“Non-linearities and upscaling in porous media“

Master’s Thesis

Sorption of methane and ethane on Belgian black shale using a manometric setup

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Abstract

The Shale gas production in the last two decades in the U.S has increased interest in this field, especially in European countries. Shale as an unconventional abundant formation has drawn much attention, since horizontal drilling and hydraulic fracturing has made the production of natural gas stored in these formations an option that should be considered. In order to estimate the gas in place in the shale and the recovery efficiency, knowledge about the quantity and the state of the gas in the formation is crucial. Adsorption as the most dominant process in gas storage is the topic of this thesis. Excess sorption capacities of Black shale from Belgium for methane and ethane was investigated. In case of methane, experiments in three different temperatures of 308 K, 318 K and 336 K and pressures up to 11 MPa are performed. The maximum methane sorption capacity of the shale is found to be 0.013-0.039 mmole per gram of sample, which tends to decrease at increasing temperature. Excess sorption experiments on ethane are performed at a temperature of 318 K and pressures up to 9 MPa. The maximum excess sorption capacity of the shale for ethane is found to be 0.7 mmole per gram of the sample, which is more than one order of magnitude higher than that of methane.
Nomenclature

Φ The ratio between the occupied adsorption sites to the total number of adsorption sites in an adsorbent
Φ(δ, τ) Fundamental dimensionless Helmholtz energy
Φ0(δ, τ) Ideal gas part of the dimensionless Helmholtz energy
Φr(δ, τ) Residual part of the dimensionless Helmholtz energy
ΔH The enthalpy of the adsorption
ΔV Volume changes defined from pump counter in volumetric method
Δm Mass changes in gravimetric method
ΔVads The changes in void volume of the sample due to the adsorption
ΔVsw The changes in void volume of the sample due to its swelling
ΔVrec The changes in void volume of the sample due to the reaction between the gas and the solid surface
δ Reduced density, ratio between the actual density of the gas and its critical density.
ρ Density of the gas
ρb Density of the gas in the bulk phase
ρeq Gas equilibrium density in step i
ρeqN−1 Gas equilibrium density in step N-1
ρeqN Gas equilibrium density in step N
ρfill Density of the gas filled in the reference cell in step i
ρfillN Density of the gas filled in the reference cell in the first step
τ Reduced temperature, ratio between the gas critical temperature and its actual temperature
A The interfacial area
a Slope of the linear regression over the results of Monte Carlo simulation in each experimental step
b The ratio between kf and Ka
Ci The virial coefficients
C Matrix (N-by-J) of excess sorption calculation by Monte Carlo method
D Matrix of N-by-1 with elements from cumulative distribution function estimated by x=J-1/2
d Intercept of linear regression over the results of Monte Carlo simulation in each experimental step
EOS Equation of state
GDS Gibbs dividing surface
\( h \) Differential enthalpies of adsorption
i, d, t, n Constants of Span-wagner and Wagner-Bücker equations of state
ci, ei, gi, bi The rest of Wagner-Bücker equation of state's constants
J Reputation number of Monte Carlo calculation
K Henry's constant
Keq The equilibrium constant
ka The equilibrium constant in adsorption process
kf The equilibrium constant in desorption process
MA McCarty and Arp equation of state for Helium
m Saturation capacity

\( m_{gas}^{exc} \) Mass of excess sorbed gas amount

\( m_{gas}^{inj} \) Mass of gas injected to the reference cell

\( m_{gas}^{unadsorbed} \) Mass of unadsorbed gas in the adsorption system

\( m_{ads}^{N-1} \) Adsorbed mass onto the sample in step N-1

\( m_{ads}^{N} \) Adsorbed mass onto the sample in step N

\( M_{w} \) Molecular weight of the gas

MSC Methane sorption capacity of the adsorbent

\( N_{i} \) constants of McCarty and Arp equation of state for Helium

N Number of experimental steps

n Total adsorbed amount

\( n^\sigma \) Molar surface excess amount

\( n^g \) Total amount of gas

\( n_{m} \) The maximum adsorbed amount

NORMINV Inverse Normal distribution function

P Pressure

R Universal gas constant

SPW Specific pore width

\( V^a \) Volume of the adsorbed layer

\( V^g \) Gas bulk phase volume

\( V^0_{sample} \) Skeletal volume which is equal to the ratio of mass to density of the sample

\( V_{void} \) Void volume measured by Helium pycnometry

\( V^N_{void} \) Void volume measured by Helium in step N

\( V^0_{void} \) Void volume measured by Helium prior to the gas adsorption experiment

\( V_{ref} \) Reference cell volume

S The total number of adsorption sites on an adsorbent

\( S_a \) The number of adsorption sites occupied by the adsorbate molecules

\( S_f \) The number of free adsorption sites

T Temperature

\( t \) Thickness of interfacial layer

TOC Total organic carbon

XRD X-Ray Diffraction, the mineral composition analysis

XRF X-Ray Fluorescence, the elemental composition analysis

Z Gas compressibility coefficient
1 Introduction

A significant amount of natural gas is stored in geological formations. This amount is not only trapped in conventional reservoirs, but also in unconventional ones. In the last century, traditional techniques have been used for production of natural gas from conventional reservoirs. Thus, the conventional reservoirs have become depleted over time, and the importance of the gas placed in unconventional reservoirs became more important. But due to the low to ultra-low permeabilities of these reservoirs, the application of traditional techniques for gas production from these reservoirs is not adequate. Therefore, great efforts have been performed to develop new techniques, that can produce noticeable amount of gas stored in the reservoir’s matrix. Recently, the development of horizontal drilling and hydraulic fracturing have made the natural gas production from unconventional reservoirs possible. However, these methods are expensive and complex.

Shale as an abundant unconventional reservoir has drawn a lot of attention during the last two decades. Considerable amounts of natural gas is stored in its matrix, but for a long period of time, the question was whether this amount could be extracted by new techniques or not. Finally in 2011, the gas production from Barnett shale in the U.S., which supplied 7% of the natural gas production of the whole continent, answered this question. This event can be considered as a milestone in shale gas history. In that year, more than twenty percent of the U.S. dry gas production was from shales [77]. Therefore, many scientists believe that in spite the costs of shale gas production, it can be a profitable energy source. Moreover, as shale gas is a light carbon fuel, its combustion generates less greenhouse per unit of energy than oil and coal and it is relatively environmentally friendly [73].

Kuuskraa et. al, considered the structural complexity of the shale basins, and reported that the shale gas in place of 32 countries around the world is about “716 trillion cubic meter”, of which “627 trillion cubic meter” are outside the U.S. Considering the dependency of the production rate on reservoir properties, shale mineralogy and geological complexity, it was estimated that “163 trillion cubic meter” of this amount is technically recoverable. Therefore, investigation on shale’s potential is an important task [43, 8].

The production of natural shale gas requires knowledge about the state of the gas in the shale matrix and knowledge of production mechanism. Studies on the stored gas in shales revealed that a considerable portion is in the adsorbed state [13]. Therefore, investigation on adsorption behaviour of natural gas components will lead to an estimation of amounts of gas in shales (gas in place), the possible production rate. The adsorption mechanisms of methane as the main component of natural gas and carbon dioxide on shales are discussed in the literature [31, 30, 55, 56]. Only few articles have dealt with high pressure ethane adsorption on coal, the second dominant component of natural gas [60, 61]. The stored amount of ethane is small in comparison to methane; However, the produced amount can be used in several industrial processes. To the author’s knowledge, no experiments on high pressure ethane adsorption on shale have been conducted.

The aim of this project is to quantify the adsorption capacity of pure methane and ethane on Belgian black shale in the North Sea basin. Moreover, the result of this work can make the quantification of the shale’s potential possible.
1 INTRODUCTION

1.1 Scope of the thesis

The scope of the thesis is:

- Measurement of methane excess sorption on Belgian Black shale at temperatures of 308 K, 318 K, and 336 K and pressures up to 10 MPa.
- Investigate the effect of temperature on the methane excess sorption capacity at high pressures.
- Measurement of the ethane excess sorption at 318 K and pressures up to 9 MPa.
- Comparison between the excess sorption of the ethane and the methane at a temperature of 318 K.
- Monte Carlo error analysis of the results of excess sorption isotherms.

The author presents essential information about shale in Chapter 2. Adsorption mechanisms and methods to quantify and measure the adsorption are discussed. Moreover, the shale gas potential in Europe is summerized. In Chapter 3, the experimental setup and the measurement method as well as the data analysis with a Monte Carlo simulation are explained. Results and discussion are presented in Chapter 4. A summary of the work and remarks on the project are given in Chapter 5.
2 Fundamentals

Shale formations are considered as a source for natural gas as they can store a noticeable amount of natural gas within their pores. In order to estimate the production rate of natural gas from these formations, knowledge about the state of the gas within the shale is essential. In Section 2.1, we discuss the origin of shale and its characteristics. Moreover, information about the shale gas potential in Europe will be presented. As most of the gas in shale is in the adsorbed state, Section 2.2 discusses the adsorption phenomena, important adsorption models and methods to measure its amount. A comprehensive literature survey on methane and ethane excess sorption measurement is provided in Section 2.3.

2.1 Shales

2.1.1 A source of natural gas

Sources for natural gas can be divided into two groups by accessibility. (1) Conventional gas reservoirs, i.e. permeable reservoirs with an intrinsic permeability\(^1\) of \(10^{-15}\)m\(^2\) (1mD) or more, in which gas can be extracted easily and inexpensively by traditional technologies. (2) Unconventional gas reservoirs, i.e. low permeable reservoirs with permeabilities of less than \(10^{-15}\)m\(^2\), for which we need to develop new techniques for extraction. These techniques can be hydraulic fracturing\(^2\), the horizontal wellbore and multilateral wellbore, which all has the aim to explore more of the reservoir to the wellbore [71].

\[\text{Figure 2.1} – \text{Fissile and laminated structure of organic rich shales [9]}\]

\(^1\)A measure for the indication of the rock ability to permit fluid flow through its matrix [81]
\(^2\)Rock fracturation by pressurized liquid [82]
Blatt et al. [6] defined shale as a geological rock formation, which is fissile and terriogenous. This characteristic makes it different from other types of mudstones. Shale as an unconventional reservoir can also act as a cap rock for oil and natural gas, preventing migration to other formations. Shale is an abundant geological formation, consisting of mostly clay and regularly derived from fine sediments. It constitutes 60% of earth’s sedimentary crusts [7].

Considering the environment in which the shale was formed, the main components of a shale are mostly clay minerals such as illite, kaolinite and smectite, along with less prominent other clay size constitutes such as quartz, char and feldspar. In addition to clay minerals, it normally contains organic particles, carbonate minerals, iron oxide minerals and sulfide minerals. Deposition of significant amounts of organic matter within the sediments may result in the presence of organic solid materials, called kerogen in shale rocks.

