lower Basin Fruitland Coal at 319.3 K (System 30, Run 5)**SI Units**

Cell T (K)	319.3
Moisture content (%)	14.8
Void volume (m ³)	0.0000560
Pump pressure (MPa)	6.95
Pump T (K)	319.3
Adsorbent mass (g)	100.6
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.74	0.203	0.206	0.049	0.050
1.58	0.308	0.317	0.049	0.050
3.01	0.408	0.432	0.048	0.051
4.20	0.444	0.485	0.048	0.052
5.61	0.436	0.497	0.048	0.054
6.98	0.432	0.524	0.048	0.058
8.32	0.410	0.548	0.050	0.067
9.62	0.398	0.659	0.067	0.111
10.90	0.312	0.707	0.074	0.169
12.36	0.234	0.652	0.070	0.194

English Engineering Units

Cell T (°F)	115.0
Moisture content (%)	14.8
Void volume (ft ³)	0.001978
Pump pressure (psia)	1008.3
Pump T (°F)	115.0
Adsorbent mass (lb)	0.2218

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
107.5	154.1	156.1	37.4	37.8
229.6	234.0	240.6	37.0	38.0
436.0	309.5	327.7	36.5	38.7
609.3	337.0	367.7	36.3	39.6
813.9	330.9	377.5	36.2	41.3
1012.7	328.0	397.5	36.5	44.2
1206.4	311.3	415.7	38.2	51.0
1395.5	301.9	500.3	50.8	84.1
1581.6	236.7	536.6	56.5	128.2
1792.2	177.8	495.0	53.0	147.5

Table 95. CO₂ Adsorption on Dry Illinois #6 Coal at 328.1 K (System 31)**SI Units**

Cell T (K)	328.2
Moisture content (%)	0
Void volume (m ³)	0.0000943
Pump pressure (MPa)	6.89
Pump T (K)	328.2
Adsorbent mass (g)	49.9
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.69	0.549	0.555	0.041	0.041
1.46	0.808	0.828	0.040	0.041
2.75	1.272	1.130	0.039	0.041
4.17	1.272	1.380	0.038	0.042
5.56	1.402	1.582	0.038	0.043
6.96	1.480	1.757	0.039	0.046
8.32	1.485	1.887	0.041	0.052
9.62	1.378	1.937	0.046	0.065
11.01	1.128	1.896	0.073	0.123
12.19	0.953	1.926	0.086	0.174
13.79	0.856	2.107	0.120	0.295

English Engineering Units

Cell T (°F)	131.0
Moisture content (%)	0
Void volume (ft ³)	0.003330
Pump pressure (psia)	998.9
Pump T (°F)	131.0
Adsorbent mass (lb)	0.1100

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
99.8	416.7	421.3	30.8	31.1
211.2	612.9	628.1	30.3	31.0
398.9	965.2	857.7	29.6	31.1
604.1	965.2	1047.4	29.0	31.5
806.7	1064.3	1200.8	28.8	32.5
1009.2	1123.7	1333.3	29.2	34.7
1206.1	1127.4	1432.1	30.8	39.2
1395.3	1046.3	1470.1	35.1	49.3
1597.2	856.1	1439.0	55.6	93.5
1768.1	723.0	1461.9	65.3	132.1
2000.3	649.9	1599.3	90.8	223.5

Table 96. CO₂ Adsorption on Dry Beulah Zap Coal at 328.1 K (System 32, Run 1)**SI Units**

Cell T (K)	328.2
Moisture content (%)	0
Void volume (m ³)	0.0000981
Pump pressure (MPa)	6.89
Pump T (K)	328.2
Adsorbent mass (g)	43.6
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.61	0.819	0.827	0.047	0.048
1.42	1.108	1.135	0.047	0.048
2.78	1.397	1.469	0.046	0.048
4.17	1.591	1.726	0.045	0.049
5.54	1.706	1.924	0.044	0.050
6.96	1.760	2.089	0.045	0.053
8.30	1.752	2.223	0.047	0.060
9.59	1.661	2.328	0.054	0.075
11.01	1.470	2.468	0.086	0.144
12.22	1.344	2.728	0.101	0.205
13.81	1.248	3.077	0.141	0.349

English Engineering Units

Cell T (°F)	131.0
Moisture content (%)	0
Void volume (ft ³)	0.003464
Pump pressure (psia)	998.9
Pump T (°F)	131.0
Adsorbent mass (lb)	0.0961

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
89.0	621.3	627.5	36.0	36.4
206.2	841.1	861.4	35.4	36.3
403.8	1060.4	1115.0	34.6	36.4
605.2	1207.3	1310.4	34.0	36.9
803.8	1294.8	1459.9	33.8	38.1
1009.8	1336.1	1585.6	34.2	40.6
1203.7	1329.6	1687.3	36.0	45.6
1391.6	1260.7	1767.0	40.8	57.2
1596.4	1115.5	1873.3	65.1	109.4
1772.1	1020.0	2070.7	76.8	156.0
2002.7	947.3	2335.3	107.3	264.5

Table 97. CO₂ Adsorption on Dry Beulah Zap Coal at 328.1 K (System 32, Run 2)**SI Units**

Cell T (K)	328.2
Moisture content (%)	0
Void volume (m ³)	0.0000989
Pump pressure (MPa)	6.92
Pump T (K)	328.2
Adsorbent mass (g)	43.3
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.67	0.825	0.834	0.047	0.047
1.51	1.126	1.155	0.046	0.047
2.78	1.386	1.457	0.045	0.047
4.19	1.585	1.721	0.044	0.048
5.58	1.694	1.912	0.044	0.050
6.97	1.750	2.078	0.045	0.053
8.34	1.712	2.178	0.047	0.060
9.53	1.631	2.272	0.053	0.074
10.96	1.455	2.427	0.086	0.143
12.17	1.324	2.667	0.101	0.204
13.73	1.275	3.118	0.142	0.347

English Engineering Units

Cell T (°F)	131.0
Moisture content (%)	0
Void volume (ft ³)	0.003494
Pump pressure (psia)	1003.2
Pump T (°F)	131.0
Adsorbent mass (lb)	0.0955

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
96.9	626.0	632.8	35.6	36.0
219.1	854.5	876.5	35.0	35.9
403.8	1051.9	1106.1	34.2	36.0
607.6	1203.0	1306.2	33.6	36.5
808.6	1286.0	1451.5	33.4	37.7
1010.6	1328.6	1577.1	33.9	40.2
1209.5	1299.5	1653.1	35.8	45.6
1382.0	1238.2	1724.4	40.4	56.3
1590.2	1104.2	1842.1	65.1	108.6
1764.4	1005.0	2024.2	77.0	155.0
1991.5	967.7	2366.6	107.7	263.4

Table 98. CO₂ Adsorption on Dry Wyodak Coal at 328.1 K (System 33)**SI Units**

Cell T (K)	328.2
Moisture content (%)	0
Void volume (m ³)	0.0000964
Pump pressure (MPa)	6.9
Pump T (K)	328.2
Adsorbent mass (g)	45.4
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.69	0.791	0.800	0.046	0.046
1.45	1.078	1.105	0.045	0.046
2.78	1.388	1.460	0.044	0.046
4.18	1.602	1.739	0.043	0.047
5.60	1.749	1.976	0.043	0.048
6.98	1.820	2.162	0.043	0.051
8.34	1.827	2.324	0.046	0.058
9.65	1.735	2.443	0.052	0.073
10.99	1.586	2.657	0.082	0.138
12.33	1.430	2.949	0.098	0.202
13.82	1.324	3.269	0.135	0.334

English Engineering Units

Cell T (°F)	131.0
Moisture content (%)	0
Void volume (ft ³)	0.003405
Pump pressure (psia)	1005.5
Pump T (°F)	131.0
Adsorbent mass (lb)	0.1001

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
100.5	600.7	607.5	34.6	35.0
210.5	818.2	838.3	34.0	34.9
403.7	1053.6	1107.8	33.3	35.0
606.0	1216.1	1320.1	32.7	35.5
812.1	1327.6	1499.7	32.4	36.7
1012.4	1381.7	1641.0	32.9	39.0
1209.8	1386.7	1764.3	34.6	44.0
1398.9	1316.5	1854.4	39.4	55.4
1593.9	1204.2	2016.9	62.4	104.4
1788.0	1085.5	2238.6	74.3	153.3
2004.8	1004.9	2481.0	102.5	253.1

Table 99. CO₂ Adsorption on Dry Upper Freeport Coal at 328.1 K (System 34)**SI Units**

Cell T (K)	328.2
Moisture content (%)	0
Void volume (m ³)	0.0000775
Pump pressure (MPa)	6.9
Pump T (K)	328.2
Adsorbent mass (g)	72.5
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
0.71	0.485	0.490	0.030	0.030
1.52	0.646	0.662	0.029	0.030
2.88	0.789	0.831	0.029	0.030
4.26	0.866	0.942	0.028	0.031
5.60	0.906	1.024	0.028	0.032
6.96	0.919	1.091	0.028	0.034
8.33	0.904	1.150	0.029	0.037
9.67	0.851	1.201	0.033	0.046
10.98	0.751	1.255	0.049	0.082
12.44	0.655	1.372	0.057	0.120
13.82	0.608	1.499	0.077	0.189

English Engineering Units

Cell T (°F)	131.0
Moisture content (%)	0
Void volume (ft ³)	0.002737
Pump pressure (psia)	1007.0
Pump T (°F)	131.0
Adsorbent mass (lb)	0.1598

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
102.7	367.8	372.1	22.4	22.7
221.1	490.1	502.8	22.1	22.7
417.1	598.7	630.7	21.7	22.8
617.2	657.4	715.0	21.4	23.3
812.6	687.9	777.2	21.3	24.1
1010.1	697.6	828.0	21.5	25.5
1208.6	686.1	872.5	22.4	28.4
1401.8	646.1	911.8	24.7	34.9
1591.9	569.9	952.4	37.0	61.9
1804.8	496.9	1041.5	43.6	91.4
2003.8	461.2	1137.8	58.1	143.3

Table 100. CO₂ Adsorption on Dry Pocahontas Coal at 319.3 K (System 35)**SI Units**

Cell T (K)	328.2
Moisture content (%)	0
Void volume (m ³)	0.0000879
Pump pressure (MPa)	6.9
Pump T (K)	328.2
Adsorbent mass (g)	55.9
Adsorbed phase density (g/cm ³)	1.027

Pressure (MPa)	Gibbs Ads (mmol/g)	Abs. Ads (mmol/g)	σ Gibbs (mmol/g)	σ Abs (mmol/g)
1.07	0.715	0.727	0.037	0.037
1.66	0.831	0.855	0.036	0.037
2.85	0.979	1.031	0.035	0.037
4.24	1.067	1.161	0.035	0.038
5.55	1.110	1.253	0.035	0.039
6.97	1.124	1.334	0.035	0.042
8.33	1.089	1.385	0.037	0.047
9.84	1.001	1.439	0.043	0.061
11.10	0.860	1.466	0.066	0.113
12.38	0.758	1.575	0.077	0.160
13.84	0.695	1.719	0.105	0.259

English Engineering Units

Cell T (°F)	131.0
Moisture content (%)	0
Void volume (ft ³)	0.003104
Pump pressure (psia)	998.9
Pump T (°F)	131.0
Adsorbent mass (lb)	0.1232

Pressure (psia)	Gibbs Ads (SCF/ton)	Abs. Ads (SCF/ton)	σ Gibbs (SCF/ton)	σ Abs (SCF/ton)
154.9	542.5	552.1	27.7	28.2
240.1	631.0	648.9	27.4	28.2
414.0	742.8	782.2	26.9	28.3
615.7	810.2	880.9	26.5	28.9
805.6	842.8	950.6	26.4	29.8
1010.8	853.1	1012.7	26.7	31.7
1208.1	826.6	1051.0	28.0	35.6
1427.3	759.9	1092.1	32.3	46.4
1610.4	652.8	1112.9	50.2	85.5
1796.1	575.2	1195.5	58.6	121.8
2007.7	527.3	1304.4	79.6	196.9

Two-Dimensional Equations-of-State Modeling and Prediction for Pure-Gas Adsorption

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Abstract

Adsorption equilibrium models are essential in optimizing coalbed methane (CBM) production and CO₂ sequestration processes. Although a number of frameworks are available for describing the adsorption phenomenon, two-dimensional (2-D) equations of state (EOSs), in particular, offer distinct advantages in modeling supercritical, high-pressure adsorption systems.

The current capability of the 2-D EOS pure-fluid modeling requires that model parameters be regressed from individual adsorption isotherms. To facilitate generalized predictions, first correlations were developed to describe the temperature dependence of the EOS parameters, and second the parameters were generalized in terms of adsorbate and adsorbent physical properties.

Model evaluations involving an extensive adsorption database for activated carbons and coals indicate that the 2-D EOS parameter correlations are capable of representing CBM-type gas adsorption on activated carbons and coals with absolute average deviations (AAD) of 2.4%, and 4.7%, respectively. In addition, the generalized EOS model parameters provide gas adsorption predictions for activated carbons within 9% AAD. However, additional work is required to develop accurate parameter generalizations for wet coals.

Keywords: Adsorption, Two-Dimensional Equation of State

Introduction

The adsorption phenomenon plays a major role in coalbed methane (CBM) production and in CO₂ sequestration; therefore, reliable adsorption equilibrium models are essential for the optimum implementation of these processes.

Although a number of frameworks are used to describe the adsorption phenomenon and correlate pure and mixture adsorption isotherms, two-dimensional (2-D) equations of state (EOSs) offer distinct advantages in modeling supercritical, high-pressure adsorption systems. First, the 2-D EOSs permit simultaneous calculation of equilibrium adsorption and volumetric properties. Second, they are amenable to model parameter generalization. Third, they are particularly suitable to extend pure adsorption isotherms to multicomponent mixture predictions using appropriate mixing rules [Zhou, 1994]. Fourth, they offer a proven model format for use in reservoir simulations.

The current capability for 2-D EOS pure-fluid modeling requires that model parameters be regressed from individual adsorption isotherms. Thus, a significant amount of experimental data is required to obtain reliable EOS predictions based on regressed model parameters.

In this study, we develop a new approach for estimating the 2-D EOS model parameters, and consequently, provide for generalized 2-D EOS pure-gas adsorption predictions. Specifically, (a) correlations are developed to describe the temperature dependence of the 2-D EOS parameters, and (b) the parameters are generalized in terms of adsorbate and adsorbent physical properties.

Two-Dimensional EOS Models

Historically, various researchers have applied the 2-D EOS to gas adsorption. Hill (1946) and de Boer (1953) have used the van der Waals (VDW) EOS to correlate pure-gas adsorption. Hoory and Prausnitz (1967) extended the 2-D VDW EOS to mixtures by introducing mixing rules. More recently, DeGance (1992) used the 2-D virial and Eyring EOS to correlate high-pressure pure adsorption isotherms.

In the early 1990's, we presented a generalized 2-D cubic EOS, which encompasses 2-D analogs of previous cubic EOS forms [see, e.g., Zhou et al. 1994]. The generalized 2-D EOS (with an additional parameter, m , for added model flexibility) is analogous to the popular three-dimensional equations of state used in vapor-liquid equilibrium calculations:

$$\left[p + \frac{a_2 \sigma^2}{1 + U b_2 \sigma + W (b_2 \sigma)^2} \right] [1 - (b_2 \sigma)^m] = \sigma R T \quad (1)$$

where π is the spreading pressure, σ is the surface density of the adsorbate, R is the universal gas constant, T is the temperature, a_2 and b_2 are the traditional EOS parameters, and numerical values of U , W , and m may be specified to give various forms of two-dimensional equations of state.

The general two-dimensional analog can be re-written as follows:

$$\left[A p + \frac{a \omega^2}{1 + U b \omega + W (b \omega)^2} \right] [1 - (b \omega)^m] = \omega R T \quad (2)$$

where A is the specific surface area, $\omega = \sigma A$ is the specific amount adsorbed, and $a = a_2/A$ and $b = b_2/A$ are model parameters. The model coefficients, U , W , and m must be specified to obtain a specific form of the 2-D EOS for application. For example,

an analog of the van der Waals (VDW) EOS is obtained by setting $m = 1$ and $U = W = 0$; similarly for the Soave-Redlich-Kwong (SRK) ($m = U = 1$ and $W = 0$); the Peng-Robinson (PR) ($m = 1$, $U = 2$, and $W = -1$); and the Eyring ($m = 1/2$ and $U = W = 0$) EOS.

This general 2-D EOS can be used to investigate EOS behaviors by specifying various combinations of model coefficients. Since the model coefficient, m , is contained in the repulsive term and has a significant effect on the shape of the pure adsorption isotherm, the selection of a value for m is most important among the EOS model coefficients. If U and W are equal to zero, then by setting m to values of 1 and 1/2, the 2-D VDW EOS and the Eyring EOS are obtained, respectively. Actually, the pure gas isotherms vary considerably in shape and Zhou had found that it is sometimes desirable to select an m value even smaller than 1/2 to describe pure isotherms. Based on extensive calculations, Zhou found that an equation with $m = 1/3$ and $U = W = 0$ (the ZGR EOS) promising [Zhou, 1994].

Equilibrium Relations

At equilibrium, the chemical potential of species i in the gas phase is equal to that in the adsorbed phase:

$$\mathbf{m}_i^a = \mathbf{m}_i^g \text{ and } d\mathbf{m}_i^a = d\mathbf{m}_i^g \quad (3)$$

$$\int_{p^*}^p d \ln \hat{f}_i^a = \int_{P^*}^P d \ln \hat{f}_i^g \quad (4)$$

Integrating Equation 4:

$$\ln \hat{f}_i^a(p) - \ln \hat{f}_i^a(p^*) = \ln \hat{f}_i^g(P) - \ln \hat{f}_i^g(P^*) \quad (5)$$

At very low pressure, $\hat{f}_i^a(p^*) = p_i^*$ and $\hat{f}_i^g(P^*) = P_i^*$

$$P_i^* \hat{f}_i^a(\mathbf{p}) = \mathbf{p}_i^* \hat{f}_i^g(P) \quad (6)$$

At very low pressure, 2-D ideal gas law applies:

$$\mathbf{p}_i^* A = \mathbf{w}_i^* RT \quad (7)$$

The Henry's constant is defined as:

$$k_i = \frac{\mathbf{w}_i^*}{P_i^*} \quad (8)$$

So:

$$A \hat{f}_i^a = A x_i \mathbf{p} \hat{\mathbf{f}}_i^a = k_i RT \hat{f}_i^g \quad (9)$$

For pure-gas adsorption:

$$\mathbf{w} Z_a \mathbf{f}^a = k_i f^g \quad (10)$$

where $\mathbf{w}$ is the amount adsorbed, Z_a is the 2-D compressibility factor, $\mathbf{f}^a$ is the fugacity coefficient using the 2-D EOS, and f^g is the fugacity for the gas phase, which was calculated by 3-D PR EOS.

Database and Data Reduction

A literature database (Table 1) and the OSU database (Table 2) are used to evaluate the capabilities of the ZGR EOS and the 2-D PR EOS to model the pure-gas adsorption.

The objective function, S , is used to correlate data with the 2-D EOSs. The function minimizes the sum of the squared-percentage deviations in predicted adsorption:

$$S = 100 \sqrt{\frac{\sum_{i=1}^{NPTS} \left[\frac{\mathbf{w}_i^c - \mathbf{w}_i^e}{\mathbf{w}_i^e} \right]^2}{NPTS}} \quad (11)$$

where w^c and w^e are the calculated and experimental adsorption amount, respectively. NPTS is the number of data points. When the experimental uncertainties are available, the objective function, S_s , is used to correlate data with the 2-D EOS models. The function minimizes the sum of the squared weighted deviations in predicted adsorption:

$$S_s = \sqrt{\frac{\sum_{i=1}^{NPTS} \left[\frac{w_i^c - w_i^e}{s_i^e} \right]^2}{NPTS}} \quad (12)$$

where, σ^e is the expected experimental uncertainty. The percentage average absolute deviation (%AAD) and root-mean-square error (RMSE) are used to evaluate the results:

$$\%AAD = \frac{100}{NPTS} \sum_{i=1}^{NPTS} \left| \frac{w_i^c - w_i^e}{w_i^e} \right| \quad (13)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{NPTS} (w_i^c - w_i^e)^2}{NPTS}} \quad (14)$$

The weighted average absolute deviation (WAAD) is also used to quantify the model evaluations when the expected experimental uncertainties are available:

$$WAAD = \frac{1}{NPTS} \sum_{i=1}^{NPTS} \left| \frac{w_i^c - w_i^e}{s_i^e} \right| \quad (15)$$

Typically, literature data do not provide the expected experimental uncertainty for each measurement; thus, the WAAD evaluation is not included in the corresponding tables.

Modeling of Pure-Gas adsorption

In this section, the correlative capabilities of the ZGR EOS and 2-D PR EOS are evaluated. In this case, the model parameters, α , β , and k , are regressed for each

isotherm. The units for the parameter, α , β , and k are $(\text{bar cm}^3 \text{ mol}^{-1} (\text{mmol/g})^{-1})$, $(\text{mmol/g})^{-1}$, and (mmol/g bar^{-1}) , respectively.

Table 3 presents summary results for the ZGR EOS representation of the literature data. The overall AAD for the 2363 literature data points is 1.7% and the overall RMSE is 0.096 mmol/g. As indicated by the results, N_2 adsorption on Columbia Grade L activated carbon at 422.0 K (System 1) has the worst quality of fit with an AAD of 6.9%, and N_2 adsorption on Coconut Shell activated carbon at 178.0 K (System 20) has the worst RMSE of 0.299 mmol/g.

Table 4 presents summary results for the 2-D PR EOS representation of the literature data. The overall AAD is 1.5% and the overall RMSE is 0.097 mmol/g. For this model, CO_2 adsorption on H-Modernite Z-900H at 323.0 K (System 31) has the worst quality of fit with an AAD of 5.9%. CO_2 adsorption on F30/470 Chemviron activated carbon at 278.0 K (System 12) has the worst RMSE of 0.273 mmol/g.

These results show that both the ZGR EOS and the 2-D PR EOS are capable of representing the pure-gas adsorption equilibrium data on the carbon adsorbents, as well as other adsorbents. Overall, the two models can represent the experimental data equally well. For a complete adsorption isotherm, the ZGR EOS represents the adsorption data better than the PR EOS at higher pressures, while at lower pressures the 2-D PR EOS represents the data more precisely. Since the amount of adsorption is small at low pressure, small absolute errors will lead to large percentage errors. This explains why the ZGR EOS represents the data with slightly higher %AAD and a lower RMSE than for 2-D PR EOS.

Table 5 presents summary results for the ZGR EOS representation of the OSU pure-gas adsorption database. The overall AAD for all 549 OSU experimental data points is 4.3% and the overall RMSE is 0.075 mmol/g. The overall WAAD is 0.6, which means the ZGR EOS can, on average, represent the experimental data within the expected experimental uncertainties. As shown in the table, CO₂ adsorption on wet Illinois #6 coal at 319.3 K (System 63) has the worst quality of fit with an AAD of 10.3% (WAAD of 1.7), and C₂H₆ adsorption on Calgon F-400 activated carbon at 318.2 K (System 50) has the worst RMSE of 0.154 mmol/g.

Table 6 presents summary results of the 2-D PR EOS representation of the OSU pure-gas adsorption database. The overall AAD for all 549 OSU experimental data points is 4.4% and the overall RMSE is 0.077 mmol/g. The overall WAAD is 0.6, which means the 2-D PR EOS can also, on average, represent the experimental data within the expected experimental uncertainties. As shown in the table, CO₂ adsorption on wet Illinois #6 coal at 319.3 K (System 63) has the worst quality of fit with an AAD of 11.5% (WAAD of 1.7), and C₂H₆ adsorption on Calgon F-400 activated carbon at 318.2 K (System 50) has the worst RMSE of 0.154 mmol/g.

In general, adsorption on wet coals is more difficult to model than adsorption on activated carbons. As shown in Tables 5 and 6, CO₂ adsorption on wet coals, in particular, is the most difficult to model. This is attributed in part to how the moisture content is accounted for in the adsorption experiments for wet coals. To account for moisture effects in the current adsorption data reduction procedures, part of the CO₂ is assumed to dissolve in water. However, no account is made of how the water molecules

would affect adsorption. This means the current data reduction procedures may not yield highly accurate adsorption results on wet coals.

Temperature Dependence of 2-D EOS Model Parameters

The results shown in the previous section are based on separate regressions for each individual isotherm. The regressed parameters show a definite temperature dependence. Therefore, temperature relations for each 2-D EOS parameter, α , β , and k , are essential to facilitate adsorption predictions.

Temperature relations for the 2-D EOS parameters can be either empirically or theoretically based. Empirical correlations (e.g., linear relations) can be used to describe the temperature dependence. However, they are rather arbitrary and may not work well for a broad temperature range. In this work, the effort was focused on theory-based relations.

de Boer (1953) related 2-D EOS parameters, a_2 and b_2 , with the 3-D EOS parameter, a and b , through:

$$a_2 = \frac{3a}{8d} \quad (16)$$

$$b_2 = \frac{3b}{4d} \quad (17)$$

where d is the diameter of the gas molecule. In doing so, he assumed that the adsorbent is inert to adsorption. Thus, he could derive the critical temperature, T_{c2} , for the 2-D EOS:

$$T_{c2} = \frac{T_c}{2} \quad (18)$$

where T_c is the critical temperature. However, because surface interactions with the gas molecules exist in the 2-D phase, the simple transformations of model parameters from

3-D EOS to 2-D EOS had few successful applications. In other words, the 2-D critical properties are not only gas dependent, but also depend on the adsorbent. If the above relations are used, we obtain:

$$\frac{\mathbf{a}}{\mathbf{b}} = \frac{a_2}{b_2} = \frac{a}{2b} \quad (19)$$

As indicated in Tables 4 and 6, the value of α for the 2-D VDW-type EOS is negative. Although the ZGR EOS forces α to be positive by revising the repulsive term in the EOS, Equation 19 is still invalid.

In this work, a different route was taken to generate the temperature relations for the 2-D EOS parameters. Here, we rely on the Ono-Kondo lattice theory and other theories to generate the temperature relations for the 2-D EOS parameters.

Temperature Dependence of β :

For the surface density of the adsorbate, $\mathbf{s}_m$ (mmol/m²), the relation below is used by Sudibandriyo [See section K-V at Page 172]:

$$\frac{d\mathbf{s}_m / dT}{\mathbf{s}_m} = -\mathbf{d} \quad (20)$$

where δ is the thermal expansion coefficient for the adsorbed gas.

β in the 2-D EOS is the inverse of the maximum adsorption capacity:

$$\mathbf{b} = \frac{I}{(\mathbf{s}_m A)} \quad (21)$$

Combining Equations 12 and 13 and integrating yields:

$$\ln\left(\frac{I}{\mathbf{b}A}\right) - \ln\left(\frac{I}{\mathbf{b}_o A}\right) = -\mathbf{d}(T - T_o) \quad (22)$$

or

$$\ln(\mathbf{b}) = dT - [dT_0 + \ln \mathbf{s}_{m,0} + \ln A] \quad (23)$$

where T_0 is set at the normal boiling point of the adsorbate (triple point for CO₂), and

$\mathbf{s}_{m,0}$ is the maximum surface density of the adsorbate at T_0 .

Temperature Dependence of Henry's Constant:

Henry's constant, k , is defined as:

$$k = \left. \frac{d\mathbf{w}_a}{dP} \right|_{P=0} \quad (24)$$

From the Ono-Kondo Lattice theory [See section K-V at Page 172]:

$$\ln \left[\frac{x_a (1 - x_b)}{x_b (1 - x_a)} \right] + ((c_p + c_v)x_a - cx_b) \frac{\mathbf{e}_{ff}}{kT} + \frac{\mathbf{e}_{fs}}{kT} = 0 \quad (25)$$

where: $x_a = \frac{\mathbf{r}_a}{\mathbf{r}_{mc}}$, $x_b = \frac{\mathbf{r}_b}{\mathbf{r}_{mc}}$, $\mathbf{r}_a$ is the adsorbed phase density, $\mathbf{r}_b$ is the bulk gas

phase density, $\mathbf{r}_{mc}$ is the maximum density defined as $\mathbf{r}_{mc} = \mathbf{s}_{m,0}/d$, $\mathbf{e}_{ff}$ is the

adsorbate-adsorbate interaction energy, $\mathbf{e}_{fs}$ is the adsorbate-adsorbent interaction energy,

and c_p , c_v , and c are model constants.

The absolute adsorption, $\mathbf{w}_a$, is defined as:

$$\mathbf{w}_a = 2C x_a = 2C \frac{\mathbf{r}_a}{\mathbf{r}_{mc}} \quad (26)$$

where $2C$ is the maximum adsorption capacity. Taking the derivative of Equation 25

with respect to pressure at the zero pressure limit yields:

$$\left. \frac{dx_a}{dP} \right|_{P=0} = \left(\frac{x_a}{x_b} \frac{dx_b}{dP} \right) \Big|_{P=0} \quad (27)$$

Thus, Henry's constant becomes:

$$k = \left. \frac{d\mathbf{w}_a}{dP} \right|_{P=0} = 2C \left. \frac{dx_a}{dP} \right|_{P=0} = 2C \frac{x_a}{x_b} \left. \frac{dx_b}{dP} \right|_{P=0} = 2C \frac{x_a}{x_b} \frac{1}{\mathbf{r}_{mc} RT} \quad (28)$$

Meanwhile, Equation 25 can be simplified at low pressure to yield:

$$\ln \left[\frac{x_a}{x_b} \right] + \frac{\mathbf{e}_{fs}}{kT} = 0 \quad (29)$$

Combining Equations 28 and 29, and identifying that $2C$ in the Ono-Kondo (OK) model is equivalent to $1/\beta$ in 2-D EOS yields:

$$k = \frac{1}{\mathbf{b} \mathbf{r}_{mc} RT} \exp \left(\frac{-\mathbf{e}_{fs}}{kT} \right) \quad (30)$$

where $\mathbf{e}_{fs}$ is the adsorbate-adsorbent or fluid-solid interaction energy.

The fluid-solid energy parameter, ϵ_{fs}/k , may be expressed in terms of the interaction of a single molecule with a single lattice plane. If z is the distance between the adsorbate molecule i and the lattice carbon plane, the potential energy can be written as follows:

$$\mathbf{F}_{i,SLP} = 4\mathbf{p} \mathbf{r}_s \mathbf{e}_{fs}^* \mathbf{s}_{fs}^2 \left[\frac{1}{5} \left(\frac{\mathbf{s}_{fs}}{z} \right)^{10} - \frac{1}{2} \left(\frac{\mathbf{s}_{fs}}{z} \right)^4 \right] \quad (31)$$

This potential energy has a minimum and its depth is given by:

$$\mathbf{e}_{fs} = \frac{6}{5} \mathbf{p} \mathbf{r}_s \mathbf{e}_{fs}^* \mathbf{s}_{fs}^2 \quad (32)$$

where $\mathbf{r}_s$ is the solid atom density of the adsorbent, $\mathbf{s}_{fs} = \frac{(\mathbf{s}_{ff} + \mathbf{s}_{fs})}{2}$ is the fluid-solid

collision diameter, and $\mathbf{e}_{fs}^* = \sqrt{\mathbf{e}_{ff}^* \mathbf{e}_{ss}^*}$ is the fluid-solid well depth potential. For carbon

adsorbent, $\mathbf{r}_s = 0.382 \text{ atom/\AA}^2$ [Do, 1998].

Temperature Dependence of α :

In 2-D EOS, only the interactions within the adsorbed phase are considered. To estimate the attractive term in the 2-D EOS, de Boer(1953) used Equation 33 to estimate a_2 :

$$a_2 = \frac{N_a^2}{2} \int_{s_{ff}}^{\infty} \frac{4e_{ff}s_{ff}^6}{r^6} 2prdr \quad (33)$$

However, in the 2-D phase, the attractive interactions are affected by the attractive force from the adsorbent surface. To estimate the attractive energy among the adsorbate molecules, a correction to Equation 33 is necessary to discount the influence of the surface interactions.

A method to evaluate a more realistic attractive term for the adsorbed gas is to deduct the attractive energy of the adsorbate-adsorbent from Equation 25. Although this is not a rigorous method, it does provide a reasonable approximation. In this study, an expression is derived for the total attractive energy between the adsorbed molecules and the solid surface, a_2' , given as:

$$a_2' = \frac{N_a^2}{2} \int_{s_{fs}}^{\infty} \frac{2pr_s e_{fs} s_{fs}^6}{r^4} 2rdr \quad (34)$$

Since α is the total attractive energy per surface area, then after correcting for the surface interactions, we obtain:

$$a = \frac{a_2 - a_2'}{A} = \left(\frac{N_a^2}{2} \int_{s_{ff}}^{\infty} \frac{4e_{ff}s_{ff}^6}{r^6} 2prdr - \frac{N_a^2}{2} \int_{s_{fs}}^{\infty} \frac{2pr_s e_{fs} s_{fs}^6}{r^4} 2rdr \right) / A \quad (35)$$

or

$$a = \left(N_a^2 p e_{ff} s_{ff}^2 - N_a^2 2pr_s e_{fs} s_{fs}^4 / 3 \right) / A \quad (36)$$

Usually, the adsorbate-adsorbent attractive energy is larger than the adsorbate-adsorbate attractive energy, which explains why the regressed parameter, α , in the 2-D PR EOS is mostly negative.

However, Equation 36 only works for 2-D VDW type of EOS. For the other 2-D EOS, such as Eyring EOS and ZGR EOS, the repulsive term was revised to obtain positive α values. The empirical revision of the repulsive term makes it more difficult to estimate α , because in both equations, α is also correlated of β . That is, empirically, α and β tend to exhibit a linear relation for a moderate temperature range.

Results for Generalization of Model Temperature Dependence

Based on the above analyses, the temperature relations for 2-D PR EOS parameters are generalized, as they relate to some of the gas properties and adsorbent characteristics. In this study, the 2-D PR EOS will be used to demonstrate the efficacy of the new temperature relations for the 2-D EOS parameters.

Table 7 summarizes the physical properties of the adsorbates investigated in this study. For the gas adsorption on activated carbons, the solid-solid interaction, e_{ss} , the maximum surface density of the adsorbate at T_0 , $S_{m,\rho}$, and the thermal expansion coefficient, d , are regressed for each adsorption system at various temperatures. The specific adsorbent surface area, A , is not a directly measured value; consequently, it is inferred from adsorption measurements using selected models. In this study, the N_2 BET surface area at 77 K is used due to availability and standardization.

Figure 1 shows the effect of variation in surface area on the adsorption representations. The adsorption in this sample calculation is for CO_2 adsorption on

activated carbon measured at OSU. From the figure, we see that a 10% variation in the surface area yields no significant difference in the correlation results; albeit, different surface area estimates produce different regressed model parameter values.

Table 8 presents summary results for the 2-D PR EOS representation of the pure-gas adsorption data on various activated carbons (Systems 1 to 25 and Systems 47 to 50). Adsorption on Zeolites was not included here, since characterization data for these adsorbents are not available. The overall AAD for the 1922 data points is 2.4 % and the overall RMSE is 0.199 mmol/g. In comparison, the overall AAD and RMSE for the adsorption on activated carbon from Tables 4 and 6 are 1.4% and 0.108 mmol/g, respectively. While errors have doubled, use of temperature relations provides for adsorption predictions over the desired temperature range.

Unlike activated carbons, the coals we investigated do not have the commercial surface area data available. Since each system includes only one isotherm, we fixed the surface density and thermal expansion coefficient for the gas adsorption on coals. Only surface area and solid-solid interaction are regressed in this case.

For the maximum surface density, we used a hexagon to represent the minimum area occupied by the gas molecule on the adsorbent surface, thus the maximum surface density:

$$s_{m,0} = \frac{I}{\left[\frac{3\sqrt{3}}{2} \left(\frac{s_{ff}}{2} \right)^2 N_a \right]} \quad (37)$$

The thermal expansion coefficient is fixed to be 0.0024 (1/K), as suggested by Sudibandriyo [Section K-IV on Page 172].

Table 9 presents summary results for the 2-D PR EOS representations of the pure-gas adsorption on wet and dry coals using the generalized temperature relations of Equations 23, 30, and 36. The overall AAD for the 432 data points is 4.7%; the overall RMSE is 0.050 mmol/g; and the overall WAAD is 0.6. As indicated in the table, CO₂ adsorption on dry Illinois #6 coal (System 77) has the worst quality of fit with AAD of 10.2% and RMSE of 0.155 mmol/g. CH₄ adsorption on wet Tiffany coal (System 68) has the worst WAAD of 1.3.

Regressing the surface area of a given matrix using various adsorbates leads to different area estimates. In addition, the value of the regressed surface area is affected by the values chosen for the maximum surface density and the thermal expansion coefficient. The results indicate that among the CBM gases (CH₄, CO₂, and N₂), N₂ accesses the least surface area and has the lowest fluid-solid interaction energy, while CO₂ accesses the most surface area and has the highest fluid-solid interaction energy.

Overall, the regression results described above using the temperature relations show that the 2-D PR EOS can be applied successfully within the experimental uncertainties (WAAD of 0.6). However, CO₂ adsorption on coals produces less favorable results. As discussed in the previous section, adsorption on wet coals is difficult to model, partly because the current procedures do not account effectively for the moisture effects in the data reduction procedures. In this case, it may also be that the thermal expansion coefficient for CO₂ is underestimated.

Predictions for Pure-Gas Adsorption on Activated Carbons

Predictions of pure-gas adsorption on activated carbon require: the surface area of the adsorbent, the solid-solid interaction of the adsorbent, the maximum surface

density of the adsorbate, and the thermal expansion coefficient of the adsorbate. Surface area of the adsorbent was taken as the N₂ BET surface area, which was available for each activated carbon.

The solid-solid interaction of the adsorbent is highly dependent on the matrix structure. However, for most of the activated carbons with the surface area of about 1000 m²/g, the solid-solid interaction parameter is approximately 40 K [Section K-IV on Page 172]. However, an activated carbon with higher surface area tends to have weaker solid-solid interaction, thus lower values for the solid-solid interaction parameter are used. For example, we use a parameter value of 20 K for the activated carbon made from Coconut Shell, which has a surface area of 3106 m²/g. Moreover, for the surface area for Charcoal in Systems 4 and 5, we use 45 K for the solid-solid interaction. All these solid-solid interaction energy values were fixed empirically from the regressed values in Table 8.

The maximum surface density can be calculated approximately from the molecular size. The maximum surface density is defined in previous section as:

$$S_{m,0} = \frac{I}{\left[\frac{3\sqrt{3}}{2} \left(\frac{S_{ff}}{2} \right)^2 N_a \right]} \quad (36)$$

Also, a value of 0.0024 (1/K) is used for the thermal expansion coefficient for all the gases considered.

Table 10 presents the 2-D PR EOS summary results for representing the pure-gas adsorption on various activated carbons. The overall AAD for the 1922 data points is 8.6% and the overall RMSE is 0.617 mmol/g. As shown in the table, CO₂ adsorption on Calgon F-400 activated carbon (System 49) has the worst quality of fit with AAD of

18.6%, and CO₂ adsorption on Norit R1 activated carbon (System 25) has the worst RMSE of 1.861 mmol/g.

Overall, the generalized model predictions yield less than 10.0 %AAD for pure-gas adsorption data on activated carbons. The results indicate that CO₂ adsorptions on activated carbons are the most difficult to predict. To achieve better prediction for all the systems of interest, improved estimates for the fluid-solid interaction and the thermal expansion coefficient of the gas are required.

Discussion

Table 11 represents the overall results of the pure-gas modeling using 2-D EOSs. Indicated by the error profiles for the data regressions, the temperature relations for the 2-D PR EOS are effective in representing the pure-gas adsorption data. Further, the pure-gas adsorption predictions for activated carbons are reasonably accurate with AAD of 8.6%, corresponding to a WAAD less than 3.0

Figure 2 illustrates the capabilities of 2-D EOS to represent and *a priori* predict pure CO₂, CH₄, N₂, and C₂H₆ adsorption on activated carbon at 318.2 K. As indicated the EOS can describe the experimental data within the expected experimental uncertainties. Similarly, excellent predictions are obtained for CH₄, N₂, and C₂H₆ adsorption on activated carbon. However, accurate predictions for CO₂ can be obtained when the surface area is increased from 950 to 1200 m²/g.

A sample calculation is given to demonstrate the 2-D PR EOS predictions involving different isotherms. In this case, CH₄ adsorption data (System 16, 12 data points) up to 5.7 MPa at 233 K were regressed to obtain the EOS parameters, the surface area and fluid-solid interaction. Using this information, the model predicted, as shown in

Figure 3, the higher-pressure adsorption of the same isotherm as well as the other adsorption isotherms over the full pressure range (System 16, 110 data points). The overall AAD and RMSE of 3.0% and 0.361 mmol/g, respectively, were obtained compared to 2.0% and 0.242 mmol/g, using parameters regressed from all the data.

These preliminary results indicate the effectiveness of the (a) newly-developed 2-D PR EOS temperature relations, and (b) parameter-calibrated predictions.

Figure 4 shows the representation and prediction results for pure CO₂ adsorption on activated carbon at four different temperatures. Both methods are capable of accurately representing of the experimental data; however, the EOS predictions underestimate the adsorption for low-temperature isotherms, and overestimate the adsorption for high-temperature isotherms. This is primarily due to the value used for the thermal expansion coefficient. As can be seen from Table 8, the regressed thermal expansion coefficient for this system is 0.0057, but a smaller value of 0.0024 is used in the prediction.

Figure 5 shows the representation results for the pure CO₂, CH₄, and N₂ adsorption on wet Fruitland coal at 319.3 K. The representations are within the expected experimental uncertainties.

The results of this study indicate that the surface area, fluid-solid interaction, maximum surface density, and thermal expansion coefficient provide effective input for EOS parameter generalization, which could facilitate *a priori* adsorption predictions.

Although the surface area for an individual adsorbent should be a unique value, different adsorbates may access different surface areas; especially when the adsorbent is porous. From the data regressions for gas adsorption on coals, we obtain similar surface areas for N₂ and CH₄ while surface areas regressed from CO₂ adsorption are usually

much higher. This may also explain, in part, why the CO₂ adsorption predictions are less satisfactory compared to the other gases.

The maximum surface density of the adsorbate is relatively independent of the adsorbent. However, the thermal expansion coefficient is highly dependent on the characteristics of the adsorbent and adsorbate. In the present predictions, a fixed value of 0.0024 is used. Thus, to predict adsorption with higher accuracy, the thermal expansion coefficient should be derived based on both the adsorbent and adsorbate properties.

For the fluid-solid interaction, we only considered the interaction of the adsorbate with carbon atoms in the adsorbent. However, different activated carbons have different additional functional groups, which may significantly impact on the adsorption.

In addition to the four model parameters discussed above, other adsorbate and adsorbent characteristics are also important for accurate adsorption predictions. For example, the carbon atom density in the adsorbent will influence the fluid-solid interaction. In this work, the carbon atom density is set to the value of graphite; albeit, this property varies for different carbon adsorbents.

Although a generalized capability has not been fully developed for wet coals, the results obtained for the activated carbon are encouraging. However, to realize this objective, attention is required to address the effect of moisture on coalbed adsorption behavior. We believe developing reliable generalized models is not complete without a proper understanding of, and rigorous accounting for, the effects of moisture on adsorption capacity, adsorbed-phase densities, and the competitive adsorption in mixtures. In fact, as stated earlier, we need to address this issue before we can develop structure-based characterizations. At present, confusion relating to the proper accounting

for moisture content significantly limits the value of the existing literature data for developing generalized predictions.

Conclusions

In summary, the 2-D EOS modeling results for pure-gas adsorption indicate that:

1. In general, both the ZGR EOS and the 2-D PR EOS can represent the pure-gas adsorption precisely within the expected experimental uncertainties of about 2%. Overall, the new temperature relations for the 2-D PR EOS enable us to represent the pure-gas adsorption within the expected experimental uncertainties without the need to regress each isotherm.
2. The revised attractive term for the 2-D PR EOS works well for all the data considered in this work, however, it does not account for temperature variations. To account for the molecular attraction more accurately, we need to delineate temperature dependence of the α function.
3. Overall, the 2-D PR EOS is capable of predicting pure-gas adsorption on activated carbons with AAD of 9%. The results are comparable to the predictions using the OK model, which yields 8 %AAD [See section K-V at Page 172]. Moreover, improved estimates for the surface area and fluid-solid interaction could be helpful in achieving higher prediction accuracy.
4. Although a generalized capability to predict CBM-type adsorption on wet coals has not been fully developed, the results obtained for the activated carbons demonstrate a realistic potential for doing so.

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Table 1. Literature Data Used for Pure-Gas Adsorption Model Evaluation

System No.	Adsorbent	Adsorbent Surf. area (m ² /g)	Adsorbate	Temp. Range (K)	Pressure Range (MPa)	Reference
1	AC, Columbia Grade L	1152	N ₂	311 - 422	0.028 – 1.50	Ray (1950)
2	AC, Columbia Grade L	1152	CH ₄	311 - 422	0.026 – 1.48	Ray (1950)
3	AC, Columbia Grade L	1152	C ₂ H ₆	311 - 478	0.007 – 1.49	Ray (1950)
4	Charcoal	1157	CH ₄	283 - 323	0.5 – 13.8	Payne (1968)
5	Charcoal	1157	C ₃ H ₈	293 - 333	8x10 ⁻⁴ – 1.35	Payne (1968)
6	AC, BPL	988	CH ₄	213 - 301	0.012 – 3.83	Reich (1980)
7	AC, BPL	988	C ₂ H ₆	213 - 301	7x10 ⁻⁴ – 1.71	Reich (1980)
8	AC, BPL	988	C ₂ H ₄	213 - 301	7x10 ⁻⁴ – 1.70	Reich (1980)
9	AC, BPL	988	CO ₂	213 - 301	0.003 – 3.84	Reich (1980)
10	AC, PCB-Calgon Corp.	1150-1250	CH ₄	296 - 480	0.27 – 6.69	Ritter (1987)
11	AC, PCB-Calgon Corp.	1150-1250	CO ₂	296 - 480	0.11 – 3.67	Ritter (1987)
12	AC F30/470, Chemviron Carbon	993.5	CO ₂	278 - 328	0.05 – 3.35	Berlier (1997)
13	AC Norit R1 Extra	1450	N ₂	298	0.03 – 5.98	Dreisbach (1999)
14	AC Norit R1 Extra	1450	CH ₄	298	0.01 – 5.75	Dreisbach (1999)
15	AC Norit R1 Extra	1450	CO ₂	298	0.008 – 6.0	Dreisbach (1999)
16	AC from Coconut shell with KOH activation	3106 (CO ₂ ads.)	CH ₄	233 - 333	0.09 – 9.40	Zhou (2000)
17	AC -Calgon F-400	850	CO ₂	303 to 318	0.02 – 20.2	Humayun (2000)
18	AC-Norit RB1	1100	CH ₄	294 - 351	0.05 – 0.8	Vaart (2000)
19	AC-Norit RB1	1100	CO ₂	294 - 348	0.05 – 0.8	Vaart (2000)
20	AC from Coconut shell with KOH activation	3106 (CO ₂ ads.)	N ₂	178 - 298	0.44 – 9.19	Zhou (2001)
21	AC F30/470, Chemviron Carbon	993.5	N ₂	303 - 383	0.39 – 9.5	Frère (2002)

Table 1. Literature Data Used for Pure-Gas Adsorption Model Evaluation - Cont'd

System No.	Adsorbent	Adsorbent Surf. area (m²/g)	Adsorbate	Temp. Range (K)	Pressure Range (MPa)	Reference
22	AC F30/470, Chemviron Carbon	993.5	CH ₄	303 - 383	0.44 – 8.98	Frère (2002)
23	AC F30/470, Chemviron Carbon	993.5	C ₃ H ₈	303 - 383	0.05 – 2.20	Frère (2002)
24	AC Norit R1	1262	N ₂	298	0.03 – 14.56	Beutekamp (2002)
25	AC Norit R1	1262	CO ₂	298	0.03 – 6.04	Beutekamp (2002)
26	Zeolite, Linde 13 X	525	N ₂	298 - 348	0.35 – 8.23	Wakasugi (1981)
27	Zeolite, Linde 5A	~400	N ₂	298 - 348	0.60 – 17.61	Wakasugi (1981)
28	Zeolite, Linde 5A	~400	CH ₄	298 - 348	0.36 – 9.18	Wakasugi (1981)
29	Zeolite, Linde 5A	~400	CO ₂	298 - 348	0.03 – 11.22	Wakasugi (1981)
30	Zeolite, Linde 5A	~400	C ₂ H ₆	298 - 348	0.07 – 5.07	Wakasugi (1981)
31	H-Modernite, Norton Co: Type Z-900H	~300	CO ₂	283 - 333	3x10 ⁻⁴ – 0.29	Talu (1986)
32	H-Modernite, Norton Co: Type Z-900H	~300	H ₂ S	283 - 368	4x10 ⁻⁴ – 0.10	Talu (1986)
33	H-Modernite, Norton Co: Type Z-900H	~300	C ₃ H ₈	283 - 324	2x10 ⁻⁵ – 0.21	Talu (1986)
34	Zeolite G5	430	CH ₄	283 - 303	0.13 – 1.15	Berlier (1995)
35	Zeolite G5	430	C ₂ H ₆	283 - 303	0.056 – 1.10	Berlier (1995)
36	Zeolite G5	430	C ₂ H ₄	283 - 303	0.056 – 1.10	Berlier (1995)
37	Zeolite13 X	383	CH ₄	298	0.15 – 15.02	Beutekamp (2002)
38	Zeolite13 X	383	C ₂ H ₆	298	0.14 – 3.95	Beutekamp (2002)

Table 2. OSU Database for Pure -Gas Adsorption Model Evaluation

System No.	Adsorbent	Adsorbate	Temp. (K)	Pressure Range (MPa)
47	Dry AC – F 400	N ₂	318	0.7 – 13.7
48	Dry AC – F 400	CH ₄	318	0.7 – 13.7
49	Dry AC – F 400	CO ₂	318	0.7 – 13.7
50	Dry AC – F 400	C ₂ H ₆	318	0.7 – 13.7
55a	Wet Fruitland Coal	N ₂	319	0.7 – 12.4
56a	Wet Fruitland Coal	CH ₄	319	0.7 – 12.4
57a	Wet Fruitland Coal	CO ₂	319	0.7 – 12.4
55b	Wet Fruitland Coal	N ₂	319	0.7 – 12.4
56b	Wet Fruitland Coal	CH ₄	319	0.7 – 12.4
57b	Wet Fruitland Coal	CO ₂	319	0.7 – 12.4
61	Wet Illinois #6 Coal	N ₂	319	0.7 – 12.4
62	Wet Illinois #6 Coal	CH ₄	319	0.7 – 12.4
63	Wet Illinois #6 Coal	CO ₂	319	0.7 – 12.4
67	Wet Tiffany Coal	N ₂	328	0.7 – 13.7
68	Wet Tiffany Coal	CH ₄	328	0.7 – 13.7
69	Wet Tiffany Coal	CO ₂	328	0.7 – 13.7
74	Wet LB Fruitland Coal	N ₂	319	0.7 – 12.4
75	Wet LB Fruitland Coal	CH ₄	319	0.7 – 12.4
76	Wet LB Fruitland Coal	CO ₂	319	0.7 – 12.4
77	Dry Illinois #6 Coal	CO ₂	328	0.7 – 13.7
78	Dry Beulah Zap Coal	CO ₂	328	0.7 – 13.7
79	Dry Wyodak Coal	CO ₂	328	0.7 – 13.7
80	Dry Upper Freeport Coal	CO ₂	328	0.7 – 13.7
81	Dry Pocahontas Coal	CO ₂	328	0.7 – 13.7

Table 3. Regression Results for Pure-Gas Adsorption Using the ZGR EOS (Literature Data)

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
1	AC, Columbia Grade L	N ₂	9	310.9	29044.0	0.1970	-0.1972	4.0	0.018
			5	338.7	38094.0	0.2317	0.2569	0.9	0.021
			9	366.5	65053.0	0.3304	0.8711	5.8	0.014
			8	394.3	92188.0	0.4234	1.2188	4.6	0.015
			5	422.0	165120.0	0.6722	1.5681	6.5	0.051
2	AC, Columbia Grade L	CH ₄	12	310.9	12826.0	0.1027	-1.5128	4.6	0.035
			10	338.7	20396.0	0.1373	-0.9923	3.0	0.062
			8	366.5	36268.0	0.1938	-0.3557	3.2	0.063
			7	394.3	45037.0	0.2327	0.0464	3.4	0.039
			8	422.0	68579.0	0.3000	0.5199	3.7	0.033
3	AC, Columbia Grade L	C ₂ H ₆	10	310.9	5088.1	0.0786	-4.8089	1.1	0.107
			9	338.7	8669.9	0.0941	-3.8745	0.4	0.016
			10	366.5	10854.0	0.0998	-3.0381	1.7	0.039
			10	394.3	10597.0	0.0953	-2.4349	2.4	0.022
			9	422.0	25601.0	0.1383	-1.6549	1.5	0.055
			5	449.8	19902.0	0.1197	-1.2724	0.6	0.022
			5	477.6	25903.0	0.1314	-0.6391	0.7	0.020
4	Charcoal	CH ₄	8	283.2	3213.3	0.0455	-2.3149	0.1	0.007
			12	293.2	3499.3	0.0469	-2.0478	0.4	0.027
			12	303.2	5048.1	0.0535	-1.7118	0.3	0.022
			10	313.2	6795.5	0.0598	-1.2870	0.8	0.044
			13	323.2	7282.7	0.0627	-1.1558	0.8	0.027
5	Charcoal	C ₃ H ₈	10	293.2	8094.2	0.0885	-6.5361	2.9	0.136
			11	303.2	2898.4	0.0769	-7.1687	1.0	0.056
			10	313.2	4564.9	0.0796	-6.4215	0.8	0.039
			11	323.2	6280.1	0.0845	-5.8480	0.6	0.032
			10	333.2	6449.8	0.0874	-5.7200	0.2	0.016

Table 3. Regression Results for Pure-Gas Adsorption Using the ZGR EOS (Literature Data) - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
6	AC, BPL	CH ₄	23	212.7	2488.2	0.0581	-4.2230	1.3	0.123
			24	260.2	4649.3	0.0638	-2.3138	1.0	0.039
			25	301.4	9887.4	0.0873	-1.1285	1.1	0.026
7	AC, BPL	C ₂ H ₆	18	212.7	4260.2	0.0833	-8.1825	2.6	0.168
			15	260.2	2714.8	0.0752	-6.1280	0.9	0.056
			16	301.4	6583.2	0.0865	-4.1326	0.7	0.031
8	AC, BPL	C ₂ H ₄	21	212.7	-1335.4	0.0518	-8.5283	2.9	0.163
			15	260.2	2473.5	0.0674	-5.4529	0.5	0.027
			16	301.4	5703.9	0.0783	-3.6855	0.6	0.028
9	AC, BPL	CO ₂	21	212.7	3346.4	0.0481	-5.8453	1.0	0.056
			14	260.2	3944.4	0.0477	-3.5773	0.3	0.020
			25	301.4	5310.8	0.0509	-2.1118	0.9	0.054
10	AC, PCB-Calgon	CH ₄	7	296.0	7504.7	0.0724	-1.8382	0.2	0.016
			8	373.0	10975.0	0.0847	-0.4204	0.7	0.025
			7	480.0	49443.0	0.1952	1.4678	1.5	0.036
11	AC, PCB-Calgon	CO ₂	4	296.0	4566.7	0.0467	-2.9818	0.1	0.022
			4	373.0	9531.0	0.0634	-0.9731	1.1	0.048
			4	480.0	23246.0	0.1057	0.5901	1.2	0.028
12	AC, F30/470 Chemviron Carbon	CO ₂	30	278.0	3770.1	0.0518	-3.8627	1.3	0.274
			19	288.0	2569.9	0.0441	-3.5255	1.1	0.156
			19	298.0	4217.3	0.0520	-3.0716	0.3	0.039
			19	303.0	4214.3	0.0520	-3.0045	0.4	0.028
			38	308.0	4193.7	0.0516	-2.9226	0.5	0.047
			19	318.0	4611.1	0.0532	-2.4638	0.5	0.039
			20	328.0	6329.5	0.0619	-2.1993	0.7	0.037

Table 3. Regression Results for Pure-Gas Adsorption Using the ZGR EOS (Literature Data) - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
13	AC, Norit R1 Extra	N ₂	10	298.0	13302.0	0.0999	-0.1924	5.0	0.074
14	AC, Norit R1 Extra	CH ₄	12	298.0	6276.9	0.0600	-1.6807	2.9	0.028
15	AC, Norit R1 Extra	CO ₂	12	298.0	3957.2	0.0377	-2.5799	3.4	0.042
16	AC, Coconut Shell	CH ₄	21	233.0	1220.3	0.0191	-3.2053	0.8	0.205
			19	253.0	1670.1	0.0208	-2.6098	0.8	0.130
			22	273.0	2029.6	0.0228	-2.2061	0.9	0.105
			21	293.0	2648.1	0.0253	-1.7117	1.0	0.070
			20	313.0	3603.1	0.0292	-1.2143	1.5	0.076
			19	333.0	4512.7	0.0323	-0.8048	1.9	0.088
17	AC, Calgon F-400	CO ₂	75	303.6	3575.1	0.0443	-2.5517	2.0	0.164
			74	305.2	4051.9	0.0444	-2.2401	3.1	0.216
			75	309.2	3731.1	0.0426	-2.1518	2.8	0.174
			76	313.2	2894.4	0.0388	-2.1469	2.7	0.126
			76	318.2	4939.2	0.0494	-1.9917	2.7	0.137
18	AC, Norit RB1	CH ₄	16	304.9	7147.5	0.0798	-2.1724	0.2	0.005
			16	311.4	11509.0	0.1019	-1.6680	0.5	0.008
			16	331.3	17080.0	0.1266	-1.2123	0.7	0.010
			16	350.5	24887.0	0.1604	-0.8182	0.9	0.009
19	AC, Norit RB1	CO ₂	16	305.2	4969.1	0.0544	-3.0951	0.1	0.005
			16	311.2	6392.0	0.0615	-2.5513	0.2	0.007
			16	329.5	8877.3	0.0733	-2.0516	0.5	0.011
			16	348.3	13363.0	0.0951	-1.6172	0.7	0.017

Table 3. Regression Results for Pure-Gas Adsorption Using the ZGR EOS (Literature Data) - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
20	AC, Coconut Shell	N ₂	10	178.0	619.8	0.0192	-3.8980	1.8	0.299
			11	198.0	1320.8	0.0233	-3.0557	0.8	0.139
			10	218.0	2044.5	0.0279	-2.3677	0.5	0.061
			10	233.0	2550.2	0.0305	-1.7953	0.2	0.023
			11	258.0	3185.9	0.0333	-1.3115	0.2	0.021
			10	278.0	3213.5	0.0336	-0.9952	0.8	0.060
			9	298.0	4605.2	0.0397	-0.5387	1.5	0.063
21	AC F30/470	N ₂	25	303.0	18796.0	0.1437	-0.1909	1.7	0.072
			19	323.0	22313.0	0.1597	0.1145	1.5	0.052
			24	343.0	28079.0	0.1818	0.5169	1.1	0.036
			24	363.0	34520.0	0.2072	0.8146	1.0	0.024
			24	383.0	38952.0	0.2264	0.9946	0.8	0.017
22	AC F30/470	CH ₄	24	303.0	14642.0	0.1055	-1.1040	2.3	0.133
			24	323.0	15027.0	0.1093	-0.9850	1.9	0.111
			25	343.0	17710.0	0.1203	-0.6642	2.2	0.121
			25	363.0	20496.0	0.1323	-0.4041	2.3	0.111
			24	383.0	24589.0	0.1458	-0.0205	1.5	0.058
23	AC F30/470	C ₃ H ₈	11	303.0	-12807.0	0.0197	-8.6208	1.4	0.129
			15	323.0	-10732.0	0.0270	-7.2295	0.8	0.061
			19	343.0	-11627.0	0.0222	-6.4518	0.5	0.037
			23	363.0	156.0	0.0826	-5.7327	0.3	0.021
			34	383.0	12755.0	0.1140	-3.9619	1.1	0.077
24	AC Norit R1	N ₂	31	298.0	11388.0	0.0880	-0.3194	3.5	0.078
25	AC Norit R1	CO ₂	29	298.0	3121.7	0.0325	-2.5906	0.8	0.070

Table 3. Regression Results for Pure-Gas Adsorption Using the ZGR EOS (Literature Data) - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
26	Zeolite, Linde 13X	N ₂	8	298.0	22294.0	0.1938	-0.1936	1.4	0.032
			8	323.0	28568.0	0.2166	0.4122	1.6	0.031
			8	348.0	36158.0	0.2412	0.9510	1.9	0.035
27	Zeolite, Linde 5A	N ₂	9	298.0	19781.0	0.1930	-0.7314	1.1	0.047
			9	323.0	19652.0	0.1902	-0.2451	1.0	0.032
			9	348.0	24782.0	0.2067	0.3614	0.8	0.021
28	Zeolite, Linde 5A	CH ₄	10	298.0	22175.0	0.1912	-1.2523	0.7	0.033
			10	323.0	24259.0	0.1993	-0.7701	0.5	0.015
			8	348.0	31317.0	0.2195	-0.0772	0.8	0.027
29	Zeolite, Linde 5A	CO ₂	11	298.0	-12794.0	0.1109	-10.5178	1.4	0.101
			15	323.0	-1151.9	0.1378	-7.9717	1.0	0.077
			15	348.0	9972.5	0.1547	-5.6726	1.1	0.054
30	Zeolite, Linde 5A	C ₂ H ₆	9	298.0	66146.0	0.3125	-0.6473	1.0	0.031
			9	323.0	43444.0	0.3027	-2.9976	1.9	0.053
			9	348.0	43720.0	0.3024	-2.4501	1.6	0.043
31	H-Modernite, Z-900H	CO ₂	18	283.0	-6929.0	0.0724	-6.2860	3.0	0.037
			41	303.0	-4483.4	0.0784	-5.1929	2.9	0.028
			34	323.0	-2785.1	0.0809	-4.1891	4.4	0.042
32	H-Modernite, Z-900H	H ₂ S	17	283.0	-6258.7	0.1294	-9.5782	0.6	0.011
			22	303.0	-1703.3	0.0647	-8.5757	0.9	0.017
			23	338.0	-2856.9	0.1389	-6.8738	2.7	0.030
			7	368.0	3036.0	0.1564	-5.6114	1.1	0.020

Table 3. Regression Results for Pure-Gas Adsorption Using the ZGR EOS (Literature Data) - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
33	H-Modernite, Z-900H	C ₃ H ₈	30	283.0	21704.0	0.4829	-8.2104	3.9	0.026
			34	303.0	56053.0	0.5645	-6.4374	5.5	0.044
			28	324.0	37815.0	0.5194	-5.9894	3.1	0.021
34	Zeolite G5	CH ₄	32	283.0	22835.0	0.1720	-1.1616	1.2	0.024
			19	303.0	27753.0	0.1873	-0.5527	2.1	0.021
35	Zeolite G5	C ₂ H ₆	22	283.0	-26948.0	0.0788	-10.9893	0.3	0.013
			18	303.0	27114.0	0.2083	-3.8318	0.5	0.018
36	Zeolite G5	C ₂ H ₄	17	283.0	-10429.0	0.1515	-12.2849	0.2	0.008
			17	303.0	-10351.0	0.1501	-10.5168	0.1	0.006
37	Zeolite 13X	CH ₄	18	298.0	25505.0	0.1829	-0.4517	1.2	0.032
38	Zeolite 13X	C ₂ H ₆	11	298.0	-32229.0	0.0260	-8.4180	1.0	0.042
Overall			2363					1.7	0.096

Table 4. Regression Results for Pure-Gas Adsorption Using the 2-D PR EOS (Literature Data)

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
1	AC, Columbia Grade L	N ₂	9	310.9	-5823.9	0.0049	1.0671	1.2	0.010
			5	338.7	-5247.7	0.0520	1.5164	1.8	0.022
			9	366.5	-4242.8	0.0622	2.0429	1.2	0.010
			8	394.3	-3604.4	0.0676	2.4025	1.3	0.007
			5	422.0	2521.0	0.4125	2.8236	1.7	0.009
2	AC, Columbia Grade L	CH ₄	12	310.9	-2716.9	0.0926	-0.1800	1.8	0.019
			10	338.7	-3558.7	0.0677	0.3407	1.5	0.041
			8	366.5	-869.5	0.1119	0.9124	1.0	0.010
			7	394.3	-5698.4	0.0448	1.3431	0.6	0.004
			8	422.0	-912.1	0.1134	1.7408	1.3	0.011
3	AC, Columbia Grade L	C ₂ H ₆	10	310.9	-7140.1	0.0959	-3.4615	1.4	0.110
			9	338.7	-7520.5	0.1090	-2.0708	1.0	0.032
			10	366.5	-8642.1	0.0945	-1.7652	0.7	0.023
			10	394.3	-10455.0	0.0595	-1.1522	1.9	0.035
			9	422.0	-8499.3	0.0552	-0.4691	3.0	0.076
			5	449.8	-8503.0	0.0343	0.1080	0.4	0.016
			5	477.6	-8661.0	0.0484	0.6463	0.7	0.016
4	Charcoal	CH ₄	8	283.2	-2417.2	0.0571	-0.7802	0.1	0.007
			12	293.2	-3142.5	0.0550	-0.6690	0.7	0.048
			12	303.2	-2640.0	0.0602	-0.3389	0.8	0.047
			10	313.2	-1858.5	0.0645	0.0765	0.3	0.033
			13	323.2	-1800.8	0.0689	0.2787	0.4	0.028
5	Charcoal	C ₃ H ₈	10	293.2	-2956.4	0.1079	-5.0547	2.3	0.133
			11	303.2	-10126.0	0.0964	-5.9586	0.6	0.051
			10	313.2	-7893.2	0.0999	-5.0624	0.7	0.038
			11	323.2	-6510.6	0.1049	-4.4225	0.5	0.032
			10	333.2	-7810.1	0.1080	-4.3602	0.3	0.015

Table 4. Regression Results for Pure-Gas Adsorption Using the 2-D PR EOS (Literature Data) - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
6	AC, BPL	CH ₄	23	212.7	-3984.9	0.0652	-2.8962	1.0	0.077
			24	260.2	-3582.1	0.0678	-0.9421	0.5	0.029
			25	301.4	-2928.2	0.0782	0.2505	0.5	0.027
7	AC, BPL	C ₂ H ₆	18	212.7	-3799.5	0.1030	-6.6951	2.7	0.177
			15	260.2	-7281.1	0.0967	-4.7486	0.9	0.059
			16	301.4	-5848.5	0.1039	-2.7450	0.6	0.025
8	AC, BPL	C ₂ H ₄	21	212.7	-8625.6	0.0724	-7.3931	2.9	0.163
			15	260.2	-6457.1	0.0871	-4.0783	0.4	0.029
			16	301.4	-5615.7	0.0933	-2.2765	0.3	0.017
9	AC, BPL	CO ₂	21	212.7	-1195.6	0.0563	-4.4091	1.0	0.071
			14	260.2	-1453.0	0.0551	-2.0637	0.4	0.019
			25	301.4	-2155.4	0.0484	-0.7352	0.4	0.026
10	AC, PCB-Calgon	CH ₄	7	296.0	-514.4	0.0890	-0.1958	0.1	0.014
			8	373.0	-5613.6	0.0594	0.9424	0.8	0.041
			7	480.0	9130.4	0.1748	2.8932	1.6	0.022
11	AC, PCB-Calgon	CO ₂	4	296.0	-1177.2	0.0557	-1.4443	0.0	0.005
			4	373.0	-2574.4	0.0457	0.3618	0.1	0.004
			4	480.0	-5103.1	0.0341	1.8489	1.1	0.047
12	AC, F30/470 Chemviron Carbon	CO ₂	30	278.0	-2526.9	0.0639	-2.3348	1.3	0.273
			19	288.0	-3492.1	0.0547	-2.0851	1.1	0.153
			19	298.0	-2952.5	0.0606	-1.6232	0.3	0.030
			19	303.0	-2876.2	0.0620	-1.5121	0.3	0.028
			38	308.0	-3126.3	0.0601	-1.3528	0.5	0.044
			19	318.0	-3689.0	0.0574	-1.0777	0.5	0.032
			20	328.0	-3930.5	0.0602	-0.8708	0.5	0.023

Table 4. Regression Results for Pure-Gas Adsorption Using the 2-D PR EOS (Literature Data) - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
13	AC, Norit R1 Extra	N ₂	10	298.0	-2097.7	0.0854	0.9155	0.7	0.016
14	AC, Norit R1 Extra	CH ₄	12	298.0	-3214.4	0.0540	-0.4825	1.5	0.041
15	AC, Norit R1 Extra	CO ₂	12	298.0	-2257.3	0.0301	-1.4047	2.1	0.086
16	AC, Coconut Shell	CH ₄	21	233.0	-1234.3	0.0186	-2.0298	1.2	0.262
			19	253.0	-961.6	0.0221	-1.3383	0.5	0.110
			22	273.0	-876.9	0.0241	-0.7778	0.4	0.145
			21	293.0	-744.8	0.0266	-0.2791	0.4	0.067
			20	313.0	-675.4	0.0281	0.1668	0.3	0.027
			19	333.0	-616.1	0.0282	0.5690	0.2	0.017
17	AC, Calgon F-400	CO ₂	75	303.6	-2320.1	0.0545	-1.0368	2.1	0.161
			74	305.2	-1458.9	0.0548	-0.6420	3.2	0.218
			75	309.2	-1975.7	0.0513	-0.6175	2.9	0.173
			76	313.2	-2869.2	0.0457	-0.6995	2.8	0.128
			76	318.2	-1796.8	0.0587	-0.4876	2.7	0.139
18	AC, Norit RB1	CH ₄	16	304.9	-5487.1	0.0418	-0.8024	0.3	0.006
			16	311.4	-5340.8	0.0434	-0.2723	0.3	0.005
			16	331.3	-5345.4	0.0450	0.1594	0.6	0.008
			16	350.5	-5233.7	0.0486	0.5498	0.7	0.008
19	AC, Norit RB1	CO ₂	16	305.2	-2566.0	0.0571	-1.6572	0.3	0.011
			16	311.2	-3182.2	0.0507	-1.1489	0.3	0.011
			16	329.5	-4007.2	0.0310	-0.6668	0.3	0.006
			16	348.3	-4290.4	0.0334	-0.2316	0.5	0.009

Table 4. Regression Results for Pure-Gas Adsorption Using the 2-D PR EOS (Literature Data) - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
20	AC, Coconut Shell	N ₂	10	178.0	-415.0	0.0273	-1.7709	0.8	0.181
			11	198.0	-288.2	0.0311	-1.2972	0.8	0.142
			10	218.0	-484.4	0.0325	-0.8288	0.4	0.078
			10	233.0	-341.4	0.0359	-0.1951	0.3	0.039
			11	258.0	-224.7	0.0383	0.2782	0.2	0.027
			10	278.0	-320.5	0.0398	0.6564	0.2	0.019
			9	298.0	-262.5	0.0417	1.0418	0.1	0.009
21	AC F30/470	N ₂	25	303.0	4199.7	0.1709	1.5391	2.1	0.079
			19	323.0	5030.7	0.1909	1.8136	1.7	0.057
			24	343.0	7517.0	0.2136	2.2385	1.7	0.044
			24	363.0	5810.4	0.2260	2.3756	1.4	0.037
			24	383.0	6225.7	0.2480	2.6005	1.3	0.027
22	AC F30/470	CH ₄	24	303.0	6139.7	0.1286	0.8751	2.2	0.129
			24	323.0	2408.0	0.1350	0.7221	1.9	0.110
			25	343.0	5518.8	0.1472	1.2113	2.3	0.121
			25	363.0	2803.0	0.1532	1.2136	2.7	0.122
			24	383.0	4319.2	0.1679	1.5901	1.9	0.069
23	AC F30/470	C ₃ H ₈	11	303.0	-22639.0	0.0380	-8.4472	1.4	0.128
			15	323.0	-21576.0	0.0496	-6.7439	0.8	0.061
			19	343.0	-21591.0	0.0424	-5.9305	0.5	0.036
			23	363.0	-19220.0	0.1051	-4.7216	0.3	0.020
			34	383.0	-5670.3	0.1402	-2.4304	1.0	0.076
24	AC Norit R1	N ₂	31	298.0	-2210.9	0.0797	0.8482	1.1	0.063
25	AC Norit R1	CO ₂	29	298.0	-1750.1	0.0313	-1.2601	1.1	0.123

Table 4. Regression Results for Pure-Gas Adsorption Using the 2-D PR EOS (Literature Data) - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
26	Zeolite, Linde 13X	N ₂	8	298.0	-643.0	0.2221	1.3707	1.3	0.033
			8	323.0	-703.5	0.2330	1.9173	1.5	0.034
			8	348.0	-1693.1	0.2286	2.3920	1.6	0.041
27	Zeolite, Linde 5A	N ₂	9	298.0	-1234.3	0.2366	0.9751	1.1	0.046
			9	323.0	-4798.5	0.2305	1.3662	1.1	0.033
			9	348.0	-4348.5	0.2462	1.9319	0.7	0.020
28	Zeolite, Linde 5A	CH ₄	10	298.0	2821.6	0.2338	0.4996	0.7	0.033
			10	323.0	1874.2	0.2448	0.9549	0.6	0.016
			8	348.0	3868.1	0.2578	1.5963	0.9	0.031
29	Zeolite, Linde 5A	CO ₂	11	298.0	-4528.7	0.1478	-10.3027	1.4	0.107
			15	323.0	-3483.7	0.1692	-7.4362	1.0	0.077
			15	348.0	-2141.0	0.1866	-4.7231	1.1	0.055
30	Zeolite, Linde 5A	C ₂ H ₆	9	298.0	48548.0	0.3594	1.1395	1.0	0.030
			9	323.0	6541.0	0.3551	-1.5561	1.7	0.054
			9	348.0	22648.0	0.3792	-0.0522	1.5	0.035
31	H-Modernite, Z-900H	CO ₂	18	283.0	-22578.0	0.1031	-5.2764	3.4	0.040
			41	303.0	-21586.0	0.1022	-4.1524	4.1	0.037
			34	323.0	-21115.0	0.0999	-3.1440	5.9	0.055
32	H-Modernite, Z-900H	H ₂ S	17	283.0	-30904.0	0.1941	-8.4583	0.6	0.011
			22	303.0	-36701.0	0.1507	-7.7711	0.9	0.072
			23	338.0	-30397.0	0.2084	-5.5962	2.6	0.030
			7	368.0	-31427.0	0.1762	-4.3822	1.1	0.018

Table 4. Regression Results for Pure-Gas Adsorption Using the 2-D PR EOS (Literature Data) - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)
					a	b	-ln(k)		
33	H-Modernite, Z-900H	C ₃ H ₈	30	283.0	-43102.0	0.6193	-6.6863	3.7	0.030
			34	303.0	-9152.4	0.6941	-4.7923	4.8	0.048
			28	324.0	-37630.0	0.06569	-4.4838	3.0	0.022
34	Zeolite G5	CH ₄	32	283.0	3851.8	0.1791	0.4151	1.0	0.022
			19	303.0	2944.3	0.1620	0.9453	0.4	0.006
35	Zeolite G5	C ₂ H ₆	22	283.0	-60077.0	0.1433	-11.2153	0.3	0.013
			18	303.0	5414.2	0.2498	2.1866	0.6	0.021
36	Zeolite G5	C ₂ H ₄	17	283.0	-57999.0	0.1823	-13.2865	0.2	0.008
			17	303.0	-54555.0	0.1872	-10.6898	0.1	0.006
37	Zeolite 13X	CH ₄	18	298.0	6817.9	0.2135	1.2033	1.1	0.041
38	Zeolite 13X	C ₂ H ₆	11	298.0	-55086.0	0.08225	-8.9521	1.0	0.042
Overall			2363					1.5	0.097

Table 5. Regression Results for Pure-Gas Adsorption Using the ZGR EOS (OSU Data)

