Application of a New Multicomponent Gas Adsorption Model to Coal Gas Adsorption Systems

C.R. Clarkson, SPE, Burlington Resources Canada Ltd.

Summary
A new multicomponent adsorption model is proposed for application to coal gas adsorption systems. The model is derived by combining the vacancy solution and Dubinin-Polanyi theories. Applications of the new adsorption model include the modeling of multicomponent adsorption processes associated with primary and enhanced coalbed methane recovery (ECBM).

In the new model, the adsorbed phase in the single-component (pure) adsorption system is treated as a binary mixture of a single-component gas with a hypothetical "vacancy" species, which also occupies adsorption space. The adsorption system is modeled as equilibrium between the gaseous phase and the adsorbed-phase vacancy solution. The Dubinin-Astakhov (D-A) equation is used to generate activity coefficients, as a function of the degree of pore-filling, for the pure component gas in the binary (adsorbate+vacancy) adsorbed-phase mixture. The Wilson equation is chosen to fit pure component (D-A-derived) activity coefficient curves by optimizing the binary interaction coefficients. These binary interaction coefficients are then used to predict multicomponent adsorption equilibrium, although only the case of binary adsorption is modeled here.

The adsorbed phase mixture for binary gas adsorption is treated as a ternary mixture of the two pure component adsorbates and the hypothetical vacancy species. Binary gas adsorption equilibrium is described by equilibrium between the gaseous components and the components in the adsorbed phase solution. Adsorbed-phase activity coefficients are calculated from the Wilson equation, with the binary interaction coefficients obtained from pure component adsorption data. Thus, only pure component adsorption data are required to make binary and multicomponent adsorption predictions with the new model.

Two binary (CH₄+CO₂) gas adsorption experimental data sets with coal as the adsorbent and one binary (CH₄+CH₄) gas adsorption data set with activated carbon as the adsorbent are used to test the predictions of the new model. In most cases the new model is able to predict binary gas adsorption accurately. The poor fit of the Wilson equation to the D-A-derived activity coefficient data for some pure component data suggests that some improvement in model predictions could be made with the choice of a different activity coefficient equation.

A unique feature of the current model is the ability to predict multicomponent gas adsorption at different temperatures from the pure component adsorption data collected at a single temperature. The temperature independence of pure component "characteristic" curves, as demonstrated in Dubinin-Polanyi theory, allows pure component adsorption to be predicted for a range of temperatures. These pure component data can then be used in modeling binary or multicomponent adsorption data at various temperatures. This is demonstrated for one experimental binary gas adsorption data set.

Introduction
Adsorption is the primary storage mechanism of gas in coal reservoirs. Adsorption models are often coupled with material balance calculations to determine coalbed gas EUR and to forecast gas production. Complicating these calculations is the fact that coalbed gas, in some cases, is composed of mixtures of components such as methane, carbon dioxide, nitrogen, and heavier hydrocarbons (>C₂), although methane is commonly the most abundant component.

During pressure depletion, the primary recovery mechanism for coalbed gas production, produced gas composition may evolve as the most strongly adsorbed components are held preferentially until relatively low pressures are reached. For example, in the San Juan Basin Fruitland coal "Fairway," coal gases initially (prior to depletion) consisted mainly of methane (>90 mole%) and carbon dioxide (<10 mole%). During primary depletion, carbon dioxide, which is more strongly adsorbed than methane, has steadily increased in concentration in the produced gas stream. Today, carbon dioxide concentrations in the produced gas stream may exceed 20 mole%. The prediction of gas composition evolution during depletion is desirable so that the commercial value of the produced gas stream may be forecast. Accurate binary gas adsorption models are thus required in some cases for economic modeling of primary coalbed gas recovery.

An additional application of binary or multicomponent adsorption models is in the prediction of methane recovery as a result of ECBM mechanisms or storage of carbon dioxide for the purposes of sequestration. The former process involves the injection of non-hydrocarbon gases, such as nitrogen or carbon dioxide, for the purpose of increasing the recovery of methane, while the latter process involves the injection of (pure) carbon dioxide or flue gases in an effort to reduce greenhouse gas emissions. The Alberta Research Council has proposed that both processes could be employed simultaneously to achieve sequestration of carbon dioxide while improving methane recoveries from coalbed gas systems. Recently, Bustin has proposed that hydrogen sulfide could also be used as an ECBM gas, which would facilitate its disposal in the subsurface.

Numerous multicomponent adsorption models have been applied to binary and tertiary component coal gas adsorption data. Some success (accurate predictions) has been achieved with both Ideal Adsorbed Solution (IAS) and 2D equation-of-state (2D EOS) models, both of which have a rigorous thermodynamic derivation. Poorer predictions are often yielded by the extended Langmuir model, which is not thermodynamically consistent. Numerous other models, which have not been used extensively for coal gas systems also exist. None of the models have been extensively tested against field data to determine their success in predicting adsorbed or produced gas compositions during primary or enhanced recovery.

The current study introduces another model for use in coal gas binary adsorption predictions. This model, which is a hybrid of Dubinin-Polanyi and vacancy solution theories, uses pure gas adsorption isotherms only for multicomponent predictions, is easily applied analytically, and has a rigorous thermodynamic derivation. One of the unique features of the model is the simple prediction of temperature effects upon multicomponent adsorption, which is a result of the use of adsorption potential theory in its derivation. For field applications, this may be of importance where injected gas (for ECBM or greenhouse gas sequestration) and reservoir gases are at different temperatures. Additionally, reservoir temperatures may vary (as a function of depth or local temperature

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236 September 2003 SPE Journal
pores. Dubinin used adsorption on zeolites as proof of the volume-fills the adsorption space by means of the mechanism of volume-filling theory. The Langmuir model is based upon the assumption that a state of dynamic equilibrium exists (at constant T and P) between adsorbed and nonadsorbed species, and that adsorption is restricted to a single monolayer. The adsorbent surface is assumed to be energetically homogeneous with respect to adsorption. The Langmuir equation has two parameters that may be optimized for fitting adsorption data (b and n_L) is simple in form, and has been fit successfully to coal methane adsorption data.