Shale oil or gas are products of the chemical decomposition of kerogen. In order to be able to describe these phenomena, we need to take a closer look at the origin of kerogen. The formation of shale starts with the sedimentation of organic remains of animals and plants to the bottom of lakes and oceans. In the anoxic environment of these water bodies, sediments can accumulate with high organic contents. During a long period of time, these sediments are buried deeper and therefore exposed to high pressure and temperature. Laminated layers of sediments are the result of this burial. Gradually, organic matter will decompose and transform to kerogen at temperatures below 50°C. This process increases the temperature in the layers to 50-150°C. During a long period of time, this temperature increment will cause its decomposition, which result in generation of oil and gas in shales [9]. On the other hand, anaerobic bacteria in this region biodegrade the organic matter and produce biogenic methane.

According to its organic content, shale can be categorized as (1) dark-colour or Black shale and (2) light-colour shales. The black colour of dark-colour shales is due to the presence of organic matter, which makes it an organic-rich formation. The sample used in this work is a black shale.

2.1.2 Shale characteristics

Important parameters to characterise shale are the shale gas type (thermogenic or biogenic), thermal maturity, total organic carbon (TOC) and the permeability of the reservoir.

Thermogenic gas is produced by cracking of organic matter or secondary oil cracking. In other words, it is a result of the maturation of the rock in a high pressure and temperature or the result of thermal decomposition of liquid hydrocarbon products. Therefore, it is expected that mature shales are a rich source of gases in comparison to immature ones [47, 65]. The thermal maturity reflects the degree of heat the organic matter has been exposed to over time (temperature history). It is described by vitrinite reflectance (\( R_o \)). Values above 1.0-1.1% indicate mature rocks. The study of vitrinite reflectance is a key method for identifying the maximum temperature history of sediments in sedimentary basins [83].

Biogenic gas is produced by anaerobic degradation of organic matter [52, 47, 48, 46, 69]. Biogenic gas can be produced both in mature and immature shales and the amount can be a considerable fraction of

---

3 Being fissile, the shale splits into thin sheets along the bedding
4 Terrigenous means that it stems from erosion of rocks on land [54]
reservoir gas. Both biogenic and thermogenic gas shales exhibit three different forms in shales; (1) free gas inside pores and fractures, (2) adsorbed gas (physically or chemically), and (3) dissolved gas on organic matter. Knowledge about the ratio between these amounts is useful for reservoir evaluation and gas production.

The total organic carbon, or TOC, is the total amount of organic matter in the rock. This value is defined as a weight percentage and it is believed that it affects the gas adsorption mechanism in shales. This phenomenon is discussed comprehensively in the literature survey.

Intrinsic permeability defines the resistance of a shale structure to gas flow, and depends on properties of the shale such as its type, pore structure, network and is independent of the type of the fluid passing through it [81].

### 2.1.3 Shale gas production

![Figure 2.2 – European shale basins [43].](image)

During the last three decades, the potential of natural gas production from shales has increased by development of new technologies. Exploitation of hydrocarbons from shale started in 1821, with the drilling

\[ k = K \frac{\mu}{\rho g}, \]  

where

- \( k \) Darcy permeability \([m^2]\)
- \( K \) Intrinsic permeability \([m/s]\)
- \( \mu \) Dynamic viscosity of the fluid \([kg/m \cdot s]\)
- \( \rho \) Density of the fluid \([kg/m^3]\)
- \( g \) Acceleration due to gravity \([m/s^2]\)
of a commercial gas well in Fredonia, New York, USA [19]. After two centuries, the production of one shale basin in the U.S. supplied 7% of the whole natural gas production in the U.S. [77]. Nowadays, shale gas production is not limited to the U.S. There are many active basins around the world with noticeable potential of shale gas production. The U.S. Energy Information Administration (EIA) [43] estimated in 2011, that there are 48 gas shale basins in 32 countries. They claimed that 11% of the world’s total natural gas resource is placed in Europe, of which more than 27% would be technically recoverable.

The relatively low recoverable amount in Europe is due to the contribution of many factors in natural gas production from shales. The application of hydraulic fracturing, the presence of potential resources in densely populated areas as well as the availability of vast conventional resources for gas production prevent investment in gas shale production. However, there are some active basins around Europe which are shown in Fig. 2.2 and summarized in Tab. 2.1. The lighter colour shows the basin area and the darker colour shows the prospective shale formation which covers less than half of the overall basin area. The prospective area has the most favourable shale characteristics for shale gas production [43].

Despite challenges in natural gas production in European shales, research on this technology and its governance in profitable regions is an important task. In order to have sufficient knowledge about production rate of a shale formation, we have to know about the amount and state of the gas in its matrix (free, adsorbed and absorbed). This cannot be obtained without comprehensive knowledge of adsorption principles.

In this work, Belgian carboniferous Black shale from the North Sea basin has been used. For more information on Shale gas production and processes, we refer to [71].
<table>
<thead>
<tr>
<th>Country</th>
<th>Shale formation</th>
<th>Location</th>
<th>Risked GIP</th>
<th>Recoverable gas</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poland</td>
<td>Silurian-age Baltic</td>
<td>North-central to southeastern</td>
<td>22.4 trillion m(^3)</td>
<td>5.3 trillion m(^3)</td>
<td>The largest in area and total GIP. Geologic features similar to Podlasie. The best reserves.</td>
</tr>
<tr>
<td></td>
<td>Lower Silurian</td>
<td>Lubian</td>
<td>5.1 trillion m(^3)</td>
<td>The largest in area and total GIP. Geologic features similar to Podlasie. The best reserves.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lower Silurian</td>
<td>Podlase</td>
<td>20.4 trillion m(^3)</td>
<td>Eastern part: Gas; western part: Water; Two geologic sub-areas: Lower and Upper. Geologic features similar to Western Europe. Oil shale potential.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Permian-Carboniferous</td>
<td>Jurassic, Lower Carboniferous</td>
<td>198 billion m(^3)</td>
<td>56.4 billion m(^3)</td>
<td>Type A: Oil/gas shale; Type B: Oil/gas shale. The largest in area and total GIP. Geologic features similar to Western Europe. Oil shale potential.</td>
</tr>
<tr>
<td></td>
<td>Jurassic, Lower Carboniferous</td>
<td>Southeast</td>
<td>28.3 billion m(^3)</td>
<td>6.5 billion m(^3)</td>
<td>Deep and very mature. Highly organic-rich shale with oil potential.</td>
</tr>
<tr>
<td></td>
<td>Permian-Carboniferous</td>
<td>Upper Jurassic Terres Noires</td>
<td>1.8 trillion m(^3)</td>
<td>453 billion m(^3)</td>
<td>Deep and very mature. Highly organic-rich shale with oil potential.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>France</td>
<td>Paris</td>
<td>Paris</td>
<td>20.4 trillion m(^3)</td>
<td>5.1 trillion m(^3)</td>
<td>High oil content; partially immature.</td>
</tr>
</tbody>
</table>
2.2 Adsorption principles

Numerous physical, chemical and biological processes can occur on the boundary of phases. Adsorption, a process that happens at the solid-fluid boundary, is such a process. In gas-solid adsorption, one or several components accumulate in the interfacial layer. Thus, their concentration will be higher in this layer compared to the neighboring zones (see Fig. 2.4). The interfacial layer includes two regions, the part of the gas phase which is under the influence of solid surface attraction forces and the solid surface layer. The adsorption process is exothermic, as it reduces the free energy and the entropy of the adsorbed gas. Important definitions in the adsorption process, that are shown in Fig. 2.3, are:

**Adsorptive** Components in the fluid bulk phase prior to adsorption.

**Adsorbate** Adsorbed molecules on the solid surface.

**Adsorbent** Bulk solid phase.

**Absorption** The dissolution of gas molecules into the solid matrix. If adsorption and absorption take place simultaneously, they cannot be distinguished and the term "Sorption" is used.

**Chemisorption** Sorption involving chemical bonding, due to electron sharing or electron transfer between the adsorbate and adsorbent.

**Physisorption** Sorption without chemical bonding by van der Waals attractions between the molecules of the surface and the gas molecules

**Desorption** The reverse process of Sorption.

![Figure 2.3](image-url) – Adsorption system consisting of two different fluid adsorptives and one solid adsorbent [40].
According to the type of sorption (chemisorption or physisorption) and the solid phase structure, i.e., porous materials, the adsorbed phase can be monolayer or multilayer and it can be localised, mobile or partially mobile [23, 22, 37]. Physisorption, or physical adsorption, is caused by physical forces, i.e., van der Waals interactions between the adsorbent and the adsorbate and those between the adsorbate molecules. The physisorption energy is below 40kJ/mole. Chemisorption, or chemical adsorption, is due to the chemical reaction between the adsorbent and the adsorbate. This type of adsorption changes the structure of the adsorbent. Moreover, the chemisorption energy is comparable to the energy of the chemical bonds and it is 80kJ/mole or more. Due to this large adsorption energy, this type of adsorption is localised, i.e., at particular sites [1].

The amount of adsorbed gas by unit mass of solid depends on temperature, pressure and the nature of the solid-gas system. The relation between the adsorbed amount and the gas equilibrium pressure in the system at constant temperature is defined as adsorption isotherm. Conversely, a desorption isotherm can also be defined. Below the critical temperature, these isotherms may deviate from each other, which cause the appearance of a loop in their graph, named adsorption hysteresis. This phenomenon is unique for each adsorption process and occurs mostly due to capillary condensation. Capillary condensation is the condensation of gas inside the adsorbent pores [21, 66]. Condensation happens when the gas vapour pressure becomes equal or higher than gas the saturation pressure, because of gas molecules interactions with the solid pore surface inside the pores [16]. At supercritical temperatures, capillary condensation does not happen and the process of pore condensation is replaced by stepwise pore filling through multilayer adsorption [57]. In this case, the interfacial layer is considered as a compressed gas, due to the absence of condensed liquid. This is one of the advantages of high pressure adsorption measurements, as it diminishes the induced complexity due to the presence of condensed liquid in calculations.

2.2.1 Langmuir adsorption isotherm

Detail of adsorption processes is highly influenced by the type of adsorbent. Results of adsorption experiments lead to use a physical model for the adsorption isotherm. Several theories based on experimental approaches have been presented in literature. The most common model in description of adsorption isotherms of gases on shales is described below.

**Langmuir monolayer model:** The first concept on monolayer adsorption on energetically homogeneous surfaces was presented by Langmuir in 1918. In this monolayer theory, the mobile adsorption is ruled out by assuming a strong bonding between adsorptive molecules and adsorbent [44, 45].