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)	WAAD
					a	b	-ln(k)			
47	AC, Calgon F-400	N ₂	22	318.2	12520.0	0.1076	0.0110	0.4	0.011	0.3
48	AC, Calgon F-400	CH ₄	22	318.2	8362.7	0.0824	-1.2223	0.5	0.024	0.7
49	AC, Calgon F-400	CO ₂	26	318.2	4732.1	0.0497	-2.1677	2.0	0.110	0.5
50	AC, Calgon F-400	C ₂ H ₆	21	318.2	1829.1	0.0744	-4.4025	6.4	0.154	0.7
55	Wet Fruitland Coal	N ₂	20	319.3	109450.0	0.7762	3.4687	2.6	0.006	0.4
56	Wet Fruitland Coal	CH ₄	40	319.3	46902.0	0.3988	1.7932	1.1	0.007	0.4
57	Wet Fruitland Coal	CO ₂	57	319.3	1050.0	0.0879	0.8713	8.7	0.123	0.9
61	Wet Illinois # 6 Coal	N ₂	37	319.3	309330.0	1.9798	4.4610	3.3	0.003	0.1
62	Wet Illinois # 6 Coal	CH ₄	20	319.3	104130.0	0.8249	2.6973	1.9	0.005	0.3
63	Wet Illinois # 6 Coal	CO ₂	40	319.3	11155.0	0.1324	1.6826	10.3	0.109	1.7
67	Wet Tiffany Coal	N ₂	21	327.5	203370.5	1.4192	4.3040	2.3	0.002	0.5
68	Wet Tiffany Coal	CH ₄	34	327.5	115540.0	0.8394	2.8661	3.1	0.011	1.1
69	Wet Tiffany Coal	CO ₂	16	327.5	62560.0	0.5405	1.2459	4.0	0.026	0.2
74	Wet LB Fruitland Coal	N ₂	17	319.3	95972.0	0.7332	4.7916	2.9	0.003	0.2
75	Wet LB Fruitland Coal	CH ₄	16	319.3	22837.0	0.3143	3.2584	2.2	0.007	0.4
76	Wet LB Fruitland Coal	CO ₂	29	319.3	103750.0	0.7905	1.5904	7.1	0.040	0.5
77	Dry Illinois # 6 Coal	CO ₂	11	328.0	5262.1	0.0679	1.0575	2.5	0.034	0.4
78	Dry Beulah Zap Coal	CO ₂	22	328.0	374.7	0.0526	0.3864	5.8	0.112	0.7
79	Dry Wyodak Coal	CO ₂	11	328.0	3467.4	0.0516	0.8258	6.7	0.123	0.8
80	Dry Upper Freeport Coal	CO ₂	11	328.0	-4205.3	0.1049	0.5818	4.2	0.044	0.4
81	Dry Pocahontash Coal	CO ₂	11	328.0	-1497.0	0.1077	0.1747	2.7	0.036	0.2
Overall			549					4.3	0.075	0.6

Table 6. Regression Results for Pure-Gas Adsorption Using the 2-D Peng-Robinson EOS (OSU Data)

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters			%AAD	RMSE (mmol/g)	WAAD
					a	b	-ln(k)			
47	AC, Calgon F-400	N ₂	22	318.2	-1567.6	0.1229	1.5551	0.4	0.015	0.3
48	AC, Calgon F-400	CH ₄	22	318.2	-2197.6	0.1004	0.3673	0.5	0.026	0.7
49	AC, Calgon F-400	CO ₂	26	318.2	-1781.7	0.0607	-0.5787	2.0	0.113	0.5
50	AC, Calgon F-400	C ₂ H ₆	21	318.2	-11251.0	0.0972	-3.1076	6.4	0.154	0.7
55	Wet Fruitland Coal	N ₂	20	319.3	-22832.0	0.2393	4.8530	2.4	0.006	0.3
56	Wet Fruitland Coal	CH ₄	40	319.3	-15173.0	0.3381	3.2015	0.9	0.005	0.4
57	Wet Fruitland Coal	CO ₂	57	319.3	-16950.0	0.0988	2.0134	8.9	0.125	0.9
61	Wet Illinois # 6 Coal	N ₂	37	319.3	-6047.6	1.1211	5.8409	1.6	0.001	0.0
62	Wet Illinois # 6 Coal	CH ₄	20	319.3	-18408.0	0.7455	4.1531	1.8	0.006	0.3
63	Wet Illinois # 6 Coal	CO ₂	40	319.3	-16580.0	0.1221	2.7488	11.5	0.120	1.7
67	Wet Tiffany Coal	N ₂	21	327.5	-43152.0	0.4537	5.7062	2.8	0.003	0.5
68	Wet Tiffany Coal	CH ₄	34	327.5	-12437.0	0.7180	4.2980	3.4	0.011	1.2
69	Wet Tiffany Coal	CO ₂	16	327.5	-2378.7	0.6593	2.9396	4.1	0.026	0.3
74	Wet LB Fruitland Coal	N ₂	17	319.3	-63209.0	0.4550	5.8280	3.8	0.004	0.3
75	Wet LB Fruitland Coal	CH ₄	16	319.3	-35702.0	0.2746	4.4951	2.9	0.009	0.5
76	Wet LB Fruitland Coal	CO ₂	29	319.3	12269.0	0.9151	3.2636	7.0	0.039	0.5
77	Dry Illinois # 6 Coal	CO ₂	11	328.0	-8979.7	0.0639	2.1918	3.0	0.037	0.5
78	Dry Beulah Zap Coal	CO ₂	22	328.0	-10799.0	0.0622	1.5280	6.3	0.116	0.8
79	Dry Wyodak Coal	CO ₂	11	328.0	-8496.1	0.0541	1.7575	7.1	0.134	0.9
80	Dry Upper Freeport Coal	CO ₂	11	328.0	-27349.0	0.1261	1.7071	4.4	0.044	0.4
81	Dry Pocahontas Coal	CO ₂	11	328.0	-23825.0	0.1074	1.3737	2.7	0.036	0.2
Overall			549					4.4	0.077	0.6

Table 7. Physical Properties of the Adsorbate and Active Site

Adsorbate	MW	Pc (MPa)	Tc (K)	Normal Boiling Point (K)	Reciprocal van der Waals co-volume (mol/liter)	S_{ff} (10^{-10} m)	e_{ff}^*/k (K)
H ₂	2.02	1.31	33.19	20.4	38.16	2.827	59.7
N ₂	28.01	3.40	126.20	77.3	25.89	3.798	71.4
H ₂ S	34.08	8.96	373.53	212.8	23.08	3.623	301.1
CO ₂	44.01	7.38	304.21	216.6 ^b	23.34	3.941	195.2
CH ₄	16.04	4.60	190.56	111.7	23.37	3.758	148.6
C ₂ H ₄	28.05	5.04	282.34	169.4	17.39	4.163	224.7
C ₂ H ₆	30.07	4.87	305.32	184.6	15.41	4.443	215.7
C ₃ H ₈	44.10	4.25	369.83	231.1	11.07	5.118	237.1
i- C ₄ H ₁₀	58.12	3.65	408.14	261.4	8.60	5.278	330.1

^b : Triple point temperature

Table 8. Regression Results for Pure-Gas Adsorption Using the 2-D PR EOS

System No.	Adsorbent	Adsorbate	NPTS	Regressed Parameters				%AAD	RMSE (mmol/g)
				A (m ² /g)	e _{ss} (k)	S _{m,0} (mmol/m ²)	d (1/K)		
1	AC, Columbia Grade L	N ₂	36	1152.0	53.01	0.0168	0.00295	3.7	0.029
2	AC, Columbia Grade L	CH ₄	45	1152.0	45.82	0.0158	0.00287	3.1	0.057
3	AC, Columbia Grade L	C ₂ H ₆	58	1152.0	49.59	0.0117	0.00317	4.5	0.152
4	Charcoal	CH ₄	55	1157.0	45.86	0.0275	0.00350	0.9	0.053
5	Charcoal	C ₃ H ₈	52	1157.0	45.68	0.0095	0.00248	3.8	0.133
6	AC, BPL	CH ₄	72	988.0	39.12	0.0189	0.00319	2.5	0.115
7	AC, BPL	C ₂ H ₆	49	988.0	46.25	0.0112	0.00313	4.4	0.207
8	AC, BPL	C ₂ H ₄	52	988.0	48.43	0.0173	0.00308	4.3	0.218
9	AC, BPL	CO ₂	60	988.0	47.40	0.0962	0.01100	3.7	0.336
10	AC, PCB-Calgon	CH ₄	21	1200.0	41.65	0.0166	0.00264	1.8	0.059
11	AC, PCB-Calgon	CO ₂	12	1200.0	38.85	0.0245	0.00561	1.8	0.187
12	AC, F30/470 Chemviron Carbon	CO ₂	164	993.5	49.52	0.0340	0.00502	2.6	0.241
13	AC, Norit R1 Extra	N ₂	10	1450.0	57.21	0.0231	0.00476	0.7	0.016
14	AC, Norit R1 Extra	CH ₄	12	1450.0	72.63	0.0889	0.01099	1.7	0.036

Table 8. Regression Results for Pure-Gas Adsorption Using the 2-D PR EOS - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	Regressed Parameters				%AAD	RMSE (mmol/g)
				A (m ² /g)	e _{ss} (k)	S _{m,0} (mmol/m ²)	d (1/K)		
15	AC, Norit R1 Extra	CO ₂	12	1450.0	53.32	0.0905	0.01328	2.1	0.086
16	AC, Coconut Shell	CH ₄	122	3106.0	23.70	0.0175	0.00277	2.0	0.242
17	AC, Calgon F-400	CO ₂	374	1200.0	43.35	0.0587	0.00994	2.7	0.286
18	AC, Norit RB1	CH ₄	64	1100.0	48.17	0.0152	0.00295	1.3	0.026
19	AC, Norit RB1	CO ₂	64	1100.0	47.05	0.0281	0.00570	1.0	0.033
20	AC, Coconut Shell	N ₂	71	3106.0	32.20	0.0183	0.00385	2.1	0.267
21	AC F30/470	N ₂	116	993.5	60.17	0.0216	0.00373	2.2	0.065
22	AC F30/470	CH ₄	122	993.5	46.23	0.0216	0.00307	1.9	0.104
23	AC F30/470	C ₃ H ₈	102	993.5	40.25	0.0102	0.00223	1.5	0.106
24	AC Norit R1	N ₂	31	1262.0	51.28	0.0188	0.00288	1.1	0.064
25	AC Norit R1	CO ₂	29	1262.0	40.03	0.0417	0.00489	1.1	0.121
47	AC, Calgon F-400	N ₂	22	950.0	31.93	0.0089	0.00001	0.4	0.018
48	AC, Calgon F-400	CH ₄	22	950.0	41.06	0.0180	0.00250	0.5	0.025
49	AC, Calgon F-400	CO ₂	50	950.0	32.83	0.0175	0.00001	1.4	0.144
50	AC, Calgon F-400	C ₂ H ₆	21	950.0	40.55	0.0099	0.00146	5.5	0.394
Overall			1922					2.4	0.199

Table 9. Regression Results for Pure-Gas Adsorption Using the 2-D PR EOS (OSU Data)

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Regressed Parameters				% AAD	RMSE (mmol/g)	WAAD
					A (m ² /g)	e _{ss} (k)	S _{m,0} (mmol/m ²)	d (1/K)			
55	Wet Fruitland Coal	N ₂	20	319.3	131.4	16.47	0.0177	0.0024	2.4	0.006	0.4
56	Wet Fruitland Coal	CH ₄	40	319.3	158.8	23.85	0.0181	0.0024	1.3	0.007	0.5
57	Wet Fruitland Coal	CO ₂	57	319.3	211.1	36.63	0.0165	0.0024	6.5	0.075	0.7
61	Wet Illinois # 6 Coal	N ₂	37	319.3	70.6	11.74	0.0177	0.0024	1.6	0.001	0.0
62	Wet Illinois # 6 Coal	CH ₄	20	319.3	84.0	19.47	0.0181	0.0024	1.9	0.006	0.3
63	Wet Illinois # 6 Coal	CO ₂	40	319.3	190.1	24.27	0.0165	0.0024	4.1	0.038	1.2
67	Wet Tiffany Coal	N ₂	21	327.5	68.1	14.98	0.0177	0.0024	2.8	0.003	0.5
68	Wet Tiffany Coal	CH ₄	34	327.5	87.6	20.04	0.0181	0.0024	3.7	0.012	1.3
69	Wet Tiffany Coal	CO ₂	16	327.5	121.5	35.83	0.0165	0.0024	9.5	0.055	0.7
74	Wet LB Fruitland Coal	N ₂	17	319.3	54.0	12.55	0.0177	0.0024	4.2	0.004	0.3
75	Wet LB Fruitland Coal	CH ₄	16	319.3	75.2	16.51	0.0181	0.0024	2.4	0.007	0.4
76	Wet LB Fruitland Coal	CO ₂	29	319.3	85.1	40.94	0.0165	0.0024	8.9	0.039	0.5
77	Dry Illinois # 6 Coal	CO ₂	11	328.0	352.5	25.87	0.0165	0.0024	10.2	0.155	0.9
78	Dry Beulah Zap Coal	CO ₂	22	328.0	363.4	37.29	0.0165	0.0024	4.6	0.080	0.6
79	Dry Wyodak Coal	CO ₂	11	328.0	403.5	31.17	0.0165	0.0024	3.9	0.067	0.6
80	Dry Upper Freeport Coal	CO ₂	11	328.0	174.3	48.64	0.0165	0.0024	5.2	0.057	0.4
81	Dry Pocahontash Coal	CO ₂	11	328.0	213.4	49.18	0.0165	0.0024	7.1	0.093	0.5
Overall			432						4.7	0.050	0.6

Table 10. Prediction Results for Pure-Gas Adsorption Using the 2-D PR EOS

System No.	Adsorbent	Adsorbate	NPTS	Parameters				%AAD	RMSE (mmol/g)
				A (m ² /g)	e _{ss} (k)	S _{m,0} (mmol/m ²)	d (1/K)		
1	AC, Columbia Grade L	N ₂	36	1152.0	40.0	0.0177	0.0024	17.8	0.106
2	AC, Columbia Grade L	CH ₄	45	1152.0	40.0	0.0181	0.0024	8.0	0.074
3	AC, Columbia Grade L	C ₂ H ₆	58	1152.0	40.0	0.0130	0.0024	14.7	0.292
4	Charcoal	CH ₄	55	1157.0	45.0	0.0181	0.0024	6.5	0.501
5	Charcoal	C ₃ H ₈	52	1157.0	45.0	0.0098	0.0024	4.5	0.154
6	AC, BPL	CH ₄	72	988.0	40.0	0.0181	0.0024	9.6	0.346
7	AC, BPL	C ₂ H ₆	49	988.0	40.0	0.0130	0.0024	11.6	0.546
8	AC, BPL	C ₂ H ₄	52	988.0	40.0	0.0148	0.0024	13.9	0.572
9	AC, BPL	CO ₂	60	988.0	40.0	0.0165	0.0024	16.9	1.092
10	AC, PCB-Calgon	CH ₄	21	1200.0	40.0	0.0181	0.0024	6.9	0.296
11	AC, PCB-Calgon	CO ₂	12	1200.0	40.0	0.0165	0.0024	12.7	0.550
12	AC, F30/470 Chemviron Carbon	CO ₂	164	993.5	40.0	0.0165	0.0024	10.8	0.945
13	AC, Norit R1 Extra	N ₂	10	1450.0	40.0	0.0177	0.0024	8.3	0.318
14	AC, Norit R1 Extra	CH ₄	12	1450.0	40.0	0.0181	0.0024	11.4	0.639

Table 10. Prediction Results for Pure-Gas Adsorption Using the 2-D PR EOS - Cont'd.

System No.	Adsorbent	Adsorbate	NPTS	Parameters				%AAD	RMSE (mmol/g)
				A (m ² /g)	e _{ss} (k)	S _{m,0} (mmol/m ²)	d (1/K)		
15	AC, Norit R1 Extra	CO ₂	12	1450.0	40.0	0.0165	0.0024	14.8	0.553
16	AC, Coconut Shell	CH ₄	122	3106.0	20.0	0.0181	0.0024	4.2	0.428
17	AC, Calgon F-400	CO ₂	374	1200.0	40.0	0.0165	0.0024	7.4	0.739
18	AC, Norit RB1	CH ₄	64	1100.0	40.0	0.0181	0.0024	8.5	0.122
19	AC, Norit RB1	CO ₂	64	1100.0	40.0	0.0165	0.0024	5.3	0.216
20	AC, Coconut Shell	N ₂	71	3106.0	20.0	0.0177	0.0024	7.4	0.971
21	AC F30/470	N ₂	116	993.5	40.0	0.0177	0.0024	6.2	0.153
22	AC F30/470	CH ₄	122	993.5	40.0	0.0181	0.0024	4.4	0.194
23	AC F30/470	C ₃ H ₈	102	993.5	40.0	0.0098	0.0024	4.9	0.262
24	AC Norit R1	N ₂	31	1262.0	40.0	0.0177	0.0024	12.3	0.250
25	AC Norit R1	CO ₂	29	1262.0	40.0	0.0165	0.0024	16.1	1.861
47	AC, Calgon F-400	N ₂	22	950.0	40.0	0.0177	0.0024	7.2	0.189
48	AC, Calgon F-400	CH ₄	22	950.0	40.0	0.0181	0.0024	1.1	0.061
49	AC, Calgon F-400	CO ₂	50	950.0	40.0	0.0165	0.0024	18.6	0.500
50	AC, Calgon F-400	C ₂ H ₆	21	950.0	40.0	0.0130	0.0024	11.5	0.707
Overall			1922					8.6	0.617

Table 11. Summaries of the Results

Cases	NPTS	%AAD	RMSE	WAAD
Regressions Based on Individual Isotherms				
ZGR EOS for Literature Data	2363	1.7	0.096	
2-D PR EOS for Literature Data	2363	1.5	0.097	
ZGR EOS for OSU Data	549	4.3	0.075	0.6
2-D PR EOS for OSU Data	549	4.4	0.077	0.6
Regressions Based on Systems				
2-D PR EOS for Activated Carbons	1922	2.4	0.199	
2-D PR EOS for Coals	432	4.7	0.050	0.6
Predictions				
2-D PR EOS for Activated Carbons	1922	8.6	0.617	

Figure 1. Effect of Surface Area to Represent Pure CO₂ Adsorption on Activated Carbon (OSU) at 318.2 K

Figure 2. Representation and Prediction of Pure-Gas Adsorption on Activated Carbon (OSU) at 318.2 K

Figure 3. 2-D PR EOS Prediction of CH₄ Absolute Adsorption on Activated Carbon (Zhou, 2000)

Figure 4. Representation and Prediction of CO₂ Adsorption on Activated Carbon at Four Different Temperatures (Vaart, 2000)

Figure 5. Representation of Pure-Gas Adsorption on Wet Fruitland Coal at 319.3 K

Two-Dimensional Equations-of-State Modeling of Mixture Adsorption

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Abstract

Adsorption equilibrium models are essential in optimizing coalbed methane production and CO₂ sequestration processes. Although a number of frameworks are available for describing the adsorption phenomenon, two-dimensional (2-D) equations of state (EOSs) offer distinct advantages in modeling supercritical, high-pressure adsorption systems.

Our previous studies involving several high-pressure adsorption mixtures have indicated the inadequacy of one-fluid mixing rules in representing the adsorption of individual components in a mixture. In this study, we have applied the Wong-Sandler excess Gibbs free energy mixing rules to the 2-D EOS.

The results indicate that the use of the excess Gibbs free energy mixing rules are effective in representing the binary mixture data considered within their experimental uncertainties.

Keywords: Adsorption, Two-Dimensional Equation of State, Mixing and Combination Rules, Wong-Sandler

Introduction

Adsorption phenomena play a major role in coalbed methane (CBM) production and in CO₂ sequestration; therefore, reliable adsorption equilibrium models are essential in the optimum implementation of these processes.

Although several frameworks have been used to describe the adsorption phenomenon and correlate pure and mixture adsorption isotherms, two-dimensional (2-D) equations of state (EOSs) offer distinct advantages in modeling supercritical, high-pressure adsorption systems. First, 2-D EOSs permit simultaneous calculation of equilibrium adsorption and volumetric properties. Second, they are amenable to model parameter generalization. Third, they are particularly suitable to extend pure adsorption isotherms to multicomponent mixture predictions using appropriate mixing rules [Do, 1998]. Fourth, they offer a proven, familiar model format for use in reservoir simulations.

One-fluid mixing rules have been partially successful in correlating high-pressure mixture adsorption. Previous studies [Zhou et al., 1994] indicate that although the one-fluid mixing rules are capable of representing the total mixture adsorption data within their experimental uncertainties; they fail to do so for the individual-components in the mixture. Specifically, the current mixing rules do not precisely describe the component partitioning (or selectivity) in the adsorbed phase of a mixture.

In this study, we incorporated the excess Gibbs free energy mixing rules in the 2-D EOSs. In so doing, we recognize differences in the molecular affinity between the adsorbate and the adsorption surface, which can result in non-random mixing.

Two-Dimensional EOS Models

Historically, various researchers have applied the 2-D EOS to gas adsorption. Hill (1946) and de Boer (1953) have used the van der Waals (VDW) EOS to correlate pure-gas adsorption. Hoory and Prausnitz (1967) extended the 2-D VDW EOS to mixtures by introducing mixing rules. More recently, DeGance (1992) used the 2-D virial and Eyring EOS to correlate high-pressure pure adsorption isotherms.

In the early 1990's, we presented a generalized 2-D cubic EOS, which encompasses 2-D analogs of previous cubic EOS forms [see, e.g., Zhou et al. 1994]. The generalized 2-D EOS (with an additional parameter, m , for added model flexibility) is analogous to the popular three-dimensional equations of state used in vapor-liquid equilibrium calculations:

$$\left[\pi + \frac{a_2 \sigma^2}{1 + U b_2 \sigma + W (b_2 \sigma)^2} \right] \left[1 - (b_2 \sigma)^m \right] = \sigma R T \quad (1)$$

where π is the spreading pressure, σ is the surface density of the adsorbate, R is the universal gas constant, T is the temperature, a_2 and b_2 are the traditional EOS parameters, and numerical values of U , W , and m may be specified to give various forms of two-dimensional equations of state.

The general two-dimensional analog can be re-written as follows:

$$\left[A \pi + \frac{a \omega^2}{1 + U b \omega + W (b \omega)^2} \right] \left[1 - (b \omega)^m \right] = \omega R T \quad (2)$$

where A is the specific surface area, $\omega = \sigma A$ is the specific amount adsorbed, and $a = a_2/A$ and $b = b_2/A$ are model parameters. The model coefficients, U , W , and m must be specified to obtain a specific form of the 2-D EOS for application. For example,

an analog of the van der Waals (VDW) EOS is obtained by setting $m = 1$ and $U = W = 0$; similarly for the Soave-Redlich-Kwong (SRK) ($m = U = 1$ and $W = 0$); the Peng-Robinson (PR) ($m = 1$, $U = 2$, and $W = -1$); and the Eyring ($m = 1/2$ and $U = W = 0$) EOS.

This general 2-D EOS can be used to investigate EOS behaviors by specifying various combinations of model coefficients. Since the model coefficient, m , is contained in the repulsive term and has a significant effect on the shape of the pure adsorption isotherm, the selection of a value for m is most important among the EOS model coefficients. If U and W are equal to zero, then by setting m to values of 1 and 1/2 the 2-D VDW EOS and the Eyring EOS are obtained, respectively. Actually, the pure gas isotherms vary considerably in shape and Zhou [Zhou et al., 1994] had found that it is sometimes desirable to select an m value even smaller than 1/2 to describe pure isotherms. Based on extensive calculations, Zhou found that an equation with $m = 1/3$ and $U = W = 0$ (the ZGR EOS) was promising.

In this work, we investigated the capabilities of the ZGR EOS and 2-D PR EOS to model the mixture adsorption.

One-Fluid Mixing Rules

Mixing rules for the model parameters are crucial for extending the 2-D EOS from pure-gas adsorption to mixture adsorption. One-fluid mixing rules are widely used in 3-D EOS applications, where the 3-D EOS parameters, a and b , for mixtures are given by:

$$a = \sum_i \sum_j x_i x_j a_{ij} \text{ and } b = \sum_i \sum_j x_i x_j b_{ij} \quad (3)$$

and:

$$a_{ij} = \sqrt{a_i a_j} (1 - C_{ij}) / 2 \quad (4)$$

$$b_{ij} = (b_i + b_j) (1 + D_{ij}) / 2 \quad (5)$$

where C_{ij} and D_{ij} are binary interaction parameters.

However, the combination rule for “a” of Equation 4 is not applicable in 2-D EOS because α values can be either positive or negative. Thus, based on practical considerations, Zhou et al. (1994) used an arithmetic mean for parameter α and geometric mean for β . The one-fluid mixing rules used are expressed empirically as:

$$\mathbf{a} = \sum_i \sum_j x_i x_j \mathbf{a}_{ij} \quad \text{and} \quad \mathbf{b} = \sum_i \sum_j x_i x_j \mathbf{b}_{ij} \quad (6)$$

and:

$$\mathbf{a}_{ij} = (\mathbf{a}_i + \mathbf{a}_j) (1 - C_{ij}) / 2 \quad (7)$$

$$\mathbf{b}_{ij} = \sqrt{\mathbf{b}_i \mathbf{b}_j} (1 + D_{ij}) / 2 \quad (8)$$

Wong-Sandler Mixing Rules to 2-D EOS

As indicated in the previous section, in order to represent mixture adsorption, a set of non-conventional combination rules (Equations 7 and 8) were used in the one-fluid mixing rules. In the regression cases, geometric or arithmetic mean for the combination rules work identically, except that the values of the regressed combination parameters, C_{ij} and D_{ij} , are different. For the prediction cases ($C_{ij}=D_{ij}=0$), however, different combination rules will lead to different results. Moreover, we recognize differences in the molecular affinity between the adsorbate and the adsorption surface, which can result in non-random mixing. Thus, we applied the Wong-Sandler mixing rules to the 2-D EOSs.

Wong-Sandler mixing rules were developed for 3-D cubic EOSs. They equate the excess Helmholtz free energy at infinite pressure from the chosen equation of state to

that from an activity coefficient model. Use of the Helmholtz free energy ensures that the second virial coefficient calculated from the equation of state has quadratic composition dependence, as required by statistical mechanics [Wong et al., 1992].

The Wong-Sandler mixing rules for 3-D cubic EOSs are [Wong et al., 1992]:

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (9)$$

$$\frac{A_\infty^{ex}}{FRT} = -\frac{a}{bRT} + \sum_i x_i \frac{a_i}{b_i RT} \quad (10)$$

where the cross term:

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{I}{2} \left[\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right) \right] (1 - C_{ij}) \quad (11)$$

and F in Equation 10 is a constant specific to the EOS chosen.

The Wong-Sandler mixing rules for the 2-D EOS are listed below. (Details are in the Appendix.)

$$\mathbf{b} - \frac{\mathbf{a}}{RT} = \sum_i \sum_j x_i x_j \left(\mathbf{b} - \frac{\mathbf{a}}{RT} \right)_{ij} \quad (12)$$

$$\frac{A_\infty^E}{RT} = -\frac{\mathbf{a}}{F \mathbf{b} RT} + \sum_i x_i \frac{\mathbf{a}_i}{F \mathbf{b}_i RT} + \left(\frac{I}{m} - 1 \right) \sum_i x_i \ln \frac{\mathbf{b}}{\mathbf{b}_i} \quad (13)$$

where the cross term:

$$\left(\mathbf{b} - \frac{\mathbf{a}}{RT} \right)_{ij} = \frac{1}{2} \left[\left(\mathbf{b}_i - \frac{\mathbf{a}_i}{RT} \right) + \left(\mathbf{b}_j - \frac{\mathbf{a}_j}{RT} \right) \right] (1 - C_{ij}) \quad (14)$$

$$\text{and } F = \sqrt{U^2 - 4W} / \ln \left(\frac{1 + \left(U - \sqrt{U^2 - 4W} \right) / 2}{1 + \left(U + \sqrt{U^2 - 4W} \right) / 2} \right)$$

If $U=W=0$, then $F=1$.

The Non-Random Two-Liquid (NRTL) model [see, e.g., Tester, 1996] was used to estimate the Helmholtz free energy, A_{∞}^E for the adsorbed phase:

$$\frac{A_{\infty}^{ex}}{RT} \approx \frac{DG^{ex}}{RT} = \sum_{l=1}^n \left[\frac{x_l \sum_{j=1}^n \mathbf{t}_{jl} G_{jl} x_j}{\sum_{k=1}^n G_{kl} x_k} \right] = \frac{1}{w} \sum_{l=1}^n \left[\frac{w_l \sum_{j=1}^n \mathbf{t}_{jl} G_{jl} w_j}{\sum_{k=1}^n G_{kl} w_k} \right] \quad (15)$$

where $\mathbf{t}_{ii} = 0$ and $G_{ji} = \exp(-\mathbf{a}_{ji} \mathbf{t}_{ji})$ with $\mathbf{a}_{ji} = \mathbf{a}_{ij}$.

Database and Data Reduction

Four cases were studied as follows:

1. Prediction capability ($C_{ij}=D_{ij}=0$) of the ZGR EOS and the 2-D PR EOS using one-fluid mixing rules
2. Representation capability (C_{ij} and D_j are regressed) of the ZGR EOS and the 2-D PR EOS using one-fluid mixing rules
3. Prediction capability of the ZGR EOS and the 2-D PR EOS using Wong-Sandler mixing rules, where the binary interaction parameter, C_{ij} , and three parameters in NRTL (α_{12} , τ_{12} , and τ_{21}) are set to zero
4. Representation capability of the ZGR EOS and the 2-D PR EOS using Wong-Sandler mixing rules, where all four adjustable parameters are regressed

In addition, two prediction cases were performed for ternary mixtures:

5. Prediction capability of the ZGR EOS and the 2-D PR EOS using one-fluid mixing rules, where C_{ij} and D_{ij} are from Case 2
6. Prediction capability of the ZGR EOS and the 2-D PR EOS using Wong-Sandler mixing rules, where all four adjustable parameters are from Case 4

Table 1 presents 6 mixture adsorption systems used for the model evaluation. Systems 1-3 are gas adsorption on dry activated carbons; Systems 4-6 are gas adsorption on wet coals. The temperature, pressure, and feed molar compositions are also listed in Table 1. These data cover a wide pressure range at temperatures close to typical CBM reservoir temperatures.

The objective function, S , was used to correlate the data. The function minimizes the sum of the squared-percentage deviations in predicted adsorption:

$$S = 100 \sqrt{\sum_{j=1}^{NC} \sum_{i=1}^{NPTS} \left[\frac{\mathbf{w}_j^e(i) - \mathbf{w}_j^c(i)}{\mathbf{w}_j^e(i)} \right]^2} \quad (16)$$

where $\mathbf{w}_j^e$ and $\mathbf{w}_j^c$ are the experimental and calculated adsorption amounts for component j , respectively, NC is the number of gas components in the mixture, and $NPTS$ is the number of data points for each component. In addition, the percentage average absolute deviation ($\%AAD \mathbf{w}_j$) and root-mean-square error ($RMSE \mathbf{w}_j$) are presented to assist in evaluating the results:

$$\%AAD \mathbf{w}_j = \frac{100}{NPTS} \sum_{i=1}^{NPTS} \left| \frac{\mathbf{w}_j^e(i) - \mathbf{w}_j^c(i)}{\mathbf{w}_j^e(i)} \right| \quad (17)$$

$$RMSE \mathbf{w}_j = \sqrt{\frac{\sum_{i=1}^{NPTS} (\mathbf{w}_j^e(i) - \mathbf{w}_j^c(i))^2}{NPTS}} \quad (18)$$

The weighted average-absolute deviation ($WAAD \mathbf{w}_j$) is also used to evaluate results when the expected experimental uncertainties, $\mathbf{s}_j^e$, are available:

$$WAAD \mathbf{w}_j = \frac{1}{NPTS} \sum_{i=1}^{NPTS} \left| \frac{\mathbf{w}_j^e(i) - \mathbf{w}_j^c(i)}{\mathbf{s}_j^e(i)} \right| \quad (19)$$

Results for Mixture Adsorption on Activated Carbons

This section presents the results of the ZGR EOS and 2-D PR EOS modeling of mixture adsorption on three dry activated carbons.

Tables 2-4 show the prediction results for binary mixture adsorption on activated carbons using Case 1. On average, both the ZGR EOS and 2-D PR EOS predict the component and total adsorption within three times the expected experimental uncertainties using one-fluid mixing rules. However, the ZGR EOS yields larger errors than the 2-D PR EOS. Typically, for the lower-adsorption component, the errors are larger than those of the higher-adsorption component.

Tables 5-7 show the representation results for binary mixture adsorption on activated carbons using Case 2. As expected, by regressing two binary interaction parameters, C_{ij} and D_{ij} , both EOSs yield better results than those in Case 1. The binary interactions, C_{ij} and D_{ij} , are larger in the 2-D PR EOS than in ZGR EOS, especially for C_{ij} . However, even with the large regressed values for C_{ij} , the results do not show significant improvement over the prediction mode. This indicates the calculated mixture adsorption is insensitive to the binary interaction parameters using the 2-D PR EOS for these systems.

Tables 8-10 show the prediction results for the ternary mixtures on activated carbons using Case 1 and Case 5. As expected, the prediction results for the ternary mixture are worse than those for binary mixture. Unexpectedly, the prediction results based on the pure-gas adsorption parameters and binary interaction parameters (Case 5) are worse than the prediction based only on pure-gas adsorption parameters (Case 1).

Tables 11-13 show the prediction results for binary mixture adsorption on activated carbons using Case 3. The results are similar to those obtained using one-fluid mixing rules; the ZGR EOS has larger errors than the 2-D PR EOS. The 2-D PR EOS predicts the lower-adsorption component with better accuracy than the ZGR EOS.

Tables 14-16 show the representation results for binary mixture adsorption on activated carbons using Case 4. In this case, both EOSs can represent most of the systems within AAD of 10%. However, the NTRL parameters are not the same as those from the vapor-liquid equilibrium (VLE) calculations. This is due largely to the presence of the adsorbent surface, which changes the local densities in the adsorbed phase. In other words, the NTRL parameters for the 2-D EOS are no longer dependent only on the gas molecules but also depend indirectly on the properties of the adsorbent.

Tables 17-19 show the prediction results for the ternary mixture adsorption on activated carbons using Case 3 and Case 6. Similar to the study using one-fluid mixing rules, the prediction results based on the pure-gas adsorption parameters and binary parameters (Case 6) do not improve predictions over those based only on the pure-gas adsorption parameters (Case 3).

Results for Mixture Adsorption on Coals

This section presents the results of the ZGR EOS and 2-D PR EOS modeling of mixture adsorption on three wet coals.

Tables 20-22 show the prediction results for binary mixture adsorption on wet coals using Case 1. Both EOSs predict the lower-adsorption component with larger error in terms of AAD and WAAD. On average, the 2-D PR EOS can predict the component and total adsorption within two times the expected experimental uncertainties except for

the methane adsorption in CH_4+CO_2 mixture on wet Tiffany coal. Overall, the ZGR EOS has a worse quality of fit than the 2-D PR EOS.

The ZGR EOS cannot predict N_2+CO_2 mixture adsorption as well as CH_4+N_2 and CH_4+CO_2 mixture adsorption on wet Fruitland coal. This is because pure N_2 and CO_2 parameters are substantially different using the ZGR EOS. The pure-gas adsorption parameters, α and β , for N_2 are about ten times larger than those of CO_2 in the ZGR EOS. In other words, the ZGR EOS interprets N_2 and CO_2 as a highly non-ideal pair, which leads to large errors in the adsorption prediction. In fact, the calculations failed to converge for the N_2+CO_2 mixture on the wet Illinois #6 coal, where the pure-gas adsorption parameter, α , for N_2 is about thirty times larger than that of CO_2 . This disparity in parameter values caused the lack of convergence in adsorption predictions.

Tables 23-25 show the representation results for binary mixture adsorption on wet coals using Case 2. By regressing two binary interaction parameters, C_{ij} and D_{ij} , the ZGR EOS can represent the experimental data within three times the expected experimental uncertainties for the adsorption on wet Tiffany coals and two times the expected experimental uncertainties for the adsorption on wet Fruitland coal and wet Illinois #6 coal. The 2-D PR EOS can represent the experimental data within two times the expected experimental uncertainties for the adsorption on wet Tiffany coal and within the expected experimental uncertainties for the wet Fruitland coal and wet Illinois #6 coal. However the binary interaction parameters are unrealistically large for the 2-D PR EOS.

Table 26 shows the prediction results for the ternary mixture on wet Tiffany coal using Case 1 and Case 5. As expected, because of the presence of methane, the prediction results for nitrogen and CO_2 component adsorption in this ternary mixture are worse than

those in N₂+CO₂ binary mixture adsorption. Similar to the ternary adsorption results on activated carbons, the prediction results based on the pure-gas adsorption parameters and binary interaction parameters do not show much improvement over the prediction based on pure-gas adsorption parameters only.

Tables 27-29 show the prediction results for binary mixture adsorption on wet coals using Case 3. The results are similar to those obtained using one-fluid mixing rules; the ZGR EOS has larger errors than the 2-D PR EOS. The 2-D PR EOS predicts the lower adsorbed component better than ZGR EOS does. The ZGR EOS does not converge for N₂+CO₂ adsorption on wet Fruitland coal and wet Illinois #6 coal. This failure to converge is partly due to reasons discussed in the one-fluid mixing rules for the adsorption and to other causes, which will be addressed in the discussion section.

Tables 30-32 show the representation results for binary mixture adsorption on wet coals using Case 4. The results are similar to those obtained using one-fluid mixing rules (Case 1).

Table 33 shows the prediction results for the ternary mixture on wet Tiffany coal using Case 2 and Case 6. These results also indicate that use of the binary mixture information does not improve the ternary mixture adsorption results.

Discussion

Because of the extra exponent (1/m) in the repulsive term in the ZGR EOS, the ZGR EOS is not actually cubic in nature. The second virial coefficient calculated from the ZGR EOS is infinite in the limit of low pressure, which is shown in the following discussion. For the generalized 2-D EOS:

$$\left[p + \frac{a\mathbf{s}^2}{1 + Ub\mathbf{s} + W(b\mathbf{s})^2} \right] [1 - (b\mathbf{s})^m] = \mathbf{s}RT \quad (20)$$

Re-writing the above equation yields:

$$Z = \frac{p}{sRT} = \frac{l}{[l - (bs)^m]} - \frac{as}{RT[l + Ubs + W(bs)^2]} \quad (21)$$

Taking the derivative of Z with respect to σ gives:

$$\frac{\partial Z}{\partial s} = \frac{mb^m s^{m-1}}{[l - (bs)^m]^2} - \frac{a}{RT[l + Ubs + W(bs)^2]} + \frac{as(Ub + 2Wb^2 s)}{RT[l + Ubs + W(bs)^2]}$$

For the 2-D EOS where $m=1$:

$$B = \left. \frac{\partial Z}{\partial s} \right|_{s=0} = b - \frac{a}{RT}$$

However, for the ZGR EOS where $m=1/3$:

$$\left. \frac{\partial Z}{\partial s} \right|_{s=0} = \left(\frac{b^{1/3} s^{-2/3}}{3[l - (bs)^{1/3}]^2} - \frac{a}{RT} \right)_{s=0} = \infty$$

Thus, when using the ZGR EOS with Wong-Sandler mixing rules, the ZGR EOS does not meet the quadratic composition dependence for the second virial coefficient, although reasonable results are obtained for most mixture calculations.

Equation 13 relates the Helmholtz free energy with the generalized 2-D EOS:

$$\frac{A_\infty^E}{RT} = -\frac{a}{FbRT} + \sum_i x_i \frac{a_i}{Fb_i RT} + \left(\frac{l}{m} - l \right) \sum_i x_i \ln \frac{b}{b_i} \quad (13)$$

Again, because of the exponent 1/3 in the ZGR EOS, the term, $\left(\frac{l}{m} - l \right) \sum_i x_i \ln \frac{b}{b_i}$, will

be large if values of β_i differ significantly from each other, which may cause the calculation to diverge. This term is the main reason why N_2/CO_2 mixture adsorption on wet Fruitland coal and wet Illinois #6 coal failed to converge using the ZGR EOS with Wong-Sandler mixing rules.

To summarize the results of mixture adsorption using different mixing rules and different EOS, Table 33 compares the results for binary mixture adsorption on activated carbons. Overall, the ZGR EOS with Wong-Sandler mixing rules predicts mixture adsorption better than that with one-fluid mixing rules. For 2-D PR EOS, the two mixing rules do not show significant difference. For the data correlation, Wong-Sandler mixing rules show better results than one-fluid mixing rules for both EOS, but they have more regressed parameters. Overall, the 2-D PR EOS show better results than the ZGR EOS in predicting and representing the mixture adsorption for both one-fluid mixing rules and Wong-Sandler mixing rules.

Table 34 compares the results for the binary mixture adsorption on wet coals. The results of N_2+CO_2 adsorption data on wet Fruitland coal and wet Illinois #6 coal are excluded because ZGR EOS failed to converge in the calculation. Overall, the ZGR EOS with Wong-Sandler mixing rules provides worse predictions for mixture adsorption than that with the one-fluid mixing rules. These ZGR EOS predictions may be attributable to the β_i parameter values for pure gases, which are significantly different. For the 2-D PR EOS, the Wong-Sandler mixing rules predict slightly better than one-fluid mixing rules. In the regression mode, however, the two mixing rules show comparable quality of fit.

Figures 1-3 show the comparison of one-fluid mixing rules and Wong-Sandler mixing rules for representing the CH_4+CO_2 mixture adsorption on activated carbon at 318.2 K using the ZGR EOS. From Figures 2 and 3, it can be seen that Wong-Sandler mixing rules represent the component adsorption better than one-fluid mixing rules. Using one-fluid mixing rules, the model underestimates the adsorption for CH_4 and

overestimates CO_2 . More generally, one-fluid mixing rules tend to underestimate the lower adsorption component and overestimate the higher adsorption component.

Figures 4-6 show comparisons of the ZGR EOS and 2-D PR EOS representation of N_2+CO_2 mixture adsorption on activated carbon at 318.2 K using Wong-Sandler mixing rules. The figures indicate that both models represent the adsorption with no significant difference.

Conclusions

1. Overall, both the ZGR EOS and the 2-D PR EOS can represent the binary mixture adsorption sets within an AAD of 12% using Wong-Sandler mixing rules and one-fluid mixing rules. Among the cases studied, 2-D PR EOS with Wong-Sandler mixing provides marginally better quality of fit, which suggests that the mixing in the adsorbed phase may be non-random, or that the additional model parameters in these mixing rules provide better precision.
2. 2-D PR EOS predicts the binary adsorption better than ZGR EOS. Further, for all the cases studied, the 2-D PR EOS with Wong-Sandler mixing rules provides more accurate binary mixture adsorption predictions. However, both EOSs predict the lower-adsorption component with higher AAD than the higher-adsorption component.
3. Use of both pure-gas and binary mixture parameters does not result in any improvement in the prediction of the ternary mixture adsorption, when compared to using only pure-gas parameters.

4. Because of the revised repulsive term in ZGR EOS, mixture calculations may fail, especially when the model parameter, β_i , varies significantly among the mixture components. This may limit the use of ZGR EOS in calculating mixture adsorption.

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Table 1. Literature Data Used for Mixture Gas Adsorption Model Evaluation

System No.	Adsorbent	Adsorbate	Temp. (K)	Pressure Range (MPa)	Feed Molar Composition	Sources
1	Dry AC – F 400	N ₂ +CH ₄	318	0.7 – 12.4	0.2, 0.4, 0.6, 0.8	Sudibandriyo (2003)
	Dry AC – F 400	CH ₄ + CO ₂	318	0.7 – 12.4	0.2, 0.4, 0.6, 0.8	Sudibandriyo (2003)
	Dry AC – F 400	N ₂ + CO ₂	318	0.7 – 12.4	0.2, 0.4, 0.6, 0.8	Sudibandriyo (2003)
	Dry AC – F 400	N ₂ +CH ₄ + CO ₂	318	0.7 – 12.4	0.1+0.4+0.5	Sudibandriyo (2003)
2	AC, BPL	CH ₄ + C ₂ H ₆	301	0.13 – 2.01	0.267,0.499,0.745*	Reich (1980)
	AC, BPL	CH ₄ + C ₂ H ₄	301	0.12 – 2.03	0.260,0.534,0.745*	Reich (1980)
	AC, BPL	C ₂ H ₆ + C ₂ H ₄	301	0.14 – 1.98	0.240,0.472,0.682*	Reich (1980)
	AC, BPL	CH ₄ + C ₂ H ₆ + C ₂ H ₄	301	0.12 – 2.97	0.624+0.174+0.202* 0.230+0.520+0.250* 0.200+0.192+0.608*	Reich (1980)
3	AC Norit R1 Extra	N ₂ + CH ₄	298	0.03 – 6.00	Not available	Dreisbach (1999)
	AC Norit R1 Extra	CH ₄ + CO ₂	298	0.03 – 6.00	Not available	Dreisbach (1999)
	AC Norit R1 Extra	N ₂ + CO ₂	298	0.03 – 6.00	Not available	Dreisbach (1999)
	AC Norit R1 Extra	N ₂ + CH ₄ + CO ₂	298	0.03 – 6.00	Not available	Dreisbach (1999)
4	Wet Tiffany Coal	N ₂ +CH ₄	328	0.7 – 13.7	0.2, 0.4, 0.6, 0.8	DOE Report (2002)
	Wet Tiffany Coal	CH ₄ + CO ₂	328	0.7 – 13.7	0.2, 0.4, 0.6, 0.8	DOE Report (2002)
	Wet Tiffany Coal	N ₂ + CO ₂	328	0.7 – 13.7	0.2, 0.4, 0.6, 0.8	DOE Report (2002)
	Wet Tiffany Coal	N ₂ +CH ₄ + CO ₂	328	0.7 – 13.7	0.1+0.4+0.5	DOE Report (2002)
5	Wet Fruitland Coal	N ₂ +CH ₄	319	0.7 – 12.4	0.2, 0.4, 0.6, 0.8	DOE Report (2003)
	Wet Fruitland Coal	CH ₄ + CO ₂	319	0.7 – 12.4	0.2, 0.4, 0.6, 0.8	DOE Report (2003)
	Wet Fruitland Coal	N ₂ + CO ₂	319	0.7 – 12.4	0.2, 0.4, 0.6, 0.8	DOE Report (2003)
6	Wet Illinois #6 Coal	N ₂ +CH ₄	319	0.7 – 12.4	0.2, 0.4, 0.6, 0.8	DOE Report (2001)
	Wet Illinois #6 Coal	CH ₄ + CO ₂	319	0.7 – 12.4	0.2, 0.4, 0.6, 0.8	DOE Report (2001)
	Wet Illinois #6 Coal	N ₂ + CO ₂	319	0.7 – 12.4	0.2, 0.4, 0.6, 0.8	DOE Report (2001)

* Gas-phase mole fraction of the first-named component at equilibria

Table 2. The 2-D EOS Predictions of Binary Mixture Adsorption on Dry Activated Carbon at 318.2 K (OSU, 2002) – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-N₂				
Methane	40	5.2	0.172	2.0
Nitrogen	40	4.7	0.063	1.1
Total	40	3.4	0.149	1.4
CH₄-CO₂				
Methane	40	6.3	0.156	1.3
CO ₂	40	11.4	0.277	2.9
Total	40	2.5	0.155	0.8
N₂-CO₂				
Nitrogen	40	13.1	0.132	2.1
CO ₂	40	11.9	0.233	2.7
Total	40	6.9	0.306	2.1
2-D PR EOS				
CH₄-N₂				
Methane	40	6.5	0.188	2.5
Nitrogen	40	4.9	0.056	1.2
Total	40	3.8	0.164	1.6
CH₄-CO₂				
Methane	40	4.6	0.123	1.0
CO ₂	40	7.4	0.188	1.8
Total	40	1.4	0.090	0.4
N₂-CO₂				
Nitrogen	40	5.5	0.068	1.0
CO ₂	40	5.3	0.120	1.2
Total	40	3.3	0.148	1.0

Table 3. The 2-D EOS Predictions of Binary Mixture Adsorption on Dry Activated Carbon at 301.4 K (Reich, 1980) – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-C₂H₆				
Methane	14	38.0	0.328	–
Ethane	14	2.6	0.097	–
Total	14	5.2	0.269	–
CH₄-C₂H₄				
Methane	15	31.8	0.289	–
Ethylene	15	3.1	0.111	–
Total	15	4.7	0.212	–
C₂H₆-C₂H₄				
Ethane	12	4.1	0.097	–
Ethylene	12	6.5	0.184	–
Total	12	4.1	0.214	–
2-D PR EOS				
CH₄-C₂H₆				
Methane	14	37.4	0.323	–
Ethane	14	2.5	0.095	–
Total	14	5.0	0.257	–
CH₄-C₂H₄				
Methane	15	30.5	0.284	–
Ethylene	15	2.8	0.105	–
Total	15	4.7	0.209	–
C₂H₆-C₂H₄				
Ethane	12	4.3	0.091	–
Ethylene	12	7.4	0.193	–
Total	12	4.1	0.208	–

Table 4. The 2-D EOS Predictions of Binary Mixture Adsorption on Dry Activated Carbon at 298.0 K (Dreisbach, 1999) – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-N₂				
Methane	24	6.8	0.224	–
Nitrogen	24	16.5	0.143	–
Total	24	4.9	0.154	–
CH₄-CO₂				
Methane	24	10.1	0.291	–
CO ₂	24	22.6	0.362	–
Total	24	3.6	0.323	–
N₂-CO₂				
Nitrogen	24	44.3	0.308	–
CO ₂	24	3.7	0.376	–
Total	24	5.3	0.478	–
2-D PR EOS				
CH₄-N₂				
Methane	24	9.2	0.255	–
Nitrogen	24	11.8	0.112	–
Total	24	3.5	0.174	–
CH₄-CO₂				
Methane	24	9.9	0.310	–
CO ₂	24	20.2	0.302	–
Total	24	3.3	0.313	–
N₂-CO₂				
Nitrogen	24	10.4	0.064	–
CO ₂	24	3.0	0.238	–
Total	24	2.9	0.264	–

Table 5. The 2-D EOS Representations of Binary Mixture Adsorption on Activated Carbon at 318.2 K (OSU, 2002) – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂	D ₁₂
ZGR EOS						
CH ₄ -N ₂					0.0753	-0.0309
Methane	40	5.3	0.165	2.1		
Nitrogen	40	2.7	0.055	0.7		
Total	40	4.0	0.169	1.7		
CH ₄ -CO ₂					0.2271	-0.0779
Methane	40	7.9	0.174	1.8		
CO ₂	40	8.1	0.201	2.0		
Total	40	0.7	0.058	0.2		
N ₂ -CO ₂					0.2851	-0.1200
Nitrogen	40	5.3	0.058	0.8		
CO ₂	40	9.5	0.207	2.2		
Total	40	3.7	0.171	1.1		
2-D PR EOS						
CH ₄ -N ₂					-0.6386	-0.1277
Methane	40	6.8	0.169	2.5		
Nitrogen	40	2.7	0.036	0.6		
Total	40	4.0	0.154	1.6		
CH ₄ -CO ₂					-0.6382	-0.1470
Methane	40	4.3	0.091	0.9		
CO ₂	40	4.8	0.140	1.2		
Total	40	1.0	0.075	0.3		
N ₂ -CO ₂					-1.0744	-0.2790
Nitrogen	40	5.0	0.071	0.9		
CO ₂	40	4.6	0.154	1.2		
Total	40	3.0	0.167	0.9		

Table 6. The 2-D EOS Representations of Binary Mixture Adsorption on Activated Carbon at 301.4 K (Reich, 1980) – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂	D ₁₂
ZGR EOS						
CH ₄ -C ₂ H ₆					0.6072	-0.4775
Methane	14	15.0	0.105	—		
Ethane	14	2.7	0.100	—		
Total	14	2.6	0.129	—		
CH ₄ -C ₂ H ₄					-0.0615	-0.1028
Methane	15	7.6	0.061	—		
Ethylene	15	3.4	0.115	—		
Total	15	2.2	0.104	—		
C ₂ H ₆ -C ₂ H ₄					0.4573	-0.2039
Ethane	12	4.6	0.096	—		
Ethylene	12	5.4	0.160	—		
Total	12	3.2	0.157	—		
2-D PR EOS						
CH ₄ -C ₂ H ₆					-0.2291	-1.0485
Methane	14	8.1	0.070	—		
Ethane	14	4.7	0.195	—		
Total	14	2.9	0.163	—		
CH ₄ -C ₂ H ₄					0.0459	-0.6458
Methane	15	6.6	0.045	—		
Ethylene	15	3.7	0.146	—		
Total	15	2.2	0.109	—		
C ₂ H ₆ -C ₂ H ₄					-0.2398	-0.3148
Ethane	12	4.5	0.092	—		
Ethylene	12	6.1	0.142	—		
Total	12	2.5	0.111	—		

Table 7. The 2-D EOS Representations of Binary Mixture Adsorption on Activated Carbon at 298.0 K (Dreisbach, 1999) – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂	D ₁₂
ZGR EOS						
CH ₄ -N ₂					0.3335	-0.1926
Methane	24	9.0	0.219	—		
Nitrogen	24	6.6	0.094	—		
Total	24	5.6	0.201	—		
CH ₄ -CO ₂					0.9357	-0.5183
Methane	24	19.6	0.437	—		
CO ₂	24	14.3	0.254	—		
Total	24	4.6	0.339	—		
N ₂ -CO ₂					0.4180	-0.2567
Nitrogen	24	9.9	0.099	—		
CO ₂	24	3.2	0.298	—		
Total	24	3.6	0.348	—		
2-D PR EOS						
CH ₄ -N ₂					-0.2546	-0.0516
Methane	24	10.8	0.262	—		
Nitrogen	24	4.5	0.081	—		
Total	24	4.6	0.225	—		
CH ₄ -CO ₂					0.1131	0.5462
Methane	24	19.5	0.485	—		
CO ₂	24	13.5	0.226	—		
Total	24	4.6	0.451	—		
N ₂ -CO ₂					-0.9042	-1.4192
Nitrogen	24	5.8	0.043	—		
CO ₂	24	3.1	0.224	—		
Total	24	2.6	0.227	—		

Table 8. The 2-D EOS Predictions of Ternary Mixture Adsorption on Dry Activated Carbon at 318.2 K – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS Based on Pure Gas Parameters				
Methane	11	3.6	0.024	0.3
Nitrogen	11	13.2	0.272	2.3
CO ₂	11	13.6	0.646	3.5
Total	11	5.8	0.370	1.9
2-D PR EOS Based on Pure Gas Parameters				
Methane	11	3.8	0.023	0.4
Nitrogen	11	18.7	0.358	3.4
CO ₂	11	11.7	0.595	2.8
Total	11	3.5	0.237	1.0
ZGR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	11	8.9	0.053	0.8
Nitrogen	11	24.0	0.398	4.6
CO ₂	11	13.9	0.701	3.5
Total	11	3.7	0.257	1.1
2-D PR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	11	6.2	0.039	0.5
Nitrogen	11	19.7	0.360	3.7
CO ₂	11	13.7	0.683	3.3
Total	11	4.5	0.294	1.3

Table 9. The 2-D EOS Predictions of Ternary Mixture Adsorption on Dry Activated Carbon at 301.4 K (Reich, 1980) – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS Based on Pure Gas Parameters				
Methane	14	49.4	0.461	–
Ethane	14	4.4	0.079	–
Ethylene	14	3.8	0.120	–
Total	14	6.2	0.459	–
2-D PR EOS Based on Pure Gas Parameters				
Methane	14	49.1	0.450	–
Ethane	14	5.1	0.090	–
Ethylene	14	3.6	0.120	–
Total	14	6.0	0.438	–
ZGR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	14	29.5	0.206	–
Ethane	14	5.2	0.096	–
Ethylene	14	3.9	0.125	–
Total	14	2.6	0.226	–
2-D PR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	14	25.7	0.189	–
Ethane	14	7.7	0.170	–
Ethylene	14	3.9	0.099	–
Total	14	2.6	0.170	–

Table 10. The 2-D EOS Predictions of Ternary Mixture Adsorption on Dry Activated Carbon at 298.0 K (Dreisbach, 1999) – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS Based on Pure Gas Parameters				
Methane	40	17.9	0.767	–
Nitrogen	40	36.1	0.436	–
CO ₂	40	22.8	0.673	–
Total	40	4.9	0.594	–
2-D PR EOS Based on Pure Gas Parameters				
Methane	40	17.3	0.733	–
Nitrogen	40	47.0	0.562	–
CO ₂	40	19.4	0.581	–
Total	40	5.6	0.696	–
ZGR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	40	21.7	0.915	–
Nitrogen	40	73.0	0.811	–
CO ₂	40	21.2	0.739	–
Total	40	9.3	0.835	–
2-D PR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	40	21.1	0.912	–
Nitrogen	40	43.6	0.519	–
CO ₂	40	17.7	0.560	–
Total	40	7.1	0.818	–

Table 11. The 2-D EOS Predictions of Binary Mixture Adsorption on Dry Activated Carbon at 318.2 K – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-N₂				
Methane	40	5.4	0.169	2.1
Nitrogen	40	2.6	0.059	0.7
Total	40	4.2	0.179	1.8
CH₄-CO₂				
Methane	40	5.3	0.159	1.2
CO ₂	40	9.8	0.237	2.5
Total	40	1.5	0.097	0.4
N₂-CO₂				
Nitrogen	40	8.7	0.081	1.2
CO ₂	40	8.7	0.195	2.0
Total	40	2.9	0.123	0.8
2-D PR EOS				
CH₄-N₂				
Methane	40	6.4	0.186	2.5
Nitrogen	40	5.3	0.057	1.3
Total	40	3.7	0.156	1.6
CH₄-CO₂				
Methane	40	4.3	0.119	1.0
CO ₂	40	7.1	0.181	1.8
Total	40	1.3	0.085	0.4
N₂-CO₂				
Nitrogen	40	5.9	0.078	1.1
CO ₂	40	5.2	0.120	1.2
Total	40	3.6	0.162	1.1

Table 12. The 2-D EOS Predictions of Binary Mixture Adsorption on Dry Activated Carbon at 318.2 K (Reich, 1980) – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-C₂H₆				
Methane	14	38.3	0.330	–
Ethane	14	2.6	0.097	–
Total	14	5.2	0.270	–
CH₄-C₂H₄				
Methane	15	39.5	0.344	–
Ethylene	15	3.1	0.123	–
Total	15	5.2	0.250	–
C₂H₆-C₂H₄				
Ethane	12	4.0	0.096	–
Ethylene	12	6.6	0.185	–
Total	12	4.2	0.218	–
2-D PR EOS				
CH₄-C₂H₆				
Methane	14	38.5	0.332	–
Ethane	14	2.5	0.095	–
Total	14	5.1	0.266	–
CH₄-C₂H₄				
Methane	15	35.7	0.316	–
Ethylene	15	2.8	0.113	–
Total	15	4.9	0.232	–
C₂H₆-C₂H₄				
Ethane	12	4.3	0.091	–
Ethylene	12	7.4	0.193	–
Total	12	4.1	0.208	–

Table 13. The 2-D EOS Predictions of Binary Mixture Adsorption on Dry Activated Carbon at 298.0 K (Dreisbach, 1999) – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-N₂				
Methane	24	9.7	0.237	–
Nitrogen	24	5.9	0.068	–
Total	24	6.3	0.240	–
CH₄-CO₂				
Methane	24	10.9	0.307	–
CO ₂	24	21.4	0.344	–
Total	24	3.7	0.335	–
N₂-CO₂				
Nitrogen	24	25.2	0.123	–
CO ₂	24	3.2	0.278	–
Total	24	3.3	0.332	–
2-D PR EOS				
CH₄-N₂				
Methane	24	9.1	0.252	–
Nitrogen	24	12.5	0.126	–
Total	24	3.6	0.164	–
CH₄-CO₂				
Methane	24	10.7	0.318	–
CO ₂	24	19.7	0.295	–
Total	24	3.4	0.319	–
N₂-CO₂				
Nitrogen	24	11.5	0.067	–
CO ₂	24	2.9	0.233	–
Total	24	2.9	0.262	–

Table 14. The 2-D EOS Representations of Binary Mixture Adsorption on Activated Carbon at 318.2 K – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂ a ₁₂	t ₁₂ t ₂₁
ZGR EOS						
CH ₄ -N ₂					-0.2502 20.0	-0.1743 -0.2677
Methane	40	1.8	0.042	0.6		
Nitrogen	40	2.7	0.048	0.8		
Total	40	0.9	0.041	0.4		
CH ₄ -CO ₂					-0.4465 20.0	-0.0028 -0.3256
Methane	40	3.0	0.060	0.6		
CO ₂	40	4.0	0.092	1.0		
Total	40	2.1	0.134	0.6		
N ₂ -CO ₂					-0.1000 20.0	-0.0949 -0.1500
Nitrogen	40	5.0	0.052	0.8		
CO ₂	40	8.6	0.179	2.0		
Total	40	4.2	0.174	1.2		
2-D PR EOS						
CH ₄ -N ₂					-0.1206 20.0	-0.0988 -0.2643
Methane	40	4.2	0.091	1.5		
Nitrogen	40	1.9	0.027	0.5		
Total	40	2.0	0.081	0.8		
CH ₄ -CO ₂					-0.1405 20.0	-0.0947 -0.2448
Methane	40	3.0	0.069	0.6		
CO ₂	40	2.7	0.074	0.7		
Total	40	1.3	0.099	0.4		
N ₂ -CO ₂					-0.1194 20.0	-0.1314 -0.0056
Nitrogen	40	3.4	0.041	0.5		
CO ₂	40	5.1	0.165	1.3		
Total	40	2.8	0.151	0.9		

Table 15. The 2-D EOS Representations of Binary Mixture Adsorption on Activated Carbon at 301.4 K (Reich, 1980) – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂ a ₁₂	t ₁₂ t ₂₁
ZGR EOS						
CH ₄ -C ₂ H ₆					0.4387 0.1851	-0.2614 -0.5461
Methane	14	14.5	0.118	—		
Ethane	14	3.0	0.116	—		
Total	14	2.3	0.120	—		
CH ₄ -C ₂ H ₄					0.0784 0.9573	-0.2540 -1.1439
Methane	15	5.1	0.042	—		
Ethylene	15	3.3	0.119	—		
Total	15	2.5	0.123	—		
C ₂ H ₆ -C ₂ H ₄					-0.2835 12.932	-0.3029 -0.2098
Ethane	12	3.0	0.060	—		
Ethylene	12	2.2	0.062	—		
Total	12	1.8	0.104	—		
2-D PR EOS						
CH ₄ -C ₂ H ₆					0.2124 1.0316	0.4684 -3.6814
Methane	14	8.3	0.074	—		
Ethane	14	4.6	0.192	—		
Total	14	2.9	0.161	—		
CH ₄ -C ₂ H ₄					0.2447 0.3000	0.0282 -1.9522
Methane	15	6.5	0.042	—		
Ethylene	15	3.6	0.132	—		
Total	15	2.1	0.099	—		
C ₂ H ₆ -C ₂ H ₄					-0.0349 8.9906	-0.7695 0.0116
Ethane	12	3.7	0.079	—		
Ethylene	12	3.4	0.079	—		
Total	12	2.5	0.122	—		

Table 16. The 2-D EOS Representations of Binary Mixture Adsorption on Activated Carbon at 298.0 K (Dreisbach, 1999) – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂ a ₁₂	t ₁₂ t ₂₁
ZGR EOS						
CH ₄ -N ₂					0.4169 0.5827	-0.0029 5.8449
Methane	24	7.9	0.183	—		
Nitrogen	24	6.6	0.062	—		
Total	24	6.4	0.211	—		
CH ₄ -CO ₂					1.1056 0.2437	4.2900 -0.0034
Methane	24	9.8	0.305	—		
CO ₂	24	6.9	0.202	—		
Total	24	4.0	0.287	—		
N ₂ -CO ₂					0.7672 0.2682	-0.5311 0.7104
Nitrogen	24	6.5	0.050	—		
CO ₂	24	3.5	0.310	—		
Total	24	3.3	0.336	—		
2-D PR EOS						
CH ₄ -N ₂					-0.1490 0.1749	-2.0331 14.477
Methane	24	8.6	0.238	—		
Nitrogen	24	3.3	0.065	—		
Total	24	5.2	0.233	—		
CH ₄ -CO ₂					0.0912 0.1437	9.1701 -0.9318
Methane	24	10.5	0.376	—		
CO ₂	24	7.5	0.235	—		
Total	24	4.0	0.354	—		
N ₂ -CO ₂					-0.0076 0.4456	-11.141 -0.7837
Nitrogen	24	5.9	0.045	—		
CO ₂	24	3.1	0.220	—		
Total	24	2.6	0.226	—		

Table 17. The 2-D EOS Predictions of Ternary Mixture Adsorption on Dry Activated Carbon at 318.2 K – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS Based on Pure Gas Parameters				
Methane	11	3.8	0.022	0.4
Nitrogen	11	28.2	0.468	5.4
CO ₂	11	13.4	0.676	3.4
Total	11	3.1	0.210	0.9
2-D PR EOS Based on Pure Gas Parameters				
Methane	11	3.8	0.023	0.4
Nitrogen	11	17.8	0.343	3.2
CO ₂	11	11.7	0.596	2.8
Total	11	3.7	0.252	1.1
ZGR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	11	5.9	0.037	0.6
Nitrogen	11	22.0	0.398	4.1
CO ₂	11	12.0	0.613	3.0
Total	11	3.0	0.197	0.9
2-D PR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	11	7.1	0.048	0.6
Nitrogen	11	21.5	0.396	4.0
CO ₂	11	13.6	0.688	3.3
Total	11	3.7	0.252	1.0

Table 18. The 2-D EOS Predictions of Ternary Mixture Adsorption on Dry Activated Carbon at 301.4 K (Reich, 1980) – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS Based on Pure Gas Parameters				
Methane	14	50.4	0.473	–
Ethane	14	4.5	0.082	–
Ethylene	14	3.6	0.119	–
Total	14	6.4	0.470	–
2-D PR EOS Based on Pure Gas Parameters				
Methane	14	49.8	0.459	–
Ethane	14	5.1	0.089	–
Ethylene	14	3.7	0.120	–
Total	14	6.1	0.446	–
ZGR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	14	31.6	0.239	–
Ethane	14	10.4	0.204	–
Ethylene	14	3.3	0.121	–
Total	14	3.9	0.233	–
2-D PR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	14	26.2	0.195	–
Ethane	14	10.3	0.252	–
Ethylene	14	4.1	0.117	–
Total	14	2.8	0.195	–

Table 19. The 2-D EOS Predictions of Ternary Mixture Adsorption on Dry Activated Carbon at 298.0 K (Dreisbach, 1999) – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS Based on Pure Gas Parameters				
Methane	40	16.8	0.705	–
Nitrogen	40	53.8	0.656	–
CO ₂	40	20.8	0.634	–
Total	40	5.8	0.705	–
2-D PR EOS Based on Pure Gas Parameters				
Methane	40	17.3	0.734	–
Nitrogen	40	46.9	0.562	–
CO ₂	40	19.0	0.571	–
Total	40	5.6	0.703	–
ZGR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	40	20.9	0.844	–
Nitrogen	40	48.9	0.584	–
CO ₂	40	29.3	0.852	–
Total	40	5.9	0.585	–
2-D PR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	40	16.7	0.700	–
Nitrogen	40	41.9	0.553	–
CO ₂	40	22.6	0.665	–
Total	40	4.7	0.565	–

Table 20. The 2-D EOS Predictions of Binary Mixture Adsorption on Wet Tiffany Coal at 327.6 K – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-N₂				
Methane	11	10.7	0.024	1.6
Nitrogen	11	5.5	0.004	0.4
Total	11	9.0	0.025	1.5
CH₄-CO₂				
Methane	11	26.6	0.037	4.4
CO ₂	11	12.7	0.057	2.7
Total	11	3.1	0.021	0.7
N₂-CO₂				
Nitrogen	11	33.9	0.012	1.2
CO ₂	11	5.9	0.043	1.0
Total	11	4.4	0.032	0.9
2-D PR EOS				
CH₄-N₂				
Methane	11	12.3	0.025	1.8
Nitrogen	11	4.4	0.004	0.3
Total	11	10.5	0.028	1.7
CH₄-CO₂				
Methane	11	24.1	0.036	3.7
CO ₂	11	10.0	0.052	1.9
Total	11	3.1	0.018	0.7
N₂-CO₂				
Nitrogen	11	52.8	0.019	1.8
CO ₂	11	7.5	0.049	1.4
Total	11	5.4	0.033	1.2

Table 21. The 2-D EOS Predictions of Binary Mixture Adsorption on Wet Fruitland Coal at 319.3 K – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-N₂				
Methane	41	5.3	0.022	0.6
Nitrogen	41	20.9	0.022	1.5
Total	41	2.3	0.011	0.3
CH₄-CO₂				
Methane	40	24.4	0.062	2.2
CO ₂	40	10.8	0.062	1.5
Total	40	9.4	0.103	1.8
N₂-CO₂				
Nitrogen	50	109.5	0.113	3.5
CO ₂	50	15.4	0.115	1.9
Total	50	22.7	0.225	3.2
2-D PR EOS				
CH₄-N₂				
Methane	41	4.0	0.017	0.4
Nitrogen	41	23.0	0.027	1.7
Total	41	3.4	0.014	0.4
CH₄-CO₂				
Methane	40	8.6	0.021	0.8
CO ₂	40	5.6	0.044	0.8
Total	40	3.7	0.046	0.7
N₂-CO₂				
Nitrogen	50	25.2	0.028	0.9
CO ₂	50	5.9	0.037	0.6
Total	50	3.1	0.025	0.3

Table 22. The 2-D EOS Predictions of Binary Mixture Adsorption on Wet Illinois #6 Coal at 319.3 K – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-N₂				
Methane	40	24.7	0.028	0.6
Nitrogen	40	29.7	0.012	0.4
Total	40	15.2	0.034	0.5
CH₄-CO₂				
Methane	40	11.7	0.019	0.5
CO ₂	40	18.2	0.090	1.4
Total	40	13.0	0.091	1.2
N₂-CO₂				
Nitrogen	–	–	–	–
CO ₂	–	–	–	–
Total	–	–	–	–
2-D PR EOS				
CH₄-N₂				
Methane	40	14.9	0.017	0.4
Nitrogen	40	15.3	0.005	0.3
Total	40	7.9	0.016	0.3
CH₄-CO₂				
Methane	40	17.7	0.021	0.7
CO ₂	40	11.7	0.054	0.8
Total	40	6.4	0.050	0.6
N₂-CO₂				
Nitrogen	40	69.1	0.017	0.7
CO ₂	40	10.4	0.046	0.7
Total	40	8.0	0.046	0.5

Table 23. The 2-D EOS Representations of Binary Mixture Adsorption Wet Tiffany Coal at 327.6 K – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂	D ₁₂
ZGR EOS						
CH ₄ -N ₂					0.0265	-0.0392
Methane	11	10.3	0.023	1.5		
Nitrogen	11	6.1	0.004	0.4		
Total	11	7.9	0.022	1.3		
CH ₄ -CO ₂					-0.1116	-0.0170
Methane	11	7.6	0.011	1.4		
CO ₂	11	13.3	0.057	3.0		
Total	11	8.3	0.051	2.1		
N ₂ -CO ₂					0.2548	-0.2723
Nitrogen	11	10.2	0.003	0.4		
CO ₂	11	5.9	0.043	1.0		
Total	11	5.4	0.041	1.0		
2-D PR EOS						
CH ₄ -N ₂					-1.0973	-3.0000
Methane	11	7.0	0.011	1.0		
Nitrogen	11	5.5	0.004	0.4		
Total	11	4.7	0.010	0.8		
CH ₄ -CO ₂					4.9538	0.03890
Methane	11	7.2	0.014	1.0		
CO ₂	11	7.7	0.038	1.6		
Total	11	5.0	0.029	1.3		
N ₂ -CO ₂					0.6113	-0.4547
Nitrogen	11	6.7	0.002	0.3		
CO ₂	11	7.4	0.048	1.3		
Total	11	6.9	0.048	1.3		

Table 24. The 2-D EOS Representations of Binary Mixture Adsorption Wet Fruitland Coal at 319.3 K – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂	D ₁₂
ZGR EOS						
CH ₄ -N ₂					0.5263	-0.4743
Methane	41	7.6	0.029	0.8		
Nitrogen	41	8.2	0.009	0.6		
Total	41	3.8	0.025	0.5		
CH ₄ -CO ₂					0.3769	-0.0985
Methane	40	5.2	0.015	0.5		
CO ₂	40	5.5	0.041	0.7		
Total	40	2.8	0.040	0.5		
N ₂ -CO ₂					0.2291	0.0364
Nitrogen	50	12.0	0.013	0.5		
CO ₂	50	7.4	0.054	0.9		
Total	50	5.0	0.052	0.7		
2-D PR EOS						
CH ₄ -N ₂					1.9927	1.8136
Methane	41	4.6	0.016	0.5		
Nitrogen	41	7.6	0.010	0.5		
Total	41	3.1	0.017	0.4		
CH ₄ -CO ₂					-0.1725	0.0159
Methane	40	3.7	0.013	0.4		
CO ₂	40	4.4	0.040	0.6		
Total	40	2.5	0.043	0.4		
N ₂ -CO ₂					0.2649	0.2556
Nitrogen	50	15.4	0.014	0.4		
CO ₂	50	6.0	0.038	0.6		
Total	50	3.3	0.031	0.4		

Table 25. The 2-D EOS Representations of Binary Mixture Adsorption Wet Illinois #6 Coal at 319.3 K – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂	D ₁₂
ZGR EOS						
CH ₄ -N ₂					0.5478	-0.3753
Methane	40	19.6	0.020	0.5		
Nitrogen	40	20.9	0.008	0.4		
Total	40	7.6	0.014	0.2		
CH ₄ -CO ₂					0.4422	-0.3346
Methane	40	11.9	0.016	0.5		
CO ₂	40	12.7	0.087	1.4		
Total	40	12.0	0.083	1.1		
N ₂ -CO ₂					—	—
Nitrogen	—	—	—	—		
CO ₂	—	—	—	—		
Total	—	—	—	—		
2-D PR EOS						
CH ₄ -N ₂					3.7989	1.2195
Methane	40	14.2	0.016	0.4		
Nitrogen	40	14.9	0.007	0.3		
Total	40	6.6	0.013	0.2		
CH ₄ -CO ₂					-0.0314	0.4156
Methane	40	15.0	0.021	0.6		
CO ₂	40	11.8	0.054	0.8		
Total	40	5.3	0.041	0.4		
N ₂ -CO ₂					-0.7207	0.7357
Nitrogen	40	51.7	0.034	0.9		
CO ₂	40	9.9	0.043	0.7		
Total	40	4.0	0.016	0.3		

Table 26. The 2-D EOS Predictions of Ternary Mixture Adsorption on Wet Tiffany Coal at 327.6 K – One-Fluid Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS Based on Pure Gas Parameters				
Methane	11	24.4	0.007	1.0
Nitrogen	11	46.2	0.030	3.0
CO ₂	11	19.4	0.075	3.6
Total	11	6.6	0.038	1.4
2-D PR EOS Based on Pure Gas Parameters				
Methane	11	19.3	0.006	0.8
Nitrogen	11	57.3	0.040	3.5
CO ₂	11	15.9	0.074	2.8
Total	11	5.2	0.031	1.1
ZGR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	11	16.2	0.005	0.6
Nitrogen	11	29.8	0.019	2.0
CO ₂	11	20.1	0.076	3.7
Total	11	11.4	0.062	2.6
2-D PR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	11	44.1	0.018	1.3
Nitrogen	11	20.9	0.011	1.5
CO ₂	11	15.6	0.068	2.8
Total	11	12.1	0.076	2.8

Table 27. The 2-D EOS Predictions of Binary Mixture Adsorption on Wet Tiffany Coal at 327.6 K – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-N₂				
Methane	11	11.2	0.025	1.7
Nitrogen	11	7.0	0.006	0.5
Total	11	10.4	0.030	1.7
CH₄-CO₂				
Methane	11	34.2	0.048	5.5
CO ₂	11	12.7	0.058	2.7
Total	11	2.0	0.012	0.5
N₂-CO₂				
Nitrogen	11	69.4	0.023	2.4
CO ₂	11	6.6	0.049	1.2
Total	11	4.4	0.029	1.0
2-D PR EOS				
CH₄-N₂				
Methane	11	11.9	0.024	1.7
Nitrogen	11	4.2	0.004	0.3
Total	11	10.1	0.026	1.6
CH₄-CO₂				
Methane	11	24.6	0.037	3.8
CO ₂	11	10.0	0.052	1.9
Total	11	3.0	0.018	0.7
N₂-CO₂				
Nitrogen	11	43.4	0.015	1.5
CO ₂	11	7.7	0.050	1.4
Total	11	5.8	0.037	1.2

Table 28. The 2-D EOS Predictions of Binary Mixture Adsorption on Wet Fruitland Coal at 319.3 K – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-N₂				
Methane	41	3.9	0.019	0.5
Nitrogen	41	29.9	0.034	2.1
Total	41	3.8	0.019	0.5
CH₄-CO₂				
Methane	40	41.9	0.087	3.6
CO ₂	40	10.9	0.063	1.5
Total	40	8.8	0.095	1.5
N₂-CO₂				
Nitrogen	–	–	–	–
CO ₂	–	–	–	–
Total	–	–	–	–
2-D PR EOS				
CH₄-N₂				
Methane	41	4.1	0.018	0.5
Nitrogen	41	22.9	0.026	1.7
Total	41	3.3	0.014	0.4
CH₄-CO₂				
Methane	40	5.7	0.018	0.6
CO ₂	40	4.9	0.042	0.7
Total	40	3.4	0.045	0.6
N₂-CO₂				
Nitrogen	50	25.8	0.029	0.9
CO ₂	50	5.9	0.037	0.6
Total	50	3.2	0.025	0.4

