

Alternative equation for sorption data interpretation

P. van Hemert, K.H.A.A. Wolf, TU Delft

ABSTRACT

Gibbs isotherm measurements are used to quantify the properties of coal-gas-water systems in the field of Enhanced Coalbed Methane production. Gibbs isotherms are measured with a volumetric sorption apparatus using a data interpretation equation which relates pressure, temperature and volume measurements to the Gibbs sorption. An alternative, more simple, equation is presented which allows easier sorption calculation and assessment of the influence of uncertainties. An example of the sensitivity of carbon dioxide Gibbs sorption on coal for the most important parameters is shown.

INTRODUCTION

The increasing demand world-wide for fossil fuels has led to renewed interest in alternative energy sources, including methane production from underground coal, known as coalbed methane (CBM). The production of CBM is already occurring commercially, i.e. in the United States, China and Australia. The production of CBM can be enhanced by injecting gas into the reservoir [1], known as enhanced coal-bed methane (ECBM) production. An additional advantage of ECBM is its potential to store undesirable gases, such as CO₂. A better understanding of ECBM reservoirs will maximize their production and storage potential. To increase the understanding of ECBM reservoirs, all aspects of the coal-gas-water systems are intensively being researched (e.g. [2], [3]); especially adsorption measurements are useful to quantify production and storage capabilities [4].

The measurement of the amount of the actual adsorbed gas is unfeasible, because the density of the sorbed phase cannot be measured independently [5]. Gibbs introduced the mathematical transformation that all changes in the properties of the sorbate and sorbent are attributed to a mathematical surface [6]. A physical interpretation of this transformation is the assumption that the sorbent is inert and that the sorbed phase and gas phase have equal density.

Gibbs isotherms of coal-gas systems are often measured using the volumetric sorption technique. However, this technique is prone to large uncertainties, as discussed by Mavor [4]. As an extension of his work, we present an alternative data interpretation equation for the calculation of Gibbs sorption isotherms from volumetric experiments. This alternative equation is easier to use and simplifies error analysis for Gibbs sorption measurements.

VOLUMETRIC SORPTION APPARATUS

The volumetric apparatus (Figure 1) is used to measure Gibbs isotherms [4, 5]. The apparatus consists of a sample cell connected to a reference cell with an external connection. The reference cell contains a built-in pressure transducer and a thermocouple.

Before an experiment the volume ratio is measured with helium expansion and then both cells are evacuated. The experimental procedure for helium expansion is identical to the experimental procedure for Gibbs sorption. An experiment is composed of two stages; an adsorption stage and a desorption stage. Multiple measurements (ten to twenty) are done in each stage. Every single measurements consists of two separate steps.

During the adsorption stage the Gibbs sorption is measured at increasing pressure. In step one of each adsorption measurement, the two cells are separated and gas is added to the

reference cell. After the pressure and temperature in the reference cell has stabilized, the two cells are connected in step two. At the end of step two, the system has attained pressure equilibrium and Gibbs sorption is measured. Step one and two are repeated for additional measurements until the maximum desired pressure is reached.

The Gibbs sorption at decreasing pressures is measured in the desorption stage. The first desorption measurement is performed after the last adsorption measurement. In step one of each desorption measurement, the two cells are separated and the reference cell is evacuated. After evacuation, the two cells are connected in step two. At the end of step two, the system is in pressure equilibrium and Gibbs sorption is measured. Step one and two are repeated for additional measurement down to atmospheric pressure.

The adsorption stage with ca. twenty measurements lasts 60 hours (Figure 2). The peaks are the step ones of the adsorption measurements and the consecutive valleys are the accompanying step two's. The desorption stage with ca. twenty measurements lasts 50 hours. The negative peaks are step ones of the desorption measurements and the consecutive plateaus the accompanying step two's. The 30 hour plateau between the two stages ensures the setup is still leak tight.