The Langmuir model considers adsorption as the condensation of molecules on the solid surface. Subsequently, desorption is explained by the evaporation of molecules. The solid surface possesses specific number of adsorption sites, $S$, from which $S_a$ is the number of sites occupied by molecules, and $S_f$ is the number of free sites. Therefore, one can write the rate of condensation and evaporation, which are proportional to $S_f$ and $S_a$, respectively. Considering the proportion of the condensation to the gas pressure, $P$, at equilibrium

$$k_a S_a = k_f P S_f = k_f P(S - S_a).$$  \hspace{1cm} (2)
The fraction of the surface, which is occupied by molecules is

\[ \phi = \frac{S_a}{S} = \frac{bP}{1 + bP}, \quad (3) \]

where

\[ b = \frac{k_f}{k_a}. \quad (4) \]

In the monolayer adsorption model, the adsorbed amount of substance in moles per gram, \( n \), is proportional to \( \phi \),

\[ n = \frac{n_m bP}{1 + bP}. \quad (5) \]

where \( n_m \) denotes the maximum adsorption amount. The Eq. 5 is called Langmuir monolayer model. According to this model, the adsorbed amount is proportional to the gas pressure at low pressures, while at high pressures, the maximum adsorption amount will be obtained.

\[ n \propto P \quad \text{at low pressures}. \quad (6) \]

\[ n \propto n_m \quad \text{at high pressures}. \quad (7) \]

### 2.2.2 Quantitative representation of adsorption

In adsorption of pure gas on a solid surface, the density of the gas, \( \rho \), decreases constantly with increasing distance until it reaches the constant gas bulk phase density, \( \rho_{gb} \). In the layer model, three zones can be distinguished: Adsorbent (zone I), adsorbed layer (zone II), adsorptive gas (zone III) as shown in Fig. 2.4. Zone III, is at sufficient distance from the adsorbent, so the solid surface forces cannot have any influence on gas molecules. The gas density only depends on equilibrium pressure and temperature. Zone II is bounded on one side by the solid surface and other side by the gas bulk phase. The force field of the solid surface on the gas causes a positive density gradient toward the surface. The local density in this layer depends on the distance from the solid surface. The volume of the adsorbed layer can be defined as,

\[ V^a = A t, \quad (8) \]

where \( A \) is the interfacial area and \( t \) the thickness of the layer. In this case, the adsorbed amount \( n \) can be found by integration of the molar density over the whole area, i.e., is

\[ n = \int_0^{V^a} \rho dV = A \int_0^t \rho dz. \quad (9) \]

By considering \( V^g \) as the volume of the gas bulk phase, the total moles of the gas, \( n^g \), is the sum of the moles present in the gas bulk phase and the adsorbed amount. This is shown in Fig. 2.4 (layer model, left
picture) and can be written as,

\[ n^g = n + \rho_b^g V^g = A \int_0^t \rho dz + \rho_b^g V^g. \]  \hspace{1cm} (10)

Obviously, in order to calculate the adsorbed amount, having information about the exact value of \( V^g \) or \( d\rho/dz \) is needed, which is not easy to obtain. More than 100 years ago, Gibbs [32] defined an approach to describe adsorption at many different interfaces. He defined the “surface excess” concept, to calculate the adsorbed amount. In his approach, the presumptive reference system is divided into two regions with the help of a geometrical plane surface parallel to the adsorbent surface. In order to have an easier interpretation, Gibbs dividing surface should be placed exactly on the solid surface layer. Gibbs’ representation is illustrated in Fig. 2.4. In this approach, the excess sorbed volume is assumed to be zero [1]. Therefore, the surface excess amount, \( n^\sigma \), is illustrated as difference between the total amount of adsorbate and the amount of gas present in the bulk phase, and it is given by

\[ n^\sigma = A \int_0^z (\rho - \rho_b^g) d\tilde{z} = n^9 - \rho_b^g (V^g + V^\sigma). \]  \hspace{1cm} (11)

**Figure 2.4** – The Gibbs representation of adsorption, density of adsorbate (\( \rho \)) and the distance from the adsorbent (\( z \)) [58]
By insertion of Eq. 10, we obtain the total adsorbed amount by

\[ n = n^\sigma + \rho_b^g V^a. \]  

(12)

In most adsorption processes, the density of the gas in the bulk phase and the adsorbed volume are relatively small and can be neglected. So the adsorbed amount is considered to be the same as the Gibbs excess adsorption amount. However, at high pressures the size of the adsorbed phase may have to be considered [58].

2.2.3 Excess sorption measurement methods

The physical quantities to determine the excess sorption are pressure, temperature and mass. Depending on which quantity is varied, different measurement methods can be distinguished, i.e., the volumetric, the manometric and the gravimetric methods. A brief explanation of these methods are supplied here. For a detailed description, we refer to Busch et al. [11] and Keller et al. [40].

**Manometric method**

A simple schematic drawing of a manometric setup is shown in Fig. 2.5. This method is based on mass conservation and an accurate measurement of the reference cell pressure and void volume. Prior to the measurement, the sample cell, which contains a certain amount of sample, is evacuated. The void volume of the sample, the volume accessible to the adsorptive gas, is measured by an inert gas. This gas is commonly Helium, as its adsorption on the sample is considered to be zero. Helium pycnometry defines the skeletal volume, \( V_{sample}^0 \), and skeletal density of the sample, \( \rho_{sample}^0 \). Then, a known amount of gas

![Figure 2.5 – Schematic drawing of a manometric setup [11]](image)

is introduced into the sample cell. This gas will expand and partially adsorb on the sample (physisorption and/or chemisorption) and partially remain in the gas bulk phase. By measuring the only variable parameter (pressure), before and after introducing the gas, the adsorption amount can be quantified. The accuracy of the measurement depends on the void volume and the accurate measurement of pressure in the reference cell in each step. Therefore, the amount of excess sorption is the difference between the mass introduced to the system through the reference cell and the mass presented in the gas bulk phase.
For the first step when the adsorbed amount of gas onto the sample cell is zero, we can write,

\[ m_{\text{exc}}^{\text{gas}} = m_{\text{inj}}^{\text{gas}} - V_{\text{void}} \rho_b^{\text{gas}}(T, P), \]

(13)

where

\begin{align*}
  m_{\text{exc}}^{\text{gas}} & \quad \text{Excess sorbed gas amount} \\
  m_{\text{inj}}^{\text{gas}} & \quad \text{Mass of gas injected to the reference cell, which is equal to } \rho_{\text{ref}}^{\text{fill}} V_{\text{ref}} \\
  V_{\text{void}} & \quad \text{Void volume measured by Helium} \\
  \rho_b^{\text{gas}} & \quad \text{Density of the gas in the bulk phase, after the first equilibrium stage.}
\end{align*}

Experimental uncertainties of a highly accurate manometric setup is discussed by van Hemert et al. [53].

**Volumetric method**

The principle is the same as that of the manometric method. Prior to the gas sorption measurement,

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{volumetric_setup.png}
\caption{Schematic drawing of a volumetric experimental setup for the gas sorption measurement[72]}
\end{figure}

Helium pycnometry is used to obtain the void volume of the sample. A simple schematic drawing of the setup is shown in Fig. 2.6. The sorption is quantified by stepwise measurement of pressure and volume at constant temperature. Continuous forward movement of a piston pump decreases the reference cell gas volume and subsequently increases gas pressure. By measuring the pressure in each step, the sorption isotherm is obtained. The amount of gas, that is introduced to the system, corresponds to the precise volume changes of the pump and can be defined by

\[ m_{\text{inj}}^{\text{gas}} = \left( \frac{P \Delta V M}{ZRT} \right)_{\text{pump}}. \]

(14)

Therefore, the excess sorption amount can be determined with

\[ m_{\text{exc}}^{\text{gas}} = m_{\text{inj}}^{\text{gas}} - m_{\text{unadsorbed}}^{\text{gas}}, \]

(15)
with

\[ m_{\text{gas}}^{\text{ads}} = \left( \frac{PV_{\text{void}}M_w}{ZRT} \right)_{\text{sample cell}}, \]  

(16)

where

- \( P \) Pressure
- \( T \) Temperature
- \( \Delta V \) Volume changes defined from pump counter
- \( V_{\text{void}} \) Void volume achieved by Helium pycnometry
- \( Z \) Gas compressibility coefficient
- \( M_w \) Molecular weight of the gas
- \( R \) Universal gas constant.

The experimental uncertainties, regarding to the measurement of excess sorption by a volumetric setup, is discussed by Mohammad et al. [51].

**Gravimetric method**

The gravimetric method is based on the measurement of the sample’s weight in a gravity field by a highly sensitive mass measuring instrument, which records precisely small changes of the mass. The physics of this method is complicated as the adsorbent is always surrounded by the adsorptive gas. The gravimetric method has been applied on a wide range of instruments, e.g., an one beam balance or a two beam balance.

The experiments are conducted at constant pressure and temperature and the excess sorption is calculated by changes in the mass of adsorbent, which consist of a buoyancy correction due to sufficient information about the density and the volume of the adsorbent in each step. The skeletal density of the sample is measured by Helium. A simple schematic of the setup is shown in Fig. 2.7. The sorbent is placed on a magnetic suspension balance which a precision about ±2µg. This is connected to a permeant magnetic, which is linked to an electro magnet at the top of the setup. As the density of the gas is measured by its mass and volume in an empty reference cell, there is no need to apply an equation of state which increases the accuracy of the method. The excess sorption in this method can be defined as,

\[ m_{\text{exc}}^{\text{gas}} = \Delta m + V^0_{\text{sample}} \rho(T, P), \]  

(17)

where

- \( \Delta m \) Changes of the mass due to the adsorption
- \( V^0_{\text{sample}} \) Skeletal volume which is equal to the ratio of mass to density of the sample
- \( \rho \) Density of the gas.

The technical equilibrium time in the gravimetric method can be defined manually or automatically by setting a criteria for the instrument. In this case, we define a lower limit for mass changes during specific time intervals (\( \Delta m/\Delta t \)). This criteria is the main advantages of gravimetric method than volumetric method [40].
Comparison between different methods

In order to choose between these methods, knowledge about their advantages and disadvantages is necessary. The advantages and disadvantages of the gravimetric method in comparison to the manometric/volumetric methods are listed below:

Advantages

- Higher accuracy of available microbalances, which results in increment of accuracy one order of magnitude at high pressures and two orders of magnitude or even more at low pressures.
- Small amounts of the adsorbent sample is needed.
- No uncertainties are caused by wall sorption, as we do not consider any mass balance for the adsorptive gas in our calculations.
- It operates in extreme pressures as the measurement method is based on the weight of the sample, which is independent of gas pressures.
- Stepwise information about kinetics are presented, even for slow adsorption processes.
- Stepwise information on the mass of sample during activation process, i.e., the leakage test and the void volume measurement.

Disadvantages
• Complexity of the measuring devices. In some cases, the sample type can also increase the complexity of the measurement, e.g. granulated particles like activated carbon can not keep the balance during the experiment and may fall from the balance.

• Difficult measuring technique: laborious experiments with complicated steps to perform [40].

In our project, excess sorption measurements of two pure gases on shale have been performed. We chose a manometric method, and our setup will be explained in details in the Chapter 3.

