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Experimental Uncertainties in Volumetric Methods for Measuring Equilibrium Adsorption

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Knowledge of adsorption equilibrium is essential in many industrial processes, including increasingly important technologies such as fuel cells and CO₂ sequestration. Developing reliable mathematical models for adsorption requires accurate experimental data. Experimental methods based on volumetric, gravimetric, and chromatographic techniques have all been used to obtain such data. Currently, two volumetric methods are widely used to measure supercritical gas adsorption on heterogeneous matrices such as activated carbon and coal. These two methods differ in the manner in which the gas is injected into the equilibrium cell for adsorption. The methods are referred to as “fixed-pressure” and “fixed-volume.” In this paper, we discuss the details of these experimental designs and error analyses for these two volumetric techniques. Case studies involving pure-fluid adsorption measurements are used to demonstrate both the efficacy and pitfalls of these volumetric methods. Further, case studies are also used to highlight differences in the uncertainties associated with calculation of excess adsorption from the experimentally measured quantities. The results indicate that the fixed-volume method is susceptible to larger experimental errors than the fixed-pressure method for equivalent experimental setups. Specifically, for the case study reported here, the average experimental uncertainties in the amount adsorbed for the fixed-pressure and fixed-volume method were 12% and 42%, respectively. These large experimental uncertainties for the fixed-volume method at the higher pressures result mainly from the uncertainty in the amount injected. Further, Monte Carlo analysis was used to validate these findings, yielding comparable results, thus providing confirmation of the analytical expressions used in the error analysis. Our analysis indicates a significant reduction in expected uncertainties of the fixed-volume injection method may be realized by utilizing an optimized ratio of cell volumes (reference and sample cells) and by having the least possible void fraction in the sample cell.

1. Introduction

Our interest in this topic arose when we undertook projects to measure adsorption isotherms to serve as a basis for simulations of coalbed methane (CBM) recovery and the design of optimal CO₂ sequestration processes. Such simulations require an accurate adsorption model to describe the adsorption phenomena, and the models must be validated and/or optimized based on quality experimental data. Since there are different methods available for the measurement of adsorption data, the selection of the most appropriate method should incorporate an analysis of experimental errors. The method that yields the least errors (uncertainties) in the acquired data should form the basis for an optimal experimental method.

The adsorption of gases on adsorbents such as coals and activated carbons increases the fluid density of the adsorbing gases near the surface of the adsorbent. This density increase explains, for example, why a coalbed methane reservoir can hold more gas than would be found in a traditional gas reservoir for the same pressure and volume.

Measuring the amount of gas adsorbed at different temperatures and pressures is not a trivial experiment. The amount of adsorption is a quantity that is calculated from primary measurements such as pressure, temperature, and volume. Further, the amount adsorbed is reported in a variety of ways to satisfy the varying interests of theorists and practitioners in

the field of adsorption. For example, a coalbed methane well operator wants to know the volume of gas that can be extracted from a ton of coal. Such practitioners often use “absolute” adsorption to estimate the amount of gas in a reservoir. A theorist considers the amount of gas adsorbed per unit of adsorbent surface area. An engineer designing compact gas storage containers optimizes the amount of gas adsorbed per unit of volume. An engineer separating gas mixtures through adsorption processes wants to know the relative amounts of each component gas adsorbed, as well as concentration differences between the adsorbed phase and the gas phase.

To limit ambiguities in reporting data, the optimum experimental approach for presenting high-pressure adsorption is to utilize the best definition for an inferred adsorption quantity with the smallest possible number of caveats associated with its inference. For adsorbing gases at high density (i.e., at high pressures), the “excess adsorption” is the experimentally determined quantity most often measured in the laboratory.

Two interlaboratory studies have been conducted to assess the laboratory-to-laboratory reproducibility of high-pressure adsorption isotherms, and the results have been published.^{1,2} However, the estimated uncertainties in the primary measurements reported by the participating laboratories ranged over several orders of magnitude. Our current work is, therefore, partly motivated by the need to (1) conduct an accurate analysis of the estimated uncertainties in the primary measurements of pressure, temperature, and volume, and (2) investigate the key factors affecting the expected uncertainties in the amounts of

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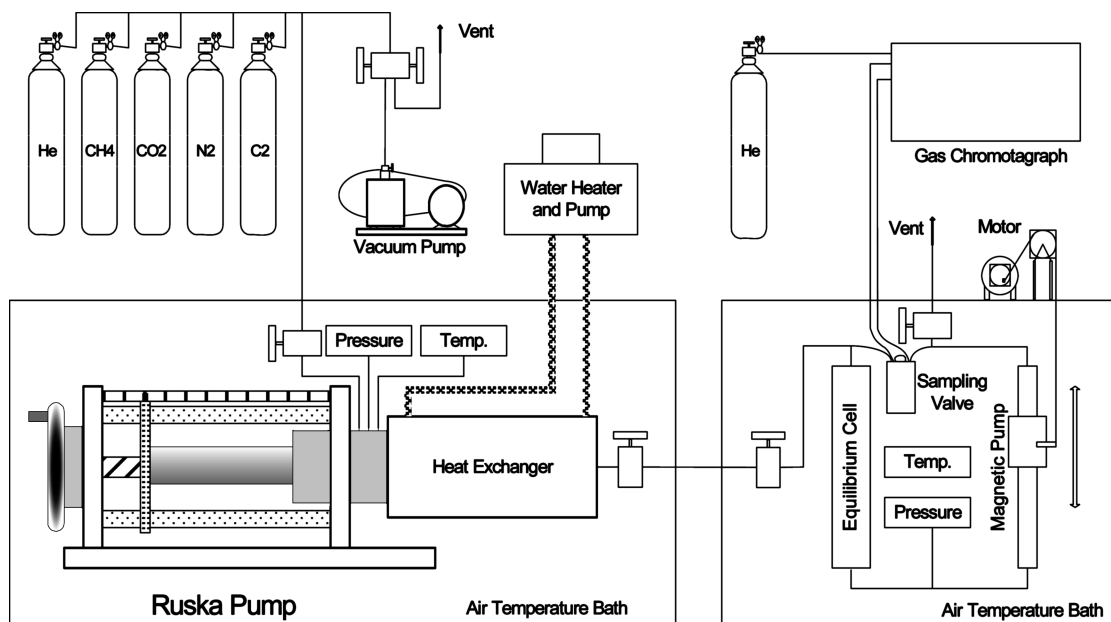


Figure 1. Schematic diagram of the experimental apparatus.

gas adsorbed, thus identifying means by which such uncertainties can be minimized.

This paper discusses the necessary assumptions for measuring the excess adsorption using two types of volumetric techniques. The basic definitions involved and the data reduction methodologies are given for pure-gas and mixed-gas adsorption. An analysis is presented to estimate the expected uncertainties in the calculated excess adsorption as a function of the errors due to random variations in primary measurements such as temperature, pressure, and volume. Case studies are given to compare the expected uncertainties in the two volumetric techniques. Finally, important design considerations that can minimize the expected uncertainties are identified, and their effects in lowering the errors are demonstrated.

2. Pure-Gas Adsorption

For pure-component gases, the excess adsorption, n^{Ex} , is defined as the amount of a gas occupying a phase volume in excess of that which would occur without the presence of a solid surface. The adsorbed gas molecules reside in one or more layers on the surface at a higher density than the gas phase. The volume of space occupied by these layers of adsorbed molecules is called the adsorbed-phase volume, V_{ads} . From a molecular perspective, V_{ads} is the near-wall space where significant fluid–solid interactions exist. The adsorbed-phase density, $\bar{\rho}_{\text{ads}}$, is a value averaged over the adsorbed-phase volume. The mass adsorbed is the amount of gas residing in the adsorbed-phase volume, often referred to as the absolute adsorption, $n_{\text{ads}}^{\text{abs}}$. The absolute adsorption concept envisions the adsorption process as resulting in two distinct, clearly definable phases, an adsorbed phase and a bulk (gas) phase. The absolute adsorption can be written as the product of the adsorbed phase density and volume:

$$n_{\text{ads}}^{\text{abs}} = \bar{\rho}_{\text{ads}} V_{\text{ads}} \quad (1)$$

and the amount unadsorbed is expressed similarly as:

$$n_{\text{unads}} = \rho_{\text{gas}} V_{\text{unads}} \quad (2)$$

However, in eq 1 the adsorbed-phase volume, the adsorbed-phase density, and the absolute adsorption cannot be measured

experimentally in a straightforward manner. This is true for essentially all experimental techniques, including adsorption measurements based on gravimetric or volumetric accounting principles. Both methods have been reviewed in detail elsewhere.³ For completeness and a new perspective, the principles of the volumetric method (used in the present study) are discussed here.

Figure 1 presents the schematic of the experimental apparatus based on fixed-pressure injection method used at Oklahoma State University (OSU). A detailed description of this experimental apparatus is given elsewhere.⁴ For an isothermal adsorption experiment using volumetric methods, a known mass of adsorbent, $m_{\text{adsorbent}}$, is placed in a container. A known amount of gas, n_{inj} , is injected (from another source) into the container with the adsorbent. Under the presumption that an experimental method exists that can measure the amount of gas that remains unadsorbed at equilibrium, n_{unads} , the difference between the amount injected into the container and the amount of unadsorbed gas is called the absolute adsorption, n^{abs} , usually reported on the basis of a unit mass of adsorbent.

$$n^{\text{abs}} = n_{\text{inj}} - n_{\text{unads}} \quad (3)$$

A major concern in determining absolute adsorption is that the amount of unadsorbed gas cannot be determined unambiguously at all experimental conditions. The amount of unadsorbed gas cannot be determined because the volume of unadsorbed gas is not constant since the volume of the adsorbed phase increases with pressure, thus reducing the volume available to the unadsorbed gas. The sum of the adsorbed gas and unadsorbed gas volumes, however, can be presumed to be constant.