Table 29. The 2-D EOS Predictions of Binary Mixture Adsorption on Wet Illinois #6 Coal at 319.3 K – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS				
CH₄-N₂				
Methane	40	19.6	0.020	0.5
Nitrogen	40	21.5	0.008	0.4
Total	40	8.0	0.016	0.3
CH₄-CO₂				
Methane	40	13.1	0.022	0.5
CO ₂	40	19.2	0.090	1.5
Total	40	15.0	0.101	1.4
N₂-CO₂				
Nitrogen	–	–	–	–
CO ₂	–	–	–	–
Total	–	–	–	–
2-D PR EOS				
CH₄-N₂				
Methane	40	14.9	0.018	0.4
Nitrogen	40	15.4	0.005	0.3
Total	40	8.0	0.017	0.3
CH₄-CO₂				
Methane	40	15.5	0.021	0.6
CO ₂	40	11.7	0.053	0.8
Total	40	5.6	0.042	0.5
N₂-CO₂				
Nitrogen	40	49.1	0.027	0.7
CO ₂	40	10.3	0.045	0.8
Total	40	4.5	0.023	0.4

Table 30. The 2-D EOS Representations of Binary Mixture Adsorption Wet Tiffany Coal at 327.6 K – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂ a ₁₂	t ₁₂ t ₂₁
ZGR EOS						
CH ₄ -N ₂					0.1615 5.9316	-0.0009 -0.6006
Methane	11	3.7	0.008	0.6		
Nitrogen	11	5.5	0.004	0.4		
Total	11	3.2	0.008	0.5		
CH ₄ -CO ₂					-0.8419 3.6242	0.2038 -1.2087
Methane	11	8.7	0.012	1.5		
CO ₂	11	4.9	0.019	1.2		
Total	11	3.0	0.016	0.9		
N ₂ -CO ₂					0.5544 2.2711	-0.3085 -2.4618
Nitrogen	11	7.1	0.002	0.3		
CO ₂	11	6.2	0.045	1.1		
Total	11	5.7	0.044	1.1		
2-D PR EOS						
CH ₄ -N ₂					0.1468 5.3000	-7.1169 -0.4682
Methane	11	9.0	0.016	1.3		
Nitrogen	11	4.4	0.003	0.3		
Total	11	7.0	0.016	1.2		
CH ₄ -CO ₂					0.5815 0.9097	0.5183 1.0000
Methane	11	4.9	0.009	0.8		
CO ₂	11	7.7	0.041	1.6		
Total	11	5.5	0.034	1.3		
N ₂ -CO ₂					0.5430 0.0135	1.1419 0.3716
Nitrogen	11	6.8	0.002	0.3		
CO ₂	11	7.4	0.049	1.4		
Total	11	6.9	0.048	1.3		

Table 31. The 2-D EOS Representations of Binary Mixture Adsorption Wet Fruitland Coal at 319.3 K – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂ a ₁₂	t ₁₂ t ₂₁
ZGR EOS						
CH ₄ -N ₂					1.0552 7.3922	-1.0275 -0.1558
Methane	41	5.8	0.021	0.6		
Nitrogen	41	6.4	0.007	0.5		
Total	41	3.3	0.021	0.4		
CH ₄ -CO ₂					0.6039 0.9791	-0.4831 -0.9208
Methane	40	5.4	0.016	0.6		
CO ₂	40	5.5	0.039	0.6		
Total	40	2.8	0.041	0.5		
N ₂ -CO ₂					—	—
Nitrogen	—	—	—	—		
CO ₂	—	—	—	—		
Total	—	—	—	—		
2-D PR EOS						
CH ₄ -N ₂					0.4095 0.6000	4.3366 1.9299
Methane	41	5.7	0.023	0.6		
Nitrogen	41	7.8	0.008	0.5		
Total	41	3.8	0.023	0.5		
CH ₄ -CO ₂					-0.0814 0.2000	0.8474 -0.9230
Methane	40	3.3	0.012	0.4		
CO ₂	40	4.2	0.040	0.6		
Total	40	2.5	0.043	0.4		
N ₂ -CO ₂					0.1853 0.0117	4.4766 0.3705
Nitrogen	50	15.2	0.014	0.5		
CO ₂	50	6.0	0.038	0.4		
Total	50	3.3	0.031	0.2		

**Table 32. The 2-D EOS Representations of Binary Mixture Adsorption
Wet Illinois #6 Coal at 319.3 K – Wong-Sandler Mixing Rules**

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂ a ₁₂	t ₁₂ t ₂₁
ZGR EOS						
CH ₄ -N ₂					0.7060 0.2688	4.4244 -2.1379
Methane	40	19.4	0.019	0.5		
Nitrogen	40	19.8	0.008	0.4		
Total	40	7.8	0.014	0.2		
CH ₄ -CO ₂					0.5460 6.1977	-0.8312 0.2455
Methane	40	11.3	0.019	0.4		
CO ₂	40	7.9	0.031	0.5		
Total	40	3.8	0.021	0.3		
N ₂ -CO ₂					—	—
Nitrogen	—	—	—	—		
CO ₂	—	—	—	—		
Total	—	—	—	—		
2-D PR EOS						
CH ₄ -N ₂					0.9307 0.2942	6.6286 1.4992
Methane	40	13.4	0.016	0.4		
Nitrogen	40	13.9	0.067	0.3		
Total	40	6.9	0.013	0.2		
CH ₄ -CO ₂					-0.0177 0.2104	1.8158 6.4210
Methane	40	14.9	0.021	0.6		
CO ₂	40	11.9	0.054	0.8		
Total	40	5.3	0.040	0.4		
N ₂ -CO ₂					-0.1918 1.6000	-6.0733 1.9089
Nitrogen	40	51.8	0.033	0.9		
CO ₂	40	9.0	0.037	0.6		
Total	40	3.4	0.014	0.3		

Table 33. The 2-D EOS Predictions of Ternary Mixture Adsorption on Wet Tiffany Coal at 327.6 K – Wong-Sandler Mixing Rules

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
ZGR EOS Based on Pure Gas Parameters				
Methane	11	30.9	0.010	1.2
Nitrogen	11	69.4	0.048	4.3
CO ₂	11	19.8	0.078	3.6
Total	11	4.2	0.024	0.9
2-D PR EOS Based on Pure Gas Parameters				
Methane	11	19.7	0.006	0.8
Nitrogen	11	53.3	0.037	3.3
CO ₂	11	16.5	0.077	2.9
Total	11	6.1	0.037	1.3
ZGR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	11	15.0	0.004	0.8
Nitrogen	11	17.9	0.009	1.3
CO ₂	11	18.0	0.068	3.3
Total	11	10.5	0.059	2.4
2-D PR EOS Based on Pure Gas and Binary Mixture Parameters				
Methane	11	37.5	0.016	1.1
Nitrogen	11	21.3	0.012	1.5
CO ₂	11	31.1	0.144	5.5
Total	11	23.4	0.149	5.3

Table 34. Summary of Mixture Adsorption on Activated Carbons

	L. A. C. *		H. A. C. *		Total	
	%AAD	RMSE	%AAD	RMSE	%AAD	RMSE
Predictions Using One-Fluid Mixing Rules						
ZGR EOS	16.0	0.202	9.0	0.253	4.4	0.265
2-D PR EOS	10.3	0.166	7.3	0.199	3.3	0.198
Predictions Using Wong-Sandler Mixing Rules						
ZGR EOS	12.2	0.180	8.3	0.224	3.7	0.222
2-D PR EOS	11.1	0.173	7.2	0.196	3.3	0.200
Regressions Using One-Fluid Mixing Rules						
ZGR EOS	8.1	0.171	7.3	0.206	3.3	0.205
2-D PR EOS	6.3	0.169	6.4	0.186	3.0	0.211
Regressions Using Wong-Sandler Mixing Rules						
ZGR EOS	5.5	0.113	5.0	0.164	3.0	0.189
2-D PR EOS	4.6	0.131	4.7	0.165	2.7	0.183

* L. A. C.: low-adsorbed component (233 data points)

H. A. C.: high-adsorbed component (233 data points)

Table 35. Summary of Mixture Adsorption on Wet Coals

	L. A. C. *		H. A. C. *		Total	
	%AAD	RMSE	%AAD	RMSE	%AAD	RMSE
Predictions Using One-Fluid Mixing Rules						
ZGR EOS	21.7	0.033	12.5	0.038	9.2	0.065
2-D PR EOS	18.0	0.021	9.2	0.038	5.5	0.034
Predictions Using Wong-Sandler Mixing Rules						
ZGR EOS	28.4	0.045	12.8	0.055	8.3	0.065
2-D PR EOS	16.5	0.020	9.0	0.038	5.3	0.032
Regressions Using One-Fluid Mixing Rules						
ZGR EOS	10.9	0.012	11.1	0.050	6.6	0.047
2-D PR EOS	9.6	0.013	8.5	0.036	4.6	0.032
Regressions Using Wong-Sandler Mixing Rules						
ZGR EOS	10.1	0.013	8.8	0.029	4.3	0.026
2-D PR EOS	9.2	0.012	8.7	0.037	4.9	0.033

* L. A. C.: low-adsorbed component (194 data points)

H. A. C.: high-adsorbed component (194 data points)

Figure 1. Representation of CH₄+CO₂ Mixture Adsorption on Activated Carbon at 318.2 K:
Total Adsorption Using the ZGR EOS

Figure 2. Representation of CH₄+CO₂ Mixture Adsorption on Activated Carbon at 318.2 K:
CH₄ Component Adsorption Using the ZGR EOS

Figure 3. Representation of CH₄+CO₂ Mixture Adsorption on Activated Carbon at 318.2 K: CO₂ Component Adsorption Using the ZGR EOS

Figure 4. Representation of N₂+CO₂ Mixture Adsorption on Activated Carbon at 318.2 K:
Total Adsorption Using Wong-Sandler Mixing Rules

Figure 5. Representation of N₂+CO₂ Mixture Adsorption on Activated Carbon at 318.2 K:
N₂ Component Adsorption Using Wong-Sandler Mixing Rules

Figure 6. Representation of N₂+CO₂ Mixture Adsorption on Activated Carbon at 318.2 K:
CO₂ Component Adsorption Using Wong-Sandler Mixing Rules

APPENDIX

Wong-Sandler Mixing Rules for the Generalized 2-D EOS

Wong-Sandler Mixing Rules for the Generalized 2-D EOS

For the 2-D EOS, $b = \mathbf{b}A$ and $a = \mathbf{a}A$. If we assume the surface area is the same among species, thus the Wong-Sandler mixing rule could extend to the generalized 2-D EOS.

$$\mathbf{b} - \frac{\mathbf{a}}{RT} = \sum_i \sum_j x_i x_j \left(\mathbf{b} - \frac{\mathbf{a}}{RT} \right)_{ij} \quad (\text{A-1})$$

$$\left(\mathbf{b} - \frac{\mathbf{a}}{RT} \right)_{ij} = \frac{I}{2} \left[\left(\mathbf{b}_i - \frac{\mathbf{a}_i}{RT} \right) + \left(\mathbf{b}_j - \frac{\mathbf{a}_j}{RT} \right) \right] (I - K_{ij}) \quad (\text{A-2})$$

Helmholtz Free Energy for the Generalized 2-D EOS

The Helmholtz free energy departure function is the difference between the molar Helmholtz free energy of pure species i and the ideal gas at the same temperature and pressure. If ϑ is the specific area of the molecule in the 2-D phase, the Helmholtz free energy departure function can be expressed as:

$$A_i(T, \mathbf{p}) - A_i^{IG}(T, \mathbf{p}) = \left(- \int_{\infty}^{\mathbf{J}} \mathbf{p} d\mathbf{J} \right) - \left(- \int_{\infty}^{\frac{RT}{\mathbf{J}}} \frac{RT}{\mathbf{J}} d\mathbf{J} \right) \quad (\text{A-3})$$

For the generalized 2-D EOS, Equation A-3 becomes:

$$\begin{aligned} A_i(T, \mathbf{p}) - A_i^{IG}(T, \mathbf{p}) = & \left(- \int_{\infty}^{\mathbf{J}} \left[\frac{RT}{\mathbf{J} - b_{2,i}^{1/m} \mathbf{J}^{1-1/m}} - \frac{a_2}{\mathbf{J}^2 + U b_{2,i} \mathbf{J} + W b_{2,i}^2} \right] d\mathbf{J} \right) - \left(- \int_{\infty}^{\frac{RT}{\mathbf{p}}} \frac{RT}{\mathbf{J}} d\mathbf{J} \right) \\ = & -RT \ln \left(\frac{\mathbf{p} (\mathbf{J}^m - b_{2,i}^m)^{1/m}}{RT} \right) - \frac{a_{2,i}}{b_{2,i} \sqrt{U^2 - 4W}} \ln \left(\frac{\mathbf{J}_i + b_{2,i} (U - \sqrt{U^2 - 4W})/2}{\mathbf{J}_i + b_{2,i} (U + \sqrt{U^2 - 4W})/2} \right) \end{aligned} \quad (\text{A-4})$$

If $U=W=0$, then

$$A_i(T, \mathbf{p}) - A_i^{IG}(T, \mathbf{p}) = -RT \ln \left(\frac{\mathbf{p}(\mathbf{J}_i^m - b_{2,i}^m)^{1/m}}{RT} \right) - \frac{a_{2,i}}{\mathbf{J}_i} \quad (\text{A-5})$$

where $a_{2,i}$ and $b_{2,i}$ are 2-D parameters for component i .

Similarly, the mixture Helmholtz free energy departure function, which is the difference between the molar Helmholtz free energy of a mixture, A_m , and that of the same mixture as an ideal gas, A_M^{IGM} , at the same temperature, pressure, and composition is:

$$A_M(T, \mathbf{p}, x) - A_M^{IGM}(T, \mathbf{p}, x) = -RT \ln \left(\frac{\mathbf{p}(\mathbf{J}_M^m - b_M^m)^{1/m}}{RT} \right) - \frac{a_M}{b_M \sqrt{U^2 - 4W}} \ln \left(\frac{\mathbf{J}_M + b_M \left(\frac{U - \sqrt{U^2 - 4W}}{2} \right)}{\mathbf{J}_M + b_M \left(\frac{U + \sqrt{U^2 - 4W}}{2} \right)} \right) \quad (\text{A-6})$$

If $U=W=0$, then

$$A_M(T, \mathbf{p}, x) - A_M^{IGM}(T, \mathbf{p}, x) = -RT \ln \left(\frac{\mathbf{p}(\mathbf{J}_M^m - b_M^m)^{1/m}}{RT} \right) - \frac{a_M}{\mathbf{J}_M} \quad (\text{A-7})$$

Thus, the excess Helmholtz free energy for mixing at constant spreading temperature and pressure, $A^E(T, \mathbf{p}, x)$, is:

$$A^E(T, \mathbf{p}, x) = A_M(T, \mathbf{p}, x) - A_M^{IGM}(T, \mathbf{p}, x) = A_M(T, \mathbf{p}, x) - \sum_i x_i A_i(T, \mathbf{p}) - RT \sum_i x_i \ln x_i$$

$$A^E(T, \mathbf{p}, x) = A_M^{IGM}(T, \mathbf{p}, x) - RT \ln \left(\frac{\mathbf{p}(\mathbf{J}_M^m - b_M^m)^{1/m}}{RT} \right) - \frac{a_M}{\mathbf{J}_M} - \sum_i x_i A_i^{IG}(T, \mathbf{p}) + RT \sum_i x_i \ln \left(\frac{\mathbf{p}(\mathbf{J}_i^m - b_i^m)^{1/m}}{RT} \right) + \sum_i \frac{x_i a_i}{\mathbf{J}_i} - RT \sum_i x_i \ln x_i \quad (\text{A-8})$$

$$A_M^{IGM}(T, \mathbf{p}, x) - \sum_i x_i A_i^{IG}(T, \mathbf{p}) = RT \sum_i x_i \ln x_i \quad (\text{A-9})$$

Thus,

$$\begin{aligned}
A^E(T, \mathbf{p}, x) &= -RT \ln \left(\frac{\mathbf{p}(\mathbf{J}_M^m - b_M^m)^{1/m}}{RT} \right) - \frac{a_M}{\mathbf{J}_M} + RT \sum_i x_i \ln \left(\frac{\mathbf{p}(\mathbf{J}_i^m - b_i^m)^{1/m}}{RT} \right) + \sum_i \frac{x_i a_i}{\mathbf{J}_i} \\
A^E(T, \mathbf{p}, x) &= -\frac{a_M}{\mathbf{J}_M} + \sum_i \frac{x_i a_i}{\mathbf{J}_i} + RT \sum_i x_i \ln \left(\frac{(\mathbf{J}_i^m - b_i^m)^{1/m}}{(\mathbf{J}_M^m - b_M^m)^{1/m}} \right)
\end{aligned} \tag{A-10}$$

Expressions for the excess Helmholtz free energy of liquid mixture have usually been derived using lattice models with the assumption that there are no free sites on the lattice. This is approximately equivalent to the assumption that in a liquid solution the molecules are so closely packed that there is not free volume; this limit in an equation of state is:

$$\lim_{\pi \rightarrow \infty} \vartheta_i = b_i$$

$$\lim_{\mathbf{p} \rightarrow \infty} \mathbf{J}_M = b_M$$

From the 2-D EOS:

$$\left[\mathbf{p} + \frac{a}{\mathbf{J}^2 + Ub\mathbf{J} + Wb^2} \right] = \frac{RT}{\mathbf{J} - b^m \mathbf{J}^{l-m}} \tag{A-11}$$

Thus

$$\mathbf{J}^m - b^m = \frac{l}{\mathbf{J}^{l-m}} \frac{RT}{\left[\mathbf{p} + \frac{a}{\mathbf{J}^2 + Ub\mathbf{J} + Wb^2} \right]} \tag{A-12}$$

$$\lim_{\mathbf{p} \rightarrow \infty} \left(\frac{(\mathbf{J}_i^m - b_i^m)^{1/m}}{(\mathbf{J}_M^m - b_M^m)^{1/m}} \right) = \left(\frac{b_m}{b_i} \right)^{1/m-l} \tag{A-13}$$

Therefore, the access Helmholtz free energy at infinite spreading pressure is:

$$A^E(T, \mathbf{p}, x) = -\frac{a_M}{b_M} + \sum_i \frac{x_i a_i}{b_i} + \left(\frac{l}{m} - l \right) RT \sum_i x_i \ln \frac{b_M}{b_i} \tag{A-14}$$

For 2-D, $b = \mathbf{b}A$, $a = \mathbf{a}A$. For simplification, let $b = b_m$ and $a = a_m$

$$\frac{A_\infty^{ex}}{RT} = -\frac{\mathbf{a}}{\mathbf{b}RT} + \sum_i x_i \frac{\mathbf{a}_i}{\mathbf{b}_i RT} + \left(\frac{l}{m} - l \right) \sum_i x_i \ln \frac{\mathbf{b}}{\mathbf{b}_i} \tag{A-15}$$

if $U \neq 0$ and/or $W \neq 0$

$$\frac{A_{\infty}^{ex}}{RT} = -\frac{\mathbf{a}}{F\mathbf{b}_{RT}} + \sum_i x_i \frac{\mathbf{a}_i}{F\mathbf{b}_i RT} + \left(\frac{l}{m} - l\right) \sum_i x_i \ln \frac{\mathbf{b}}{\mathbf{b}_i} \quad (\text{A-16})$$

$$F = \sqrt{U^2 - 4W} \Bigg/ \ln \left(\frac{l + \left(U - \sqrt{U^2 - 4W}\right)/2}{l + \left(U + \sqrt{U^2 - 4W}\right)/2} \right) \quad (\text{A-17})$$

Iteration Function Method for Mixture Adsorption Calculations
Using Two-Dimensional Equations of State

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Abstract

Adsorption equilibrium models are essential in optimizing coalbed methane production and CO₂ sequestration processes. Although several frameworks are available for describing the adsorption phenomenon, two-dimensional (2-D) equations of state (EOSs), in particular, offer distinct advantages in modeling supercritical, high-pressure adsorption systems.

Our previous studies involving high-pressure mixture adsorption have indicated the inadequacy of the simultaneous solution calculation scheme, which requires knowledge the experimental gas-phase compositions. An iteration function method (IFM) for mixture adsorption equilibrium calculations has been developed for 2-D EOS, and the robustness of the proposed method is evaluated.

Analysis of results involving many supercritical adsorption systems indicate that the new IFM algorithm is effective in performing equilibrium mixture adsorption calculations based on feed compositions. Further, use of a formulation equivalent to the Rice-Racford VLE iteration function, where the molar adsorption ratio is the iteration variable, leads to frequent adsorption calculation failures. Excellent convergence characteristics are obtained using the new IFM, which employs the amount adsorbed as the iteration variable.

Keywords: Adsorption, Two-Dimensional Equation of State, Iteration Function Method

Introduction

Adsorption phenomena play a major role in coalbed methane (CBM) production and in CO₂ sequestration; therefore, reliable adsorption equilibrium models are essential for the optimum implementation of these processes.

Although several frameworks are used to describe the adsorption phenomenon and to correlate pure and mixture adsorption isotherms, two-dimensional (2-D) equations of state (EOSs) offer distinct advantages in modeling supercritical, high-pressure adsorption systems. First, 2-D EOSs permit simultaneous calculation of equilibrium adsorption and volumetric properties. Second, they are amenable to model parameter generalization. Third, they are particularly suitable to extend pure adsorption data to multicomponent mixture predictions using appropriate mixing rules [Zhou et al., 1994; Sudibandriyo et al., 2003]. Fourth, they offer a proven model format for use in reservoir simulations.

Mixture adsorption calculations are essential in CBM recovery operations and CO₂ sequestration processes. In addition to accurate adsorption models, implementations of these processes require robust computational algorithms. For multiphase calculations, three methods may be used [see, e.g., Sofyan et al. 2003]:

1. Simultaneous solution of mass and equilibrium relations
2. Iteration function method (IFM)
3. Gibbs energy minimization (GEM) method

In our previous studies involving adsorption mixtures, the simultaneous solution method was used to perform such calculations based on experimental gas-phase compositions, y_i [Zhou, 1994]. However, in many mixture adsorption calculations, the

bulk phase compositions are not available. Moreover, the use of experimental gas-phase compositions leads to some inconsistency in the equilibrium calculations attributed to errors in the experimental gas compositions.

The most commonly used algorithm for a known phase distribution is the equal-chemical potential or equal-fugacity iteration function method, where feed gas compositions, z_i , are used to perform the calculations. In this study, an iteration function method (IFM) for mixture adsorption equilibrium calculations is developed for 2D EOS, and its robustness is evaluated for CBM-type systems.

IFM for Mixture Adsorption Calculations

In principle, the Rice-Rachford iteration function, or a similar function, can be used to perform two-phase equilibrium calculations. However, when dealing with adsorption systems, an additional degree of freedom is imposed by the presence of an adsorption matrix. For example, Smith et al. (1975) provided a phase rule for gas adsorption equilibrium to account for the spreading pressure:

$$F = N - \mathbf{p} + 3 = N - 2 + 3 = N + 1 \quad (8)$$

where F is the degrees of freedom, N is the number of components, and π is the number of the phases. The phase number π for a gas adsorption system is two. However, a more generalized point of view regards the adsorbed phase as an interface [Ross et al., 1964], where:

$$F = N - \mathbf{p} + 2 + i \quad (9)$$

and i is the number of interfaces. Thus, for a pure-gas adsorption on one adsorbent, there are two degrees of freedom. Which means, two variables, for example, T and P must be

fixed independently to establish an equilibrium state. Similarly, for a binary gas adsorption system, the degrees of freedom are three, and so on.

The total and component mass balances for a two-phase, gas-adsorption system are as follows:

$$N = N_g + N_a \quad (10)$$

$$Nz_i = N_g y_i + N_a x_i \quad (11)$$

where N is the total number of moles in the system, N_a and N_g are the number of moles of the adsorbed phase and gas phase, respectively. z_i , y_i , and x_i are the mole fractions of the feed, gas phase, and adsorbed phase, respectively.

The equilibrium requirements for a closed system at given temperature and pressure may be expressed as [Zhou et al., 1994]:

$$Z_a \hat{f}_i^a w x_i = k_i \hat{f}_i^g P y_i \quad (12)$$

where, Z_a is the compressibility factor for the adsorbed phase. $\hat{f}_i^a$ and $\hat{f}_i^g$ are the fugacity coefficient for the adsorbed phase and the gas phase, respectively. k_i is Henry's constant, and w is the total amount adsorbed per mass of adsorbent.

By definition the equilibrium constant (k -value) is:

$$K_i = \frac{y_i}{x_i} = \frac{Z_a \hat{f}_i^a w}{k_i \hat{f}_i^g P} \quad (13)$$

Now, we use Equations (10), (11), and (13) to solve for x_i and y_i :

$$x_i = \frac{z_i}{\frac{N_a}{N} + \left(1 - \frac{N_a}{N}\right) K_i} \quad \text{and} \quad y_i = \frac{K_i z_i}{\frac{N_a}{N} + \left(1 - \frac{N_a}{N}\right) K_i} \quad (14)$$

Similar to vapor-liquid equilibrium, if we define the iteration function as:

$$F\left(\frac{N_a}{N}\right) \equiv \sum_i (x_i - y_i) = 0$$

Similar to vapor-liquid equilibrium, we obtain the equivalent to the VLE Rice-Rachford iteration function [see, e.g., Sofyan et al., 2003]:

$$F = \sum_i x_i - y_i = \sum_i \frac{(1 - K_i)z_i}{\frac{N_a}{N} + \left(1 - \frac{N_a}{N}\right)K_i} \equiv 0 \quad (15)$$

For the adsorbed phase, the number of moles adsorbed, N_a , is calculated as:

$$N_a = \mathbf{w}M_a \quad (16)$$

where $\mathbf{w}$ is the total amount adsorbed per mass of the adsorbent, and M_a is the mass of adsorbent. The number of moles in the gas phase, N_g , is:

$$N_g = \mathbf{r}_g V_g \quad (17)$$

where $\mathbf{r}_g$ and V_g are the density and total volume of the gas phase, respectively. In adsorption systems, the total volume available for the gas phase is affected by the amount adsorbed [Sudibandriyo et al., 2003]; specifically,

$$V_g = V_{void} - \mathbf{w}M_a / \mathbf{r}_a \quad (18)$$

where V_{void} is the total volume available for the gas phase when there is no adsorption, and $\mathbf{r}_a$ is the adsorbed-phase density.

Expressing the adsorbed-phase molar ratio in terms of the amount adsorbed, densities and volumes, we get:

$$\frac{N_a}{N} = \frac{N_a}{N_a + N_g} = \frac{\mathbf{w}M_a}{\mathbf{w}M_a + \mathbf{r}_g V_g} = \frac{\mathbf{w}M_a}{\mathbf{w}M_a + \mathbf{r}_g (V_{void} - \mathbf{w}M_a / \mathbf{r}_a)} \quad (19)$$

Now, if we define the void volume per mass of adsorbent as:

$$v_{void} = \frac{V_{void}}{M_a} \quad (20)$$

Equation (19) can be rewritten as:

$$\frac{N_a}{N} = \frac{\mathbf{w}}{\mathbf{w} + \mathbf{r}_g (v_{void} - \mathbf{w}/\mathbf{r}_a)} \quad (21)$$

and, the working iteration function becomes:

$$F \left\{ \frac{\mathbf{w}}{\mathbf{w} + \mathbf{r}_g (v_{void} - \mathbf{w}/\mathbf{r}_a)} \right\} \equiv \sum_i \frac{(1 - K_i) z_i}{\mathbf{w} + \mathbf{r}_g (v_{void} - \mathbf{w}/\mathbf{r}_a) + (1 - \mathbf{w} + \mathbf{r}_g (v_{void} - \mathbf{w}/\mathbf{r}_a)) K_i} = 0 \quad (22)$$

This means having the feed composition at a given temperature and pressure, we can solve iteratively for the adsorbed-phase molar ratio, provided we have an adequate adsorption model for calculating the K-values.

The IFM iterative scheme for an adsorption equilibrium calculation is as follows:

1. Set initial estimates for x_i , y_i and the total adsorbed amount ω
2. Calculate the component fugacity coefficients of the adsorbed phase and the vapor phase
3. Use a numerical method to solve for N_a/N from Equation 15
4. Calculate x_i , y_i and the total adsorbed amount ω
5. Calculate K_i for each component
6. If $\left| K_i^k - K_i^{k+1} \right| > \epsilon$, where $\epsilon = 0.00001$, go back to Step 2; otherwise print results

Algorithm Robustness Analyses

The Newton-Raphson approach is used to solve for the molar adsorption ratio, N_a/N , in Equation (15) using the iteration expression:

$$\left(\frac{N_a}{N}\right)_{i+1} = \left(\frac{N_a}{N}\right)_i - \frac{F}{F'} \quad (23)$$

$$F' = -\sum_i \frac{(1 - K_i)^2 z_i}{\left[\frac{N_a}{N} + \left(1 - \frac{N_a}{N}\right)K_i\right]^2} \quad (24)$$

However, implementation of the IFM iterative scheme outlined above using the Newton-Raphson method produced poor convergence characteristics; i.e., frequent convergence failures. Our analysis indicates that the iterative values generated by the algorithm for the total amount adsorbed, ω , are the main cause for calculation failure. In the adsorption IFM scheme, unlike the VLE IFM, an estimate for the total amount adsorbed is required to initiate the calculations. Unfortunately, an error in the ω estimate is magnified in each iteration loop resulting in divergence and, thus, calculation failure. Accordingly, a new robust algorithm was developed as outlined below.

Following extensive analysis of several iterative schemes, we propose the following new iteration function for multicomponent adsorption equilibrium calculations:

$$F(\mathbf{w}) = \sum_i \frac{\left(1 - \frac{Z_a \hat{\mathbf{f}}_i^a \mathbf{w}}{k_i \hat{\mathbf{f}}_i^g P}\right) z_i}{\frac{\mathbf{w}}{\mathbf{w} + \mathbf{r}_g (v_{void} - \mathbf{w}/\mathbf{r}_a)} + \left(1 - \frac{\mathbf{w}}{\mathbf{w} + \mathbf{r}_g (v_{void} - \mathbf{w}/\mathbf{r}_a)}\right) \frac{Z_a \hat{\mathbf{f}}_i^a \mathbf{w}}{k_i \hat{\mathbf{f}}_i^g P}} \equiv 0 \quad (25)$$

In this scheme, we solve for ω instead of the N_b/N ratio. Thus, ω is the iteration variable, which we found to have excellent convergence characteristics.

Figure 1 shows a typical variation of the iteration function $F(\omega)$ with the amount adsorbed ω . As indicated, $F(\omega)$ is a monotonic function. Although the Newton-Raphson method could be used, we elected instead to use the secant method to avoid deriving the

iteration function derivative, $F'(\omega)$. As such, the iteration step for solving Equation (25) is:

$$\mathbf{w}_{i+1} = \mathbf{w}_i - \frac{F(\mathbf{w}_i)(\mathbf{w}_i - \mathbf{w}_{i-1})}{F(\mathbf{w}_i) - F(\mathbf{w}_{i-1})} \quad (26)$$

The algorithm for implementing the new IFM iterative scheme for adsorption equilibrium calculation is as follows:

1. Set the initial values of x_i , y_i and the total adsorbed amount ω ; initial values of x_i and y_i are set equal to z_i , and that of ω as $\sum_{j=1}^{NC} z_j w_j$, where NC is the number of the components, and ω_j is the pure-gas adsorption for component j .
2. Calculate the component fugacity coefficients of the adsorbed phase and the vapor phase
3. Use a numerical method to solve for ω from Equation 25
4. Calculate N_a/N
5. Calculate x_i , y_i and the total adsorbed amount ω
6. Calculate K_i for each component
7. If $|K_i^k - K_i^{k+1}| > \epsilon$, go back to Step 2; otherwise print results

Case Studies

2-D PR EOS with one-fluid mixing rules [see Section K-III on page 172] was used to demonstrate the effectiveness of the new IFM algorithm for adsorption. Several case studies were conducted involving EOS predictions ($C_{ij}=D_{ij}=0$) and model parameter regressions (regressed C_{ij} and D_{ij}). Following our previous study [see Section K-III on

page 172], the following mixture adsorption data were selected to assess the robustness of the new IFM for CBM-type systems:

1. OSU data for mixtures of methane, nitrogen, and CO₂ on activated carbon at 318.2 K
2. OSU data for mixtures of methane, nitrogen, and CO₂ on wet Tiffany coal at 328.2 K
3. OSU data for mixtures of methane, nitrogen, and CO₂ on wet Fruitland coal at 319.3 K
4. OSU data for mixtures of methane, nitrogen, and CO₂ on Wet Illinois #6 Coal 319.3 K

The objective function S was used to correlate data. The function minimizes the sum of the squared-percentage deviations in predicted adsorption:

$$S = 100 \sqrt{\sum_{j=1}^{NC} \sum_{i=1}^{NPTS} \left[\frac{\mathbf{w}_j^e(i) - \mathbf{w}_j^c(i)}{\mathbf{w}_j^e(i)} \right]^2} \quad (27)$$

Where $\mathbf{w}_j^e$ and $\mathbf{w}_j^c$ are the experimental and calculated adsorption amounts for component j , respectively. NC is the number of gas components in the mixture. NPTS is the number of data points for each component. In addition, the percentage average absolute deviation (%AAD ω_j) and root-mean-square error (RMSE ω_j) are presented to assist in evaluating the results:

$$\%AAD \ \mathbf{w}_j = \frac{100}{NPTS} \sum_{i=1}^{NPTS} \left| \frac{\mathbf{w}_j^e(i) - \mathbf{w}_j^c(i)}{\mathbf{w}_j^e(i)} \right| \quad (28)$$

$$RMSE \ \mathbf{w}_j = \sqrt{\frac{\sum_{i=1}^{NPTS} (\mathbf{w}_j^e(i) - \mathbf{w}_j^c(i))^2}{NPTS}} \quad (29)$$

The weighted average-absolute deviation (WAAD ω_j) is also used to evaluate results when the expected experimental uncertainties, $\mathbf{s}_j^e$, are available:

$$WAAD \mathbf{w}_j = \frac{1}{NPTS} \sum_{i=1}^{NPTS} \left| \frac{\mathbf{w}_j^e(i) - \mathbf{w}_j^c(i)}{\mathbf{s}_j^e(i)} \right| \quad (30)$$

Results

Tables 1 to 8 present the results for each system using the IFM algorithm. For all the systems considered totaling 404 data points, the equilibrium adsorption calculations have been successful.

Typically, fewer than ten iterations are required to solve $F(\omega)$ for ω using the secant method; two iterations for adsorption at pressures less than 1.0 MPa and about twenty iterations at pressures greater than 12.0 MPa.

Table 9 presents the overall comparison of the two calculation schemes: the simultaneous solution method using the gas phase compositions, and the IFM method using the feed compositions. Overall, the IFM algorithm produces slightly better results than the simultaneous solution method because it avoids errors introduced by imprecise gas-phase compositions. Figure 2 shows the comparison of the experimental and the calculated gas-phase composition for the $\text{CH}_4 + \text{CO}_2$ mixture adsorption on activated carbon at 318.2 K. Excellent agreement is observed for all feed compositions.

Figure 3 provides an IFM algorithm sample calculation involving the 80% $\text{N}_2 + 20\% \text{CO}_2$ mixture adsorption on activated carbon at 318.2 K. The results indicate that the IFM calculations provide smooth predictions (the solid line) in comparison to comparable results from the simultaneous solution method using experimental vapor compositions (the dash line).

Conclusions

In summary, analysis of results involving many CBM adsorption systems indicate that the new IFM algorithm for the 2-D EOS is effective in performing equilibrium mixture adsorption calculations based on feed compositions. Further, use of an equivalent formulation to the Rice-Rachford VLE iteration function, where the molar adsorption ratio is the iteration variable, leads to frequent adsorption calculation failures. Excellent convergence characteristics are obtained using the new IFM.

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Table 1. The 2-D PR EOS Predictions of Binary Mixtures Adsorption on Dry Activated Carbon at 318.2 K Using the IFM Algorithm

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
CH₄-N₂				
Methane	40	3.9	0.137	1.6
Nitrogen	40	2.9	0.052	0.8
Total	40	3.1	0.139	1.3
CH₄-CO₂				
Methane	40	2.5	0.064	0.5
CO ₂	40	3.3	0.104	0.8
Total	40	1.0	0.076	0.3
N₂-CO₂				
Nitrogen	40	5.2	0.064	1.0
CO ₂	40	2.8	0.104	0.8
Total	40	3.1	0.151	1.0

Table 2. The 2-D PR EOS Representations of Binary Mixtures Adsorption on Activated Carbon at 318.2 K Using the IFM Algorithm

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂	D ₁₂
CH₄-N₂					-0.0801	-0.0425
Methane	40	3.8	0.132	1.5		
Nitrogen	40	3.6	0.047	0.9		
Total	40	2.6	0.117	1.1		
CH₄-CO₂					-0.0856	0.0192
Methane	40	2.6	0.074	0.6		
CO ₂	40	2.3	0.077	0.6		
Total	40	0.6	0.052	0.2		
N₂-CO₂					-0.1213	0.0243
Nitrogen	40	4.1	0.043	0.6		
CO ₂	40	2.5	0.106	0.7		
Total	40	2.1	0.106	0.7		

Table 3. The 2-D PR EOS Predictions of Binary Mixtures Adsorption on Wet Tiffany Coal at 327.6 K Using the IFM Algorithm

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
CH₄-N₂				
Methane	11	13.2	0.029	1.6
Nitrogen	11	4.8	0.005	0.4
Total	11	11.3	0.033	1.6
CH₄-CO₂				
Methane	11	27.2	0.041	3.6
CO ₂	11	9.0	0.047	2.0
Total	11	2.6	0.012	0.8
N₂-CO₂				
Nitrogen	11	54.4	0.019	1.9
CO ₂	11	7.6	0.051	1.4
Total	11	5.2	0.034	1.1

Table 4. The 2-D PR EOS Representations of Binary Mixtures Adsorption Wet Tiffany Coal at 327.6 K Using the IFM Algorithm

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂	D ₁₂
CH₄-N₂					0.1205	-0.3286
Methane	11	11.8	0.025	1.4		
Nitrogen	11	7.5	0.005	0.4		
Total	11	8.2	0.021	1.1		
CH₄-CO₂					0.5129	-0.1328
Methane	11	15.0	0.023	2.7		
CO ₂	11	9.7	0.050	2.2		
Total	11	4.6	0.028	1.1		
N₂-CO₂					0.2398	-0.4310
Nitrogen	11	23.5	0.008	0.8		
CO ₂	11	7.4	0.050	1.3		
Total	11	6.1	0.043	1.2		

Table 5. The 2-D PR EOS Predictions of Binary Mixtures Adsorption on Wet Fruitland Coal at 319.3 K Using the IFM Algorithm

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
CH₄-N₂				
Methane	41	3.2	0.009	0.3
Nitrogen	41	25.9	0.033	1.9
Total	41	7.8	0.040	1.0
CH₄-CO₂				
Methane	40	7.6	0.019	0.7
CO ₂	40	5.5	0.042	0.8
Total	40	4.3	0.049	0.8
N₂-CO₂				
Nitrogen	50	30.2	0.038	1.1
CO ₂	50	2.3	0.033	0.3
Total	50	4.7	0.051	0.6

Table 6. The 2-D PR EOS Representations of Binary Mixtures Adsorption Wet Fruitland Coal at 319.3 K Using the IFM Algorithm

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂	D ₁₂
CH₄-N₂					0.7344	-0.0202
Methane	41	3.4	0.013	0.3		
Nitrogen	41	6.6	0.007	0.4		
Total	41	3.0	0.015	0.4		
CH₄-CO₂					-0.1154	0.2582
Methane	40	3.8	0.014	0.4		
CO ₂	40	4.0	0.038	0.6		
Total	40	2.4	0.040	0.4		
N₂-CO₂					0.0361	-0.0968
Nitrogen	50	14.4	0.013	0.4		
CO ₂	50	3.0	0.037	0.4		
Total	50	2.0	0.038	0.3		

Table 7. The 2-D PR EOS Predictions of Binary Mixtures Adsorption on Wet Illinois #6 Coal at 319.3 K Using the IFM Algorithm

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
CH₄-N₂				
Methane	40	13.4	0.017	0.4
Nitrogen	40	14.9	0.005	0.3
Total	40	7.1	0.016	0.3
CH₄-CO₂				
Methane	40	13.0	0.017	0.5
CO ₂	40	9.5	0.054	0.7
Total	40	6.4	0.053	0.6
N₂-CO₂				
Nitrogen	40	49.4	0.024	0.7
CO ₂	40	5.1	0.025	0.4
Total	40	2.7	0.019	0.3

Table 8. The 2-D PR EOS Representations of Binary Mixtures Adsorption Wet Illinois #6 Coal at 319.3 K Using the IFM Algorithm

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C ₁₂	D ₁₂
CH₄-N₂					0.2223	0.1834
Methane	40	13.7	0.017	0.4		
Nitrogen	40	15.3	0.005	0.3		
Total	40	7.0	0.014	0.2		
CH₄-CO₂					-0.1598	0.0979
Methane	40	11.7	0.017	0.4		
CO ₂	40	9.2	0.053	0.7		
Total	40	4.8	0.043	0.4		
N₂-CO₂					-0.5296	0.4556
Nitrogen	40	50.3	0.033	0.9		
CO ₂	40	4.9	0.024	0.4		
Total	40	2.3	0.021	0.3		

Table 9. Comparison of Mixture Adsorption Using Simultaneous Solution Method and IFM Algorithm

	L. A. C. *			H. A. C. *			Total		
	%AAD	RMSE	WAAD	%AAD	RMSE	WAAD	%AAD	RMSE	WAAD
Predictions									
NONE IFM	20.1	0.051	1.0	8.1	0.097	1.1	4.7	0.081	0.7
IFM	18.2	0.039	0.9	5.7	0.070	0.7	4.6	0.077	0.7
Regressions									
NONE IFM	12.8	0.041	0.6	7.4	0.090	1.0	3.8	0.079	0.6
IFM	12.8	0.034	0.6	5.5	0.065	0.7	3.2	0.059	0.5

* L. A. C. means lower-adsorption component (404 data points)

* H. A. C. means higher-adsorption component (404 data points)

Figure 1. A Sample Plot for the Functional Behavior of Function $F(w)$

**Figure 2. Comparison of the Experimental and Calculated Gas Phase Composition:
CH₄+CO₂ Adsorption on Activated Carbon at 318.2 K (OSU)**

**Figure 3. Comparison of the IFM and Simultaneous Solution Method:
80%N₂+20%CO₂ Adsorption on Activated Carbon at 318.2 K (OSU)**

**Simplified Local Density Model for High-Pressure
Pure-Gas Adsorption using the Peng-Robinson
Equation of State**

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Abstract

As part of our efforts to model enhanced coalbed methane recovery (CBM) and CO₂ sequestration in coalbeds, we have modified the simplified local density / Peng-Robinson model (SLD-PR) to improve its correlative capability when dealing with the adsorption of near-critical and supercritical gases of the type encountered in CBM recovery and CO₂ sequestration. Our goal of is to facilitate the use of efficient equation-of-state (EOS) computational frameworks for representing adsorption behavior, as well as improving our understanding of the phenomenon.

The ability of the modified SLD-PR to correlate accurately supercritical adsorption systems is demonstrated using several adsorption measurements from literature data as well as measurements we have made on several coals. The results indicate that our modified SLD-PR model, which incorporates an improved repulsive parameter 'b' for the PR EOS, is capable of modeling the adsorption of methane, nitrogen, and CO₂ at coalbed conditions. Using the modified SLD-PR, systems from the literature have been correlated with average absolute errors within 9% and coal systems have been correlated on average within their expected experimental uncertainties.

Our results also indicate that proper accounting of pore structure within the SLD-EOS framework is effective in improving our modeling capability for high-pressure adsorption. Further, the model (a) generates estimates for the adsorbed-phase densities, which facilitate reliable prediction of absolute gas adsorption, and (b) describes the maximum observed in Gibbs-adsorption isotherms of CO₂ at temperatures and pressures encountered in coalbeds.

Introduction

Knowledge of the adsorption behavior of coalbed gases is critical for optimum development of production processes to recover coalbed methane and to sequester carbon dioxide in coalbeds. Specifically, knowledge of methane, nitrogen, and CO₂ adsorption measurements on in-situ coal samples is necessary for conducting coalbed methane (CBM) production simulations. As part of a reservoir simulator, equilibrium modeling of physical adsorption helps determine coal-seam storage capacity, economic feasibility, and operating conditions [1].

Beyond primary and CO₂/nitrogen enhanced CBM production, coalbeds are also potentially attractive sites for sequestering CO₂ to remove it from the atmosphere. Sequestration is receiving widespread international attention, since the potential adverse environmental effects of the enormous releases of CO₂ are becoming more clearly understood. Coalbed sequestration of CO₂ could be a viable alternative to other techniques receiving current attention, such as CO₂ injection into abandoned oil and gas reservoirs, deep, confined aquifers, or into the deep ocean [2,3]. Simulations of field operations for primary and enhanced CBM production, as well as CO₂ sequestration in coalbeds require mathematical models for adsorption behavior. Ideally, such models should combine accuracy and simplicity. Thus, we have pursued a variety of model frameworks to improve the representation of adsorption behavior for pure substances and mixtures. These include (see, e. g., [4,5,6]) (a) enhanced forms of the Langmuir-type isotherms, (b) two-dimensional equations of state, (c) simplified local density models (SLD), (d) introduction of two-dimensional analogs of the activity coefficients used in

vapor-liquid equilibrium calculations, and (e) treating adsorption as a constrained form of vapor-liquid equilibrium (VLE).

In this work, we discuss the efficacy of the SLD model in modeling pure-gas adsorption in coalbeds.

The Efficacy of Sorption Models

The efficacy of sorption models is judged by two main criteria. First, the model should be able to correlate well the sorption data of interest. Second, the model should have the desired predictive capability. Specifically, the model should correlate within the experimental uncertainties:

1. The sorption of pure fluids, multicomponent mixtures, and individual components in a mixture on the adsorbents of interest
2. The sorption behavior over the ranges of temperature and pressure of interest

If the model is successful in correlating adsorption data within the desired level of uncertainty, then the model can be developed for its corresponding predictive ability. Ultimately, a generalized model should be able to predict with the desired accuracy the sorption behavior of a pure component or a multicomponent mixture from the physical-chemical characteristics of the adsorbates and the adsorbent involved. However, limitations stemming from the models and/or matrix characterization dictate, at times, the need for a matrix-calibrated model. In this case, the model is expected, for a specified adsorbent, to provide accurate predictions for:

1. High-pressure sorption from low-pressure sorption data
2. Sorption at one temperature from data at another temperature
3. Sorption behavior of one gas from other data on another gas

4. The multicomponent sorption behavior of mixed gases from their corresponding pure sorption behaviors

Although the above capabilities do not provide *a priori* predictions, they would, when fully realized, minimize the amount of data required for ECBM operations involving designated coal seams. Presently, some of these capabilities are developed and others require further refinement.

For all the correlation/predictive capabilities, the sorption model requires physical or phenomenological parameters. Typically, these parameters describe either the adsorbing fluid or the adsorbent. For example, the surface area is a characteristic parameter of the adsorbent and the gas density is a characteristic of the fluid. Models that demarcate these parameters as fluid-dependent or adsorbent-dependent generally are better suited for model parameter generalization. Moreover, existing knowledge on fluid-fluid interactions from volumetric (PVT) and vapor-liquid equilibrium (VLE) experiments and modeling can be used, thus utilizing the adsorption data solely to account for fluid-solid interaction.

The characterization of coal and other adsorbents is done frequently by regressing model parameters, such as surface area, from experimental data. More elaborate models can characterize adsorbents through statistical distributions of surface energy and pore structure [7]. Sometimes, the regressed adsorbent parameters are fluid dependent; e.g., the surface area or pore distribution of the adsorbent regressed from data on carbon dioxide is different than that regressed from nitrogen. Ideally, the same adsorbent parameters apply to each gas component, and from that, adsorption could be predicted for a variety of fluids. Realistically, each gas isotherm provides additional information about

the adsorbent properties not obtained from other gas isotherms. For our studies on coalbed methane, our present goal is an adsorption model that correlates simultaneously the adsorption behavior of carbon dioxide, methane, and nitrogen (and their mixtures) on coals with the same physical parameters for the coal.

The desired sorption model for coalbed reservoirs should:

1. Correlate pure component and mixed-gas adsorption data to within the experimental uncertainty for pressures to 1800 psia over the operating temperature range
2. Predict binary adsorption data to within the experimental uncertainty for pressures to 1800 psia over the operating temperature range
3. Possess physically meaningful parameters that can be correlated with commonly-known coal properties such as chemical composition, helium density, and vitrinite reflectance
4. Describe the dependence of the gas adsorption behavior on liquid water adsorbed/absorbed in the coalbed

The coalbed methane (CBM) industry would benefit from accurate models that lack the complexity of statistical mechanics models and the oversimplifications of rudimentary models. The computation time required to run a model is important, as CBM simulators require several function calls for each time step. CBM modelers do consider the complexity of the adsorption model, as this is a nested function within the overall simulation. To model the adsorption, CBM modelers have used variants of the well-known Langmuir isotherm. Models of this type, however, have low correlative and predictive capabilities.

The Simplified Local Density Model

Rangarajan [8] originally developed the physical premises and assumptions of SLD. Namely, (1) the chemical potential at any point next to adsorbent surface is equal to the bulk phase chemical potential, and (2) the chemical potential at any point above the surface is the sum of the fluid-fluid interaction and fluid-solid interaction potentials. An equation of state, such as the van der Waals or Peng–Robinson, provides the fluid-fluid potential information. An integrated 10-4 Lennard-Jones potential function models the fluid-solid interactions.

The SLD model is a “simplification” of local density theory. In local density theory, the local density profile is calculated by minimizing the total energy functional which is dependent on all point densities and their spatial derivatives [9]. This can be a time-intensive procedure for pure fluids; for mixture adsorption in pore distributions, the computational expense is prohibitive for engineering calculations.

The “simplification” of the SLD model assumes a mean field chemical potential; i.e. no local fluctuations. Further, the chemical potential of the fluid for each point in space is estimated from mean field theory, which is corrected for the proximity of the fluid molecule to the molecular wall of the adsorbent. The SLD model is formulated in terms of the Gibbs excess adsorption (n_{Gibbs}), defined as the excess number of moles per unit mass of adsorbent, or:

$$n_{\text{Gibbs}} = A/2 \int_{\text{Left Side of Slit}}^{\text{Right Side of Slit}} (\rho(z) - \rho_b) dz \quad (1)$$

Following Chen and Wong [10], we assume that the adsorbate molecule resides between a two-surface slit coal structure. For the slit geometry considered here and as

shown in Figure 1, we previously used [11] the lower limit of integration (the left side of slit) to be $\sigma_{ff}/2$, the center of the adsorbed molecule on the plane surface, and the upper limit of integration to be $L-\sigma_{ff}/2$, the slit width adjusted by half of the fluid diameter σ_{ff} . For this study, the lower limit of integration is set to $3/8\sigma_{ff}$ to include the density profile close to the surface wall. Additionally, we assume that for distances less than $1/8\sigma_{ff}$ away from a surface wall, the local density is effectively zero. As illustrated in Figure 1, the position within a slit is z , where z is orthogonal to the plane of the solid phase, defined as a flat surface formed by the peripheral carbon (coal) atoms. A molecule within a slit has fluid-solid interactions with both slit surfaces.

Following Chen and Wong [10], Lee's partially integrated 10-4 Lennard-Jones potential is used to describe the fluid-solid interactions. The fluid-solid potential, represented by $\Psi(z)$, is defined on a molecular basis by

$$\mu_{fs}(z) = N_A \cdot \Psi(z) \quad (2)$$

$$\Psi(z) = 4\pi\rho_{atoms}\epsilon_{fs}\sigma_{fs}^2 \left(\frac{\sigma_{fs}^{10}}{5(z')^{10}} - \frac{1}{2} \sum_{i=1}^4 \frac{\sigma_{fs}^4}{(z' + (i-1) \cdot \sigma_{ss})^4} \right) \quad (3)$$

where ϵ_{fs} is the fluid-solid interaction energy parameter and $\rho_{atoms} = 0.382 \text{ atoms/\AA}^2$.

The molecular diameter of the adsorbate and the carbon interplanar distances are σ_{ff} and σ_{ss} , respectively. The carbon interplanar distance was adopted [11] to be 0.335 nm. For convenience, the fluid-solid diameter σ_{fs} and the dummy coordinate z' are defined as $\sigma_{fs} = (\sigma_{ff} + \sigma_{ss})/2$ and $z' = z + \sigma_{ss}/2$.

The local density is determined by relating the fluid-fluid chemical potential to the fugacity f in the PR EOS, as:

$$\ln\left(\frac{f_{ff}[a(z), \mathbf{r}(z)]}{f}\right) = -\left(\frac{\Psi(z) + \Psi(L-z)}{k_B T}\right) \quad (4)$$

where k_B is Boltzmann's constant.

In studies thus far, we have used the PR EOS to determine the bulk density, the bulk fugacity and fluid fugacities. The PR EOS may be written as follows:

$$\frac{P}{\rho RT} = \frac{1}{(1-\rho b)} - \frac{a(T)\rho}{RT(1+(1-\sqrt{2})\rho b)(1+(1+\sqrt{2})\rho b)} \quad (5)$$

The bulk fugacity and the fluid fugacity for the PR EOS are:

$$\ln \frac{f}{P} = \frac{b\rho}{1-b\rho} - \frac{a(T)\rho}{RT(1+2b\rho-b^2\rho^2)} - \ln\left[\frac{P}{RT\rho} - \frac{Pb}{RT}\right] - \frac{a(T)}{2\sqrt{2}bRT} \ln\left[\frac{1+(1+\sqrt{2})\rho b}{1+(1-\sqrt{2})\rho b}\right] \quad (6)$$

$$\begin{aligned} \ln \frac{f_{ff}(z)}{P} &= \frac{b\rho(z)}{1-b\rho(z)} - \frac{a_{ads}(z)\rho(z)}{RT(1+2b\rho(z)-b^2\rho^2(z))} \\ &\quad - \ln\left[\frac{P}{RT\rho(z)} - \frac{Pb}{RT}\right] - \frac{a_{ads}(z)}{2\sqrt{2}bRT} \ln\left[\frac{1+(1+\sqrt{2})\rho(z)b}{1+(1-\sqrt{2})\rho(z)b}\right] \end{aligned} \quad (7)$$

The formulas for $a(z)$ depend on the ratio of the slit width, L , to the molecular diameter, σ_{ff} . Rangarajan [8] obtained these formulas by integrating the sum of all two-body interactions between an arbitrarily selected central molecule and all the other molecules around it. We used the results of Chen and Wong [10] for the equations describing 'a' as a function of position within a slit.

Examination of the results from the original SLD model revealed that the calculated adsorbed-phase densities from the EOS in the SLD model are too high for CO_2 and ethane. The PR covolume has a significant effect on the calculated local density of

the adsorbed fluid, especially near the surface. In Equation 7 the logarithmic repulsive term dominates the local fluid fugacity expression, especially near the surface. To illustrate this, when Equations 4, 5, and 7 are combined; the local density can be expressed as:

$$\frac{1}{\rho(z)} = b + \frac{RT}{P} \exp \left[-\frac{f_b}{P} \exp \left(\frac{-\Psi(z) - \Psi(L-z)}{kT} \right) - \lambda \right] \quad (8)$$

$$\text{where } \lambda = \frac{b\rho(z)}{1 - b\rho(z)} - \frac{a_{\text{ads}}(z)\rho(z)}{RT(1 + 2\rho(z)b - b^2\rho^2(z))} - \frac{a_{\text{ads}}(z)}{2\sqrt{2}bRT} \ln \left(\frac{1 + (1 + \sqrt{2})\rho(z)b}{1 + (1 - \sqrt{2})\rho(z)b} \right)$$

Near the surface, where the fluid-solid potential is large in magnitude, the exponential term containing the fluid-solid potential vanishes, and at moderate pressures the local density can be approximated by:

$$\frac{1}{\rho(z)} \approx b + \frac{RT}{P} \exp[-\lambda] \quad \text{Near the wall} \quad (9)$$

At higher pressures, the second term becomes small and the adsorbed density at the wall approaches the reciprocal covolume.

$$\rho(\text{wall}) \rightarrow \frac{1}{b} \quad \text{Near the wall at high pressures} \quad (10)$$

A simple empirical modification was used to account for the repulsive interactions of the high-density adsorbed fluid. Our objective was to obtain initial information regarding the impact of changes in ‘b’ on the calculated adsorption, especially for supercritical CO₂ at high pressures.

Thus, the PR covolume was empirically adjusted by the parameter Λ_b ; i.e., $b_{\text{ads}} = b \cdot \Lambda_b$. With this modification, the SLD model representations for CO₂ and

ethane on dry activated carbon were improved dramatically. Figure 2 shows the improvement for the high-pressure adsorption for both CO₂ and ethane.

Database and Data Reduction

Our ongoing effort to understand the physical mechanisms of coalbed gas sorption, and thus have predictive models for these mechanisms, led us to compile a database of the sorption behavior on three adsorbent types: activated carbons, zeolites, and coals. We used this database for comparing the efficacy of various sorption models to correlate and predict sorption behavior. Further, we tried to elucidate the predominant sorption mechanisms of the three adsorbent types by analyzing whether model inefficacy (to correlate or predict) is due to the model's incomplete physical depiction of the observed sorption. For example, we stipulate that the sorption behavior on activated carbons is less complex than that on coals, i.e., more physical mechanisms such as adsorbent swelling and CO₂ solvation may be occurring on coal than on activated carbon. Thus, a model that does not include adsorbent swelling will have greater efficacy for activated carbons than for coals. The simple sorption behavior on activated carbon can serve as a useful reference model to the presumably more complex sorption behavior on coals.

Experimental reasons exist to include activated carbons in the database. Activated carbons have much larger sorption loadings than do coals, and because of this, experimental results for activated carbons are generally more certain and more reproducible. Also, other independent laboratories may reproduce sorption results on commercial activated carbons, whereas coal samples presumably of the same type may have physical variations that confound inter-laboratory comparisons.

Zeolites can serve as a comparative basis between organic and non-organic based adsorbents. Models that refer quantitatively to gas-solid interactions may have typical values for carbon-based adsorbents such as coals and activated carbons and other values for zeolites, which normally do not contain much carbon. Such a comparative basis can help establish whether regressed model parameters make physical sense.

Understanding of the sorption phenomenon in coalbeds presents additional challenges, because the coal present in coal seams contains water. Sorption experiments are done usually on water-saturated coal rather than dry coal to simulate the *in-situ* conditions of gas sorption in wells. Dry-coal isotherms are not indicative of the actual gas adsorbed in coal seams. Experiments are usually done on either completely dry coal or water-saturated coal. A coal is said to be water-saturated when additional water added to the coal does not affect the gas adsorption isotherm. Our research group and others have done a few comparative studies for the sorption of coalbed gases on wet coals (not necessarily water-saturated) and dry coals. Water can lower the adsorptive capacity of coal by 30% for methane [12], and as much as 60% for carbon dioxide as shown in Figure 3. Thus, water significantly alters the adsorption behavior of supercritical gases on coal.

For all three adsorbent types, the database was generally limited to coalbed gases. An emphasis was placed on experimental data focused on high-pressure adsorption, particularly at supercritical temperatures.

The amount of gas sorbed onto coal often is referred to as the absolute, excess, or total adsorption. The excess adsorption is sometimes called the Gibbs excess, and it is the type of adsorption most often measured in the laboratory. Total adsorption refers to

the sum amount of adsorption resulting from all fluid species in a defined system [see, e.g., 14]. In this model development effort, we use excess Gibbs adsorption measurements. Details about how to convert excess adsorption to absolute adsorption are discussed elsewhere [11].

A database of adsorption on activated carbons and zeolites has been compiled consisting of 42 systems. In addition, a database of 17 systems has been compiled for adsorption on coals, bringing the total database to 59 systems. Each “system” consists of at least one gas isotherm on a specific adsorbent. Table 1 lists information for each of the 59 systems including the adsorbent type, the adsorbate, the temperature and pressure ranges, and the original reference. The overall distribution of pressures for the activated carbon/zeolite database is depicted in Figure 4.

A system may be analyzed separately or several systems may be analyzed together in a system group. Analyzing system groups helps establish whether a model can simultaneously correlate adsorption data of different gas species on the same adsorbent. Tables 2 and 3 presents regression results for the activated carbon/zeolites systems and the coal systems.

For each system or system group, the percent weighted absolute average deviation (WAAD) was used as an objective function in regressing the SLD model parameters. The set of parameters that minimizes the WAAD is assumed to be the best that characterizes each system or system group.

$$WAAD = \frac{1}{NPTS} \sum_i^{NPTS} \frac{abs(n_i^{\text{exp}} - n_i^{\text{model}})}{\text{weight}_i} \quad (14)$$

To establish the point estimates for the weights, we consider two cases. If the sorption data are from the OSU research group, then point estimates of the expected experimental error have been established, and the weights are set to these point estimates. Otherwise, the weights are set on a constant percent basis to each experimental point. Thus, for this scenario, the objective function will become proportional to the sum of the absolute deviations. In some cases, some experimental data points may compromise the goodness of the overall fit; the weight for such data points will be changed to accommodate this situation. A full discussion of all such cases will be contained in the results section.

All systems were regressed using only the following SLD parameters: the surface area A , the effective slit length L , the reduced fluid-solid interaction energy parameter ϵ_{fs}/k_B , and the covolume modification term, Λ_b , as given by $b_{ads} = b \cdot \Lambda_b$. In addition, a parameter 'k' was included to account for the temperature dependence on the fluid-solid interaction parameter ϵ_{fs}/k_B . The temperature dependence of Lennard-Jones 12-6 fluid-solid interaction parameters has been found by comparison to other theories [13]. A temperature-dependent ϵ_{fs} was found effective in providing better correlations for adsorption isotherms over a wide range of temperature. The linear temperature dependence used for ϵ_{fs} is given below:

$$\epsilon_{fs} = (\epsilon_{fs})_0 + kT \quad (15)$$

Only those systems or system groups that contain more than one isotherm had the parameter 'k' regressed.

For each system or system group listed in Tables 2 and 3, the following information is given: the adsorbent name, adsorbates, the number of points (NPTS) for

each adsorbate, the temperatures of all the isotherms for each adsorbate, the regressed SLD parameters, and percent average absolute deviation (%AAD), and the root mean square error (RMSE). In Table 3, the percent weighted absolute average deviation (%WAAD) is also given; here, the weights are the expected experimental uncertainties. The following equations define respectively the %AAD and the RMSE:

$$\%AAD = \frac{100}{NPTS} \sum_i \frac{abs(n_i^{\text{exp}} - n_i^{\text{model}})}{n_i^{\text{exp}}} \quad (16)$$

$$RMSE = \sqrt{\frac{1}{NPTS} \sum_i (n_i^{\text{exp}} - n_i^{\text{model}})^2} \quad (17)$$

Results and Discussion

Several regressions were performed on systems that contained more than one isotherm. For such cases, when the SLD model includes the parameter ‘k’ that modifies the temperature dependence of ϵ_{fs} , the statistical fit is much better. Moreover, without inclusion of the parameter ‘k’, the SLD model regresses a surface area that is uncharacteristically low. For example, Table 4 compares the regression results of system group 1-3 with and without the parameter ‘k’ included. With ‘k’, the regressed surface area is 1002 m²/g compared to the 275 m²/g without ‘k’. Also, the PR covolume modification terms, Λ_i , become larger. This, and the fact that the other parameters differ greatly for the two cases, suggests that the regressed values for the SLD model are sensitive to the functional temperature dependence of ϵ_{fs} .

The temperature-independent SLD-PR model is inherently deficient in correlating simultaneously the adsorption of several isotherms, but estimating the parameter ‘k’ is relatively straightforward. As shown in Table 2, the regressed values for the parameter

'k' for all system groups are negative and range from $-0.105 > k > -0.359$. Also, for all system groups except for system group 13, 22 - 24, the parameter 'k' could be regressed as gas-species independent. The zeolites tend to have larger magnitude values of 'k' compared to activated carbons. To better predict the temperature dependence of adsorption, the SLD framework should incorporate a better equation of state and should use temperature-dependent Lennard-Jones parameters available from theory.

Overall, the %AAD of adsorption of the activated carbons and zeolites was 4.1% and that of the coals was 4.4%. Figure 5 depicts the statistical distribution of percentage errors in adsorption encountered for the activated carbons and zeolites, and Figure 6 depicts the statistical distribution of weighted errors in adsorption (weighted to the experimental uncertainty) for the coals. Figure 5 presents two distribution sets: the percentage error distribution for the entire activated carbon/zeolites database and the distribution for those experimental data having pressures greater than 0.17 MPa (25 psia). Figure 7 depicts a scatter plot of the percentage errors of adsorption as a function of pressure; the percentage errors for the lower pressures are higher due to the lower experimental adsorption values.

While estimates of the experimental uncertainty are not available for the activated carbons and zeolites, estimates were available for all the coal systems. For the coal systems, the overall WAAD based on experimental uncertainties as weights is 0.56. This means that the SLD-PR can correlate the coal system isotherms to 0.56 times the experimental uncertainty, on average. While this is excellent correlative ability, one must keep in mind that several empirical modifications were used to achieve this level of fit.

The SLD model could correlate successfully the data for all systems except system 4, which had aberrant adsorption isotherm behavior for high-pressure supercritical methane. System 4 data are presented in Figure 8. The methane isotherms are still monotonously increasing at pressures past 60 MPa, where typically one should expect a Gibbs excess adsorption maximum. The carbon black may have adsorption-induced swelling, causing the aberrant behavior, or the experimental data may contain systematic errors. Nevertheless, the SLD-PR model cannot model this system accurately, and system 4 is left out of Table 2 from the regression results.

Figures 9 and 10 depict respectively the adsorption of methane and propane on charcoal at various temperatures. For both gas species, the SLD-PR model has some trouble with correlating the temperature dependence of the excess adsorption, especially at higher pressures. The SLD-PR has less trouble correlating the adsorption temperature dependence for methane on activated carbon (from KOH activated coconut shell), as shown in Figure 11.

At least two possible explanations exist for why the SLD-PR model fit is better for the activated carbon (in Figure 11) than the charcoal (in Figures 9 and 10). First, the charcoal may swell, which can change the accessible adsorbed phase volume for methane and propane. This possible swelling of the charcoal may be induced either by adsorption or by exposure to different temperatures. Second, the empirical constant ‘k’ that determines the temperature dependence of the fluid-solid interaction energy parameter, ϵ_{fs}/k , may be gas-species dependent, or the linear temperature dependence of ϵ_{fs}/k , as given by Equation 12, is not suitable. Evidence that the parameter ‘k’ is gas-species dependent is shown in systems 13, 22-24 for the F30/470 Chemviron activated carbon.

For this adsorbent, the regressed parameter 'k' is necessary for each gas species, and the magnitude of 'k' increases nearly linearly with the critical temperature of the gas. Thus, the SLD-PR would have more trouble correlating gas species of widely differing critical temperatures.

The ability of the SLD-PR to correlate isotherms from low pressures to moderately high pressures is shown in Figures 12 and 13, for a zeolite and an activated carbon, respectively. For adsorption of CO₂ on H-Modernite (Figure 12), the SLD-PR model has some trouble at the higher pressures; the model curve begins to flatten, which is indicative of a nearby maximum in the excess adsorption. The experimental data, however, clearly shows a linear dependence (in logarithmic pressure) of the excess adsorption, even at the higher pressures. The inability of the SLD-PR to correlate accurately (without the flattening at high pressures) the entire isotherm in Figure 12 may be due to the 4-order magnitude range in pressure. The modification of the PR co-volume 'b' cannot compensate for such large magnitudes in pressure.

For the adsorption of methane, nitrogen, and CO₂ on activated carbon that is depicted in Figure 13, the SLD-PR model captures the correct behavior of the adsorption isotherm at high pressures for all three gases, albeit for CO₂, the fit is not excellent. The pressures for these isotherms span 2.5 orders of magnitude; the isotherms in Figure 10 do not have as many low-pressure experimental data as the isotherms in Figure 12.

The adsorption of CO₂ on various dry coals is depicted in Figure 14. The SLD-PR model can correlatively fit these isotherms, on average, to within the expected experimental uncertainty of the measurements. For the correlation of each isotherm, however, the four regressed parameters (area, slit length, ϵ_{fs}/k_B , and Λ_i) were found to

have a high degree of correlation; thus, the parameter values that were optimized by the objective function were sometimes physically unrealistic. To reduce this problem, the fluid-solid interaction energy parameter was set to 65.2 K for all the dry coals (the value that was regressed for the dry Illinois #6 coal).

Because the modified SLD-PR has four or five regressed parameters, over-fitting the experimental data is a concern. Parameter insensitivity produces uncertain parameter values for pure components and thus hampers prediction of multi-component adsorption data. For each of the dry coal systems 55-59, four parameters regressed per isotherm is clearly an over-fit. For the wet coal systems 43-54 as shown in Figures 15-17, each wet coal has isotherms for three gases: methane, nitrogen, and CO₂. For each wet coal, values for the surface area and the slit length are common to the three gases. Thus, wet coal systems have 8 overall parameters that need to be regressed for the 3 gases, whereas the dry coal systems need 4 parameters for each gas. For an adsorbent in which all the experimental data is isothermal and there are isotherms available from N different gas species, the SLD-PR model requires $(2N+2)$ parameters to be regressed.

Conclusions

The major conclusions of this study are:

- The SLD-PR model can correlate pure-gas adsorption isotherms of many systems involving wet and dry coals, activated carbons, and zeolites over broad pressure and temperature ranges.
- For each adsorbent, common surface area and effective slit width values may be used for all gas species over all temperature and pressure ranges.
- To correlate accurately over broad pressure ranges, the SLD-PR covolume must be empirically modified; this effectively changes the adsorbed phase density.
- The SLD-PR model must be empirically modified to accurately represent isotherms over wide temperature ranges. The empirical modification of the fluid-solid interaction potential parameter ϵ_{fs}/k_B has a linear temperature dependence, which is adequate for most systems considered in this study.