2.3 Literature survey

In this section, we give a brief survey of different terms contributing to the adsorption of gases on shales. However, even if the ethane is the second most abundant component in natural gas, only a few articles discussed its sorption mechanisms. Therefore, the survey in this section is confined in methane excess sorption than that of the ethane.

2.3.1 Methane sorption on shales

In this section, methane sorption mechanisms of shale and coals are investigated. The results of adsorption on these adsorbents are comparable. According to the work of Chareonsuppanimit et al. [13], the methane sorption capacity of shale is 10-30 times lower than coals due to lower TOC amount and high ash content of the shales. The complexity of sorption on shales due to their non-homogenous individual composition as well as their pore structure was discussed by Ross and Bustin [56].

Negative sorption at high pressures, which has been also observed in this work, was discussed by several authors previously. Ross et al. [55] measured the methane excess sorption amounts on heterogenous zeolite sorbent with a pore size diameter smaller than methane molecules. As a consequence of void volume overestimation by Helium, negative adsorption values were identified. This phenomenon can be due to several reasons, i.e., Helium void volume changes by time, pressure, and temperature and the small kinematic diameter of Helium contributing its greater pore accessibility compared to the methane. Rother et al. [57] explained the negative sorption of CO$_2$ on mesoporous CPG-10 silica, by formation of a dense layer at high temperature and pressure in the middle of the pores. This results in the blocking of pores and obstructs any further adsorption. In the opinion of the author, their argument is in agreement with the specific pore width definition suggested by Kaneko et al. [39], which will be explained in the following section.

Furthermore, the swelling of the sample and reaction of the gas with the sample can cause void volume changes, which result in negative sorption. By swelling and sorption experiments of CH$_4$, N$_2$ and CO$_2$ on coal, Battistutta et al. [4] observed no swelling for methane on coals. Their results only demonstrated hysteresis and induced swelling by CO$_2$. The former is caused by improperly chosen equilibration time, presence of water in coal matrix or strong bonding due to CO$_2$ absorption which is not fully reversible. The latter causes a decline in CO$_2$ isotherm and is a fully reversible process. Furthermore, to the knowledge of the author no reaction between methane gas molecules and shale matrix has been reported. In
Table 2.2 – Investigation on the effect of different parameters on methane sorption amount on different type of samples. The effects are shown with three abbreviations: N(negative), P(positive) and NE(no effect).

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Gases</th>
<th>Sample</th>
<th>TOC</th>
<th>CR/TM</th>
<th>Moisture</th>
<th>Clay</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Krooss et al.</td>
<td>2002</td>
<td>CH₄,CO₂</td>
<td>C</td>
<td>-</td>
<td>NE</td>
<td>N</td>
<td>-</td>
<td>V</td>
</tr>
<tr>
<td>Ross et al.</td>
<td>2007</td>
<td>CH₄</td>
<td>S</td>
<td>-</td>
<td>-</td>
<td>N</td>
<td>-</td>
<td>V</td>
</tr>
<tr>
<td>Sakurovs et al.</td>
<td>2007/8</td>
<td>CH₄, CO₂, N₂</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>G</td>
</tr>
<tr>
<td>Ross et al.</td>
<td>2008</td>
<td>CH₄, CO₂</td>
<td>S,Cl</td>
<td>P</td>
<td>P</td>
<td>-</td>
<td>P</td>
<td>V</td>
</tr>
<tr>
<td>Day et al.</td>
<td>2008</td>
<td>CH₄, CO₂</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>N</td>
<td>-</td>
<td>G</td>
</tr>
<tr>
<td>Weniger et al.</td>
<td>2010</td>
<td>CH₄, CO₂</td>
<td>C, S</td>
<td>P</td>
<td>NE</td>
<td>N</td>
<td>-</td>
<td>M</td>
</tr>
<tr>
<td>Battistutta et al.</td>
<td>2011</td>
<td>CH₄, CO₂, N₂</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>N</td>
<td>-</td>
<td>V</td>
</tr>
<tr>
<td>Chareonsuppanimit et al.</td>
<td>2012</td>
<td>CH₄,CO₂, N₂</td>
<td>S</td>
<td>P</td>
<td>P</td>
<td>-</td>
<td>-</td>
<td>V</td>
</tr>
<tr>
<td>Gasparik et al.</td>
<td>2012</td>
<td>CH₄</td>
<td>S</td>
<td>NE</td>
<td>NE</td>
<td>N</td>
<td>P</td>
<td>M</td>
</tr>
<tr>
<td>Ji et al.</td>
<td>2012</td>
<td>CH₄</td>
<td>Cl</td>
<td>P</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>V</td>
</tr>
<tr>
<td>Zhang et al.</td>
<td>2012</td>
<td>CH₄</td>
<td>S</td>
<td>P</td>
<td>P</td>
<td>N</td>
<td>-</td>
<td>V</td>
</tr>
<tr>
<td>Gasparik et al.</td>
<td>2013</td>
<td>CH₄</td>
<td>S</td>
<td>P</td>
<td>P</td>
<td>N</td>
<td>NE</td>
<td>M</td>
</tr>
</tbody>
</table>

a) S:Shale, C:Coal, Cl:Clay material, A:Activated Carbon
b) Coal rank or Thermal maturity
c) V:Volumetric, M:Manometric, G:Gravimetric
d) No trend for organic-lean Sample

order to easily reference the work of different authors mentioned in this section, Table 2.2 provides an overview over the impact of different parameters on the sorption of methane investigated by different authors, methods, materials and the modeled they used.

**Temperature and Pressure:** Let us consider the sorption mechanism as

\[ A + B \rightarrow C \]

where \( A \) are the free adsorbate molecules, \( B \) are the free adsorbent surface, and \( C \) are the adsorbate molecules bound to the adsorbent surface. As seen, the sorption decreases the volume and subsequently the entropy of the system. Therefore, the increment of pressure has positive effect on the sorption. In order to determine the effect of the temperature on the sorption, consider the van’t Hoff equation,

\[
\frac{d(\ln K_{eq})}{dT} = \frac{\Delta H}{RT^2}.
\]

(18)

where \( K_{eq} \) is the equilibrium constant and \( R \) is the gas constant, and it can be rephrased as

\[
\frac{d\ln K_{eq}}{dT} = - \frac{\Delta H}{R}.
\]

(19)

As sorption is an exothermic process, the right hand side of the Eq. 19 has a positive value. Therefore, the negative effect of temperature on the sorption amount can be obtained [3].
Many authors discussed antithetic effect of these parameters experimentally, such as the precise measurements of Guo [34] in 2013. He claimed that although the increment of temperature has negative impact on the adsorbed capacity of shale, by increasing these parameters simultaneously, in the low pressures, the pressure is dominant. As the sorption capacity reaches its maximum, the influence of temperature will become more dominant. From this point on, an increment in the pressure and temperature will decreases the adsorption capacity of the shale. These formula are shown in Fig. 2.8, which we have taken from Weniger et al. [78]. In this figure, methane sorption capacity variations by depth of a coal basin are shown. By increasing depth, and subsequently pressure and temperature with different gradients, the methane sorption capacity increases until it reaches a maximum at a depth of 400-800 m. Subsequently, an increment in those will result in capacity decrement. Moreover, Sakurovs et al. [63] investigated the effect of temperature on the sorption of several gases on coals and charcoals. They confirmed its negative effect, and explained it by governing the results of Kaneko et al. [39] on pore filling behaviour of supercritical gases. In the supercritical sorption in pores, the adsorbed phase density is solely controlled by surface attraction forces, which decreases by distance from the surface. As the forces are weak in the center of large pores, the pore cannot be filled completely. Therefore, there is a specific pore width below which the surface attractions and gas density are high in the entire pore. This specific pore width increases with the pressure and in supercritical conditions, at constant temperature and increasing pressure, it reaches its maximum value. By increasing the temperature further above the critical temperature of the gas, due to its high kinematics, the effect of surface forces on the gas molecules becomes less dominant. Thus, in order to complete the filling of pores, smaller pores are needed. Therefore, it can be concluded that the specific pore width will decrease. This phenomenon describes the identi-
Total Organic Carbon (TOC): Many authors have discovered a positive effect of total organic carbon or [TOC] on methane sorption capacity. For instance, Weniger et al. [79] discovered linear trends for TOC versus adsorbed amount of methane and carbon dioxide. In 2012, by correlation between maximum methane sorption capacity and coal rank they observed that CH\textsubscript{4} is more affected by organic matter than CO\textsubscript{2}. To the knowledge of the author, only a few papers did not report any effect of this parameter on the methane sorption capacity, such as Gasparik et al. [31] and Charonsuppanimit et al. [13]. The aforementioned work were both performed on organic-lean samples. By comparison of these work with studies of Ji et al. [38] and Gasparik et al. in 2013 [30], it can be concluded that in case of organic-lean shales, and if the sample contains high amounts of smectite clay mineral, the linear relation between TOC and methane sorption capacity cannot be observed, as smectite contributes significantly to the adsorption capacity of the shale and contradicts the trend.

Moisture content: The moisture content is believed to decrease the sorption capacities of gases on coals and shales. This reduction can be described simply by a physical displacement of gas molecules by water molecules. Experimental results indicate that the increment of moisture influences the adsorption reduction to a level, in which the adsorbent reaches its critical moisture content [24]. Further increase of the moisture will not contribute to the sorption capacity. It is known that water molecules adsorb on the hydrophilic sites of coals. On the other hand, methane molecules are believed to adsorb only on hydrophobic sites. Therefore, when the moisture content is below the monolayer coverage, the presence of water molecules causes higher reduction of the carbon dioxide capacity than of the methane capacity. This is in agreement with the results of Weniger et al. [79], who found a strong reduction of CO\textsubscript{2} than that of CH\textsubscript{4} on coals. When the moisture content exceeds a monolayer coverage, water clusters are formed, as shown in Fig. 2.9. In this case, CO\textsubscript{2} molecules can adsorb on the polar sites of water clusters, while CH\textsubscript{4} molecules are restricted to hydrophobic sites. Therefore, the adsorption capacity reduction will be higher in CH\textsubscript{4} than in CO\textsubscript{2}. In experiments on a dry basis, the capacity reduction can be approximated by the moisture content. One water molecule can displace 0.3 and 0.2 molecules of CO\textsubscript{2} and CH\textsubscript{4}, respectively [24].