DATA INTERPRETATION EQUATIONS

The Gibbs sorption (n^M_{Gibbs} in mol/kg) at equilibrium step M is calculated with the material balance of the total amount of gas in the sample cell and the equilibrium amount of gas in the sample cell (equation 1). The total gas in the sample cell at step M is the amount exchanged with the reference cell summed for step 1 to M . The amount of gas exchanged is calculated from the difference in density (ρ in mol/dm³) in the reference cell between the filling and equilibrium phase. Density is a function of pressure (P in bar) and temperature (T in K). Accurate equations of state, such as [7] for carbon dioxide, are necessary to obtain accurate densities. Inaccurate equations of state, e.g. cubic ones, introduce a systematic error. The equilibrium amount of gas in the sample cell is the density at the equilibrium pressure and temperature multiplied by χ , a volume ratio of the available volumes for gas in the two cells. This difference in material balance (mol/dm³) is multiplied by the reference cell volume (V_{ref} in dm³) and divided by the sample weight (m in kg) giving Gibbs sorption (n^M_{Gibbs} in mol/kg).

$$n^M_{Gibbs} = \frac{V_{ref}}{m} \left(\left[\sum_{i=1}^M \rho(P_1^i, T_1^i) - \rho(P_2^i, T_2^i) \right] - \chi \rho(P_2^M, T_2^M) \right) \quad (1)$$

χ is the ratio of the void volume in the sample cell (V_{void} in dm³) and the reference cell volume (V_{ref} in dm³). It is measured using helium expansion (equation 2) before and after the experiment. Equation 2 can be derived from equation with the assumption that Gibbs sorption of helium is negligible. The density of helium is calculated with [8]. χ is constant throughout the experiment and is not dependent on the size of the gas molecules.

$$\chi = \frac{V_{void}}{V_{ref}} = \frac{\rho(P_2^i, T_2^i) - \rho(P_1^i, T_1^i)}{\rho(P_1^i, T_1^i) - \rho(P_2^i, T_2^i)} \quad (2)$$

Instead of Gibbs sorption, absolute sorption is sometimes reported. Absolute sorption uses an additional parameter to account for changes in the sorbent (e.g. swelling [9]) or a difference in density between the gas and sorbed phase. This practice is advised against for scientific purposes, because no accurate and independent measurements of these properties exist. The alternative equations for absolute sorption interpretation are presented for easy reference. Equation 3 contains an additional parameter (equation 4) for the volume averaged density of the sorbed phase (ρ_{sorb} in mol/dm³). Equation 5 contains an additional parameter (equation 6) for volume changes of the sorbent (ΔV_{sample} in dm³). Equation 7 contains both additional parameters.

$$n_{Abs}^M = \frac{V_{ref}}{\Theta m} \left(\left[\sum_{i=1}^M \rho(P_1^i, T_1^i) - \rho(P_2^i, T_2^i) \right] - \chi \rho(P_2^M, T_2^M) \right) \quad (3)$$

$$\Theta = \left(1 - \frac{\rho(P_2^M, T_2^M)}{\rho_{sorb}(P_2^M, T_2^M)} \right) \quad (4)$$

$$n_{Abs}^M = \frac{V_{ref}}{m} \left(\left[\sum_{i=1}^M \rho(P_1^i, T_1^i) - \rho(P_2^i, T_2^i) \right] - (\chi - \omega) \rho(P_2^M, T_2^M) \right) \quad (5)$$

$$\omega = \frac{\Delta V_{sample}}{V_{ref}} \quad (6)$$

$$n_{Abs}^M = \frac{V_{ref}}{\Theta m} \left(\left[\sum_{i=1}^M \rho(P_1^i, T_1^i) - \rho(P_2^i, T_2^i) \right] - (\chi - \omega) \rho(P_2^M, T_2^M) \right) \quad (7)$$

Equation 1 is an alternative from of the data interpretation equations as suggested by Mavor (equation 8) [4]. It is therefore informative to compare the two equations and explain their differences. The basic concept, a material balance calculation, is unchanged. Equation 8 is formulated cumulative, i.e. the sorption of each step is added to total of the sorption of the previous steps. This cumulative formulation is mathematically difficult and is easier usable when written out (equation 9). R is the universal gas constant ($\text{bar} \cdot \text{dm}^3 \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$). Z is the compressibility factor quantifying the deviation from the ideal gas law, which is a function of pressure and temperature.

$$n_{Gibbs}^M = n_{Gibbs}^{M-1} + \frac{V_{ref}}{m} \left(\frac{P_1^M T_1^M}{Z(P_1^M, T_1^M) T_1^M R} - \frac{P_2^M T_2^M}{Z(P_2^M, T_2^M) T_2^M R} \right) + \frac{V_{void}}{m} \left(\frac{P_2^{M-1} T_2^{M-1}}{Z(P_2^{M-1}, T_2^{M-1}) T_2^{M-1} R} - \frac{P_2^M T_2^M}{Z(P_2^M, T_2^M) T_2^M R} \right) \quad (8)$$

$$n_{Gibbs}^M = \frac{V_{ref}}{m} \left(\sum_{i=1}^M \frac{P_1^i T_1^i}{Z(P_1^i, T_1^i) T_1^i R} - \frac{P_2^i T_2^i}{Z(P_2^i, T_2^i) T_2^i R} \right) + \frac{V_{void}}{m} \left(\sum_{i=1}^M \frac{P_2^{i-1} T_2^{i-1}}{Z(P_2^{M-1}, T_2^{M-1}) T_2^{i-1} R} - \frac{P_2^i T_2^i}{Z(P_2^M, T_2^M) T_2^i R} \right) \quad (9)$$