Recently, Dubinin-Polanyi theory, herein referred to as the combination by Dubinin and his coworkers of the potential theory developed by Polanyi and the theory of volume filling of micropores, has been applied to methane adsorption on coal. A fundamental difference between Dubinin-Polanyi theory and Langmuir theory is in the assumed mechanism of pore-filling for microporous solids, such as activated carbons. In Langmuir theory, the adsorbed phase is assumed to occupy a monolayer on the adsorbent surface, which in turn is assumed to be homogenous. Dubinin-Polanyi theory assumes that, in micropores, the adsorbate fills the adsorption space by means of the mechanism of volume filling, and therefore does not form discrete monolayers in the pores. Dubinin used adsorption on zeolites as proof of the volume-filling mechanism.

Coal is a microporous solid; therefore, it is natural to want to apply adsorption equations that have been successful in modeling adsorption data for other microporous solids. Two equations have been developed by Dubinin and his coworkers for correlating adsorption data on microporous solids: the Dubinin-Radushkevich (D-R) equation and the D-A (Eq. 9 in this text). The Dubinin equations have been used with success to correlate a large amount of adsorption data, and have been particularly useful in application to adsorption on activated carbon. The equations, like the Langmuir equation, are simple in form. To date, however, the Dubinin equations have not been used extensively for correlating methane adsorption on coals.

Aside from the applicability of the Dubinin equations to microporous solids such as coal, Dubinin-Polanyi theory has an additional attribute that makes its application to coal desirable: prediction of temperature dependence of adsorption. As will be discussed in detail below, correlation of adsorption data at one temperature may be used to predict adsorption at other temperatures.

### Multicomponent Adsorption

The extended Langmuir model and IAS theory are most commonly used for the prediction of mixed gas adsorption on coal. Both the extended Langmuir model and IAS theory require pure component isotherm data for multicomponent predictions. The simplest model used for prediction of multicomponent adsorption isotherms is the extended Langmuir equation:

\[
n_i^* = \frac{n_i^* P_i}{1 + \sum_j b_j P_j}
\]

where \(n_i^*\) and \(b_i\) = the pure gas isotherm Langmuir constants. Partial pressures of the component gases in the free gas phase are determined with the following equation:

\[
P_i = P_i^0 e^{-\frac{H_i}{RT}}
\]

where \(P_i\) = the gas (vapor) pressure of the pure component adsorbed at the same temperature and spreading pressure as the solution, \(P_i^0\) = the gas vapor pressure of the pure component ad-sorbed at the same temperature and spreading pressure as the solution. The spreading pressure \(\gamma_i\) may be substituted for pressures in Eq. 4 to account for gas phase nonidealities. The spreading pressure for the pure components may be determined through integration of the Gibbs adsorption isotherm to the vapour pressure of the pure component, \(P_i^0\):

\[
\pi_i^0 = \frac{P_i^0}{RT} = \frac{1}{RT} \int^P P \frac{dP}{P_i^0}
\]

where \(\pi_i^0\) = the pure component adsorption isotherm. The spreading pressure \(\gamma_i\) may be defined as the reduction in surface tension of a surface owing to the spreading of the adsorbate over the surface. Any pure component isotherm equation can be used to evaluate Eq. 5.

Mole fraction constraints include

\[
\sum_{i=1}^{N} X_i = 1; \sum_{i=1}^{N} Y_i = 1
\]

The total amount of adsorbed gas in the mixture (for an ideal solution) is given by

\[
\frac{1}{n_i^*} = \sum_{i=1}^{N} \frac{X_i}{n_i^*}
\]

The actual amount of each component adsorbed in the mixture is given by

\[
n_i^* = n_i^* X_i
\]

Eq. 5 may be evaluated for each component using an isotherm equation, such as the Langmuir single-component isotherm equation, or may be determined graphically. The IAS model has also been modified to include nonidealities in the adsorbed and gaseous phases and has been used to model multicomponent coal adsorption data.

Recently, 2D EOS models have been applied to coal adsorption data with some success. These models are 2D analogs of the popular 3D EOS, such as those of van der Waals and Peng-Robinson. Hall et al. demonstrated that IAS and 2D EOS models give similar predictions for binary gas adsorption on coal, but are more accurate than the extended Langmuir equation.

### New Model Derivation

Suwanayuen and Danner applied the concept of a “vacancy” solution to the modeling of single- and multicomponent gas adsorption. The vacancy solution model (VSM), as developed by those authors, uses the concept of vacancy solutions, originally described by Dubinin, and a thermodynamic treatment similar to that of Lucassen-Reynders. Details of the VSM derivation will not be discussed here, but the conceptual model will be introduced.

The VSM treats the components in the adsorbed solution as a mixture of a hypothetical solvent called “vacancy,” with adsorbate species. The gaseous solution, in (osmotic) equilibrium with the adsorbed solution, is also treated as a mixture of these components.
The equilibrium relationship between the two vacancy solutions can be derived from basic thermodynamic principles; the equilibrium between the bulk (gaseous) solution and the 2D adsorbed phase solution is treated analogously to the equilibrium between multicomponent vapor and liquid solutions. Adsorbed solution nonideality is accounted for with the use of an activity coefficient. The main difference between the VSM of Suwanayuen and Danner,9,10 and that of Cochran et al.18 is that the compositional dependence of the activity coefficient is described by the Wilson equation in the work of the former authors and by the Flory-Huggins activity coefficient equations in the work of the latter authors.