Clay content: The exothermal heat of adsorption in clay pores is noticeably smaller than that of organic matter. Also, clay pores are easily blocked by water clusters due to their hydrophilic nature [56]. Therefore the methane sorption capacity of clay matter in presence of high amounts of kerogen is relatively small. Indeed the methane sorption capacity of kerogen is one order of magnitude higher than that of common clay minerals [84, 38]. By performing sorption experiments on clay materials, Ross and Bustin [56] claimed that clay materials incorporate sorption depending on their type. They discovered that the adsorbed gas capacity on a dried sample is in the following order: Illite > Montmorillonite > Kaolinite. In 2012, Garparik et al. [31] showed a same trend on adsorption capacity. However, one year later [30], they could not confirm any trend for clay minerals. There-
fore, they suspect that the effect of clay minerals on the adsorption capacity is due to the nature of the sample. Considering the properties of the samples they used in their experiments, they claimed that the clay mineral increases the capacity in organic-lean shales with high clay content, where the concentration of smectite is relatively high. This was in agreement with the work of Ji et al. [38], which showed that smectite has the highest methane sorption capacity among clay minerals. According to their work, methane adsorption on clay can be arranged in this order: Montmorillonite > Illite/smectite mixed layer > Kaolinite > Chlorite > Illite.

**Thermal maturity:** The effect of thermal maturity on the methane sorption capacity is still a matter of debate. Some authors did not observe any trends, while others faced negative or positive effects of thermal maturity on methane sorption capacity. For instance, among all, the results of Zhang et al. [84] for shales and for kerogen isolated parts of these shales, show that the kerogen type influences the methane sorption capacity. Induced kerogen aromaticity, which occurs during thermal maturation, contributes to an increment of the shale methane sorption capacity. They presented two equations describing the methane sorption capacity relation to vitrinite reflectance. Meanwhile, in 2012 Gasparik et al. [31] claimed that excess sorption is not associated with thermal maturity and TOC content of the shale, and only the shape of the maxima tends to be controlled by them.
2.3.2 Ethane sorption on shales

Adsorption of pure ethane on shales and coals is not widely discussed. As ethane is the second most dominant component of natural gas (Table. 2.2), the consideration of its pure adsorption mechanism for further investigations are important, because even small amount of produced ethane from shales can be used in several chemical processes, such as steam cracking for ethylene production. Commonly, ethane adsorption measurements have been performed in the low pressure regimes and there are only a few articles on high pressure ethane sorption on coals [60, 61]. To the author’s knowledge, no investigation on high pressure ethane sorption on shales is performed.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH$_4$</td>
<td>&gt;85</td>
</tr>
<tr>
<td>Ethane</td>
<td>C$_2$H$_6$</td>
<td>3-8</td>
</tr>
<tr>
<td>Propane</td>
<td>C$_3$H$_8$</td>
<td>1-5</td>
</tr>
<tr>
<td>Butane</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>1-2</td>
</tr>
<tr>
<td>Pentane$^+$</td>
<td>C$<em>5$H$</em>{12}$</td>
<td>1-5</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO$_2$</td>
<td>1-2</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H$_2$S</td>
<td>1-2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N$_2$</td>
<td>1-5</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

**Low pressure experiments:** In 1989, Schettler et al. [64] claimed that the ethane sorption capacity in Devonian shale is much higher than methane sorption capacity, due to higher polarizability of ethane molecules in comparison to that of methane. Tzabar et al. [74] and He et al. [35] found noticeably higher sorption capacities for ethane than for methane and nitrogen on activated carbon. He et al. [35] explained this phenomenon by the non-spherical shape of ethane molecules, which allow them to gain different orientations towards the surface. Ruppel et al. [59] observed the higher affinity of coals to ethane in the same pressure range. Using experiments on the same material, Choi et al. [17] interpreted the results in terms of the polarizabilities of the gases. The comparison between the study of Choudhary et al. [18] on adsorption of methane, ethane and carbon dioxide on silicate-I and previous studies revealed that in the absence of active sites on the adsorbent, the adsorption of ethane is higher than of carbon dioxide. In other words, the active cation sites caused strong interactions between carbon dioxide and the adsorbent surface and resulted in higher adsorption values for this gas.

**High pressure experiments:** Sakurovs et al. performed ethane excess sorption experiments on coals
at high pressures [60, 61]. In 2010, they revealed that excess sorption increases with the critical
temperature of the gas. This phenomenon is in contrast with the constant maximum sorption as-
sumption considered by monolayer model. Meanwhile, in case of the supercritical gas sorption, in
which the gas condensation on the surface is avoided, this conclusion is comparable to Charles’s
Law\(^6\). In 2012 [61], by comparison of the results of methane, nitrogen, ethane and carbon dioxide
maximum sorption capacities, they concluded that higher sorption capacities reported for carbon
dioxide can not be understood by the quadropole moment of its molecules and their kinematic size.
They claimed that as nitrogen molecules possess quadropole moment, but its sorption capacity is
lower than that of CO\(_2\), this cannot be a reason for higher sorption capacities of shale for CO\(_2\).
However, they did not consider the noticeable difference between the quadropole moment of CO\(_2\)
and N\(_2\) molecules. Also, they found relatively the same sorption capacities for carbon dioxide and
ethane, however ethane molecules are nonpolar. Considering that methane and ethane molecules
have the same kinematic diameter, and the ethane sorption capacity is higher than that of methane,
the sorption capacity cannot be dependant on the kinematic diameter of molecules. Their result
showed that ethane sorption capacity is analogous to CO\(_2\). Therefore they believed that critical
temperature is the only controlling parameter for maximum excess sorption.

\(^6\)Charles’s Law: For an ideal gas, if the pressure and mass of gas are constant, the changes of volume and temperature are
proportional to each other [80]
3 Excess sorption measurement: Principle and Procedure

At low pressures, the amount of adsorbed gas is negligible in comparison to the amount of unadsorbed gas. Therefore, the void volume is equal to the unadsorbed phase volume. In contrast at high pressures, the increment in adsorbed phase volume leads to larger void volumes than the unadsorbed phase volume. Thus, the assumption of zero-volume for the adsorbed phase will lead to inaccurate values for the absolute sorption. This is the main reason to use excess sorption instead of absolute sorption, as the adsorbed volume is negligible in the excess sorption definition.

The aim of this project is high pressure measurements of excess sorption of methane and ethane by a manometric setup on belgian black shale. The intrinsic reliability of the setup is discussed by Hemert et al \cite{53}. Precise measurement of temperature and pressure is performed with highly accurate instruments. The strong dependency of density to temperature at high pressures, increases the importance of using an adequate equation of state and measuring equipment, as a small change in temperature can cause a significant change in density.

In this chapter, we describe the manometric apparatus and the experimental procedure. Moreover, the adequate equations of state employed in this project will be introduced in Section 3.2. In Section 3.3, the calculation methods and the data analysis will be discussed. The last section is about Monte Carlo simulation and error analysis of the data.

3.1 Experimental method

The principle of a manometric setup is explained in Chapter 2. As already mentioned in Chapter 2, this method is based on mass conservation. In this case, excess sorption is defined as the difference between total amounts of free gas introduced to the system and the measurable amount of free gas after equilibrium in the system. Presence of any leakage in the system can influence the measurement directly.

3.1.1 Manometric Apparatus

A technical drawing of the manometric apparatus is shown in Fig. 3.1. The apparatus consists of two cells; (A) The sample cell with a volume of $7590 \pm 10 \times 10^{-8} m^3$, which is made of stainless steel and built by the Technical University of Delft. It can contain a maximum sorbent sample of $6 \times 10^{-5} m^3$. In order to minimize the leakage, it is sealed with Swagelok gaskets (SS-16-VCR-2GR). To minimize the sample loss during the desorption process and evacuation, three high porous sintered metal filters are placed at the opening of this cell. They capture particles with an aerodynamic diameter of 2 $\mu m$ or more. (B) The reference cell, which is only the tube between valve 3 and 4, has the total volume of $3524 \pm 4 \times 10^{-9} m^3$. But in case of having a better control on the amount of adsorbed and extracted gas, the volume can be extended to $12152 \pm 9 \times 10^{-9} m^3$ by opening valve 1 and including vessel C as a reference cell. All the tubes used in the manometric setup are 1/8" (316SS-Swagelok) with metal connections. Other components of the setup are listed below according to their number on Fig. 3.1. The type and manufacturer of the components are presented in Table 3.1.
Figure 3.1 – Comprehend schematic of the Manometric setup used at Technical University of Delft, Netherlands [53]

Valves (1, 2, 3, and 4) The low leakage valves, which are actuated by air. Their leakage characteristics limit the operating temperature to 340K, while their internal diameter limits the minimum applied pressure on the setup to 15 and 25 kPa.

Pressure transmitter (5) To monitor the pressure in the sample cell this transmitter is used which works in the range of 0-250 bar. The measured values by this transmitter are not accurate enough to be used in calculation of excess sorption.

Thermocouple (6) This thermocouple are used for the same purpose as (5).

Thermoelement and reader (7) The precise temperature sensor measures the temperature with the precision of about 1 K and the accuracy of 20 mK.

Pressure transmitter (8) The precise pressure sensor measures the pressure continuously with precision of 1 kPa and accuracy 0.1 kPa in temperature range of interest.

Valves (9, 10, 17) Ball valves
Gas Booster (11) The two stage air actuated booster is used to pressurize the desired gas before introducing it into the system.

Vacuum pump (13) The evacuation pump is used for gas extraction and desorption process, which evacuates the reference cell to an absolute pressure below 0.03 bar.

Data acquisition unit (15) This unit consists of Keithly KPCI-3108 data acquisition and control card, which are connected to a personal computer with a 16 channel 16 bits single ended analog input. The acquisition software is written in Testpoint V3.4. The software scans the input data every second but stores them every 10 seconds. The pressure transmitter (5) and thermocouple (6) are connected to the data acquisition and control card. The pressure transmitter (8) and thermoelement (7) are connected to the computer through RS232 interfaces. The performances of all the valves are controlled by the computer via data acquisition and control card.

Thermostatically controlled bath (16) This bath is used to keep the temperature constant during the measurement procedure. The sample cell and the reference cell are placed in the bath during the measurement. The volume of the bath is about $40 \times 10^{-3} m^3$. This bath is equipped with a temperature control device, which controls the temperature within 20 mK accuracy.

Table 3.1 – Type and manufacturer of setup elements

<table>
<thead>
<tr>
<th>Name</th>
<th>type</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves (1,2,3 and 4)</td>
<td>N60/H</td>
<td>VICI AG international</td>
</tr>
<tr>
<td>Pressure transmitter(5)</td>
<td>PTX600</td>
<td>Dr uck Nl. Bv</td>
</tr>
<tr>
<td>Thermocouple(6)</td>
<td>K-type</td>
<td>Thermocoax</td>
</tr>
<tr>
<td>Thermoelement and reader(7)</td>
<td>PT100 , F200</td>
<td>Automated system Laboratories</td>
</tr>
<tr>
<td>Pressure transmitter(8)</td>
<td>Series 9000</td>
<td>Paroscientific</td>
</tr>
<tr>
<td>Valves(9,10,17)</td>
<td>SS-43S4</td>
<td>Swagelok NS&amp;S</td>
</tr>
<tr>
<td>Gas booster(11)</td>
<td>DLE 30-75-GG</td>
<td>MAXIMATOR GmbH</td>
</tr>
<tr>
<td>Spring actuated relief valve(12)</td>
<td>SS-RL3M4-S4</td>
<td>Swagelok NS&amp;S</td>
</tr>
<tr>
<td>Vacuum pump(13)</td>
<td>N820.3FT.40.18</td>
<td>KNF</td>
</tr>
<tr>
<td>Metering valve(14)</td>
<td>SS-31-RS4</td>
<td>Swagelok NS&amp;S</td>
</tr>
<tr>
<td>Data acquisition unit (15)</td>
<td>Keithly KPCI-3108 data acquisition, control card and connection to computer by RS232 interfaces</td>
<td>TUDelft</td>
</tr>
<tr>
<td>Thermostatically controlled bath(16)</td>
<td>Proline RP485</td>
<td>Lauda</td>
</tr>
</tbody>
</table>
3.1.2 Materials

As commonly employed for excess sorption measurement, Helium pycnometry is used to calculate the
void volume. In order to verify the void volume measured by Helium, the experiment is repeated with
Argon. Moreover, the excess sorption of methane and ethane on the shale is measured.
Thermodynamic properties of these gases are described in Section 3.3. The purity of all the gases are
99.996%.