(1) Goodman, A. L.; Busch, A.; Duffy, G. J.; Fitzgerald, J. E.; Gasem, K. A. M.; Gensterblum, Y.; Krooss, B. M.; Levy, J.; Özdemir, E.; Pan, Z.; Robinson, R. L.; Schroeder, K.; Sudibandriyo, M.; White, C. M. *Energy Fuels* **2004**, *18* (4), 1175–1182.

(2) Goodman, A. L.; Busch, A.; Bustin, R. M.; Chikatamarla, L.; Day, S.; Duffy, G. J.; Fitzgerald, J. E.; Gasem, K. A. M.; Gensterblum, Y.; Hartman, C.; Jing, C.; Krooss, B. M.; Mohammed, S.; Pratt, T.; Robinson, R. L. Jr.; Romanov, V.; Sakurovs, R.; Schroeder, K.; White, C. M. *Int. J. Coal Geol.* **2007**, *72* (3–4), 153–164.

(3) Keller, J. U.; Dreisbach, F.; Rave, H.; Staudt, R.; Tomalla, M. *Adsorption* **1999**, *5* (3), 199–214.

(4) Sudibandriyo, M.; Pan, Z.; Fitzgerald, J. E.; Robinson, R. L.; Gasem, K. A. M. *Langmuir* **2003**, *19* (13), 5323–5331.

This volume is termed the “void volume” and is equal to the container volume minus the adsorbent volume. The void volume is usually calculated using a “non-adsorbing” gas such as helium; thus, it often is referred to as the helium void volume, which is the container volume excluding the volume of adsorbent that is impenetrable to helium. Equation 4 relates the various volume elements inside a container.

$$V_{\text{Void}}^{\text{He}} = V_{\text{Container}} - V_{\text{Adsorbent}}^{\text{He}} = V_{\text{ads}} + V_{\text{unads}} \quad (4)$$

In determining the helium void volume, the assumption that helium does not adsorb has been explored elsewhere in detail, and Gumma and Talu⁵ proposed a method whereby helium adsorption data are used to estimate a correction for the helium void volume. As they noted, such efforts may not be entirely necessary, and no universal method has been agreed upon to “fix” this problem. All that is required is a thermodynamic reference state, a procedure that has been formalized recently.⁶ If a “helium adsorption” correction is used, its size depends on other experimental system constraints and experimental design features. In other words, an adsorption experiment can be designed that renders the helium adsorption correction negligible in comparison to other experimental errors.

Another assumption is that the adsorbent volume impenetrable to helium is also impenetrable to all other gases. In other words, an adsorbent would not “unfold or unravel” in the presence of a gas (such as CO₂) and thereby have more volume available to that gas (a change in the void volume). These assumptions appear to be valid based on the invariance of helium void volume measurements before and after gas adsorption measurements on dry coals. Others have dealt with the possible case where the void volume changes upon adsorption due to swelling.^{7,8}

In the limit of low pressures (i.e., low amounts adsorbed), the volume of the adsorbed phase is negligible compared to the volume of the unadsorbed phase. Thus, at low pressures, the unadsorbed volume approaches that of the helium void volume:

$$V_{\text{Void}}^{\text{He}} \approx V_{\text{unads}} \quad (\text{at low pressures}) \quad (5)$$

This assumption allows for the calculation of the amount unadsorbed. The absolute amount adsorbed, then, can be calculated using eq 3 by recognizing that the amount unadsorbed is the product of the gas density and the helium void volume:

$$n^{\text{abs}} \approx n_{\text{inj}} - \rho_{\text{gas}} V_{\text{Void}}^{\text{He}} \quad (\text{at low pressures}) \quad (6)$$

In eq 6, the assumption of a zero-volume adsorbed phase affects the accuracy of the inferred absolute amount adsorbed. As pressure increases, the adsorbed-phase volume will grow in size, and the helium void volume will be larger than the actual unadsorbed phase volume. Thus, at higher pressures, eq 6 will underpredict the absolute amount adsorbed. In general, the absolute amount adsorbed cannot be determined experimentally with confidence at high-pressure conditions.

An alternative definition of the amount adsorbed can be defined that is valid at both high- and low-pressure conditions — the “excess” adsorption:

$$n^{\text{Ex}} \equiv n_{\text{inj}} - \rho_{\text{gas}} V_{\text{Void}}^{\text{He}} \quad (\text{all pressures}) \quad (7)$$

As noted earlier, the excess adsorption becomes identical to the absolute adsorption in the limit of zero pressure.

Equation 7 is written from the perspective of the experimentalist, that is, in terms of directly measurable quantities. As mentioned previously, the only assumptions present in eq 7 is the validity of the method used to determine the helium void volume, and whether this volume is applicable to gases other than helium. Another convenient way of writing eq 7 is to define the second term as the Gibbsian unadsorbed amount, which is the amount of gas unadsorbed if it occupied the entire helium void volume:

$$n_{\text{unads}}^{\text{Gibbs}} \equiv \rho_{\text{gas}} V_{\text{Void}}^{\text{He}} \quad (8)$$

The term Gibbsian is used here to distinguish the actual amount of gas unadsorbed, n_{unads} , from the amount unadsorbed assuming a zero-volume adsorbed phase.

$$n_{\text{unads}}^{\text{Gibbs}} = n_{\text{unads}} + \rho_{\text{gas}} V_{\text{ads}} = \rho_{\text{gas}} (V_{\text{unads}} + V_{\text{ads}}) \quad (9)$$

This terminology allows for a more concise definition for the excess adsorption:

$$n^{\text{Ex}} = n_{\text{inj}} - n_{\text{unads}}^{\text{Gibbs}} \quad (10)$$

Combining eqs 1–4 and 7 provides:

$$n^{\text{Ex}} = (\bar{\rho}_{\text{ads}} - \rho_{\text{gas}}) V_{\text{ads}} \quad (11)$$

The above expression furnishes clear insight into the physical meaning of the excess adsorption. It is the difference in the amount of material adsorbed ($\bar{\rho}_{\text{ads}} V_{\text{ads}}$) and the amount ($\rho_{\text{gas}} V_{\text{ads}}$) of material that would occupy the same volume if filled with the bulk gas (i.e., if no adsorption had occurred). Further, since $n^{\text{abs}} = \bar{\rho}_{\text{ads}} V_{\text{ads}}$, eq 11 may be rearranged to yield the relationship between the excess and absolute adsorptions in terms of phase densities:

$$n^{\text{abs}} = \frac{n^{\text{Ex}}}{\left(1 - \frac{\rho_{\text{gas}}}{\bar{\rho}_{\text{ads}}}\right)} \quad (12)$$

3. Mixed-Gas Adsorption

Applying basic mass and volume conservation principles allows for definitions of the amount of excess adsorption of gas mixture components. Consider, at equilibrium, a system volume containing an adsorbent and a gas mixture. The volume balance described by eq 4 applies for mixtures: a mixture occupies space, either in the adsorbed or unadsorbed phase volumes. Each component has a molar composition in each of these phase volumes and an overall molar composition (or feed composition). As in the case for pure-component adsorption, the adsorbed-phase density or adsorbed-phase volume for mixture adsorption is not experimentally accessible. For mixtures, the molar composition of the adsorbed phase, x_i^{abs} , is also inaccessible.

Consider an amount of gas mixture, n_{inj} , having known feed mole fractions, z_i , being injected into the system volume containing an adsorbent. After equilibrium is reached, the mole fractions in the unadsorbed gas mixture, y_i , are measured. A mass balance can be stated for each component i :

$$z_i n_{\text{inj}} = V_{\text{ads}} \bar{\rho}_{\text{ads}} x_i^{\text{abs}} + V_{\text{unads}} \rho_{\text{gas}} y_i \quad (13)$$

where ρ_{gas} is the density of the gas-phase mixture.

In eq 13, the situation is analogous to that described previously for pure gas adsorption; that is, the unadsorbed-phase

(5) Gumma, S.; Talu, O. *Adsorption* **2003**, 9 (1), 17–28.

(6) Myers, A. L. *AIChE J.* **2002**, 48 (1), 145–160.

(7) Ozdemir, E.; Morsi, B. I.; Schroeder, K. *Langmuir* **2003**, 19 (23), 9764–9773.

(8) Day, S.; Fry, R.; Sakurovs, R. *Int. J. Coal Geol.* **2008**, 74 (1), 41–52.