The model developed in the current work uses the concept of equilibrium between the gaseous phase and an adsorbed-phase vacancy solution. The single-component isotherms utilized in the new model are based upon the Dubinin-Polanyi theory. Significant procedural differences exist between the current VSM approach and that of other authors because of the treatment of the gaseous and liquid solutions as bulk solutions, as with traditional vapor-liquid equilibria. The concept of a spreading pressure, as used for 2D adsorbed phase treatments, is thus eliminated. The development of the new VSM, referred to as VSM-DA, is detailed below for single- and binary-gas adsorption. The new model combines the analytical simplicity of the models described previously, is thermodynamically rigorous, and has the added feature of being able to predict temperature dependence of adsorption.

**Single-Component Adsorption.** As with the VSM, the current model treats single-component adsorption as a binary mixture of a single-component gas with a hypothetical vacancy species that also occupies spaces that could be filled with adsorbate. The D-A equation is used to generate activity coefficients for the single-component gas in the binary mixture.

Chen and Yang23 demonstrated that the D-R and D-A equations were approximations of an adsorption isotherm equation that they derived from statistical thermodynamic principals. A theoretical basis for the D-R and D-A equations was thus established. The equivalence of the D-A equation with Chen and Yang's isotherm is shown with the following equation (Eq. 30 in Chen and Yang23):

\[
\ln \theta = \frac{kT}{\beta F} \ln \left( \frac{P}{P_o} \right) - \frac{RT}{\beta F} \ln \left( \frac{P}{P_o} \right) = \frac{RT}{\beta F} \ln \left( \frac{P}{P_o} \right) \tag{9}
\]

where \( \theta = W/W_o \).

Eq. 9 is the D-A equation with the following constraint:

\[
\alpha = \frac{\beta}{RT} \quad \tag{10}
\]

Eq. 9 was derived by equating the chemical potential for the bulk (gas) phase and the adsorbed phase at temperature \( T \) for two different gas pressures, \( P \) and \( P_o \). The two relationships were summed and several further approximations yielded Eq. 9. The following critical approximation was used in the derivation of Eq. 9:

\[
\ln \theta = \left[ \frac{kT}{\beta F} \ln \left( \frac{P}{P_o} \right) \right] \tag{11}
\]

which is approximately valid for moderate values of \( \theta \). If this assumption is not made, then Eq. 9 may be rewritten with some algebraic manipulation as

\[
\ln \theta + \frac{RT}{\beta F} (-\ln \theta)^{1/\alpha} \ln \left( \frac{P}{P_o} \right) = 0 \quad \tag{12}
\]

Using Eq. 10, Eq. 12 becomes

\[
\ln \theta + \frac{RT}{\beta F} (-\ln \theta)^{1/\alpha} \ln \left( \frac{P}{P_o} \right) = 0 \quad \tag{13}
\]

which is a more general form of the D-A equation. This equation may be fitted to experimental isotherm by optimizing the parameters \( W_o, n, \) and \( D = \frac{E_\beta}{RT} \). Despite the successful application of the D-A equation to many adsorption systems, the D-A equation (as well as the D-R equation) has been criticized because of an incorrect low-pressure limit. Recently, Sundaram24 proposed a modification to the Dubinin isotherm that incorporates a Henry's law limit.

In the current work, the adsorbed phase is treated as a bulk mixture of the hypothetical vacancy species and the single-component adsorbate. Nonideal solution theory may then be used to model the adsorbed-phase behavior, starting with the definition of the chemical potential of the single component (nonvacancy) in the adsorbed and gaseous phases.

**Adsorbed Phase.**

\[
\mu^s = \mu_0^s + RT \ln \gamma^s X^s \quad \tag{14}
\]

where

\[
\gamma^s = \frac{P}{X^s P_o} \quad \tag{15}
\]

If \( \gamma^s = 1 \), then Raoult's law results.

**Gaseous Phase.** Assuming ideal gas behavior,

\[
\mu^g = \mu_0^g + RT \ln \left( \frac{P}{P_o} \right) \quad \tag{16}
\]

If the chemical potential of the component in the gas phase and adsorbed phase are equated (equilibrium),

\[
\mu^s + RT \ln \gamma^s X^s - \mu^g - RT \ln \left( \frac{P}{P_o} \right) = 0 \quad \tag{17}
\]

If the reference state for the gas phase is chosen as the saturated vapor pressure at temperature \( T \), then

\[
\ln \gamma^s X^s - \ln \left( \frac{P}{P_o} \right) = 0 \quad \tag{18}
\]

In the work by Suwanayuen and Danner,9 the assumption was made that the mole fraction of the adsorbed phase (nonvacancy) component was equal to the fractional coverage. If the assumption is made that the degree of pore-filling is equal to the mole fraction of the adsorbate in the current work, then Eq. 18 becomes

\[
\ln \gamma^s X^s - \ln \left( \frac{P}{P_o} \right) = 0 \quad \tag{19}
\]

A method of determining the adsorbed-phase activity coefficient is obtained if Eq. 19 and Eq. 13 are equated (noting that \( P^s = P_o \)):

\[
\ln \gamma^s + \frac{\beta E_\beta}{RT} (-\ln \theta)^{1/\alpha}, \quad \exp \left[ \ln \theta + \frac{\beta E_\beta}{RT} (-\ln \theta)^{1/\alpha} \right] = \exp \left[ \frac{\beta E_\beta}{RT} (-\ln \theta)^{1/\alpha} \right] \quad \tag{20a}
\]

If Eq. 9 is used in the derivation of the activity coefficient instead of Eq. 13, then

\[
\gamma^s = \frac{\beta E_\beta}{RT} (-\ln \theta)^{1/\alpha} \quad \tag{20b}
\]

Thus, a method for generating adsorbed phase activity coefficients is obtained.

