Adsorption of carbon dioxide
and a hydrogen-carbon dioxide mixture

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ABSTRACT

Methane can be converted into hydrogen, but removal of byproduct carbon dioxide is expensive. Methane production from coalbed reservoirs can be increased by injecting carbon dioxide, storing the carbon dioxide. To examine the potential of using the hydrogen-carbon dioxide as an injectant in coalbed methane reservoir to enhance methane production and store carbon dioxide without loss of hydrogen details on the sorption properties of such a system must be known. The Gibbs sorption of a hydrogen-carbon dioxide (80-20 mole %) mixture and pure carbon dioxide is measured on a water equilibrated medium rank coal at ~322 K to 150 bar. To ensure the reliability of the data duplicate experiments are performed in separate setups. The sensitivity of volumetric sorption measurements for systematic uncertainties is demonstrated.

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 carbon dioxide (CO_2). Better understanding of the physics of ECBM reservoirs allows full exploitation of their production and storage potential. For example, the produced methane can be converted into hydrogen-carbon dioxide and injected into the coalbed to enhance methane production and filter the carbon dioxide out of the mixture. In order to ensure the feasibility of this technique, the behavior of hydrogen-carbon dioxide-methane-water- coal systems must be understood. Some work has been done on the behavior of carbon dioxide-methane-water-coal has been done (e.g. [2] and [3]), but data on hydrogen is not available.

The aim of this study is to measure Gibbs sorption isotherms for CO_2 and a hydrogen-carbon dioxide (H_2:CO_2 80-20 mole %) mixtures at reservoir conditions. The measurement of the actually adsorbed gas is impossible, because the density of the sorbed phase cannot be measured independently [4]. Gibbs introduced the mathematical transformation that all changes in the properties of the sorbate and sorbent are attributed to a mathematical surface [5]. A physical interpretation of this transformation is the assumption that the sorbate phase is inert and that the sorbed and gas phase have equal density.

A modified version of the volumetric sorption apparatus [6] has been constructed and two preliminary carbon dioxide and two hydrogen-carbon dioxide mixture experiments on medium rank coal have been performed.

MATERIAL AND METHODS

Volumetric sorption apparatus

The setup (Figure 1) is based on the experimental setups of Mavor (Figure 2) [6].The basic apparatus consists of a sample cell and a reference cell. The reference cell contains a built-in pressure transducer and a thermocouple. The main improvement in this new setup is the inclusion of two inline sample valves. The inline sample valves which allow direct sampling to the gas chromatograph with minimal system disturbance (sample volume ~0.1 µL). The setup contains two similar identical sorption setups to allow for duplicate experimentation. The entire setup is in a water filled thermostatic bath kept at ~322 K.

Before an experiment the volume ratio is measured with helium expansion and then both cells are evacuated. The experimental procedure is identical to the experimental procedure for Gibbs sorption. The experiment is composed of two stages; an adsorption stage and a desorption stage. Each stage consists of multiple measurements and each measurement is made up of two 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 (step 2). The Gibbs sorption is measured after equilibration. Step one and two are repeated for additional measurements until the maximum pressure is reached.

In the desorption stage the Gibbs sorption is measured at decreasing pressures. It is performed directly 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 (step 2). The Gibbs sorption is measured after equilibration. Step one and two are repeated for additional measurement down to atmospheric pressure.

The adsorption stage with ca. twenty measurements lasts 60 hours (Figure 3). 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 the step one's of the desorption measurements and the consecutive plateaus the accompanying step two's. The 30 hour plateau between the two stages is used to verify the setup is still leak tight.

The experiments were done at actual in-situ conditions (Table 1). The pressure and temperature in the reference cells is recorded every ten seconds. The system is considered at equilibrium when the pressure change is less than 0.2 bar/h. The temperatures are measured with type K thermocouples; the random uncertainty is 0.02 K averaged over fifty measurements. There was a variation of 0.05 to 0.1 K in the temperature due to the day-night cycle. The pressures are measured using a Drück^{TM} PTX 611 pressure transducers, the random uncertainty is 0.002 bar averaged over fifty measurements. The pressures of the evacuated reference cells could not reliably be measured and is assumed to be 0.01 bar.