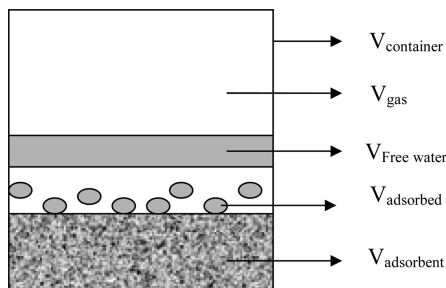


Figure 2. Equilibrium cell and associated volumes (highly idealized view).

volume and the adsorbed-phase volume are inaccessible experimentally, in general. The absolute adsorption for each component can be expressed using either the adsorbed-phase volume or the unadsorbed-phase volume:

$$n_i^{\text{Abs}} = V_{\text{ads}} \bar{\rho}_{\text{ads}} x_i^{\text{Abs}} = z_i n_{\text{inj}} - V_{\text{unads}} \rho_{\text{gas}} y_i \quad (14)$$

Analogous to the case for pure adsorption, the excess adsorption for mixtures is defined by replacing the experimentally inaccessible unadsorbed-phase volume with the helium void volume:

$$n_i^{\text{Ex}} = z_i n_{\text{inj}} - V_{\text{Void}}^{\text{He}} \rho_{\text{gas}} y_i \quad (15)$$

Equation 15 defines the excess adsorption for a component in a gas mixture in terms of experimentally measurable quantities, if we assume the gas-phase density is known from experiment or a suitable equation of state.

4. Adsorption on Wet Adsorbents

When performing experiments on wet adsorbents for temperatures greater than those at which solid-phase water occurs, the water can be present as a component in as many as three phases: the adsorbed fluid, a water-rich phase, and the gas phase. The presence of water in a volumetric adsorption experiment requires special attention because the total amount of water in the system container does not change with pressure (assuming dry injection gas).

For helium void volume determination (and the subsequent gas isotherms) in our recent works with coals, the coal under investigation is at its equilibrium saturation state with water; that is, no water-rich phase is assumed to exist. The water in a system container $V_{\text{Container}}$ is thus adsorbed completely and has a volume of $V_{\text{ads}}^{\text{Water}}$. In a helium void volume determination, the helium gas is assumed to be unadsorbed in the water. This is justified by available experimental data on helium solubility in water and by the fact that the measured helium void volume does not vary with pressure.

The helium void volume determination of a wet adsorbent takes into account the volume occupied by the adsorbed water.

$$V_{\text{Void}}^{\text{He}} = V_{\text{Container}} - (V_{\text{adsorbent}} + V_{\text{ads}}^{\text{Water}}) \text{ Wet adsorbent} \quad (16)$$

Figure 2 is a highly idealized visualization of the different volumes in the sample cell. As shown in the figure, the sample cell (container) volume is comprised of the adsorbent volume, adsorbed-phase volume, free-water volume (if any), and bulk-gas volume.

For dry adsorbents, the material balance of eq 3 accounts for the injected material residing in the adsorbed and unadsorbed phases. This assumption does not hold true for wet adsorbents because gases such as CO_2 are soluble in water. Thus, eq 3

must be modified to account for the solubility of gas in water (n_{sol}), to yield:

$$n_{\text{inj}} = n^{\text{abs}} + n_{\text{unads}} + n_{\text{sol}} \quad (17)$$

Thus, the amount of gas in the adsorbed and unadsorbed phases can be accounted for by reducing the amount injected by the amount dissolved in the water ($n_{\text{inj}} - n_{\text{sol}}$):

$$n_{\text{inj}} - n_{\text{sol}} = n^{\text{abs}} + n_{\text{unads}} \quad (18)$$

Equation 18 illustrates how a correction is made for the solubility of the gas in the water-rich adsorbed phase. The amount of gas dissolved, n_{sol} , is presumed known based on independent measurements of the gas solubility in water at the conditions existing in the adsorption experiment.

For mixture adsorption on a wet adsorbent, the experimental excess adsorption is defined by eq 15, but with the amount injected corrected for gas solubility in the water phase:

$$n_i^{\text{Ex}} = (z_i n_{\text{inj}} - n_i^{\text{sol}}) - V_{\text{Void}}^{\text{He}} \rho_{\text{gas}} y_i \quad (19)$$

As shown in eq 19, the calculated excess adsorption for a wet adsorbent is lowered by the amount of gas soluble in the adsorbed water. This quantity, however, cannot be determined by any elementary experimental methods. A first estimate is to assume that a component is soluble in the adsorbed water to the same extent it would be in liquid water:

$$n_i^{\text{sol,ads}} = n_i^{\text{sol,water}} \text{ (assumption for wet adsorbents)} \quad (20)$$

In mixture studies, the solubility of component i was further assumed to be equal to its pure component solubility evaluated at a pressure equal to its partial pressure ($P y_i$). The above assumption was invoked in the data reduction procedures for wet adsorption measurements at OSU. Also, for measurements at OSU to date, the gas phase is assumed to be water-free (e.g., $y_{\text{water}} = 0$). Further, in mixed-gas adsorption, the calibrated gas-chromatograph response for gases under study was assumed invariant to concentrations of water in the gas phase.

4.1. Adsorption on a Mass-of-Adsorbent Basis. The excess adsorption is often reported on a unit mass basis. For wet adsorbents, it is presented on a dry basis.

$$n^{\text{Ex}} = \frac{1000 n_{\text{ads}}}{(1 - \lambda_{\text{water}}) L} \quad (21)$$

Here, λ_{water} is water mass fraction. The relationships given above form the basis for analysis of experimental errors in adsorption measurements.

5. Analysis of Experimental Errors

The method used to estimate the expected uncertainties in the reported adsorption data is based on the theory of multivariate error propagation (see, e.g., Morrison⁹). This method of error analysis accounts for the way in which random errors in the experimental measurements are propagated into errors in the quantities calculated from the measurements.

To determine the expected uncertainty in a given quantity, we express the desired quantity as an analytical function of the measured variables. Specifically, for a given quantity, y (e.g., amount adsorbed), calculated from a set of input variables, $x_1, x_2, \dots, x_{\text{NV}}$ (e.g., pressure, temperature, etc.) the uncertainty σ_y is:

(9) Morrison, D. F., *Multivariate Statistical Methods*; McGraw Hill: New York, 1967.

$$\sigma_y^2 = \sum_{i=1}^{NV} \left[\left(\frac{\partial y}{\partial x_i} \right)^2 \sigma_{x_i}^2 \right] \quad (22)$$

where NV is the number of measured variables, i is the variable index, and σ_{x_i} is the standard deviation of the measurement x_i . The uncertainty expression above assumes that the input variables are uncorrelated, and that first-order approximations are sufficient; that is,

$$\frac{\partial y}{\partial x} \Delta x \gg \frac{\partial^2 y}{\partial x^2} (\Delta x)^2 \quad (23)$$

where Δx is the deviation in the measurement x for a given point.

Random errors are defined in the context that if the experiment were built and operated in the same way many times, the variance in all the measured variables would affect the calculated excess adsorption value. Errors that are systematic (not random) will not be addressed here. These include assumptions used in the data reduction technique (e.g., no water exists in the equilibrium gas phase).

5.1. Error in the Amount Adsorbed. The amount of gas adsorbed is expressed as the difference between the amount injected and the amount unadsorbed. Further, for wet adsorbents, the amount of gas dissolved in water is also taken into account. Therefore, the amount of gas adsorbed is given as:

$$n_{\text{ads}} = n_{\text{inj}} - n_{\text{unads}} - n_{\text{sol}} \quad (24)$$

Applying eq 22 to the above equation yields:

$$\sigma_{n_{\text{ads}}}^2 = \left(\frac{\partial n_{\text{ads}}}{\partial n_{\text{inj}}} \right)^2 \sigma_{n_{\text{inj}}}^2 + \left(\frac{\partial n_{\text{ads}}}{\partial n_{\text{unads}}} \right)^2 \sigma_{n_{\text{unads}}}^2 + \left(\frac{\partial n_{\text{ads}}}{\partial n_{\text{sol}}} \right)^2 \sigma_{n_{\text{sol}}}^2 \quad (25)$$

Thus, the error in the amount adsorbed is given as:

$$\sigma_{n_{\text{ads}}}^2 = \sigma_{n_{\text{inj}}}^2 + \sigma_{n_{\text{unads}}}^2 + \sigma_{n_{\text{sol}}}^2 \quad (26)$$

where $\sigma_{n_{\text{ads}}}$, $\sigma_{n_{\text{inj}}}$, $\sigma_{n_{\text{unads}}}$, and $\sigma_{n_{\text{sol}}}$ are the uncertainties in the amount of gas adsorbed, injected, unadsorbed in the cell, and dissolved in water, respectively. Therefore, the squared error estimate (\sim variance) in the amount of gas adsorbed is the simple sum of squared error estimates in the amount of gas injected into the cell, the amount of unadsorbed gas in the cell, and the amount of gas dissolved in adsorbed water. Following are the relevant expressions for these quantities.

5.2. Error in the Amount Injected. **5.2.1. Fixed-pressure Injection.** The data reduction differs in the amount injected for the two volumetric techniques considered here. For the fixed-pressure/variable-volume technique, the amount injected from the “pump” section is:

$$n_{\text{inj}} = \rho_{\text{gas}}(V_{\text{initial}} - V_{\text{final}}) \text{ at fixed pressure} \quad (27)$$

The initial volume and final volume are read on the volume scale of the pump; however, these volumes do not represent the true volume in the pump, since there is additional gas volume in dead space outside the pump (in connecting valves, fittings, and tubing). The true gas volume for use in eq 27 is related to the volume read on the pump scale, V^{Read} ; the maximum scale volume, V^{Scale} (the reading when the piston is in the full forward position in the pump); and the dead volume, V^{Dead} (which is the remaining gas volume when $V^{\text{Read}} = V^{\text{Scale}}$). V^{Dead} and V^{Scale} are constant and do not change for a given experimental setup. In our case, the typical maximum volume, V^{Scale} , for a Ruska pump is 250 or 500 cm³, depending on the pump being used.