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Table 1. Literature Data Used for Pure Gas Adsorption Model Evaluations

System No.	Adsorbent	Adsorbent Surf. area (m²/g)	Adsorbate	Temp. Range (K)	Pressure Range (MPa)	Reference
1	AC, Columbia Grade L	1152	N ₂	311 - 422	0.028 – 1.50	Ray (1950)
2	AC, Columbia Grade L	1152	CH ₄	311 - 422	0.026 – 1.48	Ray (1950)
3	AC, Columbia Grade L	1152	C ₂ H ₆	311 - 478	0.007 – 1.49	Ray (1950)
4	Carbon Black	123	CH ₄	311 - 394	0.05 – 65.6	Stacy (1968)
5	Charcoal	1157	CH ₄	283 - 323	0.5 – 13.8	Payne (1968)
6	Charcoal	1157	C ₃ H ₈	293 - 333	8x10 ⁻⁴ – 1.35	Payne (1968)
7	AC, BPL	988	CH ₄	213 - 301	0.012 – 3.83	Reich (1980)
8	AC, BPL	988	C ₂ H ₆	213 - 301	7x10 ⁻⁴ – 1.71	Reich (1980)
9	AC, BPL	988	C ₂ H ₄	213 - 301	7x10 ⁻⁴ – 1.70	Reich (1980)
10	AC, BPL	988	CO ₂	213 - 301	0.003 – 3.84	Reich (1980)
11	AC, PCB-Calgon Corp.	1150-1250	CH ₄	296 - 480	0.27 – 6.69	Ritter (1987)
12	AC, PCB-Calgon Corp.	1150-1250	CO ₂	296 - 480	0.11 – 3.67	Ritter (1987)
13	AC F30/470, Chemviron Carbon	993.5	CO ₂	278 - 328	0.05 – 3.35	Berlier (1997)
14	AC Norit R1 Extra	1450	N ₂	298	0.03 – 5.98	Dreisbach (1999)
15	AC Norit R1 Extra	1450	CH ₄	298	0.01 – 5.75	Dreisbach (1999)
16	AC Norit R1 Extra	1450	CO ₂	298	0.008 – 6.0	Dreisbach (1999)
17	AC from Coconut shell with KOH activation	3106 (CO ₂ ads.)	CH ₄	233 - 333	0.09 – 9.40	Zhou (2000)
18	AC -Calgon F-400	850	CO ₂	303 to 318	0.02 – 20.2	Humayun (2000)
19	AC-Norit RB1	1100	CH ₄	294 - 351	0.05 – 0.8	Vaart (2000)
20	AC-Norit RB1	1100	CO ₂	294 - 348	0.05 – 0.8	Vaart (2000)
21	AC from Coconut shell with KOH activation	3106 (CO ₂ ads.)	N ₂	178 - 298	0.44 – 9.19	Zhou (2001)

Table 1. Literature Data Used for Pure Gas Adsorption Model Evaluation (Continued)

System No.	Adsorbent	Adsorbent Surf. Area (m²/g)	Adsorbate	Temp. Range (K)	Pressure Range (MPa)	Reference
22	AC F30/470, Chemviron Carbon	993.5	N ₂	303 - 383	0.39 – 9.5	Frère (2002)
23	AC F30/470, Chemviron Carbon	993.5	CH ₄	303 - 383	0.44 – 8.98	Frère (2002)
24	AC F30/470, Chemviron Carbon	993.5	C ₃ H ₈	303 - 383	0.05 – 2.20	Frère (2002)
25	AC Norit R1	1262	N ₂	298	0.03 – 14.56	Beutekamp (2002)
26	AC Norit R1	1262	CO ₂	298	0.03 – 6.04	Beutekamp (2002)
27	AC –Calgon F-400	850	N ₂	298	0.67 – 12.9	OSU
28	AC –Calgon F-400	850	CH ₄	298	0.67 – 12.9	OSU
29	AC –Calgon F-400	850	CO ₂	298	0.67 – 12.9	OSU
30	AC –Calgon F-400	850	C ₂ H ₆	298	0.67 – 12.9	OSU
31	Zeolite, Linde 13 X	525	N ₂	298 - 348	0.35 – 8.23	Wakasugi (1981)
32	Zeolite, Linde 5A	~400	N ₂	298 - 348	0.60 – 17.61	Wakasugi (1981)
33	Zeolite, Linde 5A	~400	CH ₄	298 - 348	0.36 – 9. 18	Wakasugi (1981)
34	Zeolite, Linde 5A	~400	CO ₂	298 - 348	0.03 – 11. 22	Wakasugi (1981)
35	Zeolite, Linde 5A	~400	C ₂ H ₆	298 - 348	0.07 – 5.07	Wakasugi (1981)
36	H-Modernite, Norton Co: Type Z-900H	~300	CO ₂	283 - 333	3x10 ⁻⁴ – 0.29	Talu (1986)
37	H-Modernite, Norton Co: Type Z-900H	~300	C ₃ H ₈	283 - 324	2x10 ⁻⁵ – 0.21	Talu (1986)
38	Zeolite G5	430	CH ₄	283 - 303	0.13 – 1.15	Berlier (1995)
39	Zeolite G5	430	C ₂ H ₆	283 - 303	0.056 – 1.10	Berlier (1995)
40	Zeolite G5	430	C ₂ H ₄	283 - 303	0.056 – 1.10	Berlier (1995)
41	Zeolite13 X	383	CH ₄	298	0.15 – 15.02	Beutekamp (2002)
42	Zeolite13 X	383	C ₂ H ₆	298	0.14 – 3.95	Beutekamp (2002)

Table 1. Literature Data Used for Pure Gas Adsorption Model Evaluation (Continued)

System No.	Adsorbent	Adsorbent Surf. Area (m²/g)	Adsorbate	Temp. (K)	Pressure Range (MPa)	Reference
43	Wet Fruitland Coal #2	--	N ₂	319.3	0.7 – 12.4	OSU
44	Wet Fruitland Coal #2	--	CH ₄	319.3	0.7 – 12.4	OSU
45	Wet Fruitland Coal #2	--	CO ₂	319.3	0.7 – 12.4	OSU
46	Wet Illinois #6 Coal	--	N ₂	319.3	0.7 – 12.4	OSU
47	Wet Illinois #6 Coal	--	CH ₄	319.3	0.7 – 12.4	OSU
48	Wet Illinois #6 Coal	--	CO ₂	319.3	0.7 – 12.5	OSU
49	Wet Tiffany Coal	--	N ₂	327.5	0.7 – 13.8	OSU
50	Wet Tiffany Coal	--	CH ₄	327.5	0.4 – 13.6	OSU
51	Wet Tiffany Coal	--	CO ₂	327.5	0.5 – 13.6	OSU
52	Wet LB Fruitland Coal	--	N ₂	319.3	1.5 – 12.4	OSU
53	Wet LB Fruitland Coal	--	CH ₄	319.3	1.4 – 12.5	OSU
54	Wet LB Fruitland Coal	--	CO ₂	319.3	0.7 – 12.4	OSU
55	Dry Illinois #6 Coal	--	CO ₂	328	0.7 – 13.8	OSU
56	Dry Beulah Zap Coal	--	CO ₂	328	0.6 – 13.8	OSU
57	Dry Wyodak Coal	--	CO ₂	328	0.7 – 13.8	OSU
58	Dry Upper Freeport Coal	--	CO ₂	328	0.7 – 13.8	OSU
59	Dry Pocahontas Coal	--	CO ₂	328	1.1 – 13.8	OSU

Table 2. Results of SLD-PR Model for Pure Gas Adsorption on Activated Carbons and Zeolites

System No(s).	Adsorbent	Adsorbate	NPTS	T (K)	Parameters					%AAD	RMSE (mmol/g)
					Area (m ² /g)	L (nm)	(e _{fs}) ₀ /k _B (K)	L _b	k/k _B (K)		
1-3	AC, Columbia Grade L	N ₂ CH ₄ C ₂ H ₆	139	310.9 338.7 366.5 394.3 422.0 449.8 477.6	1002	1.26	85.0 107.2 130.9	2.67 2.02 1.62	-0.115	4.9	0.160
5- 6	Charcoal	CH ₄ C ₃ H ₈	107	283.2 293.2 303.2 313.2 323.2 293.2 303.2 313.2 323.2 333.2	997.8	1.17	97.6 118.6	1.38 1.02	-0.105	4.6	0.230
7-10	AC, BPL	CH ₄ C ₂ H ₆ C ₂ H ₄ CO ₂	212	212.7 260.2 301.4	1332.4	1.07	110.4 132.4 133.6 120.5	2.16 1.73 1.78 1.68	-0.196	5.4	0.325

Table 2. Results of SLD-PR Model for Pure Gas Adsorption on Activated Carbons and Zeolites (Continued)

System No(s).	Adsorbent	Adsorbate	NPTS	T (K)	Parameters					%AAD	RMSE (mmol/g)
					Area (m ² /g)	L (nm)	(e _{fs}) ₀ /k _B (K)	L _b	k/k _B (K)		
11-12	AC, PCB-Calgon Carbon	CH ₄ CO ₂	34	296 373 480	1079.2	1.226	104.4 115.5	1.81 1.49	-0.127	5.2	0.240
14-16	AC, Norit R1 Extra	N ₂ CH ₄ CO ₂	34	298	1062.9	1.37	47.8 70.6 77.8	2.14 1.64 1.37	--	4.7	0.246
17, 21	AC, Coconut Shell	CH ₄ N ₂	193	233 253 273 293 313 333 178 198 218 233 258 278 298	1831.9	1.50	96.9 75.4	1.32 1.46	-0.140	2.5	0.302

Table 2. Results of SLD-PR Model for Pure Gas Adsorption on Activated Carbons and Zeolites (Continued)

System No(s).	Adsorbent	Adsorbate	NPTS	T (K)	Parameters					%AAD	RMSE (mmol/g)
					Area (m ² /g)	L (nm)	(e _{fs}) ₀ /k _B (K)	L _b	k/k _B (K)		
18	AC, Calgon F-400	CO ₂	116	303.6 305.2 309.2 313.2 318.2	590.9	1.36	203.3	1.17	-0.359	7.8	0.40
19-20	AC, Norit RB1	CH ₄	128	304.9 311.4 331.3 350.5	1228.7	1.23	122.9	2.60	-0.176	3.4	0.140
		CO ₂		305.2 311.2 329.5 348.3			181.8	1.82			
13, 22-24	AC, F30/470 Chemiviron Carbon	CO ₂	504	278 288 298 303 308 318 328	1147.0	1.42	189.5	1.74	-0.356	2.6	0.147
				303			122.8	2.05	-0.187		
				323			283.8	1.74	-0.515		
				343			75.0	2.30	-0.117		
				363							
				383							
		CH ₄		303			122.8	2.05	-0.187		
		C ₃ H ₈		343			283.8	1.74	-0.515		
		N ₂		363			75.0	2.30	-0.117		
				383							

Table 2. Results of SLD-PR Model for Pure Gas Adsorption on Activated Carbons and Zeolites (Continued)

System No(s).	Adsorbent	Adsorbate	NPTS	T (K)	Parameters					%AAD	RMSE (mmol/g)
					Area (m ² /g)	L (nm)	(e _{fs}) ₀ /k _B (K)	L _b	k/k _B (K)		
25-26	AC, Norit R1	N ₂	60	298	650.0	1.11	55.7	1.26	--	3.2	0.164
		CO ₂					74.3	0.783			
27-30	AC Calgon F-400	N ₂	127	318.2	620.9	1.20	48.7	1.51	--	3.3	0.167
		CH ₄					71.9	1.33			
		CO ₂					86.7	1.11			
		C ₂ H ₆					92.7	1.14			
31	Zeolite, Linde 13X	N ₂	24	298 323 348	494.7	1.29	111.1	2.04	-0.191	1.6	0.026
32-35	Zeolite, Linde 5A	N ₂	123	298 323 348	271.4	0.987	141.2	1.11	-0.230	3.1	0.112
		CH ₄					153.9	1.22			
		CO ₂					246.5	0.90			
		C ₂ H ₆					174.0	1.00			

Table 2. Results of SLD-PR Model for Pure Gas Adsorption on Activated Carbons and Zeolites (Continued)

System No(s).	Adsorbent	Adsorbate	NPTS	T (K)	Parameters					%AAD	RMSE (mmol/g)
					Area (m ² /g)	L (nm)	(e _{fs}) ₀ /k _B (K)	L _b	k/k _B (K)		
36- 37	H-Modernite, Norton Co: Type Z-900H	CO ₂	185	283.0	300.0	1.02	180.7	0.763	-0.268	8.8	0.065
		C ₃ H ₈		303.2			177.1	1.42			
				324.3							
38-40	Zeolite G5	CH ₄	125	283	623.1	1.13	96.9	1.28	-0.140	2.4	0.091
		C ₂ H ₄		303			132.7	1.14			
		C ₂ H ₆					114.6	1.13			
41-42	Zeolite 13X	CH ₄	29	298.2	408.5	0.60	52.3	0.90	--	1.2	0.046
		C ₂ H ₆					55.7	0.69			
Overall Statistics for Activated Carbons and Zeolites			2140							4.1	0.133

Table 3. Results of SLD-PR Model for Pure Gas Adsorption on Coals

System No(s).	Adsorbent	Adsorbate	NPTS	T (K)	Parameters				WAAD	%AAD	RMSE (mmol/g)
					Area (m ² /g)	L (nm)	(e _{fs}) ₀ /k _B (K)	L _b			
43-45	Wet Fruitland Coal #2	N ₂	134	319.3	63.7	1.02	31.7	1.00	0.53	4.5	0.058
		CH ₄					56.1	0.77			
		CO ₂					58.4	0.68			
46-48	Wet Illinois#6 Coal	N ₂	70	319.3	47.1	1.46	22.0	1.14	0.34	4.8	0.040
		CH ₄					48.5	1.00			
		CO ₂					77.1	0.90			
49-51	Wet Tiffany Coal	N ₂	63	327.5	36.1	1.07	29.3	1.12	0.77	3.6	0.011
		CH ₄					52.0	0.83			
		CO ₂					66.6	0.74			
52-54	Wet Lower Basin Fruitland Coal	N ₂	81	319.3	23.0	1.03	32.4	0.99	0.55	5.6	0.026
		CH ₄					54.3	0.69			
		CO ₂					64.1	0.62			
55	Dry Illinois #6 Coal	CO ₂	11	328	136.0	1.70	65.2	1.14	0.29	1.8	0.025
56	Dry Beulah Zap Coal	CO ₂	11	328	135.1	1.13	65.2	0.86	0.96	4.0	0.059

Table 3. Results of SLD-PR Model for Pure Gas Adsorption on Coals (Continued)

System No(s).	Adsorbent	Adsorbate	NPTS	T (K)	Parameters				WAAD	%AAD	RMSE (mmol/g)
					Area (m ² /g)	L (nm)	(e _{fs}) ₀ /k _B (K)	L _b			
57	Dry Wyodak Coal	CO ₂	11	328	140.0	1.27	65.2	0.92	0.95	4.2	0.062
58	Dry Upper Freeport Coal	CO ₂	11	328	74.6	1.02	65.2	0.83	0.61	2.7	0.023
59	Dry Pocahontas Coal	CO ₂	11	328	99.9	1.02	65.2	0.89	0.51	2.3	0.023
Overall Statistics for Coals			403						0.56	4.4	0.023

Table 4. Comparing the SLD-PR Model with and without the Parameter ‘k’

System No(s).	Adsorbent	Adsorbate	NPTS	T (K)	Parameters					%AAD	RMSE (mmol/g)
					Area (m ² /g)	L (nm)	- e _{fs} /k _B (K)	L _b	k/k _B (K)		
1-3 No ‘k’	AC, Columbia Grade L	N ₂ CH ₄ C ₂ H ₆	139	310.9 338.7 366.5 394.3 422.0 449.8 477.6	275.3	1.18	88.3 70.3 98.2	0.606 0.699 0.526	--	7.2	0.197
1-3 ‘k’ include- ed	AC, Columbia Grade L	N ₂ CH ₄ C ₂ H ₆	139	310.9 338.7 366.5 394.3 422.0 449.8 477.6	1002	1.26	85.0 107.2 130.9	2.67 2.02 1.62	-0.115	4.9	0.160

Figure 1. Depiction of Slit Model Used for the SLD Model Calculations

Figure 2. Effect of Covolume Modification in the SLD-PR Model on the Excess Adsorption of CO₂ and Ethane on Calgon F-400 Activated Carbon at 318.2 K

Figure 3. Effect of Moisture Content on the CO_2 Adsorption on Argonne Premium Illinois #6 Coal

Figure 4. Cumulative Distribution Function of Pressure For Pure-Gas Adsorption on Activated Carbons and Zeolites (2140 data points)

Figure 5. Cumulative Distribution Function of Percentage Errors of Adsorption for Activated Carbons and Zeolites

Figure 6. Cumulative Distribution Function of Weighted Percentage Errors of Adsorption for Coals

Figure 7. Scatter Plot of Percentage Errors of Adsorption for Activated Carbons and Zeolites

Figure 8. Methane Adsorption on Carbon Black at Various Temperatures (System 4)

Figure 9. Methane Adsorption on Charcoal at Various Temperatures (System 5)

Figure 10. Propane Adsorption on Charcoal at Various Temperatures (System 6)

Figure 11. Methane Adsorption on Activated Carbon from Coconut Shell with KOH Activation at Various Temperatures (System 17)

Figure 12. CO₂ Adsorption on H-Modernite at Various Temperatures (System 37)

Figure 13. Adsorption on Norit R1 Extra Activated Carbon at 298 K (Systems 15-17)

Figure 14. Adsorption of CO₂ on Various Dry Coals at 328 K (Systems 55-59)

Figure 15. Adsorption of Methane on Various Wet Coals (Systems 44, 47, 50, 53)

Figure 16. Adsorption of Nitrogen on Various Wet Coals (Systems 43, 46, 49, 52)

Figure 17. Adsorption of CO₂ on Various Wet Coals (Systems 45, 48, 51, 54)

**Ono-Kondo Lattice Model for High-Pressure
Pure-Gas Adsorption**

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Abstract

Theoretically-based models for adsorption behavior are needed to develop optimal strategies for enhanced coalbed methane (CBM) recovery operations. Although a number of frameworks are available for describing the adsorption phenomenon, the Ono-Kondo (OK) lattice model offers several practical advantages in modeling supercritical, high-pressure adsorption systems.

In this study, we evaluated the OK lattice model for correlating high-pressure, supercritical adsorption isotherms encountered in CBM recovery and CO₂ sequestration. Specifically, the parameters of the OK model were evaluated to obtain reliable representation of pure-gas adsorption on carbon adsorbents. Generalized model parameters were developed to relate the parameters with gas properties and adsorbent characterizations and to generate the temperature relations for the OK model parameters.

The results indicate that the OK monolayer model appears effective in modeling pure-gas adsorption on carbon matrices. The model can represent the isotherm adsorption on activated carbon and coals within their experimental uncertainties with about 3.6% AAD. The generalized model can predict the adsorption isotherms on activated carbon with about 7% AAD. Moreover, the generalized model can also predict the other gas adsorption isotherms based on the parameters obtained from one gas adsorption isotherm. The generalized model also appears effective for the pure-gas adsorption on wet coals when the moisture content in the coals is above their equilibrium value. The model parameters in this condition, however, are affected by the presence of water.

Keywords: Adsorption, High-Pressure, Coalbed Methane, OK Lattice Model

Introduction

A practically useful adsorption theory should be capable of handling different adsorbate/adsorbent systems over the whole range of operating conditions. Among the theories widely used for adsorption are the Langmuir model, ideal adsorbed solution (IAS) theory (Myers and Prausnitz, 1965), heterogeneous ideal adsorbed solution (HIAS) (Myers, 1987), vacancy solution model (VSM) (Suwanayuen and Danner, 1980; Cochran et al., 1985), theory of volume filling micropores (TVFM) (Dubinin, 1966), two-dimensional equations of state model (2-D EOS) (Hoory and Prausnitz, 1967; Hall et al., 1994, Zhou et al., 1994; Sudibandriyo et al., 2003), and the simplified local density (SLD) model (Chen et al., 1997; Fitzgerald et al., 2003). In general, all the models work well for low-pressure adsorptions. However, for high-pressure adsorption, where the effect of adsorbed-phase density becomes significant, the models that do not include this effect are inadequate.

In this study, we evaluate and further develop the Ono-Kondo (OK) lattice model to correlate high-pressure, supercritical adsorption isotherms encountered in CBM recovery and CO₂ sequestration. In general, the OK model lies between the SLD and 2-D EOS models in the practicality of its theory and its ease of computation and applicability. Specifically, the OK model:

1. Is based on a well-developed lattice theory
2. Describes monolayer and multilayer adsorption
3. Describes adsorption behavior based on the physical properties of the adsorbates and the accessible characterization of the adsorbent

Application of the model to pure gas adsorption on activated carbon has been demonstrated by Aranovich and Donohue (1996) and Benard and Chahine (1997 and 2001). The results show that the model is in good agreement with the experimental data considered. However, the regressed model parameters obtained in their study were not suitable for other similar systems in the high-pressure, supercritical region. These results reveal that, even though the OK model has the potential to represent gas adsorption, the model parameters must be determined with care. This includes: (a) determination of the optimal number of layers used to describe the adsorbed phase for a specific system, (b) a general formulation that will produce reasonable estimates for each parameter, and (c) describing the parameters in terms of accessible adsorbate-adsorbent characteristics. These general formulations are important for predicting adsorption of systems beyond those where experimental data are available. Moreover, the temperature dependence of the parameters must also be evaluated.

In this study, the correlative capability of the OK model is evaluated. Model parameters were regressed to obtain precise representations for pure-gas, high-pressure adsorption on carbon adsorbents involving adsorbates in the near critical and supercritical regions. Also, generalized model parameters were developed which can predict the adsorption equilibrium to within twice the expected experimental uncertainties.

Extending the mathematical models to describe adsorption behavior on coals is complicated by (a) the difficulty in characterizing the coal matrix adequately and (b) assessing the effect of water (found in essentially all coalbeds) on the adsorption behavior. As a result, we decided to perform initial studies (a) on a more readily characterized carbon matrix and (b) in the absence of water. This led to our choice of dry

activated carbon. Our rationale is that useful models should be expected to fit data on activated carbon prior to extending them to include the effects of the complex adsorbent structure of coals and/or the presence of water.

To apply the OK model, the number of layers must be specified. Therefore, before performing model parameter evaluations, we determined the number of layers required to best describe the systems considered. The multilayer and monolayer adsorption models were compared, and the appropriate model was used for the rest of the study.

Ono-Kondo Lattice Model for Adsorption

An adsorption model based on lattice theory was proposed first by Ono and Kondo in 1960. In the lattice model, the fluid system is assumed to be composed of layers of lattice cells that contain fluid molecules and vacancies. For the case of adsorption, more fluid molecules reside in the cells of the adsorbed-phase layers than in the cells of the bulk-phase layers. Molecular interactions are assumed to exist only between nearest neighboring molecules. When equilibrium exists between the gas-phase and the multilayer adsorbed phase, the expression for the thermodynamic equilibrium for pure-component adsorption can be written as (Aranovich and Donohue, 1996):

$$\ln[x_t(1-x_b)/x_b(1-x_t)] + z_0(x_t - x_b)e_{ii}/kT + (x_{t+1} - 2x_t + x_{t-1})e_{ii}/kT = 0 \quad (1)$$

for $t = 2, 3, \dots, m$, number of layer.

$$\ln[x_1(1-x_b)/x_b(1-x_1)] + (z_1x_1 + x_2 - z_0x_b)e_{ii}/kT + e_{is}/kT = 0 \quad (2)$$

for the 1st adsorbed layer.

In these equations, x_t is the reduced density or fraction of sites occupied by adsorbed molecules in layer t , and x_b is the fraction of sites occupied by fluid molecules in the

bulk. For a hexagonal configuration of lattice cells, the coordination numbers z_0 and z_1 are 8 and 6, respectively; and by definition, $z_2 = (z_0 - z_1)/2$. The fluid-fluid interaction energy is expressed by e_{ii}/kT , and the fluid-solid surface interaction energy is expressed by e_{is}/kT , where k is Boltzman's constant, and T is the absolute temperature.

The analytical expression for the Gibbs excess adsorption from this model is:

$$G = C \sum_t^m (x_t - x_b) \quad (3)$$

where C is a prefactor related to the capacity of the adsorbent for a specific gas, and m is the maximum number of adsorbed layers in an adsorption isotherm. The reduced densities x_t and x_b are expressed as $x_t = \mathbf{r}_t / \mathbf{r}_{mc}$ and $x_b = \mathbf{r}_b / \mathbf{r}_{mc}$, where $\mathbf{r}_t$ and $\mathbf{r}_b$ are the adsorbed and the bulk density of the adsorbate at layer t , respectively and $\mathbf{r}_{mc}$ is the adsorbed phase density at maximum capacity.

For monolayer adsorption inside a slit, the equilibrium expression can be written as (Benard and Chahine, 1997):

$$\ln[x_{ads}(1 - x_b) / x_b(1 - x_{ads})] + ((z_1 + 1)x_{ads} - z_0 x_b) e_{ii} / kT + e_{is} / kT = 0 \quad (4)$$

The Gibbs excess adsorption then simplifies to:

$$\Gamma = 2C (x_{ads} - x_b) = 2C \left(\frac{\mathbf{r}_{ads}}{\mathbf{r}_{mc}} - \frac{\mathbf{r}_b}{\mathbf{r}_{mc}} \right) \quad (5)$$

Determination of the Number of Layers

As described in the previous section, the OK lattice model can be applied to monolayer or multilayer adsorption. We used selected experimental data to evaluate the number layers required to adequately represent the systems considered. Specifically, our

measurements at 318 K for pure adsorption of nitrogen, methane and CO₂ on activated carbon were used to represent adsorption in the supercritical region; the CO₂ adsorption data on activated carbon conducted by Humayun (2000) at 304 K were used to represent the adsorption in the near-critical region; and our CO₂ adsorption data on dry coal (Illinois #6) were used to represent an adsorbent with a wide pore-size distribution.

Table 1 presents a summary of our model evaluation results for the monolayer and three-layer models we used to correlate the selected data. The model parameters, given in Table 1, were determined by minimizing the sum of squares of weighted absolute deviations in the calculated adsorption, w , for the pure gas of interest. The quality of the fit, expressed in terms of absolute average percentage deviation (%AAD) and weighted average absolute deviations (WAAD), is also given in Table 1 for both monolayer and multilayer models. Figures 1 and 2 illustrate the quality of representation produced by the models. Both models show excellent representation within the expected experimental uncertainties; as such, comparable representation is observed for the monolayer and multilayer models. The results suggest that the simpler monolayer model is appropriate for the systems considered. The results are not surprising, considering that the adsorption of small molecules occurs mostly in the micropore structure (Gan et al., 1972; Medek et al., 1977; Benard and Chahine, 1977). Perhaps because the size of the micropores is only several times the diameter of the molecules and the phase conditions are removed from the critical region, monolayer adsorption is adequate.

In conclusion, the monolayer model appears effective in modeling pure-gas adsorption on carbon matrices. Therefore, this approach was used for further evaluation.

Modeling of Pure-Gas Adsorption on Activated Carbon (AC)

The Maximum Adsorbed-Phase Density Estimate

The OK model has four parameters: r_{mc} , e_{ii}/k , e_{is}/k and C . To reduce the number of regressed parameters in the model, the maximum adsorbed-phase density, r_{mc} , is usually estimated independently. A commonly used approximation is the liquid density at the normal boiling point, as was done by Arri and Yee (1992). However, examination of the results from the OK model reveals that the adsorbed-phase densities generated by the OK model, as presented in Table 2, are less than the boiling point estimates and are closer to the reciprocal van der Waals co-volume estimates. Moreover, the adsorbed-phase densities generated by the OK model and the reciprocal van der Waals co-volume estimates were also close to the “graphical estimate” based on the Gibbs adsorption definition: $G = V_{ads}(r_{ads} - r_{gas})$, as illustrated by Figure 3. V_{ads} is the adsorbed-phase volume and r_{ads} and r_{gas} are the density of the adsorbed phase and the gas phase, respectively. As shown in the figure for CO₂, if the absolute adsorption, $V_{ads}r_{ads}$, becomes constant at high pressures, then the Gibbs adsorption should show a linear decrease with increasing r_{gas} . Extrapolation of this linear relation yields an x-axis intercept where $r_{ads} = r_{gas} = r_{mc}$. Figure 3 indicates that $r_{ads} = 22.5$ mol/L or 1.02 g/cm³. Use of this technique requires sufficient data in the linear (high pressure) region beyond the maximum in the Gibbs adsorption; thus, an estimate is shown in Table 2 only for carbon dioxide. For the other adsorbates, the available data do not extend to the linear region.

In our recent publication on the simplified local density (SLD) modeling (Fitzgerald, et al., 2003), a theoretical explanation was offered for why the adsorbed-phase densities are close to the equation of state (EOS) reciprocal co-volumes. The SLD model can show that, at high pressures, the adsorbed-phase density approaches the reciprocal co-volume.

The Fluid-fluid Energy Parameter Estimate

In the present work, the fluid-fluid energy parameter, $\mathbf{e}_{ii}/k$, was estimated to be proportional to the Lennard-Jones well depth energy parameter. For the Lennard-Jones 12-6 potential, the pair-wise interaction between two molecules separated by a distance r is given by

$$\mathbf{F}(r) = 4\mathbf{e}^* \left[\left(\frac{\mathbf{s}}{r} \right)^{12} - \left(\frac{\mathbf{s}}{r} \right)^6 \right] \quad (4)$$

where $\mathbf{F}(r)$ is the potential energy, $\mathbf{e}^*$ is the well depth of the potential, and $\mathbf{s}$ is the collision diameter, which is defined as the distance at which the potential energy is zero. If the adsorbed molecules are randomly distributed, the total energy of interaction between a molecule and all the surrounding molecules is:

$$U_1 = \int_s^\infty \mathbf{F}(r) \frac{N}{A} 2\pi r dr = -\frac{6\mathbf{p}}{5} \mathbf{e}^* \mathbf{s}^2 \frac{N}{A} \quad (5)$$

where N is the number of molecules on the surface and A is the surface area. The total energy due to the molecular interaction is then simply (Do, 1998)

$$U_T = \frac{N}{2} U_1 = -\frac{3\mathbf{p}}{5} \mathbf{e}^* \mathbf{s}^2 \frac{N^2}{A} \quad (6)$$

In OK model, the total energy due to molecular interactions is expressed in terms of the coordination number and the fractional coverage. Equating the two total energy expressions, for $z_0 = 8$ (hexagonal configuration), results in

$$U_T = \frac{z_0}{2} N e_{ii} = 4 N e_{ii} = \left| -\frac{3p}{5} \mathbf{e}^* \mathbf{s}^2 \frac{N^2}{A} \right| \quad (7)$$

or

$$\mathbf{e}_{ii} = \frac{3p}{20} \mathbf{e}^* \mathbf{s}^2 \frac{N}{A} \quad (8)$$

When the spherical particles are closely packed, the fraction occupied by those particles is 0.907 (Do, 1998), and we write:

$$\frac{p}{4} N \frac{a^2}{A} = 0.907 \quad (9)$$

Here, a is the distance between the two particles at the minimum energy potential, $a = (2)^{1/6} \mathbf{s}$. Combining Equation (8) and (9) results in the following estimate for the fluid-fluid energy parameter in the OK model:

$$\mathbf{e}_{ii} = 0.432 \mathbf{e}^* \quad (10)$$

The fluid-fluid energy parameters obtained for the gas adsorptions on activated carbon shown in Table 1 are reasonably close to the ones obtained from the above expression; for example, the regressed value of $\mathbf{e}_{ii}/k$ for CO₂ is 82 K compared to the 84.3 K value estimated using Equation (10). Further, the value of the calculated Gibbs excess adsorption is not highly sensitive to small deviations in $\mathbf{e}_{ii}/k$ obtained from Equation (10); for example, a ten percent deviation in $\mathbf{e}_{ii}/k$ can still produce reasonable values of the Gibbs excess adsorption. We also observed that the fluid-fluid energy parameters are positive values, which represents a repulsive energy potential. These results confirm the

observations of Benard and Chahine (1997) and also agree with molecular simulation results obtained recently by Aranovich (2001). This phenomenon is similar to the negative values obtained for parameter α in two-dimensional equation of state (Zhou, 1994) and is not totally unexpected in light of the fact that surface forces are significant in the adsorbed phases. The effect of solid surface potential on adsorbed molecules may affect the molecular energy at conditions such that the interaction between them becomes repulsive.

Because the lattice model was also assumed for the gas phase, the positive fluid-fluid energy parameter is also repulsive in the gas phase, which might be unreasonable. The use of an accurate equation of state to calculate the chemical potential in the gas phase might be more appropriate; this approach is scheduled for future study.

Two-Parameter OK Model

The adsorbed-phase density and the fluid-fluid energy parameters can be estimated from the reciprocal van der Waals co-volume and from a proportional relation to the well depth of the Lennard-Jones 12-6 potential, respectively. For further generalization, the above estimates were applied for modeling of (a) selected gas adsorption on activated carbon and zeolites reported in the literature and (b) our gas adsorption measurements on activated carbon. In this case, the fluid-solid energy parameter, e_{is}/k , was regressed for each *system* and the parameter C was regressed for each adsorption *isotherm*. Because no detailed information was given on uncertainties in the selected literature experimental data, the percentage average deviation of the Gibbs excess adsorption (% AAD) was used as the objective function to determine the two model parameters.

Table 3 presents the results of our model representation of the above selected data. Overall, for 2242 data points, the OK model with two regressed parameters (one common e_{is}/k for each system, and individual C for each isotherm) represents the data with about 3.6% AAD. However, some significantly larger errors were observed, especially for the CO₂ and propane isotherms. These larger errors are partly due to the high uncertainty in the CO₂ and propane bulk density calculations. Also, the percentage deviation is exaggerated when the Gibbs excess adsorption becomes exceedingly small; i.e. at lower pressures, at high temperatures, or at nearly full coverage adsorption at higher pressures. For the OSU adsorption data set (Systems 47-50), the OK model is capable on average of representing the data within their experimental uncertainties.

Figure 4 shows the percentage deviation plot for the OK model representation of the adsorption data on activated carbon. About 90% of the data can be represented by the model within 8.4 % AAD. As mentioned above, the large percentage deviations occurred mainly when the Gibbs excess adsorption values are small at relatively low pressures. Figure 5 illustrates the OK model representation of System 15 (CO₂ on Norit R1 Extra activated carbon), where the percentage deviations are large (9.5 % AAD). As shown in the figure, the model can actually represent the experimental data reasonably well at pressure above 0.5 MPa. The nitrogen and methane adsorption on the same activated carbon are also shown in the figure for comparison.

Figure 6 illustrates the OK model representation of a system with significant temperature range. As shown in this figure, the model is capable of describing the temperature variation.

Basis for Generalization

Based on our preliminary evaluation of the regressed parameter C presented in Table 3, it appears that, for a given adsorbate at fixed temperature, the value of C increases as the surface area of the adsorbent increases. This suggests that the maximum adsorption capacity, C , can be divided into two contributions; i.e. the contribution from the adsorbent characteristics, represented by surface area (A , m^2/g), and the contribution from the adsorbate characteristic(s). In this study, we proposed the following simple relation for the maximum adsorption capacity, C :

$$C(T) = \frac{AC_a(T)}{2} \quad (11)$$

C_a is the surface adsorbed-phase density (mmol/m^2), with its value depending only on the adsorbate.

C is also temperature dependent. As reported in Table 3, the value of C increases as temperature decreases. This temperature dependence of the maximum adsorption capacity is not uncommon, based on the previous studies. Benard and Chahine (1997; 2001) reported the temperature dependence of C , and they proposed an empirical temperature relation for C . Similarly, Do (1998) asserted that the maximum adsorption capacity in the Langmuir model was a function of temperature. He described this temperature dependence as due to the thermal expansion of the adsorbed phase.

Because of its theoretical basis, we adopted Do's approach and used the following thermal expansion expression for evaluating the surface adsorbed-phase density:

$$\frac{dC_a / dT}{C_a} = -\alpha \quad (12)$$

Integrating Equation (12) and combining with Equation (11) results in:

$$\ln(1/C) = dT - [\ln C_{a,o} + dT_o + \ln(A/2)] \quad (13)$$

where T_o (K) is chosen at the normal boiling point of the adsorbate (triple point for CO_2), T (K) is the absolute temperature, $C_{a,o}$ is the maximum surface adsorbed-phase density at T_o , and d is the thermal expansion coefficient of the adsorbed phase.

For a given system, Equation (13) yields a linear correlation if $\ln(1/C)$ is plotted against temperature, T . Figure 7 presents the correlation between $\ln(1/C)$ obtained from Table 3 for gas adsorption on BPL activated carbon (Reich, 1980) and temperature, T . The linear relationship shown in this figure suggests that Equation (13) provides a good representation of the temperature dependence of the maximum adsorption capacity, C .

The values of $C_{a,o}$ and d depend only on the adsorbate; therefore, a linear correlation should also be obtained if C is plotted against A at constant temperature. Figure 8 presents the plots of parameter C obtained in Table 3 against the surface area, A . The values of the surface areas, in most cases, were reported by the investigators. In a few cases, however, they were obtained from the information provided by the adsorbent production company or estimated from the literature. Although the accuracy of the reported surface areas is questionable, Figure 8 still shows a reasonable linear correlation between the parameter C and the surface area, A . This observation further supports the assumption made in Equation (11).

The fluid-solid energy parameter, e_{is}/k , was generalized based on the interaction of a single molecule with a single lattice plane. If z is the distance between the adsorbate molecule i and the lattice carbon plane, the potential energy can be written as:

$$F_{i,SLP} = 4pr_c e_{ic}^* s_{ic}^2 \left[\frac{1}{5} \left(\frac{s_{ic}}{z} \right)^{10} - \frac{1}{2} \left(\frac{s_{ic}}{z} \right)^4 \right] \quad (14)$$

The potential energy has a minimum at a depth given by:

$$\mathbf{e}_{is} = \frac{6}{5} \mathbf{p} \mathbf{r}_c \mathbf{e}_{ic}^* \mathbf{s}_{ic}^2 \quad (15)$$

where $\mathbf{r}_c = 0.382 \text{ atom/\AA}^2$ is the area density of carbon atoms in a graphite plane. The adsorbate-carbon collision diameter is estimated as $\mathbf{s}_{ic} = \frac{1}{2}(\mathbf{s}_{ii} + \mathbf{s}_{cc})$. The adsorbate-carbon well depth potential is estimated as $\mathbf{e}_{ic}^* = \sqrt{\mathbf{e}_{ii}^* \mathbf{e}_{cc}^*}$.

Generalization of the model parameters was performed by evaluating $C_{a,o}$, $\mathbf{d}$ and $\mathbf{e}_{cc}^*$ of the systems studied. All other physical properties of the adsorbate and carbon atom used are listed in Table 4. Five case studies described in Table 5 were explored. For each case, 1520 independent adsorption data points were employed. These data include all the activated carbon systems shown in Table 3, excluding systems that have only one adsorption isotherm. These systems were used later to validate the generalized model.

In Case 1, all the parameters, $C_{a,o}$, $\mathbf{d}$ and $\mathbf{e}_{cc}^*$, were optimized simultaneously, while the surface area was taken from information provided in the literature. Table 6 shows the parameters obtained in Case 1. The regressed solid-solid energy parameter, $\mathbf{e}_{cc}^* / k$, varied from 38 to 43 K.

For all components studied, except CO₂, the mean thermal expansion coefficient of the adsorbed phase, $\mathbf{d}$, was approximately 0.0024 K⁻¹. This value is close to the 0.0025 K⁻¹ value estimated by Wakasugi (1981) for all components. However, the regressed $\mathbf{d}$ for CO₂ is much higher (0.0039 K⁻¹).

The maximum surface adsorbed-phase density at T_o (normal boiling point), $C_{a,o}$, obtained in Case 1 was correlated with the diameter of the adsorbed molecules. Figure 9 shows a linear correlation between $C_{a,o}$ and the reciprocal square of the molecule diameter. This finding is not unexpected since for a close-packed hard sphere molecule, the surface density will be equal to $\sqrt{2} / N_{av} \sigma^2$, where N_{av} is the Avogadro's number. However, $C_{a,o}$ is much higher for CO_2 , and it does not follow the observed linear trend for the other adsorbates.

In Case 2, the general linear correlation for $C_{a,o}$ obtained in Case 1 was applied. A constant δ obtained in Case 1 was also used in Case 2. As shown in Table 5, the overall percentage deviations obtained in Case 1 is practically the same as for Case 2. The overall percentage deviations did not change significantly (about 7% AAD) when the solid-solid energy parameter, e_{cc}^* / k , was set constant at 40 K in Case 3.

Slightly better results were obtained when the surface area was regressed, as in Case 4 (6.4 %AAD). In this case, the regressed surface area deviated up to 8% from the reported surface area. Moreover, as shown in Case 5, using the regressed surface area and a constant solid-solid energy parameter, $e_{cc}^* / k = 40$ K, the model can predict the adsorption isotherms with an AAD of 7%.

Figure 10 shows the percentage deviation plot for the generalized OK model prediction of the adsorption data on activated carbon. About 90% of the data can be predicted by the generalized model within 14.5 % AAD. Figure 11 illustrates the comparison of generalized (Case 5) and two-parameter OK model representation of methane adsorption on activated carbon (System 22). As illustrated in the figure, the generalized model can predict the adsorption isotherms about twice the error of the two-

parameter OK model. The results of the five cases above suggest that the gas adsorption can be predicted using the generalized OK model with the average deviation of about 7% AAD.

Several gas adsorption systems were subsequently used to validate this generalized OK model. Figure 12 shows the generalized OK model prediction of our gas adsorption measurements on activated carbon at 318.2 K. A surface area of 920 m²/g and the solid-solid energy parameter, e_{cc}^*/k , of 39 K, were obtained from the best fit of the CO₂ adsorption data. Using this information and the generalized $C_{a,o}$ and δ , the adsorption isotherms for the other three gases were then *predicted*. A similar prediction procedure was applied for the other systems, confirming that the gas adsorption on activated carbon can be predicted using the generalized OK model with about 7% AAD or about twice the error of the two-parameter OK model.

Modeling of Pure-Gas Adsorption on Coals

Two-Parameter OK Model for Pure-Gas Adsorption on Coals

Similar to our treatment of pure-gas adsorption on activated carbon, we modeled pure-gas adsorption on coals using the adsorbed-phase density and the fluid-fluid energy parameters estimated from the reciprocal van der Waals co-volume and from the Lennard-Jones 12-6 potential, respectively. Our gas adsorption measurements on several coals were used to evaluate the fluid-solid energy parameter, e_{is}/k , and the parameter C in the OK model. The weighted average deviation of the Gibbs excess adsorption (WAAD) was used as the objective function to determine the two model parameters.

Table 7 presents the results of our model representation of the above selected data. Overall, for 308 data points, the OK model with two regressed parameters can represent the data within the expected experimental uncertainties, which corresponds to 3.3% AAD. Specifically, the two-parameter OK model representation of gas adsorption on wet Fruitland coal gives comparable results to three-parameter models such as LRC and 2-D EOS used by Zhou (1994).

Model Generalization for Pure-Gas Adsorption on Coals

The same approach used for activated carbon was used to determine the parameter C in the gas adsorption model on coals. Specifically, we used a generalized $C_{a,o}$ and δ obtained from the modeling on activated carbon. The surface area of the coals, however, was regressed from the experimental adsorption data, since the surface area is very specific to the coal samples and is also dependent on the wetness of the coals studied.

The fluid-solid energy parameter, e_{is}/k , for adsorption on coals, as shown in Table 7, is much lower than that on activated carbon. This lower value might be attributed to the mean position of a molecule in the structure of the coals and the presence of water. Figure 13 illustrates the molecule positions in the slit of the activated carbon and coals. In activated carbon, the distance between a molecule and surface plane, z , is approximately equal to the collision diameter of the two atoms, i.e. $z = s_{ic}$. Due to wider slit length of the coals (Gan, 1972), the distance between a molecule and surface plane of the coal might be slightly higher than s_{ic} . Therefore, the fluid-solid energy for pure adsorption on coals was calculated according to Equation (14) instead of Equation (15). Furthermore, the chemical structure of the coal is much more complex than that of

activated carbon. The wetness of the coal might also affect the regressed overall fluid-solid energy. Therefore, we proposed a modification of Equation (14):

$$F_{i,SLP} = e_{is} / k = 4pr_c e_{ic}^* s_{ic}^2 j_c (1 + x_f) \left[\frac{1}{5} \left(\frac{s_{ic}}{z} \right)^{10} - \frac{1}{2} \left(\frac{s_{ic}}{z} \right)^4 \right] \quad (16)$$

A correction, j_c was introduced to take into account for the effect of adsorbent chemical structure on the adsorbate. This value is close to zero for adsorption on activated carbon, and was generalized based on the chemical composition of the coals. A moisture correction effect, f_c , was calculated as a function of the ash-free coal not occupied by equilibrium moisture content. This value of f_c is available experimentally. A more rigorous way to handle the water effect would be to use a multi-component model by treating the water as an additional adsorbed component. In our current stage of study, however, such a model is still under development. For simplicity, therefore, the correction above was introduced in this study.

In summary, the model generalization for gas adsorption on coals was performed in the following sequence:

1. Parameter C was calculated using Equation (10), where generalized $C_{a,o}$ and d as shown in Table 5, Case 2, were applied. The surface area, A , was optimized for each coal.
2. The fluid-solid energy parameter, e_{is}/k , was calculated using Equation (13), where the distance between a molecule and surface plane, z , was optimized for each coal, and the correction j_c was optimized for a specific adsorbate-coal system. The solid-solid energy parameter, e_{cc}^* / k , was set at 40 K.

3. The correction γ_f was generalized by the following contribution method:

$$\mathbf{x}_f = R_{VC}(ax_O + bx_H + cx_N + dx_S + e) \quad (17)$$

where R_{VC} is the ratio of the volatile to the fixed carbon contents (on dry basis) and x_O , x_H , x_N and x_S are the oxygen, hydrogen, nitrogen and sulfur contents in the coals (on dry basis), respectively.

Many researchers have tried to correlate the gas adsorption capacity in terms of the carbon contents or the ratio of the volatile to the fixed carbon content and the oxygen content (Moffat and Weale, 1955, Toda et al., 1970, Joubert et al., 1974, Levy et al., 1997, McCutcheon et al., 2003). Their hypothesis is that the chemical contents of the coal might produce specific available surface area of the coal. However, the chemical contents also reflect the types of functional group attached in carbon matrices, which affect the fluid-solid interaction energy. We do not evaluate the chemical contents effect on the surface area, and the surface area is regressed in this study. However, we used an empirical correlation shown by Equation (17) to account for the effect of chemical content on the fluid-solid interaction energy.

Our pure-gas adsorption data on activated carbon, Fruitland coal, Lower Basin (LB) Fruitland coal and Illinois #6 coal were employed to evaluate the correction function in Equation (17). Because of the limited available data, only three factors in Equation (17) were considered in the evaluation, i.e. the ratio of the volatile-to-the-fixed carbon contents, the oxygen content and the hydrogen content (the coefficients c and d are assumed zero). Regression results yielded the coefficients in Equation (17) as: $a =$

0.141, $b = 0$, $e = 0.075$ for CO₂; $a = 0$, $b = 0.166$, $e = 0.033$ for methane; and all coefficients are zero for nitrogen.

Tables 8 and 9 show the parameters used in the generalized OK model for pure-gas adsorption on wet and dry coals. The generalized OK model can represent the data with about 5.3% AAD and 3.0% AAD for the gas adsorption on wet coals and dry coals, respectively. Figures 14-17 show the comparison of the two-parameter OK model representations and generalized OK model predictions for gas adsorption on wet coals (Figure 14-16) and CO₂ adsorption on dry coals (Figure 17). As shown in the figures, the generalized model can predict the data almost as well as the two-parameter model does. Larger deviations, however, are obtained for the CO₂ adsorption in the region above 8 MPa. The low-sorbing nature of coal and the high uncertainty of the CO₂ bulk density may have amplified the deviations in this region. The possibility of coal swelling when CO₂ is adsorbed at high pressure might also contribute to this large deviation.

Pure-gas adsorption on Tiffany coal at 327.6 K was used to validate this generalized OK model. Figure 18 shows the generalized OK model prediction of our gas adsorption measurements on Tiffany coal. The surface area, $A=100 \text{ m}^2/\text{g}$, and the distance between a molecule and surface plane, $z = 1.29s_{ic}$, are obtained from the best fit for the CO₂ adsorption. Then, using this information and the generalized $C_{a,o}$, δ and γ_f , the nitrogen and methane gas adsorption isotherms are predicted. As shown in this figure, the gas adsorption on coal can be predicted using the generalized OK model within the expected experimental uncertainties.

Application of the generalized model to our recent CO₂ adsorption on wet Illinois #6 Argonne Coal, however, gave marginal results. About 11 % AAD was obtained using

this generalized model. Specifically, the generalized model over-predicted the fluid-solid energy parameter, which resulted in high estimates for the predicted Gibbs adsorption at lower pressures. These results suggest that the water effect on the fluid-solid energy parameter is more complicated than that shown in Equation (17). As stated earlier, the adsorption on the wet substrate should be treated as a multicomponent adsorption, where water is an adsorbed component. Further study on the modeling of water effect on adsorption is needed. To support this study, additional data for other adsorbates (methane and nitrogen) on wet coals at water contents less than equilibrium moisture value are needed. In addition, the measurement of pure-water adsorption on the dry coals might be needed.

Summary

We have shown in this study that the OK monolayer model appears effective in modeling pure-gas adsorption on carbon matrices. On average, the OK model with two regressed parameters (one common e_{is}/k for each system, and individual C for each isotherm) can represent the adsorption on activated carbon with about 3.6% AAD. Specifically, for the OSU adsorption data set, the two-parameter OK model is capable on average of representing the data within their experimental uncertainties. The adsorbed-phase density and the fluid-fluid energy parameters in the OK model can be estimated from the reciprocal van der Waals co-volume and from a proportional relation to the well depth of the Lennard-Jones 12-6 potential, respectively.

Generalization of the model parameters was performed using adsorbent surface area and adsorbates physical properties. The results show that the generalized OK model can predict the adsorption isotherms on activated carbon with about 7% AAD or twice

the deviation of the two-parameter OK model. Moreover, the model can also predict the other gas adsorption isotherms based on the parameters (surface area and the solid-solid energy, e_{cc}^* / k) obtained from one gas at given temperature.

The generalized OK model also appears effective for pure-gas adsorption on wet coals when the moisture content in the coal is above its equilibrium moisture content (EMC). The model parameters in this condition, however, are affected by the presence of water. Moreover, the generalized model was unable to predict the adsorption on wet coal, which has moisture content less than its EMC. These results suggest that the water effect on the fluid-solid energy parameter is more complicated than that shown in the generalized model. Furthermore, the adsorption on the wet substrate should be treated as a multi-component adsorption, where water is recognized as one of the adsorbed components. Further study on the modeling of water effect on adsorption, however, needs additional data for other adsorbates (methane and nitrogen) on dry coals and wet coals with water contents less than their equilibrium moisture value.

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Table 1. Comparison of Monolayer and Multilayer Modeling Results for Selected Systems

Model Parameters	AC (OSU, 2002)			AC (Humayun, 2000)	Dry Illinois #6 Coal
	Nitrogen	Methane	CO ₂	CO ₂	CO ₂
Monolayer Model					
ϵ_{is}/k (K)	-1032	-1385	-1690	-1610	-1170
ϵ_{ii}/k (K)	41	64	82	100	60
ρ_{mc} (g/cc)	0.67	0.34	0.98	0.98	0.95
C (mmol/g)	2.72	3.26	4.53	5.27	1.19
NPTS	22	18	52	28	11
% AAD	0.3	0.6	2.8	4.3	2.9
WAAD	0.3	0.6	0.9	0.8	0.7
Three-layer Model					
ϵ_{is}/k (K)	-1020	-1380	-1650	-1570	-1160
ϵ_{ii}/k (K)	50	64	82	110	70
ρ_{mc} (g/cc)	0.67	0.40	1.02	0.99	0.98
C (mmol/g)	2.81	3.20	4.58	5.45	1.23
NPTS	22	18	52	28	11
% AAD	0.3	0.6	3.4	4.3	3.0
WAAD	0.3	0.7	1.0	0.8	0.6

Table 2. Adsorbed-Phase Densities Estimated by Different Methods

Method	Adsorbed-Phase Density (g/cm ³)		
	Methane	Nitrogen	CO ₂
Ono-Kondo model	0.345	0.673	0.977
Zhou-Gasem-Robinson (ZGR) EOS	0.345	0.839	0.982
Liquid density estimate	0.421	0.808	---
Solid density estimate	---	---	1.18
Reciprocal van der Waals covolume	0.374	0.725	1.03
Graphical estimate from the Gibbs adsorption	---	---	1.02

Table 3. Results of Two-Parameter OK Model for Pure-Gas Adsorption

System No.	Adsorbent	Adsorbent Surface Area (m ² /g)	Gas	NPTS	T (K)	Parameters		%AAD	RMSE (mmol/g)	Reference
						- e _{is} /k (K)	C (mmol/g)			
1	AC, Columbia Grade L	1152	N ₂	36	310.9 338.7 366.5 394.3 422.0	1090	3.071 2.947 2.724 2.583 2.756	3.1	0.015	Ray (1950)
2	AC, Columbia Grade L	1152	CH ₄	45	310.9 338.7 366.5 394.3 422.0	1410	3.692 3.546 3.217 2.847 2.737	2.6	0.049	Ray (1950)
3	AC, Columbia Grade L	1152	C ₂ H ₆	58	310.9 338.7 366.5 394.3 422.0 449.8 477.6	2190	3.574 3.147 2.865 2.706 2.434 2.381 2.159	4.4	0.145	Ray (1950)
4	Charcoal	1157	CH ₄	55	283.2 293.2 303.2 313.2 323.2	1330	5.037 4.834 4.710 4.521 4.332	1.2	0.051	Payne (1968)

Table 3. Results of Two-Parameter OK Model for Pure-Gas Adsorption (Continued)

System No.	Adsorbent	Adsorbent Surface Area (m ² /g)	Gas	NPTS	T (K)	Parameters		%AAD	RMSE (mmol/g)	Reference
						- e _{is} /k (K)	C (mmol/g)			
5	Charcoal	1157	C ₃ H ₈	52	293.2 303.2 313.2 323.2 333.2	2490	3.774 3.662 3.592 3.486 3.375	6.7	0.200	Payne (1968)
6	AC, BPL	988	CH ₄	72	212.7 260.2 301.4	1320	4.515 3.880 3.279	3.1	0.112	Reich (1980)
7	AC, BPL	988	CO ₂	60	212.7 260.2 301.4	1520	9.753 6.344 5.110	4.9	0.325	Reich (1980)
8	AC, BPL	988	C ₂ H ₆	49	212.7 260.2 301.4	2000	4.090 3.588 3.157	6.3	0.318	Reich (1980)
9	AC, BPL	988	C ₂ H ₄	52	212.7 260.2 301.4	1935	4.387 3.758 3.281	4.5	0.234	Reich (1980)
10	AC, PCB-Calgon	1150-1250	CH ₄	22	296 373 480	1380	3.994 3.191 2.547	3.2	0.066	Ritter (1987)
11	AC, PCB-Calgon	1150-1250	CO ₂	12	296 373 480	1600	6.123 4.170 2.910	4.6	0.230	Ritter (1987)

Table 3. Results of Two-Parameter OK Model for Pure-Gas Adsorption (Continued)

System No.	Adsorbent	Adsorbent Surface Area (m ² /g)	Gas	NPTS	T (K)	Parameters		%AAD	RMSE (mmol/g)	Reference
						- e _{is} /k (K)	C (mmol/g)			
12	AC, F30/470 Chemviron Carbon	993.5	CO ₂	164	278	1625	5.741	1.2	0.138	Berlier (1997)
					288		5.620			
					298		5.341			
					303		5.326			
					308		5.143			
					318		4.808			
					328		4.598			
13	AC, Norit R1 Extra	1450	N ₂	10	298	1050	3.409	3.3	0.021	Dreisbach (1999)
14	AC, Norit R1 Extra	1450	CH ₄	12	298	1390	4.335	3.3	0.124	Dreisbach (1999)
15	AC, Norit R1 Extra	1450	CO ₂	12	298	1600	6.773	9.5	0.267	Dreisbach (1999)
16	AC, Coconut Shell	3106	CH ₄	122	233	1140	11.650	3.0	0.237	Zhou (2000)
					253		11.221			
					273		10.578			
					293		9.926			
					313		9.301			
					333		8.647			
17	AC, Calgon F-400	850	CO ₂	116	303.6	1700	4.847	8.8	0.306	Humayun (2000)
					305.2		4.843			
					309.2		4.667			
					313.2		4.530			
					318.2		4.443			

Table 3. Results of Two-Parameter OK Model for Pure-Gas Adsorption (Continued)

System No.	Adsorbent	Adsorbent Surface Area (m ² /g)	Gas	NPTS	T (K)	Parameters		%AAD	RMSE (mmol/g)	Reference
						- e _{is} /k (K)	C (mmol/g)			
18	AC, Norit RB1	1100	CH ₄	64	304.9 311.4 331.3 350.5	1480	3.731 3.171 3.024 2.875	1.5	0.030	Vaart (2000)
19	AC, Norit RB1	1100	CO ₂	64	305.2 311.2 329.5 348.3	1655	5.839 4.788 4.301 3.884	1.7	0.060	Vaart (2000)
20	AC, Coconut Shell	3106	N ₂	71	178 198 218 233 258 278 298	880	11.026 10.664 9.823 9.000 8.537 7.703 7.424	1.5	0.162	Zhou (2001)
21	AC F30/470	993.5	N ₂	116	303 323 343 363 383	1135	2.617 2.457 2.284 2.134 2.008	2.0	0.044	Frère (2002)
22	AC F30/470	993.5	CH ₄	122	303 323 343 362 383	1395	3.625 3.420 3.207 2.987 2.809	2.2	0.094	Frère (2002)

Table 3. Results of Two-Parameter OK Model for Pure-Gas Adsorption (Continued)

System No.	Adsorbent	Adsorbent Surface Area (m ² /g)	Gas	NPTS	T (K)	Parameters		%AAD	RMSE (mmol/g)	Reference
						- e _{is} /k (K)	C (mmol/g)			
23	AC F30/470	993.5	C ₃ H ₈	102	303 323 343 363 383	2550	3.045 2.877 2.802 2.654 2.487	2.3	0.173	Frère (2002)
24	AC Norit R1	1262	N ₂	31	298	1070	3.655	1.5	0.035	Beutekamp (2002)
25	AC Norit R1	1262	CO ₂	29	298	1500	7.513	3.6	0.269	Beutekamp (2002)
26	Zeolite, Linde 13X	525	N ₂	24	298 323 348	1185	1.627 1.480 1.329	2.2	0.042	Wakasugi (1981)
27	Zeolite, Linde 5A	~400	N ₂	27	298 323 348	1310	1.525 1.403 1.284	1.3	0.032	Wakasugi (1981)
28	Zeolite, Linde 5A	~400	CH ₄	28	298 323 348	1600	1.559 1.449 1.336	2.7	0.048	Wakasugi (1981)
29	Zeolite, Linde 5A	~400	CO ₂	41	298 323 348	2500	2.136 2.060 1.990	5.6	0.317	Wakasugi (1981)
30	Zeolite, Linde 5A	~400	C ₂ H ₆	27	298 323 348	2600	1.158 1.098 1.023	2.1	0.051	Wakasugi (1981)
31	H-Modernite, Z-900H	~300	CO ₂	93	283 303 323	2600	1.634 1.548 1.434	11.2	0.090	Talu (1986)

Table 3. Results of Two-Parameter OK Model for Pure-Gas Adsorption (Continued)

System No.	Adsorbent	Adsorbent Surface Area (m ² /g)	Gas	NPTS	T (K)	Parameters		%AAD	RMSE (mmol/g)	Reference
						- e _{is} /k (K)	C (mmol/g)			
32	H-Modernite, Z-900H	~300	H ₂ S	69	283 303 338 368	3550	2.108 1.998 1.847 1.734	2.2	0.032	Talu (1986)
33	H-Modernite, Z-900H	~300	C ₃ H ₈	92	283 303 324	3150	0.618 0.603 0.562	7.2	0.045	Talu (1986)
34	Zeolite G5	430	CH ₄	51	283 303	1200	3.352 3.100	3.9	0.055	Berlier (1995)
35	Zeolite G5	430	C ₂ H ₆	40	283 303	2525	1.699 1.620	1.3	0.044	Berlier (1995)
36	Zeolite G5	430	C ₂ H ₄	34	283 303	2630	1.923 1.798	1.1	0.048	Berlier (1995)
37	Zeolite 13X	383	CH ₄	12	298	1500	1.699	9.8	0.131	Beuterkamp (2002)
38	Zeolite 13X	383	C ₂ H ₆	11	298	2380	1.575	2.1	0.062	Beuterkamp (2002)
47	AC, Calgon F-400	850-998	N ₂	22	318.2	1060	2.577	0.4	0.012	OSU (2001)
48	AC, Calgon F-400	850-998	CH ₄	40	318.2	1385	3.164	1.4	0.064	OSU (2001)
49	AC, Calgon F-400	850-998	CO ₂	52 10	318.2 328.2	1710	4.500 4.259	4.4 3.8	0.222 0.206	OSU (2001)
50	AC, Calgon F-400	850-998	C ₂ H ₆	21	318.2	2135	2.835	6.4	0.153	OSU (2001)
Overall				2243				3.6		

Table 4. Physical Properties of the Adsorbates ^a and Active Sites

Adsorbate	MW	Pc (MPa)	Tc (K)	Normal Boiling Point (K)	Reciprocal van der Waals co-volume (mol/L)	S (x10 ⁻¹⁰ m)	e [*] /k (K)
H ₂	2.02	1.31	33.19	20.4	38.16	2.827	59.7
N ₂	28.01	3.40	126.20	77.3	25.89	3.798	71.4
H ₂ S	34.08	8.96	373.53	212.8	23.08	3.623	301.1
CO ₂	44.01	7.38	304.21	216.6 ^b	23.34	3.941	195.2
CH ₄	16.04	4.60	190.56	111.7	23.37	3.758	148.6
C ₂ H ₄	28.05	5.04	282.34	169.4	17.39	4.163	224.7
C ₂ H ₆	30.07	4.87	305.32	184.6	15.41	4.443	215.7
C ₃ H ₈	44.10	4.25	369.83	231.1	11.07	5.118	237.1
i- C ₄ H ₁₀	58.12	3.65	408.14	261.4	8.60	5.278	330.1
C						3.4 ^c	28 ^c
O(Zeolite)						3.04 ^d	139.96 ^d

^a Reid (1987)

^b Triple point temperature

^c Steele (1974)

^d Mellot (1996)

Table 5. Description of the Cases Studied in Model Generalization

Case No	Description	Overall %AAD
1	Based on reported surface area, A $C_{a,o}$ and δ are regressed for specific adsorbate ϵ_{cc}/k is regressed for specific activated carbon	7.25
2	Based on reported surface area, A Generalized $C_{a,o}$ and δ : For CO ₂ : $C_{a,o} = 0.0142 \text{ mmol/m}^2$; $\delta = 0.0039 \text{ (K}^{-1}\text{)}$ For other component: $C_{a,o} = 0.102/\sigma^2 + 0.0034$; σ in Å $\delta = 0.0024 \text{ (K}^{-1}\text{)}$ $\epsilon_{cc}/k \text{ (K)}$ is obtained from Case 1 (varied from 38 to 43)	7.33
3	Based on reported surface area, A Generalized $C_{a,o}$ and δ : For CO ₂ : $C_{a,o} = 0.0142 \text{ mmol/m}^2$; $\delta = 0.0039 \text{ (K}^{-1}\text{)}$ For other component: $C_{a,o} = 0.102/\sigma^2 + 0.0034$; σ in Å $\delta = 0.0025 \text{ (K}^{-1}\text{)}$ $\epsilon_{cc}/k \text{ (K)} = 40$	7.44
4	Surface area, A , is regressed Generalized $C_{a,o}$ and δ : For CO ₂ : $C_{a,o} = 0.0142 \text{ mmol/m}^2$; $\delta = 0.0039 \text{ (K}^{-1}\text{)}$ For other component: $C_{a,o} = 0.102/\sigma^2 + 0.0034$; σ in Å $\delta = 0.0023 \text{ (K}^{-1}\text{)}$ $\epsilon_{cc}/k \text{ (K)}$ is obtained from Case 1 (varied from 38 to 43)	6.34
5	Surface area, A , is regressed Generalized $C_{a,o}$ and δ : For CO ₂ : $C_{a,o} = 0.0142 \text{ mmol/m}^2$; $\delta = 0.0039 \text{ (K}^{-1}\text{)}$ For other component: $C_{a,o} = 0.102/\sigma^2 + 0.0034$; σ in Å $\delta = 0.0023 \text{ (K}^{-1}\text{)}$ $\epsilon_{cc}/k \text{ (K)} = 40$	7.00

Table 6. Parameters Used in Case 1 of Model Generalization

Component	$C_{a,o}$ (mmol/m ²)	d (K ⁻¹)	e_{cc}/k (K)
N ₂	0.0105	0.0024	38 - 43
CH ₄	0.0106	0.0024	
C ₂ H ₄	0.00945	0.0024	
C ₂ H ₆	0.00831	0.0024	
C ₃ H ₈	0.00735	0.0024	
CO ₂	0.0142	0.0039	
Activated Carbon			

Table 7. Results of Two-Parameter OK Model for Pure-Gas Adsorption on Coals

System No.	Adsorbent	Adsorbate	NPTS	T (K)	Parameters		%AAD	RMSE (mmol/g)	WAAD
					$-e_{is}/k$ (K)	C (mmol/g)			
55a	Wet Fruitland Coal #1	N ₂	20	319.3	610	0.572	1.3	0.005	0.2
56a	Wet Fruitland Coal #1	CH ₄	20	319.3	990	0.650	0.8	0.004	0.2
57a	Wet Fruitland Coal #1	CO ₂	14	319.3	1340	0.853	5.1	0.091	0.5
55b	Wet Fruitland Coal #2	N ₂	20	319.3	575	0.495	1.8	0.004	0.2
56b	Wet Fruitland Coal #2	CH ₄	20	319.3	960	0.663	0.8	0.005	0.4
57b	Wet Fruitland Coal #2	CO ₂	20	319.3	1280	0.887	6.7	0.087	0.7
61	Wet Illinois #6 Coal	N ₂	20	319.3	450	0.331	2.4	0.002	0.2
62	Wet Illinois #6 Coal	CH ₄	20	319.3	780	0.468	1.7	0.005	0.3
63	Wet Illinois #6 Coal	CO ₂	20	319.3	1100	0.735	3.2	0.033	0.5
67	Wet Tiffany Coal	N ₂	21	327.5	530	0.287	3.3	0.003	0.4
68	Wet Tiffany Coal	CH ₄	22	327.5	930	0.356	3.4	0.012	0.6
69	Wet Tiffany Coal	CO ₂	16	327.5	1385	0.433	4.2	0.022	0.6
74	Wet LB Fruitland Coal	N ₂	16	319.3	530	0.213	4.3	0.004	0.4
75	Wet LB Fruitland Coal	CH ₄	16	319.3	815	0.327	2.6	0.007	0.5
76	Wet LB Fruitland Coal	CO ₂	29	319.3	1300	0.354	5.4	0.023	0.6
77	Dry Illinois #6 Coal	CO ₂	11	328	1250	1.204	5.1	0.067	0.9
78	Dry Beulah Zap Coal	CO ₂	22	328	1375	1.3540	3.3	0.071	0.5
79	Dry Wyodak Coal	CO ₂	11	328	1270	1.5039	2.9	0.064	0.5
80	Dry Upper Freeport Coal	CO ₂	11	328	1480	0.6768	2.2	0.026	0.4
81	Dry Pocahontash Coal	CO ₂	11	328	1540	0.7979	1.8	0.023	0.3
Overall			360				3.1		0.5

Table 8. Summary Results for the OK Model of Pure-Gas Adsorption on Wet Coals

Model Parameters	Pure-Gas Adsorbed		
	Methane	Nitrogen	CO ₂
<i>Wet Fruitland Coal ($f_c=0.97$)</i>			
A (m ² /g)	194		
z	1.296 s_{ic}		
NPTS	20	20	20
% AAD	3.2	4.8	8.5
RMSE (mmol/g)	0.019	0.013	0.087
<i>Wet Illinois #6 Coal ($f_c=0.97$)</i>			
A (m ² /g)	150		
z	1.448 s_{ic}		
NPTS	20	20	20
% AAD	2.6	4.4	3.5
RMSE (mmol/g)	0.008	0.004	0.037
<i>Wet LB Fruitland ($f_c=0.95$)</i>			
A (m ² /g)	77		
z	1.296 s_{ic}		
NPTS	16	16	29
% AAD	4.9	6.4	8.3
RMSE (mmol/g)	0.019	0.007	0.036

Table 9. Summary Results for the OK Model of CO₂ Adsorption on Dry Coals

Model Parameters	Beulah Zap	Wyodak	Illinois #6	Upper Freeport	Pocahontas
A (m ² /g)	298	332	251	149	177
z	1.657 s_{ic}	1.653 s_{ic}	1.530 s_{ic}	1.277 s_{ic}	1.163 s_{ic}
NPTS	22	11	11	11	11
% AAD	3.3	2.9	4.4	2.5	1.8
RMSE (mmol/g)	0.068	0.058	0.062	0.025	0.024

Figure 1. Comparison of Monolayer and Three-Layer OK Model Representations of Pure-Gas Adsorption on Activated Carbon

Figure 2. Comparison of Monolayer and Three-Layer OK Model Representations of Pure CO₂ Adsorption on Illinois #6 Coal

Figure 3. Graphical Method for Estimating Adsorbed-Phase Density: CO₂ Adsorption on Activated Carbon at 318.2 K

Figure 4. Deviation Plot for Two-Parameter OK Model Representations of Gas Adsorption on Activated Carbon

Figure 5. OK Model Representations of Gas Adsorption on Norit R1 Extra Activated Carbon at 298 K (Dreisbach, 1999)

Figure 6. OK Model Representations of Methane Adsorption on Activated Carbon (Zhou, 2000)

Figure 7. Temperature Dependence of the Maximum Adsorption Capacity, C , (Reich, 1980)

Figure 8. Correlation of the Maximum Adsorption Capacity, C , with Surface Area at Constant Temperature

Figure 9. Variation of the Maximum Surface Adsorbed-Phase Density, $C_{a,o}$, with the Diameter of the Molecules, σ

Figure 10. Deviation Plot for the Generalized OK Model Predictions of Gas Adsorption on Activated Carbon

Figure 11. Comparison of the Generalized Predictions and two-Parameter OK Model Representations of Methane Adsorption on Activated Carbon (Frere, 2000)

Figure 12. OK Model Predictions of Gas Adsorption on Activated Carbon at 318.2 K (OSU, 2000)

Figure 13. Molecule Positions in the Slit of the Activated Carbon and Coal

Figure 14. OK Model Representations of Nitrogen Adsorption on Wet Coals at 319.3 K

Figure 15. OK Model Representations of Methane Adsorption on Wet Coals at 319.3 K

Figure 16. OK Model Representations of CO₂ Adsorption on Wet Coals at 319.3 K

Figure 17. OK Model Representations of CO₂ Adsorption on Dry Coals at 328.2 K

Figure 18. OK Model Predictions of Pure-Gas Adsorption on Wet Tiffany Coal at 327.6 K

Ono-Kondo Lattice Model for High-Pressure Mixture Adsorption

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Abstract

Theoretically-based models for adsorption behavior are needed to develop optimal strategies for enhanced coalbed methane (CBM) recovery operations. Although a number of frameworks are available for describing the adsorption phenomenon, the Ono-Kondo (OK) lattice model offers several practical advantages in modeling supercritical, high-pressure adsorption systems.

Our recent studies have indicated that the OK lattice model has the capability to represent high-pressure, pure-gas adsorption data. The goal of the present work is to extend the OK framework to mixture predictions. Specifically, the OK model parameters obtained from pure-gas adsorption were used to predict gas mixture adsorption for selected multicomponent adsorption systems. Binary interaction parameters (BIP) were used to improve the model representations to within the expected experimental uncertainties.

The results indicate that the OK model can be used to (a) predict binary gas adsorption within twice the experimental uncertainties on average, and to (b) represent total and individual adsorptions to within the expected experimental uncertainties with the use of one binary interaction parameter, C_{ij} . In addition, improved representations were obtained when two binary interaction parameters (C_{ij} and E_{ij}) were applied, as indicated by a significant reduction in the average weighted error.

Keywords: Adsorption, Mixture, High-Pressure, Coalbed Methane, OK Lattice Model

Introduction

Our recent studies have indicated that the Ono-Kondo (OK) lattice model has the capability to represent high-pressure, pure-gas adsorption data. The goal of the present work is to extend the OK framework to mixture predictions. Specifically, we have:

1. Derived a general equilibrium equation for monolayer, random mixed-gas adsorption
2. Evaluated the predictive capability, where the OK model parameters obtained from pure-gas adsorption are used to predict gas mixture adsorption for selected multicomponent adsorption systems,
3. Evaluated the predictive capability of the model, where binary interaction parameters (BIP) are used to examine the model representation of the mixture data.

The model development/evaluation was conducted using our newly-acquired data and data from the literature.

As in the modeling of the pure adsorption, we first performed studies on dry activated carbon matrices, followed by the studies on wet coals. Data in the literature on high-pressure multicomponent gas adsorption, however, are not as plentiful as for pure fluids. Thus, the following mixture adsorption data on activated carbon were selected for the model evaluation:

1. Mixture adsorption of methane, nitrogen and CO₂ on Calgon F-400 activated carbon at 318.2 K (Sudibandriyo, 2003).
2. Mixture adsorption of methane, nitrogen and CO₂ on Norit R1-Extra activated carbon at 298 K (Dreisbach et. al., 1999).

3. Mixture adsorption of methane, ethane, and ethylene on BPL activated carbon at 301.4 K (Reich et. al., 1980).

A few experimental studies have examined high-pressure multi-component gas adsorption on coals (Arri et. al., 1992, DeGance, 1992; Harpalani and Pariti, 1993; Greaves et. al., 1993; Clarkson and Bustin, 2000). Limited information, however, was given on the experimental data in most of those references. Therefore, we decided to use only OSU mixture adsorption measurements on various wet coals for model evaluation.

Ono-Kondo Lattice Model for Mixture Adsorption

A general equilibrium equation for monolayer, random mixed-gas adsorption was derived as:

$$\ln \frac{x_i (1 - \sum_{j=1}^n x_{j,b})}{x_{i,b} (1 - \sum_{j=1}^n x_j)} + \sum_{j=1}^n \frac{e_{ij}}{kT} [z_1 + 1] x_j - z_0 x_{j,b} + \frac{e_{is}}{kT} = 0 \quad (1)$$

In this equation, x_i is the reduced density or fraction of sites occupied by adsorbed molecules i , and $x_{i,b}$ is the fraction of sites occupied by fluid molecules i in the gas phase. For a hexagonal configuration of lattice cells, the coordination numbers z_0 and z_1 are 8 and 6, respectively; and by definition, $z_2 = (z_0 - z_1)/2$. The fluid-fluid interaction energy is expressed by e_{ij}/kT , and the fluid-solid surface interaction energy is expressed by e_{is}/kT , where k is Boltzmann's constant, and T is the absolute temperature.

A geometric combination rule was used to evaluate the interaction energy between molecule i and j ; i.e.: $e_{ij} = (1 + C_{ij}) \sqrt{e_{ii} e_{jj}}$. Here, a regressed binary interaction

parameter C_{ij} was introduced to account for unlike molecular interactions, which deviate from the geometric mean relation.

The Gibbs excess adsorption for each component was calculated using the following expression:

$$G_i = 2C_i(x_i - x_{i,b}) \quad (2)$$

The fractional coverage in the bulk-phase, $x_{i,b}$ was obtained from the following equation

$$x_{i,b} = \frac{y_i \mathbf{r}_b}{\mathbf{r}_{mc}} \quad (3)$$

where the bulk density, $\mathbf{r}_b$, was calculated using the Benedict-Webb-Rubin (BWR) equation of state (see e.g., Bishnoi, 1972). Since little information is known about the mixture adsorbed phase density, the maximum density, ρ_{mc} , was estimated using the following ideal mixing rules:

$$\frac{1}{\mathbf{r}_{mc}} = \frac{x_A^{Abs}}{\mathbf{r}_{mc,A}} + \frac{x_B^{Abs}}{\mathbf{r}_{mc,B}} \quad (4)$$

The absolute adsorbed phase mole fractions, x_A^{Abs} and x_B^{Abs} are used in this equation.

A correction factor was introduced to calculate the Gibbs adsorption for each component, considering that the maximum capacity of a component might be different for pure and mixture adsorption. In this case, Equation (2) was modified as:

$$G_i = 2C_i(x_i - x_{i,b}) C_{corr} \quad (5)$$

The correction factor was evaluated through the following empirical expression:

$$C_{corr} = \sum_i^n \sum_j^n x_i^{Abs} x_j^{Abs} E_{ij} \quad (6)$$

Additional regressed binary interaction parameter, E_{ij} , is introduced in this expression, in which $E_{ii} = E_{jj} = 1$.

Iteration Function Method (IFM)

In general, the Gibbs excess adsorption can be calculated using a model if the pressure, temperature and the equilibrium composition in the gas phase are known. In our previous study (Sudibandriyo et. al., 2003), the equilibrium mole fraction in the gas phase is obtained from the experimental adsorption data. Although the gas composition obtained from the experiment is adequate to calculate the individual Gibbs excess adsorption, error in the gas composition measurement can worsen the model representation. Moreover, using the experimental gas compositions can only permit Gibbs adsorption calculations at the conditions where the experiment measurements are available. In addition, in coalbed methane production simulation, the overall gas composition information is more readily obtained than the equilibrium gas composition. To overcome these problems, the iteration function method, which is similar to a flash calculation in vapor-liquid equilibrium, is used to determine the adsorption equilibrium gas mole fraction for given pressure, temperature, feed composition and specific void volume (void volume per unit amount of adsorbent) of the system.

If z_i represents the mole fraction of each component (i) in the feed, then by a molar balance, we can express z_i in terms of the other experimentally accessible variables as:

$$z_i = \frac{(n_{Gibbs})_i + V_{void} \mathbf{r}_b y_i}{n_{Gibbs}^{total} + V_{void} \mathbf{r}_b} \quad (7)$$

The component Gibbs adsorption is first calculated using the OK model of Equations (1) and (2). The solution, however, is contingent on equilibrium mole fractions, y_i , as they are needed to calculate the gas density using the BWR EOS and to calculate the individual fractional coverage in the bulk-phase, $x_{i,b}$, as defined in Equation (3). The gas mole fractions were initialized with the available experimental values to speed the calculation (although any reasonable initial values could be used).

The next step is to evaluate Equation (7) for each component. If Equation (7) is not satisfied for each component, then a new set of equilibrium mole fractions is used to calculate the next trial adsorbed amount. The procedure is repeated until Equation (7) is satisfied. The Newton-Raphson's method with numerical derivatives was used to solve Equation (7).

Modeling Mixed-Gas Adsorption on Dry Activated Carbon

Methane, Nitrogen and CO₂ Mixture Adsorption on Calgon F-400 (OSU Data)

Our measurements on pure and mixture adsorption of methane, nitrogen and CO₂ on activated carbon at 318.2 K and pressures to 13.6 MPa were used to evaluate the OK modeling capability. The experimental data are given in a recent publication (Sudibandriyo et. al., 2003) and also documented in a DOE Report (Gasem et.al., 2002). The binary mixture adsorption includes methane/CO₂, nitrogen/CO₂, and methane/nitrogen at nominal molar feed gas compositions of 20, 40, 60 and 80% with a specific void volume ranging from 2.04-2.57 cm³/g. Adsorption isotherms were also measured for a single methane/nitrogen/CO₂ ternary mixture at the nominal molar feed composition was 10/40/50 with a specific void volume of 2.10 cm³/g.

Because adsorption calculations are very sensitive to inaccuracies in experimental mole fraction, in general, using the “iteration function method” (IFM) to predict the gas composition, gives better results than using the experimental gas compositions. Therefore, in this study, we only present the results based on the iteration function method. The sum of squares of weighted absolute errors in the calculated adsorption was selected for the objective function to determine the binary interaction parameters.

Evaluation of the pure adsorption has been conducted in study of the Ono-Kondo lattice model for high-pressure pure-gas adsorption, and the OK model parameters used to fit the pure adsorption data were given in that study (Section K-VI of Page 172).

Table 1 presents the results of the OK model predictions for binary mixture adsorption on dry activated carbon. The results are based solely on parameters from fits to pure component data ($C_{ij}=0$). On average, the OK model can predict the binary adsorption data with about 1.6 times the expected experimental uncertainties. The OK model can predict the total and the more-adsorbed component adsorptions within 7.5% AAD. Although the RMSE is small, the percentage deviation for the lesser-adsorbed component adsorptions is large as the Gibbs excess adsorption becomes exceedingly small. For example, in the nitrogen/CO₂ system, 81% AAD and 0.20 mmol/g RMSE were obtained for nitrogen adsorption, compared to 7.5% AAD and 0.33 mmol/g RMSE for total adsorption in the same system. However, worse results were generally obtained for the predictions of the lesser-adsorbed component adsorptions, as indicated by larger WAAD (up to 3.5 for nitrogen adsorption in nitrogen/CO₂ system).

Here, we evaluate the capability of the generalized pure adsorption model described in the previous study to predict mixture adsorption. Accordingly, pure-

adsorption model parameters based on the generalized model were used for mixture adsorption predictions. The results presented in Table 1 show that slightly better predictions are obtained than those based on the pure-adsorption model regressions. On average, the generalized OK model can predict the binary adsorption data with about 1.4 times the experimental uncertainties. However, using the generalized pure-component parameters results in poor predictions for the pure-component adsorption (up to three times the experimental uncertainties for methane adsorption).

Figures 1 and 2 show the OK model predictions of the individual component adsorption of methane/CO₂ system. As shown in these figures, on average, the OK model can predict the binary mixture adsorptions within twice the experimental uncertainties. In addition, the model can also predict a maximum in the Gibbs adsorption as experimentally observed for the lesser-adsorbed component.

Table 2 presents the OK model representation of binary mixture adsorption based on only one binary interaction parameter, C_{ij} , in the fluid-fluid energy parameter, e_{ij} . Significant improvement has been obtained, especially for the nitrogen component adsorption in the nitrogen/CO₂ system; specifically, a reduction in WAAD from 3.5 to 0.6 is observed with the use of one binary interaction parameter. On average, the OK model can represent the binary adsorption data with about 0.8 times the experimental uncertainties with the maximum error obtained for representing the CO₂ component adsorption in the nitrogen/CO₂ mixture, which yielded 1.4 times the expected experimental uncertainties.

The binary interaction parameters obtained, however, are relatively large ($C_{ij} = 0.658, 0.335$ and 0.198 for nitrogen/CO₂, methane/CO₂ and methane/nitrogen system,

respectively). This is, at least in part, due to influence of the quadrupole moment of the CO₂ affected by the fluid-solid interaction energy. Exact calculations of this effect are complicated, but it appears that the nitrogen/CO₂ system shows more non-ideality than the other systems. Other reasons for the large C_{ij} include the inadequacy of the mixing/combining rules applied in OK model to predict binary adsorption.

The relatively large values of C_{ij} also suggest that the correlative burden of the binary adsorption modeling has mainly rested on the correction in the fluid-fluid interaction energy. For future study, application of the surface heterogeneity through the fluid-solid energy distribution should be considered, while the chemical potential in the gas phase should be calculated using an accurate equation of state.

Table 2 also presents the results when two binary interaction parameters are regressed to represent the binary mixture adsorption. As presented in Table 2, on average, the deviation obtained is about 0.5 times the experimental uncertainties. The second binary interaction parameters, E_{ij} , for methane/CO₂ and methane/nitrogen system are close to the nominal one; for nitrogen/CO₂ system, however, significant correction is needed ($E_{ij}=0.871$).

Figures 1 and 2 also show the OK representations of the individual component adsorption of methane/CO₂ system. For completeness, pure-substance adsorption is included in each figure. As shown in these figures, the OK model can represent the binary mixture adsorptions very well within the experimental uncertainties, as indicated by the error bars in the figures.

Figure 3 presents an example for a comparison between the gas compositions obtained from experimental measurements and the ones obtained from the IFM

calculations. The figure shows that the gas compositions obtained from IFM calculations produce an excellent fit to the experimental values. Slight deviations, however, occur at lower pressures. This might be due to a modeling deficiency or an experimental error, where the equilibrium condition may have not been reached in the earlier stages of adsorption even though the system had been allowed 24 hours to reach equilibrium.