Comparing equation 1 to 9 shows the differences of the alternative formulation to the classic formulation. The real gas law in equation 9 has been substituted by the density function (equation 10). Density is physically more simple to understand and simplifies the calculation considerably. The redundant summation of the difference in equilibrium densities is replaced by the single remaining term. This makes the formula more concise and thus easier to calculate.

Incorporating these redundant terms would overestimate the experimental uncertainty of the measurements. The equilibrium term in equation 9 is multiplied with the void volume, where as the equilibrium term in equation 1 is multiplied by χ and all density terms are multiplied by the reference volume. χ is an independently measured parameter, where as V_{void} is calculated from V_{ref} and χ (equation 2). The use of dependent parameter V_{void} unnecessarily complicates error analysis.

$$\rho(P,T) = \frac{n(P,T)}{V} = \frac{P}{RTZ(P,T)} \quad (10)$$

ERROR ANALYSIS

Error in a scientific measurement is the inevitable uncertainty that is present in all measurements [10]. Without a reported uncertainty a measurement is severely reduced in value, because the accuracy of the final result is an important factor. The uncertainty of a measurement is the standard deviation of repeated similar experiments. The uncertainty of direct measurements can be estimated a priori from the properties of the measuring equipment. Uncertainty of indirectly measured quantities can be estimated a priori from the properties of the measuring equipment combined with error propagation.

The uncertainty in the indirectly measured quantities of Gibbs sorption depends on the uncertainties of the directly measured quantities; pressures, temperatures, reference cell volume, volume ratio and sample weight (equation 11, or equation 12 for independent random errors). Formulas for the partial derivatives are presented in Appendix A.

$$\begin{aligned} \delta n_{Gibbs}^M \leq & \frac{\partial n_{Gibbs}^M}{\partial V_{ref}} \delta V_{ref} + \frac{\partial n_{Gibbs}^M}{\partial m} \delta m + \sum_{i=1}^M \sum_{k=1}^2 \frac{\partial n_{Gibbs}^M}{\partial P_k^i} \delta P_k^i + \\ & + \sum_{i=1}^M \sum_{k=1}^2 \frac{\partial n_{Gibbs}^M}{\partial T_k^i} \delta T_k^i + \frac{\partial n_{Gibbs}^M}{\partial \chi} \delta \chi \end{aligned} \quad (11)$$

$$\delta n_{Gibbs}^M = \sqrt{\left(\frac{\partial n_{Gibbs}^M}{\partial V_{ref}} \delta V_{ref} \right)^2 + \left(\frac{\partial n_{Gibbs}^M}{\partial m} \delta m \right)^2 + \left(\frac{\partial n_{Gibbs}^M}{\partial m} \delta m \right)^2 + \sum_{i=1}^M \sum_{k=1}^2 \left(\frac{\partial n_{Gibbs}^M}{\partial P_k^i} \delta P_k^i \right)^2 + \sum_{i=1}^M \sum_{k=1}^2 \left(\frac{\partial n_{Gibbs}^M}{\partial T_k^i} \delta T_k^i \right)^2 + \left(\frac{\partial n_{Gibbs}^M}{\partial \chi} \delta \chi \right)^2} \quad (12)$$

Two types of errors are distinguished; random and systematic errors. Random errors can be revealed by repeating the experiment, whereas systematic errors cannot [10]; i.e. the magnitude of the random error depends on the measurements being compared.

- Measurements on an identical sample performed in the same setup should not deviate more than the random error introduced by the random uncertainty in the pressure, temperature measurements and the determined χ .
- Measurements on an identical sample performed in the different setups should not deviate more than the random error introduced by the random uncertainty in the pressure, temperature and determined χ and V_{ref} .

When measurements on identical samples do not agree within the random uncertainty, some systematic uncertainty must exist in one of the experiments. Significant differences in sample preparation, such as water equilibration procedure, are sometimes referred to as

systematic errors. More correctly, the existence of these differences violates the identical sample condition and precludes any comparison for error analysis.