The steps taken for a gas injection are shown schematically in Figure 3. In the following discussion, the unit of pressure is

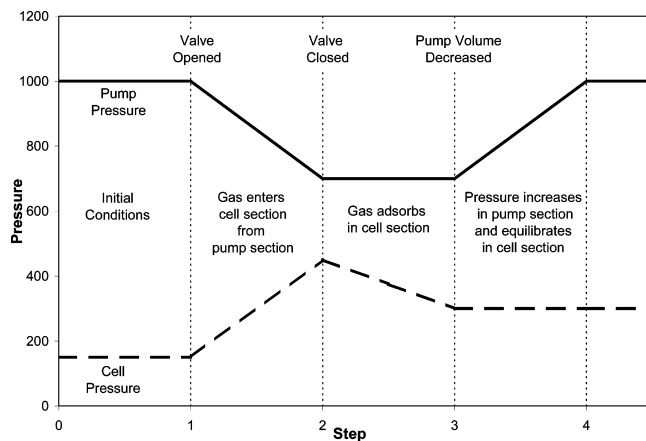


Figure 3. Procedure for gas injection at fixed pressure.

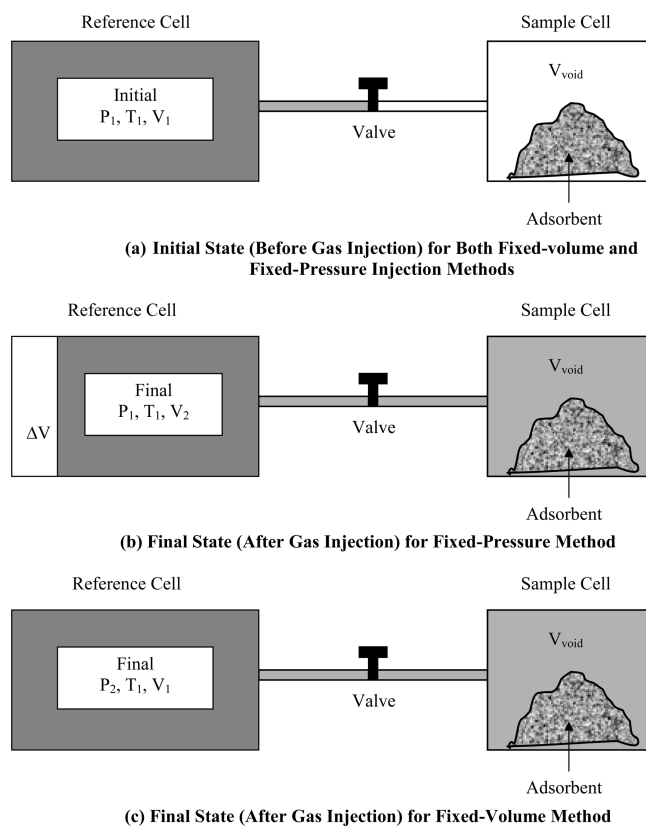


Figure 4. Schematic representations of the sample and reference cell conditions before and after gas injection. (a) Initial state (before gas injection) for both fixed-volume and fixed-pressure injection methods. (b) Final state (after gas injection) for fixed-pressure method. (c) Final state (after gas injection) for fixed-volume method.

“psia”, since the isotherm injections in our work are carried out in increments of 200 psia (1.38 MPa).

The initial pump pressure may be higher or lower than the cell pressure. Typically, in our studies, the initial pump pressure is set to about 1000 psia because this is about the average pressure for a measured isotherm, 2000 psia. (Because CO₂ and ethane are in the near-critical region at 1000 psia, pressures other than 1000 psia are used to minimize the sensitivity of ρ_{gas} to errors in the measured pressure). If the initial pump pressure is higher than the cell pressure, then the intermediary valve is opened between the pump and cell section. The valve is closed when the appropriate amount of gas has entered the cell section (isotherm equilibrium pressure increments are usually about 200

psia). If the initial pump pressure is lower than the cell pressure, then the pump volume is decreased until the pump pressure is high enough to facilitate injection (and to prevent the backflow of cell-section gas into the pump).

This technique assumes that the final pressure and temperature in the pump are identical to the initial values. However, moving the pump back after an injection to its initial pressure–temperature state introduces some random errors associated with the precision of pressure and temperature measurements after an injection. The initial and final state of the pump (reference) and sample cell section are illustrated in Figure 4, panels a and b, respectively.

Using these concepts, the amount injected can be calculated from the pump volumes in the first to the second positions as:

$$n_{2,1}^{\text{inj}} = n_1^{\text{pump}} - n_2^{\text{pump}} = \rho_1(V^{\text{Scale}} - V_1^{\text{Read}} + V^{\text{Dead}}) - \rho_2(V^{\text{Scale}} - V_2^{\text{Read}} + V^{\text{Dead}}) \quad (28)$$

Next, we assume that the final pump volume reading from one injection step is the initial volume in the subsequent injection (as usually done in practice). For each of $(N - 1)$ volume changes, there are two independent measurements each of the pump pressure, temperature, and volume. Again, the dead volume and scale volume are constants that do not physically change.

$$n_{\text{inj}} = n_{n,1}^{\text{inj}} = \rho_1(V^{\text{Scale}} - V_1^{\text{Read}} + V^{\text{Dead}}) - \rho_n(V^{\text{Scale}} - V_n^{\text{Read}} + V^{\text{Dead}}) \quad (29)$$

The error in the amount injected is thus:

$$\sigma_{n_{\text{inj}}}^2 = \left(\frac{\partial n_{\text{inj}}}{\partial \rho_n}\right)^2 \sigma_{\rho_n}^2 + \left(\frac{\partial n_{\text{inj}}}{\partial \rho_1}\right)^2 \sigma_{\rho_1}^2 + \left(\frac{\partial n_{\text{inj}}}{\partial V_n^{\text{Read}}}\right)^2 \sigma_{V_n^{\text{Read}}}^2 + \left(\frac{\partial n_{\text{inj}}}{\partial V_1^{\text{Read}}}\right)^2 \sigma_{V_1^{\text{Read}}}^2 \quad (30)$$

If we assume that the random errors in the temperature, pressure, and volume readings are the same at initial “1” and final injection step “ N ” (i.e., $\sigma_{T_n} = \sigma_{T_1}$, $\sigma_{\rho_n} = \sigma_{\rho_1} = \sigma_{\rho}^{\text{pump}}$), and $\rho_1 = \rho_n = \rho^{\text{pump}}$, then the above expression can be rewritten as:

$$\sigma_{n_{\text{inj}}}^2 = ((V^{\text{Scale}} + V^{\text{Dead}} - V_n^{\text{Read}})^2 + (V^{\text{Scale}} + V^{\text{Dead}} - V_1^{\text{Read}})^2) \sigma_{\rho^{\text{pump}}}^2 + 2(\rho^{\text{pump}})^2 \sigma_{V^{\text{Read}}}^2 \quad (31)$$

As evident in the expression above, the actual gas volume takes part in determining the expected error in the amount injected. In practice, this means to minimize errors in the amount injected requires minimizing the dead volume, V^{Dead} , and using the highest possible initial value of V^{Read} (which minimizes the volume of gas inside the pump, which is $V^{\text{Scale}} - V^{\text{Read}}$) that will complete the isotherm. For example, a volume injected of 100 cm³ has less expected error in the amount injected if the actual volumes are 125 and 25 cm³, than if they were 225 and 125 cm³. As such, the volume of gas remaining in the pump after each injection should be a minimum.

5.2.2. Fixed-volume Injection. The fixed-volume/variable-pressure technique consists of a series of injections from a reference cell of known, constant volume into a sample cell containing the adsorbent. In general, the amount injected into the sample cell from the j th state (which is the higher-pressure initial state before the injection) to the k th state of the reference cell is:

$$n_{j,k}^{\text{inj}} = n_j^{\text{Ref}} - n_k^{\text{Ref}} = V^{\text{Ref}}(\rho_j - \rho_k) = \frac{V^{\text{Ref}}}{R} \left(\frac{P_j}{T_j Z_j} - \frac{P_k}{T_k Z_k} \right) \text{fixed volume} \quad (32)$$

The initial and final state of the reference and sample cell section is illustrated in Figure 4, panels a and c, respectively. These figures depict a single injection, and these injections are repeated to yield the complete isotherm.