Sample preparation

A medium rank (*Rmax=0.53*) coal sample from the Nottinghamshire and North Derbyshire Coalfield, referred to as Tupton, was selected for use because of its availability. The coal was broken into small particles by consecutive use of a hammer, steel crushing jaw and a grinder. These particles were sieved into two fractions; smaller and larger than 2.0 mm fraction; the larger than 2.0 mm fraction was selected for experimentation. The sieving and breaking procedures were kept as brief as possible, to minimize fracturing of the coal to dust. The fractions were split into batches of ~70 cm^3 and stored in glass jars with an argon atmosphere in a refrigerator at ~5°C.

Before an experiment, the sample is equilibrated with moisture at 96 to 97 % relative humidity at 30 °C. The procedure is based on the ASTM standard for equilibrium moisture determination [7]: The coal sample is completely saturated with water and then equilibrated in a desiccator with a saturated solution of K_2SO_4 at 30°C at 0.1 bar for several weeks. The weight of the water equilibrated coal starts decreasing as soon as the sample is removed from the desiccator. The coal is built into the sample cell as fast as possible to minimize the loss of water. In contrast, the weight at the end of the experiment is stable implying water equilibrium.

Data interpretation equations

The Gibbs sorption (n^M_{Gibbs} in mol/kg) at equilibrium step M for experiments with pure gas 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) [8]. The total gas in the sample cell at step M is the amount exchanged with the reference cell summed for measurement *1* to *M*. The amount of gas exchanged in one step is calculated from the difference in density (ρ in mol/dm^3) in the reference cell between the filling and equilibrium phase. Density is a function of pressure (P in bar) and temperature (T in K). Reference equations, such as [9] for carbon dioxide, are necessary to obtain accurate densities. Inaccurate equations of state, such as cubic ones, introduce a systematic error. An accurate equation of state for hydrogen-carbon dioxide mixtures has not yet been found. To demonstrate our first results, the ideal gas law has been used. This introduces a systematic error in the Gibbs isotherms, and the preliminary status of these results is emphasized. The equilibrium amount of gas in the sample cell is the density at the equilibrium pressure and temperature multiplied by χ, the volume ratio of the available volumes for gas in the two cells. This difference in material balance in mol/dm^3 is multiplied by the reference cell volume (V_{ref} in dm^3) and divided by the sample weight (m in kg) giving Gibbs sorption (n^M_{Gibbs} in mol/kg).

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

χ, the ratio of the volume accessible to gas in the sample cell (V_{cell} in dm^3) and the reference cell volume (V_{ref} dm^3), is measured using helium expansion (Equation 2). Helium density is calculated with [10]. Helium sorption is assumed negligible when determining χ. Use of χ in Equation 1 implicitly assumes it is constant for gas type, pressure, temperature, sorption and time.

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

To calculate total Gibbs sorption at equilibrium step M for a mixture, Equation 1 is modified to incorporate the dependence of density on composition (Equation 3). The composition of a gas is defined by the mole fractions (x) of the different components (N is the number of components).

$$n^M_{Gibbs} = \frac{V_{ref}}{m}\left(\left[\sum_{i=1}^{M}\rho(P_1^i,T_1^i,\sum_{k=1}^{N-1}x_1^{i,k}) - \rho(P_2^i,T_2^i,\sum_{k=1}^{N-1}x_1^{i,k})\right] + -\chi\rho(P_2^M,T_2^M,\sum_{k=1}^{N-1}x_1^{M,k})\right) \tag{3}$$

To calculate the Gibbs sorption of component α at equilibrium step M Equation 3 is modified from a general to a component specific material balance (Equation 4).

$$n^{M,\alpha}_{Gibbs} = \frac{V_{ref}}{m}\left(\left[\sum_{i=1}^{M}x_1^{i,\alpha}\rho(P_1^i,T_1^i,\sum_{k=1}^{N-1}x_1^{i,k}) - x_2^{i,\alpha}\rho(P_2^i,T_2^i,\sum_{k=1}^{N-1}x_1^{i,k})\right] + -x_2^{M,\alpha}\chi\rho(P_2^M,T_2^M,\sum_{k=1}^{N-1}x_1^{M,k})\right) \tag{4}$$