The most dangerous systematic errors in volumetric sorption experiments (Figure 4) is a changing volume ratio. The sensitivity of Gibbs sorption with changes in χ means that care should be taken in its measurement and the assumption of its independency of pressure, temperature and time during an experiment. The volume ratio has to be measured both before and after the experiment. A procedure for measuring its changes during an experiment is preferred.

Other common systematic errors are inaccuracies in the pressure and temperature measurements (Figure 4). The influence of such calibration errors becomes larger if the gas is near to its critical point, such as carbon dioxide at the conditions of the Recopol project (<http://recopol.nitg.tno.nl>). Near the critical point large density changes occur with small pressure and temperature changes increasing the influence of systematic errors. This can explain some of the discrepancies in measured CO₂ Gibbs sorption isotherms [11].

SUMMARY

We present an alternative and more simple material balance formulation for Gibbs Excess Surface isotherms measured with a volumetric sorption apparatus. We emphasize that Gibbs sorption is sensitive to random and systematic uncertainties due to the nature of the experiment, which measures the difference between the large quantities of total and equilibrium gas in the setup. To facilitate error analysis we present the equations necessary for the estimation of the random and systematic uncertainties in Appendix A.

APPENDIX A

The partial derivatives of n^M_{Gibbs} with respect to the different direct variables are shown; The partial derivative of density with respect to pressure and/or temperature is best numerically evaluated.

$$\frac{\partial n^M_{Gibbs}}{\partial V_{ref}} = \frac{n^M_{Gibbs}}{V_{ref}} \quad (\text{A.1})$$

$$\frac{\partial n^M_{Gibbs}}{\partial m} = \frac{n^M_{Gibbs}}{m} \quad (\text{A.2})$$

$$\frac{\partial n^M_{Gibbs}}{\partial P_1^i} = \frac{V_{ref}}{m} \frac{\partial \rho(P_1^i, T_1^i)}{\partial P_1^i}, i \leq M \quad (\text{A.3})$$

$$\frac{\partial n^M_{Gibbs}}{\partial T_1^i} = \frac{V_{ref}}{m} \frac{\partial \rho(P_1^i, T_1^i)}{\partial T_1^i}, i \leq M \quad (\text{A.4})$$

$$\frac{\partial n^M_{Gibbs}}{\partial P_2^i} = \frac{-V_{ref}}{m} \frac{\partial \rho(P_2^i, T_2^i)}{\partial P_2^i}, i < M \quad (\text{A.5})$$

$$\frac{\partial n^M_{Gibbs}}{\partial T_2^i} = \frac{-V_{ref}}{m} \frac{\partial \rho(P_2^i, T_2^i)}{\partial T_2^i}, i < M \quad (\text{A.6})$$

$$\frac{\partial n^M_{Gibbs}}{\partial P_2^M} = \frac{-V_{ref}}{m} \left(\frac{\partial \rho(P_2^M, T_2^M)}{\partial P_2^M} + \chi \frac{\partial \rho(P_2^M, T_2^M)}{\partial P_2^M} \right) \quad (\text{A.7})$$

$$\frac{\partial n^M_{Gibbs}}{\partial T_2^M} = \frac{-V_{ref}}{m} \left(\frac{\partial \rho(P_2^M, T_2^M)}{\partial T_2^M} + \chi \frac{\partial \rho(P_2^M, T_2^M)}{\partial T_2^M} \right) \quad (\text{A.8})$$

$$\frac{\partial n^M_{Gibbs}}{\partial \chi} = \frac{-V_{ref} \rho(P_2^M, T_2^M)}{m} \quad (\text{A.9})$$

NOMENCLATURE

m	Sample weight	(kg)
n_{Gibbs}	Gibbs sorption	(mole/kg)
n_{Abs}	Absolute sorption	(mole/kg)
P	Absolute pressure	(bar)
R	universal gas constant	(mole·K·bar ⁻¹ ·cm ⁻³)
T	Absolute temperature	(K)
V_{ref}	Volume accessible to gas in reference cell	(dm ³)
V_{void}	Volume accessible to gas in sample cell	(dm ³)
Z	Compressibility factor	(-)
χ	Ratio between V_{void} and V_{ref}	(-)
ρ	Density of gas	(mole·dm ⁻³)

Subscripts

1	denotes step 1 in the experimental procedure
2	denotes step 2 in the experimental procedure
k	denotes the first or second experimental step

Superscripts

i	denotes the i^{th} measurement step
M	denotes the Gibbs sorption measurement of interest
N	denotes the number of components

ACKNOWLEDGMENTS

We thank the CATO-programme and Shell for the fundings that made this project possible. We express the greatest thank to Hans Bruining and Niels van Wageningen for advise on reporting the findings, and to Jos Maas for valuable discussion on experimental uncertainties.