Accordingly, the total amount injected from the reference cell to the sample cell and from the first through the N th injection is:

$$n_N^{\text{inj}} = \sum_{j=1, k=j+1}^N n_{j,k}^{\text{inj}} \quad (33)$$

In this technique, after N injections have been made from the reference cell to the sample cell, there are $2N$ independent measurements each of the temperature and pressure and one volume measurement (of the reference cell). The expected squared error in the amount injected at the N th injection is the resultant sum of the expected squared errors for each injection from the j th to the k th state:

$$\sigma_{n_N^{\text{inj}}}^2 = \sum_{j=1, k=j+1}^N \sigma_{n_{j,k}^{\text{inj}}}^2 \quad (34)$$

The expected error of an injection from the j th to the k th state is:

$$\sigma_{n_{j,k}^{\text{inj}}}^2 = \left(\frac{\partial n_{j,k}^{\text{inj}}}{\partial V^{\text{Ref}}}\right)^2 \sigma_{V^{\text{Ref}}}^2 + \left(\frac{\partial n_{j,k}^{\text{inj}}}{\partial \rho_j}\right)^2 \sigma_{\rho_j}^2 + \left(\frac{\partial n_{j,k}^{\text{inj}}}{\partial \rho_k}\right)^2 \sigma_{\rho_k}^2 \quad (35)$$

which yields the following:

$$\sigma_{n_{j,k}^{\text{inj}}}^2 = (\rho_j - \rho_k)^2 \sigma_{V^{\text{Ref}}}^2 + (V^{\text{Ref}})^2 (\sigma_{\rho_j}^2 + \sigma_{\rho_k}^2) \quad (36)$$

The error in the amount injected from the j th to the k th state can be related to the amount injected:

$$\sigma_{n_{j,k}^{\text{inj}}}^2 = (n_{j,k}^{\text{inj}})^2 \left(\frac{\sigma_{V^{\text{Ref}}}}{V^{\text{Ref}}} \right)^2 + (V^{\text{Ref}})^2 (\sigma_{\rho_j}^2 + \sigma_{\rho_k}^2) \quad (37)$$

Thus, the error in the amount injected at the N th injection is:

$$\sigma_{n_N^{\text{inj}}}^2 = \left(\frac{\sigma_{V^{\text{Ref}}}}{V^{\text{Ref}}} \right)^2 (n_N^{\text{inj}})^2 + (V^{\text{Ref}})^2 \sum_{j,k=1}^N (\sigma_{\rho_j}^2 + \sigma_{\rho_k}^2) \quad (38)$$

As evident from eq 38, the error in the amount injected depends on the uncertainty in the volume of the reference container. Also, unlike the fixed-pressure method, the initial pressure in the reference cell must be higher than the pressure in the sample cell.

5.2.3. Error in the Amount Injected for a Specific Gas. To calculate the excess adsorption for a specific component i (as given by eq 15), the feed fraction of that component, z_i , is needed in addition to the overall amount injected, n_{inj} . The usual situation during the course of an isotherm measurement is that the molar composition of the feed is constant. Given these assumptions, the expected squared error for the molar amount injected of component i , or $z_i n_{\text{inj}}$ is:

$$\sigma_{z_i n_{\text{inj}}}^2 = z_i^2 \sigma_{n_{\text{inj}}}^2 + n_{\text{inj}}^2 \sigma_{z_i}^2 \quad (39)$$

This expression is valid for both the fixed-volume and fixed-pressure methods, provided that the corresponding expressions for the error in the amount injected are used.

5.3. Error in Density. As evident from the above discussion, the error in the amount injected is dependent on the error in the density of gas, σ_{ρ} . The density may be expressed in terms of gas compressibility factor as:

$$\rho = \frac{P}{ZRT} \quad (40)$$

Thus, the error in the density is given as:

$$\begin{aligned} \sigma_\rho^2 &= \left(\frac{\partial \rho}{\partial P}\right)^2 \sigma_P^2 + \left(\frac{\partial \rho}{\partial T}\right)^2 \sigma_T^2 + \left(\frac{\partial \rho}{\partial Z}\right)^2 \sigma_Z^2 \\ &= \rho^2 \left(\frac{1}{P} - \frac{1}{Z} \frac{\partial Z}{\partial P}\right)^2 \sigma_P^2 + \rho^2 \left(\frac{1}{T} + \frac{1}{Z} \frac{\partial Z}{\partial T}\right)^2 \sigma_T^2 + \rho^2 \left(\frac{1}{Z}\right)^2 \sigma_Z^2 \end{aligned} \quad (41)$$

The derivatives of the compressibility factor can be evaluated at the nominal pressure and temperature using an accurate equation of state.

5.4. Error in the Gibbsian Amount Unadsorbed. The “Gibbsian unadsorbed amount” may be defined as being equal to $\rho_{\text{gas}} V_{\text{void}}^{\text{He}}$. The error estimation is the same for both the fixed-volume and fixed-pressure methods, because those methods differ only in their gas injection techniques.

$$n_{\text{unads}}^{\text{Gibbs}} = V_{\text{void}}^{\text{He}} \rho_{\text{gas}}^{\text{Cell}} \quad (42)$$

$$\sigma_{n_{\text{unads}}^{\text{Gibbs}}}^2 = (V_{\text{void}}^{\text{He}})^2 \sigma_{\rho_{\text{gas}}^{\text{Cell}}}^2 + (\rho_{\text{gas}}^{\text{Cell}})^2 \sigma_{V_{\text{void}}^{\text{He}}}^2 \quad (43)$$

This expression can be rewritten, with the use of eq 41, to establish a proportional relationship between the expected error in the Gibbsian amount unadsorbed and the amount itself:

$$\begin{aligned} \sigma_{n_{\text{unads}}^{\text{Gibbs}}}^2 &= (n_{\text{unads}}^{\text{Gibbs}})^2 \left(\left(\frac{1}{P} - \frac{1}{Z} \frac{\partial Z}{\partial P} \right)^2 \sigma_P^2 + \right. \\ &\quad \left. \left(\frac{1}{T} + \frac{1}{Z} \frac{\partial Z}{\partial T} \right)^2 \sigma_T^2 + \rho^2 \left(\frac{1}{Z} \right)^2 \sigma_Z^2 + \left(\frac{\sigma_{V_{\text{void}}^{\text{He}}}}{V_{\text{void}}^{\text{He}}} \right)^2 \right) \end{aligned} \quad (44)$$

As shown, the Gibbsian amount unadsorbed and its expected error can be minimized by reducing the percentage error in the helium void volume by as much as possible. This is accomplished by packing the adsorbent into all the available volume of the sample cell. This task also minimizes the systematic error possibility of adsorbed water being stripped from the adsorbent into the gas phase.

To calculate the excess adsorption for a specific component i (as given by eq 15), the equilibrium composition of that component, y_i , is needed in addition to the Gibbsian amount unadsorbed. The expected error is:

$$\sigma_{y_i n_{\text{unads}}^{\text{Gibbs}}}^2 = (n_{\text{unads}}^{\text{Gibbs}})^2 \sigma_{y_i}^2 + y_i^2 \sigma_{n_{\text{unads}}^{\text{Gibbs}}}^2 \quad (45)$$

5.5. Error Due to Correction for Adsorption on Wet Adsorbents. Wet adsorbents have a correction that accounts for the fact that the void volume determined by helium is affected by the presence of adsorbed water. The correction for this experimental artifact is to subtract the amount of gas soluble in the water from the excess amount adsorbed (calculated in the normal manner for dry adsorbents). Correlations exist that will give gas solubility in water as a function of pressure, temperature, and composition. The expected error in gas solubility from random errors in pressure, temperature, or the amount of water in the sample cell probably is much less than the systematic errors. Nevertheless, a reasonable compromise assumption is that the error in the amount of gas soluble in the adsorbed water is proportional to the amount of dissolved gas:

$$\sigma_{\text{gas}}^{\text{Sol, Water}} = k_{\text{sol}} n_{\text{gas}}^{\text{Sol, Water}} \quad (46)$$

where a value of 0.05 for k_{sol} might be a reasonable estimate. Errors in this correction can be expected to be greatest in

magnitude for gases that are highly soluble in water, such as CO_2 .

5.6. Error in the Gibbsian (Excess) Amount Adsorbed.

The excess adsorption is typically presented in units of mmol/gm dry adsorbent. Therefore,

$$n^{\text{Ex}} = \frac{1000 n_{\text{ads}}}{(1 - \lambda_{\text{water}}) L} \quad (47)$$

The error in the excess amount of gas adsorbed then becomes:

$$\sigma_{n^{\text{Gibbs}}}^2 = \left(\frac{\partial n^{\text{Gibbs}}}{\partial n_{\text{ads}}} \right)^2 \sigma_{n_{\text{ads}}}^2 + \left(\frac{\partial n^{\text{Gibbs}}}{\partial L} \right)^2 \sigma_L^2 + \left(\frac{\partial n^{\text{Gibbs}}}{\partial \lambda_{\text{water}}} \right)^2 \sigma_{\lambda_{\text{water}}}^2 \quad (48)$$

$$\begin{aligned} \sigma_{n^{\text{Gibbs}}}^2 &= \left(\frac{1000}{(1 - \lambda_{\text{water}}) L} \right)^2 \sigma_{n_{\text{ads}}}^2 + \left(\frac{1000 n_{\text{ads}}}{(1 - \lambda_{\text{water}}) L^2} \right)^2 \sigma_L^2 + \\ &\quad \left(\frac{1000 n_{\text{ads}}}{\lambda_{\text{water}}^2 L} \right)^2 \sigma_{\lambda_{\text{water}}}^2 \end{aligned} \quad (49)$$

Equation 49 is valid for estimating the experimental uncertainty in the amount of gas adsorbed from the two injection methods discussed above. Further, the corresponding expressions for the error in the amount injected for the fixed-pressure and fixed-volume methods are used in conjunction with eq 49 to estimate the experimental uncertainty from the two methods.

6. Comparison of Error in Fixed-Volume and Fixed-Pressure Methods

6.1. Gas Injection into an Empty Sample Cell. An analysis of which injection method yields lower uncertainties is complicated by the fact that many types of isotherms are possible: low-pressure versus high-pressure measurements, ideal gases versus compressible fluids, and high-adsorbing versus low-adsorbing adsorbents. Our analysis involves estimating the errors in pressure, temperature, and volume measurements for the two methods. For both methods, expected errors in the reported adsorption can be decreased by reducing the experimental errors.