3.1.3 Sample preparation

The carboniferous Black shale from Belgium is used in our experiments. Our sample was taken from a
mine in Zolder, in the north of Belgium in the Campina Basin. The characteristics and preparation of the
sample is described below.

Granulation and sieving: After choosing sample pieces of 2-5 cm, they are granulated and sieved to a
size of 50-100 µm.

X-Ray Fluorescence (XRF): To determine the elemental composition of the sample, X-Ray Fluorescence
analysis is performed. The results reveal that the main part of the shale sample is SiO$_2$ (see
Fig. 3.2)

X-Ray Diffraction (XRD): To evaluate the mineral composition of the sample, X-Ray diffraction analysis
is performed. According to the result (Fig. 3.2), the shale sample consists of about 54% clay
minerals, i.e., illite, Na-albite, Chlorite and Kaolinite, around 27% quartz and 6.6% organic matter
and 7.4% Siderite.

![Figure 3.2 – Result of XRD (right) and XRF (left) analysis of Belgian black Shale](image)

Mass measurement of the empty sample cell: The cell together with the filters and the covers should
be weight prior to filling. So, all the parts are placed in a plastic container as it is shown in Fig. 3.3.
Filling the sample cell: The filling is done with the help of a funnel. In order to get an optimal packing the sample cell is shaken smoothly every few seconds during the filling procedure. After filling, a filter is placed at the opening of the sample cell to avoid sample loss during desorption or evacuation processes.

![Figure 3.3](image)

Figure 3.3 – The method to measure the empty sample cell prior to filling (left), Sample cell filling procedure (middle), placing the filter on the opening of the sample cell (right)

Evacuation of the sample cell: Prior to the experiment, the shale sample should be placed in an oven for 24 hours at 378 K under vacuum conditions. To apply the vacuum pressure, the opening of the cell will be connected to a vacuum pump inside the oven (Fig. 3.4). In order to obtain optimal experimental condition, we tried to achieve the minimum possible moisture content.

![Figure 3.4](image)

Figure 3.4 – Evacuation of the sample cell

Shale sample mass calculation: After the evacuation procedure, the sample cell should be closed immediately. Then it is placed and weight in the same plastic container as used before. Then, the weight difference of the shale containing cell and the empty sample cell is used to determine the shale sample’s weight.
3.1.4 Experimental procedure

Each set of excess sorption measurements consist of four steps. Prior to the measurement, the setup is evacuated for 24 hours at a chosen experimental temperature.

1) Helium leakage test: The first step is to verify whether the system is leak free or not. For this purpose, Helium will be injected in the sample cell through the reference cell. When pressure in the sample cell reaches a value of 18 MPa, valve 3 will be closed and valve 4 will be kept open until the equilibrium is reached (see Fig. 3.1). The equilibration time depends on the type of the gas and its temperature and it can be determined by the plot of the pressure versus logarithmic time as shown in Fig. 3.5 [4]. In case of Helium and Argon, temperature does not change the equilibration time. Therefore, a constant equilibrium time of 1 hour was determined for these components.

![Figure 3.5](image-url) – The pressure versus logarithmic time scale graph of helium in the first adsorption stage at temperatures of 308 K. Reaching a relatively constant pressure shows that the equilibrium is attained in the system. The equilibration time of Helium is about one hour.

2) Helium pycnometry: As mentioned before, Helium is used to measure the void volume of the sample. The system pressure is 18 MPa after the leakage test. The first step after the Helium leakage test is evacuation. For this purpose, the vacuum pump is connected to the reference cell. In order to evacuate the sample cell stepwise, we follow the following procedure in each step, first the reference cell is evacuated and stabilized for an hour until absolute pressure of 0.027 ± 0.03 bar is reached. Then the valve between these two cells (valve 4) is opened for one hour to decrease the pressure in the sample cell. Afterwards, it is closed again and the reference cell is evacuated until the pressure in the sample cell falls below 3 MPa. Then the program is stopped and by keeping both valves open, deep evacuation of the sample cell takes place.
In the next step, the booster is connected to the system and the compression process is performed stepwise in analogy to the evacuation. This means that in each step, the reference cell is filled with the gas at the pressure of 18 MPa. Then it is stabilized for an hour and subsequently valve 4 is opened for an hour to allow the gas to reach its equilibrium. This step is repeated until the equilibrium pressure reaches the desired pressure. In our experiments, the equilibrium pressure of the last stage is between 11-12 MPa. The pressure and temperature data are stored in the computer every 10 seconds.

3) Methane or Ethane excess sorption/desorption experiment: This step is performed for each gas individually. The procedure is exactly the same as for Helium pycnometry. For methane, the experiments are done at three different temperatures, i.e., 308 K, 318 K and 336 K and at pressures up to 11 MPa. For ethane, due to some difficulties, two experiments were performed both at 318 K and up to 9 MPa. No experiments was performed on other temperatures. Subsequently, each sorption experiment is followed by a desorption experiment, which is done by stepwise evacuation of system with the help of a vacuum pump.

4) Verification of the void volume: Finally, the void volume estimation is repeated with Argon to validate the void volume measured in the Helium sorption experiment. Certainly, the results of these two measurements are not exactly the same as He and Ar molecules have different kinematic diameters, but the relative error is below 0.8%.

3.2 Application of adequate equation of state

One of the sources of the uncertainties in the manometric method, is connected to the choice of equation of state, which is required for the density determination. Therefore, the choice of an appropriate equation of state (EOS) is an important step.

For choosing the right EOS, apart from accuracy, the degree of complexity needs to be considered. Numerous equations of state are provided in the literature, but our aim is to find simple but accurate EOSs that are valid in our experimental region for ethane, methane, argon, and helium. Important properties of the gases are defined in Table. 3.2.

3.2.1 Helium

In 1990, McCarty and Arp [50] proposed an equation of state (MA) for Helium in the temperature range of 0.8 to 1500 K and the pressures up to 2000 MPa. Prior to their work, all the presented EOSs consisted of two distinct equations for normal Helium and superfluid Helium without any relation between these two equations. However, the MA equation distinguishes these two states of Helium, there is a smooth transition between these two phases. The MA EOS is based on an algorithm with 32 terms. These terms are selected from the Jacobsen EOS, which is a modification of the Benedict-Webb-Rubin EOS.
3.2 EXCESS SORPTION MEASUREMENT: PRINCIPLE AND PROCEDURE

Table 3.2 – Important properties of the gases used in this project

<table>
<thead>
<tr>
<th>Component</th>
<th>( M_a ),[\text{g} \cdot \text{mol}^{-1}]</th>
<th>\text{Kinematic diameter [nm]}</th>
<th>Critical point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium (He)</td>
<td>4.0026 [50]</td>
<td>0.26 [68]</td>
<td>( P_c = 0.227\text{MPa} ) [50]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( T_c = 5.1953\text{K} )  [50]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \rho_c = 69.64\text{kg.m}^{-3} ) [50]</td>
</tr>
<tr>
<td>Methane (CH(_4))</td>
<td>16.0428 [25]</td>
<td>0.38 [61]</td>
<td>( P_c = 4.5402\text{MPa} ) [70]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( T_c = 190.564\text{K} )  [67]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \rho_c = 162.66\text{kg.m}^{-3} ) [67]</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>39.948 [68]</td>
<td>0.34 [61]</td>
<td>( P_c = 4.0597\text{MPa} ) [70]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( T_c = 150.687\text{K} )  [33]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \rho_c = 535.6\text{kg.m}^{-3} ) [33]</td>
</tr>
<tr>
<td>Ethane (C(_2)H(_6))</td>
<td>30.069 [29]</td>
<td>0.38 [61]</td>
<td>( P_c = 4.8722\text{MPa} ) [28]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( T_c = 305.322\text{K} )  [28]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \rho_c = 206.18\text{kg.m}^{-3} ) [28]</td>
</tr>
</tbody>
</table>

* Molecular weight

\[ \rho = \rho RT \quad + \rho^2 (N_1 T + N_2 T^{1/2} + N_3 + N_4/T + N_5/T^2) + \rho^3 (N_6 T + N_7 + N_8/T + N_9/T^2) \]
\[ + \rho^4 (N_{10} T + N_{11} + N_{12}/T) + \rho^5 (N_{13}) + \rho^6 (N_{14}/T + N_{15}/T^2) + \rho^7 (N_{16}/T) \]
\[ + \rho^8 (N_{17}/T + N_{18}/T^2) + \rho^9 (N_{19}/T^2) + \rho^{10} (N_{20}/T^2 + N_{21}/T^3) \exp(-\tau \rho^2) \]
\[ + \rho^{11} (N_{22}/T^2 + N_{23}/T^4) \exp(-\tau \rho^2) + \rho^{12} (N_{24}/T^2 + N_{25}/T^3) \exp(-\tau \rho^2) \]
\[ + \rho^{13} (N_{26}/T^2 + N_{27}/T^4) \exp(-\tau \rho^2) + \rho^{14} (N_{28}/T^2 + N_{29}/T^3) \exp(-\tau \rho^2) \]
\[ + \rho^{15} (N_{30}/T^2 + N_{31}/T^3 + N_{32}/T^4) \exp(-\tau \rho^2) \quad (20) \]

The constants of Eq. 20 are given in Table 3.3. The reduced temperature \( \tau \) is the ratio of gas actual temperature to its critical temperature. The pressure, temperature and density units are MPa, K, and mole/L, respectively. The MA EOS is well known and widely used for Helium pycnometry [11].