Mole fractions are calculated from the number of moles (s) of each component (Equation 5) as measured by the GC (Equation 6).Where k^α mole·V^{-1}·s^{-1}·dm^{-3} is the calibration factor of component α converting the measured peak area (A^α in V·s) to molar density (mol·dm^{-3}).

$$x^\alpha = \frac{s^\alpha}{\sum\limits_{k=1}^{N} s^k} \tag{5}$$

$$s^\alpha = k^\alpha A^\alpha \tag{6}$$

Unfortunately, in these experiments with the hydrogen-carbon dioxide mixture, only carbon dioxide could reliably be measured. The hydrogen peaks were undetectable or overlapped with the larger carbon dioxide peaks. Therefore, Equation 5 is replaced by Equation 7 resulting in Equation 8.

$$x^\alpha = \frac{s^\alpha}{\rho\left(P,T,\sum\limits_{k=1}^{N-1} x^k\right)} \tag{7}$$

$$n_{Gibbs}^{M,\alpha} = \frac{V_{ref}}{m}\left(\left[\sum\limits_{i=1}^{M} s_1^{i,\alpha} - s_2^{i,\alpha}\right] - \chi s_2^{M,\alpha}\right) \tag{8}$$

RESULTS & DISCUSSION

The sensitivity of Gibbs sorption with carbon dioxide is demonstrated in Figure 4. The following systematic errors explain the factor two deviation; A systematic uncertainty of one K in the temperature measurements, two percent in the pressure measurements and a change in the void volume of four percent. The pressure and temperature systematic uncertainties were independently confirmed. The change in void volume is caused by the loss of water during the evacuation procedure. Coal swelling may also contribute to changes in void volume. This sensitivity partly explains the large spread in Gibbs sorption of carbon dioxide on identical samples in an inter-laboratory comparison [11].

The sensitivity of Gibbs sorption with carbon dioxide at reservoir conditions is evident from the peaks and valleys at 100 bar. Carbon dioxide at typical reservoir conditions (e.g. 100 bar and 322 K, see e.g. http://recopol.nitg.tno.nl) is near its critical point, where small changes in pressure and/or temperature have large influence on the density. A small uncertainty in pressure and temperature has a significant influence on the calculated density which has a large influence on the Gibbs sorption.

The dependence of Gibbs sorption on the density equation (e.g. Equation 1) shows that accurate equations of state are necessary for volumetric measurements. For few mixtures accurate measurements on the density behavior with compositions exist. The use of an inaccurate density, such as ideal density, introduces systematic deviations in the material balance (Figure 5). The deviation between the adsorption and desorption isotherms and the increasing behavior of the desorption isotherm is caused by these material balance errors. The cause of the deviation between the duplicate experiments (< 5 %) is under investigation.

The importance of compositional equilibration is demonstrated in Figure 6. The two measurements of carbon dioxide Gibbs sorption in a hydrogen-carbon dioxide mixture vary significantly and even show some negative carbon dioxide sorption. These effects are experimental artifacts caused by insufficient mixing of the gas. In Equation 4, compositional equilibration of the gas in the entire is implicitly assumed. Compositional equilibration is attained through gas diffusion with a diffusion coefficient of 10^{-7} m^2/s at 100 bar [12]; resulting in a characteristic time of ~40 days for a reference cell length of 1 m. The equilibration time of the pressure was in the order of hours (Figure 3), precluding the compositional equilibration assumption and explaining the experimental artifacts.

CONCLUSION

1. A set-up in which simultaneous two independent sorption experiments can be performed has been constructed.
2. Equation 1 and related equations show that Gibbs sorption measurements require accurate knowledge of the gas density. No accurate model for multi-component gas density exists, limiting the usefulness of multi-component sorption experiments.
3. Gibbs sorption measurements are very sensitive for changes and errors in the volume ratio of the void volume and the reference cell.
4. Gibbs sorption measurements with carbon dioxide at reservoir conditions (100 bar, 322 K) are very sensitive to inaccuracies in the pressure and temperature measurements. Such reservoir conditions are near the critical point of carbon dioxide, where the density of carbon dioxide strongly depends on pressure and temperature.
5. Gas diffusion at high pressures is too slow for compositional equilibration during an experiment, impairing the validity of compositional measurements. One possible remediation of this problem is the implementation of a magnetic pump.