Table 3 presents the model predictions for the ternary mixture adsorption on dry activated carbon at 318.2 K. The predictions based on pure adsorption parameters produce deviations of about 1.8 times the experimental uncertainties, on average. Larger deviations are seen for the lesser-adsorbed component adsorption; i.e. nitrogen (about three times the experimental uncertainties). Table 3 also presents the component adsorption predictions of the ternary mixture based on the pure and the binary interaction parameters (BIP) obtained from binary adsorption data. As expected, the use of binary interaction parameters not only reduces the calculated deviations for the binary systems, but also improves the predictions for the component ternary adsorption. The prediction based on pure and binary adsorption parameters produce errors of about 0.8 and 0.7 times the experimental uncertainties when using one and two binary interaction parameters, respectively. The slight difference from the two results indicates that using only one binary interaction parameter may be sufficient to represent the mixture adsorption.

Figure 4 shows the OK model predictions for the ternary mixture adsorption on activated carbon, based on pure-component data and with two binary interaction parameters from the binary adsorption data. As shown in the figure, the OK model can predict all the ternary mixture adsorptions well and within the experimental uncertainties

(represented by the error bars in the figures) when the binary interaction parameters are included.

Methane, Nitrogen and CO₂ Mixture Adsorption on Norit R1-Extra (Dreisbach, 1999)

The measurements from other investigators were used to validate the mixture adsorption model. Pure and mixture adsorption of methane, nitrogen and CO₂ on Norit R1-Extra activated carbon at 298 K (Dreisbach, 1999) were used to evaluate the OK modeling capability. Because no detailed information was given on the uncertainties of the experimental data selected, the percentage average error of the Gibbs excess adsorption (%AAD) was used for the objective function to determine the model parameters. Evaluation of the pure adsorption has been conducted in the previous study (Section K-VI of Page 172), where the OK model parameters used to fit the pure adsorption data were reported.

Also, because no detailed information was given on the feed composition and the specific void volume of the system, the IFM procedure cannot be employed in the modeling effort. In this case, the gas-phase equilibrium mole fractions obtained from the adsorption measurements were smoothed using a regressed logarithmic function, before they were used to calculate the individual Gibbs excess adsorption.

Table 4 presents the prediction of binary mixture adsorption on dry Norit R1-Extra activated carbon at 298 K based on pure component parameters. As presented in the Table, the OK model can predict the total adsorption data within 6% AAD (about 0.4 mmol/g in RMSE). However, the prediction for individual component adsorption produces only mediocre results (12 to 139% AAD or 0.18 to 0.57 mmol/g in RMSE). These unsatisfactory prediction results are, in part, due to the large uncertainties in the

equilibrium mole fractions in the gas phase data obtained from the adsorption measurements. Not unexpectedly, the worst predictions are for the nitrogen adsorption in nitrogen/CO₂ system (139% AAD). For this system, the RMSE of the nitrogen adsorption is 0.32 mmol/g, which is actually smaller than the RMSE of the total adsorption (0.36 mmol/g) with only 6% AAD. The higher %AAD in nitrogen adsorption is mainly due to its lower adsorption in this mixture.

Using the parameters based on the generalized pure adsorption model improves the individual adsorption prediction, especially the nitrogen adsorption in nitrogen/CO₂ system (38% AAD). As in the case of OSU data, however, using these generalized pure component parameters results in unsatisfactory prediction of the pure-component adsorption.

Table 5 presents the OK model representation of binary mixture adsorption based on only one binary interaction parameter, C_{ij} , in the fluid-fluid energy parameter, e_{ij} . Significant improvement from the predictive case has been obtained. The total adsorption can be represented within 6.4% AAD and the individual component adsorption can be represented with deviations from 5.7 to 17.8% AAD.

Table 5 also presents the results when two binary interaction parameters are applied to represent the binary mixture adsorption. As presented in Table 5, only slight improvement has been attained compared to the results obtained by using only one binary interaction parameter. The total adsorption can be represented with AAD from 3 to 5% and the individual component adsorption can be represented from 6 to 17% AAD.

Table 6 presents the model prediction results for the ternary mixture adsorption on dry Norit R1-Extra activated carbon. The total adsorption can be predicted based on pure

adsorption parameters to within 12% AAD. The OK model can predict the more-adsorbed component adsorptions within 18% AAD. The percentage deviations for the lesser-adsorbed component adsorptions, however, are large as the Gibbs excess adsorption becomes very small. Application of the binary interaction parameters does not appear to improve the predictions for this adsorption system. In fact, about the same magnitude of deviations were also obtained by Dreisbach (1999) for ternary adsorption predictions using a dual-site Langmuir model.

Inaccuracy in experimental gas mole fractions may have contributed to the larger deviations in the mixture adsorption predictions. In his study, Dreisbach used two different methods to obtain the bulk-phase compositions. For binary adsorption, he used an equation of state to infer both the bulk-phase composition and density from P-T measurements and system volume calibrations, while for ternary adsorption he used a gas chromatograph to measure the bulk-phase composition.

Methane, Ethane, and Ethylene Mixture Adsorption (Reich, 1980)

Zhou (1994) used data for methane, ethane, and ethylene on activated carbon at 301.4 K [Reich et al., 1980] for model comparisons. For the same reason, the OK model was also used to represent those data and compared with the modeling results obtained by Zhou.

Because no detailed information was given on the uncertainties of the experimental data selected, the percentage average error of the Gibbs excess adsorption (%AAD) was used for the objective function to determine the model parameters. Also, because no detailed information was given on the specific void volume of the system, the

IFM calculation procedure could not be employed in the modeling effort. The feed compositions are the same as the gas-phase equilibrium mole fractions in their adsorption measurements. These experimental equilibrium gas mole fractions were used to calculate the individual Gibbs excess adsorption.

Table 7 presents the comparison of models predictions and representations for mixture adsorption of methane, ethane and ethylene on dry BPL activated carbon at 301.4 K. As exhibited in the table, on average, the OK model predicts the total and more-adsorbed component adsorption very well (with 4% AAD). The model, however, is unable to provide good estimates for the lesser-adsorbed component (up to 35% AAD). For individual adsorption, the OK model prediction gives better results compared to the Langmuir model and gives comparable results to the 2-D EOS (EOS-S) model. In addition, for total adsorption predictions, the OK model has better performance than the other models (on average, the %AAD are 3.8, 6.0, and 6.4 for the OK, Langmuir and EOS-S model, respectively).

As other models do, the OK model can also predict the ethane/ethylene adsorptions very well within 6% AAD. Pure ethane and ethylene have very similar adsorption on activated carbon. Therefore, the adsorbed phase is expected to form an ideal mixture.

The use of optimum interaction parameters significantly improves the predictions of methane adsorption in the binary and ternary systems. The average deviations for methane adsorption were reduced from 35.2% to 23.8% for methane/ethane and from 33.9% to 15.2% for methane/ethylene. For the ternary system, using the binary interaction parameter obtained from binary data, the OK model reduced average

deviations in predicting the amount of methane adsorbed from 52.2 % to 39.1%. However, application of the second binary interaction parameters (E_{ij}) in these systems does not improve the mixture adsorption representations.

The binary interaction parameters for the OK model are reported in Table 8. Interestingly, negative values of C_{ij} were also obtained for these systems, as was the case of interaction parameters obtained by Zhou using a two-dimensional equation of state model (2-D EOS). As expected, only small C_{ij} ($= -0.037$) was obtained for the ethane/ethylene system.

Figures 5 and 6 show the OK model predictions and representations of the methane/ethane mixture adsorption on dry BPL activated carbon. For completeness, pure adsorption is also included in each figure. As shown in the figures, using the binary interaction parameters improves the model in representing the methane adsorption data. However, the model always underestimates the methane adsorption in the methane/ethane and methane/ethylene systems, especially at higher pressures.

Modeling of Mixed-Gas Adsorption on Coals

Data Employed

Pure and binary mixture adsorption of methane, nitrogen and CO₂ on wet Fruitland coal at 319.3 K and pressures to 12.4 MPa have been measured at OSU as documented by Hall (1993). The mixture data include methane/CO₂, nitrogen/CO₂, and methane/nitrogen adsorption isotherms at nominal molar feed gas compositions of 20, 40, 60 and 80% with a specific void volume ranging from 1.22-1.29 cm³/g and moisture content ranging from 8% to 14%.

The adsorption data on Fruitland coal reported by Hall were reanalyzed from primary PVTy measurements since the Redlich-Kwong (RK) equation of state was used to determine the gas compressibility factors. The RK predictions are inadequate in this near-critical portion of the CO₂ phase diagram. Therefore, in present data-reduction calculations, the raw measurements were reprocessed using highly-precise equations of state (Span and Wagner, 1996; Pan, 2003) to obtain the Gibbs excess adsorptions, which were used for this model evaluation.

The adsorption of pure and binary mixture adsorption of methane, nitrogen and CO₂ on wet Illinois #6 at 319.3 K and pressures to 12.4 MPa have been measured at OSU and documented in a DOE Report (Gasem et al., 2001). The mixture data include methane/CO₂, nitrogen/CO₂, and methane/nitrogen adsorption isotherms at nominal molar feed gas compositions of 20, 40, 60 and 80% with a specific void volume ranging from 1.00-1.69 cm³/g and moisture content ranging from 5% to 23%.

The low-adsorptive nature of the Illinois #6 coal makes the adsorption measurement very sensitive to the bulk-gas composition measurement, especially for the methane/CO₂, nitrogen/CO₂ systems. In this case, the gas-phase equilibrium mole fractions obtained from the adsorption measurements were smoothed using a regressed logarithmic function for methane/CO₂ system and using IFM procedure for the nitrogen/CO₂ system. The smoothed gas-phase equilibrium mole fractions were then used to reprocess the data-reduction calculations for the earlier reported data (Gasem, 2001), so as to obtain Gibbs excess adsorption isotherms.

Adsorption isotherms were measured at OSU for the methane/nitrogen, methane/CO₂ and nitrogen/CO₂ binary mixtures on wet, mixed Tiffany coal at 327.6 K

and pressures to 13.8 MPa. The coal sample was from an equal-mass mixture of coals from BP Amoco Tiffany Injection Wells #1 and #10. These measurements were conducted for a single molar feed composition for each mixture with specific void volume about 0.89 cm³/g and moisture content about 11%. Adsorption isotherms were also measured for a single methane/nitrogen/CO₂ ternary mixture on wet, mixed Tiffany coal at 327.6 K and pressures to 13.8 MPa. The nominal molar feed composition was 10/40/50 with specific void volume of 0.89 cm³/g and moisture content of 10%. The adsorption data for those measurements were documented in a DOE report (Gasem et al., 2000) and also in a topical report (Gasem et al., 2002).

Results

The IFM procedure was used for the model evaluation, and the sum of squares of weighted absolute errors in the calculated adsorption was selected for the objective function to determine the binary interaction parameters.

The model evaluation for the pure adsorption and the corresponding OK model parameters, are presented in the Section K-VI of Page 172.

Tables 9-11 present the results of the OK model adsorption predictions for the binary mixture on the wet selected coals. On average, the OK model can predict the binary adsorption data within twice the expected experimental uncertainties. However, high WAAD of 4.5 was observed for methane adsorption in the methane/CO₂ adsorption on wet Tiffany coal. It appears that the model underestimates the methane adsorption in this system, especially at higher pressures.

The OK model can predict the total and the more-adsorbed component adsorptions within 17% AAD. However, the percentage deviation for the lesser-adsorbed

component adsorptions is large as the Gibbs excess adsorption becomes exceedingly small. For example, the AAD of the nitrogen adsorption in the nitrogen/CO₂ adsorption on wet Tiffany coal reaches 156%, although the RMSE is only 0.015 mmol/g.

Tables 9 and 10 also present the results when the parameters based on a generalized pure-adsorption model were used to predict the mixture adsorption. Comparable statistical results to the case without generalization were obtained.

Tables 12-14 present the OK model representation of binary mixture adsorption using binary interaction parameters. Significant improvement has been obtained, especially for the lesser-adsorbed component adsorptions. For example, a reduction in WAAD from 4.5 to 1.0 is observed for methane component adsorption in the methane/CO₂ adsorption on wet Tiffany coal with the use of one binary interaction parameter, C_{ij} . Also, a reduction from 152 to 67 %AAD is observed for nitrogen component adsorption in nitrogen/CO₂ adsorption on wet Fruitland coal. On average, the OK model can represent the binary adsorption on wet coals data about 0.8 times the expected experimental uncertainties. Better representations were further obtained when two binary interaction parameters were applied, as indicated by a WAAD of about 0.5.

The binary interaction parameters obtained from the adsorption on Fruitland coal are similar in order to those obtained from the adsorption on dry activated carbon, i.e. C_{ij} = 0.438, 0.126 and 0.099 for nitrogen/CO₂, methane/CO₂ and methane/nitrogen system, respectively. But the binary interaction parameters obtained from the adsorption on Illinois #6 and Tiffany coals do not show similar trend to those obtained from the adsorption on dry activated carbon.

The second binary interaction parameters, E_{ij} , for most of the systems are less than the values obtained from the adsorption on dry activated carbon. This indicates that the model without interaction parameters overestimates the individual component adsorption on the wet coals. The chemical structure of the coal and the presence of water in the coal affect the predictive capability of the model. Further, separating the two factors affecting the mixture adsorption modeling would require additional data, especially mixture adsorption data on dry coals.

Figure 7 shows an example of the OK predictions and representations for the binary mixture adsorption on wet coal. For completeness, the corresponding pure-substance adsorption isotherms are included in the figure. As shown in the figure, the OK model can represent all the binary mixture adsorptions within the experimental uncertainties (represented by the error bars in the figures) when two binary interaction parameters are used.

Table 15 presents the model predictions for the ternary mixture adsorption on wet Tiffany coal. For the total adsorption in this system, the OK model can predict data within the expected experimental uncertainties (within 8.5% AAD). The predictions based on pure-adsorption parameters produce deviations about 1.5 times the expected experimental uncertainties, on average. The larger deviations are exhibited by the lesser-adsorbed component adsorption; i.e., nitrogen (about 2.6 times the experimental uncertainties). The ternary mixture adsorption predictions based on the pure and the binary interaction parameters (BIP) obtained from binary adsorption data were also presented in Table 15. As the case for adsorption on dry activated carbon, the use of binary interaction parameters not only can reduce the observed deviations for the binary

systems, but they also improve the predictions for the ternary adsorption systems. On average, the use of both one and two binary interaction parameters in the model can predict the ternary adsorption within the expected experimental uncertainties.

Figure 8 shows the OK model predictions for the ternary mixture adsorption on wet Tiffany coal, based on pure-component data and with two binary interaction parameters from the binary adsorption data. As shown in the figure, the OK model can predict almost all total and individual component adsorptions in the ternary mixture system within the experimental uncertainties when the binary interaction parameters are included.

Summary

The OK model can be used to predict individual component adsorption in the binary and ternary system within twice the experimental uncertainties, on average. In general, the model can also predict the total adsorption in the binary system within the expected experimental uncertainties. Worse results were generally obtained for the predictions of the lesser-adsorbed component adsorptions, as indicated by larger WAAD (3.5 for nitrogen adsorption in the nitrogen/CO₂ adsorption on activated carbon, and 4.5 for methane adsorption in the methane/CO₂ adsorption on wet Tiffany coal).

The predictions of the binary adsorption on the dry activated carbon systems based on the generalized pure adsorption model produced slightly better results than those based on the correlative pure-adsorption model. In the wet coal systems, comparable results were obtained for both cases.

In general, the use of one binary interaction parameter, C_{ij} , significantly improved the binary mixture adsorption representation. Specifically, the lesser-adsorbed

components can be represented to within the expected experimental uncertainties with the use of C_{ij} . Better representations were further obtained when two binary interaction parameters (C_{ij} and E_{ij}) were applied, as indicated by a WAAD of about 0.5.

Relatively large values of C_{ij} in some system suggests that the correlative burden of the binary adsorption modeling has mainly rested on correcting values for the fluid-fluid interaction energy. Application of the surface heterogeneity, such as the fluid-solid energy distribution, and application of an accurate equation of state with adequate mixing rules to calculate the chemical potential in the gas phase, should be considered in future studies.

The second binary interaction parameters, E_{ij} , for most of the wet coal systems are less than the values obtained from the adsorption on dry activated carbon. This indicates that the model without interaction parameters overestimates the individual component adsorptions on the wet coals. The chemical structure of the coal and the presence of water in the coal affect the predictive capability of the model. Further, separating the two factors affecting the mixture adsorption modeling would require additional data, especially mixture adsorption data on dry coals.

Comparison of the OK model to the other models in mixture adsorption on BPL activated carbon (Reich, 1980) shows that the OK model produced better predictions, for individual adsorption, compared to Langmuir model and gave comparable results to the 2-D EOS model. For the total adsorption predictions, the OK model has a better performance than the other models.

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Table 1. OK Model Predictions of Binary Mixture Adsorption on Dry Activated Carbon at 318.2 K (OSU, 2002)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
Based on Parameters from the Pure-Adsorption Model				
CH₄-N₂				
Methane	40	2.5	0.080	1.0
Nitrogen	40	11.7	0.064	1.7
Total	40	0.7	0.029	0.3
CH₄-CO₂				
Methane	40	17.8	0.132	2.1
CO ₂	40	4.1	0.113	1.0
Total	40	4.0	0.206	1.1
N₂-CO₂				
Nitrogen	40	81.1	0.199	3.5
CO ₂	40	4.6	0.152	1.2
Total	40	7.5	0.335	2.4
Based on Generalized Pure-Adsorption Model				
CH₄-N₂				
Methane	40	3.3	0.096	1.2
Nitrogen	40	6.9	0.070	1.5
Total	40	2.9	0.098	1.2
CH₄-CO₂				
Methane	40	18.7	0.126	1.9
CO ₂	40	3.1	0.130	0.8
Total	40	1.5	0.087	0.4
N₂-CO₂				
Nitrogen	40	71.0	0.164	2.6
CO ₂	40	3.8	0.127	1.0
Total	40	5.6	0.277	1.8

Table 2. OK Model Representations of Binary Mixture Adsorption on Dry Activated Carbon at 318.2 K (OSU, 2002)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C_{ij}	E_{ij}
Based on One Regressed Parameter (C_{ij})						
CH4-N2					0.198	1.0
Methane	40	2.8	0.073	1.1		
Nitrogen	40	5.0	0.032	0.7		
Total	40	1.8	0.065	0.8		
CH4-CO2					0.335	1.0
Methane	40	4.8	0.047	0.4		
CO2	40	2.7	0.147	0.7		
Total	40	2.2	0.152	0.6		
N2-CO2					0.658	1.0
Nitrogen	40	8.2	0.045	0.6		
CO2	40	4.4	0.255	1.4		
Total	40	4.1	0.262	1.4		
Based on Two Regressed Parameters						
CH4-N2					0.351	1.078
Methane	40	1.5	0.036	0.6		
Nitrogen	40	2.0	0.020	0.5		
Total	40	0.7	0.033	0.3		
CH4-CO2					0.280	0.956
Methane	40	4.2	0.033	0.4		
CO2	40	2.1	0.101	0.5		
Total	40	1.7	0.107	0.5		
N2-CO2					0.446	0.871
Nitrogen	40	17.6	0.044	0.7		
CO2	40	2.3	0.130	0.7		
Total	40	2.6	0.162	0.8		

Table 3. OK Model Predictions of Ternary Mixture Adsorption on Dry Activated Carbon at 318.2 K

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
Based on Parameters from the Pure -Adsorption Model				
Methane	11	8.9	0.040	0.7
Nitrogen	11	540	0.201	3.3
CO₂	11	3.1	0.107	0.9
Total	11	6.8	0.335	2.2
Based on Generalized the Pure -Adsorption Model				
Methane	11	11.4	0.054	0.9
Nitrogen	11	474	0.158	2.3
CO₂	11	1.7	0.077	0.5
Total	11	4.9	0.275	1.6
Based on Pure and One Binary Interaction Parameter (C_{ij})				
Methane	11	2.6	0.012	0.2
Nitrogen	11	37.6	0.022	0.4
CO₂	11	4.3	0.290	1.2
Total	11	4.2	0.299	1.3
Based on Pure and Two Binary Interaction Parameters				
Methane	11	4.2	0.017	0.5
Nitrogen	11	121	0.052	0.9
CO₂	11	2.5	0.139	0.7
Total	11	3.2	0.177	0.9

Table 4. OK Model Predictions of Binary Mixture Adsorption on Dry Activated Carbon at 298 K (Dreisbach, 1999)

Systems	NPTS	%AAD	RMSE (mmol/g)
Based on Two-Parameter Pure-Adsorption Model			
CH₄-N₂			
Methane	24	12.2	0.352
Nitrogen	24	22.3	0.181
Total	24	4.3	0.197
CH₄-CO₂			
Methane	24	13.4	0.207
CO ₂	24	18.8	0.569
Total	24	5.8	0.487
N₂-CO₂			
Nitrogen	24	139	0.317
CO ₂	24	7.6	0.483
Total	24	6.0	0.364
Based on Generalized Pure-Adsorption Model			
CH₄-N₂			
Methane	24	7.4	0.240
Nitrogen	24	12.8	0.113
Total	24	4.6	0.192
CH₄-CO₂			
Methane	24	10.2	0.319
CO ₂	24	31.3	0.571
Total	24	8.3	0.584
N₂-CO₂			
Nitrogen	24	38.2	0.100
CO ₂	24	13.2	0.597
Total	24	11.9	0.609

Table 5. OK Model Representations of Binary Mixture Adsorption on Dry Activated Carbon at 298 K (Dreisbach, 1999)

Systems	NPTS	%AAD	RMSE (mmol/g)	C_{ij}	E_{ij}
Based on One Regressed Parameter (C_{ij})					
CH4-N2				0.610	1.0
Methane	24	14.8	0.345		
Nitrogen	24	5.8	0.119		
Total	24	6.4	0.291		
CH4-CO2				0.294	1.0
Methane	24	6.8	0.182		
CO2	24	10.1	0.451		
Total	24	6.2	0.540		
N2-CO2				0.832	1.0
Nitrogen	24	17.8	0.087		
CO2	24	5.7	0.344		
Total	24	4.8	0.327		
Based on Two Regressed Parameters					
CH4-N2				0.665	1.197
Methane	24	11.0	0.214		
Nitrogen	24	8.2	0.204		
Total	24	2.9	0.100		
CH4-CO2				0.319	1.206
Methane	24	3.7	0.097		
CO2	24	9.4	0.257		
Total	24	4.8	0.276		
N2-CO2				0.832	0.971
Nitrogen	24	17.2	0.079		
CO2	24	5.9	0.363		
Total	24	4.9	0.342		

Table 6. OK Model Predictions of Ternary Mixture Adsorption on Dry Activated Carbon at 298 K (Dreisbach, 1999)

Systems	NPTS	%AAD	RMSE (mmol/g)
Based on Parameters from the Pure-Adsorption Model			
Methane	40	13.4	0.514
Nitrogen	40	45.0	0.446
CO ₂	40	12.5	0.261
Total	40	8.7	0.794
Based on Pure and One Binary Interaction Parameter (C_{ij})			
Methane	40	17.2	0.661
Nitrogen	40	48.5	0.5
CO ₂	40	14.2	0.34
Total	40	11.9	1.09
Based on Pure and Two Binary Interaction Parameters			
Methane	40	17.9	0.638
Nitrogen	40	47.2	0.473
CO ₂	40	14.9	0.393
Total	40	9.1	0.731

Table 7. Comparison of Model Predictions and Representation for Mixture Adsorption of CH₄, C₂H₆ and C₂H₄ on Dry Activated Carbon at 301.4 K (Reich, 1980)

Systems	NPTS	% AAD						RMSE (mmol/g)		
		Lang-muir	2D-EOS	2D-EOS (C_{ij})	OK	OK (C_{ij})	OK (C_{ij} & E_{ij})	OK	OK (C_{ij})	OK (C_{ij} & E_{ij})
CH ₄ -C ₂ H ₆										
Methane	14	36.7	39.8	19.5	35.2	23.8	23.7	0.329	0.169	0.168
Ethane	14	4.4	2.4	2.3	3.8	2.5	2.4	0.142	0.086	0.084
Total	14	5.8	7.2	3.5	4.5	2.3	2.2	0.226	0.125	0.153
CH ₄ -C ₂ H ₄										
Methane	15	28.9	33.9	8.8	29.9	15.2	14.0	0.297	0.110	0.104
Ethylene	15	5.4	2.9	3.3	3.8	3.2	1.9	0.148	0.113	0.088
Total	15	5.8	6.3	2.7	3.1	2.8	2.2	0.172	0.126	0.141
C ₂ H ₆ -C ₂ H ₄										
Ethane	12	5.2	4.6	5.0	4.3	5.1	4.1	0.099	0.110	0.084
Ethylene	12	8.3	6.8	5.7	5.7	5.0	3.3	0.187	0.185	0.116
Total	12	6.4	5.6	5.1	3.8	3.3	1.3	0.193	0.176	0.080
CH ₄ -C ₂ H ₆ -C ₂ H ₄										
Methane	14	59.3	51.2	33.5	52.2	39.1	38.1	0.486	0.303	0.285
Ethane	14	3.7	3.5	4.8	5.6	4.7	5.4	0.122	0.093	0.102
Ethylene	14	4.9	4.4	5.5	4.9	4.9	5.5	0.133	0.154	0.131
Total	14	9.5	8.4	5.5	5.7	3.9	3.9	0.420	0.334	0.287

* The results presented in the third to fifth columns are taken from Zhou (1994).

Table 8. Binary Interaction Parameters Used in OK Model for Mixture Adsorption of CH₄, C₂H₆ and C₂H₄ on Dry Activated Carbon at 301.4 K (Reich, 1980)

System	C_{ij}	E_{ij}
One Binary Interaction Parameter		
CH ₄ -C ₂ H ₆	-0.569	1.0
CH ₄ -C ₂ H ₄	-0.550	1.0
C ₂ H ₆ -C ₂ H ₄	-0.037	1.0
Two Binary Interaction Parameters		
CH ₄ -C ₂ H ₆	-0.577	0.972
CH ₄ -C ₂ H ₄	-0.642	0.890
C ₂ H ₆ -C ₂ H ₄	-0.037	1.088

Table 9. OK Model Predictions of Binary Mixture Adsorption on Wet Fruitland Coal at 319.3 K (OSU, 2000)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
Based on Two-Parameter Pure-Adsorption Model				
CH₄-N₂				
Methane	40	3.1	0.014	0.3
Nitrogen	40	16.4	0.019	0.9
Total	40	5.1	0.023	0.6
CH₄-CO₂				
Methane	40	8.9	0.012	0.5
CO ₂	40	5.7	0.036	0.8
Total	40	4.7	0.040	0.7
N₂-CO₂				
Nitrogen	40	152	0.026	1.0
CO ₂	40	7.1	0.059	0.9
Total	40	11.3	0.078	1.2
Based on the Generalized Pure-Adsorption Model				
CH₄-N₂				
Methane	40	3.1	0.012	0.3
Nitrogen	40	29.4	0.023	1.5
Total	40	4.0	0.016	0.4
CH₄-CO₂				
Methane	40	29.5	0.036	1.3
CO ₂	40	9.5	0.049	1.2
Total	40	4.2	0.034	0.6
N₂-CO₂				
Nitrogen	40	130	0.016	0.6
CO ₂	40	6.2	0.045	0.6
Total	40	5.9	0.053	0.6

Table 10. OK Model Representations of Binary Mixture Adsorption on Wet Fruitland Coal at 319.3 K (OSU, 2000)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C_{ij}	E_{ij}
Based on One Regressed Parameter (C_{ij})						
CH4-N2					0.099	1.0
Methane	40	3.1	0.015	0.3		
Nitrogen	40	17.7	0.018	1.0		
Total	40	4.6	0.020	0.5		
CH4-CO2					0.126	1.0
Methane	40	8.8	0.013	0.4		
CO2	40	5.6	0.040	0.7		
Total	40	3.8	0.035	0.6		
N2-CO2					0.438	1.0
Nitrogen	40	67.1	0.014	0.6		
CO2	40	8.1	0.073	1.0		
Total	40	9.9	0.073	1.1		
Based on Two Regressed Parameters						
CH4-N2					-0.241	0.825
Methane	40	3.4	0.011	0.3		
Nitrogen	40	10.5	0.012	0.6		
Total	40	1.7	0.011	0.2		
CH4-CO2					0.012	0.891
Methane	40	7.8	0.017	0.5		
CO2	40	2.7	0.017	0.3		
Total	40	2.1	0.018	0.3		
N2-CO2					0.152	0.681
Nitrogen	40	82.3	0.010	0.4		
CO2	40	4.3	0.034	0.5		
Total	40	3.5	0.035	0.4		

Table 11. OK Model Predictions of Binary Mixture Adsorption on Wet Illinois #6 Coal at 319.3 K (OSU, 2001)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
Based on Two-Parameter Pure-Adsorption Model				
CH₄-N₂				
Methane	40	12.6	0.018	1.0
Nitrogen	40	85.2	0.013	0.8
Total	40	13.5	0.030	1.2
CH₄-CO₂				
Methane	40	17.6	0.017	1.1
CO ₂	40	9.8	0.054	1.2
Total	40	8.7	0.058	1.3
N₂-CO₂				
Nitrogen	40	44.3	0.004	0.5
CO ₂	40	9.5	0.045	1.6
Total	40	7.6	0.042	1.3
Based on the Generalized Pure-Adsorption Model				
CH₄-N₂				
Methane	40	26.5	0.039	2.0
Nitrogen	40	31.9	0.005	0.6
Total	40	16.8	0.038	1.5
CH₄-CO₂				
Methane	40	21.2	0.021	1.5
CO ₂	40	8.3	0.045	1.0
Total	40	8.0	0.053	1.2
N₂-CO₂				
Nitrogen	40	207	0.018	1.6
CO ₂	40	11.9	0.054	1.9
Total	40	6.8	0.036	1.1

Table 12. OK Model Representations of Binary Mixture Adsorption on Wet Illinois #6 Coal at 319.3 K (OSU, 2001)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C_{ij}	E_{ij}
Based on One Regressed Parameter (C_{ij})						
CH4-N2					1.094	1.0
Methane	40	11.1	0.021	0.9		
Nitrogen	40	27.3	0.005	0.5		
Total	40	9.4	0.023	0.8		
CH4-CO2					0.180	1.0
Methane	40	18.7	0.015	0.9		
CO2	40	10.4	0.060	1.2		
Total	40	8.0	0.055	1.1		
N2-CO2					-0.306	1.0
Nitrogen	40	34.1	0.003	0.4		
CO2	40	9.2	0.040	1.5		
Total	40	8.3	0.042	1.4		
Based on Two Regressed Parameters						
CH4-N2					0.403	0.740
Methane	40	3.2	0.006	0.2		
Nitrogen	40	54.5	0.007	0.6		
Total	40	4.2	0.010	0.4		
CH4-CO2					-0.104	0.799
Methane	40	12.0	0.010	0.6		
CO2	40	7.9	0.034	0.9		
Total	40	5.7	0.032	0.8		
N2-CO2					-0.618	0.715
Nitrogen	40	86.0	0.006	0.5		
CO2	40	1.3	0.009	0.2		
Total	40	1.4	0.010	0.2		

Table 13. OK Model Predictions of Binary Mixture Adsorption on Wet Tiffany Coal at 327.6 K (OSU, 2002)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
CH₄-N₂				
Methane	11	6.9	0.018	1.0
Nitrogen	11	5.3	0.003	0.3
Total	11	6.5	0.020	1.0
CH₄-CO₂				
Methane	11	45.7	0.055	4.5
CO ₂	11	16.9	0.072	2.5
Total	11	3.5	0.020	0.6
N₂-CO₂				
Nitrogen	11	156	0.015	1.5
CO ₂	11	7.8	0.049	1.0
Total	11	5.9	0.036	0.9

Table 14. OK Model Representations of Binary Mixture Adsorption on Wet Tiffany Coal at 327.6 K (OSU, 2002)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C_{ij}	E_{ij}
Based on One Regressed Parameter (C_{ij})						
CH₄-N₂					-0.364	1.0
Methane	11	7.0	0.019	1.0		
Nitrogen	11	8.1	0.004	0.4		
Total	11	5.0	0.016	0.8		
CH₄-CO₂					-0.692	1.0
Methane	11	12.5	0.021	1.0		
CO ₂	11	12.9	0.049	2.0		
Total	11	7.0	0.030	1.2		
N₂-CO₂					-1.239	1.0
Nitrogen	11	52.5	0.005	0.5		
CO ₂	11	6.0	0.036	0.8		
Total	11	5.1	0.031	0.7		

Table 14. OK Model Representations of Binary Mixture Adsorption on Wet Tiffany Coal at 327.6 K (Continued)

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD	C_{ij}	E_{ij}
Based on Two Regressed Parameters						
CH₄-N₂					0.108	1.179
Methane	40	2.7	0.005	0.2		
Nitrogen	40	6.6	0.003	0.3		
Total	40	2.6	0.006	0.4		
CH₄-CO₂					-1.074	0.764
Methane	40	8.9	0.015	0.7		
CO ₂	40	4.4	0.017	0.7		
Total	40	1.8	0.007	0.4		
N₂-CO₂					-1.230	1.036
Nitrogen	40	53.1	0.005	0.5		
CO ₂	40	6.1	0.037	0.8		
Total	40	5.2	0.032	0.7		

Table 15. OK Model Predictions of Ternary Mixture Adsorption on Wet Tiffany Coal at 327.6 K

Systems	NPTS	%AAD	RMSE (mmol/g)	WAAD
Based on Parameters from Pure-Adsorption Model				
Methane	11	34.0	0.010	0.7
Nitrogen	11	85.8	0.037	2.6
CO₂	11	19.3	0.073	2.1
Total	11	5.1	0.028	0.6
Based on Pure and One Binary Interaction Parameters (C_{AB})				
Methane	11	7.0	0.002	0.1
Nitrogen	11	40.7	0.017	1.2
CO₂	11	15.3	0.051	1.6
Total	11	8.5	0.034	1.0
Based on Pure and Two Binary Interaction Parameters				
Methane	11	29.2	0.010	0.6
Nitrogen	11	48.4	0.021	1.4
CO₂	11	13.1	0.042	1.4
Total	11	7.5	0.030	0.9

Figure 1. CH₄ Gibbs Adsorption of CH₄/CO₂ on Dry Activated Carbon at 318.2 K and Various Feed Gas Composition (OSU Data)

Figure 2. CO₂ Gibbs Adsorption of CH₄/CO₂ on Dry Activated Carbon at 318.2 K and Various Feed Gas Composition (OSU Data)

Figure 3. Comparison between the Gas Compositions Obtained from Experiment Measurements And from the Flash Calculation

Figure 4. OK Model Predictions of a 10/40/50 Mol % CH₄/N₂/CO₂ Feed Mixture Adsorption on Dry Activated Carbon at 318.2 K (OSU Data)

Figure 5. CH₄ Adsorption of CH₄/C₂H₆ on Dry Activated Carbon at 301.4 K and Various Feed Gas Composition (Reich)

Figure 6. C_2H_6 Adsorption of CH_4/C_2H_6 on Dry Activated Carbon at 301.4 K and Various Feed Gas Composition (Reich)

Figure 7. Gibbs Adsorption of a 50/50 Mol % CH₄/N₂ Feed Mixture on Wet Tiffany Coal at 327.6 K (OSU Data)

Figure 8. OK Model Predictions of a 10/40/50 Mol % $\text{CH}_4/\text{N}_2/\text{CO}_2$ Feed Mixture Adsorption on Wet Tiffany Coal at 327.6 K (OSU Data)

**Correlating Compressibility Factors of Coalbed Gases Using
the Benedict-Webb-Rubin (BWR) Equation of State**

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Abstract

We have recently been studying the adsorption of pure and mixed coalbed gases (methane, nitrogen and carbon dioxide) on selected coals. Our measurements utilize a volumetric experimental technique, which requires high-accuracy gas compressibility factors as input in the data reduction procedure. Thus, as part of these studies we have re-optimized parameters for the Benedict-Webb-Rubin equation-of-state (both pure-component parameters and the binary interaction parameters) to improve compressibility factor predictions for the gases of interest. A database of 1442 gas-phase data points involving pure, binary, and ternary mixture PVT data was used in the parameter regressions, including some PVT measurements we made for selected compositions at 326.7 K and pressures to 13.9 MPa.

Four parameter-optimization scenarios were evaluated to ensure the best quality fit for the data considered. As expected, a simultaneous optimization of pure-component, binary, and ternary data provides the best overall fit to the database, with an average absolute deviation (AAD) of 0.1% and a maximum deviation of 1.4%.

In addition, a sensitivity analysis was conducted to demonstrate the effect of variability in compressibility factors on the calculated mixture adsorption for one of our adsorption experiments. The results indicate that a 0.5% error in the compressibility factor is multiplied six-fold (3.0% error) in total adsorption and almost seventeen-fold (8.5%) in the component adsorption.

Keywords: Compressibility Factor, Benedict-Webb-Rubin (BWR), Equation of State, PVT Mixture Data, Coalbed Gases

Introduction

Adsorption equilibrium models are essential in process simulators used to optimize coalbed methane production and carbon dioxide (CO_2) sequestration processes. To develop reliable adsorption models requires accurate pure and mixture adsorption data. In turn, proper reduction of experimental adsorption data requires accurate gas-phase compressibility (Z) factors for methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2), and their mixtures.

A careful evaluation of the current literature led us to conclude that an adequate predictive capability for the mixture compressibility factors does not exist. Therefore, we elected to develop such a capability using the Benedict-Webb-Rubin (BWR) equation of state.

Specifically, we have used the available pure-fluid and binary mixture data to refit the parameters in the BWR equation to improve its compressibility factor predictions based on (a) the available experimental volumetric data from the literature, and (b) supplementary measurements we have conducted. Experimental data at temperatures from 300 to 350 K and pressures to 20 MPa were used to evaluate and further develop the BWR EOS. These data reflect coalbed reservoir temperature and pressure conditions.

Background

Our experimental technique for measuring adsorption isotherms employs a mass balance method, utilizing volumetric accounting principles; therefore, accurate gas-phase compressibility (Z) factors from outside sources are required for methane, nitrogen and CO_2 and their mixtures to properly analyze our experimental adsorption data [1]. Our objective has been to minimize the uncertainties in our reported adsorption results that are caused by errors in the input information on compressibility factors.

To illustrate the need for accurate compressibility factors, Figures 2 and 3 show the impact of uncertainties in the compressibility factor on the adsorption results for both pure CO₂ and CO₂ component adsorption in a CH₄-CO₂ binary mixture adsorbing on activated carbon at 113 °F. The figures present, as a function of pressure, the effects of uncertainties in Z on the uncertainty in the amount adsorbed. Figure 2 presents results for pure CO₂, and Figure 3 shows similar results for the amount of CO₂ adsorbed from a CH₄ + CO₂ mixture at a gas composition of 60% CO₂. These figures reveal that significant errors begin to occur in the amount adsorbed when the compressibility factor errors are as low as about 0.5%. The apparent “breaks” in the smoothness of the curves as a function pressure are the result of the detailed experimental protocol used in the experiments illustrated; e.g., the point at which the injection pump had to be refilled part way through the experiment. (Details of the equations used in adsorption data reduction are presented elsewhere [1], including the exact manner in which the Z factors enter the governing equations.)

Since we are engaged in adsorption measurements involving pure, binary and ternary gas systems, we require compressibility factors of such gas systems. Following is a brief description of how we met our needs in recent studies.

For **pure** methane, nitrogen and CO₂, we employ highly accurate equations of state from the literature [2,3]. These EOS models predict the compressibility factors within 0.1% AAD.

For gas mixtures, we have used available pure-fluid and **binary** mixture data to refit the BWR equation and improve its accuracy significantly; in general, the new BWR EOS parameters yield deviations in the compressibility factor within 0.5%. This level of accuracy is deemed satisfactory for our needs.

The present study was motivated by our need to reduce adsorption data for ternary gas systems, where we encountered the fact that ternary Z data were extremely scarce. As

a result, we decided to perform a limited number of binary (CH₄/N₂) and ternary (CH₄/N₂/CO₂) compressibility factor measurements at 130°F and pressures to 2000 psia. These newly acquired data were combined with available data from the literature on pure substances and binary systems to improve the BWR EOS compressibility factor predictions.

Model Development

The BWR EOS is widely used in the hydrocarbon industry for correlating and predicting fluid densities [4]. In this study, we employ the eight-parameter BWR EOS to correlate the PVT data of coalbed gases methane, nitrogen, CO₂ and their mixtures [4]:

$$Z = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3} \right) \rho + \left(b - \frac{a}{RT} \right) \rho^2 + \frac{a\alpha}{RT} \rho^5 + \frac{c\rho^2}{RT^3} (1 + \gamma\rho^2) e^{-\gamma\rho^2} \quad (1)$$

where T is temperature, ρ is density, R is the universal gas constant, and a-c, A-C, and α and γ are EOS parameters. To apply the BWR to mixtures, mixing and combination rules are required. A variety of combinations rules were evaluated, including those employing composition-dependent interaction parameters [5]; however, for simplicity, we have used the following mixing rules suggested by Bishnoi et al. [4]:

$$B_0 = \sum_{i=1}^n \sum_{j=1}^n x_i x_j B_{0ij} \quad \text{where } B_{0ij} = \sqrt{B_{0i} B_{0j}}$$

$$A_0 = \sum_{i=1}^n \sum_{j=1}^n x_i x_j A_{0ij} \quad \text{where } A_{0ij} = \sqrt{A_{0i} A_{0j}} (1 - k_{ij})$$

$$C_0 = \sum_{i=1}^n \sum_{j=1}^n x_i x_j C_{0ij} \quad \text{where } C_{0ij} = \sqrt{C_{0i} C_{0j}} (1 - k_{ij})^3$$

$$b = \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n x_i x_j x_k (b_{ij} b_{jk} b_{ik})^{1/3} \quad \text{where } b_{ij} = \sqrt{b_i b_j}$$

$$a = \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n x_i x_j x_k (a_{ij} a_{jk} a_{ik})^{1/3} \quad \text{where } a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$$

$$\begin{aligned}
c &= \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n x_i x_j x_k (c_{ij} c_{jk} c_{ik})^{1/3} & \text{where } c_{ij} &= \sqrt{c_i c_j} (1 - k_{ij})^3 \\
\alpha &= \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n x_i x_j x_k (\alpha_{ij} \alpha_{jk} \alpha_{ik})^{1/3} & \text{where } \alpha_{ij} &= \sqrt{\alpha_i \alpha_j} \\
\gamma &= \sum_{i=1}^n \sum_{j=1}^n x_i x_j \gamma_{ij} & \text{where } \gamma_{ij} &= \sqrt{\gamma_i \gamma_j}
\end{aligned} \tag{2}$$

Here, n is the number of components, x is the mole fraction of component i in the gas phase, and k_{ij} is the binary interaction parameter. Following customary notation, for a given parameter β , $\beta_{ii} = \beta_i$, and the pure-fluid interaction parameters are equal to zero (or $k_{ii} = k_{jj} = 0$).

Database and Data Reduction

Literature Data: Table 1 presents the literature data used in this work. Pure-gas and mixture data ranging in temperature from 279 to 350 K and pressures to 20.4 MPa are included.

New Measurements: Our experimental Z factor measurements were done in the same apparatus used for adsorption studies (but with no adsorbent in the equilibrium cell). The technique employs a mass balance method, utilizing volumetric accounting principles. The experimental apparatus, shown schematically in Figure 1, has been used successfully in our previous adsorption measurements [1]. Brief descriptions of the experimental apparatus and procedures follow.

The entire apparatus (both Pump and Cell sections) is maintained in a constant temperature air bath. A highly accurate variable-volume Ruska pump is used for the injections of the pure gases from the Ruska pump into the equilibrium cell (EC, Figure 1); the injections are made at constant pressure and temperature. A magnetic pump circulates the gas to ensure proper mixing. The temperature and pressure are recorded at equilibrium.

The equilibrium cell is placed under vacuum prior to gas injection. The volume of the equilibrium cell and associated tubing, V_{cell} , is then determined by injecting a known quantity of helium from a calibrated injection pump, as follows:

$$V_{\text{cell}} = n_{\text{He}} (Z_{\text{He}} RT / P)_{\text{cell}} \quad (3)$$

$$n_{\text{He}} = (PV / Z_{\text{He}} RT)_{\text{pump}} \quad (4)$$

In these equations, n_{He} is the number of moles of helium injected into the cell, V is the volume of gas injected from the pump, Z_{He} is the compressibility factor of helium, R is the universal gas constant, T is the temperature, P is the pressure, and the subscripts "cell" and "pump" refer to conditions in the cell and pump sections of the apparatus, respectively. In these calibration measurements, values of Z_{He} were taken from highly accurate literature data [1].

Once V_{cell} was determined from multiple replications of the experimental technique, the targeted gas(es) was injected and allowed to reach equilibrium. For the mixtures, pure gases were injected in sequence, with the pump cleaned and evacuated prior to introduction of each gas. The total amount of each gas injected was thus known, and the gas composition in the equilibrium cell could be calculated by mass balance, based on the amount of each gas injected. For example, in the CH_4/N_2 system, CH_4 might be injected first to reach some desired initial pressure in EC, and then sequential injections of N_2 could be made, with equilibrium established after each injection. Thus, the pressure would increase after each N_2 injection, as would the total amount of gas, n_{total} , and the mole fraction of N_2 in the EC mixture. The compressibility factor for the mixture in the EC was calculated after each injection step as:

$$Z = \frac{PV_{\text{cell}}}{n_{\text{total}} RT} \quad (5)$$

The estimated uncertainties in each of the experimentally measured quantities are as follows: temperature 0.2°F, pressure 1.0 psia, injected gas volumes 0.02 cc, gas-phase composition 0.001 in mole fraction. The expected uncertainties in the compressibility factors are estimated using error propagation in all the measured variables and confirmed by replicate runs.

The newly acquired PVT measurements for the selected mixtures and the associated expected experimental uncertainties appear in Table 2. (Note that the experimental technique used leads to changing gas composition (mole fraction) as the pressure changes.) These data, combined with the literature data, were used to regress the BWR parameters and conduct our model evaluations.

Data Reduction: The percentage root-mean-square (%RMS) error was used as an objective function to correlate the data with the BWR EOS. The function minimizes the sum of the squared-percentage deviations in compressibility factors:

$$\%RMS = 100 \sqrt{\frac{\sum_{i=1}^{NPTS} \left(\frac{Z_{exp} - Z_{calc}}{Z_{exp}} \right)^2}{NPTS}} \quad (6)$$

Here, NPTS is the number of data points, Z_{calc} and Z_{exp} are the calculated and the experimental compressibility factor for datum point “i”. The average absolute deviation (%AAD) and the weighted RMS are also presented to further quantify our regressed parameter evaluations:

$$\%AAD = \frac{100}{NPTS} \sum_{i=1}^{NPTS} \text{abs} \left(\frac{Z_{calc} - Z_{exp}}{Z_{exp}} \right) \quad (7)$$

$$\text{RMS} = \sqrt{\frac{\sum_{i=1}^{\text{NPTS}} (z_{\text{exp}} - z_{\text{calc}})_i^2}{\text{NPTS}}} \quad (8)$$

Case Studies

Four different parameter-optimization scenarios were evaluated to ensure the best BWR quality fit for the data. Specifically, we conducted the following case studies:

- Case 1: This is the base case; the original BWR model parameters were used, as reported by Bishnoi and Robinson [4]. Both their pure component parameters and binary interaction parameters were employed.
- Case 2: Sequential parameter regressions were conducted. First the pure-component BWR parameters were regressed from pure PVT data for each of the Systems 1, 2 and 3; then the binary interaction parameters were regressed using both binary and ternary data simultaneously (Systems 4 to 17).
- Case 3: Simultaneous parameter regressions were conducted. Both the pure-component BWR parameters and the binary interaction parameters were regressed simultaneously using all the data (Systems 1 to 17).
- Case 4: Regressions were done for a restricted range of conditions. Simultaneous parameter regressions were conducted covering only the temperature range of primary interest (307 to 338 K). Both pure-component BWR parameters and binary interaction parameters were regressed from all data points at temperatures from 307 K to 338 K and pressures up to 13.7 MPa.

Results and Discussion

The BWR EOS parameters for the various case studies are listed in Table 3. An overall summary of results generated by these parameters is presented in Table 4. These results indicated that the overall %AAD range from 0.1 to 0.4 for the cases considered and the maximum percentage deviations range from -5.9% to 14.6% (Case 2). As expected, Case 4, where we conducted simultaneous regression of pure, binary, and ternary data covering our experimental temperature and pressure range, produces the best overall fit and the least maximum deviation (0.07 %AAD and -1.5% maximum deviation).

Tables 5 to 8 present detailed results for Cases 1-4. The three binary systems show comparable quality of fit for the best cases (Cases 3 and 4). The largest errors tend to occur at high CO₂ compositions, particularly at conditions near the CO₂ critical point. The ternary data is also well represented, with data from the present work showing the highest deviations (about 0.6 %AAD). This is not unexpected, since those data covered the widest composition range and had higher estimated experimental uncertainties than the other two sources of ternary data.

Figures 4, 6, 8, and 10 show deviation plots for the Z factors for the various mixtures for each of the case studies. A gradual improvement in the quality of fit is observed proceeding from Case 1 to Case 4. The figures indicate that while the N₂-CO₂ binary data tend to exhibit the largest deviations, although this is less pronounced in the best cases (cases 3 and 4).

Figures 5, 7, 9, and 11 show the deviation plots for the pure components for the various case studies. These plots are useful in comparing the quality of the fit for the pure components, and especially to reveal potential loss of accuracy when conducting simultaneous regressions (Cases 3 and 4). Our objective was to gain model flexibility through simultaneous treatment of all data, but not at any significant expense to the pure-component predictions.

The pure-component deviation plots indicate that CO₂ (System 3) consistently exhibits the largest deviations in all scenarios. For pure gases, the BWR EOS can predict compressibility factors for CH₄ and N₂ within 0.3% for all four cases. However, for CO₂, the absolute deviations are as much as 3% for Case 1 and within 0.8% for Cases 2 to 4. The CO₂ Z factors are most difficult to represent as a result of the near-critical behavior of CO₂ in the range of temperatures and pressures of interest in this work.

Our recent adsorption isotherm measurements for the CH₄-CO₂ binary on dry activated carbon are used to demonstrate how compressibility factors in the bulk phase affect the total adsorption as well as the component adsorption in mixtures [15]. The molar feed composition of the mixture is 40% methane, and the equilibrium temperature is 113 °F. Figure 12 shows the effect of 0.5%, 1.0% and 2.0% change in the compressibility factor on the total and the component CO₂ *Gibbs* adsorption. The observed percentage change in the amount adsorbed ranges corresponding to 0.5 and 2.0% variability in the compressibility factor are: from 1.6 to 6.2% in total adsorption, from 0.9 to 3.7% in CO₂ component adsorption and from 5.9 to 23.1% in CH₄ component adsorption.

Conclusions

The major conclusions of this study are:

- Mixture adsorption calculations are sensitive to the accuracy of compressibility factor predictions.
- Regressing the BWR EOS parameters using both pure and mixture PVT data simultaneously yielded improved compressibility factor predictions without the need for complicated combination and/or mixing rules.
- The modified BWR parameters (Cases 3 and 4) yield Z factors that are adequate for coalbed adsorption data reductions.

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Table 1. Experimental Data Used

System No.	System	Temperature Range, (K)	Pressure Range, (MPa)	Composition Range, 1 st Component	NPTS	Reference
1	CH ₄	300.0 - 350.0	0.03 - 15.01	1.0000	27	[9]
2	N ₂	300.0 - 350.0	0.01 - 20.01	1.0000	68	[10]
3	CO ₂	300.0 - 350.0	0.01 - 15.01	1.0000	55	[8]
4	CH ₄ - N ₂	327.6	3.78 - 13.44	0.1912 - 0.8237	12	[This Work]
5		308.4 - 330.0	0.39 - 12.00	0.1354 - 0.8976	391	[2]
6	CH ₄ - CO ₂	315.0 - 330.0	2.45 - 19.31	0.0205 - 0.1011	57	[14]
7		300.0 - 350.0	2.11 - 13.87	0.0989 - 0.9017	38	[7]
8		300.0 - 330.0	0.08 - 12.00	0.5239 - 0.8052	200	[2]
9		300.0 - 310.0	2.25 - 15.65	0.0205 - 0.1011	34	[14]
10		320.0	0.19 - 9.47	0.0999 - 0.9001	80	[11]
11	N ₂ - CO ₂	300.0 - 350.0	1.11 - 17.66	0.0908 - 0.8944	130	[6]
12		273.1 - 330.0	0.09 - 11.91	0.5530 - 0.8990	168	[2]
13		320.0	0.84 - 16.24	0.0908 - 0.8944	71	[12]
14		305.0 - 330.0	2.26 - 15.05	0.0180 - 0.8237	48	[13]
15	Ternary	327.6	6.27 - 13.89	0.1510 - 0.4520	14	[This Work]
16		279.4 - 308.4	3.73 - 6.27	0.2482, 0.2497*	33	[2]
17		300.0 - 340.0	3.99 - 20.41	0.9595, 0.0201*	16	[14]

* Single measurement compositions: y_{CO_2} , y_{N_2}

Table 2. Experimental Compressibility Factors for Mixtures at 327.6K

Pressure (Psia)	y_{CH_4}	y_{CO_2}	y_{N_2}	Z_{exp}	Experimental Uncertainty in Z (%)
CH₄+N₂ System					
3.776	0.6662	0.0000	0.3338	0.9764	0.6
5.569	0.4548	0.0000	0.5452	0.9831	0.5
8.492	0.3013	0.0000	0.6987	0.9932	0.5
11.284	0.2296	0.0000	0.7704	1.0056	0.4
13.713	0.1912	0.0000	0.8088	1.0176	0.4
3.982	0.2964	0.0000	0.7036	0.9942	0.6
6.133	0.6422	0.0000	0.3578	0.9731	0.5
10.721	0.7530	0.0000	0.2470	0.9400	0.4
13.438	0.8064	0.0000	0.1936	0.9234	0.4
5.085	0.8237	0.0000	0.1763	0.9571	0.5
6.425	0.6555	0.0000	0.3445	0.9623	0.5
9.020	0.4727	0.0000	0.5273	0.9743	0.5
CH₄+CO₂+N₂ System					
6.487	0.4800	0.5200	0.0000	0.86446	0.5
6.929	0.0000	0.7897	0.2103	0.81313	0.5
6.884	0.0000	0.5164	0.4836	0.90761	0.5
6.479	0.2428	0.7572	0.0000	0.80687	0.5
6.482	0.0000	0.5840	0.4160	0.89179	0.5
8.236	0.2322	0.7678	0.0000	0.74606	0.5
6.275	0.4092	0.4883	0.1024	0.88580	0.5
7.855	0.4010	0.4345	0.1645	0.87463	0.5
11.666	0.4053	0.4696	0.1251	0.81424	0.4
9.006	0.4520	0.4582	0.0898	0.84397	0.5
8.283	0.1755	0.4258	0.3987	0.90046	0.5
10.282	0.1610	0.5020	0.3371	0.84894	0.4
8.416	0.2371	0.4455	0.3174	0.88338	0.5
13.894	0.1510	0.4994	0.3496	0.81858	0.4

Table 3. BWR EOS Parameters for Pure Gases

Component	$B_0 \cdot 10^2$	A_0	$C_0 \cdot 10^{-5}$	$b \cdot 10^3$	a	$a \cdot 10^5$	$c \cdot 10^{-4}$	$g \cdot 10^3$	$k_{ij} \cdot 10^2^*$
Case 1									
CH ₄	4.3203	1.8712	0.2350	3.9787	0.0692	9.6836	0.3018	5.7118	3.0000
CO ₂	3.2015	1.8367	1.7603	6.2536	0.2420	4.8784	1.9008	4.2808	3.0000
N ₂	4.0743	1.0536	0.0806	2.3277	0.0251	12.7200	0.0728	5.3000	3.0000
Case 2									
CH ₄	4.3658	1.7825	0.3034	3.4320	0.0728	39.7800	0.4220	14.4131	3.1025
CO ₂	3.1735	1.9668	1.6296	2.8034	0.0844	10.4177	1.2458	5.0744	8.4725
N ₂	4.0681	0.9599	0.1386	2.0797	0.0279	29.0908	0.1107	0.0000	-2.2938
Case 3									
CH ₄	4.4122	1.8538	0.2407	4.7569	0.1128	11.0522	0.4852	6.3824	2.4740
CO ₂	3.2649	1.8396	1.7706	6.2334	0.2441	5.3636	1.9339	4.5487	2.8084
N ₂	4.2007	1.0946	0.0466	2.6731	0.0374	7.8119	0.0868	4.4634	-5.5230
Case 4									
CH ₄	4.8871	2.0094	0.2042	4.0428	0.0943	22.2778	0.4791	10.4556	2.0940
CO ₂	3.2518	1.8450	1.7621	6.2767	0.2450	5.3354	1.9330	4.5528	1.2785
N ₂	4.3979	1.1378	0.0414	2.0963	0.0244	20.4833	0.0668	9.0570	-6.7309

* k_{13} , k_{12} , k_{23}

T: K

P: atm

ρ : mol/liter

Table 4. Overall Quality of BWR Compressibility Factor Predictions

Case	Errors in Predicted Z Factor			
	RMS (x1000)	%RMS	%AAD	Range of % Deviations
1	5.0	0.84	0.38	-3.3 to 7.5
2	5.1	1.10	0.41	-5.8 to 14.6
3	1.3	0.18	0.10	-1.4 to 1.4
4	1.0	0.13	0.07	-1.5 to 0.8

Table 5. Quality of BWR Compressibility Factor Predictions: Case 1

System No.	System	Errors in Predicted Z Factor			
		RMS (x1000)	%RMS	%AAD	Range of % Deviations
1	CH ₄	1.6	0.18	0.17	-0.3 to 0.0
2	N ₂	1.6	0.16	0.14	-0.3 to 0.0
3	CO ₂	3.2	0.70	0.35	-3.1 to 0.5
4	CH ₄ - N ₂	4.0	0.41	0.33	-1.0 to 0.0
5		1.8	0.19	0.18	-0.5 to 0.4
6	CH ₄ - CO ₂	2.7	0.53	0.41	-1.9 to 0.9
7		2.4	0.34	0.27	-1.2 to 0.4
8		0.6	0.08	0.05	-0.3 to 0.1
9		3.2	0.83	0.54	-3.3 to 1.0
10		0.8	0.09	0.06	-0.3 to 0.1
11	N ₂ - CO ₂	12.4	2.25	1.48	-0.6 to 7.5
12		5.4	0.62	0.39	0.0 to 2.8
13		9.3	1.44	0.93	-0.5 to 4.1
14		3.2	0.94	0.69	-1.3 to 2.6
15	Ternary	5.3	0.62	0.53	-0.9 to 1.4
16		1.0	0.11	0.10	0.1 to 0.1
17		2.9	0.77	0.57	-0.8 to 1.9
Overall		5.0	0.84	0.38	-3.3 to 7.5

Table 6. Quality of BWR Compressibility Factor Predictions: Case 2

System No.	System	Errors in Predicted Z Factor			
		RMS (x1000)	%RMS	%AAD	Range of % Deviations
1	CH ₄	0.3	0.03	0.02	-0.1 to 0.0
2	N ₂	0.2	0.02	0.01	0.0 to 0.0
3	CO ₂	1.1	0.18	0.12	-0.5 to 0.7
4	CH ₄ - N ₂	2.6	0.27	0.21	-0.7 to 0.2
5		0.5	0.05	0.03	-0.3 to 0.6
6	CH ₄ - CO ₂	3.2	0.62	0.51	-1.8 to 1.5
7		4.9	0.70	0.52	-1.4 to 1.9
8		4.3	0.54	0.34	0.0 to 2.2
9		7.2	2.03	1.38	-5.9 to 3.3
10		2.7	0.33	0.20	0.0 to 1.2
11	N ₂ - CO ₂	11.8	2.75	1.40	-2.5 to 14.6
12		4.5	0.53	0.33	-2.8 to 0.0
13		7.3	1.35	0.73	-1.6 to 7.3
14		7.3	2.25	1.48	-1.1 to 5.9
15	Ternary	6.0	0.70	0.54	-1.5 to 0.1
16		1.9	0.21	0.20	0.1 to 0.3
17		6.4	1.96	1.38	-0.4 to 4.3
Overall		5.1	1.10	0.41	-5.9 to 14.6

Table 7. Quality of BWR Compressibility Factor Predictions: Case 3

System No.	System	Errors in Predicted Z Factor			
		RMS (x1000)	%RMS	%AAD	Range of % Deviations
1	CH ₄	0.7	0.08	0.07	-0.1 to 0.2
2	N ₂	0.5	0.05	0.04	-0.1 to 0.1
3	CO ₂	2.0	0.30	0.21	-0.6 to 0.9
4	CH ₄ - N ₂	2.7	0.28	0.21	-0.8 to 0.2
5		0.5	0.06	0.03	-0.3 to 0.6
6	CH ₄ - CO ₂	2.0	0.28	0.22	-0.7 to 0.6
7		1.6	0.25	0.15	-1.0 to 0.5
8		0.5	0.06	0.05	-0.1 to 0.2
9		2.0	0.47	0.35	-1.2 to 1.4
10		0.6	0.08	0.05	-0.1 to 0.2
11	N ₂ - CO ₂	2.1	0.25	0.18	-0.7 to 0.7
12		0.7	0.07	0.05	-0.1 to 0.2
13		1.2	0.14	0.10	-0.5 to 0.2
14		1.3	0.30	0.24	-0.7 to 0.5
15	Ternary	5.3	0.63	0.56	-1.4 to -0.2
16		0.7	0.08	0.08	0.1 to 0.1
17		1.5	0.32	0.23	-0.8 to 0.4
Overall		1.3	0.18	0.10	-1.4 to 1.4

Table 8. Quality of BWR Compressibility Factor Predictions: Case 4*

System No.	System	Errors in Predicted Z Factor			
		RMS (x1000)	%RMS	%AAD	Range of % Deviations
1	CH ₄	1.1	0.12	0.10	-0.1 to 0.3
2	N ₂	0.7	0.07	0.04	-0.3 to 0.1
3	CO ₂	1.9	0.29	0.21	-0.4 to 0.8
4	CH ₄ - N ₂	2.7	0.27	0.22	-0.7 to 0.2
5		0.5	0.05	0.02	-0.3 to 0.6
6	CH ₄ - CO ₂	1.8	0.26	0.20	-0.6 to 0.6
7		1.7	0.23	0.19	-0.7 to 0.4
8		0.4	0.05	0.03	-0.2 to 0.2
9		2.6	0.68	0.49	-1.7 to 1.9
10		0.4	0.05	0.03	-0.2 to 0.2
11	N ₂ - CO ₂	2.6	0.41	0.25	-2.3 to 0.8
12		0.4	0.04	0.03	-0.1 to 0.2
13		1.2	0.13	0.09	-0.6 to 0.2
14		1.1	0.25	0.19	-0.6 to 0.7
15	Ternary	6.0	0.71	0.65	-1.5 to -0.2
16		0.1	0.02	0.01	0.0 to 0.0
17		1.5	0.35	0.27	-0.8 to 0.4
Overall		1.4	0.22	0.10	-2.3 to 1.9

*Results for predictions for complete T, P ranges of data, based on parameters from fits to reduced ranges of Case 4

Figure 1. Schematic Diagram of the Experimental Apparatus

Figure 2. Effect of Compressibility Factor Uncertainty on the Expected Uncertainties in Adsorption: Pure CO₂ on Activated Carbon at 113 °F

**Figure 3. Effect of Compressibility Factor Uncertainty on the expected
Uncertainties in Adsorption: CO₂ Component Adsorption in
40%CH₄+60%CO₂ on Activated Carbon at 113 °F**

Figure 4. Overall Summary Results for Case 1

Figure 5. Pure-Component Summary Results for Case 1

Figure 6. Overall Summary Results for Case 2

Figure 7. Pure-Component Summary Results for Case 2

Figure 8. Overall Summary Results for Case 3

Figure 9. Pure-Component Summary Results for Case 3

Figure 10. Overall Summary Results for Case 4

Figure 11. Pure-Component Summary Results for Case 4

Figure 12. Gibbs Adsorption Sensitivity to Variability in Compressibility
Factor: 40%CH₄+60%CO₂ on Activated Carbon at 113 °F

Adsorption of Methane, Nitrogen, Carbon Dioxide and their Binary Mixtures on Dry Activated Carbon at 318.2 K and Pressures to 13.6 MPa

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Abstract

A detailed experimental study has been made of the adsorption of pure methane, nitrogen and carbon dioxide and their binary mixtures on dry activated carbon (Filtrisorb 400, 12x40 mesh, Calgon Carbon) at 318.2 K and pressures to 13.6 MPa. The mixture measurements were made at nominal feed-gas compositions of 20, 40, 60 and 80 mole percent. The mixture data clearly elucidate the competitive nature of the individual-component adsorption from the mixtures.

Measurements were made using a volumetric technique, coupled with gas chromatographic analysis of the equilibrium gas phase compositions. Error propagation analysis reveals expected average experimental uncertainties in the amount adsorbed of 2% for pure methane and nitrogen and 6% for CO₂. For the mixture measurements, uncertainties are estimated to be about 3% for the total adsorption, while the individual-component uncertainties vary from 0.02 to 0.2 mmol/g activated carbon, depending on the mixture composition.

The data were correlated using the two-dimensional Zhou-Gasem-Robinson (ZGR) equation of state model. The model fits the pure component adsorption data within their experimental uncertainties, while the total and individual-component

adsorptions in the binary systems are represented within one to two times the expected experimental uncertainties.

As an additional benefit, the good agreement between the present data and those of Humayun and Tomasko for pure carbon dioxide (using two very different experimental techniques) suggests that these data provide a useful reference for benchmarking new experimental apparatus/techniques intended for high pressure adsorption measurements of supercritical gases.

Keyword: high pressure; adsorption; methane; nitrogen; carbon dioxide; activated carbon

1. Introduction

The authors' long-range objective is to develop reliable models to predict the adsorption behavior of supercritical gases on coals, with specific applications to (a) coalbed methane production and (b) the use of coalbeds to sequester the greenhouse gas carbon dioxide. In pursuit of that objective, we have performed both experimental¹ and modeling²⁻⁵ studies.

Evaluating mathematical models to describe adsorption behavior on coals is complicated by (a) the difficulty in characterizing the coal matrix adequately and (b) assessing the effect of water (found in essentially all coalbeds) on the adsorption behavior. As a result, we decided to perform studies on a more readily characterized carbon matrix and in the absence of water. This led to the choice of dry activated carbon for the present study. Our rationale is that useful models should be expected to fit the data on activated carbon prior to extending them to include the effects of the complex adsorbent structure of coals and/or the presence of water.

An added incentive was the fact that Humayun and Tomasko⁶ recently measured the adsorption of carbon dioxide on activated carbon using a gravimetric method. Combined, their data and ours could be used to confirm the mutual viability of the two experimental techniques employed. This is especially useful, since the gravimetric technique involves different experimental considerations than the volumetric method of our work.

Several theories and models have been developed to correlate high-pressure pure adsorption data and to predict gas mixture adsorption. In this study, we used the two-dimensional Zhou-Gasem-Robinson (ZGR) equation of state to demonstrate its ability

to correlate the experimental data. More general, detailed evaluations of the ZGR and other models (e.g., Ono-Kondo and Simplified Local Density) for adsorption on activated carbon and coals will soon appear elsewhere ^{7,8}.

2. Experimental Methods and Procedures

2.1 Adsorption Measurements

The experimental method is based on a mass balance principle, which employs precise measurements of pressures, volumes and temperatures. A brief description of the apparatus and procedures follows.

The experimental apparatus, shown schematically in Figure 1, has been used successfully in previous studies ¹. The pump and cell sections of the apparatus are maintained in two constant temperature air baths at 318.2 K. The equilibrium cell has a volume of 110 cm³ and is filled with the adsorbent to be studied. The cell is placed under vacuum prior to gas injection. The void volume V_{void} in the equilibrium cell is then determined by injected known quantities of helium from a calibrated injection pump (Ruska Pump). Since helium is not significantly adsorbed, the void volume can be determined from measured values of temperature, pressure and amount of helium injected into the cell. Several injections made into the cell at different pressures show consistency in the calculated void volume. Generally, the void volume calculated from sequential injections varies less than 0.3 cm³ from the average value (of approximately 100 cm³) based on at least five injections. The mass-balance equation, expressed in volumetric terms, is

$$V_{void} = \frac{\left(\frac{P\Delta V}{ZT} \right)_{pump}}{\left(\frac{P_2}{Z_2 T} - \frac{P_1}{Z_1 T} \right)_{cell}}, \quad (1)$$

where ΔV is the volume injected from the pump, Z is the compressibility factor of helium, T is the temperature, P is the pressure, subscripts “cell” and “pump” refer to conditions in the cell and pump sections of the apparatus, respectively, and “1” and “2” refer to conditions in the cell before and after injection of gas from the pump, respectively. During each injection step, the pressure in the pumps at the end of the injection is adjusted to the initial value, about 6.8 MPa (although the pressure in the pumps during the injection may vary). The void volume from these measurements is then used in subsequent measurements of adsorption, as follows.

The Gibbs adsorption (also known as the excess adsorption) can be calculated directly from experimental quantities. For pure-gas adsorption measurements, a known quantity, n_{inj} , of gas (e.g., methane) is injected from the pump section into the cell section. Some of the injected gas will be adsorbed, and the remainder, n_{unads}^{Gibbs} , will exist in the equilibrium bulk (gas) phase in the cell. A molar balance is used to calculate the amount adsorbed, n_{ads}^{Gibbs} , as

$$n_{ads}^{Gibbs} = n_{inj} - n_{unads}^{Gibbs} \quad (2)$$

The amount injected can be determined from pressure, temperature and volume measurements of the pump section:

$$n_{inj} = \left(\frac{P\Delta V}{ZRT} \right)_{pump} \quad (3)$$

The amount of unadsorbed gas is calculated from conditions at equilibrium in the cell:

$$n_{unads}^{Gibbs} = \left(\frac{PV_{Void}}{ZRT} \right)_{cell} \quad (4)$$

In Eqs. 3 and 4, Z is the compressibility of the pure gas at the applicable conditions of temperature and pressure.

The above steps are repeated at sequentially higher pressures to yield a complete adsorption isotherm. The amount adsorbed is usually presented as an intensive quantity (mmol adsorbed / g adsorbent or mmol/g) by dividing n_{ads}^{Gibbs} by the mass of adsorbent in the cell. Inspection of Eqs. 2-4 reveals that the amount adsorbed may be calculated in a straightforward manner from experimental measurements of pressures, temperatures and volumes, coupled with independent knowledge of the gas compressibility factors, Z (from experimental data or a suitably accurate equation of state).

For mixed-gas adsorption measurements, a volumetrically prepared gas mixture of known composition (z_i) is injected; thus, the total amount of each component in the cell is known. A magnetic pump is used to circulate the fluid mixture to ensure that equilibrium is reached. The composition (y_i) of the gas phase in the cell at equilibrium is determined by chromatographic analysis. A pneumatically controlled sampling valve, contained in the air bath at cell temperature, sends a 20 μ L sample to the gas chromatograph (GC) for analysis. The amount of each individual component adsorbed is calculated using component material balances; for component “i” in the mixture, the relations are

$$n_{ads(i)}^{Gibbs} = n_{inj(i)} - n_{unads(i)}^{Gibbs} = n_{inj} z_i - n_{unads}^{Gibbs} y_i \quad (5)$$

where

$$n_{inj(i)} = \left(\frac{P\Delta V}{ZRT} \right)_{pump} z_i \quad (6)$$

and Z is the compressibility of the *feed* gas mixture at pump conditions, and

$$n_{unads(i)}^{Gibbs} = \left(\frac{PV_{Void}}{ZRT} \right)_{cell} y_i \quad (7)$$

where Z is the compressibility of the *equilibrium* gas mixture at cell conditions.

2.2 Relationship between Gibbs and Absolute Adsorption

Adsorption data may also be reported in terms of *absolute* adsorption. Calculations for the Gibbs and absolute adsorption differ in the manner by which n_{unads} is calculated. The Gibbs adsorption calculation, described above, neglects the volume occupied by the adsorbed phase in calculating the amount of unadsorbed gas (i.e., in Eq. 4, the entire void volume, V_{void} , is viewed as being available to the unadsorbed gas).

Following is a discussion to clarify the relationships between the Gibbs and absolute adsorption and to highlight the approximate nature of the calculated absolute adsorption. In addition, expressions are presented which facilitate calculation of the absolute component adsorption, $n_{ads(i)}^{Abs}$, and the adsorbed-phase mole fraction, x_i^{Abs} , in terms of the experimental Gibbs adsorption results.

Pure Component Adsorption: First, consider the various volumes that can be used to characterize the state existing in the equilibrium cell. Using a representation that

envision two distinct, homogeneous fluid phases (bulk gas and adsorbed phase), the total system volume V_{total} of the experimental apparatus is the sum of the volumes of solid adsorbent (V_{solid}), gas (V_{gas}), and adsorbed-phase (V_{ads}), as follows:

$$V_{total} = V_{solid} + V_{gas} + V_{ads} \quad (8)$$

The void volume, having been determined by helium injection, is related to these quantities as follows:

$$V_{void} = V_{gas} + V_{ads} = V_{total} - V_{solid} \quad (9)$$

Now, consider the amount of material adsorbed at equilibrium, which may be written in molar terms as follows:

$$n_{ads} = n_{total} - n_{unads} \quad (10)$$

The difference in the definitions of the Gibbs and total adsorption resides in the manner in which n_{unads} is related to the volume terms. As stated previously, in the Gibbs calculation, the volume occupied by the condensed phase is neglected in calculating n_{unads} , and the amount of unadsorbed gas is calculated using the entire void volume; thus, Eq. 10 becomes, using Eq. 9 for V_{void} ,

$$n_{ads}^{Gibbs} = n_{total} - V_{void} \mathbf{r}_{gas} \quad (11)$$

where $\mathbf{r}$ denotes density. In the calculation of the absolute adsorption, n_{unads} is determined using the volume actually available to the bulk gas phase (accounting for the reduction of volume accessible to the gas as a result of the volume occupied by the adsorbed phase):

$$n_{ads}^{Abs} = n_{total} - V_{gas} \mathbf{r}_{gas} \quad (12)$$

By combining Eqs. 11 and 12 to eliminate n_{total} , the following relation between Gibbs and absolute adsorption is obtained:

$$n_{ads}^{Gibbs} = n_{ads}^{Abs} - V_{ads} \mathbf{r}_{gas} \quad (13)$$

The volume of the adsorbed phase may be expressed in terms of the amount adsorbed and the density of the adsorbed phase as

$$V_{ads} = n_{ads}^{Abs} / \mathbf{r}_{ads} \quad (14)$$

Combining Eqs. 13 and 14 yields

$$n_{ads}^{Gibbs} = V_{ads} (\mathbf{r}_{ads} - \mathbf{r}_{gas}) \quad (15)$$

Eq. 15 clearly illustrates the physical interpretation of the Gibbs adsorption, namely, the amount adsorbed in excess of that which would be present if the adsorbed phase volume were filled with bulk gas. Combining Eqs. 14 and 15 leads to:

$$n_{ads}^{Abs} = n_{ads}^{Gibbs} \left(\frac{\mathbf{r}_{ads}}{\mathbf{r}_{ads} - \mathbf{r}_{gas}} \right) \quad (16)$$

An important consideration in the calculation of the absolute adsorption is that it requires knowledge of the adsorbed phase density, $\mathbf{r}_{ads}$, which is not readily accessible by experimental measurement. Thus, estimates of $\mathbf{r}_{ads}$ are usually employed. A commonly used approximation is the liquid density at the atmospheric pressure boiling point, as was done by Arri and Yee⁹. In this study, however, we

used model-regressed estimates for the adsorbed-phase density, as discussed in Section 3.

Adsorption from Mixtures: For absolute adsorption, the component mole fractions in the adsorbed phase, x_i^{Abs} , may be calculated from the component Gibbs adsorptions; however, this requires some assumption regarding the density, ρ_{ads} , of the adsorbed phase *mixture*. In the following discussion, ρ_{ads} is approximated using the assumption of ideal mixing in the adsorbed phase, where the pure-component adsorbed-phase density estimates are used to calculate the mixture adsorbed-phase density. The component Gibbs adsorption (amount of component “i” in the adsorbed phase in excess of the amount that would be present if the bulk equilibrium gas mixture occupied the volume of the adsorbed phase) may be written using a component material balance as

$$n_{ads(i)}^{Gibbs} = n_{ads}^{Abs} x_i^{Abs} - V_{ads} \rho_{gas} y_i = V_{ads} \left(\rho_{ads} x_i^{Abs} - \rho_{gas} y_i \right) \quad (17)$$

For convenience, we define a fractional component Gibbs adsorption, q_i^{Gibbs} , as

$$q_i^{Gibbs} \equiv \frac{n_{ads(i)}^{Gibbs}}{n_{ads}^{Gibbs}} \quad (18)$$

(Note that, although Eq. 18 has the appearance of a mole fraction, the Gibbs adsorption is an excess quantity, not a total quantity for a specified phase; thus q_i , rather than x_i , is used to denote the quantity.)