3.2.2 Methane and Argon

In 1992, Span and Wagner [70] developed a special equation of state for Methane and Argon in the temperature range of 270 to 350 K and the pressures up to 30 MPa. The proposed EOS is based on
the fundamental dimensionless Helmholtz energy \( \Phi = A/(RT) \). It possesses two parts, i.e., an ideal gas part and a residual part. The latter part takes into account the real fluid behaviour. Moreover, all the thermodynamic properties of the gases can be calculated by combination of these parts and their derivatives. Generally, it is defined as,

\[
\Phi(\delta, \tau) = \Phi^0(\delta, \tau) + \Phi^r(\delta, \tau),
\]

with \( \delta \) and \( \tau \), as reduced density and inverse reduced temperature, respectively,

\[
\delta = \rho/\rho_c, \tag{22}
\]

\[
\tau = T_c/T. \tag{23}
\]

where \( \rho_c \) and \( T_c \) are critical density and critical temperature.

As the EOS is only valid for a specific range of temperature and pressure, the residual part includes only a simple polynomial expansion, without any exponential term. The relation between pressure, temperature and density using the residual part of the Helmholtz energy is,

\[
\frac{p(\delta, \tau)}{\rho RT} = 1 + \delta \Phi^r_\delta, \tag{24}
\]

where pressure is in [Pa], Temperature in [K] and density in \([kg \cdot m^{-3}]\). According to Span and Wagner result,

\[
\Phi^r_\delta = \sum_{i=1}^{I} n_i d_i \delta^i \tau^{-1}, \tag{25}
\]
and by inserting the Eq. 25 in Eq. 24:

\[
\frac{p(\delta, \tau)}{pRT} = 1 + \sum_{i=1}^{I} n_i d_i \delta^{d_i} \tau^{t_i}. \tag{26}
\]

The constants in Eq. 26 for Methane and Argon are presented in Table 3.4. The uncertainties in density calculation are

\[
\frac{\Delta \rho}{\rho} \leq \pm0.02\% \quad P \leq 12 MPa, \tag{27}
\]

\[
\frac{\Delta \rho}{\rho} \leq \pm0.05\% \quad P \geq 12 MPa. \tag{28}
\]

The Span and Wagner equation of state is widely accepted for high pressure excess sorption determination of methane [11].

<table>
<thead>
<tr>
<th>i</th>
<th>d_i</th>
<th>t_i</th>
<th>n_i</th>
<th>d_i</th>
<th>t_i</th>
<th>n_i</th>
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<tr>
<td>1</td>
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<td>-0.25</td>
<td>0.251330485 \times 10^0</td>
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<td>2</td>
<td>0.25</td>
<td>0.854553290 \times 10^{-1}</td>
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<td>5</td>
<td>2</td>
<td>3.00</td>
<td>0.204359144 \times 10^0</td>
<td>2</td>
<td>2.75</td>
<td>0.152713256 \times 10^0</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>5.50</td>
<td>-0.100523656 \times 10^0</td>
<td>3</td>
<td>-0.50</td>
<td>0.994079499 \times 10^{-2}</td>
</tr>
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<td>2.50</td>
<td>-0.359988775 \times 10^{-1}</td>
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<tr>
<td>8</td>
<td>3</td>
<td>2.25</td>
<td>-0.598532889 \times 10^{-1}</td>
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<td>0.25</td>
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<tr>
<td>9</td>
<td>3</td>
<td>5.00</td>
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<td>4.00</td>
<td>-0.496627097 \times 10^{-1}</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>1.25</td>
<td>0.957140954 \times 10^{-2}</td>
<td>12=I</td>
<td>8</td>
<td>4.25</td>
</tr>
</tbody>
</table>

### 3.2.3 Ethane

At constant temperature and around the critical pressure of the gas, a small change in pressure leads to a significant shift in density values. Our experiments with ethane have been performed at a temperature of 318 K, which is relatively close to ethane’s critical temperature (T_c = 305.322 K). Therefore, it is important to choose an accurate EOS that describes the critical behaviour of the ethane adequately.

In 2006, Wagner and Bücker (WB) [76] introduced an equation of state for ethane, which present accurate
results in temperatures ranging from ethane’s melting point ($T_m = 90$ K) to 570 K and pressures up to 900 MPa. Their work contains a good overview on all the previous equations of state used in science and industry. They used the same fundamental equation for deriving ethane’s EOS as Span and Wagner (Eq. 21 and Eq. 24). The EOS is fitted on the highly accurate experimental data using Funke et al. [28, 29] and Claus et al. [20]. According to their work, the ideal fluid part of the Helmholtz energy was derived based on the thermodynamic behaviour of the ethane, whereas the real fluid part of the Helmholtz energy is obtained empirically. Thus, the EOS for ethane is given as,

$$
\frac{p(\delta, \tau)}{\rho RT} = 1 + \sum_{i=1}^{5} n_i d_i \delta^{d_i} \tau^{t_i} + \sum_{i=6}^{39} n_i e^{-\delta^{c_i} \tau^{c_i}} [\delta^{d_i} \tau^{t_i} (d_i - c_i \delta^{c_i})] 
+ \sum_{i=40}^{44} n_i e^{-\delta^{c_i} \tau^{c_i}} [(d_i - 2 \eta_i \delta - \varepsilon_i)^2] [\delta^{d_i} \tau^{t_i} (d_i - c_i \delta^{c_i})].
$$

(29)

The coefficients and exponents of Eq. 29 are presented in Table 3.5. This EOS shows deviation less than 0.02% from the experimental results of Funke et al., and 0.02%-0.03% from the experimental results of Claus et al.. In the critical region, the total experimental uncertainties reported by Funke et al. are about 0.007%-0.016% at $298 \leq T \leq 318$. The equation of state presented by Friend et al. [27], which is commonly used for ethane, possesses a noticeable systematic error in this region [76]. In the gas phase region, and at high temperatures and pressures, the deviation of the results of Friend’s EOS from the precise experimental results of Funke et al. and Claus et al. exceeds +0.3%.
Table 3.5 – Coefficient and exponents of Wagner and Bücker EOS [76]

<table>
<thead>
<tr>
<th>i</th>
<th>n_i</th>
<th>c_i</th>
<th>d_i</th>
<th>t_i</th>
<th>η_i</th>
<th>β_i</th>
<th>γ_i</th>
<th>ε_i</th>
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<td>-</td>
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<tr>
<td>5</td>
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<td>-</td>
<td>4</td>
<td>0.75</td>
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</tr>
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<td>-</td>
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<td>2</td>
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<td>37</td>
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<td>4</td>
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<td>38</td>
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<td>39</td>
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<td>10</td>
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<td>1.05</td>
<td>1</td>
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<td>3.00</td>
<td>15</td>
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<td>1.05</td>
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<td>400</td>
<td>1.16</td>
<td>1</td>
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</table>
3.3 Data Analysis

The method to measure pressure, temperature and the weight of the sample is described in the previous section. In the next step, the density of the gas is calculated from the measured temperature and pressure using a proper equation of state. Analysis of these data in each sorption experiment are described in following paragraphs. The sorption experiment starts with filling the reference cell with a known amount of gas as shown in Fig. 3.6. Then, the valve between the two cells will be opened and the system will be equilibrated during equilibration time, which is different for each gas. Assuming a constant mass before and after opening the valve 4 in the system we can write

$$\rho_N^{V_{ref}} + \rho_{eq}^{N-1}V_{void} + m_{ads}^{N-1} = \rho_{eq}^N V_{ref} + \rho_{eq}^N V_{void} + m_{ads}^N,$$

therefore the adsorbed amount of gas in each step will be,

$$m_{ads}^N - m_{ads}^{N-1} = (\rho_{fill}^N - \rho_{eq}^N)V_{ref} + (\rho_{eq}^{N-1} - \rho_{eq}^N)V_{void} ,$$

where

- $\rho_{fill}^N$: Density of the gas filled in the reference cell in the first step
- $V_{ref}$: Reference cell volume
- $\rho_{eq}^{N-1}$: Gas equilibrium density in step N-1
- $\rho_{eq}^N$: Gas equilibrium density in step N
- $V_{void}$: Void volume measured by Helium
- $m_{ads}^{N-1}$: Adsorbed mass onto the sample in step N-1
- $m_{ads}^N$: Adsorbed mass onto the sample in step N.

Figure 3.6 – Simple schematic of the sorption experiment, left: filling the reference cell; Right: connecting the reference cell to sample cell and letting the system to equilibrate.
3.3.1 Helium void volume calculation method

Many authors agreed on using Helium for measuring the void volume in a system. However there are some consideration and uncertainties, that should be taken into account. As Helium is an inert gas, its sorption quantity is considered to be zero. Therefore, the void volume measured by Helium corresponds to the accessible volume of the adsorbent. Ross et al. [55] discussed effects of different parameters on the Helium void volume. For instance, high pressure contributes to higher penetration ability of Helium molecules. Furthermore, employing Helium as a non-adsorbing gas results in an overestimation of the void volume as Helium molecules have a smaller kinematic diameter than other gases and can penetrate in holes that others cannot. Other aspects that need to be taken into account are swelling of the sample cell [4] and reaction of the sorbed gas such as CO\textsubscript{2} with the adsorbent, i.e. mineral trapping [10, 2, 26]. Therefore, the void volume in each step should be considered different from the next step. So by rewriting the Eq. 31 for \( n = 1 \ldots N \) steps and summing up all of them, the following equation will be derived,

\[
m_{ads}^N = \sum_{i=1}^{N} (\rho_i^{fill} - \rho_i^{eq}) V_{ref} - \rho_{eq}^N V_{void}.
\]

Therefore, in calculation of total adsorbed mass, the only void volume needed is \( V_{void} \) at the present step, \( N \).

Modification of the void volume can be done through considering the effect of different factors, i.e, the volume occupied by adsorbed Helium on the shale, \( \Delta V_{ads} \), swelling of the sample due to its infinite weight, \( \Delta V_{sw} \), and the reaction of adsorbed gas with the shale \( \Delta V_{rec} \). If we consider the stepwise modification of void volume, the outcome for \( N \) steps will be,

\[
V_{void}^N = V_{void}^0 - \sum_{i=1}^{N} \Delta V_{ads} - \sum_{i=1}^{N} \Delta V_{sw} - \sum_{i=1}^{N} \Delta V_{rec}.
\]

As Helium is a non-sorbing, inert gas and we measure the excess sorption quantity, that is based on zero-adsorbed volume assumption, the void volume is considered to be constant during the whole measurement.