Both methods use essentially the same relations to calculate the Gibbsian amount unadsorbed in the sample cell; the methods differ in calculating the amount of gas injected. Therefore, a prudent comparison of the two methods requires an analysis of the amount of gas injected. The amount of gas injected into a sample cell at a specific pressure is a function of the adsorption characteristics of the adsorbent and the void volume per unit mass of adsorbent. To simplify the analysis of both methods, we consider the amount of gas injected into an empty sample cell (i.e., no adsorbent).

Recent interest in CO_2 adsorption led to an analysis of the error in CO_2 injection. For this case analysis, the values of random errors in the temperature and pressure were taken as 0.1 K and 1 psia for both the fixed-pressure and fixed-volume methods. For the fixed-pressure method, estimate of the random error in V^{Read} is set to 0.01 cm^3 , and V^{Dead} is set to 50 cm^3 . These values are typical of the work performed at OSU.

For both methods, we consider CO_2 at 318 K being injected into an empty sample cell at 318 K. Injection steps are taken such that the sample cell pressure is increased at interval steps of 200 psia. For the fixed-pressure method, one pressure in the injection pump (to be determined) is used to make all the injections. For the fixed-volume method, the initial pressure in the reference vessel is selected to cause the equilibrium cell pressure to increase by 200 psia and result in equal pressures in the equilibrium and reference cell at the end of each injection

Table 1. Error Analysis for CO₂ Injection in an Empty Cell at 318 K Using the Fixed-Volume Method

<i>j, k</i>	$P_k = P^{\text{cell}}$ (psia)	P_k/Z_k (psia)	$V^{\text{cell}}/V^{\text{ref}}$				
			0.05	0.10	0.15	0.20	0.25
			P_j (psia)				
1	200	212	209	219	228	237	246
2	400	454	409	418	428	437	446
3	600	738	609	618	627	636	645
4	800	1088	809	817	826	835	843
5	1000	1554	1008	1016	1024	1032	1040
6	1200	2284	1207	1214	1221	1228	1234
7	1400	3846	1409	1416	1424	1432	1440
8	1600	5277	1617	1636	1656	1678	1702
9	1800	5876	1812	1827	1842	1857	1873
10	2000	6236	2012	2024	2037	2050	2063
<i>j, k</i>	$P_k = P^{\text{cell}}$ (psia)	ρ_N (mol/L)	$(\sigma(n_N^{\text{inj}})/n_N^{\text{inj}}) \times 100\%$				
1	200	0.553	15.10	7.58	5.07	3.82	3.07
2	400	1.184	10.80	5.42	3.64	2.74	2.21
3	600	1.925	9.01	4.53	3.04	2.30	1.86
4	800	2.837	8.12	4.09	2.75	2.08	1.69
5	1000	4.050	7.93	4.01	2.70	2.05	1.67
6	1200	5.952	9.18	4.70	3.20	2.45	2.00
7	1400	10.025	10.86	5.64	3.82	2.90	2.34
8	1600	13.755	9.68	4.92	3.29	2.47	1.98
9	1800	15.314	9.34	4.71	3.14	2.36	1.89
10	2000	16.254	9.08	4.57	3.05	2.29	1.83

step (this will minimize the error in the amount injected and is the ideal situation for this method). Thus, the value of ρ_k and its expected error, can be calculated easily for all the pressure intervals in the fixed volume method. The initial pressure in the reference cell necessary for each injection for a given $V^{\text{cell}}/V^{\text{ref}}$ is calculated using the following expression:

$$\frac{P_j}{Z_j} = \frac{P_k}{Z_k} \left(1 + \frac{V^{\text{cell}}}{V^{\text{ref}}} \right) - \frac{P_{k-1}}{Z_{k-1}} \left(\frac{V^{\text{cell}}}{V^{\text{ref}}} \right) \quad (\text{at constant temperature}) \quad (50)$$

where subscripts *j* and *k* refer to the initial and final state, respectively.

The squared error in the amount injected can be obtained as:

$$\left(\frac{\sigma_{n_N^{\text{inj}}}}{n_N^{\text{inj}}} \right)^2 = \left(\frac{\sigma_V^{\text{ref}}}{V^{\text{ref}}} \right)^2 + \left(\frac{V^{\text{ref}}}{V^{\text{cell}}} \right)^2 \sum_{k=1}^N \rho_k^2 \left(\left(\frac{1}{P_k} - \frac{1}{Z_k} \frac{\partial Z_k}{\partial P_k} \right)^2 \sigma_{P_k}^2 + \left(\frac{1}{T_k} + \frac{1}{Z_k} \frac{\partial Z_k}{\partial T_k} \right)^2 \sigma_{T_k}^2 \right) + \left(\frac{V^{\text{ref}}}{V^{\text{cell}}} \right)^2 \sum_{j=1}^N \rho_j^2 \left(\left(\frac{1}{P_j} - \frac{1}{Z_j} \frac{\partial Z_j}{\partial P_j} \right)^2 \sigma_{P_j}^2 + \left(\frac{1}{T_j} + \frac{1}{Z_j} \frac{\partial Z_j}{\partial T_j} \right)^2 \sigma_{T_j}^2 \right) \quad (51)$$

As evident from eq 51, the fractional error in the volume of the reference cell contributes directly to the fractional error in the amount injected. A reasonable assumption is that $\sigma_V^{\text{ref}}/V^{\text{ref}}$ is less than 0.3%. This is generally the error obtained from an error analysis of the helium void volume for volumes between 50 and 150 cm³ in volumetric methods.⁴ Table 1 presents values of P_j for various values of the ratio $V^{\text{cell}}/V^{\text{ref}}$. Also presented in Table 1 is the expected percentage error in the amount injected. As shown in the table, large values of $V^{\text{cell}}/V^{\text{ref}}$ give smaller values of the percentage error in n_{inj} . Large values of $V^{\text{cell}}/V^{\text{ref}}$, however, lead to large required pressures of P_j , and pressure transducers tend to compromise precision and accuracy (in absolute terms) in the pressure measured for a larger range measurement. At a given pressure in the sample cell, percent errors in the amount injected tend to increase linearly with the ratio $V^{\text{ref}}/V^{\text{cell}}$. Percent errors have a maximum near 1400 psia due to the sensitivity of the CO₂ density to pressure and

temperature. The density and its partial derivatives with respect to temperature and pressure were calculated using an accurate equation of state.¹⁰

For adsorption studies involving CO₂ adsorption, an optimized procedure would use a large reference cell at low pressures and a small reference cell at high pressures; this would simultaneously minimize errors in the amount injected while constraining the initial pressures, P_i , to reasonable values. This procedure would generally lower errors at the lower pressures; errors at the higher pressures of the isotherm are governed primarily by the magnitude of the injection pressure P_i (or equivalently, the magnitude of $V^{\text{cell}}/V^{\text{ref}}$).

Table 2 presents the error analysis of the amount injected for the fixed-pressure method. A 500 cm³ scale volume pump is used to make CO₂ injections at various injection pressures. The initial volume readings are presented for each pump pressure and sample cell volume (save for the five that are empty to indicate that 500 cm³ pump is not large enough for those situations). These readings are calculated on the basis that at the end of the last injection step ($P_{\text{cell}} = 2000$ psia), the final volume reading is 500 cm³. Table 2 also presents the percent error in the amount injected for the various cases of cell volume size, pump pressure, and cell pressure.

There are several notable characteristics of the error analysis in Table 2. At any specific pressure in the cell and for any pump pressure, larger cell volumes lead to smaller percent errors for the amount injected. Also, the percent errors increase linearly with the reciprocal density of the sample for all the various cases of pump pressure and sample cell volume. For the cases where the pump pressure is 1400 psia, the percent error is higher than for the cases where pressures are 1200 and 1800 psia. This analysis shows for pump pressures above the pressure of the pressure-density inflection point, lower percent errors in the amount injected are possible than for pressures below that inflection point.

6.2. Case Studies and Discussion. To confirm the analytical expressions for the errors in the amounts adsorbed, Monte Carlo sensitivity analysis was performed for the CO₂ adsorption for both the fixed-volume and fixed-pressure methods. To conduct this sensitivity analysis, all independent variables were perturbed with a normally distributed random error. The experimental estimates for the uncertainties in the primary measured quantities of pressure, volume, and temperature were used as the random error of the corresponding perturbed variable in the Monte Carlo analysis. The Monte Carlo analysis was conducted for approximately 1000 sets of these perturbed variables. Thus, for each set of perturbed variables, an amount adsorbed was evaluated. The average of these runs at each pressure was taken as the amount adsorbed at that pressure for a given set of perturbed variables. Further, the standard deviation of the amount adsorbed evaluated from these 1000 sets was taken as the estimate of the uncertainty in the acquired data for comparison with the experimental error derived analytically.

Figure 5 presents a comparison of the analytical and Monte Carlo error estimates using the fixed-volume method for adsorption of CO₂ on a dry coal. Similarly, Figure 6 presents the comparison between analytical and Monte Carlo error estimates using the fixed-pressure method for adsorption of CO₂ on a dry coal. In this figure, sections marked as I, II, and III represent the three separate loadings of pump that were required to complete the isotherm. (Note the differences in the y-axis scales in the two figures.) The discontinuities at pressures around

(10) Span, R.; Wagner, W. *J. Phys. Chem. Ref. Data* **1996**, 25 (6), 1509–1596.