A method for predicting multicomponent activity coefficients from the single-component data (binary vacancy solutions) is required to model multicomponent adsorption data. The Wilson equation is chosen to fit the activity coefficients calculated from Eq. 20 by optimizing the binary interaction coefficients. The equation for the adsorbate component (nonvacancy) in the adsorbed phase is

\[
\gamma^s = \exp \left[ \frac{1 - \ln (X^s_{11} + X^s_{1v})}{X^s_{11} + X^s_{1v}} \right] \quad \tag{21}
\]

**Multicomponent Adsorption.** The case of binary gas adsorption is used here, but the following procedures may be extended to.
multicomponent adsorption. For binary gas adsorption, vacancy solution theory requires that binary equilibrium adsorption be treated as equilibrium between ternary vacancy solutions (two adsorbates+vacancy). The chemical potential of an adsorbate component in the adsorbed and gaseous phases becomes:

**Adsorbed Phase.**

\[ \mu_i = \mu_i^* + RT \ln \gamma_i X_i^s \]  
where \( i = 1, 2 \) for adsorbed (nonvacancy) components.

**Gaseous Phase.** Assuming ideal gas behavior,

\[ \mu_i = \mu_i^s + RT \ln \left( \frac{P_i^s}{P} \right) \]  

If the chemical potential of the component in the gas phase and adsorbed phase are equated (equilibrium),

\[ \mu_i^s + RT \ln \gamma_i X_i^s + RT \ln \left( \frac{P_i^s}{P} \right) \]  

Because the standard state for the adsorbed and gaseous components are assumed to be equal, then

\[ \ln \gamma_i X_i^s = \ln \left( \frac{P_i^s}{P} \right) \]  

As with Suwanayuen and Danner,\(^{10}\) the following relationships are assumed:

\[ X_i^s = X_i \theta, \]  
where \( \theta = \frac{n_i^s}{n_i^o}. \)

Substituting Eq. 26 into Eq. 25,

\[ \ln \gamma_i X_i \theta = \ln \left( \frac{Y_i P_i^s}{P} \right) \]  
where Dalton’s law is assumed for component partial pressure.

The activity coefficient for each component in the ternary adsorbed solution may be described by the Wilson equation:

\[ \gamma_i^s = \exp \left[ \frac{1 - \ln(X_i^s + X_j^s \Lambda_j + X_k^s \Lambda_k)}{X_i^s + X_j^s \Lambda_j + X_k^s \Lambda_k + X_i^s \Lambda_j + X_i^s \Lambda_k + X_j^s \Lambda_j + X_k^s \Lambda_k} \right] \]  

where \( i, j = 1, 2, 3. \)

An expression is now required for \( n_i^m \), the maximum total number of moles in the adsorbed mixture. The expression utilized by Suwanayuen and Danner\(^ {10} \) for the adsorbed vacancy solution is adopted here:

\[ n_i^m = \gamma_i X_i^s \]  

**Calculation Procedure.**

The following procedure is required to calculate mixed gas adsorption equilibrium compositions and total mixed gas adsorption isotherms from the pure component data, using the example of binary gas adsorption:

1) Use Eq. 13 or Eq. 9 to obtain the parameters \( W, n, \) and \( E \) for each component through regression from experimental data. \( P_i^s \) in Eq. 13 or Eq. 9 is calculated using the reduced Kirchoff equation (Kapoor et al.\(^ {25} \)). In the case of experimental data expressed as \( n_i^f \) as a function of pressure, \( \theta = n_i^f / n_i^o \), and therefore \( n_i^m \) is optimized instead of \( W \). In the current work, a least-squares routine coupled with a multiparameter optimization algorithm in MATLAB\(^ {30} \) was used to optimize the isotherm parameters. Multiparameter optimization runs were re-initiated at several starting points to ensure that the convergence to the same point occurred.

2) Calculate the activity coefficients as a function of degree of filling for each component using the regressed parameters, calculated in Step 1, and Eq. 20.

3) Calculate binary interaction coefficients \( A_{ij}, A_{ji} \) by fitting Eq. 21 to the activity coefficient curve generated by Eq. 20 (Step 2); for simplification, \( \Lambda_{11}, \Lambda_{1n} \) may be assumed equal to unity.

4) Assume a value for \( X_1 \) (\( X_2 = 1 - X_1 \)).

5) Calculate \( n_i^m \) from Eq. 29.

6) Use Eq. 28 to calculate the activity coefficients for the adsorbed components.

7) Solve the two equilibrium equations (components \( i \) and \( j \)) derived from Eq. 27 simultaneously for \( Y_1 \) (\( Y_2 = 1 - Y_1 \)) and \( n_i^m \).

**Temperature Invariance Condition**

Eq. 9 and the D-R equation (assuming \( n = 2 \)) were derived from the following relation:

\[ \frac{\theta}{E} = \frac{A}{E} \]  
where

\[ A = RT \ln \left( \frac{P}{P_i^s} \right) \]  

and

\[ E = E \beta \]  

A unique feature of Dubinin-Polanyi theory is that characteristic curves, or plots of \( \theta \) vs. \( A \), are temperature-invariant for many adsorption systems (particularly for gas and vapor adsorption on carbonaceous adsorbents). If this is the case for a given adsorption system, then \( E \) and \( n \) are also temperature-invariant. Thus, if \( E \) and \( n \) are derived from an isotherm at one temperature, then isotherms at different temperatures may be easily derived. Dubinin\(^ {3} \) discusses the range of \( \theta \) for which the temperature-invariance condition holds.