NOMENCLATURE.

k	Calibration factor for converting measurements	$(\text{mole}\cdot\text{dm}^{-3}\cdot\text{V}^{-1}\cdot\text{s}^{-1})$
m	Sample weight	(kg)
n_{Gibbs}	Gibbs sorption	(mole/kg)
s	Amount of gas	(mole)
x	Mole fraction	(-)
A	Area response of gas chromatograph	$(\text{V}\cdot\text{s})$
P	Absolute pressure	(bar)
R	universal gas constant	$(\text{mole}\cdot\text{K}\cdot\text{bar}^{-1}\cdot\text{cm}^{-3})$
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	$(\text{mole}\cdot\text{dm}^{-3})$

*Subscript*s

1	denotes step 1 in the experimental procedure
2	denotes step 2 in the experimental procedure

Superscripts

i	denotes the ith measurement
k	denotes the kth component
M	denotes the Gibbs sorption measurement of interest
N	denotes the number of components
α	denotes a component of interest, e.g. carbon dioxide

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Table 1: Details of the experiments.

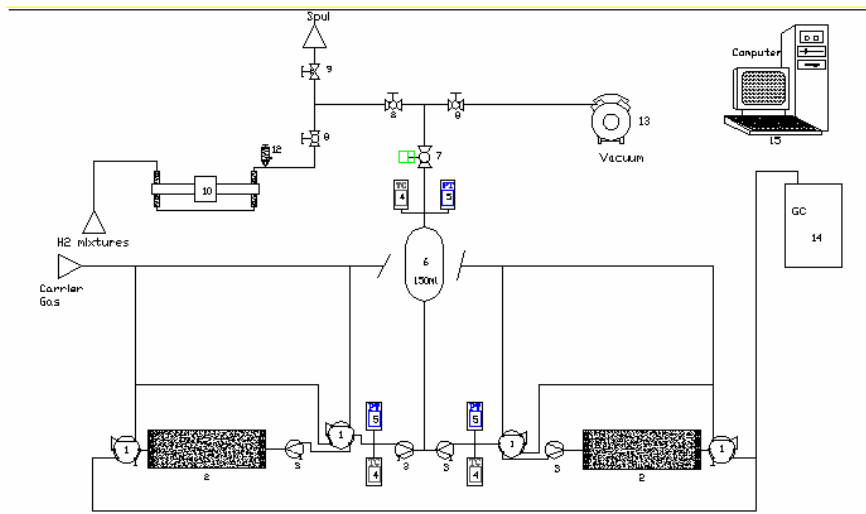| Experiment	Gas	start weight (g)	end weight (g)	start X (-)	end X (-)	T (k)	P max (bar)
1	CO_2	40.79	38.87	6.089	-	321.5	141
2	CO_2	42.51	41.84	5.636	-	322.8	149
3	H_2-CO_2 8:2 mole	38.9	37.7871	6.267	6.288	322.3	155
4	H_2-CO_2 8:2 mole	41.0	40.0938	5.877	5.875	322.4	159