REFERENCES

1. Puri, R. and D Yee, 1990: "Enhanced coalbed methane recovery"; SPE 20732, presented at the 65th Annual Technical Conference of the Society of Petroleum Engineers, New Orleans, Louisiana, p.193-202.
2. Hildenbrand A., B.M. Krooss, A. Busch and R. Gaschnitz, 2006: "Evolution of methane sorption capacity of coal seams as a function of burial history – a case study from the Campine Basin, NE Belgium"; International Journal of Coal Geology, V. 66, no. 3, p. 179-203.
3. Harpalani, S. and G.L. Chen, 1995: "Estimation of changes in fracture porosity of coal with gas emission"; Fuel, V. 74, No. 10, p. 1491-1498.
4. Mavor M.J. and C. Hartman, 2004; "Uncertainty in Sorption Isotherm Measurements", Proceedings of the 2004 International Coalbed Methane Symposium, Tuscaloosa, Alabama.
5. Gumma S. and O. Talu, 2003; "Gibbs Dividing Surface and Helium Adsorption"; Adsorption, 9, p. 17-28.
6. Gibbs, J.W., 1928; The Collected Works of J.W. Gibbs: New York, Longmans and Green.
7. Sun L.X., S.B. Kiselev, J.F. Ely, 2005: " Multiparameter crossover equation of state: Generalized algorithm and application to carbon dioxide"; Fluid Phase Equilibria, V. 233, No. 2, p. 204-219.
8. McCarthy R.D. and V.D. Arp, 1990: "A New Wide Range equation of State for Helium"; Adv. Cryo. Eng., V. 35, p. 1465-1475.
9. Romanov V.N., A.L. Goodman and J.W. Larsen, 2006: "Errors in CO₂ adsorption measurements caused by coal swelling"; Energy & Fuels, V. 20, No. 1, p. 416-416.
10. Taylor J.R., 1997: An Introduction To Error Analysis, The Study of Uncertainties in Physical Measurements, 2nd Edition, University Science Books, Sausalito, California (1997), p. 75 & p. 106.
11. Goodman A.L., A. Busch, G.J. Duffy, J.E. Fitzgerald, K.A.M. Gasem, Y. Gensterblum, B.M. Krooss, J. Levy, E. Ozdemir, Z. Pan, R.L. Robinson, K. Schroeder, M. Subidandriyo and C.M. White, 2004; "An inter-laboratory comparison of CO₂ isotherms measured on Argonne premium coal samples"; Energy & Fuels, V. 18, No. 4, p. 1175-1182.
12. van Hemert P., K.H.A.A. Wolf and J.G. Maas, 2006: "Adsorption of carbon dioxide and a hydrogen-carbon dioxide mixture", Proceedings of the 2006 International Coalbed Methane Symposium, Tuscaloosa, Alabama.

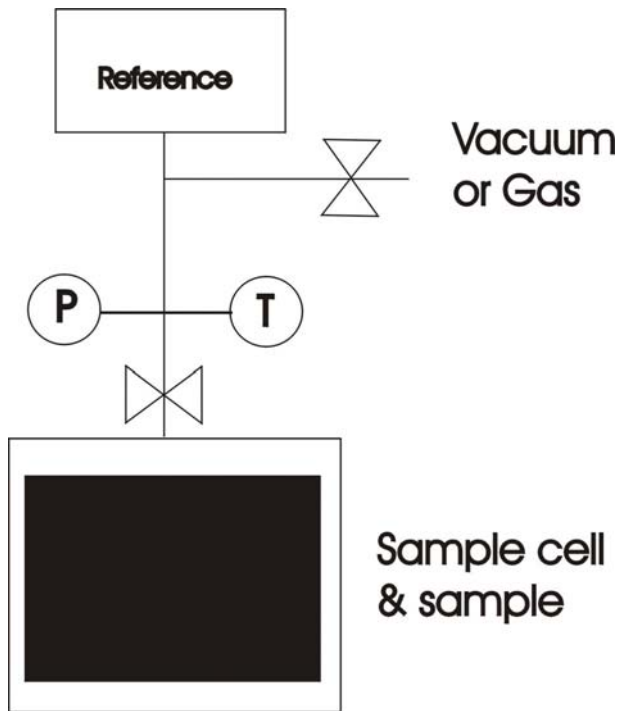


Figure 2: Schematic drawing of classic experimental setup for volumetric measurements of Gibbs sorption [4].