Illustrations of how the temperature-invariance principle can be used to calculate single-component isotherms for coal gas systems at different temperatures have been discussed elsewhere (i.e., Ruppel et al.\(^ {13} \) and Clarkson et al.\(^ {14} \)). The current study uses the new multicomponent adsorption model derived above to calculate binary gas total adsorption at different temperatures. Procedurally, this is achieved as follows:

1) Follow Steps 1 and 2 in the previous section using single-component isotherms at one temperature.

2) Recalculate \( D = \frac{E \beta}{RT} \) for both component gases at the new temperature(s), assuming \( E \) is temperature-invariant.

3) Follow Steps 2 through 7 in the previous section to calculate binary adsorption amounts at the new temperature.

Implicit in the above procedure is that \( n_i^m \) or \( W \) is temperature-invariant. Dubinin\(^ {3} \) provides a method for correcting for the temperature dependence of the maximum adsorbed amount.

**Application of Model to Binary Gas Adsorption Data Sets**

Three binary gas adsorption data sets were chosen to test the new model predictions: \( \text{CH}_4+\text{CO}_2 \) binary gas adsorption on moist Fruitland coal data of Hall et al.\(^ {6} \), \( \text{CH}_4+\text{CO}_2 \) binary gas adsorption on dry Westcliff Bulli seam-coal data of Stevenson et al.\(^ {17} \), and \( \text{CH}_4+\text{C}_2\text{H}_6 \) binary gas adsorption on activated carbon data of Reich et al.\(^ {28} \). The new model predictions are compared graphically against those of IAS theory,\(^ {16} \) using the Langmuir equation to model single-component adsorption data.
and for their binary mixtures at 115°F on moist Fruitland coal at pressures up to 1,800 psia. Only the CH$_4$+CO$_2$ data is modeled here. CO$_2$ isotherm data for pressures below 1,010 psia were used because of the inflection adsorption data at higher pressures, as discussed in Hall et al.$^6$ The feedgas compositions used for binary adsorption were 20, 40, 60, and 80%, thus providing a large range in compositions that are ideal for model testing.

The fit of the D-A equation (Eq. 13 is plotted) to CH$_4$ and CO$_2$ isotherm data is shown in Fig. 1a. Eq. 9 gave a very similar match, and is not plotted. The quality of fit (%AAD, see Table 1 for definition) for the D-A and Langmuir equation is also shown in Fig. 1a. Note that the %AAD is given for the D-A Eq. 9 instead of Eq. 13 (which is plotted in the figure). The reason for this is that Eq. 9 can be written explicitly in terms of the adsorbed amount (Eq. 13 cannot), facilitating a direct comparison with the Langmuir equation because the adsorbed amount is used in the least-squares function for both Eq. 9 and the Langmuir equation (as opposed to ln$P/P_0$ for Eq. 13).

Fig. 1—(a) Hall et al.$^6$ CH$_4$ and CO$_2$ isotherm data (115°F) and model fits; (b) Stevenson et al.$^{17}$ CH$_4$ and CO$_2$ isotherm data (86°F) and model fits.

Optimized parameters for the D-A and Langmuir equations are given in Tables 2a and 2b. The optimized parameters for the D-A equations (Eq. 9 and Eq. 13) were obtained from using ln$P/P_0$ (experimental and calculated) in the least-squares function, as opposed to adsorbed amount (experimental and calculated) for the Langmuir equation.

The Langmuir equation fit to the data is not as good as the D-A equation, as discussed previously.$^{27}$ This is because the D-A equation has three optimized parameters vs. two for the Langmuir equation.

The pure component gas adsorbed-phase activity coefficients generated from the D-A equation (Eq. 20a and Eq. 20b) for CH$_4$ and CO$_2$ are shown in Figs. 2 and 3, along with the Wilson equation fit to the activity coefficient curves. The Wilson equation was fit to the activity coefficient curve over the pore-filling range represented by the experimental data. The Wilson equation fit is not particularly good over the range of pore-filling shown, suggesting that another activity coefficient equation may be more
appropriate for binary interaction parameter calculation. Equilibrium (isobaric) compositional diagrams at 1,800, 1,000, and 120 psia are shown in Figs. 4a through 6a. The new model predictions (using activity coefficients calculated from Eq. 20a and Eq. 20b), along with those of IAS theory, are shown. The new model predictions are comparable, if not slightly better than, IAS theory. The predictions using Eq. 20b to model single-component adsorbed phase activity coefficients are better than those using Eq. 20a, as demonstrated in Table 1, which summarizes the relative error calculations for total adsorption and gaseous-phase mole fraction.

Total adsorption vs. gaseous-phase mole fraction is shown in Figs. 4b through 6b for 1,800, 1,000, and 120 psia. At 1,800 psia, the new model underpredicts the total adsorption for high values of CO₂ gaseous-phase mole fraction because of the inflection in CO₂ adsorption at high pressures. Overall, the model predictions for total adsorption are very good, being within 10% of the experimental data.

CH₄+CO₂ Adsorption Data on Dry Bulli Seam Coal. Stevenson et al.¹⁷ collected adsorption data for pure CH₄ and CO₂ (as well as N₂) and their binary and ternary mixtures at 86°F on dry Westcliff Bulli seam coal at pressures up to 850 psia. Again, only the CH₄+CO₂ data are modeled. The feedgas compositions for the Stevenson et al.¹⁷ binary data set span a wide range as with the Hall et al.⁶ data set. The new model predictions, using Eq. 20b to calculate pure component adsorbed-phase coefficients, are shown only.