Inserting this definition into Eq. 17, we obtain

$$n_{ads}^{Gibbs} q_i^{Gibbs} = n_{ads}^{Abs} \left(x_i^{Abs} - y_i \frac{\rho_{gas}}{\rho_{ads}} \right) \quad (19)$$

Combining Eq. 16 with Eq. 19,

$$x_i^{Abs} = \mathbf{q}_i^{Gibbs} \left(1 - \frac{\mathbf{r}_{gas}}{\mathbf{r}_{ads}} \right) + y_i \left(\frac{\mathbf{r}_{gas}}{\mathbf{r}_{ads}} \right) \quad (20)$$

Eq. 20 reveals that x_i^{Abs} and $\mathbf{q}_i^{Gibbs}$ become identical in the limit of low pressure (where $\mathbf{r}_{gas}$ becomes small).

Inspection of Eq. 20 reveals that all quantities on the right hand side can be obtained directly from experimental measurements except $\mathbf{r}_{ads}$, for which some approximation must be made. If ideal mixing is used to represent $\mathbf{r}_{ads}$ in terms of the pure component adsorbed-phase densities, we have

$$\frac{1}{\mathbf{r}_{ads}} = \frac{x_1^{Abs}}{\mathbf{r}_{ads(1)}} + \frac{x_2^{Abs}}{\mathbf{r}_{ads(2)}} \quad (21)$$

where the subscripts “1” and “2” refer to pure components. Then, Eq. 20 may be written as

$$x_1^{Abs} = 1 - x_2^{Abs} = \frac{\mathbf{q}_1^{Gibbs} \mathbf{r}_{ads(2)} + \mathbf{r}_{gas} (y_1 - \mathbf{q}_1^{Gibbs})}{\mathbf{r}_{ads(2)} + \mathbf{r}_{gas} (y_1 - \mathbf{q}_1^{Gibbs}) \left(1 - \frac{\mathbf{r}_{ads(2)}}{\mathbf{r}_{ads(1)}} \right)} \quad (22)$$

and the absolute component adsorption can be calculated as follows:

$$n_{ads(i)}^{Abs} = n_{abs}^{Abs} x_i^{Abs} \quad (23)$$

with Eq. 16 used to calculate the *total* mixture adsorption, n_{ads}^{Abs} , where the densities, $\mathbf{r}_{ads}$ and $\mathbf{r}_{gas}$, refer to mixtures of compositions x_i^{Abs} and y_i , respectively.

2.3 Gas Compressibility Factors

As indicated by Eqs. 3 through 7, accurate gas-phase compressibility (Z) factors are required for methane, nitrogen and carbon dioxide and their mixtures to properly analyze the experimental data. The compressibility factors for pure methane,

nitrogen, and CO₂ were determined from highly accurate equations of state ¹⁰⁻¹². For void volume determination, the helium compressibility factor is given by ¹³

$$Z_{He} = 1 + (0.001471 - 0.000004779T + 0.00000000492T^2) / P \quad (24)$$

where T is in Kelvins and P is in atmospheres. This expression is based on the experimental data from National Bureau of Standards Technical Note 631 for helium.

A careful evaluation of the current literature led us to conclude that an adequate predictive capability for the mixture Z factors did not exist. Therefore, we elected to use available pure-fluid and binary mixture data to refit the Benedict-Webb-Rubin equation of state (BWR EOS) and improve its accuracy significantly. In general, the new BWR parameters yield deviations in the Z factors of less than 0.5%. This allowed us to address our compressibility factor needs for binary adsorption mixtures. Details of the BWR equation expressions are given elsewhere ¹⁴.

2.4 Materials

The pure gases used in this work were obtained from Airgas-Pennsylvania with reported purities of about 99.99% and were used as received. A bituminous-coal-based activated carbon (Filtrisorb 400, 12x40 mesh, Calgon Carbon) was used as the adsorbent; its compositional analysis is presented in Table 1. The composition of activated carbon is less complex than coals. In particular, it has a higher carbon content (ultimate and proximate) and significantly less volatile matter than typical coals, leading to a less complex characterization problem when interpreting solid-fluid interactions in the adsorption process. The activated carbon was washed in demineralized water, then dried under vacuum at 230°F for two days before being

used in the adsorption measurements. The nitrogen BET surface area at 77 K has been reported to be 850 m²/g ⁶.

2.5 Calibrations

Calibrations were performed routinely during the course of the experiments. The temperature measuring devices were calibrated against a Minco platinum resistance reference thermometer, and the pressure transducers were calibrated against a Ruska deadweight tester with calibration traceable to the National Institute of Science and Technology.

The gas chromatograph was calibrated against volumetrically-prepared mixtures at the nominal feed-gas concentrations. The GC used for composition analysis is a Varian Chrompack CP-3800 with the helium carrier gas maintained at a 0.25-mL/s flow rate. A 10-ft Haysep D packed-column was used for CH₄/CO₂ and N₂/CO₂ systems, and a molecular sieve 13X column was used for the CH₄/N₂ system; column temperature was 80°C. A thermal conductivity detector was used for all of the binary systems studied; its bath temperature was set at 100°C. The chromatographic response factor, defined as $(A_2 / A_1)(y_1 / y_2)$ where A is the GC response area, was found to depend slightly on pressure; as such, the GC was calibrated for each nominal composition at pressure intervals of 1.4 MPa.

The uncertainties in the experimentally measured quantities after calibrations were estimated as follows: temperatures, 0.1 K; pressures, 6.9 kPa; injected gas volumes, 0.02 cm³; gas mixture compositions, 0.002 mole fraction.

A detailed error propagation analysis was performed, which indicates that the average uncertainties for the pure adsorption measurements are approximately 1.8%

(0.065-0.069 mmol/g) for methane adsorption, 2.3% (0.054-0.056 mmol/g) for nitrogen and 6.4 % (0.269-0.342 mmol/g) for CO₂ adsorption. The higher percentage uncertainty for CO₂ is due mainly to the lower value of the Gibbs adsorption for CO₂ at the higher pressure and the higher uncertainty in the CO₂ compressibility factor (due to its proximity to its critical point).

The uncertainties for the binary mixture adsorptions vary with composition. Uncertainties for all the binary gas *total* adsorption measurements are within 4%. The percent uncertainty of component gas adsorption, however, can become high at low concentrations of the less adsorbed gases (i.e., nitrogen in the nitrogen/CO₂ system). Table 2 presents estimated uncertainties for the mixed gas adsorption measurements.

3. Experimental Results

3.1 Pure Gas Adsorption

The experimental data for pure gas adsorption are listed in Tables 3-5. Two independent sets of measurements (Runs 1 and 2) for each component were performed to confirm the reproducibility of the data. The results, shown in Figure 2, verify the reproducibility of our procedures, since the replicate measurements agree within expected experimental uncertainties.

Figure 2 presents both the Gibbs and absolute adsorption behaviors of methane, nitrogen and CO₂ on activated carbon. Both methane and CO₂ exhibit maxima in the Gibbs adsorption. Further, the absolute adsorption of CO₂ on activated carbon is about 60% greater than methane and 120% greater than nitrogen. Also shown in the figure are predictions of absolute adsorption from the ZGR equation of state, as

described in Section 4, below. Selected experimental uncertainty bars are shown on the CO₂ data for illustrative purposes.

In calculating the absolute adsorption, we used a constant adsorbed-phase-density assumption. The densities employed, generated by the Ono-Kondo model ⁵, are 0.354 g/cm³, 0.701 g/cm³ and 0.996 g/cm³ for methane, nitrogen and CO₂, respectively. As shown in Table 6, the adsorbed-phase densities from the Ono-Kondo model ⁵ are less than the boiling point estimates and close to the van der Waals estimates. Also shown in Table 6 is an entry labeled “Graphical estimate from the Gibbs adsorption isotherm,” which is based on Eq. 15 and illustrated by Figure 3. As shown in the figure for CO₂, when the absolute adsorption, $V_{ads}r_{ads}$, becomes constant at high pressures, then the Gibbs adsorption shows a linear decrease with increasing r_{gas} . Extrapolation of this linear relation yields an x-axis intercept where $r_{ads} = r_{gas}$. In this illustration, the graph indicates that $r_{ads} = 22.5$ mol/L or 1.02 g/cm³. Use of this technique requires sufficient data in the linear (high pressure) region beyond the maximum in the Gibbs adsorption; thus, an estimate is shown in Table 6 only for carbon dioxide.

Figure 4a presents a comparison of the present data for pure CO₂ with the previous measurements of Humayun and Tomasko ⁶. The measurements from their gravimetric flow apparatus are almost continuous (in frequency of acquisition), so their results appear as a continuous line in the figure. Close comparison (using a deviation plot, Figure 4b) reveals that the two data sets agree within their combined experimental uncertainties throughout most of the range of data. This provides a very

useful confirmation of both groups' experimental results. Figure 4b also illustrates that the ZGR model fits the data within their experimental uncertainties.

3.2 Binary Gas Adsorption

Tables 7-9 present the experimental data for CH₄/N₂, CH₄/CO₂, and N₂/CO₂ at nominal molar feed gas compositions of 20, 40, 60 and 80% with a specific void volume ranging from 2.04-2.57 cm³/g. A maximum in the Gibbs adsorption is observed for the lesser-adsorbed component at all feed compositions while the same phenomenon is only observed at higher feed compositions for the more highly adsorbed component. Beyond this maximum, the amount adsorbed decreases with increasing pressure. In fact, negative values for the Gibbs adsorption of nitrogen occur at feed composition of 40% and 20% nitrogen in the nitrogen/CO₂ system at high pressures. Physically, this means that less nitrogen is present in the adsorbed phase than would be present if the equilibrium bulk-phase gas replaced the condensed phase; this reflects the high selectivity for CO₂ over N₂ in the adsorbed phase, which leads to low nitrogen concentrations (g mol N₂/m³) in that phase.

Figures 5-10 show the absolute adsorption of individual components from the mixtures. For completeness, pure substance adsorption is included in each figure. For each of the binary systems, the more volatile (lower critical temperature) gas is the more strongly adsorbed component only when its equilibrium gas composition is high (greater than 80%N₂ in CH₄/N₂; greater than 75%CH₄ in CH₄/CO₂; greater than 90%N₂ in N₂/CO₂).

Dreisbach and co-workers have studied the adsorption behavior of these gases on a similar adsorbent, Norit R1 Extra activated carbon, at room temperature and

pressures to 6 MPa using a gravimetric method ¹⁵. Their study differs in several aspects from the present work. For binary adsorption, they used an equation of state to infer both the *bulk phase composition* and *density* from P-T measurements and system volume calibrations, while we used an EOS to infer the *density* from P-T-y measurements. Also, our measurements extend to much higher pressures (13.6 MPa) because at such higher pressures the adsorption data exhibit maxima for carbon dioxide and methane ^{6,16-20}.

4. Equation-of-State Modeling

Over the years, various researchers have applied two-dimensional equations of state (2-D EOS) to gas adsorption. Hill ²¹ and de Boer ²² used the van der Waals (VDW) EOS to correlate pure-gas adsorption. Hoory and Prausnitz ²³ extended the 2-D VDW EOS to mixtures by introducing mixing rules. More recently, Degance ²⁴ used the 2-D virial and Eyring EOS to correlate high-pressure pure adsorption isotherms.

In the early 1990's, we developed a generalized 2-D cubic EOS, which encompasses 2-D analogs of all the previous cubic EOS forms ². The generalized 2-D EOS is analogous to the popular three-dimensional equations of state used in vapor-liquid equilibrium calculations; in generalized form:

$$\left[P + \frac{a\mathbf{r}^2}{1 + Ub\mathbf{r} + W(b\mathbf{r})^2} \right] [1 - b\mathbf{r}] = \mathbf{r}RT \quad (25)$$

Where a and b are the traditional EOS parameters, and numerical values of U and W may be specified to give various forms of three-dimensional equations of state. In the most general form, the two-dimensional analog of the generalized cubic equation can be expressed as follows (with an additional parameter m for added model flexibility):

$$\left[A\mathbf{p} + \frac{\mathbf{a}\mathbf{w}^2}{1+U\mathbf{b}\mathbf{w}+W(\mathbf{b}\mathbf{w})^2} \right] \left[1 - (\mathbf{b}\mathbf{w})^m \right] = \mathbf{w}RT \quad (26)$$

where A is the specific surface area, $\mathbf{p}$ is the spreading pressure, $\mathbf{w}$ is the specific amount adsorbed (mmol/g of adsorbent), and $\mathbf{a}$ and $\mathbf{b}$ are (regressed) model parameters. The model coefficients, U , W , and m must be specified to obtain a specific form of the 2-D EOS for application. For example, an analog of the van der Waals (VDW) EOS is obtained by setting $m = 1$ and $U = W = 0$, and similarly for the Soave-Redlich-Kwong (SRK) ($m = U = 1$ and $W = 0$), the Peng-Robinson (PR) ($m = 1$, $U = 2$, and $W = -1$), and the Eyring ($m = 1/2$ and $U = W = 0$) EOS.

This general 2-D EOS can be used to investigate EOS behaviors by specifying various combinations of model coefficients. The model coefficient m has been found to be the most important among the EOS model coefficients, because it has a significant effect on the shape of the pure adsorption isotherm. If U and W are equal to zero, then by setting m to values of ∞ , 1, and 1/2, we obtain the 2-D ideal gas law, the VDW EOS, and the Eyring EOS, respectively.

Actually, pure gas isotherms vary considerably in shape and Zhou² found that it is sometimes desirable to select an m value even smaller than 1/2 to describe pure isotherms. He determined that an equation with $m = 1/3$ and $U = W = 0$ (the Zhou-Gasem-Robinson [ZGR] EOS) showed considerable promise and that the 2-D EOS could be applied to adsorbed phases containing mixtures by utilizing the traditional mixing rules (where x is the mole fraction in the adsorbed phase):

$$\mathbf{a} = \sum_i \sum_j x_i x_j \mathbf{a}_{ij} \quad (27)$$

$$\mathbf{b} = \sum_i \sum_j x_i x_j \mathbf{b}_{ij} \quad (28)$$

along with the non-traditional combination rules:

$$\begin{aligned} \mathbf{a}_{ij} &= (1 - C_{ij})(\mathbf{a}_i + \mathbf{a}_j)/2 \\ \mathbf{b}_{ij} &= \sqrt{\mathbf{b}_i \mathbf{b}_j} (1 + D_{ij}) \end{aligned} \quad (29)$$

where C_{ij} and D_{ij} are empirical binary interaction parameters.

The absolute adsorption of the pure and binary gas systems was correlated with the two-dimensional on ZGR EOS, which is described in detail elsewhere ². The equilibrium between the adsorbed phase and the gas phase will lead to the following relation ²:

$$Ax_i \mathbf{p} \hat{\mathbf{f}}_i^a = k_i RT \hat{\mathbf{f}}_i^g \quad (30)$$

where $\hat{\mathbf{f}}_i^a$ is the coefficient fugacity in the adsorbed phase obtained from 2D EOS model, $\hat{\mathbf{f}}_i^g$ is fugacity in the gas phase obtained from 3D EOS, and k_i represents the slope of the pure component ($\mathbf{w}$ vs. P) isotherm at the origin. For the ZGR EOS, the fugacity expression is:

$$\ln \hat{\mathbf{f}}_i^a = \frac{2 \sum_j \mathbf{b}_{ij} \mathbf{w}_j - \mathbf{b} \mathbf{w}}{(\mathbf{b} \mathbf{w})^{l-m} - \mathbf{b} \mathbf{w}} - \frac{l}{m} \ln [l - (\mathbf{b} \mathbf{w})^m] - \ln Z_a - \frac{2}{RT} \sum_j \mathbf{a}_{ij} \mathbf{w}_j \quad (31)$$

where $Z_a = \mathbf{p} A / \mathbf{w} RT$. In the present work, the gas phase fugacities were calculated using a modified Redlich-Kwong EOS ².

Regressions used to determine the model coefficients minimized the sum of squares of the relative errors in the predicted amounts adsorbed. The optimized parameters included a and β for each pure component, as well as the k (in Eq. 30) for each pure system and the interaction parameters, C_{ij} and D_{ij} , for each binary system.

Figure 2 shows the two-dimensional ZGR-EOS representation of the pure-component adsorption. The model shows excellent fit, within the experimental uncertainties. Table 10 presents the parameters used to fit the pure adsorption data.

The parameters obtained from the pure adsorption, plus the two optimized binary interaction parameters were used to represent the binary adsorption data. Table 11 contains the binary interaction parameters used for these mixtures. Figures 5-10 show the model representation for component adsorption of the binary systems studied. The figures show that the model represents the mixture data within one-to-two times the experiment uncertainties. We anticipate that representation of the data can be improved, however, by use of improved mixing rules in the ZGR EOS modeling and by inclusion of non-ideal mixing rules for the adsorbed phase density in the data reduction (in place of Eq. 21).

5. Conclusion

The adsorption of methane, nitrogen, CO₂ and their binary mixtures was measured on dry activated carbon at 318.2 K and pressures to 13.6 MPa using a volumetric/gas chromatographic method. Both Gibbs and absolute adsorption results are presented. The ZGR equation of state is shown to be capable of describing the pure component data within their experimental uncertainties and the mixture data within one-to-two times the expected uncertainties. Finally, the data for CO₂ are recommended as a reference data set for evaluation of experimental apparatus/techniques for measuring high-pressure adsorption from supercritical gases.

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Table 1. Analysis of Calgon Activated Carbon Used in This Study

Analysis	Units	Value	Lower Limit	Upper Limit
<i>Manufacturer specification*</i>				
Abrasion Number		87	75	-
Apparent Density	g/cm ³	0.53	0.44	-
Skeleton Density	g/cm ³	2.02		
Ash	%	7	-	9
Effective Size	mm	0.64	0.55	0.75
Iodine Number	mg/g	1046	1000	-
US Sieve Series on 12	%	1	-	5
US Sieve Series –40 Mesh	%	1	-	4
<i>Ultimate**</i>				
Carbon	%	88.65		
Hydrogen	%	0.74		
Oxygen	%	3.01		
Nitrogen	%	0.40		
Sulfur	%	0.73		
Ash	%	6.47		
<i>Proximate**</i>				
Vol. Matter	%	3.68		
Fixed Carbon	%	89.85		
Ash	%	6.47		

* Calgon Carbon Corp., Pittsburgh, Pennsylvania.

** Huffman Laboratories, Inc., Golden, Colorado.

Table 2. Expected Uncertainties in Binary Mixture Adsorption Measurements

System	Feed Gas Composition %	Total		CH ₄		N ₂		CO ₂	
		σ	% σ	σ	% σ	σ	% σ	σ	% σ
CH ₄ /N ₂	20/80	0.083	3.1	0.034	3.6	0.059	3.3	-	-
	40/60	0.075	2.4	0.051	2.7	0.038	3.1	-	-
	60/40	0.080	2.5	0.068	2.6	0.029	4.5	-	-
	80/20	0.085	2.4	0.081	2.4	0.020	10.0	-	-
CH ₄ /CO ₂	20/80	0.200	3.7	0.040	17.7	-	-	0.189	3.7
	40/60	0.165	3.3	0.056	5.5	-	-	0.135	3.4
	60/40	0.159	3.5	0.078	4.1	-	-	0.098	3.7
	80/20	0.162	3.9	0.116	4.0	-	-	0.057	4.3
N ₂ /CO ₂	20/80	0.141	2.8	-	-	0.034	39.5	0.144	2.9
	40/60	0.130	3.1	-	-	0.050	27.9	0.124	3.3
	60/40	0.124	3.5	-	-	0.059	6.6	0.100	3.8
	80/20	0.116	4.1	-	-	0.077	4.4	0.055	4.6

σ : Average absolute uncertainty, mmol/g

% σ : Average absolute percent uncertainty, %

Table 3. Pure Methane Adsorption on Activated Carbon at 318.2K

Run 1			Run 2		
Pressure (MPa)	Gibbs Adsorption (mmol/g)	Absolute Adsorption (mmol/g)	Pressure (MPa)	Gibbs Adsorption (mmol/g)	Absolute Adsorption (mmol/g)
0.55	1.870	1.888	0.88	2.394	2.432
1.23	2.762	2.822	1.56	3.082	3.170
2.55	3.586	3.755	2.86	3.778	3.985
3.48	3.891	4.149	4.29	4.156	4.513
4.80	4.145	4.541	5.33	4.310	4.786
6.18	4.283	4.835	6.95	4.427	5.101
7.64	4.339	5.066	8.36	4.445	5.301
9.03	4.337	5.238	9.74	4.412	5.450
10.37	4.286	5.357	11.08	4.357	5.576
11.76	4.209	5.459	12.45	4.269	5.677
13.25	4.106	5.549			

Table 4. Pure Nitrogen Adsorption on Activated Carbon at 318.2 K

Run 1			Run 2		
Pressure (MPa)	Gibbs Adsorption (mmol/g)	Absolute Adsorption (mmol/g)	Pressure (MPa)	Gibbs Adsorption (mmol/g)	Absolute Adsorption (mmol/g)
0.69	0.996	1.007	0.89	1.190	1.206
1.73	1.741	1.788	1.81	1.795	1.845
2.86	2.224	2.324	2.80	2.217	2.314
4.10	2.566	2.735	4.19	2.600	2.775
5.53	2.823	3.078	5.56	2.841	3.100
6.97	2.990	3.338	6.96	3.005	3.354
8.31	3.086	3.522	8.29	3.105	3.543
9.66	3.155	3.683	9.70	3.173	3.707
11.10	3.199	3.826	11.19	3.214	3.850
12.46	3.199	3.916	12.45	3.229	3.952
13.66	3.197	3.994	13.65	3.235	4.041

Table 5. Pure CO₂ Adsorption on Activated Carbon at 318.2 K

Run 1			Run 2		
Pressure (MPa)	Gibbs Adsorption (mmol/g)	Absolute Adsorption (mmol/g)	Pressure (MPa)	Gibbs Adsorption (mmol/g)	Absolute Adsorption (mmol/g)
0.36	2.962	2.982	0.59	3.831	3.870
0.73	4.170	4.223	1.15	5.051	5.155
1.19	5.064	5.172	1.89	5.878	6.086
1.79	5.783	5.976	2.63	6.343	6.672
2.52	6.300	6.611	3.47	6.682	7.172
3.30	6.650	7.106	5.94	6.873	7.987
4.29	6.962	7.641	6.84	6.748	8.188
5.56	7.078	8.101	7.96	6.395	8.393
7.01	6.882	8.434	8.64	5.993	8.515
8.30	6.348	8.623	9.17	5.434	8.512
9.64	4.810	8.577	10.02	4.188	8.390
11.06	3.449	8.781	11.11	3.335	8.569
13.36	2.638	8.924	12.90	2.706	8.751

Table 6. Adsorbed-Phase Densities Estimated by Different Methods

Method	Adsorbed-Phase Density (g/cm ³)		
	Methane	Nitrogen	CO ₂
Ono-Kondo model	0.354	0.701	0.996
ZGR EOS	0.345	0.839	0.982
Liquid density estimate	0.421	0.808	---
Solid density estimate	---	---	1.18
Van der Waals covolume	0.374	0.725	1.03
Graphical estimate from the Gibbs adsorption isotherm	---	---	1.02

Table 7. Methane/Nitrogen Adsorption on Dry Activated Carbon
at 318.2 K

Pressure (MPa)	Methane Gas Mole Fraction	Methane Adsorption (mmol/g)		Nitrogen Adsorption (mmol/g)	
		Gibbs	Absolute	Gibbs	Absolute
Methane Feed Composition: 81.7%, Specific Void Volume = 2.57 cm ³ /g					
0.65	0.649	1.600	1.613	0.227	0.234
1.39	0.674	2.372	2.416	0.293	0.314
2.76	0.703	3.193	3.317	0.330	0.382
4.21	0.721	3.598	3.822	0.309	0.396
5.65	0.732	3.877	4.214	0.267	0.390
6.94	0.744	3.994	4.442	0.257	0.411
8.35	0.752	4.082	4.657	0.224	0.414
9.74	0.759	4.123	4.828	0.195	0.419
11.05	0.763	4.145	4.976	0.156	0.414
12.44	0.768	4.132	5.099	0.130	0.423
Methane Feed Composition: 60.0%, Specific Void Volume = 2.57 cm ³ /g					
0.75	0.370	1.156	1.164	0.491	0.504
1.43	0.394	1.692	1.714	0.647	0.682
2.70	0.424	2.318	2.380	0.764	0.848
4.20	0.451	2.756	2.879	0.802	0.951
5.52	0.468	3.006	3.190	0.793	1.002
6.97	0.482	3.193	3.451	0.763	1.040
8.36	0.491	3.342	3.675	0.702	1.047
9.71	0.501	3.405	3.814	0.660	1.067
11.07	0.509	3.459	3.948	0.611	1.083
12.43	0.513	3.520	4.089	0.541	1.081
Methane Feed Composition: 40.0%, Specific Void Volume = 2.57 cm ³ /g					
0.77	0.204	0.735	0.739	0.731	0.745
1.60	0.230	1.155	1.169	1.058	1.104
2.85	0.240	1.593	1.627	1.261	1.366
4.16	0.251	1.917	1.977	1.343	1.521
5.53	0.271	2.115	2.210	1.404	1.660
6.98	0.284	2.278	2.414	1.408	1.750
8.29	0.291	2.415	2.589	1.368	1.792
9.62	0.298	2.514	2.729	1.322	1.829
11.01	0.305	2.574	2.835	1.277	1.869
12.44	0.315	2.593	2.903	1.255	1.931
Methane Feed Composition: 20.0%, Specific Void Volume = 2.57 cm ³ /g					
0.76	0.094	0.326	0.328	0.915	0.929
1.50	0.100	0.520	0.525	1.348	1.389
2.77	0.106	0.754	0.766	1.754	1.856
4.16	0.112	0.942	0.965	1.987	2.169
5.55	0.119	1.075	1.112	2.116	2.386
6.95	0.128	1.158	1.211	2.200	2.560
8.36	0.131	1.248	1.317	2.213	2.669
9.70	0.137	1.292	1.379	2.231	2.777
11.07	0.143	1.317	1.424	2.232	2.870
12.44	0.147	1.348	1.473	2.210	2.940

Table 8. Methane/CO₂ Adsorption on Dry Activated Carbon
at 318.2 K

Pressure (MPa)	Methane Gas Mole Fraction	Methane Adsorption (mmol/g)		CO ₂ Adsorption (mmol/g)	
		Gibbs	Absolute	Gibbs	Absolute
Methane Feed Composition: 80.0%, Specific Void Volume = 2.57 cm ³ /g					
0.77	0.890	1.930	1.960	0.567	0.571
1.46	0.886	2.515	2.591	0.784	0.794
2.81	0.884	3.035	3.225	1.057	1.082
4.12	0.883	3.237	3.556	1.249	1.291
5.55	0.877	3.317	3.789	1.396	1.462
6.92	0.871	3.322	3.951	1.495	1.588
8.30	0.866	3.252	4.042	1.562	1.684
9.67	0.861	3.166	4.127	1.616	1.771
11.04	0.856	3.060	4.194	1.649	1.839
12.41	0.852	2.943	4.253	1.664	1.892
Methane Feed Composition: 60.0%, Specific Void Volume = 2.57 cm ³ /g					
0.68	0.777	1.475	1.500	1.182	1.189
1.42	0.775	1.938	2.009	1.705	1.726
2.77	0.766	2.240	2.418	2.275	2.329
4.17	0.755	2.306	2.614	2.667	2.767
5.56	0.744	2.267	2.717	2.949	3.103
6.95	0.727	2.215	2.810	3.099	3.323
8.30	0.720	2.063	2.811	3.252	3.543
9.66	0.707	1.946	2.848	3.310	3.683
11.04	0.700	1.788	2.859	3.377	3.838
12.41	0.688	1.674	2.908	3.344	3.903
Methane Feed Composition: 40.1%, Specific Void Volume = 2.57 cm ³ /g					
0.68	0.618	1.044	1.066	1.922	1.935
1.44	0.610	1.328	1.391	2.737	2.777
2.75	0.603	1.436	1.591	3.567	3.670
4.18	0.582	1.403	1.671	4.107	4.300
5.54	0.560	1.330	1.713	4.426	4.726
6.90	0.548	1.189	1.700	4.680	5.102
8.29	0.529	1.077	1.718	4.769	5.341
9.69	0.513	0.940	1.723	4.805	5.547
11.01	0.500	0.820	1.741	4.754	5.677
12.43	0.486	0.699	1.774	4.641	5.776
Methane Feed Composition: 20.0%, Specific Void Volume = 2.57 cm ³ /g					
0.68	0.391	0.558	0.574	2.876	2.901
1.35	0.382	0.657	0.699	3.865	3.932
2.75	0.366	0.648	0.756	4.991	5.179
4.21	0.340	0.580	0.764	5.588	5.945
5.58	0.323	0.475	0.737	5.920	6.470
6.95	0.302	0.400	0.741	6.018	6.807
8.32	0.286	0.299	0.727	5.984	7.054
9.66	0.270	0.204	0.720	5.762	7.157
11.00	0.256	0.159	0.790	5.556	7.385
12.41	0.244	0.106	0.862	5.162	7.503

Table 9. Nitrogen/CO₂ Adsorption on Dry Activated Carbon
at 318.2 K

Pressure (MPa)	Nitrogen Gas Mole Fraction	Nitrogen Adsorption (mmol/g)		CO ₂ Adsorption (mmol/g)	
		Gibbs	Absolute	Gibbs	Absolute
Nitrogen Feed Composition: 80.0%, Specific Void Volume = 2.04 cm ³ /g					
0.79	0.954	0.959	0.975	0.357	0.358
1.53	0.945	1.398	1.443	0.563	0.566
2.74	0.944	1.792	1.902	0.827	0.833
4.18	0.946	2.015	2.221	1.090	1.101
5.57	0.947	2.099	2.408	1.312	1.330
6.95	0.946	2.118	2.537	1.503	1.527
8.34	0.942	2.102	2.637	1.663	1.696
9.70	0.937	2.061	2.711	1.792	1.835
11.12	0.934	1.994	2.766	1.919	1.974
12.65	0.929	1.909	2.813	2.032	2.101
Nitrogen Feed Composition: 58.1%, Specific Void Volume = 2.04 cm ³ /g					
0.90	0.888	0.808	0.831	0.949	0.952
1.54	0.880	1.042	1.095	1.365	1.373
2.74	0.872	1.234	1.363	1.957	1.976
4.26	0.866	1.265	1.511	2.543	2.581
5.56	0.853	1.222	1.578	2.926	2.987
6.96	0.843	1.121	1.603	3.278	3.368
8.31	0.831	1.011	1.618	3.552	3.675
9.67	0.817	0.898	1.631	3.766	3.930
11.12	0.808	0.740	1.616	3.988	4.197
12.54	0.795	0.603	1.615	4.137	4.397
Nitrogen Feed Composition: 40.0%, Specific Void Volume = 2.04 cm ³ /g					
0.78	0.794	0.585	0.606	1.472	1.477
1.43	0.779	0.742	0.796	2.166	2.181
2.72	0.767	0.791	0.934	3.149	3.192
4.15	0.749	0.697	0.957	3.922	4.009
5.53	0.724	0.574	0.953	4.456	4.600
6.97	0.693	0.449	0.953	4.839	5.062
8.26	0.673	0.310	0.934	5.129	5.432
9.87	0.637	0.214	0.970	5.267	5.699
11.23	0.619	0.074	0.954	5.400	5.942
12.66	0.604	-0.080	0.937	5.521	6.187
Nitrogen Feed Composition: 20.0%, Specific Void Volume = 2.04 cm ³ /g					
0.66	0.582	0.316	0.333	2.243	2.255
1.46	0.567	0.359	0.414	3.540	3.583
2.79	0.521	0.289	0.423	4.777	4.900
4.13	0.471	0.207	0.420	5.478	5.718
5.53	0.432	0.104	0.401	5.941	6.333
6.98	0.394	0.019	0.401	6.183	6.771
8.35	0.366	-0.068	0.397	6.278	7.083
9.73	0.341	-0.146	0.402	6.245	7.305
11.12	0.320	-0.232	0.405	6.122	7.475
12.52	0.299	-0.290	0.429	5.826	7.510

Table 10. ZGR EOS Representation of Pure Gas Adsorption
on Dry Activated Carbon at 318.2 K

Component	Regressed Parameters			NPTS	%AAD
	<i>a</i>	<i>b</i>	$\ln k$		
Methane	8.1826E+3	0.081454	1.22264	21	0.5
Nitrogen	1.2231E+4	0.106498	-0.00272	22	0.4
CO ₂	4.7611E+3	0.049399	2.15519	22	1.4

%AAD = average absolute percent deviation

NPTS = number of data points evaluated.

Table 11. ZGR EOS Representation of Binary Mixed Gas Adsorption
on Dry Activated Carbon at 318.2 K

System	NPTS	% AAD			Regressed Parameters	
		Comp. 1	Comp. 2	Total	C_{ij}	D_{ij}
CH ₄ /N ₂	40	4.6	3.1	3.6	-0.0247	0.0209
CH ₄ /CO ₂	40	8.6	9.5	1.2	0.1061	-0.0097
N ₂ /CO ₂	40	5.4	10.8	4.6	0.2495	-0.1657

Figure 1. Schematic Diagram of the Experimental Apparatus

Figure 2. Pure Gas Adsorption on Dry Activated Carbon at 318.2 K

Figure 3. The Graphical Method for Estimating the Adsorbed-Phase Density:
CO₂ Adsorption on Activated Carbon at 318.2 K

Figure 4a. Measurement Comparison for the Adsorption of Pure CO₂ on Dry Activated Carbon

Figure 4b. Deviation of Data from ZGR EOS Fit to the Adsorption Data for Pure CO₂ on Dry Activated Carbon

Figure 5. Absolute Adsorption of Methane/Nitrogen on Dry Activated Carbon at 318.2 K:
Methane Adsorption

Figure 6. Absolute Adsorption of Methane/Nitrogen on Dry Activated Carbon at 318.2 K:
Nitrogen Adsorption

Figure 7. Absolute Adsorption of Methane/CO₂ on Dry Activated Carbon at 318.2 K:
Methane Adsorption

Figure 8. Absolute Adsorption of Methane/CO₂ on Dry Activated Carbon at 318.2 K:
CO₂ Adsorption

Figure 9. Absolute Adsorption of Nitrogen/CO₂ on Dry Activated Carbon at 318.2 K:
Nitrogen Adsorption

Figure 10. Absolute Adsorption of Nitrogen/CO₂ on Dry Activated Carbon at 318.2 K:
CO₂ Adsorption

**Modeling the Adsorption of Pure Gases
on Coals with the SLD Model**

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Abstract

The simplified local density / Peng-Robinson model (SLD-PR) was modified to improve its predictive capability when dealing with near-critical and supercritical adsorption systems of the type encountered in coalbed methane recovery and CO₂ sequestration. The goal was to develop efficient equation-of-state (EOS) computational frameworks for representing adsorption behavior, as well as to improve our understanding of the phenomenon.

The ability of the modified SLD-PR to correlate accurately data for supercritical adsorption systems is demonstrated using adsorption measurements on activated carbon, Illinois #6 coal, Fruitland coal, and Lower-Basin Fruitland coal. The results indicate that the modified SLD-PR model, which incorporates a modified repulsive parameter 'b' for the PR EOS, is capable of modeling the adsorption of pure methane, nitrogen, and CO₂ at coalbed conditions. Inclusion of a slit geometry in the adsorbent matrix yields results superior to our previous two-dimensional EOS models for the adsorbates considered.

The results also indicate that accounting for the adsorption surface structure within the SLD-EOS framework is effective in improving modeling capability for high-pressure adsorption phenomena. An explanation is offered as to why the adsorbed-phase densities are close to the EOS reciprocal co-volumes. Further, the model (a) generates direct estimates for the adsorbed-phase densities (which facilitate reliable prediction of absolute gas adsorption) and (b) readily describes the observed maximum in Gibbs-adsorption isotherms of CO₂ at the temperatures and pressures encountered in coalbeds.

Keywords: A. Coal, Activated carbon; B. High pressure; C. Adsorption properties; D. Gas storage

1. Introduction

Knowledge of the adsorption behavior of coalbed gases is necessary for optimum development of production processes to recover coalbed methane and to sequester CO₂ in coalbeds. Specifically, methane, nitrogen, and CO₂ adsorption measurements on in-situ coal samples are valuable input to coalbed methane (CBM) production simulations. As part of a reservoir simulator, equilibrium modeling of physical adsorption helps determine coal-seam storage capacity, economic feasibility, and operating conditions [1].

Beyond primary and CO₂/nitrogen enhanced coalbed methane production, coalbeds are also potentially attractive sites for sequestering CO₂ to remove it from the atmosphere. Sequestration is receiving widespread international attention. Currently, coalbed sequestration of CO₂ could be a viable alternative to other proposed techniques, such as CO₂ injection into abandoned oil and gas reservoirs, deep, confined aquifers, and the deep ocean [2,3].

Simulations of field operations for primary and enhanced CBM production, as well as CO₂ sequestration in coalbeds, require mathematical models for adsorption behavior. Ideally, such models would combine accuracy and simplicity. Thus, we have pursued a variety of model frameworks to improve the representation of adsorption behavior for pure substances and mixtures.

We are currently investigating five avenues for representing adsorption equilibrium [4-6]. These include (a) enhanced forms of Langmuir-type isotherms, (b) two-dimensional equations of state, (c) the simplified local density models (SLD), (d) introduction of two-dimensional analogs of the activity coefficients used in vapor-liquid equilibrium calculations, and (e) treating adsorption as a constrained form of vapor-liquid equilibrium (VLE). The latter approach attempts to extend the utility of the efficient EOS framework to near-critical adsorption by employing concepts similar to the Polanyi potential theory to account for fluid-solid site interactions. In each of these modeling efforts, our

objective is to develop reliable, simple analytic models capable of describing multilayer adsorption of near-critical and supercritical components on heterogeneous surfaces.

In the present study, we investigate the abilities of the SLD-PR model to correlate the behavior of supercritical adsorption systems of the type encountered in CBM recovery and CO₂ sequestration. Our newly acquired measurements on an activated carbon, Illinois #6 coal, Lower Basin Fruitland coal, and our previous data on Fruitland coal [4,6] are employed for this purpose. Specifically, the SLD-PR is used to correlate Gibbs excess adsorption data for methane, ethane, nitrogen, and CO₂ on dry activated carbon, and on wet Lower-Basin Fruitland, Fruitland, and Illinois #6 coals. The modeling objectives are to (a) demonstrate the viability of the SLD model for correlating isotherms past the Gibbs excess maximum; (b) establish the utility of the SLD model in estimating absolute adsorption from the Gibbs excess adsorption; and (c) highlight the different adsorption behaviors of activated carbon and coals.

2. SLD Slit Theory

Following Chen et al. [9], we assume that the adsorbate molecule resides between a two-surface slit structure. As illustrated in Figure 1, the position within a slit is z , where z is orthogonal to the plane of the solid phase, defined as a flat surface formed by the peripheral carbon (coal) atoms. A molecule within a slit has fluid-solid interactions with both slit surfaces. The subscripts 'fs₁' and 'fs₂' denote the chemical potential arising from the first and second surface, respectively.

For the slit geometry considered here, the lower limit of integration $\sigma_{ff}/2$ is the location of the center of an adsorbed molecule touching the left plane surface, and the upper limit, $L-\sigma_{ff}/2$, is the location of an adsorbed molecule touching the right plane surface. Using this geometry, the SLD model is formulated in terms of the Gibbs excess adsorption (n_{Gibbs}), defined as the excess number of moles per unit mass of adsorbent, or:

$$n_{\text{Gibbs}} = A/2 \int_{\sigma_{\text{ff}2}}^{L-\sigma_{\text{ff}2}} (\rho(z) - \rho_b) dz \quad (1)$$

The SLD model asserts that (a) the chemical potential at any point above the adsorbent surface is equal to the bulk phase chemical potential, and (b) the molar chemical potential at any point above the surface is the sum of the fluid-fluid interaction and fluid-solid interaction potentials [7,8]. Accordingly, the equilibrium chemical potential is calculated by contributions from fluid-fluid and fluid-solid interactions as:

$$\mu(z) = \mu_{\text{ff}}(z) + \mu_{\text{fs}1}(z) + \mu_{\text{fs}2}(L - z) = \mu_{\text{bulk}} \quad (2)$$

where the subscript bulk refers to the bulk fluid, ff refers to fluid-fluid interactions, and fs refers to the fluid-solid interactions. An EOS (e.g., van der Waals or Peng–Robinson) provides the fluid-fluid potential information.

Figure 1. SLD Slit Geometry

Lee's partially integrated 10-4 Lennard-Jones potential [10] is used to describe the fluid-solid interactions. It is represented by $\mu(z)$ and defined on a molecular basis as:

$$\mu_{\text{fs}}(z) = N_A \cdot \Psi(z) \quad (3)$$

$$\Psi(z) = 4\pi\rho_{\text{atoms}} \varepsilon_{\text{fs}} \sigma_{\text{fs}}^2 \left(\frac{\sigma_{\text{fs}}^{10}}{5(z')^{10}} - \frac{1}{2} \sum_{i=1}^4 \frac{\sigma_{\text{fs}}^4}{(z' + (i-1) \cdot \sigma_{\text{ss}})^4} \right) \quad (4)$$

where ε_{fs} is the fluid-solid interaction energy parameter and $\rho_{\text{atoms}} = 0.382 \text{ atoms}/\text{\AA}^2$. The molecular diameter of the adsorbate and the carbon interplanar distances are σ_{ff} and σ_{ss} , respectively. The carbon interplanar distance is taken to be that of graphite, 0.335 nm.

For convenience, the fluid-solid diameter σ_{fs} and the dummy coordinate z' are defined as:

$$\sigma_{\text{fs}} = \frac{\sigma_{\text{ff}} + \sigma_{\text{ss}}}{2} \quad (5)$$

$$z' = z + \sigma_{\text{ss}}/2 \quad (6)$$

The local density is determined by relating the fluid-fluid chemical potential to the fugacity f in the PR EOS, as:

$$\ln \left(\frac{f_{\text{ff}}[a(z), \rho(z)]}{f} \right) = - \left(\frac{\Psi(z) + \Psi(L-z)}{kT} \right) \quad (7)$$

In this study, we have used the PR EOS to determine the bulk density, the bulk fugacity and fluid fugacities. The PR EOS may be written as follows:

$$\frac{P}{RT} = \frac{1}{(1-b)} - \frac{a(T)}{RT \left[1 + (1-\sqrt{2})b \right] \left[1 + (1+\sqrt{2})b \right]} \quad (8)$$

$$\text{where} \quad a(T) = 0.45724\alpha(T)R^2T_c^2/P_c \quad (9)$$

$$b = 0.077796RT_c/P_c \quad (10)$$

For $\alpha(T)$, we used the Mathias-Copeman expression with parameters regressed by Hernandez-Garduza [11]. Constants C_1 - C_3 appear in Table 1.

$$\alpha(T) = 1 + C_1 \left(1 - \sqrt{T/T_c} \right) + C_2 \left(1 - \sqrt{T/T_c} \right)^2 + C_3 \left(1 - \sqrt{T/T_c} \right)^3 \quad (11)$$

Table 1. Physical Fluid Parameters

	T _c (K)	P _c (MPa)	σ _{ff} (nm)	C ₁	C ₂	C ₃
Nitrogen	126.19	3.396	0.3798	0.43694	-0.07912	0.32185
Methane	190.56	4.599	0.3758	0.41108	-0.14020	0.27998
CO ₂	304.13	7.377	0.3941	0.71369	-0.44764	2.43752
Ethane	305.30	4.872	0.4443	0.52005	0.00430	0.10292

The bulk fugacity and the fluid fugacity for the PR EOS are:

$$\ln \frac{f}{P} = \frac{bp}{1-bp} - \frac{a(T)p}{RT(1+2bp-b^2p^2)} - \ln \left[\frac{P}{RTp} - \frac{Pb}{RT} \right] - \frac{a(T)}{2\sqrt{2}bRT} \ln \left[\frac{1+(1+\sqrt{2})pb}{1+(1-\sqrt{2})pb} \right] \quad (12)$$

$$\ln \frac{f_{ff}(z)}{P} = \frac{bp(z)}{1-bp(z)} - \frac{a_{ads}(z)p(z)}{RT(1+2bp(z)-b^2p^2(z))} - \ln \left[\frac{P}{RTp(z)} - \frac{Pb}{RT} \right] - \frac{a_{ads}(z)}{2\sqrt{2}bRT} \ln \left[\frac{1+(1+\sqrt{2})p(z)b}{1+(1-\sqrt{2})p(z)b} \right] \quad (13)$$

The parameter ‘a’ in the Peng-Robinson EOS is a function of position within the slit when calculating the local-phase density. We used the suggestion of Chen et al. [9] for the equations describing ‘a’ as a function of position.

Once the local-density profile is determined across the slit, the Gibbs excess can be obtained by integrating Eq. (1) numerically. In this work, we subdivided half of the slit into 50 intervals and solved Eq. (1) for each interval. The amount adsorbed was calculated by numerical integration using Simpson’s rule.

3. Background on Gibbs Excess and Absolute Adsorption

To provide a basis for estimating the absolute adsorption from Gibbs excess, a brief background is necessary. We specifically limit the scope to supercritical adsorption so that condensation effects can be ignored. Within this scope, the Gibbs excess is the experimentally relevant quantity at high pressures:

$$n_{\text{Gibbs}} = V_a (\bar{\rho}_a - \rho_b) = n_{\text{tot}} - V_{\text{void}} \rho_b \quad (14)$$

The subscripts “a” and “b” refer to the adsorbed phase and the bulk phase. The void volume V_{void} is determined by helium injection, and n_{tot} is the total fluid amount in the volume V_{void} . The overbar signifies the average adsorbed density over the adsorbed-phase volume V_a . The adsorbed-phase volume V_a has units of volume per unit mass of adsorbent. In a container with a helium volume of V_{void} , the Gibbs excess adsorption is the amount in excess of what would be present if V_{void} was filled completely with the bulk fluid (i.e., if no adsorption occurred).

The Gibbs excess adsorption levels off at higher pressures as the first layer of fluid molecules near full occupancy on the surface. Other layers will form depending on the affinity of the fluid molecule for the surface at larger distances. At sufficiently high pressures the Gibbs excess adsorption will show a maximum. After this maximum, the Gibbs excess adsorption decreases nearly linearly with bulk density. The linearity in this region can be explained by assuming that no additional adsorption is occurring. The actual amount adsorbed can be significantly different from the experimentally inferred Gibbs excess adsorption, especially past the Gibbs excess maximum. The actual adsorption (hereafter called the absolute adsorption) is estimated from a model that provides either the adsorbed-phase volume or the average adsorbed-phase density. These physical parameters are obtainable through regression of experimental data using the SLD model. The absolute adsorption is simply the product of the adsorbed-phase volume and the average adsorbed density.

$$n_{\text{abs}} = V_a \bar{\rho}_a \quad (15)$$

4. Database Employed in this Study

Gas adsorption measurements have been conducted at Oklahoma State University (OSU) [4,6] on a number of coal samples and on activated carbon. Adsorption isotherms for pure methane, ethane, nitrogen, and CO_2 on dry activated carbon, and similar measurements of methane, nitrogen, and CO_2 on

wet Illinois #6, Fruitland, and Lower-Basin (LB) Fruitland coals were measured at pressures to 12.4 MPa (1800 psia). All activated carbon measurements were at 318.15 K (113.0°F), and all coal measurements were at 319.3K (115.0°F). All experimental data are presented on a dry basis (e.g., mmol adsorbed/g dry adsorbent).

Pure gases were obtained from commercial vendors with reported purities of 99.95% or higher. The ultimate and proximate analyses of the adsorbents were conducted by Huffman Laboratories and are presented in Table 2.

Comparisons of the SLD model with the experimental data appear in Figures 2-6, where the error bars signify one standard deviation uncertainty in the measurements. We assumed normal distributions in the errors in the primary measurements for pressure, temperature, volume, and weight. To estimate the error in the Gibbs excess adsorption, error was propagated from these primary measurements, including effects of the temperature and pressure sensitivity of the bulk-phase compressibility factor.

Table 2. Compositional Analysis of Adsorbents Used in This Study

Analysis	Activated Carbon	Fruitland OSU Coal (#2)	Illinois #6 Coal	Lower Basin Fruitland Coal OSU (#3b)
<i>Ultimate</i>				
Carbon %	88.65	66.58	71.47	40.20
Hydrogen %	0.74	4.23	5.13	3.10
Oxygen %	3.01	5.08	9.85	2.87
Nitrogen %	0.40	1.47	1.46	0.89
Sulfur %	0.73	0.72	1.27	2.14
Ash %	6.46	21.92	10.81	50.81
<i>Proximate</i>				
Vol. Matter %	3.68	20.33	30.61	14.00
Fixed Carbon %	89.86	57.75	55.90	35.19

4.1 Activated Carbon

Figure 2 presents Gibbs excess data for all four gases on dry activated carbon (Filtrisorb 400, 12x40 mesh, Calgon Carbon). CO₂ and ethane each display a maximum. Methane and nitrogen show less

pronounced maxima at higher pressures. The OSU measurements are compared with the data of Humayun and Tomasko [12] for CO₂ in Figure 3. Agreement is within the combined experimental uncertainties. Humayun measured CO₂ adsorption using a gravimetric technique; this method required no helium void volume measurement, in contrast to the volumetric method we use. The excellent agreement between the gravimetric and the volumetric method implies that the void volume does not change appreciably during the adsorption process for the activated carbon, as well as demonstrating the accuracy of both data sets.

4.2 Fruitland Coal

Amoco Corporation [13,14] and OSU [4,6] have performed several adsorption measurements on Fruitland coal. These measurements span several years, so the coal samples may be slightly different due to variation in handling, oxidation, drying, and rewetting. For modeling purposes in this paper, we use only recent measurements on Fruitland coal where ultimate and proximate analyses are available for the samples used. The adsorption isotherms for this coal are shown in Figures 4-6. For CO₂ measurements at pressures above 9 MPa, the reproducibility is visibly lower. We suspect an experimental artifact due to CO₂'s leaching of water from the coal. Water miscible in the bulk CO₂ fluid will cause the fluid density to appreciably change. Impurities such as water can have an effect on the density of supercritical fluids near the critical temperature [15,16]. This effect is also noticeable in the Illinois #6 and Lower Basin Fruitland coal.

4.3 Illinois #6 Coal

The adsorption measurements on wet Illinois #6 are presented in Figures 4-6. These measurements indicate that both methane and nitrogen adsorption on wet Illinois #6 are about half that adsorbed on wet Fruitland coal at the same conditions. Replicate runs were conducted for each gas to confirm the

precision of our measurements and to investigate the effect of variations in moisture content and coal sample preparation on the adsorption behavior.

The Illinois #6 data were acquired using two coal samples of different moisture content. Both measurement sets indicate that water content values above the equilibrium water content do not significantly affect the adsorption behavior. These findings supports similar conclusions reached in previous studies [4,6].

4.4 Lower-Basin Fruitland Coal

Adsorption isotherms for pure methane, nitrogen, and CO₂ on wet Lower-Basin (LB) Fruitland coal are also presented in Figures 4-6. For CO₂, two replicate isotherms show an anomalous “bump” near 9MPa. The increased uncertainty of the CO₂ bulk density at these pressure-temperature conditions amplifies the expected uncertainty in the amount adsorbed. In addition, water in the CO₂ bulk fluid may explain this anomalous behavior, as mentioned previously.

Figure 2. Gibbs Excess Adsorption of CO₂, Methane, Nitrogen, and Ethane on Filtrasorb 400 Activated Carbon at 45°C (113°F) with Modified SLD Model

Figure 3. Comparison of CO₂ Adsorption Data on Filtrasorb 400 Activated Carbon at 45°C (113°F)

Figure 4. Methane Adsorption on Wet Coals at 46.1°C (115°F) with Modified SLD Model

Figure 5. Nitrogen Adsorption on Wet Coals at 46.1°C (115°F) with Modified SLD Model

Figure 6. CO₂ Adsorption on Wet Coals at 46.1°C (115°F) with Modified SLD Model

5. Data Reduction Procedure

To correlate data with the SLD model, we used the objective function WRMS, which minimizes the sum of the squared weighted deviations in the predicted Gibbs excess adsorption:

$$\text{WRMS} = \sqrt{\frac{\sum_{i=1}^N \left(\frac{n_{\text{exp}} - n_{\text{calc}}}{s_{\text{exp}}} \right)^2}{N}} \quad (16)$$

Here, N is the number of data points, n_{calc} is the calculated Gibbs excess, and n_{exp} is the experimental Gibbs excess, and s_{exp} is the expected experimental uncertainty. Detailed procedures for data reduction are given by Gase m et al. [17]. The weighted average-absolute deviation (WAAD) is also used to quantify our model evaluations:

$$\text{WAAD} = \frac{1}{N} \sum_{i=1}^N \left| \frac{n_{\text{calc}} - n_{\text{exp}}}{s_{\text{exp}}} \right| \quad (17)$$

The average absolute percent error (%AAD) is also given for reference. This is defined by:

$$\%AAD = \frac{1}{N} \sum_{i=1}^N \left| \frac{n_{\text{calc}} - n_{\text{exp}}}{n_{\text{exp}}} \right| \cdot 100 \quad (18)$$

6. Modeling Results and Discussion

6.1 Original SLD Predictions

To model the adsorption of methane, ethane, nitrogen, and CO₂ on activated carbon and coals, the SLD theory first implemented by Chen et al. [9] was used. The model contains three regressed parameters: the surface area A, the slit width L, and the fluid-solid interaction energy parameter ϵ_{fs} . As shown in Figure 7, the original SLD model yields poor representation for CO₂ and ethane on activated carbon. The model cannot simultaneously correlate the experimental data over the entire pressure range; thus, the results shown in Figure 7 are based on regressions at pressures below the Gibbs excess maximum. At higher pressures, the observed deviations for both systems are well outside the expected experimental uncertainties. Chen et al. [9] experienced similar difficulties in modeling CO₂ adsorption on another activated carbon.

Figure 7. Improvement of the SLD Model Predictions by PR Covolume Modification

Examination of the results from the original SLD model revealed that the calculated adsorbed-phase densities from the EOS in the SLD model are too high for CO₂ and ethane. If the assumption is made that, at sufficiently high pressures, no further adsorption occurs ($V_a \bar{\rho}_a$ becomes constant), then Eq. (14) reveals that a plot of n_{Gibbs} versus ρ_b should become linear with a slope of $-V_a$. Further, this linear relation (extrapolated) will reach $n_{\text{Gibbs}} = 0$ when $\bar{\rho}_a = \bar{\rho}_b$.

Figure 8 indicates that the adsorbed-phase densities for CO₂ and ethane at zero Gibbs excess are 22.6 mole/L and 14.8 mole/L, respectively (assuming a linear variation in Gibbs excess adsorption with density). The SLD adsorbed-phase density estimates at zero Gibbs excess (obtained from data below the Gibbs maximum) are 36.0 and 24.3 mole/L. We attribute this significant disagreement in adsorbed-phase density estimates to inadequate accounting for repulsive interactions by the original EOS used in the SLD model.

Figure 8. Determination of Adsorbed-Phase Density on Activated Carbon at 45°C

6.2 Modified SLD Predictions

The PR covolume, b , has a significant effect on the calculated local density of the adsorbed fluid, especially near the surface. In Eq. (13) the logarithmic repulsive term dominates the local fluid fugacity expression, especially near the surface. To illustrate this, when Eqs. (7), (12), and (13) are combined, the local density can be expressed as:

$$\frac{1}{\rho(z)} = b + \frac{RT}{P} \exp \left[-\frac{f_b}{P} \exp \left(\frac{-\Psi(z) - \Psi(L-z)}{kT} \right) - \lambda \right] \quad (19)$$

$$\text{where } \lambda = \frac{b\rho(z)}{1 - b\rho(z)} - \frac{a_{\text{ads}}(z)\rho(z)}{RT(1 + 2\rho(z)b - b^2\rho^2(z))} - \frac{a_{\text{ads}}(z)}{2\sqrt{2}bRT} \ln \left(\frac{1 + (1 + \sqrt{2})\rho(z)b}{1 + (1 - \sqrt{2})\rho(z)b} \right)$$

Near the surface, where the fluid-solid potential is large in magnitude, the exponential term containing the fluid-solid potential vanishes, and at moderate pressures the local density can be approximated by:

$$\frac{1}{\rho(z)} \approx b + \frac{RT}{P} \exp[-\lambda] \quad \text{Near the wall} \quad (20)$$

At higher pressures, the second term becomes small and the adsorbed density at the wall approaches the reciprocal covolume.

$$\rho(\text{wall}) \rightarrow \frac{1}{b} \quad \text{Near the wall at high pressures} \quad (21)$$

The covolume is the dominant factor that determines the adsorbed-density profile in the high-pressure limit. Thus, the accuracy of the repulsive expression is predominant in modeling the local density. Soule et al. [18] used the Elliot-Suresh-Donohue equation of state to better account for the subdivision of attractive and repulsive interactions for adsorption modeling in the SLD framework. Compared to the van der Waals and PR equations of state, the ESD equation more accurately described the temperature dependence of adsorption.

Instead of incorporating a more accurate repulsive term in expression for the model, we used a simple empirical modification to account for the repulsive interactions of the high-density adsorbed fluid. Our objective was to obtain initial information regarding the impact of changes in ‘b’ on the calculated adsorption, especially for supercritical CO₂ at high pressures. Thus, the PR covolume was empirically adjusted by the parameter Λ_b :

$$b_{\text{ads}} = b \cdot (1 + \Lambda_b) \quad (22)$$

Eq. (13) then becomes:

$$\ln \frac{f_{\text{ff}}(z)}{P} = \frac{b_{\text{ads}} \rho(z)}{1 - b_{\text{ads}} \rho(z)} - \frac{a_{\text{ads}}(z) \rho(z)}{RT [1 + 2b_{\text{ads}} \rho(z) - b_{\text{ads}}^2 \rho(z)^2]} - \ln \left[\frac{1 - b_{\text{ads}} \rho(z)}{RT \rho(z)} \right] - \frac{a_{\text{ads}}(z)}{2\sqrt{2}b_{\text{ads}} RT} \ln \left[\frac{1 + (1 + \sqrt{2})\rho(z)b_{\text{ads}}}{1 + (1 - \sqrt{2})\rho(z)b_{\text{ads}}} \right] \quad (23)$$

6.3 Modeling Dry Activated Carbon Adsorption

With the above modification, the SLD model representations for CO₂ and ethane on dry activated carbon were improved dramatically. Table 3 presents the regressed parameters for modified case. For CO₂, when the covolume was increased by 52% ($\Lambda_b = 0.5184$), the adsorbed-phase density at zero Gibbs excess was in better agreement with our graphical estimates. Ethane had similar improvements when its covolume was increased by 56%. Figure 7 shows the improvement for the high-pressure adsorption for both CO₂ and ethane. Figure 9 demonstrates the effect of the modified covolume on the CO₂ local density profile at two pressures. Figure 10 normalizes the local density for CO₂ to the modified covolume b_{ads} . Even at 0.69 MPa, the wall density is roughly 96% of $1/b_{ads}$. As the pressure increases, the wall density approaches $1/b_{ads}$ as indicated by Eqs. (20) and (21), thus validating their use.

As shown in Table 3 (and later in Table 4), the surface area was allowed to differ from gas to gas. This can be rationalized as the fluid species having different accessibility to the pore sites and thus different surface areas.

Table 3. Modified SLD Model Results on Activated Carbon at 45°C (113°F)

	CO₂	Ethane	Methane	Nitrogen
A (m ² /g)	1131	1126	774	643
ϵ_{fs}/k (K)	78.5	83.0	77.6	57.1
L ₀ (nm)	1.11	1.11	1.11	1.11
Λ_b	0.52	0.56	0.52	0.55
NPTS	51	32	22	22
% AAD	2.5	4.9	0.6	0.3
WRMS	0.78	1.54	0.60	0.26
WAAD	0.64	1.19	0.47	0.24

6.4 Modeling Wet Coal Adsorption

Table 4 presents the summary results for our evaluation of gas adsorption on wet coals. In general, the modified SLD-PR model is capable of representing the adsorption data considered in this study within

their experimental uncertainties. Due to the lower reproducibility of CO₂ sorption data in the high-pressure region, as shown in Figure 6, we set the covolume parameter Λ_b to 0.30 for modeling the wet coals rather than regressing it. Regression results show that the value of Λ_b is smaller than that observed for the dry activated carbon. A constrained value of 0.30 for Λ_b for CO₂ was used to achieve an adsorbed-phase density (at zero Gibbs excess) comparable to that obtained for CO₂ adsorption on activated carbon (~1.0 g/cm³). Failing to constrain Λ_b produces model results implying that the adsorbed-phase densities are high (~1.3 - 1.8 g/cm³ for CO₂).

The wet coal isotherms differ from the dry activated carbon isotherms in at least two respects. First, the presence of water lowers the adsorptive capacity of the adsorbent and alters the shape of the isotherms. (The amount of gas *absorbed* in the water was accounted for in the experimental measurements so that only physical adsorption on the coal is considered.) Second, the coals have significantly lower surface areas than the activated carbon, as shown in Tables 3 and 4.

Figure 9. Effect of PR Covolume on Local Density: CO₂ at 45°C

Figure 10. Effect of PR Covolume on Normalized Local Density: CO₂ at 45°C

Table 4. Summary Results for the Modified SLD-PR Adsorption Model

Model Parameters	Pure Gas Adsorbed		
	Methane	Nitrogen	CO ₂
Wet Fruitland Coal			
A (m ² /g)	104	72	99
ϵ_{fs}/k (K)	61	35	95
L (nm)	1.60	1.60	1.60
Λ_b	0.30	0.30	0.30
NPTS	40	37	52
% AAD	1.2	3.0	8.8
WRMS	0.36	0.52	1.28
WAAD	0.27	0.42	0.91
Wet Illinois #6 Coal			
A (m ² /g)	67	51	90
ϵ_{fs}/k (K)	49	24	70
L (nm)	1.62	1.62	1.62
Λ_b	0.30	0.30	0.30
NPTS	20	20	30
% AAD	3.0	3.4	10.9
WRMS	0.46	0.19	0.82
WAAD	0.33	0.17	0.61
Wet LB Fruitland			
A (m ² /g)	56	31	66
ϵ_{fs}/k (K)	47	32	65
L (nm)	1.12	1.12	1.12
Λ_b	0.30	0.30	0.30
NPTS	16	17	48
% AAD	4.8	4.7	6.9
WRMS	0.95	0.52	0.89
WAAD	0.83	0.42	0.68

6.5 Absolute Adsorption Calculations

Absolute adsorption can be calculated readily from the regressed SLD-PR parameters for a given adsorbent as follows:

$$n_{\text{abs}} = n_{\text{Gibbs}} + \frac{A}{2}(L - \sigma_{\text{ff}})p_{\text{b}} \quad (24)$$

In Eq. (24), the absolute adsorption was calculated from the Gibbs excess adsorption using the SLD adsorbed-phase volume, V_{a} , and the PR bulk gas density. For this study, the SLD adsorbed-phase volume for a slit geometry is the product of half the surface area, A , and the effective slit width, $L - \sigma_{\text{ff}}$; this is the volume where the spherical fluid molecules can reside without intersecting the hypothetical flat-plane carbon surface, i.e., the center of a fluid molecule cannot move closer than a distance of $\sigma_{\text{ff}}/2$ from each wall of the slit. The resultant absolute adsorption isotherms on dry activated carbon are depicted in Figure 11; and similar isotherms for the wet coals are shown in Figures 12-14. Note that for ethane and CO_2 on activated carbon, the capacity for the absolute adsorption corresponds to the zero-density intercept of the linearly regressed line in Figure 8. As indicated by Figure 11, methane and nitrogen adsorption isotherms have not reached their maximum adsorption capacity at 14 MPa, the highest pressure of this study.

Figure 11. Absolute Adsorption Calculated by SLD Model for Activated Carbon

Figure 12. Absolute Adsorption Calculated by SLD Model for Fruitland Coal

Figure 13. Absolute Adsorption Calculated by SLD Model for Lower Basin Fruitland

Figure 14. Absolute Adsorption Calculated by SLD Model for Illinois #6 Coal

7. Conclusions

The major conclusions of this study are as follows:

- The modified SLD-PR model is better equipped than the original model to represent adsorption isotherms encountered in CBM production and CO₂ sequestration, including those exhibiting Gibbs excess adsorption maxima.
- Simple modification of the PR EOS covolume improves both the Gibbs excess adsorption and the adsorbate-phase density predictions. Further study is needed to improve the description of the repulsive forces in the EOS used in SLD calculations.
- The SLD-PR model can be used to facilitate reliable representation of Gibbs excess or absolute adsorption behaviors.

Nomenclature

A	surface area
a	Peng-Robinson attractive parameter
a _{ads}	local Peng-Robinson attractive parameter for adsorbed phase
AAD	average absolute deviation
b	Peng-Robinson covolume
b _{ads}	modified Peng-Robinson covolume for adsorbed phase
f	fugacity
i	dummy index
k	Boltzmann constant
L	slit width; defined as the normal distance between the carbon planes
N	number of points in regression
N _A	Avogadro's number
n	amount in moles
n _{Gibbs}	the Gibbs excess adsorption
P	pressure
R	universal gas constant
T	temperature
V _a	adsorbed-phase volume
V _{void}	void volume (system volume minus adsorbent volume determined by helium)
v	specific volume of fluid
WAAD	weighted average absolute deviation
WRMS	weighted root mean square deviation
z	normal position between carbon planes; zero at one plane
z'	dummy position variable: $z' = z + \sigma_{ff}/2$

Z compressibility factor

Subscripts

a adsorbed-phase property
b bulk property
c critical condition
ff fluid-fluid interaction
fs fluid-solid interaction
ss solid-solid interaction

Greek

α temperature dependent function for Peng-Robinson EOS
 ϵ_{fs} fluid-solid interaction parameter
 Λ_b modification parameter to Peng-Robinson covolume
 λ defined by Eq. (19)
 μ chemical potential
 ρ density
 σ particle diameter
 σ_{exp} expected experimental uncertainty
 Ψ fluid-solid potential function

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Adsorption of Pure Methane, Nitrogen, and Carbon Dioxide and Their Mixtures on Wet Tiffany Coal

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A. Executive Summary

The major objectives of this project were to (a) measure the adsorption behavior of pure methane, nitrogen, CO₂ and their binary and ternary mixtures on wet Tiffany coal at 130°F and pressures to 2000 psia; (b) correlate the equilibrium adsorption isotherm data using the extended Langmuir model, the Langmuir model, the loading ratio correlation and the Zhou-Gasem-Robinson equation of state; and (c) establish sorption-time estimates for the pure components. Specific accomplishments are summarized below regarding the complementary tasks involving experimental work and data correlation.

Experimental Work

- Representative coal samples from BP Amoco Tiffany Injection Wells #1 and #10 were prepared, as requested. The equilibrium moisture content and particle size distribution of each coal sample were determined. Compositional coal analyses for both samples were performed by Huffman Laboratories, Inc.
- Pure gas adsorption for methane on wet Tiffany coal samples from Injection Wells #1 and #10 was measured separately at 130°F (327.6 K) and pressures to 2000 psia (13.7 MPa). The average expected uncertainty in these data is about 3% (9 SCF/ton). Our measurements indicate that the adsorption isotherms of the two coal samples exhibit similar Langmuir-type behavior. For the samples from the two wells, a maximum variation of about 5% in the amount adsorbed is observed at 2000 psia.
- Gas adsorption isotherms were measured for **pure** methane, nitrogen and CO₂ on a wet, mixed Tiffany coal sample. The coal sample was an equal-mass mixture of coals from Well #1 and Well #10. The adsorption measurements were conducted at 130°F at pressures to 2000 psia. The adsorption isotherms have average expected experimental uncertainties of 3% (9 SCF/ton), 6% (8 SCF/ton), and 7% (62 SCF/ton) for methane, nitrogen, and CO₂, respectively.

In addition, sorption times for pure methane, nitrogen and CO₂ were measured and correlated using a Langmuir-type correlation.

- Adsorption isotherms were measured for methane/nitrogen, methane/CO₂ and nitrogen/CO₂ **binary mixtures** on wet, mixed Tiffany coal at 130°F and pressures to 2000 psia. These measurements were conducted for a single molar feed composition for each mixture. The expected uncertainties in the amount adsorbed for these binary mixtures vary with pressure and composition. In general, average uncertainties are about 5% (19 SCF/ton) for the total adsorption; however, the expected uncertainties in the amount of individual-component adsorption are significantly higher for the less-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20/80 nitrogen/CO₂ system).
- Adsorption isotherms were measured for a single methane/nitrogen/CO₂ **ternary mixture** on wet, mixed Tiffany coal at 130 °F and pressures to 2000 psia. The

nominal molar feed composition was 10/40/50. The average expected uncertainty for the total adsorption and CO₂ adsorption is about 5% (16 SCF/ton). However, the low adsorption of nitrogen and methane in this ternary yield average experimental uncertainties of 14% (9 SCF/ton) and 27% (9 SCF/ton), respectively.

- Limited binary and ternary gas-phase compressibility factor measurements at 130°F and pressures to 2000 psia involving methane, nitrogen, and CO₂ were conducted to facilitate reduction of our ternary adsorption data. These newly acquired data (and available data from the literature) were used to improve the Benedict-Webb-Rubin (BWR) equation-of-state (EOS) compressibility factor predictions, which are used in material balance calculations for the adsorption measurements. In general, the optimized BWR EOS represents the experimental compressibility factor data within 0.5% AAD.

Data Correlation

- The Langmuir/loading ratio correlation (LRC) and the Zhou-Gasem-Robinson (ZGR) two-dimensional EOS were used to analyze the newly acquired adsorption data. Model parameters were obtained for the systems studied.
- The LRC and ZGR EOS were used to **correlate** the adsorption data for methane, nitrogen, and CO₂ and their mixtures on wet Tiffany coal. The model parameters were determined by minimizing the sum of squares of weighted errors in the calculated amounts of gas adsorbed. The results demonstrate the ability of the LRC and ZGR EOS to represent the total pure, binary and ternary systems within their expected experimental uncertainties. Specifically, representations with average absolute percentage errors (AAD) of 1-3% (2-15 SCF/ton), 1-8% (1-25 SCF/ton), and 2-10% (7-37 SCF/ton) were obtained for the pure, total binary, and total ternary adsorption isotherms, respectively. However, the quality of fit for the individual-component adsorption varies significantly, ranging from 3% for the more-adsorbed methane or CO₂ to 32% for the less-adsorbed nitrogen.
- The LRC and ZGR EOS are capable of **predicting** binary adsorption isotherms based solely on pure-fluid adsorption parameters within twice their experimental uncertainties (1-50 %AAD, 5-40 SCF/ton). In comparison, the ternary predictions based on pure-fluid parameters yield three times the experimental uncertainties (4-56 %AAD, 2-60 SCF/ton). The quality of the model predictions indicate that although the two models are capable of predicting total adsorption isotherms adequately, they predict individual-component adsorption in mixtures poorly, especially when dealing with the less-adsorbed component of the mixture.
- Sorption-time estimates for pure methane, nitrogen, and CO₂ were represented using a Langmuir-type correlation with average errors of about 8%.

B. Introduction

The specific objectives of the adsorption measurements and correlations for BP Amoco Tiffany coal were to:

- Prepare representative coal samples from Injection Well #1 and Injection Well #10.
- Determine (a) equilibrium moisture content, (b) particle size distribution, (c) compositional analyses, and (d) vitrinite reflectance analysis for each coal sample.
- Measure the adsorption behaviors of pure methane, nitrogen, CO₂ and their binary and ternary mixtures on a Tiffany equal-mass, mixed-coal sample from Injector Wells #1 and #10 at 130°F and pressures to 2000 psia. The nominal molar feed compositions for the methane/nitrogen, methane/CO₂, and nitrogen/CO₂ binary mixtures were specified at 50/50, 40/60, and 20/80, respectively. The nominal molar feed composition for the methane/nitrogen/CO₂ ternary mixture was 10/40/50.
- Correlate the equilibrium adsorption isotherm data using the extended Langmuir model, the Langmuir model, the loading ratio correlation and the Zhou-Gasem-Robinson equation of state.
- Establish sorption-time estimates for the pure components.

C. Experimental Work

1. Experimental Facility

The experimental apparatus was developed in previous work for Amoco Corporation and the Oklahoma Center for the Advancement of Science and Technology. As a precursor to the present data acquisition, the apparatus was thoroughly re-tested and revised as necessary. The equipment is described in detail elsewhere [1,2].

Recently, we enhanced our experimental facility to include the ability to measure adsorption kinetics for systems encountered in coalbed methane production and sequestration of CO₂. Brief descriptions of experimental methods and procedures are given in the following section.

2. Experimental Methods and Procedures

(a) Adsorption Measurements

Our experimental technique employs a mass balance method, utilizing volumetric accounting principles. The experimental apparatus, shown schematically in Figure

1, has been used successfully in previous measurements [1, 2]. Brief descriptions of the experimental apparatus and procedures follow.

The entire apparatus (both Pump and Cell sections) is maintained in a constant temperature air bath. The equilibrium cell (EC, Figure 1) is filled with the coal to be studied, and the cell is placed under vacuum prior to gas injection. The void (gas) volume, V_{void} , in the equilibrium cell is then determined by injecting a known quantity of helium from a calibrated injection pump. Since helium is not adsorbed, the void volume can be determined from measured values of the temperature, pressure and amount of helium injected into the cell. The void volume equations are

$$V_{\text{void}} = n_{\text{He}} (Z_{\text{He}} RT / P)_{\text{cell}} \quad (1)$$

$$n_{\text{He}} = (PV / Z_{\text{He}} RT)_{\text{pump}} \quad (2)$$

In these equations, n_{He} is the number of moles of helium injected into the cell, V is the volume of gas injected from the pump, Z_{He} is the compressibility factor of helium, R is the universal gas constant, T is the temperature, P is the pressure, and the subscripts "cell" and "pump" refer to conditions in the cell and pump sections of the apparatus, respectively.

The amount of gas (methane, for example) adsorbed at a given pressure can be calculated based on the preliminary calibrations done above. First, a given quantity of methane, n_{inj} , is injected into the cell. This amount is determined by an equation analogous to Equation 2, above. A magnetic recirculating pump is used to circulate methane over the adsorbent until equilibrium is reached, where no further methane is adsorbed. The amount of unadsorbed methane, n_{unads} , is then determined based on the fact that any unadsorbed methane will remain in the void volume (determined from the helium calibration). The expression for this quantity is

$$n_{\text{unads}} = (PV_{\text{void}} / Z_{\text{methane}} RT)_{\text{cell}} \quad (3)$$

where the pressure P is measured after equilibrium is reached in the cell. In addition, we estimate the amount of gas dissolved in water, n_{dis} , using correlations for gas solubility [2]. The amount of adsorbed methane, n_{ads} , is then calculated by difference as

$$n_{\text{ads}} = n_{\text{inj}} - n_{\text{unads}} - n_{\text{dis}} \quad (4)$$

These steps are repeated at sequentially higher pressures to yield a complete adsorption isotherm.

In mixture studies, a gas mixture of known composition is injected, so the total amount of each gas fed into the cell is known. The amount of unadsorbed gas at each pressure is calculated by Equation 3 with Z_{methane} replaced by Z_{mix} , the gas mixture compressibility factor. The composition of the gas mixture in the void volume is determined by chromatographic analysis using a microliter-size sample

captured in a sampling valve (SV1). This permits the total amount of unadsorbed gas to be apportioned among the various components according to their mole fractions in the gas. Equation 4 can be then applied to each component in the gas mixture. For methane/nitrogen/CO₂ mixtures, the mixture Z factors (Z_{mix}) are determined accurately from the BWR EOS, as described below.

The estimated uncertainties in each of the experimentally measured quantities are as follows: temperature 0.2°F, pressure 1.0 psia, injected gas volumes 0.02 cc, bulk gas-phase composition 0.001 in mole fraction. The expected uncertainties in the amount adsorbed are estimated using error propagation in all the measured variables and confirmed by replicate runs.

Compressibility Factors

As indicated by Equations 1-3, accurate gas-phase compressibility (Z) factors are required for methane, nitrogen and carbon dioxide and their mixtures to properly analyze our experimental adsorption data. The compressibility factors for **pure** methane, nitrogen and CO₂ were determined from highly accurate equations of state [3-5]. However, a careful evaluation of the current literature led us to conclude that an adequate predictive capability for the **mixture** Z factors does not exist. Therefore, we elected to develop such a capability using the Benedict-Webb-Rubin (BWR) equation of state.

Specifically, we used available pure-fluid and **binary** mixture data to refit the BWR equation and improve its accuracy significantly; in general, the new BWR EOS parameters yield deviations in the Z factor within 0.2%. This allowed us to address our compressibility factor needs for binary adsorption mixtures.

To facilitate our **ternary** adsorption measurements, we conducted a limited number of binary and ternary compressibility factor measurements involving methane, nitrogen, and CO₂ at 130°F and pressures to 2000 psia. These newly acquired data and available data from the literature were used to improve the BWR EOS compressibility factor predictions. In general, the optimized BWR EOS represents the compressibility factor data within 0.5% AAD [11].