Figure 1: Technical drawing of new experimental setup which allows two simultaneous volumetric Gibbs sorption experiments with in-line gas chromatography valves for compositional measurements.
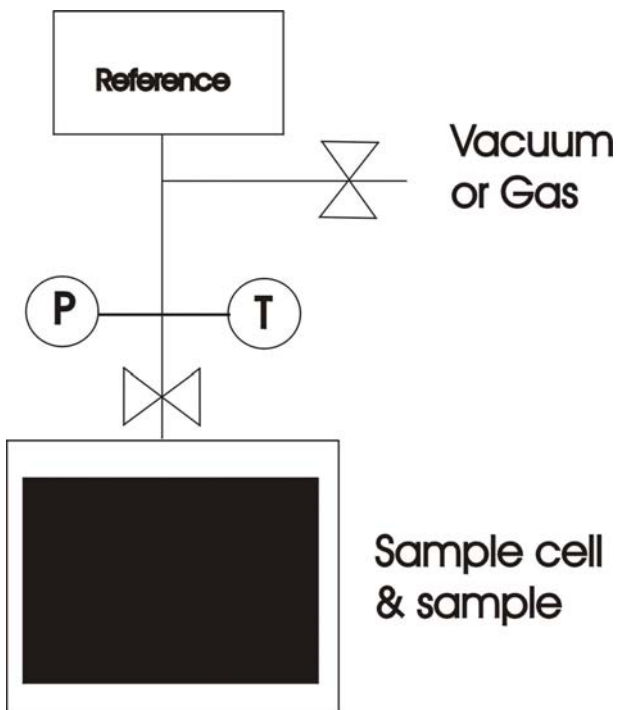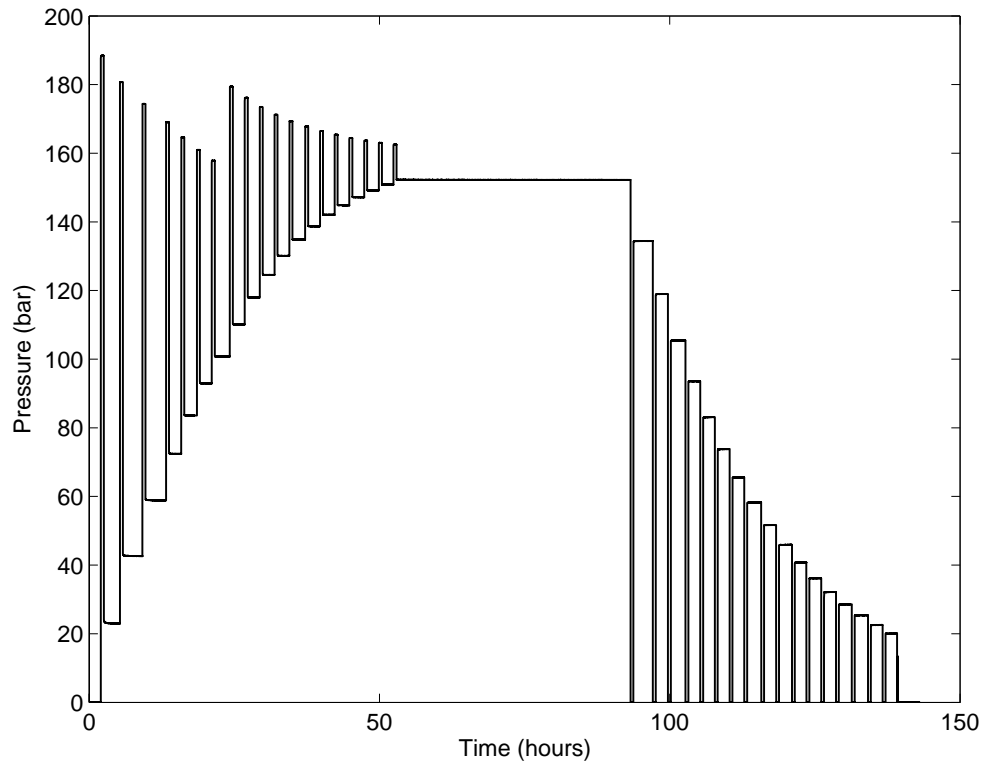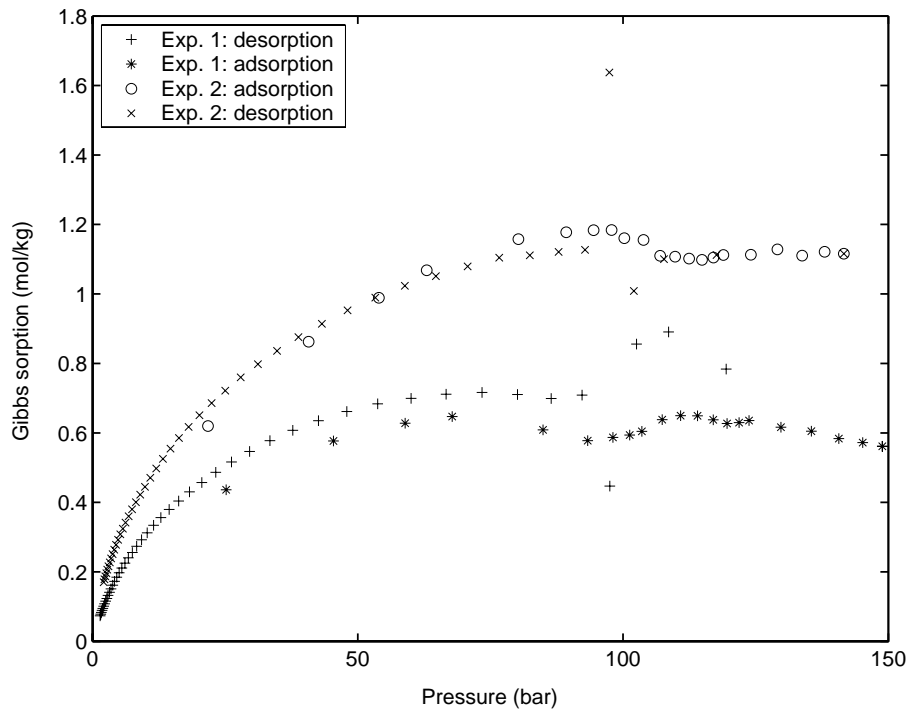