The fit of the D-A equation (Eq. 13 is plotted) to CH₄ and CO₂ isotherm data is shown in Fig. 1b. As with Fig. 1a, %AAD is given for the D-A Eq. 9 (using adsorbed amount in the least-squares function) instead of Eq. 13. Optimized parameters for the D-A and Langmuir equations are given in Tables 3a and 3b. The optimized parameters for the D-A equations (Eq. 9 and Eq. 13) were obtained from using lnP/Po (experimental and calculated) in the least-squares function, whereas the adsorbed amount (experimental and calculated) was used for the Langmuir equation. The Langmuir equation fit to the data is also shown, and is not as good as the D-A Eq. 9, as with the Hall et al.⁶ data set. Note that the units of adsorption in Fig. 1 are kept consistent with the original authors, even though the pressure axis was changed from units of kPa to psia.

CH₄+C₂H₆ Adsorption Data on Activated Carbon: Temperature Dependence Predictions. The CH₄+C₂H₆ pure and binary gas adsorption data of Reich et al.²⁶ are used to test the predictions of the new model for adsorption at various temperatures. This data set was chosen as the pure, and binary data was collected at various temperatures.

The ability of the new multicomponent adsorption model to predict adsorption as a function of temperature is contingent upon the temperature invariance of the characteristic energy of adsorption, E, and the D-A exponent n. The CH₄ and C₂H₆ pure component isotherms at 8.7°F were first fit with Eq. 9, and the parameters n₁°, n₂°, and D, obtained from nonlinear regression. The pure component isotherms at 82.9°F were then predicted from the 8.7°F isotherm data by recalculating the D parameter at 82.9°F. This is done by assuming E is temperature-invariant, and by using the following relation:

<table>
<thead>
<tr>
<th>Adsorte</th>
<th>Temperature (°F)</th>
<th>D-A (Eq. 9)</th>
<th>D-A (Eq. 13)</th>
<th>VSM-D-A (using Eq. 20a)</th>
<th>VSM-D-A (using Eq. 20b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>115</td>
<td>1.112</td>
<td>1.049</td>
<td>25.593</td>
<td>8.399</td>
</tr>
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<td></td>
<td></td>
<td>2.962</td>
<td>2.053</td>
<td>0.304</td>
<td>1.852</td>
</tr>
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<td></td>
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<td>1.641</td>
<td>2.579</td>
<td>18.307</td>
<td>8.426</td>
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<td>CO₂</td>
<td>115</td>
<td>1.475</td>
<td>1.475</td>
<td>8.671</td>
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<tr>
<td></td>
<td></td>
<td>2.713</td>
<td>1.205</td>
<td>1.815</td>
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</tr>
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\[ \text{%AAD} = \frac{100}{N_f} \sum_{j=1}^{N_p} \text{abs} \left[ \frac{n_{\text{calcd}}(j) - n_{\text{exp}}(j)}{n_{\text{exp}}(j)} \right] \text{ for each } n_{\text{calcd}}, \text{ and percent average absolute deviation} \]

\[ \text{%AAD} = \frac{100}{N_f N_p} \sum_{j=1}^{N_p} \sum_{i=1}^{N_c} \text{abs} \left[ \frac{Y_{\text{calcd}}(j) - Y_{\text{exp}}(j)}{Y_{\text{exp}}(j)} \right] \text{ for each } Y_{\text{calcd}}, \text{ where } N_f = \text{number of data points and } N_p = \text{number of components} \]
The pure component isotherms are then calculated at the new temperature (82.9°F) using the $D$ parameter, adjusted for temperature, $n$, and $n_1$, calculated from the 8.7°F pure component data. In this analysis, $n_1^\infty$ is not adjusted for the thermal expansion of the adsorbate (i.e., Dubinin). The procedure for calculating the binary gas equilibrium at the new temperature then follows that described in the Calculation Procedure section given above.

The fit of the D-A Eq. 9 to the pure component data at 8.7°F, the 82.9°F predictions, and the experimental data are shown in Fig. 2.

![Graphs](image)

**Fig. 2**—(a) CO$_2$ activity coefficient plot, derived from D-A (Eq. 20a); (b) CH$_4$ activity coefficient plot, derived from D-A (Eq. 20a).
Optimized parameters (using $\ln(P/P_0)$ in least-squares function) for the D-A equation are given in Table 5. The prediction of adsorption at 82.9°F is reasonable at low pressures, but some deviation occurs at high pressures. The deviation is likely caused by the fact that $n_1$ was not corrected for thermal effects.

Table 6 summarizes the relative error calculations for the VSM-D-A model applied to the 8.7°F binary (74.5% CH$_4$/25.5% C$_2$H$_6$) adsorption data.

The predictions for binary (74.5% CH$_4$/25.5% C$_2$H$_6$) gas total adsorption at 82.9°F are shown in Fig. 10b. The predictions are very good, with only small deviation occurring at high pressure.

**Discussion**

The proposed multicomponent adsorption model, which is a hybrid of the Dubinin-Polanyi and vacancy solution theories, describes binary gas adsorption behavior of coal systems quite well, although some improvements could possibly be made.

The Wilson equation has been used to model pure gas (binary with inclusion of vacancy species) adsorbed-phase activity coefficients, as well as the binary gas (ternary with inclusion of vacancy species) adsorbed-phase activity coefficients. It is apparent that the Wilson equation fit to the pure component data is not optimal, and is likely the cause of some error in binary predictions. The original vacancy solution theory also utilized the Wilson equation to model nonideality in the adsorbed-phase solution, but improvements were later made by incorporating the Flory-Huggins activity coefficient equations. Future studies will include the application of other activity coefficient equations and their effect upon the new model predictions.