Table 2. Error Analysis for CO₂ Injection in an Empty Cell at 318 K Using the Fixed-pressure Method

V^{cell} (cm ³)	P_{pump} (psia)				
	800	1000	1200	1400	1800
	V^{read} for 500 cm ³ scale pump				
10	206.19	309.21	386.14	452.71	486.32
50		148.69	276.91	387.86	443.86
100			140.36	306.78	390.79
150			3.81	225.71	337.72

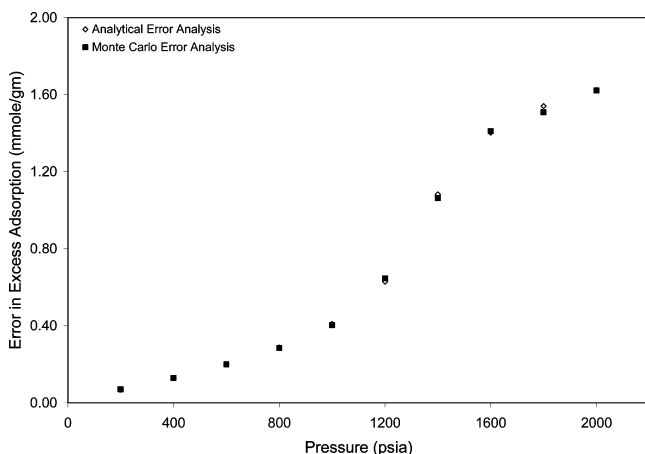
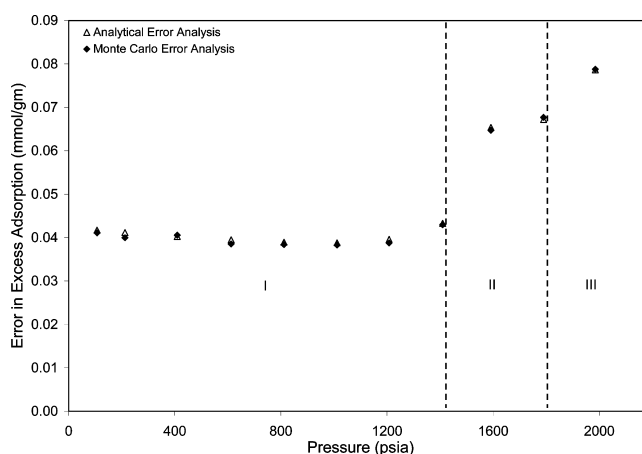
P_{cell} (psia)	P_{pump} (psia)					P_{pump} (psia)				
	800	1000	1200	1400	1800	800	1000	1200	1400	1800
	$(\sigma(n_N^{\text{inj}})/n_N^{\text{inj}}) \times 100\%$ for $V^{\text{cell}} = 10 \text{ cm}^3$					$(\sigma(n_N^{\text{inj}})/n_N^{\text{inj}}) \times 100\%$ for $V^{\text{cell}} = 50 \text{ cm}^3$				
200	46.71	48.16	64.99	111.57	26.67	15.96	21.54	36.97	8.78	
400	21.75	22.43	30.26	51.95	12.42	7.38	9.96	17.10	4.06	
600	13.33	13.74	18.54	31.82	7.61	4.49	6.06	10.40	2.47	
800	9.00	9.28	12.52	21.49	5.14	3.00	4.05	6.96	1.65	
1000	6.26	6.46	8.71	14.96	3.58	2.07	2.79	4.78	1.14	
1200	4.22	4.35	5.87	10.08	2.41	1.37	1.84	3.16	0.75	
1400	2.45	2.53	3.42	5.86	1.40	0.76	1.03	1.77	0.42	
1600	1.76	1.81	2.44	4.19	1.00	0.53	0.71	1.22	0.29	
1800	1.56	1.61	2.18	3.74	0.89	0.46	0.63	1.08	0.26	
2000	1.47	1.51	2.04	3.50	0.84	0.43	0.58	1.00	0.24	
	$(\sigma(n_N^{\text{inj}})/n_N^{\text{inj}}) \times 100\%$ for $V^{\text{cell}} = 100 \text{ cm}^3$					$(\sigma(n_N^{\text{inj}})/n_N^{\text{inj}}) \times 100\%$ for $V^{\text{cell}} = 150 \text{ cm}^3$				
200			16.11	27.65	6.55			14.30	24.54	5.81
400			7.43	12.75	3.02			6.58	11.30	2.67
600			4.50	7.72	1.83			3.98	6.83	1.62
800			3.00	5.14	1.22			2.64	4.54	1.07
1000			2.05	3.51	0.83			1.80	3.09	0.73
1200			1.34	2.30	0.55			1.18	2.02	0.48
1400			0.74	1.27	0.30			0.64	1.10	0.26
1600			0.51	0.87	0.21			0.44	0.75	0.18
1800			0.44	0.76	0.18			0.39	0.66	0.16
2000			0.41	0.71	0.17			0.36	0.62	0.15

1500 psia and 2000 psia are due to the reloading of pump necessary for higher pressure injections. Figures 5 and 6 indicate that the Monte Carlo and analytical error estimation methods give comparable results. Thus, these results provide confirmation of the analytical expressions for the estimated uncertainties in the amount of gas adsorbed. Figure 7 presents the histogram and cumulative distribution of these errors, where “X”, “Xbar” and “Sigma” represent the sample observation, mean, and standard deviation of the distribution. As evident from the figure, the distribution displays essentially normal error distribution behavior.

Figure 8 presents a CO₂ adsorption isotherm on a wet coal at 318 K and the expected errors in the amount adsorbed for the two injection methods (Case a). For a meaningful comparison, both methods used identical cell volumes and amounts of coal. Moreover, the expected uncertainties used for pressure, temperature, volume, and mass measurements were the same

for both methods. Specifically, the reference cell and sample cell volumes for both methods were 500 and 125 cm³, respectively, and 65 g of coal sample were used. In the error propagation for both methods, we used experimental uncertainties of 0.1 K in temperature, 1 psia in pressure, and 0.3% in void volume, 0.02 cm³ in the reference cell volume, and 0.01 g. in the amount of coal.

As evident from Figure 8, adsorption data using the fixed-volume method have larger experimental uncertainties (uncertainties higher than 20% for pressures above 1200 psia). The average experimental uncertainties in the amount adsorbed for the fixed-pressure and fixed-volume method were 12 and 42%, respectively. Thus, errors from a different injection technique for this experimental set up can differ by about 3-fold, on average. These large experimental uncertainties at the higher pressures are caused mainly by the uncertainty in the amount injected. This relates directly to the injection technique used in

**Figure 5.** Comparison of Monte Carlo and analytical error analyses for CO₂ adsorption with the fixed-volume method.**Figure 6.** Comparison of Monte Carlo and analytical error analyses for CO₂ adsorption with the fixed-pressure method.

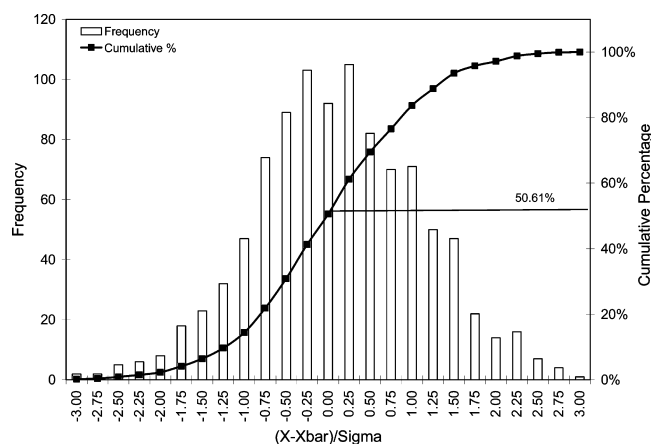


Figure 7. Histogram for the distribution of errors evaluated from the Monte Carlo error analysis for CO₂ adsorption with the fixed-pressure method.

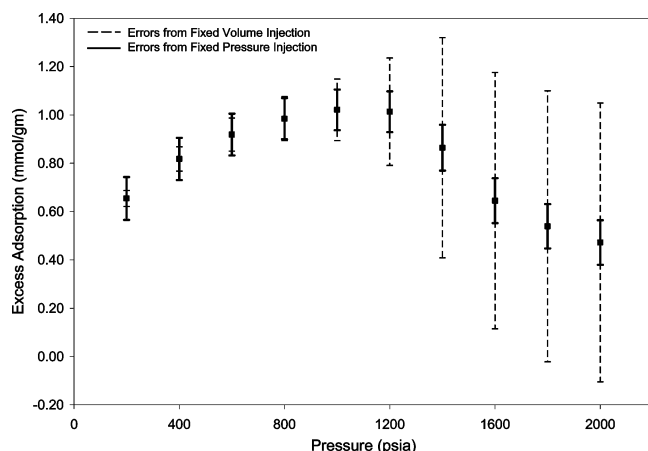


Figure 8. Comparison of analytical error analysis for fixed-volume and fixed-pressure methods for CO₂ adsorption (Case a).

the fixed-volume method, where in this case study we used the idealized case corresponding to minimum error.