Figure 2: Schematic drawing of classic experimental setup for volumetric measurements of Gibbs sorption [6].

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: The adsorption and desorption isotherms of the two independent carbon dioxide sorption measurements.
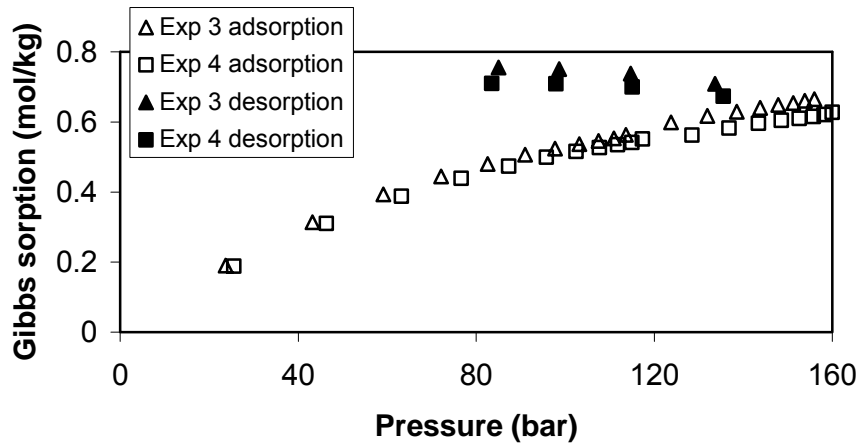
Figure 5: Total sorption of 80-20% hydrogen-carbon dioxide mixture on wet Tupton coal at ~322 K.
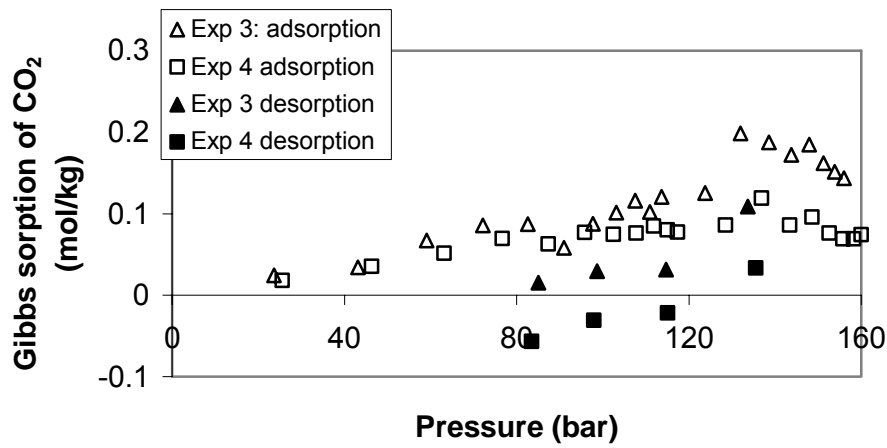

Figure 6: Sorption of carbon dioxide in a 80-20% hydrogen-carbon dioxide mixture on wet Tupton coal at ~322 K.