Relationship between Gibbs and Absolute Adsorption

By definition, Gibbs adsorption considers the gas-phase volume as the sum of the gas (V_{gas}) and adsorbed phase (V_{ads}) volumes (ignoring the reduction in gas-phase volume due to presence of the adsorbed phase.) Expressing Gibbs adsorption in terms of vapor volume (V_{gas}) and adsorbed-phase volume (V_{ads}), and using the specific molar volume (v_{gas} and v_{ads}), we obtain:

$$n_{\text{ads}}^{\text{Gibbs}} = n_{\text{inj}} - \left[\frac{V_{\text{gas}} + V_{\text{ads}}}{v_{\text{gas}}} \right] \quad (5)$$

For absolute adsorption, the amount adsorbed within the equilibrium cell is given as:

$$n_{ads}^{Abs} = n_{inj} - \left[\frac{V_{gas}}{v_{gas}} \right] \quad (6)$$

By combining Equations 5 and 6, the Gibbs adsorption expression can be rewritten as:

$$n_{ads}^{Abs} = n_{ads}^{Gibbs} + \left[\frac{V_{ads}}{v_{gas}} \right] \quad (7)$$

Since

$$V_{ads} = n_{ads}^{Abs} v_{ads} \quad \text{and} \quad v_{ads} = \frac{1}{\rho_{ads}}$$

Then

$$n_{ads}^{Abs} = \frac{n_{ads}^{Gibbs}}{\left[1 - \left(\frac{\rho_{gas}}{\rho_{ads}} \right) \right]} \quad (8)$$

where ρ is density. At low pressures, the density-ratio correction is negligible, but at higher pressures it becomes significant.

A common approximation for the density of an adsorbed phase is to use the liquid density at the atmospheric pressure boiling point, as done by Yee [6]. However, more accurate estimates for the adsorbed-phase density are required when the adsorbed-phase density approaches the bulk gas density.

For multicomponent systems, the adsorbed-phase density, ρ_{ads} , in Equation 8 is replaced with the mixture adsorbed-phase density, which is assumed to be the adsorbed mole fraction weighted average of the pure-component phase volumes ($1/\rho_{ads,i}$), i.e.:

$$\rho_{ads} = \frac{1}{\sum \frac{x_i^{Abs}}{\rho_{ads,i}}} \quad (9)$$

Component Absolute Adsorption

The component mole fraction in the adsorbed phase, x_i^{Abs} , is calculated based on the following derivation. Note that abbreviated subscripts are used for volumes to simplify documentation (g=gas, a=ads, and c=void).

$$n_{inj}(i) = \frac{V_g}{V_g} y_i + \frac{V_a}{V_a} x_i^{Abs} \quad (10)$$

Since

$$V_c = V_g + V_a = V_{void}$$

and substituting for n_{ads}^{Abs} then

$$n_{inj}(i) = \left[\frac{(V_c - V_a)}{V_g} \right] y_i + \left[\frac{n_{ads}^{Gibbs}}{1 - \frac{V_a}{V_g}} \right] x_i^{Abs} \quad (11)$$

or

$$n_{inj}(i) = \frac{V_c}{V_g} y_i - \frac{V_a}{V_g} y_i + \left[\frac{n_{ads}^{Gibbs}}{1 - \frac{V_a}{V_g}} \right] x_i^{Abs} \quad (12)$$

Noting that

$$n_{ads}^{Gibbs} = \frac{V_a}{V_a} \left[1 - \frac{V_a}{V_g} \right] = \left(\frac{V_a}{V_a} - \frac{V_a}{V_g} \right),$$

which upon rearrangement leads to

$$\frac{V_a}{V_g} = \frac{n_{ads}^{Gibbs}}{\left(1 - \frac{V_a}{V_g} \right)} - n_{ads}^{Gibbs} = \left[\frac{1}{\left(1 - \frac{V_a}{V_g} \right)} - 1 \right] n_{ads}^{Gibbs} = \left[\frac{\frac{V_a}{V_g}}{\left(1 - \frac{V_a}{V_g} \right)} \right] n_{ads}^{Gibbs}$$

Therefore, Equation 12 becomes

$$n_{inj}(i) - \frac{V_c}{V_g} y_i = - \left[\frac{\frac{V_a}{V_g}}{\left(1 - \frac{V_a}{V_g} \right)} \right] n_{ads}^{Gibbs} y_i + \left[\frac{n_{ads}^{Gibbs}}{1 - \frac{V_a}{V_g}} \right] x_i^{Abs} \quad (13)$$

or

$$\left(n_{inj}(i) - \frac{V_c}{V_g} y_i \right) \left(1 - \frac{V_a}{V_g} \right) = \left[x_i^{Abs} - y_i \left(\frac{V_a}{V_g} \right) \right] n_{ads}^{Gibbs} \quad (14)$$

By definition

$$x_i^{Gibbs} = \frac{n_{ads}^{Gibbs}(i)}{n_{ads}^{Gibbs}}$$

Then

$$x_i^{Gibbs} = \frac{\left(n_{inj}(i) - \frac{V_c}{V_g} y_i \right)}{n_{ads}^{Gibbs}}$$

Then Equation 14 can be written as

$$x_i^{Gibbs} \left(1 - \frac{V_a}{V_g} \right) = x_i^{Abs} - y_i \left(\frac{V_a}{V_g} \right) \quad (15)$$

For a binary system, Equation 15 becomes two equations:

$$x_1^{Gibbs} = x_1^{Abs} + (x_1^{Gibbs} - y_1) \left[\frac{V_{a1}}{V_g} x_1^{Abs} + \frac{V_{a2}}{V_g} x_2^{Abs} \right] \quad (16)$$

and

$$x_2^{Gibbs} = x_2^{Abs} + (x_2^{Gibbs} - y_2) \left[\frac{V_{a1}}{V_g} x_1^{Abs} + \frac{V_{a2}}{V_g} x_2^{Abs} \right] \quad (17)$$

Given the Gibbs adsorbed-phase compositions $(x_1^{Gibbs}, x_2^{Gibbs})$ and the experimental gas-phase compositions (y_1, y_2) , absolute adsorbed-phase compositions are obtained by solving Equations 16 and 17 simultaneously. Once these compositions are obtained, the absolute adsorption of each individual component is calculated as follows:

$$n_{ads}^{Abs}(i) = x_i^{Abs} n_{ads}^{Abs} \quad (18)$$

(b) Determination of Coal Particle Size Distribution

A sieve analysis was used to determine the macro-particle size distribution. A series of meshes was selected: They were No. 3.5, 8, 10, 12, 20, 30, 40, 50 and 60 with

respective openings of 5.66, 2.38, 2.00, 1.70, 0.85, 0.60, 0.425, 0.300, 0.250 mm. The analysis was performed on a pre-weighed in-situ coal sample. The sieves were stacked in order of mesh size. After sufficiently shaking the sample, we measured the weight of the contents remaining in each sieve to determine the respective proportion of the coal particle size distribution.

(c) Determination of Coal Moisture Content

A pre-weighed, as-received wet coal sample was placed into a pre-weighed container. The container was subjected to a continuous vacuum in a 215-220°F oven. Vacuum was applied overnight to remove moisture. After the moisture was removed, the container was re-weighed, and the difference was assumed to be from the moisture loss.

Another wet sample was placed on a flat pan in a 35.0°C air atmosphere at 97-99% relative humidity. The sample weight was determined periodically to gauge the constancy of weight, which indicates the approach of the sample to equilibrium moisture content. Once a constant sample weight was achieved, the sample was assumed to be at its “equilibrium moisture content” or EMC.

The equilibrium sample was then placed in a continuous vacuum at 215-220°F. The moisture loss determined by weight difference was used to calculate the EMC. For the Tiffany samples considered in this study, the moisture content of the as-received samples was found to be higher than the EMC.

(d) Sorption-Time Measurements for Pure Gases

To facilitate sorption-time measurements, an analog acquisition card was installed in our pressure console. Thus, a graphic representation of how pressure varies with time can be displayed *in real time* using conventional Excel tools. Temperature was also measured by a thermocouple and sent to an analog converter and then to the analog computer acquisition board.

A desorption step is initiated by reducing the equilibrium pressure of the adsorbed gas. This adsorption pressure reduction is accomplished by opening a valve connecting the equilibrium cell (where the coal sample is in contact with the adsorbate) to the injection pump, which is set at lower pressure. The valve between the cell and injection pump is opened as quickly as possible to simulate a step change in pressure. The coal sample then desorbs its gas, and the pressure rises from the initial desorption pressure (P_0) to a new equilibrium pressure (P_f). The pressure at any given time (P_t) is monitored and recorded along with time (t) by the data acquisition module. Thus, the sorption-time estimates are generated from the desorption-time increment involving P_0 and P_f , as depicted by the illustration below.

The pressure fractional uptake, Δ , is defined as:

$$\Lambda = (P_t - P_0)/(P_f - P_0) \quad (19)$$

Here P_0 is the initial desorption pressure, P_f is the final desorption pressure, and P_t is the pressure at time t . Typically, a scaled-time plot produces a generalizeable desorption profile for different equilibrium pressures.

An alternative representation for the adsorption kinetics may be expressed in terms of sorption fractional uptake, defined as:

$$\Theta = (\omega_t - \omega_0)/(\omega_f - \omega_0) = (V_{SCF_t} - V_{SCF_0})/(V_{SCF_f} - V_{SCF_0}) \quad (20)$$

where ω is the amount of gas adsorbed, and V_{SCF} is the corresponding volume at the standard conditions. If a Langmuir-type model is used to correlate the equilibrium sorption data, then Equation 20 can be rewritten as:

$$\Theta = \Lambda \left(\frac{1 + BP_f}{1 + BP_t} \right) \quad (21)$$

where B is the Langmuir constant regressed from sorption experimental data.

D. Data Correlation

The newly acquired adsorption data on the Tiffany coal samples were correlated using (a) the extended Langmuir model, (b) the loading ratio correlation, and (c) the Zhou-Gasem-Robinson (ZGR) two-dimensional equation of state. Following is a brief description of the models used. An assessment for the quality of their

representation and prediction of the present pure and mixture Tiffany coal data is presented in Section E.

(a) Langmuir/Loading Ratio Correlation

Historically, simple models have been used to represent the behavior of pure and mixed gas adsorption on coal. The extended Langmuir model is used almost exclusively in literature studies [e.g., 6], although the Ideal Adsorbed Solution (IAS) model has also been employed [7, 8]. Both of these models work well for essentially ideal adsorbed solutions, but neither is capable of handling nonidealities in the adsorbed phase with any accuracy. The extended Langmuir model is shown below as an illustration of the simple modeling approach used in most previous studies. For mixtures, it takes the form

$$\theta_i = \frac{\omega_i}{L_i} = \frac{B_i P y_i}{1 + \sum_j B_j P y_j} \quad (22)$$

where ω_i is the amount of component "i" adsorbed (SCF of "i" adsorbed per ton of coal), L_i and B_i are Langmuir constants for "i", P is pressure, and y_i is the mole fraction of "i" in the gas phase. This relation allows mixture adsorption to be predicted from pure-component data, since values of L_i and B_i may be determined from the pure-component form of Equation 22. For pure-fluid adsorption, Equation 22 reduces to the Langmuir model:

$$\theta = \frac{\omega}{L} = \frac{BP}{1 + BP} \quad (23)$$

The combined Langmuir-Freundlick adsorption isotherm, expressed in terms of ω_i , yields the loading ratio correlation (LRC) for mixtures:

$$\theta_i = \frac{\omega_i}{L_i} = \frac{(B_i P y_i)^{\eta_i}}{1 + \sum_j (B_j P y_j)^{\eta_j}} \quad (24)$$

The additional parameter (η_i) in the LRC lends the Langmuir model more flexibility. Although the simplicity of Langmuir models is attractive, our data show that they are inadequate to represent the behavior of mixtures of the gases CO₂, methane, and nitrogen. In fact, previously we found errors greater than 100% when the extended Langmuir model was applied to our data on the adsorption of nitrogen from nitrogen + CO₂ mixtures [2].

(b) ZGR Equation of State

Simulations of coalbed gas recovery and CO₂ sequestering require reliable, yet simple, analytic models beyond Langmuir-type correlations. Equation-of-state (EOS) frameworks offer an attractive potential for such requirements. A general two-dimensional EOS can be written as follows [9]:

$$\left[A\pi + \frac{\alpha\omega^2}{1+U\beta\omega+W(\beta\omega)^2} \right] [1-(\beta\omega)^m] = \omega RT \quad (25)$$

where A is the specific surface area, π is the spreading pressure, ω is the specific amount adsorbed, and α , β and m are model parameters. The model coefficients, U , W , and m must be specified to obtain a specific form of the 2-D EOS for application. For example, an analog of the van der Waals (VDW) EOS is obtained by setting $m = 1$ and $U = W = 0$; similarly for the Soave-Redlich-Kwong (SRK) ($m = U = 1$ and $W = 0$); the Peng-Robinson (PR) ($m = 1$, $U = 2$, and $W = -1$); and the Eyring ($m = 1/2$ and $U = W = 0$) EOS.

This general 2-D EOS can be used to investigate EOS behaviors by specifying various combinations of model coefficients. Selection of the model coefficient m is the most important among the EOS model coefficients, because it has a significant effect on the shape of the pure adsorption isotherm. If U and W are equal to zero, then by setting m to values of ∞ , 1 , and $1/2$, we obtain the 2-D ideal gas law, the VDW EOS, and the Eyring EOS, respectively. Actually, the pure gas isotherms vary considerably in shape and we have found that it is sometimes desirable to select an m value even smaller than $1/2$ to describe pure isotherms. We have determined that an equation with $m = 1/3$ and $U = W = 0$ (the ZGR EOS) is promising [9]. The 2-D EOS can be applied to adsorbed phases containing mixtures by utilizing the traditional mixing rules (where x is the mole fraction in the adsorbed phase):

$$\alpha = \sum_i \sum_j x_i x_j \alpha_{ij} \quad (26)$$

$$\beta = \sum_i \sum_j x_i x_j \beta_{ij} \quad (27)$$

along with the non-traditional combination rules [9],

$$\begin{aligned} \alpha_{ij} &= (1 - C_{ij})(\alpha_i + \alpha_j)/2 \\ \beta_{ij} &= (1 + D_{ij})\sqrt{\beta_i \beta_j} \end{aligned} \quad (28)$$

where C_{ij} and D_{ij} are the EOS binary interaction parameters.

E. Results and Discussion

1. Experimental Data

(a) Comparison of Tiffany Coal Samples

Coal characterization measurements are presented in Tables 1-3 and Figures 2-4. Table 1 presents the compositional analyses for coal samples from Wells #1 and #10. Table 2 and Figures 2-4 present the coal particle size distribution for the two samples. The analyses indicate that the two coal samples are similar in composition and particle size distribution.

The density of the compact solid coal is called the coal helium density, in reference to the helium displacement measurements used to determine the adsorbent density [10]. We have measured the coal helium densities for Well #1, Well #10, and the mixed sample. They are 1.73, 1.57, and 1.67 ± 0.07 g/cc, respectively. The equilibrium moisture content of Well #1 coal sample is $3.8 \pm 0.2\%$ and the equilibrium moisture content of Well #10 coal sample is $3.7 \pm 0.2\%$.

Vitrinite reflectance analyses conducted by National Petrographic Services indicate that the present Tiffany coal samples are medium volatility bituminous coal. As summarized in Table 3, Wells #1 and 10 have average oil-based vitrinite reflectance values of 1.31 and 1.35, respectively.

Initial methane adsorption isotherms were measured separately for Wells #1 and #10. Results are presented in Tables 4 and 5 (on moisture-free and ash-free bases) and Figure 5. They indicate that the adsorption capacities of samples from the two wells are comparable with a maximum variation of 5% in the amount adsorbed at 2000 psia.

Because of the similarity in the methane adsorption behavior for Tiffany Well #1 and Well #10 coal samples, and upon agreement with BP Amoco personnel, coal samples from the two wells were mixed on an equal-mass basis. Large chunks of coal (dime-size) were broken up and the coal mixture was gently shaken to ensure a final homogenous mixture. The coal samples were placed into a tightly-capped jar. Helium was injected into the jar to prevent oxidation of the coal.

(b) Adsorption Isotherms

Pure Gas Adsorption

Gas adsorption measurements for pure methane, nitrogen and CO₂ were conducted on wet Tiffany coal samples at 130°F and pressures to 2000 psia. Our error analysis indicates that the average uncertainties for the methane, nitrogen, and CO₂ adsorption measurements are approximately 3% (9 SCF/ton), 6% (8 SCF/ton) and 7% (62 SCF/ton), respectively. These estimates, which are depicted as error bars in some of the figures, were generated by error propagation of uncertainties in all

measured quantities. The repeated isotherms confirm the estimated precision of the measurements.

The adsorption data are presented in Tables 4-8 and Figures 5-10. Figure 6 presents the Gibbs adsorption isotherms for methane, nitrogen, and CO₂, respectively. The absolute adsorption data for these gases are presented in Figures 7-10. In this study, unless otherwise noted, we use the adsorbed-phase density approximation suggested by Yee [6]. For nitrogen, methane, and CO₂, densities of 0.808, 0.421, and 1.18 g/cm³, respectively, were used to convert the Gibbs to absolute adsorption.

Tables 4 and 5 present isotherms for methane on Well #1 and Well #10 coal samples, respectively. Replicate runs were conducted to confirm our measurements. These measurements show good agreement between the replicate runs, which yield an expected uncertainty of about 5%. A four-point adsorption isotherm was measured on the Tiffany mixed coal sample, as presented in Table 6. As expected, the mixed coal sample produced an intermediate adsorption capacity; i.e., it shows less adsorption than the Well #1 coal sample and more than the Well #10 sample.

The replicate runs for methane (Figure 5 and Tables 4-6) show good agreement. The average expected uncertainty for these measurements is approximately 3% (9 SCF/ton), as depicted by the error bars in Figure 5. (Notice that error bars are included only for one run).

The adsorption isotherm for pure nitrogen on the mixed Tiffany coal sample is presented in Table 7 and Figure 8. As indicated by Figure 8, no significant differences exist between the replicate runs. The average expected uncertainty for these measurements is approximately 6% (8 SCF/ton). Similarly, adsorption isotherm measurements for pure CO₂ on wet Tiffany mixed coal sample are given in Table 8 and Figure 9. The replicate runs show reasonable agreement with an average expected uncertainty of about 7% (62 SCF/ton).

Both methane and nitrogen adsorption measurements on Tiffany coal indicate lower adsorption capacity than the adsorption on the Fruitland coal reported previously [1]. The measurements on Tiffany coal are about one half that on Fruitland coal at the same conditions. This difference might be due to variations in coal composition. Ash content in Tiffany coal is about twice that of the Fruitland coal. In contrast, the carbon content in Tiffany coal is about two thirds that in Fruitland coal. Nevertheless, the new measurements agree with the previous ones in the *relative* amounts of nitrogen, methane and CO₂ adsorbed, which are in the approximate ratio of 1 : 2.7 : 5 at 1000 psia.

As previously reported [1], a slightly different moisture content in each measurement set indicates that water content values beyond the equilibrium water content have no significant effect the adsorption behavior. In contrast, the adsorbed-phase density estimates may affect the calculated absolute adsorption isotherm. Figure 10

illustrates the effect of variation in the adsorbed-phase density on the CO₂ absolute adsorption. Here, three estimates are used: (1) the triple point liquid density (1.18 g/cm³), (2) the ZGR model estimate (1.25 g/cm³), and (3) a graphical estimate based on the Gibbs adsorption isotherm (1.40 g/cm³). Differences in the calculated adsorption increase with pressure, rising to as much as 15% at 2000 psia.

Binary Mixture Adsorption

Adsorptions isotherms were measured for methane/nitrogen, methane/CO₂ and nitrogen/CO₂ on wet, mixed Tiffany coal at 130 °F and pressures to 2000 psia. The measurements were conducted at one feed composition for each mixture. The expected uncertainties in the amount adsorbed for these binary mixtures vary with pressure and composition. In general, percent average uncertainties are below 5% (19 SCF/ton) for total adsorption; however, the expected uncertainties in the amount of individual-component adsorption are significantly higher for the less-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20/80 nitrogen/CO₂ system).

Mixture absolute adsorption estimates were calculated assuming ideal-solution additive volumes in the condensed phase (i.e., the mixture volume is the mole-fraction-weighted average of the pure component volumes). The traditional values of 0.808 g/cm³, 0.421 g/cm³, and 1.18 g/cm³, were used to estimate the adsorbed-phase density of methane, nitrogen, and CO₂, respectively.

Table 9 and Figure 11 present the experimental data for methane/nitrogen adsorption at the nominal molar feed composition of 50% methane. In general, the average expected uncertainties in the amount of individual-component adsorption are 7% (13 SCF/ton) for methane, and 17% (8 SCF/ton) for nitrogen. The total adsorption has estimated uncertainties of 7% (15 SCF/ton). Figure 12 presents the absolute adsorption for this binary system, including predictions from the LRC and ZGR models. As shown in Figures 11 and 12, methane is more strongly adsorbed than nitrogen.

Table 10 and Figure 13 present the experimental data of methane/CO₂ adsorption at a nominal molar feed composition of 40% methane. The average expected uncertainties in the amount of individual-component adsorption are 7% (10 SCF/ton) for methane, and 6% (17 SCF/ton) for CO₂. The total adsorption has estimated uncertainties of 4% (20 SCF/ton). Figure 14 presents the absolute adsorption of this system, which indicates that the amount of CO₂ adsorbed is almost three times that observed for methane.

Table 11 and Figure 15 present the experimental data of nitrogen/CO₂ adsorption at the nominal molar feed composition of 20% nitrogen. A small amount of nitrogen is adsorbed at this feed composition. This results in higher uncertainties for the nitrogen component adsorption, which could be around 29% (8 SCF/ton). In comparison, the CO₂ component adsorption has estimated uncertainties 6% (23 SCF/ton), and the total adsorption has estimated uncertainties of 5% (22 SCF/ton).

Figure 16 presents the absolute adsorption of this binary system, which indicates that the amount of CO₂ adsorbed is almost 20 times that observed for nitrogen.

Ternary Mixture Adsorption

The ternary adsorption of methane/nitrogen/CO₂ on wet, mixed Tiffany coal at 130 °F and pressures to 2000 psia was conducted at 10/40/50 mole % feed composition. Table 12 and Figure 17 present the excess Gibbs adsorption data for this mixture, and Figure 18 depicts the absolute adsorption isotherms. The average expected uncertainty for the total adsorption and CO₂ adsorption is about 5% (17 SCF/ton). However, the low adsorption of nitrogen and methane in this ternary yielded experimental uncertainties of 14% (9 SCF/ton) and 27% (9 SCF/ton), respectively. The absolute adsorption data for this ternary were generated using the same procedure used for the binary mixtures.

(c) Sorption-Time Estimates for Pure Gases

Tables 13-16 present the desorption data for pure methane, nitrogen and CO₂, respectively. The tables provide a record for a number of desorption runs for each gas off the Tiffany coal samples, where values for the initial desorption pressure, final desorption pressure and the time of desorption are given. In addition, information is shown for the 90% pressure fractional uptake, Λ ; and the 63% sorption fractional uptake, Θ .

Figure 19 presents three methane desorption runs for the Well #1 coal sample. Similarly, Figure 20 presents two methane desorption runs for Well #10 coal sample. The results for three nitrogen runs and six CO₂ desorption runs off the Tiffany mixed coal sample are given in Figures 21 and 22, respectively. Other runs for the various gases, which are not included, show the same trend.

For the Well #1 coal sample, the sorption time at 90% pressure uptake for methane varies from 8 minutes to 140 minutes depending on the pressure. For the Well #10 coal sample, the 90% sorption time for methane varies from 4 minutes to 50 minutes depending on the pressure. Accordingly, methane desorption on Well #10 coal is faster than on Well #1 coal. Moreover, desorption at higher pressures is faster than desorption at lower pressures. Similar trends for the effect of pressure on sorption time are observed for nitrogen and CO₂ on the Tiffany mixed coal sample.

2. Data Correlation and Model Evaluation

(a) Adsorption Isotherms

The data correlation and model evaluation effort undertaken here addresses two important issues: (a) the ability of the LRC and ZGR EOS to correlate or represent the acquired adsorption data, and (b) the ability of the two models to predict the binary and ternary mixture adsorptions. Thus, beyond establishing the model precision in summarizing existing data, we are also interested in evaluating the efficacy of such models in using pure and/or binary measurements to provide accurate predictions for ternary and other multicomponent mixtures.

Accordingly, in the following discussion two case studies are considered. First, we evaluate model **representations** of the Tiffany adsorption data, where the model parameters (L , B , and η for the LRC; α , β , C_{ij} , D_{ij} for ZGR EOS) are regressed to correlate the data considered and to establish the quality of precision attainable for the present models. Next, we examine binary model **predictions** based on pure-fluid parameters, and ternary predictions based on pure or a combination of pure and binary parameters.

The following weighted-error objective function was used to regress model parameters:

$$SS = \sum_i \sum_j \left(\frac{\omega_{ij}^{\text{calc}} - \omega_{ij}^{\text{exp t}}}{\sigma_{ij}^{\text{exp t}}} \right)^2 \quad i=1, \text{NPTS}; j=1, \text{NC} \quad (29)$$

Here, j and i are component and data point indices, respectively, NC the total number of components in the mixture, NPTS the total number of data points, and $\sigma_{ij}^{\text{exp t}}$ is the expected experimental uncertainty for the individual data point. The root-mean-square error (RMSE) and the %AAD for the individual isotherms, calculated as

$$\text{RMSE} = \sqrt{\frac{\sum_i^{\text{NPTS}} (\omega_i^{\text{calc}} - \omega_i^{\text{exp t}})^2}{\text{NPTS}}}$$
$$\% \text{AAD} = 100 \sum_i^{\text{NPTS}} \left| \frac{\omega_i^{\text{calc}} - \omega_i^{\text{exp t}}}{\omega_i^{\text{exp t}}} \right|$$

were used to express the quality of fit in our model evaluations. Similar expressions were used for the overall fit.

Pure Adsorption

Tables 17-20 present a summary of our model evaluation results for the three models used to correlate the present adsorption data for methane, nitrogen, and CO₂. The model parameters, shown in Tables 17-20, were determined by minimizing the sum of squares of weighted errors in the calculated adsorption, ω , for the pure gas of interest (Equation 29).

Table 17 presents the results for the Langmuir model. AADs of 2 to 4% (4-17 SCF/ton) were obtained for the systems considered. Table 18 presents the results for the LRC using system-specific pressure exponents (η_i). The results indicate that the LRC produces better quality fit than the Langmuir correlation for the three gases studied. This in part reflects the added flexibility gained by the additional parameter η_i in the regressions. AADs of 1 to 2% (2-12 SCF/ton) were observed for the systems considered. When a common pressure exponent (η_i) was forced on the model, a value of 0.90 was obtained. Table 19 presents the results of this LRC using the common exponent, which yielded an AAD of 1-2% (2-12 SCF/ton).

Table 20 presents a summary of our model evaluation results for ZGR EOS. These results reveal the ability of the ZGR EOS to represent the adsorption of CO₂, methane and nitrogen on Tiffany coals within their expected experimental uncertainties. Similar to the LRC results, fits with 2 to 3% AAD (3-15 SCF/ton) were obtained.

Figures 7-10 illustrate the abilities of the LRC and ZGR models to describe the present pure-fluid adsorption data.

Binary Mixture Adsorptions

Figures 12, 14, and 16 present the LRC **representations** of the binary absolute adsorption data. The LRC parameters generated for these mixtures and the model statistics are given in Table 21. In general, AADs of 1-10% (1-19 SCF/ton) are observed for the individual-component adsorption. However, an AAD of 32% (11 SCF/ton) was obtained for the nitrogen adsorption in the nitrogen/CO₂ mixture adsorption.

Table 22 summarizes the results for the **LRC predictions** based on pure-gas adsorption data. As shown in this table, the LRC model predicts the methane/nitrogen and methane/CO₂ binary adsorptions within the experimental uncertainties (2-21%, 5-42 SCF/ton) using pure-fluid adsorption parameters; however, the model predictions for the nitrogen/CO₂ binary are less accurate (AAD of 39% or 14 SCF/ton for the nitrogen adsorption). Moreover, variation of the pressure exponent η does not significantly change the results. Figures 23-25 illustrate the quality of the LRC predictions for the binary mixtures.

Table 25 presents a summary of the evaluation results for ZGR EOS, where various binary parameter regressions have been considered. The results indicate that using two interaction parameters (C_{ij} and D_{ij}) leads to the best overall fit for the Tiffany coal adsorption data. **Representations** within the expected experimental uncertainty (AAD of 3-15%, 3-33 SCF/ton) are obtained for the three binaries. Figures 12, 14, and 16 illustrate the abilities of the ZGR EOS to describe the present binary mixture adsorption data. In most cases, the ZGR and LRC give comparable results, with slightly better statistics for the LRC.

In addition, Table 25 summarizes the results for the **ZGR predictions** based on pure-gas adsorption data. As shown in this table and Figures 23-25, the ZGR EOS predicts the binary adsorption isotherms of methane/nitrogen and methane/CO₂ within twice the experimental uncertainty (about 1-27%, 5-35 SCF/ton). Significantly higher deviations, however, are observed for the less-adsorbed nitrogen (up to 49% AAD, 13 SCF/ton) in the nitrogen/CO₂ binary.

Ternary Mixture Adsorption

Figure 18 presents the LRC **representations** of the ternary adsorption data. The LRC parameters generated for this mixture and the model statistics are given in Table 23. AAD of 3-12% (4-17 SCF/ton) are observed for the individual adsorption, and 3% (16 SCF/ton) for the total adsorption. The results suggest that the quality of fit is directly related to the amount adsorbed.

The **predictive capability** of the LRC is examined in Figure 26 and Table 24. In this case, the LRC model parameters obtained from the pure adsorption were used to predict the ternary mixture adsorption on wet Tiffany coal. Poor model predictions were obtained for this ternary when only pure-adsorption data are utilized in model optimization. AAD of 5-45% (2-55 SCF/ton) were observed for the individual-component isotherms. This translates roughly to prediction errors within one to four times the expected experimental uncertainty. Variation in the pressure exponent η did not alter the results significantly.

Table 25 presents a summary the evaluation results for ZGR EOS, which indicate the ability of the ZGR EOS to predict the methane/nitrogen/CO₂ ternary adsorption isotherms within three times their expected experimental uncertainties (4-56% AAD, 5-52 SCF/ton). The ZGR **representations** using binary interaction parameters (C_{ij} , D_{ij}) are comparable to those obtained by the LRC using the same amount of input data. The ZGR binary interaction parameters generated for this mixture are also given in Table 25.

The **predictive capability** of the ZGR EOS is examined in Figure 26 and Table 25. The ZGR predictions based on pure (α_i , β_i , $\ln k_i$) and binary (C_{ij} , D_{ij}) parameters are within three times the experimental uncertainty (10-32% AAD, 5-49 SCF/ton). However, the results indicate that for the present mixtures little improvement is realized by predicting the individual-component ternary isotherms based on

parameters generated from both pure and binary adsorption data. Further, the quality of the model predictions indicate that although the LRC and ZGR EOS are capable of predicting total adsorption isotherms adequately, they predict the individual-component isotherms poorly, especially when dealing with the less-adsorbed component of the mixture. In fact, diminishing the influence of the less-adsorbed components on the parameter regressions, by using a least-squares (un-weighted) objective function, improves the ternary model predictions based on pure and binary data.

These results suggest significant model improvements are required to realize the expected benefit of improving multicomponent predictions using binary adsorption measurements.

(b) Sorption-Time Estimates for Pure Gases

An empirical correlation was used to represent the sorption fractional uptake, Θ :

$$\Theta = \frac{\beta t^\alpha}{1 + \beta t^\alpha} \quad (30)$$

where

$$\alpha = (aP^2 + bP + 0.5)c$$

The coefficients β , a , b and c are regressed from sorption time data [8]. For the systems considered in this study, Equation 30 represents the sorption-time estimates on average within 8%. Table 26 lists the regressed parameters for the gases considered, and Figures 27-30 present the correlated sorption curves for methane, nitrogen and CO₂, respectively.

Table 27 and Figure 31 present time estimates for liberated gas off the Tiffany coal samples. The plot indicates that CO₂ has the fastest sorption time followed by nitrogen and methane. Moreover, the sorption time for the three gases is within 12 minutes for 63% adsorbed-gas liberation.

F. Conclusions

- Characterizations of BP Amoco Tiffany coal samples from Injection Wells #1 and #10 were done. Results for (a) particle size distribution, (b) composition, (c) equilibrium moisture content, and (d) vitrinite reflectance indicate similarity of the two samples.
- The vitrinite reflectance analysis indicates that the samples represent medium volatility bituminous coals.
- Adsorption isotherms for pure methane on the two wet Tiffany coal samples (Wells #1 and #10) at 130°F and pressures to 2000 psia confirmed the similarity of the two samples.
- Adsorption isotherms were then measured for **pure** methane, nitrogen and CO₂ on a mixed Tiffany coal sample. The coal sample was an equal-mass mixture of coals from Well #1 and Well #10. The adsorption measurements were conducted at 130°F and pressures to 2000 psia. The adsorption capacity of the mixed sample is intermediate to that observed for Well #1 and Well #10 samples. The pure adsorption data have average expected experimental uncertainties of 3% (9 SCF/ton), 6% (8 SCF/ton) and 7% (62 SCF/ton) for methane, nitrogen, and CO₂, respectively.
- Sorption times were measured for pure methane, nitrogen and CO₂. The measurements were correlated using a Langmuir-type equation, which yielded average errors within 8%.
- **Binary** adsorption of methane/nitrogen, methane/CO₂ and nitrogen/CO₂ on a wet Tiffany mixed coal at 130 °F and pressures to 2000 psia were measured at one feed composition for each mixture. The expected uncertainties in the amount adsorbed for these binary mixtures vary with pressure and composition. In general, percent average uncertainties are about 7% (19 SCF/ton) for total adsorption; however, the expected uncertainties in the amount of individual-component adsorption are significantly higher, especially at lower feed gas mole fractions (i.e., nitrogen in the nitrogen/CO₂ system at 20/80 mole % feed composition).
- **Ternary** adsorption was measured for methane/nitrogen/CO₂ on a wet Tiffany mixed coal at 130°F and pressures to 2000 psia for a 10/40/50 mole % feed composition. The average expected uncertainty for the total adsorption and CO₂ adsorption is about 5% (17 SCF/ton). However, the low adsorption of nitrogen and methane in this ternary yielded experimental uncertainties of 14% (9 SCF/ton) and 27% (9 SCF/ton), respectively.
- Our newly acquired compressibility factor measurements for mixtures of methane/nitrogen/CO₂ allowed us to optimize the BWR EOS to predict accurately the Z factors required for use in reduction of our mixture adsorption data.

- The total adsorption data can be **correlated** within their experimental uncertainties by the loading ratio correlation (LRC) and the 2D Zhou-Gasem-Robinson (ZGR) equation of state (EOS).
- The present results suggest that both the LRC and ZGR EOS are capable of **predicting** binary adsorption isotherms based on pure-fluid adsorption parameters within twice their experimental uncertainties. In comparison, the ternary predictions based on pure-fluid parameters yield three times the experimental uncertainties. Further, for the present system, little improvement is realized by predicting the individual-component ternary isotherms based on parameters generated from both pure and binary adsorption data.
- The quality of the model predictions indicate that although the LRC and ZGR EOS are capable of predicting the total adsorption adequately, they predict the individual-component adsorption poorly, especially when dealing with the less-adsorbed component of the mixture. This suggests significant model improvements are required to realize the full benefit of improving multicomponent predictions using input from binary adsorption measurements.

G. References

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Table 1. Compositional Analyses of Tiffany Coal Samples*

Analysis	Well #1	Well #10	Well #1 Dried Basis	Well #10 Dried Basis
Dry Loss %	6.85	18.33		
Carbon %	44.51	46.35	47.78	56.75
Hydrogen %	3.20	4.30	2.62	2.77
Oxygen %	11.85	20.51	6.19	5.16
Nitrogen %	0.86	0.83	0.92	1.02
Sulfur %	0.53	0.42	0.57	0.52
Ash %	46.30	38.99	49.71	47.74
Proximate				
Volatile Matter %	14.41	12.54	15.48	15.35
Fixed Carbon %	32.43	30.14	34.82	36.91

*Analysis was conducted on a mass basis by Huffman Laboratories, Inc., 4630 Indiana Street, Golden, CO 80405.

Table 2. Tiffany Coal Particle Size Distribution

Size Range (mm)		Well #1 (% mass)	Well #10 (% mass)
From	To		
0.00	0.25	4.0	5.0
0.25	0.30	4.5	1.4
0.30	0.425	7.5	3.3
0.425	0.60	10.9	8.2
0.60	0.85	13.9	15.0
0.85	1.70	45.7	41.0
1.70	2.00	2.5	5.6
2.00	2.38	6.2	4.3
2.38	5.66	4.7	15.6
5.66	∞	0.0	0.6

Table 3. Vitrinite Reflectance Analysis*

	Well #1	Well #10
Average VRO	1.31	1.35
Range	1.19-1.43	1.21-1.50
Grain Count	50	50
Rank	Medium Volatility Bituminous Coal	Medium Volatility Bituminous Coal

*Analysis was conducted by National Petrographic Service, Inc., 5933 Bellaire Blvd. Suite 108, Houston, TX 77081.

**Table 4. Pure Methane Adsorption on Wet Tiffany Well #1 Coal at 130 °F:
5.6% Moisture Content**

Run 1 (Moisture Free Basis)			Run 2 (Moisture Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)*	Absolute Adsorption (SCF/ton)	Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
62.0	43.2	43.5	322.5	141.7	146.4
139.3	79.7	80.8	657.3	199.7	214.0
298.3	138.6	142.8	1129.1	245.7	278.7
485.0	176.9	186.0	1840.3	260.8	325.9
655.5	205.9	220.6			
898.3	234.1	258.0			
1057.1	246.1	276.6			
1235.1	254.7	292.9			
1446.4	260.5	308.1			
1728.1	264.2	324.9			
1960.3	267.8	340.5			

Run 1 (Moisture and Ash Free Basis)			Run 2 (Moisture and Ash Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)	Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
62.0	85.9	86.5	322.5	281.8	291.1
139.3	158.4	160.7	657.3	397.1	425.5
298.3	275.6	284.0	1129.1	488.5	554.2
485.0	351.8	369.8	1840.3	518.6	648.1
655.5	409.4	438.6			
898.3	465.5	513.0			
1057.1	489.3	550.1			
1235.1	506.4	582.4			
1446.4	518.0	612.7			
1728.1	525.3	646.0			
1960.3	532.5	677.0			

* 1 mmol/g = 758.98 SCF/ton

**Table 5. Pure Methane Adsorption on Wet Tiffany Well #10 Coal at 130 °F:
16.5% Moisture Content**

Run 1 (Moisture Free Basis)			Run 2 (Moisture Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)	Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
81.2	48.8	49.1	251.1	108.3	111.0
191.1	94.1	95.9	681.6	199.0	213.8
375.5	145.5	151.1	1137.8	232.8	264.4
591.6	189.8	201.9	1665.4	238.0	290.4
809.1	219.3	239.2			
1018.2	230.2	257.6			
1194.5	238.6	273.0			
1393.2	241.9	284.1			
1599.8	243.5	294.1			
1807.4	246.9	307.1			
1975.9	250.6	319.4			

Run 1 (Moisture and Ash Free Basis)			Run 2 (Moisture and Ash Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)	Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
81.2	93.4	94.1	251.1	207.2	212.6
191.1	180.0	183.6	681.6	380.8	409.2
375.5	278.4	289.2	1137.8	445.4	506.1
591.6	363.2	386.3	1665.4	455.5	555.7
809.1	419.6	457.6			
1018.2	440.5	492.8			
1194.5	456.6	522.3			
1393.2	462.9	543.6			
1599.8	465.9	562.8			
1807.4	472.5	587.6			
1975.9	479.5	611.1			

**Table 6. Pure Methane Adsorption on Wet Tiffany Mixed Coal Sample at 130 ° F:
11.7% Moisture Content**

(Moisture Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
255.9	114.0	117.0
824.9	223.1	243.9
1210.2	247.4	283.6
1796.9	254.8	316.6

**Table 7. Pure Nitrogen Adsorption on Wet Tiffany Mixed Coal Sample at
130 ° F: 11.7% Moisture Content**

Run 1 (Moisture Free Basis)			Run 2 (Moisture Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)	Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
126.8	23.5	23.7	106.6	18.0	18.1
222.7	35.2	35.9	202.9	29.4	29.9
418.3	54.3	56.4	406.0	51.0	52.9
615.7	67.8	71.7	602.7	66.0	69.7
808.7	81.7	88.0	795.6	82.0	88.1
1008.9	91.9	100.8	1000.2	93.4	102.3
1211.4	99.8	111.6	1202.5	102.1	113.9
1404.6	108.4	123.4	1410.9	111.2	126.6
1615.8	118.9	138.1	1604.9	119.0	138.0
1817.6	125.8	148.9	1806.2	124.5	147.2
1994.8	132.5	159.5			

**Table 8. Pure CO₂ Adsorption on Wet Tiffany Mixed Coal Sample at 130 °F:
11.7% Moisture Content**

Run 1 (Moisture Free Basis)			Run 2 (Moisture Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)	Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
69.5	149.6	150.6	97.3	175.1	176.7
204.5	273.1	278.8	526.8	383.0	406.6
400.7	362.8	378.8	1028.3	417.2	486.1
624.3	408.0	439.4	1504.0	357.1	515.4
813.3	422.3	469.5	1956.1	281.5	575.6
1010.0	423.0	490.6			
1209.1	403.6	496.8			
1402.1	372.3	501.2			
1590.5	335.2	520.2			
1784.6	303.4	555.7			
1976.5	271.0	560.1			

Table 9. Methane/Nitrogen Adsorption on a Wet Tiffany Mixed Coal Sample at 130 °F: 10.5% Moisture Content

Pressure (psia)	Adsorption (SCF/ton dry coal)						Phase Compositions (Mole Fraction Methane)	
	Total		Methane		Nitrogen		Gas	Adsorbed*
	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute		
	Methane Feed Composition: 50.0%							
118.5	45.9	46.4	36.9	37.1	9.0	9.3	0.432	0.799
220.1	79.2	80.8	63.8	64.5	15.3	16.3	0.436	0.798
400.0	120.0	124.7	98.4	100.6	21.6	24.1	0.444	0.806
611.6	155.5	165.1	126.6	130.9	28.9	34.1	0.454	0.793
813.8	180.4	195.7	152.1	159.1	28.3	36.6	0.456	0.813
1005.9	199.1	220.4	167.3	177.1	31.8	43.3	0.461	0.804
1208.5	212.7	240.7	183.2	196.2	29.4	44.5	0.464	0.815
1409.7	223.8	258.7	193.4	209.5	30.4	49.3	0.467	0.810
1609.6	233.7	276.6	203.6	223.8	30.1	52.8	0.469	0.809
1812.8	241.5	292.5	207.8	231.9	33.7	60.6	0.473	0.793
2010.8	251.5	311.6	216.4	244.9	35.1	66.7	0.474	0.786

* - Based on absolute adsorption

Table 10. Methane/CO₂ Adsorption on a Wet Tiffany Mixed Coal Sample at 130 °F: 11.4% Moisture Content

Pressure (psia)	Adsorption (SCF/ton dry coal)						Phase Compositions (Mole Fraction Methane)	
	Total		Methane		Carbon Dioxide		Gas	Adsorbed*
	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute		
	Methane Feed Composition: 41.4%							
105.3	136.1	137.5	35.9	36.7	100.2	100.9	0.541	0.267
210.0	209.7	214.1	49.6	52.0	160.1	162.1	0.530	0.243
402.4	288.6	301.1	67.7	73.8	220.9	227.2	0.500	0.245
601.4	334.6	357.0	70.7	81.7	263.9	275.4	0.488	0.229
820.7	361.7	397.0	76.0	92.7	285.8	304.4	0.473	0.234
1010.0	374.4	422.2	75.4	97.6	299.0	324.6	0.465	0.231
1214.0	379.1	441.7	79.2	107.7	299.9	334.0	0.455	0.244
1409.3	376.8	454.6	80.6	115.4	296.2	339.1	0.449	0.254
1609.3	370.4	464.6	82.6	124.2	287.8	340.3	0.443	0.268
1806.7	361.5	473.1	85.4	134.2	276.1	338.9	0.438	0.284
2034.8	344.0	474.7	90.2	146.7	253.7	328.0	0.432	0.309

* - Based on absolute adsorption

Table 11. Nitrogen/CO₂ Adsorption on a Wet Tiffany Mixed Coal Sample at 130 °F: 10.4% Moisture Content

Pressure (psia)	Adsorption (SCF/ton dry coal)						Phase Compositions (Mole Fraction Nitogen)	
	Total		Nitrogen		Carbon Dioxide			
	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	Gas	Adsorbed*
	Nitrogen Feed Composition: 20.1 %							
91.8	143.1	144.4	4.3	4.8	138.7	139.6	0.363	0.033
196.3	230.7	235.1	6.6	8.0	224.1	227.1	0.325	0.034
402.7	324.7	338.4	6.5	10.5	318.2	327.9	0.289	0.031
602.9	371.4	396.3	6.9	13.6	364.5	382.8	0.268	0.034
824.4	398.4	438.1	5.5	15.5	392.9	422.6	0.253	0.035
1011.5	405.4	458.7	9.9	22.7	395.5	436.0	0.241	0.050
1213.7	403.4	472.8	8.5	24.7	394.9	448.2	0.233	0.052
1407.7	395.2	481.5	8.7	28.3	386.5	453.2	0.227	0.059
1604.3	376.1	479.3	6.5	29.5	369.5	449.8	0.223	0.062
1805.2	352.6	473.7	5.4	31.9	347.2	441.8	0.219	0.067
2004.2	336.8	478.6	4.2	34.9	332.6	443.7	0.216	0.073

* - Based on absolute adsorption

**Table 12. Adsorption of a 10/40/50 Mole % Methane/Nitrogen/CO₂ Feed Mixture
on a Wet Tiffany Mixed Coal Sample at 130 °F: 10.5% Moisture Content**

Pressure (psia)	Adsorption (SCF/ton dry coal)							
	Total		Methane		Nitrogen		Carbon Dioxide	
	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute
102.3	95.4	96.2	9.1	9.2	14.6	15.1	71.7	71.9
199.3	158.9	161.7	13.3	13.6	19.4	21.0	126.2	127.0
393.1	239.4	248.1	18.1	19.1	23.4	28.2	197.9	200.8
612.6	291.6	308.8	20.8	22.7	26.9	36.0	243.8	250.1
807.2	319.5	345.4	21.9	24.8	30.1	43.2	267.6	277.4
1008.8	337.1	372.7	21.7	25.7	30.6	48.2	284.8	298.8
1206.4	345.1	390.5	22.0	27.1	31.5	53.4	291.7	310.0
1410.7	349.8	406.1	20.7	27.0	30.9	57.6	298.2	321.5
1607.6	346.9	413.0	21.6	28.9	32.3	63.2	293.0	320.8
1808.6	344.2	420.4	22.8	31.2	34.0	69.4	287.3	319.8
2005.4	342.7	429.4	25.2	34.5	35.6	75.6	281.9	319.2

**Table 12. (Continued) Adsorption of a 10/40/50 Mole % Methane/Nitrogen/CO₂ Feed Mixture
on a Wet Tiffany Mixed Coal Sample at 130 °F: 10.5% Moisture Content**

Pressure (psia)	Phase Compositions (Mole %)					
	Methane		Nitrogen		Carbon Dioxide	
	Gas	Adsorbed*	Gas	Adsorbed*	Gas	Adsorbed*
102.3	0.107	0.095	0.543	0.157	0.350	0.748
199.3	0.112	0.084	0.537	0.130	0.352	0.786
393.1	0.112	0.077	0.514	0.114	0.374	0.810
612.6	0.111	0.074	0.491	0.116	0.398	0.810
807.2	0.111	0.072	0.476	0.125	0.414	0.803
1008.8	0.110	0.069	0.464	0.129	0.426	0.802
1206.4	0.109	0.069	0.455	0.137	0.436	0.794
1410.7	0.109	0.067	0.448	0.142	0.443	0.792
1607.6	0.107	0.070	0.442	0.153	0.451	0.777
1808.6	0.106	0.074	0.436	0.165	0.457	0.761
2005.4	0.105	0.081	0.432	0.176	0.463	0.743

* - Based on absolute adsorption

Table 13. Desorption Time for Methane on Wet Tiffany Well #1 Coal Sample at 130 °F

Equilibrium Pressures (psia)			Time at L=0.9 (min)	Time at Q=0.63 (min)
Initial System	Desorption			
	From	To		
1958.2	1697.1	1722.8	7.5	0.6
1722.8	1496.9	1519.4	11.1	0.9
1519.4	1288.7	1310.6	17.4	1.4
1310.6	1098.4	1115.7	21.8	1.7
1115.7	894.4	911.8	28.2	2.2
911.8	682.3	704.6	44.0	3.5
704.6	484.3	505.6	56.3	4.5
283.9	43.1	87.1	169.0	14.6

Table 14. Desorption Time for Methane on Wet Tiffany Well #10 Coal Sample at 130 °F

Equilibrium Pressures (psia)			Time at L=0.9 (min)	Time at Q=0.63 (min)
Initial System	Desorption			
	From	To		
1976.4	1650.0	1678.2	4.4	0.3
1678.2	1351.0	1377.2	8.0	0.6
1377.2	1071.5	1098.7	8.8	0.7
649.1	430.4	460.1	8.4	0.7
460.1	242.4	324.7	26.1	2.3
324.7	142.4	238.1	40.3	3.7

Table 15. Desorption Time for Nitrogen on Wet Tiffany Mixed Coal Sample at 130 °F

Equilibrium Pressures (psia)			Time at L=0.9 (min)	Time at Q=0.63 (min)
Initial System	Desorption			
	From	To		
1954.4	1304.4	1310.1	22.0	4.0
1310.1	716.0	728.7	30.0	5.6
728.7	325.0	332.2	60.0	7.2
332.2	40.7	42.3	60.0	12.0

Table 16. Adsorption Time for CO₂ on Wet Tiffany Mixed Coal Sample at 130°F

Equilibrium Pressures (psia)			Time at L=0.9 (min)	Time at Q=0.63 (min)
Initial System	Adsorption			
	From	To		
3.0	159.2	69.5	39.5	2.9
69.5	462.0	400.7	27.6	2.5
400.7	662.0	624.3	22.0	2.2
624.3	834.0	813.3	15.6	2.0
813.3	1031.0	1010.0	10.7	1.8
1010.0	1233.0	1209.1	8.4	1.6

Table 17. Langmuir Model Representation of Adsorption on Wet Tiffany Coals at 130 °F

Pure Gas	L (SCF/ton)	Bx1000 (psia ⁻¹)	h	RMSE (SCF/ton)	%AAD
CH ₄ (Well #1)	432.0	1.6107	1.0	4.2	1.9
CH ₄ (Well #10)	417.5	1.5654	1.0	2.6	1.1
CH ₄ (Mixed Coal)	434.9	1.5074	1.0	7.2	2.6
N ₂ (Mixed Coal)	266.9	0.6303	1.0	3.9	3.5
CO ₂ (Mixed Coal)	590.9	4.5121	1.0	16.6	2.0

Table 18. LRC Model Representation of Adsorption on Wet Tiffany Coals at 130 °F

Pure Gas	L (SCF/ton)	Bx1000 (psia ⁻¹)	h	RMSE (SCF/ton)	%AAD
CH ₄ (Well #1)	509.0	1.1089	0.89	2.9	0.8
CH ₄ (Well #10)	440.7	1.3946	0.96	2.8	0.9
CH ₄ (Mixed Coal)	491.8	1.1113	0.91	7.4	2.3
N ₂ (Mixed Coal)	416.3	0.2708	0.87	2.2	2.1
CO ₂ (Mixed Coal)	631.2	3.9299	0.91	12.4	1.8

Table 19. LRC Model Representation of Adsorption on Wet, Mixed Tiffany Coals at 130 °F (common h)

Pure Gas	L (SCF/ton)	Bx1000 (psia ⁻¹)	h	RMSE (SCF/ton)	%AAD
CH ₄	504.4	1.0854	0.90	7.6	2.3
N ₂	364.6	0.3512	0.90	2.4	2.3
CO ₂	634.8	3.8024	0.90	12.2	1.8

Table 20. ZGR Equation-of-State Representation of Adsorption on Wet, Mixed Tiffany Coals at 130 °F

Pure Gas	a	b	- ln k	RMSE (SCF/ton)	%AAD
CH ₄	144770	1.0140	2.84	8.1	3.0
N ₂	193160	1.3926	4.29	1.7	2.3
CO ₂	74425	0.6069	1.26	15.4	2.1

Table 21. LRC Model Representation of Binary Adsorption on Wet Tiffany Coals at 130 °F

Mixture	L (SCF/ton)	Bx1000 (psia ⁻¹)	h	RMSE (SCF/ton)	%AAD
CH₄ - N₂:					
CH ₄	435.8	1.522	0.96	16.6	9.7
N ₂	366.6	0.337	0.89	5.8	9.0
Total				20.9	8.2
CH₄ - CO₂:					
CH ₄	435.8	1.522	0.96	12.0	7.3
CO ₂	702.6	2.868	0.80	17.0	4.2
Total				5.5	1.2
N₂ - CO₂:					
N ₂	366.6	0.337	0.89	11.3	31.6
CO ₂	702.6	2.868	0.80	36.2	6.7
Total				26.2	4.7
Pure:					
CH ₄	435.8	1.522	0.96	8.3	3.3
N ₂	366.6	0.337	0.89	2.9	2.7
CO ₂	702.6	2.868	0.80	12.6	2.1

Table 22. LRC Model Predictions of Binary Adsorption on Wet Tiffany Coals at 130 °F

Mixture	h= 1 (Langmuir)		Regressed h		h= 0.90	
	RMSE (SCF/ton)	%AAD	RMSE (SCF/ton)	%AAD	RMSE (SCF/ton)	%AAD
CH₄ - N₂:						
CH ₄	29.5	15.8	15.5	9.0	23.2	12.0
N ₂	3.8	6.2	4.0	8.3	3.8	9.3
Total	30.2	12.2	16.2	6.4	21.7	8.2
CH₄- CO₂:						
CH ₄	36.5	25.9	31.3	21.1	31.4	21.0
CO ₂	39.1	9.0	42.5	10.1	44.1	10.5
Total	4.9	1.2	11.2	1.9	12.8	2.2
N₂ - CO₂:						
N ₂	15.2	44.9	14.1	38.9	13.7	37.3
CO ₂	27.7	5.2	35.6	5.9	33.1	5.7
Total	15.9	3.5	22.7	3.8	21.1	3.8

Table 23. LRC Model Representation of Ternary Adsorption on Wet Tiffany Coals at 130 °F

Individual Adsorption	L (SCF/ton)	Bx1000 (psia ⁻¹)	h	RMSE (SCF/ton)	%AAD
CH ₄	478.2	1.8205	0.97	4.2	9.0
N ₂	212.8	2.0495	1.30	8.1	11.7
CO ₂	631.2	4.4225	1.05	12.8	3.3
Total				1.7	0.5

Table 24. LRC Model Predictions of Ternary Adsorption on Wet Tiffany Coals at 130 °F

Individual Adsorption	L (SCF/ton)	BX1000 (psia ⁻¹)	h	RMSE (SCF/ton)	% AAD
Parameters based on pure data					
h= 1 (Langmuir)					
CH ₄	434.9	1.507	1.0	5.9	20.7
N ₂	266.9	0.630	1.0	29.8	47.8
CO ₂	590.9	4.512	1.0	49.6	13.2
Total				14.9	2.9
h Regressed					
CH ₄	491.8	1.111	0.91	2.1	5.3
N ₂	416.3	0.271	0.87	29.6	46.1
CO ₂	631.2	3.930	0.91	61.4	17.7
Total				30.5	6.7
h= 0.90					
CH ₄	504.4	1.085	0.90	2.2	5.2
N ₂	364.6	0.351	0.90	28.2	44.5
CO ₂	634.8	3.802	0.90	54.7	15.8
Total				24.9	5.4
Parameters based on pure and binary data					
CH ₄	435.8	1.522	0.96	4.6	16.6
N ₂	366.6	0.337	0.89	25.1	45.8
CO ₂	702.6	2.868	0.80	43.9	12.0
Total				26.1	6.0

Table 25. ZGR EOS Representation of Mixtures on Tiffany Mixed Coal at 130 °F

Mixture			%AAD			RMSE (SCF/ton coal)		
C _{ij} = D _{ij} =0								
	C _{ij}	D _{ij}	ω ₁	ω ₂	Total	ω ₁	ω ₂	Total
CH ₄ / N ₂	0.000	0.000	11.9	10.0	11.5	20.5	6.7	26.3
CH ₄ / CO ₂	0.000	0.000	27.0	10.4	1.4	30.2	35.0	5.4
N ₂ / CO ₂	0.000	0.000	48.7	4.9	3.5	13.1	25.4	15.6
Regressed C _{ij} (D _{ij} =0)								
	C _{ij}	D _{ij}	ω ₁	ω ₂	Total	ω ₁	ω ₂	Total
CH ₄ / N ₂	-0.090	0.000	10.6	7.3	7.6	18.8	3.9	17.5
CH ₄ / CO ₂	-0.125	0.000	8.4	10.6	6.1	11.2	32.9	25.4
N ₂ / CO ₂	-0.140	0.000	16.0	4.1	3.2	3.9	20.9	17.7
Regressed D _{ij} (C _{ij} =0)								
	C _{ij}	D _{ij}	ω ₁	ω ₂	Total	ω ₁	ω ₂	Total
CH ₄ / N ₂	0.000	-0.068	10.6	7.1	7.5	18.4	3.8	16.9
CH ₄ / CO ₂	0.000	-0.090	7.7	11.0	6.6	9.6	34.7	28.6
N ₂ / CO ₂	0.000	-0.108	14.5	4.3	3.5	3.3	21.8	19.0
Regressed C _{ij} and D _{ij}								
	C _{ij}	D _{ij}	ω ₁	ω ₂	Total	ω ₁	ω ₂	Total
CH ₄ / N ₂	-0.060	-0.023	10.6	7.2	7.5	18.7	3.8	17.3
CH ₄ / CO ₂	-0.098	-0.019	8.2	10.7	6.2	10.9	33.2	26.1
N ₂ / CO ₂	-0.011	-0.100	14.6	4.3	3.4	3.4	21.7	18.9
Predicted Ternary								
Mixture	%AAD				RMSE (SCF/ton coal)			
From pure data C _{ij} = D _{ij} =0								
	ω ₁	ω ₂	ω ₃	Total	ω ₁	ω ₂	ω ₃	Total
CH ₄ / N ₂ / CO ₂	21.6	55.9	17.6	4.3	4.9	29.2	51.5	18.1
C _{ij} from Binary (D _{ij} =0)								
	ω ₁	ω ₂	ω ₃	Total	ω ₁	ω ₂	ω ₃	Total
CH ₄ / N ₂ / CO ₂	18.0	32.8	17.4	9.3	4.6	17.1	48.1	35.2
D _{ij} from Binary (C _{ij} =0)								
	ω ₁	ω ₂	ω ₃	Total	ω ₁	ω ₂	ω ₃	Total
CH ₄ / N ₂ / CO ₂	18.3	31.6	17.7	9.7	4.8	16.1	49.6	37.9
C _{ij} and D _{ij} from Binary								
	ω ₁	ω ₂	ω ₃	Total	ω ₁	ω ₂	ω ₃	Total
CH ₄ / N ₂ / CO ₂	18.6	31.9	17.6	9.6	4.8	16.4	49.1	37.1

Table 26. Sorption Fractional Uptake Correlation

Pure Gas	$a = (aP^2 + bP + 0.5)c$	b	%AAD
CH ₄ (Well #1)	$(-5.530 \times 10^{-8} \times P^2 + 2.960 \times 10^{-4} \times P + 0.5)(1.030)$	0.4570	4.1
CH ₄ (Well #10)	$(1.251 \times 10^{-8} \times P^2 + 7.397 \times 10^{-4} \times P + 0.5)(1.327)$	0.3912	6.4
N ₂ (Mixed Coal)	$(0.5) \times 1.700$	0.2833	7.2
CO ₂ (Mixed Coal)	$1.264 \times 10^{-7} \times P^2 + 9.497 \times 10^{-5} \times P + 0.5)(1.066)$	0.6404	2.2

Table 27. Sorption-Time Estimates on Wet Tiffany Coal Samples at 130 °F for 63% Desorption

Starting Desorption Pressure (psia)	Methane on Well #1 (min)	Methane on Well #10 (min)	Nitrogen on Mixed Coal (min)	CO ₂ on Mixed Coal (min)
2000	9.3	8.4	8.2	4.7
1800	9.4	8.4	8.2	4.7
1600	9.5	8.5	8.2	4.7
1400	9.6	8.5	8.2	4.7
1200	9.8	8.5	8.2	4.7
1000	9.9	8.6	8.2	4.7
800	10.2	8.6	8.2	4.7
600	10.5	8.7	8.2	4.7
400	10.9	8.8	8.2	4.8
200	11.6	9.0	8.2	4.8

Figure 1. Schematic Diagram of Adsorption Apparatus

Figure 2. Tiffany Well #1 Coal Particle Size Distribution

Figure 3. Tiffany Well #10 Coal Particle Size Distribution

Figure 4. Tiffany Well #1 and Well #10 Coal Particle Size Distributions

**Figure 5. Pure Methane Absolute Adsorption on Tiffany Coal Samples
at 130 °F**

Figure 6. Pure Gas Gibbs Adsorption on Tiffany Coals at 130 °F

Figure 7. Pure Gas Absolute Adsorption on Tiffany Coals at 130 °F

**Figure 8. Pure Nitrogen Absolute Adsorption on Tiffany Mixed Coal
Sample at 130 °F**

Figure 9. Pure CO₂ Absolute Adsorption on Tiffany Mixed Coal
Sample at 130 °F

**Figure 10. CO₂ Absolute Adsorption on Tiffany Mixed Coal Sample
Using Different Adsorbed-Phase Densities**

**Figure 11. Gibbs Adsorption of a 50/50 Mole % Methane/Nitrogen Feed Mixture
on a Wet Tiffany Mixed Coal Sample at 130 °F**

Figure 12. Absolute Adsorption for 50/50 Mole % Methane/Nitrogen Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

Figure 13. Gibbs Adsorption of a 40/60 Mole % Methane/CO₂ Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

Figure 14. Absolute Adsorption for 40/60 Mole % Methane/CO₂ Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

Figure 15. Gibbs Adsorption of a 20/80 Mole % Nitrogen/CO₂ Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

Figure 16. Absolute Adsorption for 20/80 Mole % Nitrogen/CO₂ Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

Figure 17. Gibbs Adsorption of a 10/40/50 Mole % Methane/Nitrogen/CO₂ Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

Figure 18. Absolute Adsorption for 10/40/50 Mole % Methane/Nitrogen/CO₂ Feed on Wet Tiffany Mixed Coal Sample at 130 °F

**Figure 19. Fractional Uptake of Methane Desorption on Tiffany Well #1
Coal at 130 °F**

**Figure 20. Fractional Uptake of Methane Desorption on Tiffany
Well #10 Coal at 130 °F**

**Figure 21. Fractional Uptake of Nitrogen on Tiffany Mixed Coal
at 130 °F**

**Figure 22. Fractional Uptake of CO₂ Adsorption on Tiffany Mixed Coal
at 130°F**

Figure 23. Model Predictions of Absolute Adsorption for 50/50 Mole % Methane/Nitrogen Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

Figure 24. Model Predictions of Absolute Adsorption for 40/60 Mole % Methane/CO₂ Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

Figure 25. Model Predictions of Absolute Adsorption for 20/80 Mole % Nitrogen/CO₂ Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

Figure 26 Model Predictions of Absolute Adsorption for 10/40/50 Mole % Methane/Nitrogen/CO₂ Feed on a Wet Tiffany Mixed Coal Sample at 130 °F

**Figure 27. Desorption Curve for Methane on Tiffany Well #1 Coal
at 130 °F**

**Figure 28. Desorption Curve for Methane on Tiffany Well #10 Coal
at 130 °F**

**Figure 29. Desorption Curve for Nitrogen on Tiffany Mixed Coal
at 130 °F**

**Figure 30. Adsorption Curve for CO₂ on Tiffany Mixed Coal
at 130 °F**

**Figure 31. Liberated Gas from Tiffany Coal Samples:
2000 to 14.7 psia**

CO₂ Adsorption on Selected Coals

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1. Introduction

The Department of Energy - National Energy Technology Laboratory (NETL) in Pittsburgh has organized a "round robin" for CO₂/coal adsorption isotherm measurements. The goal is to (a) assess the reproducibility of CO₂/coal adsorption isotherm measurements, and (b) develop a standard method for measuring coal adsorption isotherms.

The purpose of this report is to present the adsorption measurements conducted at Oklahoma State University. CO₂ adsorption isotherms at 131 °F (328.2 K) and pressures to 2000 psia (13.8 MPa) were measured on five coal samples from the Argonne National Laboratory. The coals considered in this study were:

1. Beulah-Zap
2. Wyodak
3. Illinois #6
4. Upper Freeport
5. Pocahontas #3

The measurements were performed on dry coal samples, as prescribed by the NETL drying protocol.

2. Experimental Methods and Procedures

2.1 Adsorption Measurements

The experimental method is based on a mass balance principle, which employs precise measurements of pressures, volumes and temperatures. A brief description of the apparatus and procedures follows.

The experimental apparatus, shown schematically in Figure 1, has been used successfully in previous studies¹. The pump and cell sections of the apparatus are maintained in a constant temperature air bath at 113 °F (318.2 K). The equilibrium cell has a volume of

110 cm³ and is partially filled with the adsorbent to be studied. The cell is placed under vacuum prior to gas injection. The void volume V_{void} in the equilibrium cell is then determined by injecting known quantities of helium from a calibrated injection pump (Ruska Pump). Since helium is not significantly adsorbed, the void volume can be determined from measured values of temperature, pressure and amount of helium injected into the cell. Several injections made into the cell at different pressures show consistency in the calculated void volume. Generally, the void volume calculated from sequential injections varies less than 0.3 cm³ from the average value (of approximately 77-98 cm³) based on at least five injections. The mass-balance equation, expressed in volumetric terms, is

$$V_{void} = \frac{\left(\frac{P\Delta V}{ZT} \right)_{pump}}{\left(\frac{P_2}{Z_2 T} - \frac{P_1}{Z_1 T} \right)_{cell}}, \quad (1)$$

where ΔV is the volume injected from the pump, Z is the compressibility factor of helium, T is the temperature, P is the pressure, subscripts “cell” and “pump” refer to conditions in the cell and pump sections of the apparatus, respectively, and “1” and “2” refer to conditions in the cell before and after injection of gas from the pump, respectively. During each injection step, the pressure in the pump at the end of the injection is adjusted to the initial value, about 6.8 MPa (although the pressure in the pumps during the injection may vary). The void volume from these measurements is then used in subsequent measurements of adsorption, as follows.

The Gibbs adsorption (also known as the excess adsorption) can be calculated directly from experimental quantities. For pure-gas adsorption measurements, a known quantity, n_{inj} , of gas (e.g., CO₂) is injected from the pump section into the cell section. Some of the injected gas will be adsorbed, and the remainder, n_{unads}^{Gibbs} , will exist in the equilibrium bulk (gas) phase in the cell. A molar balance is used to calculate the amount adsorbed, n_{ads}^{Gibbs} , as

$$n_{ads}^{Gibbs} = n_{inj} - n_{unads}^{Gibbs} \quad (2)$$

The amount injected can be determined from pressure, temperature and volume measurements of the pump section:

$$n_{inj} = \left(\frac{P\Delta V}{ZRT} \right)_{pump} \quad (3)$$

The amount of unadsorbed gas is calculated from conditions at equilibrium in the cell:

$$n_{unads}^{Gibbs} = \left(\frac{PV_{Void}}{ZRT} \right)_{cell} \quad (4)$$

where the pressure P is measured after equilibrium is reached in the cell. A circulating pump is used to circulate CO_2 over the adsorbent (coal) until equilibrium is reached (usually within 6 to 12 hours, depending on the adsorption capacity of the coal), where no further CO_2 is adsorbed.

In Eqs. 3 and 4, Z is the compressibility of the CO_2 at the applicable conditions of temperature and pressure.

The above steps are repeated at sequentially higher pressures to yield a complete adsorption isotherm. The amount adsorbed is usually presented as an intensive quantity (mmol adsorbed / g adsorbent or mmol/g) by dividing n_{ads}^{Gibbs} by the mass of adsorbent in the cell. Inspection of Eqs. 2-4 reveals that the amount adsorbed may be calculated in a straightforward manner from experimental measurements of pressures, temperatures and volumes, coupled with independent knowledge of the gas compressibility factors, Z (from experimental data or a suitably accurate equation of state).

The desorption was performed similarly to the adsorption procedure described above. In the desorption, the adsorbed gas was released from the cell section to the pump section.

2.2 Gas Compressibility Factors

As indicated by Eqs. 3 and 4, accurate gas-phase compressibility (Z) factors are required for carbon dioxide to properly analyze the experimental data. The compressibility factor for CO_2 was determined from highly accurate equations of state ². For void volume determination, the helium compressibility factor is given by ³

$$Z_{He} = 1 + (0.001471 - 0.000004779T + 0.00000000492T^2)P \quad (5)$$

where T is in Kelvins and P is in atmospheres. This expression is based on the experimental data from National Bureau of Standards Technical Note 631 for helium ⁴.

2.3 Materials

The pure CO_2 used in this work was obtained from Airgas-Pennsylvania with reported purity of about 99.99% and was used as received. Five types of coal samples prepared by Argonne National Laboratory were used as the adsorbent; the proximate analyses of the five coals we have studied are presented in Table 1. The coals were dried under vacuum in the equilibrium cell at 80°C for 36 hours before being used in the adsorption measurements.

2.4 Calibrations

Calibrations were performed routinely during the course of the experiments. The temperature measuring devices were calibrated against a Minco platinum resistance reference thermometer, and the pressure transducers were calibrated against a Ruska deadweight tester with a calibration traceable to the National Institute of Science and Technology.

The uncertainties in the experimentally measured quantities after calibrations were estimated as follows: temperatures, 0.1 K; pressures, 6.9 kPa; injected gas volumes, 0.02 cm³; void volume, 0.2 cm³.

A detailed error propagation analysis was performed, which indicates that the average uncertainty for the CO₂ adsorption measurements is approximately 4.5% (0.04-0.1 mmol/g). The highest percentage uncertainty is usually obtained at the higher pressures, which is due mainly to the lower value of the Gibbs adsorption for CO₂ at the higher pressures and the higher uncertainty in the CO₂ compressibility factor (due to its proximity to its critical point).

3. Experimental Results

The experimental data for CO₂ adsorption and desorption on all five Argonne coals at 131 °F are presented in Tables 2-6. The data are presented on a dry basis. The expected experimental uncertainties, σ , for the adsorption measurements are also included in those tables. *Appendix A contains our adsorption data on a dry, ash-free basis.*

Figure 2 presents the Gibbs adsorption and desorption behaviors of CO₂ on the five coals. Figure 2A in Appendix A presents the CO₂ Gibbs adsorptions on dry, ash-free basis. All the coals studied exhibit maxima in the Gibbs adsorption. Further, at 1000 psia, the adsorptions of CO₂ on the five coals are in the order of (from the highest to the lowest): Wyodak, Beulah-Zap, Illinois #6, Pocahontas #3, and Upper Freeport.

Figure 2 also shows that the adsorption and desorption data are almost identical within expected uncertainties for three Argonne coals: Pocahontas #3, Illinois #6 and Upper Freeport. The Wyodak and Beulah-Zap coal, however, shows some hysteresis. The observed behavior may be related to the specific structure of these coals. Tentatively, it may be attributed to irreversible matrix swelling or “ink-bottle” pores that can trap adsorbate⁵. However, further investigation is required to explain the specific behavior of this coal.

The lower adsorption on higher rank coal, which is related to the water equilibrium content in our preliminary report, apparently does not apply for all the five coals studied. Figure 3A shows the variation in the CO₂ Gibbs adsorption capacity at 1000 psia with the water equilibrium content on an ash-free basis. As indicated in this figure, the adsorption capacity exhibits a maximum at a water equilibrium content of about 25%.

Figure 4A presents the variation in the CO₂ Gibbs adsorption capacity at 1000 psia with fixed carbon content (dry, ash-free basis). The results indicate that the adsorption capacity first decreases with increasing rank, then it increases slightly. This trend produces a minimum adsorption capacity for a coal with a 70% fixed carbon content. Similar results are obtained when the adsorption capacity at 1000 psia is plotted against the ratio of fixed carbon content to volatile matter content (see Figure 5A). The minimum adsorption capacity is observed at a ratio of about 3. This type of behavior has been observed elsewhere^{6,7,8}.

4. Conclusions

The adsorption and desorption of CO₂ were measured on five different rank coals at 131 °F (318.2 K) and pressures to 2000 psia (13.8 MPa) using a volumetric method. The average expected uncertainty in these data is about 4.5% (0.04-0.1 mmol/g). The results indicate that while the adsorption and desorption data are almost identical (within expected uncertainties) for the Pocahontas #3, Illinois #6 and Upper Freeport coals, the data for the Wyodak and Beulah-Zap coals show some hysteresis. Further investigation is needed to explain the specific behavior of these coals.