The development of the new model assumed that the gaseous phase behaved ideally, and thus activity coefficients for the gaseous phase were not included. Although this assumption is not necessary, it reduces computational complexity. Some insight into the effect of noninclusion of gas-phase nonideality corrections...
upon predictions may be obtained from a study by Manik. In this study, predictions of binary gas adsorption were compared by using IAS theory with (IAS-RG) and without (IAS-PG) correction for gas-phase nonideality. The data set of Stevenson et al. was used. Equilibrium concentration and adsorption capacity predictions for IAS-RG and IAS-PG appear to be in good agreement for low (120 psia) and high (800 psia) pressures. The impact of the ideal gas assumption upon binary gas prediction for the new model is similarly expected to be small, but will be studied in future work.

**Conclusions**

1. A new multicomponent adsorption model, which was derived by combining the vacancy solution and Dubinin-Polanyi theories, is reasonably accurate for binary gas/coal adsorption systems.
2. Adsorbed-phase activity coefficient curves derived for pure component adsorption are not accurately fit by the Wilson equation, causing some error in binary gas predictions.
3. Improvements to the new model could be made through the use of different activity coefficient equations and the incorporation of gaseous-phase activity coefficients.
4. The prediction of adsorption temperature dependence is easily achieved with the new model, owing to the incorporation of Dubinin-Polanyi theory. Limited testing of the model (over a small temperature range) illustrates these predictions to be accurate.

**Nomenclature**

- $A$: specific surface area of adsorbent, $m^2/g$
- $b$: Langmuir model constant, $1/psi$
- $D$: $E_B T$, D-A equation parameter, dimensionless
- $E_o$: characteristic energy of adsorption for standard vapor, $J/mol$
- $k$: Boltzmann’s constant, $1.381 \times 10^{-23}$ $J/K$
- $K$: constant in Eq. 9
- $n$: constant in Dubinin-Astakhov equation, dimensionless
- $n_L$: Langmuir model constant, $mol/g$
- $n'$: number of moles of pure component in the adsorbed phase (Eq. 1), $mol/g$
- $n_i'$: number of moles of component $i$ in the adsorbed phase mixture, $mol/g$
Fig. 5—(a) Binary CH₄+CO₂ equilibrium compositions; (b) binary CH₄+CO₂ total adsorption: 1,000 psi.

\( n_i^{eq} \) = amount of pure component adsorbed from pure gas at the same temperature and spreading pressure as the adsorbed mixture (Eq. 7), mol/g

\( n_i^{\infty} \) = maximum number of moles of component \( i \) in the adsorbed phase mixture, mol/g

\( n_m^s \) = number of moles of mixture in the adsorbed phase, mol/g

\( n_m^{\infty} \) = maximum number of moles of mixture in the adsorbed phase, mol/g

\( N_c \) = number of components

\( N_A \) = Avogadro’s number, \( 6.022 \times 10^{23} \) mol\(^{-1}\)

\( P \) = pressure of the gas phase, psi

\( P_i^* \) = reference-state pressure of the pure component \( i \) chosen as saturated vapor pressure of component \( i \) at the same temperature as adsorbed solution, psi

\( P_o \) = saturated vapor pressure, psi

\( P_i^* \) = reference-state pressure of the pure gaseous component \( i \), or gas (vapor) pressure of the pure component adsorbed at the same temperature and spreading pressure as the solution (Eqs. 4 and 5), psi

\( R \) = universal gas constant, \( 8.314 \) J/mol·K

\( T \) = absolute temperature, K

\( W \) = adsorbed amount at pressure, \( P \), cm\(^3\)/g

\( W_o \) = adsorbed amount at saturated vapor pressure (limiting volume of the adsorption space), cm\(^3\)/g

\( X_i \) = mole fraction of component \( i \) in the adsorbed phase (no vacancy), dimensionless

\( X_i^{eq} \) = mole fraction of component \( i \) in the adsorbed phase vacancy solution, dimensionless

\( Y \) = mole fraction of component \( i \) in the gaseous phase, dimensionless

\( \beta \) = similarity coefficient, dimensionless
Fig. 6—(a) Binary CH₄+CO₂ equilibrium compositions; (b) binary CH₄+CO₂ total adsorption: 120 psi.

\[ \gamma_i \] = activity coefficient of component \( i \) in adsorbed phase vacancy solution, dimensionless

\[ \theta \] = dimensionless loading

\[ \Lambda_i, \Lambda_{ij} \] = Wilson equation parameter, binary interaction constant between components \( i \) and \( j \), dimensionless

\[ \mu_i^\circ \] = reference-state chemical potential of component \( i \) in adsorbed phase vacancy solution, J/mol

\[ \mu_i^o \] = chemical potential of component \( i \) in gaseous phase, J/mol

\[ \mu_i^{\circ g} \] = reference state chemical potential of component \( i \) in gaseous phase, J/mol

\[ \pi \] = spreading pressure, N/m

### TABLE 3A—PARAMETERS OF THE VSM-D-A MODEL DERIVED FROM THE SINGLE-COMPONENT ISOTHERM DATA OF STEVENSON ET AL.¹⁷

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Temperature (°F)</th>
<th>( \rho_i^A ) (g-mole/kg)</th>
<th>( D )</th>
<th>( n )</th>
<th>( \rho_i^{\circ A} ) (g-mole/kg)</th>
<th>( D )</th>
<th>( n )</th>
<th>( \Lambda_{ij} )</th>
<th>( \Lambda_{ji} )</th>
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</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>86</td>
<td>0.824</td>
<td>3.941</td>
<td>1.990</td>
<td>0.733</td>
<td>3.063</td>
<td>4.020</td>
<td>42.091</td>
<td>1.145</td>
</tr>
<tr>
<td>CO₂</td>
<td>86</td>
<td>1.135</td>
<td>3.475</td>
<td>1.518</td>
<td>1.133</td>
<td>2.482</td>
<td>1.747</td>
<td>20.708</td>
<td>2.019</td>
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</table>