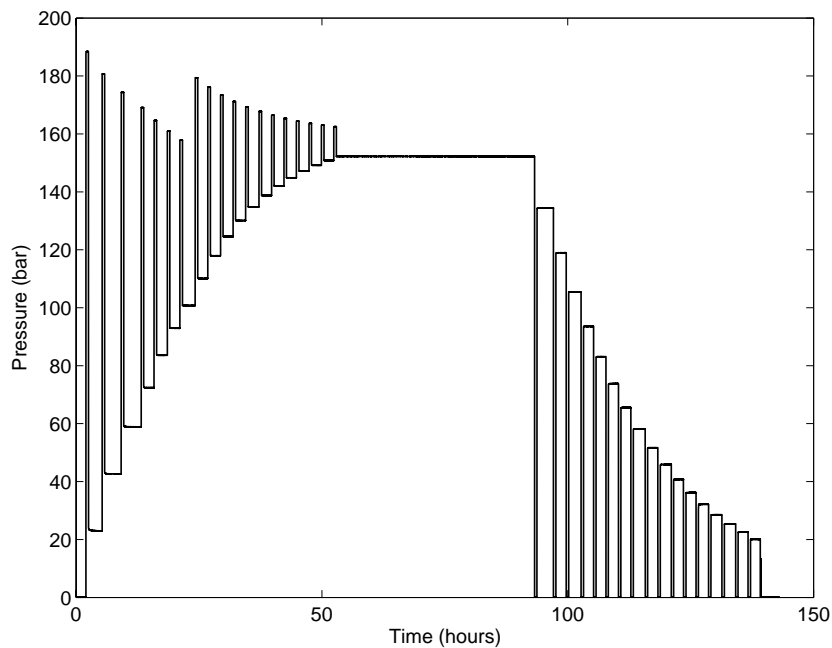


Figure 3: Pressure development in reference cell during measurement of the Gibbs adsorption (0 to 60 hours) and Gibbs desorption (90 to 140 hours) isotherms.

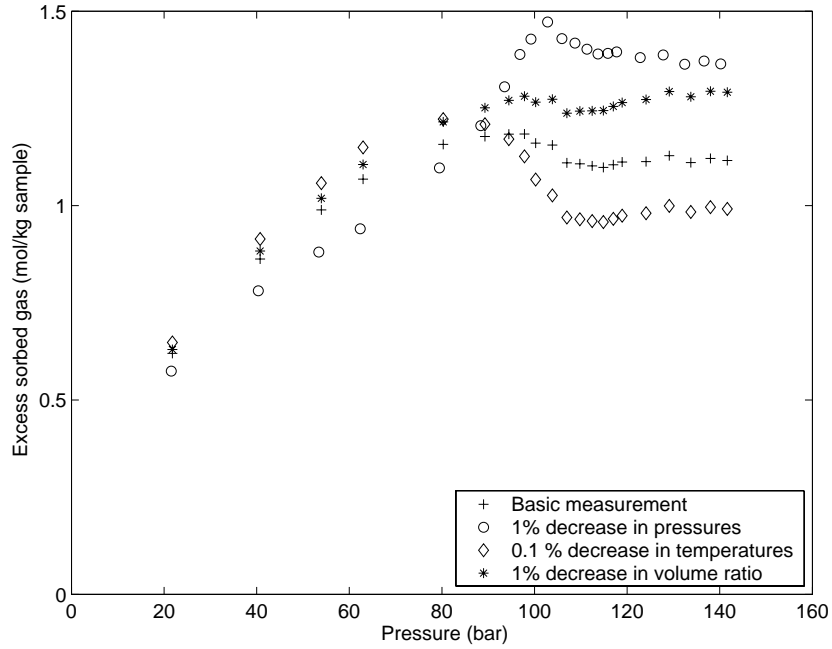


Figure 4: Gibbs adsorption isotherm of carbon dioxide on wet Tupton coal at 322 K [12]. The influence of small systematic uncertainties in the P, T or χ parameters on the calculated Gibbs sorption is demonstrated.