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Table 1. Analysis of Coals Used in This Study

Analysis*	Beulah Zap	Wyodak	Illinois-6	Upper Freeport	Pocahontas
<i>Ultimate</i>					
Carbon %	72.9	75.0	77.7	85.5	91.1
Hydrogen %	4.83	5.35	5.00	4.70	4.44
Oxygen %	20.3	18.0	13.5	7.5	2.5
Sulfur %	0.80	0.63	4.83	2.32	0.66
Ash %	9.7	8.8	15.5	13.2	4.8
<i>Proximate</i>					
Moisture %	32.2	28.1	8.0	1.1	0.7
Vol. Matter %	30.5	32.2	36.9	27.1	18.5
Fixed Carbon %	30.7	33.0	40.9	58.7	76.1
Ash %	6.6	6.3	14.3	13.0	4.7
Fixed Carbon %; dry, ash-free basis	50.2	50.3	52.6	68.3	80.4

* Analyses were provided by the Argonne National Laboratory

Table 2. CO₂ Adsorption and Desorption on Beulah-Zap Coal at 131 °F

Coal wet = 64.7 g Coal (after drying) = 43.6 g Void volume = 98.1 cm ³ P _{pump} = 998.9 psia T _{pump} = 131 °F						
Adsorption				Desorption		
ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Adsorption (mmol/g)	Experimental Uncertainty, σ (mmol/g)	ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Desorption (mmol/g)
16.13	89	0.819	0.047		2003	1.248
12.19	206	1.108	0.047	40.6	1819	1.314
19.58	404	1.397	0.046	67.35	1620	1.470
21.15	605	1.591	0.045	74.25	1417	1.676
23.27	804	1.706	0.044	51.70	1212	1.812
28.70	1010	1.760	0.045	36.10	1007	1.863
34.52	1204	1.752	0.048	27.90	802	1.863
46.16	1392	1.661	0.055	53.62*	611	1.817
72.50	1596	1.470	0.087	51.19*	406	1.697
63.69	1772	1.344	0.093	141.25**	194	1.420
53.98	2003	1.248	0.105			

* P_{pump} = 498.3 psia

** P_{pump} = 197.7 psia

Table 3. CO₂ Adsorption and Desorption on Illinois #6 Coal at 131 °F

Coal wet = 54.5 g Coal (after drying) = 49.9 g Void volume = 94.3 cm ³ P _{pump} = 998.9 psia T _{pump} = 131 °F						
Adsorption				Desorption		
ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Adsorption (mmol/g)	Experimental Uncertainty, σ (mmol/g)	ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Desorption (mmol/g)
14.34	100	0.549	0.041		2000	0.856
11.55	211	0.808	0.040	38.43	1819	0.919
18.40	399	1.075	0.039	62.44	1625	1.087
21.09	604	1.272	0.038	72.27	1415	1.364
23.28	807	1.402	0.038	54.20	1185	1.499
27.61	1009	1.480	0.039	32.30	994	1.478
33.92	1206	1.485	0.041	62.05*	808	1.413
44.55	1395	1.378	0.047	58.70*	603	1.280
67.68	1597	1.128	0.074	135.30**	410	1.109
58.74	1768	0.953	0.099	137.20**	204	0.827
52.46	2000	0.856	0.099			

* P_{pump} = 498.3 psia

** P_{pump} = 197.7 psia

Table 4. CO₂ Adsorption and Desorption on Pocahontas #3 Coal at 131 °F

Coal wet = 56.3 g Coal (after drying) = 55.9 g Void volume = 87.8 cm ³ P _{pump} = 998.9 psia T _{pump} = 131 °F						
Adsorption				Desorption		
ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Adsorption (mmol/g)	Experimental Uncertainty, σ (mmol/g)	ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Desorption (mmol/g)
20.98	155	0.715	0.037		2008	0.707
7.63	240	0.832	0.036	31.85	1842	0.735
15.14	414	0.980	0.035	63.05	1628	0.853
18.38	616	1.069	0.035	62.29	1442	0.970
19.52	806	1.113	0.035	53.78	1212	1.057
25.28	1011	1.127	0.035	32.43	1007	1.089
31.17	1208	1.094	0.037	25.00	802	1.082
50.23	1427	1.007	0.044	50.11*	603	1.042
59.86	1610	0.869	0.067	43.37*	405	0.985
58.29	1796	0.769	0.085	119.59**	201	0.818
42.70	2008	0.707	0.088			

* P_{pump} = 498.3 psia

** P_{pump} = 197.7 psia

Table 5. CO₂ Adsorption and Desorption on Wyodak Coal at 131 °F

Coal wet = 62.8 g Coal (after drying) = 45.5 g Void volume = 96.4 cm ³ P _{pump} = 1005.5 psia T _{pump} = 131 °F						
Adsorption				Desorption		
ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Adsorption (mmol/g)	Experimental Uncertainty, σ (mmol/g)	ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Desorption (mmol/g)
16.73	100	0.791	0.046		2005	1.324
11.54	210	1.078	0.045	42.58	1808	1.410
19.19	404	1.388	0.044	58.9	1629	1.582
21.05	606	1.602	0.043	76.08	1415	1.775
24.02	812	1.749	0.043	52.26	1199	1.910
27.58	1012	1.820	0.043	34.12	998	1.948
34.62	1210	1.827	0.046	22.53	830	1.930
45.75	1399	1.735	0.052	63.24*	604	1.852
67.81	1594	1.586	0.082	48.96*	407	1.700
67.21	1788	1.430	0.098	140.6**	191	1.386
47.95	2005	1.324	0.135			

* P_{pump} = 504.7 psia

** P_{pump} = 203.9 psia

Table 6. CO₂ Adsorption and Desorption on Upper Freeport Coal at 131 °F

Coal wet = 73.5 g Coal (after drying) = 72.5 g Void volume = 77.5 cm ³ P _{pump} = 1007.0 psia T _{pump} = 131 °F						
Adsorption				Desorption		
ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Adsorption (mmol/g)	Experimental Uncertainty, σ (mmol/g)	ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Desorption (mmol/g)
15.25	103	0.485	0.030		2004	0.608
10.1	221	0.646	0.029	30.05	1827	0.640
15.4	417	0.789	0.029	52.47	1625	0.731
16.25	617	0.866	0.028	60.3	1412	0.843
17.75	813	0.906	0.028	46.35	1165	0.918
21.33	1010	0.919	0.028	22.8	992	0.933
27.47	1209	0.904	0.029	20.35	799	0.925
37.45	1402	0.851	0.033	42.53*	605	0.892
52.49	1592	0.751	0.049	38.85*	407	0.828
58.06	1805	0.655	0.057	121.06**	173	0.658
34.57	2004	0.608	0.077			

* P_{pump} = 506.2 psia

** P_{pump} = 205.4 psia

Figure 1. Schematic Diagram of the Experimental Apparatus

Figure 2. Gibbs Adsorption (closed symbols) and Desorption (open symbol) of CO₂ on Dry Coals at 131 °F

APPENDIX A

CO₂ Adsorption on Dry, Ash-Free Basis

Table 1A. CO₂ Adsorption and Desorption on Dry, Ash-Free Beulah-Zap Coal at 131 °F

Coal wet = 64.7 g ; Ash content = 6.59 % Coal (after drying) = 43.6 g Void volume = 98.1 cm ³ P _{pump} = 998.9 psia T _{pump} = 131 °F						
Adsorption (DAF)				Desorption (DAF)		
ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Adsorption (mmol/g)	Experimental Uncertainty, σ (mmol/g)	ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Desorption (mmol/g)
16.13	89	0.907	0.047		2003	1.383
12.19	206	1.227	0.047	40.6	1819	1.456
19.58	404	1.548	0.046	67.35	1620	1.629
21.15	605	1.763	0.045	74.25	1417	1.857
23.27	804	1.890	0.044	51.70	1212	2.007
28.70	1010	1.950	0.045	36.10	1007	2.064
34.52	1204	1.941	0.048	27.90	802	2.064
46.16	1392	1.840	0.055	53.62*	611	2.013
72.50	1596	1.629	0.087	51.19*	406	1.880
63.69	1772	1.489	0.093	141.25**	194	1.573
53.98	2003	1.383	0.105			

* P_{pump} = 498.3 psia

** P_{pump} = 197.7 psia

Table 2A. CO₂ Adsorption and Desorption on Dry, Ash-Free Illinois #6 Coal at 131 °F

Coal wet = 54.5 g ; Ash content = 14.25 % Coal (after drying) = 49.9 g Void volume = 94.3 cm ³ P _{pump} = 998.9 psia T _{pump} = 131 °F						
Adsorption (DAF)				Desorption (DAF)		
ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Adsorption (mmol/g)	Experimental Uncertainty, σ (mmol/g)	ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Desorption (mmol/g)
14.34	100	0.650	0.041		2000	1.014
11.55	211	0.957	0.040	38.43	1819	1.088
18.40	399	1.273	0.039	62.44	1625	1.287
21.09	604	1.506	0.038	72.27	1415	1.615
23.28	807	1.660	0.038	54.20	1185	1.775
27.61	1009	1.752	0.039	32.30	994	1.750
33.92	1206	1.758	0.041	62.05*	808	1.673
44.55	1395	1.632	0.047	58.70*	603	1.516
67.68	1597	1.336	0.074	135.30**	410	1.313
58.74	1768	1.128	0.099	137.20**	204	0.979
52.46	2000	1.014	0.099			

* P_{pump} = 498.3 psia

** P_{pump} = 197.7 psia

Table 3A. CO₂ Adsorption and Desorption on Dry, Ash-Free Pocahontas #3 Coal
at 131 °F

Coal wet = 56.3 g; Ash content = 4.74 % Coal (after drying) = 55.9 g Void volume = 87.8 cm ³ P _{pump} = 998.9 psia T _{pump} = 131 °F						
Adsorption (DAF)				Desorption (DAF)		
ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Adsorption (mmol/g)	Experimental Uncertainty, σ (mmol/g)	ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Desorption (mmol/g)
20.98	155	0.751	0.037		2008	0.742
7.63	240	0.873	0.036	31.85	1842	0.772
15.14	414	1.029	0.035	63.05	1628	0.895
18.38	616	1.122	0.035	62.29	1442	1.018
19.52	806	1.168	0.035	53.78	1212	1.110
25.28	1011	1.183	0.035	32.43	1007	1.143
31.17	1208	1.148	0.037	25.00	802	1.136
50.23	1427	1.057	0.044	50.11*	603	1.094
59.86	1610	0.912	0.067	43.37*	405	1.034
58.29	1796	0.807	0.085	119.59**	201	0.859
42.70	2008	0.742	0.088			

* P_{pump} = 498.3 psia

** P_{pump} = 197.7 psia

Table 4A. CO₂ Adsorption and Desorption on Dry, Ash-Free Wyodak Coal
at 131 °F

Coal wet = 62.8 g; Ash content = 6.31 % Coal (after drying) = 45.4 g Void volume = 96.4 cm ³ P _{pump} = 1005.5 psia T _{pump} = 131 °F						
Adsorption (DAF)				Desorption (DAF)		
ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Adsorption (mmol/g)	Experimental Uncertainty, σ (mmol/g)	ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Desorption (mmol/g)
16.73	100	0.845	0.046		2005	1.413
11.54	210	1.151	0.045	42.58	1808	1.505
19.19	404	1.482	0.044	58.9	1629	1.689
21.05	606	1.710	0.043	76.08	1415	1.895
24.02	812	1.867	0.043	52.26	1199	2.038
27.58	1012	1.943	0.043	34.12	998	2.079
34.62	1210	1.950	0.046	22.53	830	2.060
45.75	1399	1.851	0.052	63.24*	604	1.977
67.81	1594	1.693	0.082	48.96*	407	1.815
67.21	1788	1.527	0.098	140.6**	191	1.479
47.95	2005	1.413	0.135			

* P_{pump} = 504.7 psia

** P_{pump} = 203.9 psia

Table 5A. CO₂ Adsorption and Desorption on Dry, Ash-Free Upper Freeport Coal
at 131 °F

Coal wet = 73.5 g; Ash content = 13.03 % Coal (after drying) = 72.5 g Void volume = 77.5 cm ³ P _{pump} = 1007.0 psia T _{pump} = 131 °F						
Adsorption (DAF)				Desorption (DAF)		
ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Adsorption (mmol/g)	Experimental Uncertainty, σ (mmol/g)	ΔV_{pump} (cm ³)	Pressure (Psia)	Gibbs Desorption (mmol/g)
15.25	103	0.557	0.030		2004	0.699
10.1	221	0.742	0.029	30.05	1827	0.736
15.4	417	0.907	0.029	52.47	1625	0.840
16.25	617	0.996	0.028	60.3	1412	0.969
17.75	813	1.042	0.028	46.35	1165	1.055
21.33	1010	1.057	0.028	22.8	992	1.072
27.47	1209	1.039	0.029	20.35	799	1.064
37.45	1402	0.979	0.033	42.53*	605	1.026
52.49	1592	0.863	0.049	38.85*	407	0.952
58.06	1805	0.753	0.057	121.06**	173	0.757
34.57	2004	0.699	0.077			

* P_{pump} = 506.2 psia

** P_{pump} = 205.4 psia

Figure 2A. Gibbs Adsorption (closed symbols) and Desorption (open symbol) of CO₂ on Dry, Ash-Free Coals at 131 °F

Figure 3A. Variation of the CO₂ Gibbs adsorption capacity of the Argonne coals with moisture content at 1000 psia and 131 °F (DAF basis)

Figure 4A. Variation of the CO₂ Gibbs adsorption capacity of the Argonne coals with fixed carbon content at 1000 psia and 131 °F (DAF basis)

Figure 5A. Variation of the CO₂ Gibbs adsorption capacity of the Argonne coals with (fixed carbon / volatile matter) ratio at 1000 psia and 131 °F (DAF basis)

Two-Dimensional Equation-of-State Modeling for Mixture Adsorption

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Abstract

Adsorption equilibrium models are essential in optimizing coalbed methane production and CO₂ sequestration processes. Although a number of frameworks are available for describing the adsorption phenomenon, two-dimensional (2-D) equations of state (EOS), in particular, offer distinct advantages in modeling supercritical, high-pressure adsorption systems.

Our previous studies involving several high-pressure adsorption mixtures have indicated the inadequacy of one-fluid mixing rules in representing the component adsorption isotherms. In this study, we have (a) applied the Wong-Sandler excess Gibbs free energy mixing rules to the 2-D EOS, and (b) augmented the 2-D one-fluid mixing rules with new accessible-area combination rules.

The results indicate that use of the excess Gibbs free energy mixing rules or accessible-surface one-fluid mixing rules is effective in representing the binary mixtures considered within their experimental uncertainties.

Keywords: Adsorption, Two-Dimensional Equation of State, Mixing and combination rules, Wong-Sandler

Introduction

The adsorption phenomenon plays a major role in coalbed methane (CBM) production and in CO₂ sequestration; therefore, reliable adsorption equilibrium models are essential in the optimum implementation of these processes.

Although a number of frameworks are used to describe the adsorption phenomenon and correlate pure and mixture adsorption isotherms, two-dimensional (2-D) equations of state (EOS) offer distinct advantages in modeling supercritical, high-pressure adsorption systems. First, 2-D EOS permit

simultaneous calculation of equilibrium adsorption and volumetric properties. Second, they are amenable to model parameter generalization. Third, they are particularly suitable to extend pure adsorption isotherms to multicomponent mixture predictions using appropriate mixing rules [Do, 1998]. Fourth, they offer a proven model format for use in reservoir simulations.

The one-fluid mixing rules have been partially successful in correlating high-pressure mixture adsorption isotherms. Previous studies [Zhou et al., 1994] indicate that although the one-fluid mixing rules are capable of representing the total mixture adsorption isotherms within their experimental uncertainties, they fail to do so for the individual-component isotherms of the mixture. Specifically, the current mixing rules do not describe precisely the component partitioning (or selectivity) in the adsorbed phase of a mixture.

In this study, we investigate two new approaches for improving the 2-D EOS mixing rules, and consequently, the 2-D EOS mixture predictions.

First, we hypothesize that different molecules have different accessible adsorption surface areas. Accordingly, we re-derive the one-fluid mixing rules to account for the component-accessible surface area. Second, we incorporate the excess Gibbs free energy mixing rules in the 2-D EOS. In so doing, we recognize differences in the molecular affinity between the adsorbate and the adsorption surface, which can result in non-random mixing.

Our newly acquired pure and binary gas adsorption measurements involving methane (CH_4), nitrogen (N_2) and carbon dioxide (CO_2) on activated carbon [Sudibandriyo, 2002] are used to evaluate the new approaches and for comparisons with the original one-fluid model.

Two-Dimensional EOS Models

Over the years, various researchers have applied the 2-D EOS to gas adsorption. Hill (1946) and de Boer (1953) have used the van der Waals (VDW) EOS to correlate pure-gas adsorption. Hoory and Prausnitz (1967) extended the 2-D VDW EOS to mixtures by introducing mixing rules. More recently, Degance (1992) used the 2-D virial and Eyring EOS to correlate high-pressure pure adsorption isotherms.

In early 1990's, we have developed a generalized 2-D cubic EOS, which encompasses 2-D analogs of all the previous cubic EOS forms [see, e.g., Zhou et al. 1994]. The generalized 2-D EOS is analogous to the popular three-dimensional equations of state used in vapor-liquid equilibrium calculations:

$$\left[p + \frac{ap^2}{1 + Ub\rho + W(b\rho)^2} \right] [1 - b\rho] = \rho RT \quad (1)$$

Where a and b are the traditional EOS parameters, and numerical values of U and W may be specified to give various forms of three-dimensional equations of state.

The general two-dimensional analog can be written as follows (with an additional parameter m for added model flexibility):

$$\left[A\pi + \frac{\alpha\omega^2}{1 + U\beta\omega + W(\beta\omega)^2} \right] [1 - (\beta\omega)^m] = \omega RT \quad (2)$$

Where A is the specific surface area, π is the spreading pressure, σ is the surface density of the adsorbate, $\omega = \sigma A$ is the specific amount adsorbed, and $\alpha = a/A$ and $\beta = b/A$ are model parameters. The model coefficients, U , W , and

m must be specified to obtain a specific form of the 2-D EOS for application. For example, an analog of the van der Waals (VDW) EOS is obtained by setting $m = 1$ and $U = W = 0$; similarly for the Soave-Redlich-Kwong (SRK) ($m = U = 1$ and $W = 0$); the Peng-Robinson (PR) ($m = 1$, $U = 2$, and $W = -1$); and the Eyring ($m = 1/2$ and $U = W = 0$) EOS.

This general 2-D EOS can be used to investigate EOS behaviors by specifying various combinations of model coefficients. Selection of the model coefficient m is the most important among the EOS model coefficients, because it is in the repulsive term and has a significant effect on the shape of the pure adsorption isotherm. If U and W are equal to zero, then by setting m to values of ∞ , 1 , and $1/2$, we obtain the 2-D ideal gas law, the 2-D VDW EOS, and the Eyring EOS, respectively. Actually, the pure gas isotherms vary considerably in shape and Zhou had found that it is sometimes desirable to select an m value even smaller than $1/2$ to describe pure isotherms. Based on extensive calculations, Zhou found that an equation with $m = 1/3$ and $U = W = 0$ (the ZGR EOS) is promising [Zhou, 1994].

EOS Mixing Rules

Following is a brief description of the mixing rules evaluated in this study.

1. One-Fluid Mixing Rules

When extending 2-D EOS to multicomponent adsorption, one-fluid mixing rules are applied by analogy to 3-D EOS mixture modeling. The mixing rules we have used in our previous studies are as follows [Zhou et al., 1994]:

$$\alpha = \sum_i \sum_j x_i x_j \alpha_{ij} \quad \text{and} \quad \beta = \sum_i \sum_j x_i x_j \beta_{ij} \quad (3)$$

Here, the cross coefficients are defined by the combining rules:

$$\begin{aligned}\alpha_{ij} &= (\alpha_i + \alpha_j)(1 - C_{ij})/2 \\ \beta_{ij} &= \sqrt{\beta_i \beta_j} (1 + D_{ij})\end{aligned}\tag{4}$$

2. Accessible-Area One-fluid Mixing Rules

The one fluid-mixing rules and the associated combining rules for 3-D EOS are:

$$\begin{aligned}a &= \sum_i \sum_j x_i x_j a_{ij} \quad \text{and} \quad b = \sum_i \sum_j x_i x_j b_{ij} \\ a_{ij} &= \sqrt{a_i a_j} (1 - C_{ij}) \\ b_{ij} &= (b_i + b_j)(1 + D_{ij})/2\end{aligned}\tag{5}$$

When transforming these mixing rules into 2-D EOS analog, the EOS constants a and b are replaced by α and β , where by definition $\alpha = a/A$ and $\beta = b/A$.

Here, we assume that different adsorbates may see slightly different surface area on the same adsorbent; i.e., different molecules may have different accessible adsorption area. These considerations lead to the following mixing rules for a binary system, assuming a linear combination rule for both a and b :

$$A\alpha = \sum_i \sum_j x_i x_j a_{ij} = x_1^2 A_1 \alpha_1 + x_1 x_2 (\alpha_1 A_1 + \alpha_2 A_2)(1 - C_{12}) + x_2^2 A_2 \alpha_2\tag{6}$$

where

$$A = \sum_i \sum_j x_i x_j A_{ij} = x_1^2 A_1 + x_1 x_2 (A_1 + A_2)(1 - L_{12}) + x_2^2 A_2\tag{7}$$

In addition, If we let the area ratio $E_{21} = A_2 / A_1$, then:

$$\alpha = (x_1^2 \alpha_1 + x_1 x_2 (\alpha_1 + \alpha_2 E_{21})(1 - C_{ij}) + x_2^2 \alpha_2 E_{21}) / \tilde{A} \quad (8)$$

and similarly,

$$\beta = (x_1^2 \beta_1 + x_1 x_2 (\beta_1 + \beta_2 E_{21})(1 + D_{ij}) + x_2^2 \beta_2 E_{21}) / \tilde{A} \quad (9)$$

where the accessible area is:

$$\tilde{A} = x_1^2 + x_1 x_2 (1 + E_{21})(1 - L_{ij}) + x_2^2 E_{21} \quad (10)$$

The above derivation indicates that the new mixing rules contain a maximum of four adjustable parameters per binary: C_{ij} , D_{ij} , E_{21} , and L_{12} .

3. Excess Gibbs Free Energy Mixing Rules

The presence of an adsorbent promotes adsorption to occur and for the adsorbed-phase to form. Since the adsorptive affinities of molecules are different for different adsorbents leading to preferential molecular arrangement, we hypothesize that non-random mixing occurs during adsorption. To test this hypothesis, we have derived and implemented the 2-D analog to the Wong-Sandler (WS) mixing rules designed for cubic EOS. These mixing rules are implemented within the ZGR EOS.

The 3-D WS mixing rules are as follows [Wong 1992]:

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (11)$$

$$\frac{A_\gamma^{\text{ex}}}{CRT} = -\frac{a}{bRT} + \sum_i x_i \frac{a_i}{b_i RT} \quad (12)$$

where the cross term is given as:

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2} \left[\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right) \right] (1 - C_{ij}) \quad (13)$$

and C is a constant specific to the EOS chosen. Since $b = \beta A$, $a = \alpha A$, then the WS mixing rule incorporated in the 2-D ZGR EOS as:

$$\xi = \beta - \frac{\alpha}{RT} = \left(\sum_i \sum_j x_i x_j \left(\beta - \frac{\alpha}{RT} \right)_{ij} \right) / \tilde{A} \quad (14)$$

$$\left(\beta - \frac{\alpha}{RT} \right)_{ij} = \frac{1}{2} \left[\left(\beta_i - \frac{\alpha_i}{RT} \right) E_i + \left(\beta_j - \frac{\alpha_j}{RT} \right) E_j \right] (1 - C_{ij}) \quad (15)$$

Derivation of the Helmholtz free energy departure function for ZGR is given as:

$$\frac{A_\gamma^{\text{ex}}}{RT} = -\frac{\alpha}{\beta RT} + \sum_i x_i \frac{\alpha_i}{\beta_i RT} + (m-1) \sum_i x_i \ln \frac{\beta \tilde{A}}{\beta_i E_i} \quad (16)$$

We use numerical methods to solve the following equations for β, α :

$$\beta = \xi / \left(1 - \sum_i x_i \frac{\alpha_i}{\beta_i RT} + \frac{A_\gamma^{\text{ex}}}{RT} - (m-1) \sum_i x_i \ln \frac{\beta \tilde{A}}{\beta_i E_i} \right) \quad (17)$$

$$\frac{\alpha}{RT} = \beta - \xi \quad (18)$$

Various expressions for the Helmholtz free energy departure function may be used [see e.g., Tester, 1996]. In this study, we use the non-random two-liquid model (NTRL) of Renon and coworkers:

$$\frac{A_{\gamma}^{\text{ex}}}{RT} \approx \frac{G_{\gamma}^{\text{ex}}}{RT} = x_1 x_2 \left(\frac{\tau_{12} G_{12}}{x_1 + x_2 G_{12}} + \frac{\tau_{21} G_{21}}{x_2 + x_1 G_{21}} \right) \quad (19)$$

Case Studies

We have conducted six case studies to evaluate the various mixing rules:

Case 1: One-fluid mixing rules predictions – no regressed binary interaction parameters ($C_{12}=D_{12}=0$)

Case 2: One-fluid mixing rules - binary interaction parameters, C_{12} and D_{12} , are regressed

Case 3: Accessible area one-fluid mixing rules - binary interaction parameters, C_{12} and D_{12} , and surface area ratio, E_{21} , are regressed ($L_{12}=0$)

Case 4: Accessible area one-fluid mixing rules - binary interaction parameters, C_{12} and D_{12} , surface area ratio, E_{21} , and surface interaction parameter, L_{12} , are regressed

Case 5: Accessible area one-fluid mixing rules - only surface area ratio, E_{21} , is regressed

Case 6: Wong-Sandler mixing rules with NRTL model - interaction parameter, C_{ij} , and NRTL parameters, τ_{12} , τ_{21} and α_{12} , are regressed

Database and Data Reduction

Gas adsorption measurements have been conducted at Oklahoma State University (OSU) on activated carbon. Adsorption isotherms for pure methane, nitrogen, CO_2 and their binary mixtures were measured on dry activated carbon at 318.2 K (113 °F) and pressures to 12.4 MPa (1800 psia). The nominal molar

feed compositions of the mixtures considered are: 20%/80%, 40%/60%, 60%/40% and 80%/20% [Sudibandriyo, 2002].

Our error analysis indicates that the experimental uncertainties for the adsorption measurements vary with composition. Uncertainties for the binary gas *total* adsorption measurements are within 4%. (Detailed description of the newly-acquired experimental data will be forthcoming in a separate publication.)

The objective function RMSE is used to correlate data with the ZGR EOS model. The function minimizes the sum of the squared-percentage deviations in predicted adsorption:

$$\text{RMSE} = \sqrt{\frac{\sum_i^N \left(\frac{n_{\text{exp}} - n_{\text{calc}}}{n_{\text{exp}}} \right)_i^2}{N}} \quad (20)$$

Here, N is the number of data points, n_{calc} and n_{exp} are the calculated and the experimental adsorption for data point “i”. The average absolute deviation (%AAD) and the weighted average-absolute error (WAAE) are also used to quantify our model evaluations:

$$\% \text{AAD} = \frac{100}{N} \sum_{i=1}^N \text{abs} \left(\frac{n_{\text{calc}} - n_{\text{exp}}}{n_{\text{exp}}} \right) \quad (21)$$

$$\text{WAAE} = \frac{1}{N} \sum_{i=1}^N \text{abs} \left(\frac{n_{\text{calc}} - n_{\text{exp}}}{s_{\text{exp}}} \right) \quad (22)$$

Here, σ_{exp} is the expected experimental uncertainty.

Results and Discussion

Table 1 presents the summary results of our model evaluation for binary mixture adsorption. The one-fluid mixing model prediction (Case 1) results in deviation of one to two times the experimental uncertainties for the total adsorption (1-4% AAD) and about two to four times the experimental uncertainties for the component adsorptions (3-11% AAD).

The one-fluid mixing model correlation (Case 2) results in deviation of one to two times the experimental uncertainties for the total adsorption (1-5% AAD) and about two to four times the experimental uncertainties for the component adsorptions (3-11% AAD). These results indicate that while the one-fluid mixing model correlates the total adsorption adequately, it correlates the individual component-adsorption isotherms poorly. Further, regressing binary interaction parameters does not improve the results significantly.

The model representations are improved when accounting for the accessible surface (Case 3). The total adsorptions and the component adsorptions are improved to within 4% AAD and 7% AAD, respectively. Slightly better results are obtained when additional binary surface interaction parameter, L_{ij} , is introduced to the model (Case 4). Moreover, if we only regress the accessible surface area ratio for the binary adsorption systems (Case 5), the total adsorptions and the component adsorptions are to within 3% AAD and 7% AAD, respectively. This result is comparable to Case 3 and 4 and better than Case 2.

These results indicate that accounting for accessible surface area in the mixing rules improves the individual component representation significantly.

As shown by Cases 3, 4 and 5 in Table 1, the values of the regressed area parameter, E_2 , are 1.01, 0.96, and 0.95 for CH_4/N_2 , CH_4/CO_2 , and N_2/CO_2 , respectively. These surface area ratios are internally consistent for these three

gases on the same adsorbent, i.e., a third ratio can be determined knowing the other two ratios.

The WS mixing rules with the NRTL model (Case 6) represent the CH₄/N₂ and CH₄/CO₂ systems with further refinement in the fit. The total adsorptions and the component adsorptions fits are improved to within 2% AAD and 4% AAD, respectively. The WAAE for total adsorptions and the component adsorptions are less than 1.7 for the systems considered. However, for N₂/CO₂ system, the results are only comparable to the one-fluid mixing rules. Although more detailed studies are required to evaluate the SW mixing rules, these preliminary empirical results suggest that mixture adsorption on the surface is non-random.

Figures 1-3 show the results for CH₄/CO₂ systems for Case 2. As indicated by the figures, the one-fluid mixing model does not correlate the adsorption isotherms within their experimental uncertainties when the feed composition of CH₄ is 20% and 80%. Figures 4-6 show the results for CH₄/CO₂ systems for Case 6. Here, the quality of representation obtained from the WS mixing rules is uniformly better than the other cases for all feed conditions.

Conclusions

The major conclusions of this study are:

- Use of accessible-surface, one-fluid mixing rules or the excess Gibbs free energy mixing rules is effective in representing the binary mixture data within their experimental uncertainties.
- Accessible surface area plays an important role in one-fluid mixing rules. These results also support the assumption that different adsorbates access different surface area on the same adsorbent.
- Wong-Sandler mixing rules can be applied successfully to 2-D EOS adsorption modeling. This suggests that mixture adsorption on the surface is non-random.

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Table 1. Summary Results for Different Mixing Rules

	CH ₄	N ₂	CO ₂	Total	C _{ij}	D _{ij}	E ₂₁	L _{ij}
Case 1: One-fluid mixing predictions based on pure-component parameters								
CH₄-N₂					-	-	-	-
%AAD	4.8	2.9	-	3.7				
WAAE	2.0	0.9	-	1.6				
CH₄-CO₂					-	-	-	-
%AAD	6.1	-	10.6	1.8				
WAAE	2.3	-	4.4	0.9				
N₂-CO₂					-	-	-	-
%AAD	-	9.3	10.1	3.7				
WAAE	-	2.1	4.2	1.9				
Case 2: One-fluid mixing regressions – C_{ij} and D_{ij}								
CH₄-N₂					0.000	0.000	-	-
%AAD	4.8	2.9	-	3.7				
WAAE	2.0	0.9	-	1.6				
CH₄-CO₂					0.108	-0.041	-	-
%AAD	8.7	-	9.6	1.2				
WAAE	3.1	-	4.0	0.6				
N₂-CO₂					0.260	-0.172	-	-
%AAD	-	5.4	10.8	4.6				
WAAE	-	1.3	4.4	2.4				
Case 3: Accessible-area, one-fluid mixing regressions – C_{ij}, D_{ij} and E₂₁								
CH₄-N₂					0.006	-0.000	1.008	-
%AAD	5.0	2.4	-	3.6				
WAAE	2.1	0.7	-	1.6				
CH₄-CO₂					0.015	0.007	0.960	-
%AAD	4.8	-	5.8	2.5				
WAAE	1.8	-	2.4	1.2				
N₂-CO₂					-0.002	-0.006	0.950	-
%AAD	-	4.9	6.5	2.7				
WAAE	-	1.3	2.8	1.5				

Table 1. Summary Results for Different Mixing Rules – continued

	CH₄	N₂	CO₂	Total	C_{ij}	D_{ij}	E₂₁	L_{ij}
Case 4: Accessible-area, one-fluid mixing regressions – C_{ij}, D_{ij}, E₂₁ and L_{ij}								
CH₄-N₂					0.007	0.002	1.007	-0.007
%AAD	4.9	2.4	-	3.6				
WAAE	2.1	0.7	-	1.6				
CH₄-CO₂					0.168	-0.069	0.959	-0.012
%AAD	4.5	-	5.6	2.3				
WAAE	1.7	-	2.3	1.1				
N₂-CO₂					0.151	-0.177	0.955	0.235
%AAD	-	4.5	6.1	2.6				
WAAE	-	1.3	2.5	1.4				
Case 5: Accessible-area, one-fluid mixing regressions – E₂₁								
CH₄-N₂					-	-	1.006	-
%AAD	4.9	2.9	-	3.4				
WAAE	2.0	0.9	-	1.5				
CH₄-CO₂					-	-	0.966	-
%AAD	4.7	-	7.0	1.5				
WAAE	1.7	-	2.8	0.7				
N₂-CO₂					-	-	0.949	-
%AAD	-	5.2	6.5	2.9				
WAAE	-	1.3	2.8	1.6				
Case 6: Wong-Sandler mixing rules with NRTL model – C_{ij}, t₁₂, t₂₁ and a₁₂,								
	CH₄	N₂	CO₂	Total	C_{ij}	t₁₂	t₁₂	a₁₂
CH₄-N₂					-0.087	-0.139	-0.185	107.5
%AAD	1.9	2.0	-	0.6				
WAAE	0.7	0.7	-	0.3				
CH₄-CO₂					-0.458	0.052	-0.352	20.2
%AAD	3.3	-	4.2	2.4				
WAAE	1.2	-	1.7	1.1				
N₂-CO₂					-0.181	-0.106	-0.188	20.0
%AAD	-	5.2	9.5	5.2				
WAAE	-	1.3	3.8	2.6

Figure 1. Case 2: CH₄/CO₂ Adsorption on Activated Carbon at 113 °F

Figure 2. Case 2: CH₄/CO₂ Adsorption on Activated Carbon at 113 °F

Figure 3. Case 2: CH₄/CO₂ Adsorption on Activated Carbon at 113 °F

Figure 4. Case 6: CH₄/CO₂ Adsorption on Activated Carbon at 113 °F

Figure 5. Case 6: CH₄/CO₂ Adsorption on Activated Carbon at 113 °F

Figure 6. Case 6: CH₄/CO₂ Adsorption on Activated Carbon at 113 °F

**Modeling the Adsorption of Methane, Carbon Dioxide,
Nitrogen and their Binary Mixtures on Activated Carbon
Using the Simplified Local Density Model**

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Abstract

The simplified local density / Peng-Robinson model (SLD-PR) was extended to correlate the gas adsorption of mixtures for near-critical and supercritical adsorption systems of the type encountered in coalbed methane recovery and CO₂ sequestration. The goal was to develop efficient equation-of-state (EOS) computational frameworks for representing adsorption behavior, as well as to improve our understanding of the phenomenon.

The ability of the modified SLD-PR to correlate accurately data for the binary adsorption is demonstrated using recent adsorption measurements on activated carbon. The results indicate that the modified SLD-PR model, which incorporates a modified repulsive parameter 'b' for the PR-EOS, is capable of correlating 335 adsorption data points within their experimental uncertainties using 11 regressed parameters. The data set used includes adsorption isotherms of pure and binary mixtures of methane, nitrogen and CO₂ on dry activated carbon at 113.0 °F and pressures to 1800 psia. Nominal molar feed compositions of the fluid mixtures for adsorption were 20%/80%, 40%/60%, 60%/40%, and 80%/20%.

Keywords: coal, activated carbon, high pressure, adsorption properties, gas storage

1. Introduction

Deep coalbeds retain large quantities of gases such as methane, nitrogen, and CO₂ through adsorption. When a gas adheres to the surface of coal, the solid-gas interactions present can change the apparent gas density to that comparable to liquids. In coalbeds, methane resides inside the microporous coal structure at higher densities than the free-gas phase due to physical adsorption. Gas species other than methane also reside in the coal seam: typically 90% is methane, 8% CO₂, 2% nitrogen, with traces of other hydrocarbons (1). U.S. coalbeds alone hold about 95 trillion cubic feet of recoverable gas. The implementation of coalbed methane technology accounted for 6% of the U.S. natural gas production in 1997 (2).

Through a process called enhanced coalbed methane recovery (ECMR), nitrogen injection is used to increase production of the coalbed methane (3). By combining CO₂ with nitrogen, ECMR can displace more methane from the coalbed than with nitrogen alone (4). Nitrogen injection raises the reservoir pressure to improve gas flow but does not displace selectively the adsorbed methane gas. CO₂ injection selectively frees adsorbed methane gas from the coal because CO₂ equilibrium adsorption is greater than that of methane (3, 5).

Nitrogen injection results in rapid breakthrough in the recovered natural gas, which consequently raises separation costs. CO₂, however, can displace adsorbed methane from the coalbed and has a delayed breakthrough in the recovered gas. While the injection of CO₂ has more technical benefits than that of nitrogen, a mixture of CO₂ and nitrogen would have better economics (6). Economic feasibility studies and subsequent optimization hinge on coalbed equilibrium models that predict the quality and quantity of natural gas recovered.

Injection of CO₂ into reservoirs may provide also an environmental benefit. Beyond primary and CO₂/nitrogen enhanced coalbed methane production, coalbeds are also potentially attractive sites for sequestering CO₂ to remove it from the atmosphere. Sequestration is receiving widespread international attention. Coalbed sequestration of CO₂ could be a viable alternative to other proposed techniques, such as CO₂ injection into abandoned oil and gas reservoirs, deep, confined aquifers, and the deep ocean (7, 8).

Our objective is to identify / develop models capable of correlating high-pressure adsorption of the type encountered in CBM reservoirs. Because enhanced CBM recovery or CO₂ sequestration involves many possible fluid mixtures in the reservoir, models should have the flexibility to correlate reasonably mixture adsorption for many mixtures. To accomplish this task, we have extended the SLD-PR model to describe mixture adsorption. We test the model against recently acquired data on activated carbon. Rather than coal, activated carbon was chosen because the experimental uncertainties for its adsorption are lower than the uncertainty for coal, thus providing a more rigorous test for the model. Because coal is a more complex structure than activated carbon, the adsorption on activated carbon serves as a reference for the more complicated adsorption/absorption on water-saturated coal.

2. Mixture Gas Adsorption at High Pressures

High-pressure mixture adsorption is expressed in different terms than traditional mixture vapor-liquid systems; high-pressure adsorption is measured as an *excess* quantity. No clear experimental method is capable of measuring the volume of the adsorbed phase, its average density, or its component fractions. Experimental methods can measure, however, these quantities in relationship to bulk phase properties.

To illustrate, consider a system volume that contains activated carbon. A gas feed mixture of a given composition is introduced into the system. At equilibrium, the feed gas is distributed between two phases, the bulk-gas phase and the adsorbed phase. The bulk-gas density and the component mole fractions are defined as ρ_b and y_i , respectively. Each gas component (i) adsorbs onto the activated carbon. An excess quantity can be measured and is designated the Gibbs excess adsorption, $(n_{Gibbs})_i$.

Adsorption for a pure component can be described as the product of an averaged phase density $\langle \mathbf{r}_{ads} \rangle$ over an adsorbed-phase volume, V_{ads} , near the adsorbent surface. The measurable Gibbs excess adsorption is then:

$$n_{Gibbs} = V_{ads} (\langle \mathbf{r}_{ads} \rangle - \mathbf{r}_b) \quad (1)$$

In the adsorbed phase, the molar concentration and adsorbed-phase density change as functions of position whereas, in the bulk phase, the density and mole concentrations are uniform. For a component in a mixture, the excess adsorption is defined as:

$$(n_{Gibbs})_i = V_{ads} (\langle \mathbf{r}_{ads} x_i \rangle - \mathbf{r}_b y_i) \quad (2)$$

In experimental studies, helium injection is used to measure the volume of the adsorbent in relationship to the total system volume. The volume in the system that is available to helium (per gram of adsorbent) is designated the “helium void volume”, V_{void} . The helium void volume is measured at the same temperature as the gas mixture.

For coalbed methane production, a retrieved core sample can be analyzed by measuring the pressure, temperature, equilibrium mole fractions y_i , and a helium void volume. If z_i represents the mole fraction of each component (i) in the feed, then by a molar balance, we can express z_i in terms of the other experimentally accessible variables.

$$z_i = \frac{(n_{Gibbs})_i + V_{void} \mathbf{r}_b y_i}{n_{Gibbs}^{total} + V_{void} \mathbf{r}_b} \quad (3)$$

For mixture adsorption, we assume that the available surface area is identical for all gases. In addition, we assume that helium has access to the same pore volume as the other gases. Recent evidence suggests that this is true (at least for CO_2 on activated carbon recently studied) because gravimetric and volumetric techniques yield virtually identical adsorption isotherms for CO_2 (9, 10). Humayun (9) measured CO_2 adsorption using a gravimetric technique; this method required no helium void volume measurement, in contrast to the volumetric method we use. That the gravimetric method and the volumetric method yield virtually identical isotherms implies that the void volume does not change appreciably during the adsorption process for the

activated carbon, and that the volume available to CO₂ is identical to the volume available to helium.

3. SLD Slit Theory

The SLD model incorporates multi-layered adsorption, uses readily-available fluid property information from well-known equations of state such as the PR, and accounts for fluid-solid interactions by familiar potential functions. The SLD model is a “simplification” of local density theory because it assumes a mean field chemical potential; i.e., no local fluctuations.

Rangarajan (11) originally developed the physical premises and assumptions of SLD. Namely, (1) the chemical potential at any point next to adsorbent surface is equal to the bulk phase chemical potential, and (2) the molar chemical potential at any point above the surface is the sum of fluid-fluid and fluid-solid interaction potentials. An equation of state, such PR, can provide the fluid-fluid potential information. An integrated 10-4 Lennard-Jones potential function models the fluid-solid interactions. Chen and Wong (12), Subramanian (13), and Soule (14) also have used the SLD model for adsorption.

The SLD model has been formulated in terms of the Gibbs excess adsorption (n_{Gibbs}), defined as the excess number of moles per unit mass of adsorbent. Following Chen and Wong (12), we assume that the adsorbate molecule resides between a two-surface slit coal structure. For a slit geometry with surface area A (per gram of adsorbent) and a slit width of L, the Gibbs excess becomes:

$$n_{Gibbs} = A/2 \int_{\sigma_{ff}/2}^{L-\sigma_{ff}/2} (\rho(z) - \rho_b) dz \quad (4)$$

The lower limit of integration $\sigma_{ff}/2$ is the center of the adsorbed molecule on the plane surface; and the upper limit is $L-\sigma_{ff}/2$, where σ_{ff} is the fluid molecule diameter. The coordinate ‘z’ is orthogonal to the adsorbent wall.

4. Adsorption for Mixtures using SLD

Soule (15) used the SLD framework in conjunction with the ESD equation of state to model binary adsorption. Our modeling technique is different than Soule's in three ways:

1. The component adsorbed fraction is allowed to vary in the adsorbed phase as a function of position
2. One-fluid solution thermodynamics is used to describe the fugacity of a component in the adsorbed and bulk phase
3. Our model evaluations are conducted against higher-pressure data (1800 psia to his 300 psia) for many mixture combinations.

Soule did not attempt to optimize model parameters against mixture data, but rather predicted mixture adsorption from pure-component data. Here, we have performed model predictions based on the pure-component parameters and on optimized model parameters against mixture adsorption data.

For mixture adsorption, the amount of each component adsorbed depends on the component mole fractions in the bulk and adsorbed phase. That is:

$$(n_{Gibbs})_i = A/2 \int_{s_{ff}/2}^{L-s_{ff}/2} (\mathbf{r}(z)x_i(z) - \mathbf{r}_b y_i) dz \quad (5)$$

In this study, we used the PR-EOS to determine the bulk density and local density. For the Soave-type modifier for the EOS attraction law constant, $\alpha(T)$, in the PR EOS, we used the Mathias-Copeman expression with parameters regressed by Hernandez-Garduza (16). The local density and the mole fractions of the components at each position 'z' can be calculated by a local equilibrium relationship:

$$\ln \left(\frac{\hat{f}_i^{ads}(\bar{x}(z), \mathbf{r}(z))}{\hat{f}_i^{bulk}} \right) + \frac{\Psi_i^{fs}(z) + \Psi_i^{fs}(L-z)}{kT} = 0 \quad (6)$$

In the adsorbed phase, the fugacity of component ‘i’ in a mixture solution is a function of the local composition, local density, pressure, and temperature. In the bulk phase, the fugacity of component ‘i’ in a mixture solution is solved at the bulk density, pressure, and temperature. The fluid-solid potential is a function of slit geometry and position. Following Chen and Wong (12), Lee’s partially integrated 10-4 Lennard-Jones potential is used to describe the fluid-solid interactions for each component:

$$\Psi_i^{fs}(z) = 4\rho_{atoms}(\mathbf{e}_{fs})_i(\mathbf{s}_{fs})_i^2 \left(\frac{(\mathbf{s}_{fs})_i^{10}}{5(z')^{10}} - \frac{1}{2} \sum_{i=1}^4 \frac{(\mathbf{s}_{fs})_i^4}{(z' + (i-1)\mathbf{s}_{ss})^4} \right) \quad (7)$$

Here, ϵ_{fs} is the fluid-solid interaction energy parameter and $\rho_{atoms} = 0.382 \text{ atoms/\AA}^2$. The molecular diameter of the adsorbate and the carbon interplanar distances are σ_{ff} and σ_{ss} , respectively. The carbon interplanar distance was adopted from Subramanian (13) to be 0.335 nm, and fluid diameters are 0.3758 nm, 0.3798 nm and 0.3941 nm for methane, nitrogen, and CO₂, respectively. For convenience, the fluid-solid diameter σ_{fs} and the dummy coordinate z are defined as $\mathbf{s}_{fs} = (\mathbf{s}_{ff} + \mathbf{s}_{ss})/2$ and $z' = z + \sigma_{ss}/2$.

In the bulk phase, we use a linear mixing rule and a quadratic mixing rule for ‘b’ and ‘a’, respectively. The fugacity for the bulk phase using the PR-EOS is:

$$\ln \left(\frac{\hat{f}_i^{bulk}}{y_i P} \right) = \frac{b_i}{b}(Z-1) - \ln \left(Z - \frac{pb_i}{RT} \right) + \frac{b_i RT}{2\sqrt{2}a_i} \left(\frac{b_i}{b} - \frac{2\sum_j y_j a_{ij}}{a} \right) \ln \left(\frac{(1 + \mathbf{r}b(1 + \sqrt{2}))}{(1 + \mathbf{r}b(1 - \sqrt{2}))} \right) \quad (8)$$

In the adsorbed phase, we use quadratic mixing rules for both the covolume ‘b’ and the attraction law constant ‘a’. Using these rules, the fugacity in the adsorbed phase is:

$$\ln\left(\frac{\hat{f}_i^{ads}(z)}{x_i(z)P}\right) = \frac{2\sum_j x_j(z)b_{ij} - b}{b} \left(\frac{P}{\mathbf{r}(z)RT} - 1 \right) - \ln\left(\frac{P}{\mathbf{r}(z)RT} - \frac{Pb}{RT} \right) \\ + \frac{a(z)}{2\sqrt{2}RTb} \left(\frac{2\sum_j x_j(z)b_{ij} - b}{b} - \frac{2\sum_j x_j(z)a_{ij}(z)}{a} \right) \ln\left(\frac{(1 + \mathbf{r}(z)b(1 + \sqrt{2}))}{(1 + \mathbf{r}(z)b(1 - \sqrt{2}))} \right) \quad (9)$$

The formulas for $a(z)$ depend on the ratio of the slit width, L , to the molecular diameter, $(\sigma_{ff})_i$. Rangarajan (11) obtained these formulas by integrating the sum of all two-body interactions between an arbitrarily selected central molecule and all the other molecules around it. We used the results of Chen and Wong (12) for the equations describing ‘ a ’ as a function of position within a slit. Combining rules for a_{ij} follow the geometric mean. In this paper, we assume that C_{ij} is equal to zero for all component interactions in the bulk phase, but we regress those C_{ij} for the adsorbed phase:

$$(a_{ads})_{ij} = \sqrt{(a_{ads})_i (a_{ads})_j} (1 - C_{ij}) \quad (10)$$

In this work, we have adjusted the covolume, ‘ b_i ’, by an empirical parameter Λ_i . At high adsorptive loadings, the local fluid density at the wall decreases with increasing values of the parameter Λ_i , which is nominally unity (10). We use a linear combining rule for the covolume interaction in the adsorbed phase:

$$(b_{ads})_{ij} = \left(\frac{b_i(1 + \Lambda_i) + b_j(1 + \Lambda_j)}{2} \right) \quad (11)$$

5. Database and Data Reduction

Gas adsorption measurements have been conducted at Oklahoma State University (OSU) on activated carbon. Adsorption isotherms for pure methane, nitrogen, CO₂ and their binary mixtures were measured on dry activated carbon at 318.2 K (113 °F) and pressures to 12.4 MPa (1800 psia) (17).

Our error analysis indicates that the experimental uncertainties for the adsorption measurements considered here range from 2 to 6% for the pure gases. Uncertainties for the binary mixtures vary with composition. Uncertainties for all the binary gas *total* adsorption measurements are within 4% (17).

The objective function WAAE (weighted average absolute error) is used to correlate data with the SLD-PR model. The function represents the average of the weighted deviations in predicted Gibbs excess adsorption:

$$WAAE = \frac{1}{N} \sum_{i=1}^N abs \left(\frac{n_{calc} - n_{exp}}{\sigma_{exp}} \right) \quad (12)$$

Here, N is the number of data points, n_{calc} and n_{exp} are the calculated and the experimental Gibbs excess for datum ‘i’, and σ_{exp} is the expected experimental uncertainty for datum ‘i’.

6. Calculation Details

The temperature, pressure, feed mole fractions, and void volume (per gram adsorbent) are needed as information to perform an adsorption flash calculation. Once accomplished, the flash calculation provides the component Gibbs adsorption and the equilibrium mole fraction in the bulk phase for each component.

In this work, we subdivided half of the adjusted slit width, $L - (\sigma_{ff})_i$, into 50 intervals. At each interval, the local density and the adsorbed mole fractions were calculated by

simultaneously solving Eq. 6 for all components and using the mole fraction summation requirement, $\sum_i x_i = 1$. The adsorbed mole fractions were initialized to the feed mole fractions, i.e., $x_i = z_i$ for all components 'i'. The solution, however, is contingent on *equilibrium* (not feed) mole fractions, y_i , as they are needed to solve for the bulk-phase fugacity in Eq. 6. The bulk mole fractions were initialized with the available experimental values to speed the calculation (although any reasonable initial values could be used). Once the local density and the adsorbed mole fractions are calculated for each interval, a trial adsorbed amount was calculated by numerical integration using Simpson's rule in accordance with Eq. 5.

The next step is to evaluate Eq. 3 for each component. If Eq. 3 is not satisfied for each component, then a new set of equilibrium mole fractions is used to calculate the next trial adsorbed amount. The procedure is repeated until Eq. 3 and the adsorbed mole fraction summation is satisfied. A Newton-Raphson method with numerical derivatives is used to solve Eq. 6 and then Eq. 3.

7. Case Studies

Two independent cases were explored in this study. For each case, we correlate all 335 independent adsorption data using 11 regressed parameters.

1. We consider that the adsorbed material may reside in the slit from $\sigma_{ff}/2$ to $L - \sigma_{ff}/2$. No adsorbed material is allowed within $\sigma_{ff}/2$ adjacent to the wall. The pore volume is taken as $A (L - \sigma_{ff})/2$.
2. Next, we consider the adsorbed material to reside in the slit from $3/8\sigma_{ff}$ to $L - 3/8\sigma_{ff}$. This accounts for almost all of the adsorbed material not included in the first case. We presume that the pore volume is $A (L)/2$.

Case 1 assumes that the fluid molecule may not penetrate the wall at all and the local density from the wall to $\sigma_{ff}/2$ is zero. We assume in Case 1 that since the fluid molecule cannot

reside in the distance from the wall to $\sigma_{ff}/2$ (or from $L-\sigma_{ff}/2$), that the volume contained there is excluded from the pore volume. Hence, the pore volume is taken as $A/2 (L - \sigma_{ff})$.

Case 2 assumes that the fluid molecule may reside anywhere in the slit. The pore volume is taken to include the entire volume covered by the slit, $A/2 (L)$. Though the fluid may reside anywhere, the density is negligibly small in the distance from the wall to about $3/8\sigma_{ff}$. Thus we assumed that the second integral in Eq. 13 was accordingly zero, as shown below:

$$(n_{Gibbs})_i = A/2 \int_{3/8\sigma_{ff}}^{L-3/8\sigma_{ff}} (\mathbf{r}(z)x_i(z) - \mathbf{r}_b y_i) dz + A \int_{3/8\sigma_{ff}}^0 (\mathbf{r}(z)x_i(z) - \mathbf{r}_b y_i) dz \quad (13)$$

8. Results and Discussion

Table 1 presents a summary of the results of our model evaluation, and Figures 1-6 show the model representations of the experimental data (Case 2). In general, the SLD-PR model is capable of representing the adsorption data considered in this study within their experimental uncertainties (represented by error bars in the figure). On average, Case 2 correlates all the data slightly better than Case 1. On average, The SLD-PR model fits all the adsorption data (all 335 points) within one experimental standard deviation.

The SLD-PR model can correlate adsorption isotherms which exhibit maximums and other features. Of particular interest is the nitrogen adsorption in the 40%/60% and 20%/80% nitrogen/CO₂ mixtures (Figure 5). These two isotherms each exhibit a maximum, inflect and become concave up with pressure, and finally crossover and become negative. We are unaware of any other published experimental data that exhibit these features for a binary system. The SLD-PR model can correlate such behavior surprisingly well.

To test the *predictive* capability of the SLD-PR model, we regressed the pure component isotherms as described in Case 2. Using only these parameters, we predicted the mixture adsorption (setting all binary interaction parameters, C_{ij} , to zero). Figures 1-6 show the isotherms predicted in this manner. These model predictions, based solely on pure-substance

adsorption data, are within twice the experimental uncertainties for the methane/nitrogen mixture isotherms, and they are within three times the experimental uncertainties for methane/CO₂ and nitrogen/CO₂ mixture isotherms.

The *correlative* model is least accurate for the methane adsorption at high methane concentrations of methane-nitrogen mixtures. Also, for pure CO₂ at high pressures, the model is noticeably higher than the data. These errors could be in part due to systematic experimental error (for methane adsorption), and in part due to inadequate fluid property accuracy (for CO₂ near the critical point).

As shown in Table 2, the regressed parameters for Case 1 and Case 2 have a few similarities, but some parameters are strikingly different from one another. The surface area for Case 1 is higher than Case 2 because the molecular diameter of the pore volume was excluded for Case 1. While the surface area differs between the two cases, the pore volumes for the two cases are quantitatively similar.

The parameter Λ_b is higher for Case 2 than Case 1. Higher values of Λ_b mean proportionally lower values of the local density near the wall. Case 2 has lower values of Λ_b because, for this case, we include the pore volume close to the wall. This added volume decreases the average local density across the pore volume and offsets the need for a correction from Λ_b . The ratio of the Λ_b values for each case and for each component are very similar, suggesting that a decrease in defined pore volume can be offset by a roughly proportional increase in Λ_b . Thus, definition of the pore volume is very important, as different pore volume definitions lead to different regressed parameters.

The attraction interactions for methane-CO₂ and nitrogen-CO₂ have small corrections (C_{ij}) in Case 1, and methane-nitrogen and methane-CO₂ have small corrections in Case 2. This suggests that predictions of nitrogen-CO₂ mixture adsorption from pure component isotherms would be better predicted if Case 1 were used. In contrast, methane-nitrogen mixture adsorption would be better predicted if Case 2 were used. The size of the correction for methane-nitrogen in Case 1 and nitrogen-CO₂ in Case 2 is rather large. This suggests that one-fluid mixing rules

may not be sufficient to predict binary adsorption. Other possibilities owing to the large correction factors include an inadequate SLD theory describing fluid interactions, or the inaccuracy of the PR-EOS repulsive pressure, $RT/(v-b)$. Future work will address these matters.

9. Conclusions

Major conclusions of this study are:

- The SLD-PR *predicts* mixture adsorption within twice the experimental uncertainty on average, based solely on pure-component adsorption isotherms.
- The SLD-PR model *correlates* the binary mixture adsorption behavior of the systems considered within one standard deviation of experimental error. This includes component-adsorption isotherms exhibiting excess adsorption maxima and negative excess adsorption.
- The one-fluid mixing rules are suitable for the task of correlation; however, they require large corrections for some binary interactions.
- Case studies show that the SLD pore volume definition has a significant effect on the values of regressed parameters, such as surface area.

Nomenclature

A	surface area of coal
a	PR attractive parameter
a_{ads}	local PR attractive parameter for adsorbed phase
b	PR covolume
b_{ads}	modified PR covolume for adsorbed phase
C_{ij}	binary interaction parameter for fluids ‘i’ and ‘j’
f	fugacity
k	Boltzmann constant
L	slit width; defined as the normal distance between the carbon planes
N	number of points in regression
n_{Gibbs}	the Gibbs excess adsorption
P	pressure
R	universal gas constant

T	temperature
V_{ads}	adsorbed-phase volume
V_{void}	void volume (system volume minus adsorbent volume determined by helium)
WAAE	weighted average absolute error
x_i	mole fraction of adsorbed phase of component ‘i’
y_i	equilibrium mole fraction of bulk phase of component ‘i’
z	normal position between carbon planes; zero at one plane
z_i	feed gas concentration of component ‘i’
z'	dummy position variable: $z' = z + \sigma_{\text{ff}}/2$

Subscripts

a	adsorbed-phase property
b	bulk property
c	critical condition
calc	calculated
exp	experimental
ff	fluid-fluid interaction
i	dummy index, or component ‘i’
j	dummy index, or component ‘j’
fs	fluid-solid interaction
ss	solid-solid interaction

Greek

α	temperature dependent function for PR-EOS
ϵ_{fs}	fluid-solid interaction parameter
Λ_{b}	modification parameter to PR covolume
ρ	density
σ	particle diameter
σ_{exp}	expected experimental uncertainty
Ψ	fluid-solid potential function

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Table 1: Statistical Results for Model Regressions

	Average Absolute Deviation from Experimental Uncertainty			
Pure Gases	Case 1		Case 2	
Methane	1.4		1.2	
Nitrogen	1.0		1.0	
CO ₂	1.2		1.2	
Feed Mixture	Case 1		Case 2	
Methane/Nitrogen	methane	nitrogen	methane	nitrogen
20/80	0.24	0.97	0.33	0.97
40/60	1.5	0.88	1.42	0.86
60/40	1.4	0.37	1.28	0.21
80/20	1.4	0.89	1.37	0.75
Methane/CO ₂	methane	CO ₂	methane	CO ₂
20/80	0.79	0.81	0.66	0.93
40/60	0.51	0.66	0.50	0.54
60/40	0.66	0.57	0.57	0.40
80/20	0.21	0.75	0.21	0.63
Nitrogen/CO ₂	nitrogen	CO ₂	nitrogen	CO ₂
20/80	0.73	0.76	0.73	0.78
40/60	0.63	0.54	0.53	0.67
60/40	0.66	1.1	0.78	1.2
80/20	0.21	1.1	0.42	0.79

Table 2: Regressed Parameters for SLD Model

	<i>Case 1</i>			<i>Case 2</i>		
Surface Area (m ² /g)	844			604		
Slit Length (nm)	1.13			1.09		
<i>Binary Interaction, C_{ij}</i>						
Methane-Nitrogen	0.229			0.078		
Methane-CO ₂	0.066			-0.0013		
Nitrogen-CO ₂	-0.021			-0.247		
	<i>methane</i>	<i>nitrogen</i>	<i>CO₂</i>	<i>methane</i>	<i>nitrogen</i>	<i>CO₂</i>
ε _{fs} /k (K)	76.1	50.0	88.3	70.5	49.7	76.9
Λ _b	1.62	1.85	1.29	1.23	1.43	1.00

Figure 1: SLD Model of Methane Adsorption in Methane/Nitrogen Mixtures (Solid Line is Correlative, Dashed Line for Mixtures is Predictive)

Figure 2: SLD Model of Nitrogen Adsorption in Methane/Nitrogen Mixtures (Solid Line is Correlative, Dashed Line for Mixtures is Predictive)

Figure 3: SLD Model of Methane Adsorption in Methane/CO₂ Mixtures (Solid Line is Correlative, Dashed Line for Mixtures is Predictive)

Figure 4: SLD Model of CO₂ Adsorption in Methane/CO₂ Mixtures (Solid Line is Correlative, Dashed Line for Mixtures is Predictive)

Figure 5: SLD Model of Nitrogen Adsorption in Nitrogen/CO₂ Mixtures (Solid Line is Correlative, Dashed Line for Mixtures is Predictive)

Figure 6: SLD Model of CO₂ Adsorption in Nitrogen/CO₂ Mixtures (Solid Line is Correlative, Dashed Line for Mixtures is Predictive)

Extension of the Ono-Kondo Lattice Model to High-pressure Mixture Adsorption

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Abstract

Our recent studies have indicated that the Ono-Kondo (OK) lattice model has excellent capability of representing the high-pressure, pure gas adsorption data. The goal of the present work is to extend the OK framework to mixture predictions.

The ability of the Ono-Kondo (OK) lattice model to correlate precisely data for supercritical binary adsorption systems is demonstrated using our recent measurements for the adsorption of pure carbon dioxide, methane and nitrogen and their binary mixtures on activated carbon at 318 K and pressures to 12.5 MPa.

Results indicate that the extended OK model represents these binary adsorption measurements within their experimental uncertainties. The calculations require (a) good estimates for the pure-component parameters, and (b) two interaction parameters to account for difference in species molecular interactions with the adsorbent.

Key words: high pressure; adsorption; methane; nitrogen; carbon dioxide; activated carbon; Ono-Kondo model

Introduction

The authors' long-range objective is to develop reliable models to predict the adsorption behavior of supercritical gases on coals, with specific applications to (a) coalbed methane (CBM) production and (b) the use of coalbeds to sequester the greenhouse gas CO₂. In pursuit of that objective, we have performed both experimental [Hall, 1994] and modeling [Zhou, 1994; Gasem, 2001 and 2002; Pan, 2002] studies.

Evaluating mathematical models to describe adsorption behavior on coals is complicated by (a) the difficulty in characterizing the coal matrix adequately, and (b) assessing the effect of water (found in essentially all coalbeds) on the adsorption behavior. As a result, we decided to perform studies on a more readily characterized carbon matrix and in the absence of water. This led to the choice of dry activated carbon for the present study. Our rationale is that useful

models should be expected to fit the data on activated carbon before including the effects of the complex adsorbent structure of coals and/or the presence of water.

Several theories and models have been developed to correlate high-pressure pure adsorption data and to predict gas mixture adsorption. These include (a) enhanced forms of the Langmuir-type isotherms, (b) two-dimensional equations of state, (c) the simplified local density models (SLD), and (d) the Ono Kondo (OK) model. In this study, we demonstrate the ability of the Ono Kondo (OK) lattice model to correlate high-pressure, supercritical adsorption isotherms encountered in CBM recovery and CO₂ sequestration. In addition to its strong theoretical basis, the lattice theory offers several practical advantages. Specifically the OK model:

1. Describes monolayer and multilayer adsorption
2. Represents both Gibbs and absolute adsorption
3. Has a potential to describe the adsorption behavior based on the physical properties of the adsorbates and the accessible characterization of the adsorbent
4. Is structured to incorporate accurate density calculations, which may reduce the correlative burden of the adsorption modeling

The objectives of this study were to (a) evaluate the abilities of the OK model to correlate gas adsorption isotherms over an extended pressure range, including the Gibbs adsorption maximum exhibited by many high-pressure adsorption systems; and (b) extend the utility of this model to mixture adsorption correlation and prediction based on model parameters obtained from pure-component adsorption isotherms.

The Ono-Kondo Model

In the lattice model, the fluid system is assumed to be composed of layers of lattice cells that contain fluid molecules and vacancies. For the case of adsorption, as shown in Figure 1, more fluid molecules reside in the cells of the adsorbed-phase layers than in the cells of the bulk-phase layers. Molecular interactions are assumed to exist only between the nearest neighboring molecules. When equilibrium exists between the gas-phase and multilayer adsorbed phase, the expression for the thermodynamic equilibrium can be written as [Aranovich, 1995]:

$$\ln(x_i(1-x_b)/(x_b(1-x_i))) + z_0(x_i - x_b)\epsilon/kT + z_2(x_{i+1} - 2x_i + x_{i-1})\epsilon/kT = 0; \quad i = 2, 3, \dots \quad (1)$$

with the following boundary condition:

$$\ln(x_1(1-x_b)/(x_b(1-x_1))) + (z_1x_1 + z_2x_2 - z_0x_b)\epsilon/kT + \epsilon_s/kT = 0 \quad (2)$$

In these equations, x_i is the reduced density or fraction of sites occupied by adsorbed molecules in layer i , and x_b is the fraction of sites occupied by fluid molecules in the bulk. For a cubic lattice, the coordination numbers z_0 and z_1 are 6 and 4, respectively; and by definition, we set $z_2 = (z_0 - z_1)/2$. The adsorbate-adsorbate energy interaction parameter is expressed by ϵ/kT , and the adsorbate-adsorbent surface energy interaction parameter is expressed by ϵ_s/kT , where k is Boltzman's constant, and T is the absolute temperature.

The analytical expression for Gibbs excess adsorption for this model is:

$$n_{Gibbs} = C \sum_i^M (x_i - x_b) \quad (3)$$

where C is a prefactor related to the capacity of adsorbent for a specific gas, and M is the maximum number of layers that can be fit in an adsorption isotherm. The reduced densities x_i and x_b are expressed as $x_i = \mathbf{r}_i / \mathbf{r}_{mc}$ and $x_b = \mathbf{r}_b / \mathbf{r}_{mc}$, where $\mathbf{r}_i$ and $\mathbf{r}_b$ are the adsorbed and the bulk density of the adsorbate, respectively. The bulk density for pure methane, nitrogen, and CO₂ were determined from highly accurate equations of state (Angus, 1978 and 1979; Span, 1996). The maximum adsorbed-phase density $\mathbf{r}_{mc}$ may be estimated in various ways. Arri (1992) used the saturated liquid density at atmospheric pressure and Hocker and Donohue (1999) suggested a theoretical value from close-packed molecules. Application of these estimates, however, does not produce optimum fits of the Ono-Kondo model isotherms for pure methane, nitrogen, and CO₂ on activated carbon. Shown below, better results are obtained when this maximum adsorbed-phase density is treated as a regressed parameter.

The structure of the activated carbon, as illustrated in Figure 2, is similar to a graphite with the spacing between adjacent graphite planes is only a few molecular diameters. Therefore in this study, following Benard and Chahine (1997), we assume a monolayer adsorption, in which the adsorbed molecules are directly mapped onto parallel graphite planes, as shown in Figure 3.

Furthermore, we choose the 2D-hexagonal configuration to match the graphite molecular structure. These assumptions simplify the thermodynamic equilibrium expression of Eqs. (1) and (2) to:

$$\ln [x_{ads} (1 - x_b) / x_b (1 - x_{ads})] + (7x_{ads} - 8x_b)\epsilon / kT + \epsilon_s / kT = 0 \quad (4)$$

Also, the Gibbs excess adsorption expression, Eq. (3), simplifies to:

$$\Gamma = 2C (x_{ads} - x_b) = 2C \left(\frac{\rho_{ads}}{\rho_{mc}} - \frac{\rho_b}{\rho_{mc}} \right) \quad (5)$$

Extending OK Model to Mixtures

In our previous studies, we have established the viability of the OK model for correlating pure-component adsorption of the targeted gases on a variety of adsorbents over a wide range of pressure [Gasem, 2002]. In this study, we extend the OK model to mixture predictions. Specifically, we incorporate mixing rules into the OK model and evaluate its ability to correlate/predict the mixture total and component adsorptions.

For a binary mixed gas containing components A and B, the equality of the chemical potential in the adsorbed and bulk phases for each component leads to the following equilibrium equations for monolayer, binary, and mixed-gas adsorption:

$$\ln \frac{x_A (1 - x_{A,b} - x_{B,b})}{x_{A,b} (1 - x_A - x_B)} + \frac{\epsilon_{AA}}{kT} ((z_1 + 1)x_A - z_0 x_{A,b}) + \frac{\epsilon_{AB}}{kT} ((z_1 + 1)x_B - z_0 x_{B,b}) + \frac{\epsilon_{As}}{kT} = 0 \quad (6)$$

and

$$\ln \frac{x_B (1 - x_{A,b} - x_{B,b})}{x_{B,b} (1 - x_A - x_B)} + \frac{\epsilon_{BB}}{kT} ((c_p + 1)x_B - c x_{B,b}) + \frac{\epsilon_{AB}}{kT} ((c_p + 1)x_A - c x_{A,b}) + \frac{\epsilon_{Bs}}{kT} = 0 \quad (7)$$

A linear combination rule is used to evaluate the interaction energy between molecule A and B; i.e.:

$$\mathbf{e}_{AB} = (1 + C_{AB})(\mathbf{e}_{AA} + \mathbf{e}_{BB}) / 2. \quad (8)$$

This combination rule is chosen in anticipation of different signs for $\mathbf{e}_{AA}$ and $\mathbf{e}_{BB}$. Also, a regressed binary interaction parameter C_{AB} is introduced to account for unlike interactions.

For a binary mixture, the non-linear equations, Eqs. (6) and (7), are solved using the Newton-Raphson method to obtain x_A and x_B . In addition, we needed to extend Eq. (5) to mixtures and calculate the amount of individual component adsorption in a binary mixture. For components A and B, the equation becomes:

$$\Gamma_A = 2C_A(1 + S_{AB})(x_A - x_{A,b}) = 2C_A(1 + S_{AB}) \left(\frac{\mathbf{r}_A}{\mathbf{r}_{mc,A}} - \frac{y_A \mathbf{r}_b}{\mathbf{r}_{mc,A}} \right) \quad (9)$$

and

$$\Gamma_B = 2C_B(1 - S_{AB})(x_B - x_{B,b}) = 2C_B(1 - S_{AB}) \left(\frac{\mathbf{r}_B}{\mathbf{r}_{mc,B}} - \frac{y_B \mathbf{r}_b}{\mathbf{r}_{mc,B}} \right) \quad (10)$$

Here S_{AB} is another binary interaction parameter that accounts for difference in species-molecular interactions with the adsorbent. The mixture bulk density is calculated separately using a modified BWR equation of state [Gasem, 2002].

Database and Data Reduction

Gas adsorption measurements have been conducted at Oklahoma State University (OSU) on activated carbon. Adsorption isotherms for pure methane, nitrogen, CO₂ and their binary mixtures were measured on dry activated carbon at 318.2 K (113 °F) and pressures to 12.4 MPa (1800 psia). Pure gases were obtained from Airgas-Pennsylvania with reported purities of 99.99% or better. Activated carbon (Filtrisorb 400, 12x40 mesh, Calgon Carbon) was used as the adsorbent. The activated carbon was dried under vacuum at 230 °F for two days before being used in the adsorption measurements. The nitrogen BET surface area of the activated carbon at 77 K has been reported to be 850 m²/g (Humayun, 2000).

Our error analysis indicates that the experimental uncertainties for the adsorption measurements range from 2 to 6% for the pure adsorption. The uncertainties for the binary mixture adsorptions vary with composition. Uncertainties for all the binary gas *total* adsorption measurements are within 4%. (Detailed description of the newly-acquired experimental data will be forthcoming in a separate publication [Sudibandriyo et al., 2002].)

The objective function WRMSE is used to correlate data with the OK model. The function minimizes the sum of the squared weighted deviations in predicted Gibbs excess adsorption:

$$WRMSE = \sqrt{\frac{\sum_{i=1}^N \left(\frac{n_{exp} - n_{calc}}{s_{exp}} \right)^2}{N}} \quad (11)$$

Here, N is the number of data points, n_{calc} and n_{exp} are the calculated and the experimental adsorption for data point “i”. The average absolute deviation (%AAD) and the weighted average-absolute error (WAAE) are also used to quantify our model evaluations:

$$\%AAD = \frac{100}{N} \sum_{i=1}^N abs \left(\frac{n_{calc} - n_{exp}}{n_{exp}} \right) \quad (12)$$

$$WAAE = \frac{1}{N} \sum_{i=1}^N abs \left(\frac{n_{calc} - n_{exp}}{s_{exp}} \right) \quad (13)$$

Results and Discussion

1. Pure Adsorption

Table 1 presents the summary results of our model evaluation, and Figure 4 shows the model representations of the pure adsorption experimental data. In general, the OK model represents the adsorption data within their experimental uncertainties (represented by error bars in the figure). The average absolute percent deviation (AAPD) for methane, nitrogen and CO₂ are 0.8%, 0.3% and 3.3%, respectively.

The quality of the mixture adsorption predictions and representations is dependent on good estimates for the pure-component parameters. Table 1 also presents the OK parameters for the pure adsorptions. Our model parameters show reasonable agreement with the parameters obtained by Benard and Chahine (1997) for methane adsorption on activated carbon. Application of the parameters obtained by Aranovich and Donohue (1995), however, does not give satisfactory results for the system studied. This is because Donohue used data from the

subcritical region (except for methane) to evaluate parameters in his model. Better representations of our model for the high-pressure adsorptions are mainly attributed to more accurate representation of the maximum adsorbed-phase densities. Interestingly, the maximum adsorbed-phase densities obtained in our evaluation for all components are comparable to the van der Waals co-volume estimates, as indicated by Table 2. Furthermore, the CO₂ adsorbed-phase density is essentially the same as that obtained graphically in Figure 5, which indicates that the adsorbed-phase densities for CO₂ at zero Gibbs excess are 1.02 g/cm³ (assuming a linear variation in Gibbs excess adsorption with density).

In the present work, we maintain the adsorbate-adsorbate energy interaction parameter, ϵ/kT , for each component proportional to its Lennard-Jones depth well energy potential [Do, 1998]. The regressed adsorbate-adsorbent energy interaction parameters, ϵ_s/kT , are also equal to with the values obtained for a molecule adsorbed on a graphite plane; i.e., 1206 K, 937 K, 1631K for methane, nitrogen, and CO₂, respectively [Do, 1998]. Further, as indicated by Table 1, while the adsorbate-adsorbent energy interaction parameters, ϵ_s/kT , are all negative, the adsorbate-adsorbate ϵ/kT values are positive. These results confirm the observations of Benard (1997) and Aranovich et al. (2001), that the “attractive” force between adsorbate-adsorbate ϵ/kT might be repulsive, i.e., it might be null or positive.

2. Mixture Adsorption

Table 3 presents the summary results of our model evaluation for binary mixture adsorption. The OK model predictions based solely on pure-substance parameters ($C_{AB}=S_{AB}=0$) result in deviations of one to two times the experimental uncertainties for the total adsorption (1-10% AAD) and about two to three times the experimental uncertainties for the component adsorptions (4-74% AAD). These results indicate that while the OK model predicts the total adsorption adequately, it predicts the individual component-adsorption isotherms poorly.

The model representations are improved when accounting for the interaction between two different adsorbed molecules, C_{AB} , (Case 1). The total adsorptions and the component adsorptions are improved to within 8% AAD and 13% AAD, respectively. However, the best

results are obtained when additional binary interaction parameter, S_{AB} , is introduced to the model (Case 2). This S_{AB} parameter accounts for difference in molecular interactions with the adsorbent. As presented in Case 2 of Table 3, the OK model is capable of representing all total adsorption data with less than 4% AAD and component adsorption data within 10% AAD. The WAAE for all total adsorptions and the component adsorptions are less than 1.1, except for CO₂ adsorption in the nitrogen-CO₂ binary (WAAE=1.8).

Figure 6 shows the OK model representation for the methane-CO₂ mixture adsorption for Case 2. In general, the OK model is capable of representing all total and component adsorption data considered in this study within their experimental uncertainty (represented by error bars in the figure). Similar results are obtained for methane-nitrogen and nitrogen-CO₂ mixture adsorptions.

Conclusions

Major conclusions of this study are as follows:

- Pure-component adsorption measurements for CO₂, methane, and nitrogen on activated carbon were successfully correlated using the OK model within their expected experimental uncertainties.
- The OK model is capable of predicting total adsorption for binary systems adequately. The extended OK model represents the binary adsorption data within their experimental uncertainties by using (a) good estimates for the pure-component parameters, and (b) two interaction parameters to account for difference in species-molecular interactions with the adsorbent.

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Table 1. Summary Results for the OK Model for Pure Adsorption

OK Parameters	This Work	Benard (1997)	Donohue (95-99)
M	2	2	3
z_0	8	8	6
z_1	6	6	4
$z_2=(z_0-z_1)/2$	1	1	1
Methane			
ϵ_s/k (K)	-1385	-1332	-1187
ϵ/k (K)	64	50	-173
ρ_{mc} (g/cc)	0.38	0.38	$\rho = \sqrt{2} / (A_v \sigma^3) = 0.70$
C (mmol/g AC)	3.21	3.20	2.30
%AAD	0.8	0.9	5.5
CO₂			
ϵ_s/k (K)	-1690		-1093
ϵ/k (K)	82		-260
ρ_{mc} (g/cc)	1.00		$\rho = \sqrt{2} / (A_v \sigma^3) = 1.14$
C (mmol/g AC)	4.52		2.24
%AAD	3.3		27.8
Nitrogen			
ϵ_s/k (K)	-1032		-504
ϵ/k (K)	41		-69
ρ_{mc} (g/cc)	0.70		$\rho = \sqrt{2} / (A_v \sigma^3) = 1.30$
C (mmol/g AC)	2.72		6.67
%AAD	0.3		31.4

A_v = Avogadro's number

Table 2. Adsorbed-Phase Densities Estimated by Different Methods

Method	Adsorbed-Phase Density (g/cm ³)		
	Methane	Nitrogen	CO ₂
Ono-Kondo model (regressed)	0.38	0.70	1.00
Zhou-Gasem-Robinson EOS (regressed)	0.35	0.84	0.98
Liquid density estimate (at normal b.p.)	0.42	0.81	
Solid density estimate (at triple pt.)			1.18
van der Waals covolume	0.37	0.72	1.03
Graphical estimate from the Gibbs adsorption isotherm			1.02
Hard-Sphere Packing: $r = \sqrt{2} / (A_v \sigma^3)$	0.70	1.30	1.14
Hard-Sphere Packing: $r = q / (A_v \rho \sigma^3 / 6)$; $q = 0.7$	0.66	1.23	1.08

$\sigma_{CO_2} = 4.49$ nm; $\sigma_{CH_4} = 3.78$ nm; $\sigma_{N_2} = 3.70$ nm

Table 3. Summary Results for the OK Model for Binary Adsorption

	Methane	Nitrogen	CO2	Total	C _{ij}	S _{ij}
Prediction Based on Pure-Component Parameters: C_{AB}=0, S_{AB}=0						
CH₄-N₂					-	-
%AAD	4.1	13.2	-	1.1		
WAAE	1.6	2.1	-	0.5		
CH₄-CO₂					-	-
%AAD	18.3	-	10.3	4.8		
WAAE	2.2	-	2.5	1.3		
N₂-CO₂					-	-
%AAD	-	73.5	13.9	9.7		
WAAE	-	2.8	3.1	2.8		
Case 1: One Regressed Binary Interaction Parameter, C_{AB} (S_{AB}=0)						
CH₄-N₂					0.1830	-
%AAD	4.3	5.3	-	2.2		
WAAE	1.7	0.9	-	0.9		
CH₄-CO₂					0.3108	-
%AAD	6.5	-	6.6	2.9		
WAAE	0.7	-	1.5	0.7		
N₂-CO₂					0.4278	-
%AAD	-	11.2	13.1	7.7		
WAAE	-	0.9	3.2	2.3		
Case 2: Two Regressed Binary Interaction Parameters						
CH₄-N₂					0.1397	0.0318
%AAD	2.4	6.1	-	1.9		
WAAE	0.8	1.0	-	0.8		
CH₄-CO₂					0.3251	0.0333
%AAD	6.8	-	4.7	2.4		
WAAE	0.8	-	1.1	0.6		
N₂-CO₂					0.5109	0.0742
%AAD	-	10.6	8.0	4.0		
WAAE	-	1.1	1.8	1.1

Figure 1. Multilayer Adsorption

Figure 2. Activated Carbon Structure [Jankowska, 1991]

Figure 3. Monolayer Adsorption on Two Parallel Graphite Planes

Figure 4. OK Model Representations to the Pure Gas Adsorption on Activated Carbon at 113 °F

Figure 5. Adsorbed-Phase Density Estimation for CO₂ Adsorption Using a Graphical Method

Figure 6. OK Model Representations of CH₄/CO₂ Adsorption on Activated Carbon at 113 °F : (a) Total Adsorption (b) CH₄ Adsorption and (c) CO₂ Adsorption