September 2003 SPE Journal
Table 3B—Parameters of the Langmuir Model Derived from Single-Component Isotherm Data of Stevenson et al.17

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Temperature (°F)</th>
<th>Langmuir Isotherm Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>86</td>
<td>(n_i) (g-mole/kg)</td>
</tr>
<tr>
<td>CO₂</td>
<td>86</td>
<td>0.662</td>
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<tr>
<td></td>
<td></td>
<td>1.050</td>
</tr>
</tbody>
</table>

\(\pi^*\) = reduced spreading pressure, Eq. 5, mol/g  
\(\Phi\) = potential energy between adsorbate and adsorbent  
(see Chen and Yang²³)  

\(\text{subscripts:}\)  
\(\text{calc}\) = calculated  
\(\text{exp}\) = experimental  
\(i\) = component \(i\)  
\(L\) = Langmuir  
\(m\) = mixture  
\(l\) = adsorbate  
\(v\) = vacancy

Fig. 7—(a) CO₂ activity coefficient plot, derived from D-A (Eq. 20b); (b) CH₄ activity coefficient plot, derived from D-A (Eq. 20b).
Superscripts

- $g$ = gaseous phase value
- $o$ = reference state
- $s$ = adsorbed phase value
- $\infty$ = maximum adsorption limit value

Acknowledgments

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References


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**TABLE 4—PREDICTIONS OF VSM-D-A MODEL FOR METHANE AND CARBON DIOXIDE MIXTURE ADSORPTION DATA OF STEVENSON ET AL.**

<table>
<thead>
<tr>
<th>Quantities</th>
<th>Data Points</th>
<th>Quality of Fit (%AAD*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_f$</td>
<td>30</td>
<td>33</td>
</tr>
<tr>
<td>$n^*_a$</td>
<td>30</td>
<td>3</td>
</tr>
</tbody>
</table>

*Percent average absolute deviation $= \frac{100}{N_p} \sum_{j=1}^{N_p} \frac{\text{abs}[n^*_a(j) - n^*_a \text{exp}(j)]}{n^*_a \text{exp}(j)}$ for $n^*_a$, and percent average absolute deviation $= \frac{100}{N_p} \sum_{j=1}^{N_p} \sum_{i=1}^{N_c} \frac{\text{abs}[Y_{\text{calc}}(j) - Y_{\text{exp}}(j)]}{Y_{\text{exp}}(j)}$ for $y_i$, where $N_p$ = number of data points and $N_c$ = number of components.
Fig. 10—Reich et al. CH₄ and C₂H₆: (a) isotherm data and model fits; (b) binary (CH₄+C₂H₆) total adsorption data. The prediction of temperature dependence is shown.

17. Stevenson, M.D. et al.: “Adsorption/Desorption of Multicomponent Gas Mixtures at In-Seam Conditions,” paper SPE 23026 presented at
Christopher R. Clarkson is a senior reservoir engineer with Burlington Resources Canada Ltd. e-mail: cclarkson@br-inc.ca. His work focus has been on exploration for and development of coalbed methane reservoirs. He has studied both primary and enhanced coalbed methane recovery processes in the San Juan basin of New Mexico/Colorado and is particularly interested in the application of reservoir simulation to optimize coalbed gas recovery and well performance. Clarkson holds a PhD degree in geological engineering from the U. of British Columbia, Canada.

TABLE 5—PARAMETERS OF THE VSM-DA MODEL DERIVED FROM SINGLE-COMPONENT ISOTHERM DATA OF REICH ET AL.26

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Temperature (°F)</th>
<th>D-A Isotherm Parameters (D-A (Eq. 9))</th>
<th>Binary Interaction Coefficients From Wilson Equation (VSM-D-A (Eq. 20b))</th>
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</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>8.7</td>
<td>6.300</td>
<td>4.370</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>8.7</td>
<td>6.381</td>
<td>5.197</td>
</tr>
<tr>
<td>CH₄</td>
<td>82.9</td>
<td>6.300</td>
<td>3.773</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>82.9</td>
<td>6.381</td>
<td>4.486</td>
</tr>
</tbody>
</table>


SI Metric Conversion Factors

°F (°F–32)/1.8 = °C

psi × 6.894 757 = E+00 = kPa

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TABLE 6—PREDICTIONS OF VSM-D-A MODEL FOR METHANE AND ETHANE MIXTURE ADSORPTION DATA (74.5–25.5 MOL%, 8.7°F) OF REICH ET AL.26

<table>
<thead>
<tr>
<th>Quantities</th>
<th>Data Points</th>
<th>Quality of Fit (%AAD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>yᵢ</td>
<td>3</td>
<td>VSM-D-A (using Eq. 206)</td>
</tr>
<tr>
<td>nᵢₑ</td>
<td>3</td>
<td>6</td>
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</tbody>
</table>

*Percent average absolute deviation = \( \frac{100}{N_p} \sum_{i=1}^{N_p} | nᵢₑ(j) - nᵢₑ(exp)(j)| / nᵢₑ(exp)(j) \) for nᵢₑ, and percent average absolute deviation = \( \frac{100}{N_p N_c} \sum_{i=1}^{N_p} \sum_{j=1}^{N_c} | Yᵢₑ(j) - Yₑ(exp)(j)| / Yₑ(exp)(j) \) for yᵢ, where N_p = number of data points and N_c = number of components.