We further note that the fixed-volume method can yield lower uncertainties than the fixed-pressure methods at low to medium pressures (below 800 psia), as shown in Figure 8; however, the uncertainties for the fixed-volume method increase sharply at higher pressures, as discussed earlier.

In practice, the fixed-volume method is often used with smaller cell volumes containing small amounts of coal (e.g., see Goodman et al.¹), resulting in even larger experimental uncertainties. One such fixed-volume apparatus is compared below with the fixed-pressure method. Figure 9 presents two experimental runs for adsorption of CO₂ on a wet coal at 318 K and the expected errors in the amount adsorbed that would be obtained using the two injection methods (Case b). A typical fixed-volume method reported in the literature¹ was used for this case study. The fixed-pressure method reported is the one being utilized at OSU.

Error propagation for the fixed-volume method used experimental uncertainties of 0.1 K in temperature, 1 psia in pressure, 0.1 cm³ for the void volume, and 0.1 cm³ for the reference volume. Error propagation for the fixed-pressure method used experimental uncertainties that were used for Figure 8. As shown in Figure 9, the fixed-volume method yields large experimental uncertainties especially at the higher pressures.

The experimental uncertainties from the fixed-volume method are also highly sensitive to small errors in the void volume. A standard error of 0.1 cm³ in the void volume contributes 70–75% of the total estimated error for pressures greater than 200 psia. This

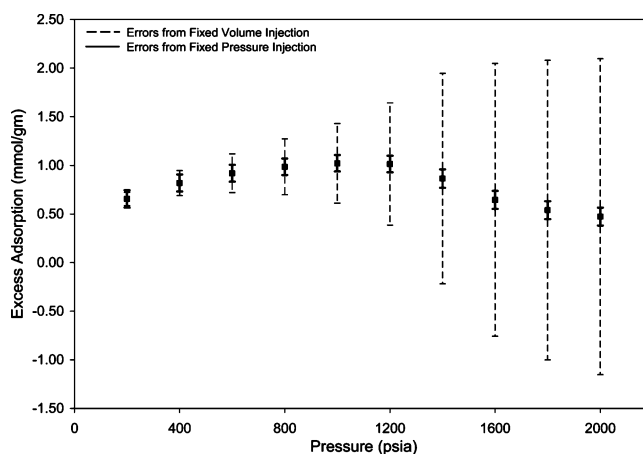


Figure 9. Comparison of analytical error analysis for fixed-volume and fixed-pressure methods for CO₂ adsorption (Case b).

is mainly due to the large ratio of void volume to adsorbent mass used. To avoid these large errors, more coal should be packed into the sample cell to diminish the void volume size. As mentioned previously, most fixed-volume apparatuses are used with small amounts of coal and a large void volume, and therefore, large experimental errors are more probable from the fixed-volume method than the fixed-pressure method.

The coals that were used for the case studies discussed above were similar to Fruitland coal from the San Juan Basin. Further, the Monte Carlo analysis was performed on Upper Freeport and Pocahontas coals. Regardless of the actual coal used, the qualitative nature of these results does not change.

The case studies above clearly demonstrate that there is an increase in the experimental uncertainties depending on the injection method utilized. Further, the larger void volume typically used in fixed-volume method also contributes to the higher uncertainties.

We have also performed an analysis to ascertain the sensitivity of errors in the adsorbed amounts as a function of precision in pressure, temperature, and volume for both fixed-volume and fixed-pressure methods. Specifically, we have looked at the ratio of the errors in the amount adsorbed in the two methods as a function of precision in these primary variables, when each variable is considered separately. This analysis was performed on the CO₂ adsorption isotherm that was also used in Figure 8 (case a). The results indicate that the two methods respond differently to a specified uncertainty in a given variable, and this difference appears to be unaffected by the level of measurement uncertainty in these primary variables (e.g., if a temperature precision of 1 K is used in both methods instead of 0.1 K, the uncertainties in the amounts adsorbed in each of the methods increase, but their ratio remains the same).

6.3. Design Considerations for Minimizing Experimental Errors. The larger uncertainties obtained using the fixed-volume injection method in the case studies discussed above can be reduced by methodical, error-analysis-driven design of the experimental apparatus. Specifically, the factors critical in minimizing the expected uncertainties in the amounts adsorbed measured with a fixed-volume injection method are (1) the ratio of the sample cell to the reference cell, for which we recommend a ratio of about 2.0. A ratio of greater than 2.0 could yield even lower errors; however, a ratio of 2.0 would be the upper limit for most situations because of the constraint on the maximum injection pressure possible practically; (2) the void volume, which must be reduced by using as much coal as possible in a given cell volume.

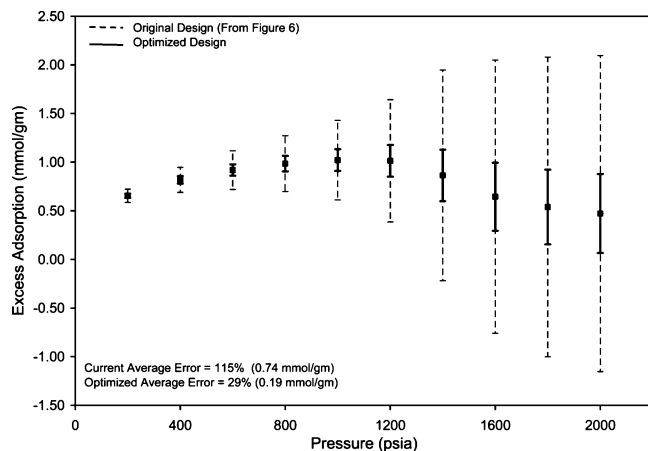


Figure 10. Minimization of errors for fixed-volume method for CO₂ adsorption.

Our analysis indicates that the sample cell must be larger than the reference cell to minimize the error. However, this imposes a constraint because the initial pressure necessary for the highest pressure injections increases rapidly with a decrease in the reference cell volume. We optimized this ratio with this constraint and found a practical value of $(V^{\text{cell}})/(V^{\text{Ref}}) = 2.0$ yields the lowest error for a given set of errors in the primary variables of pressure, temperature, and volumes. As mentioned above, a ratio larger than 2.0 would require unrealistically high initial pressures in the reference volume for the later injections of an isotherm.

Therefore, the sample cell should be about twice the size of the reference volume, and the void volume in the sample cell should be minimized by packing as much coal as possible into the cell to lower the expected uncertainties. Figure 10 illustrates the result of this minimization of experimental errors. Specifically, the figure was generated by utilizing the experimental uncertainties used in Figure 9 with volume ratio, $(V^{\text{cell}})/(V^{\text{Ref}})$, of 1.62 for the cell volumes instead of an original ratio of less than 1.0. As evident from Figure 10, the optimized ratio results in lowering the error significantly. Specifically, the average experimental uncertainties for the isotherm decreased from 115% (0.74 mmol/gm) to about 29% (0.19 mmol/gm). Therefore, with careful design, it is possible to lower errors from the fixed-volume injection method.

Finally, while the comparisons presented herein are typical of current experimental studies, they are highly dependent on the uncertainties assigned to the measured variables.

7. Conclusions

Analytical expressions were derived for the data reduction of adsorption measurements at high pressures using the volumetric method. Data reduction for two methods of

measuring the injected amounts of gas into a sample cell was described: injection at fixed-volume and at fixed-pressure. Key assumptions were explained for the provided methods.

Analytical expressions were derived for the expected error in the excess adsorption. The total error is composed of parts arising from the amount injected, the amount unadsorbed, and the mass of the adsorbent. Results show that the fixed-volume method can yield larger uncertainties than the fixed-pressure method for the same experimental set up. The larger errors are a result of the injection method used in the fixed-volume method. Further, minimizing the void volume of the sample cell can diminish the expected error in the amount adsorbed. This is accomplished by packing as much adsorbent as possible into the sample cell.

Fortunately, with careful design, lower errors can be obtained for the fixed-volume injection method. Specifically, using a ratio of sample cell to reference cell of around 2.0 and reducing the void volume in the sample cell can result in significant reduction in expected uncertainties in the amount of gas adsorbed.

Nomenclature

- ρ = bulk gas pressure
- T = temperature
- z = gas compressibility factor
- V_{ads} = adsorbed phase volume
- V_{unads} = unadsorbed phase volume
- V^{ref} = reference volume
- V^{Cell} = cell volume
- $V_{\text{Void}}^{\text{He}}$ = helium void volume
- n_{inj} = amount injected
- n_{unads} = amount unadsorbed
- n_{sol} = amount of gas dissolved in water
- n^{Ex} = excess adsorption
- $n_{\text{ads}}^{\text{abs}}$ = absolute adsorption
- $\bar{\rho}_{\text{ads}}$ = average adsorbed phase density
- ρ_{gas} = gas density
- L = mass of the coal sample
- λ_{water} = mass fraction of water in the coal sample
- z_i = feed mole fraction
- y_i = gas phase mole fraction
- x_i^{abs} = adsorbed phase mole fraction (absolute)
- σ_{ρ}^2 = uncertainty in density
- σ_L^2 = uncertainty in the mass of coal sample
- $\sigma_{n_{\text{inj}}}^2$ = uncertainty in amount injected
- $\sigma_{n_{\text{unads}}}^2$ = uncertainty in amount unadsorbed
- $\sigma_{n_{\text{sol}}}^2$ = uncertainty in amount dissolved in water
- $\sigma_{n_{\text{ads}}}^2$ = uncertainty in amount adsorbed

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