Consider again the mass conservation before and after opening the valve 4. In case of Helium, we have \( m_{ads}^N = m_{ads}^{N-1} = 0 \). Therefore,

\[
V_{ref}(\rho_{fill}^N - \rho_{eq}^N) = V_{void}(\rho_{eq}^N - \rho_{eq}^{N-1}).
\]

Now we can define a parameter called volume ratio (\( \chi \)), which is

\[
\chi = \frac{V_{void}}{V_{ref}} = \frac{(\rho_{fill}^N - \rho_{eq}^N)}{(\rho_{eq}^N - \rho_{eq}^{N-1})}.
\]
By insertion of Eq. 35 in Eq. 31, the cumulative excess sorption equation can be derived,

\[ m_{ads}^N - m_{ads}^{N-1} = (\rho_{fill}^N - \rho_{eq}^N)V_{ref} + (\rho_{eq}^{N-1} - \rho_{eq}^N)\chi V_{ref}. \]  

### 3.4 Monte Carlo Method

The random errors in the experimental measurements can be simulated by a Monte Carlo error analysis. According to Eq. 36, the input parameters to calculate the excess sorption amount are the reference volume \( V_{ref} \), the density of filling in each step \( \rho_{fill}^N \), the volume ratio \( \chi \) and the equilibrium density of each step \( \rho_{eq}^N \) and its previous step \( \rho_{eq}^{N-1} \). The densities are calculated from the measured pressure and temperature at each step. Therefore, we consider a random error for each of these parameters. In case of temperature and pressure, the precision of their measuring devices are considered as the random error for the calculation, which are 20 mK and 0.01 bar, respectively [75]. For the volume of the reference cell and the volume ratio, the error is considered to have a random source.

In order to conduct a Monte Carlo simulation, we need to generate random numbers for our input parameters. In this regard, a random value is added to the experimental measured value. Normally, random errors in the experimental procedure are non-uniform and possess Gaussian distribution [41]. Therefore, we govern a normal distribution function with a standard deviation equal to the error in our measuring devices for temperature and pressure, and in case of the reference cell volume and the volume ratio, the measured random error.

After applying the random errors on input parameters, the following steps are conducted:

1. **Calculation of the excess sorption matrix, \( C \):** To calculate the excess sorption amount with the help of Eq. 36, we repeated the calculation 205 times \( J = 205 \). The more the calculation is repeated, the higher will be the precision of the results. As the sorption experiments are stepwise, for an experiment with \( N \) equilibrium stages, the result will be a matrix of N-by-J.

2. **Sorting the matrix \( C \):** We sort the rows of the matrix \( C \) in ascending order.

3. **The column matrix, \( D \):** We define a column matrix (N-by-1), with each elements from cumulative distribution function estimated by \( x = J - 1/2 \), where \( J \) is the row number in the matrix \( C \). By inversion of the elements on the column matrix to their standard normal form, we obtain the matrix \( D \).

4. **The linear regression:** The linear regression of each row of \( C \) on \( D \) \( (C = aD + d) \) results in \( N \) linear equations, in which the slope of the line, \( a \), is the error bar and the intercept, \( d \), is the excess sorption amount. The obtained values are in the mole basis, so they have to be devided by the sample mass to achieve the excess sorption amount on mass basis.

5. **The adsorption isotherm with error analysis:** The last step is to plot the excess sorption quantities versus equilibrium pressure at each step and place the error bars on each point.
4 Results and discussion

The following experiments are performed on dried Black shale sample from Belgium by the highly precise manometric setup; [1] sorption and desorption of $\text{CH}_4$ at temperatures of 336.03 K, 318.26 K and 308.73 K up to the pressure of 11 MPa; [2] sorption and desorption of $\text{C}_2\text{H}_6$ at temperatures of 318.69 K and 318.34 K up to the pressure of 9 MPa. The condition and parameters of the sorption experiment are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Temperature [K]</th>
<th>Equilibration time [h]</th>
<th>Sample weight [g]</th>
<th>Volume ratio ($\chi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>336.03</td>
<td>$\sim$ 30 [4]</td>
<td>50</td>
<td>15.67 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>318.26</td>
<td>$\sim$ 252 [4]</td>
<td>50</td>
<td>16.3 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>308.73</td>
<td>$\sim$ 1</td>
<td>66</td>
<td>15 ± 0.05</td>
</tr>
<tr>
<td>Ethane</td>
<td>318.69</td>
<td>$\sim$ 2</td>
<td>64.2</td>
<td>15.14 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>318.34</td>
<td>$\sim$ 2</td>
<td>64.2</td>
<td>15.19 ± 0.03</td>
</tr>
</tbody>
</table>

4.1 Equilibration time

In order to measure the excess sorption in each step, it is necessary to wait until the gas pressure reaches equilibrium. The equilibration time depends on the gas and the temperature of the measurement, and it can be obtained experimentally by plotting the gas pressure versus logarithmic time scale [4]. As discussed in Chapter 3, in case of Helium, the equilibration time did not show any significant dependency on the temperature and it was always about one hour. For the methane experiments at 336 K and 318 K, the equilibration times are reported by Battistutta et al. [4]. As the reported equilibration time of the methane at 318 K was relatively high (10 days), our experiments with methane were performed assuming a fixed equilibration time of 5.5 hours. For the methane experiment at 308 K as well as the ethane experiment at 318 K, the equilibration times are one hour and two hours, respectively. This can be observed in Fig. 4.1. At the beginning of the measurement in each step, the pressure transducer showed a noticeable increase in the pressure, which is due to the adiabatic temperature effect in the cell. As the setup is placed in a thermostatic bath, the temperature equilibration is fast and the pressure decreases until it reaches equilibrium. The pressure increment is not shown in Fig. 4.1.

4.2 Measurements with methane

The result of the methane excess sorption at 336.03 K is presented in Fig. 4.2. The maximum excess sorption is $0.0137 \pm 0.0064 \text{ mmol/g}_{\text{sample}}$ in the pressure range of 3-5 MPa. This value is in the range reported by Beaton et al. in 2010 [5] (0.012-0.029 mmol/g). After that, the maximum excess sorption
Figure 4.1 – Determination of the equilibration time by plotting the pressure versus the logarithmic time scale. The result of the first equilibration stages show equilibration time of one hour for methane at 308K (up graph) and two hours for ethane at 318K (bottom graph)

decreases until it reaches zero at a pressure of about 9 MPa. To our knowledge, the decline of the excess sorption values can be determined by (1) the overestimation of the void volume measured by Helium and (2) the finite volume of the sorbent [55]. Since, we could not observe any reaction during the methane sorption on shale, and the sample weight was the same before and after the experiment, we concluded that no reaction occurred. Moreover we did not observe swelling of the sample, as the void volume measured by Argon at the end of each set of experiment was almost the same as the Helium void volume. The same behaviour was reported by Battistutta et al. [4] for methane.
Excess sorption of methane at 318.26 K is presented in Fig. 4.3. The maximum excess sorption is the value of $0.0213 \pm 0.0062$ mmole/g$_{sample}$ in the pressure range of 4-6 MPa. The excess sorption value increases until it reaches its maximum and then decreases until it reaches zero at about 10 MPa. After this point, negative excess sorption has been observed. This can be due to the same reasons as the result of methane at 336 K.

Excess sorption of methane at 308.73 K is presented in Fig. 4.4. The maximum excess sorption is $0.0398 \pm 0.0084$ mmole/g$_{sample}$ in the pressure range of 6-7 MPa. The excess sorption capacity of the shale is in the range reported by Weniger et al. [79] (0.03 - 0.47 mmol/g). By considering the error bars in each point, a Langmuir shape for methane excess sorption in this temperature range can be drawn; the same behaviour was observed by other authors.

By comparison of the methane experiment results at three different temperatures, the dependency of the excess sorption on the temperature can be observed (Fig. 4.5). In all the works on this topic to the moment, the negative impact of temperature has been proven (see Chapter 2, Section 2.3). Moreover, the effect of temperature on void volume can also be distinguished. At increasing temperature, the methane excess sorption capacity of the shale tends to reach zero and negative values faster, which can be attributed to the change in measured Helium void volume. This is also in agreement with the work of Ross et al. [55].

### 4.3 Measurements with ethane

Ethane excess sorption measurements have been performed at temperatures of 318.69 K (Experiment 1) and 318.34 K (Experiment 2) up to the pressures of 6 MPa and 9 MPa, respectively. The results are
Figure 4.3 – Methane excess sorption isotherm at temperature of 318.26 K and pressures up to 11 MPa on Belgian black shale using a manometric setup.

Figure 4.4 – Methane excess sorption isotherm at a temperature of 308.73 K and pressures up to 11 MPa on Belgian black shale using the manometric setup.

presented in Fig. 4.6. For the purpose of comparison, both results without error analysis are plotted in Fig. 4.7. In order to interpret the results, we divide the graphs into three regions: (1) \( P \leq 4 \) MPa, (2) \( 4 < P < 6 \) MPa, (3) \( 6 \) MPa \( \geq P \).

Region (1): The results in both experiments are similar. First we have a small increase in the excess
Region (2): In experiment 1, the excess sorption quantity tends to increase, whereas in experiment 2, it is decreasing until it reaches its minimum at 6 MPa. To our knowledge, if the negative sorption values in this region were due to the interaction between the shale and the ethane gas, it had to be observable in both experiments. Moreover, we could not observe any reaction during the ethane sorption on the shale, and the sample weight did not change during the experiment. As the temperature in these experiments are almost the same. Therefore, we focus on the gas behaviour in this region. The critical pressure of the ethane is at 4.8 MPa. Regarding to the ethane’s density measurements by Funke et al. [28, 29] and Claus et al. [20], no special behaviour for ethane above its critical point was reported. A comparison of both experiments shows only a small difference with respect to the equilibrium pressure, which has caused the divergence between the results. On the other hand, due to the negative impact of temperature on sorption capacity of shale, the excess sorption capacity of shale in experiment 2 is expected to be higher than experiment 1. Therefore, the result of a negative sorption in experiment 2 and the lower sorption amount in this experiment can not be explained physically and might be caused by uncertainties of the EOS around the critical point of ethane.

In Fig. 4.8, we plotted the excess sorption results of the second experiments versus equilibrium density. As can be observed, the excess sorption values could decrease and become negative before the critical region of the ethane. To our knowledge, this behaviour could be due to the application of EOS on manometric setup. In Fig. 4.9, we considered a higher experimental temperature (318.69 K, the temperature of experiment 1) for experiment 2 and we calculated the densities and subsequently the excess sorption quantity. As it can be seen, in this graph the excess sorption quantity versus equilibrium density looks more logical than Fig. 4.8. In our opinion, the measurement uncertainties close to the critical point of

![Figure 4.5 – Comparison of the results of methane excess sorption at temperatures of 308 K (red line), 318 K (green line), and 336 K (blue line)](image)
ethane is the reason for negative sorption quantities observed in the second experiment.

**Region(3):** In this region, the excess sorption value tends to increase in both experiments. A sharp jump can be observed, which result in the maximum excess sorption value of $0.70 \pm 0.01\text{mmole/g sample}$ at the pressure of 9 MPa. It can be seen clearly in Fig. 4.8 that this sharp jump occurs exactly beyond the critical point of ethane. This can be due to the fact that after critical point, a small change in the pressure at the constant temperature causes a significant change in the density. Therefore, this would lead to higher excess sorption values. In both experiments, we did not observe a swelling of the sample, as the void volume measured by Argon at the end of each set of experiment confirmed the void volume measurement.
RESULTS AND DISCUSSION

Figure 4.7 – Comparison between the results of the ethane excess sorption at temperatures of 318.34 K (blue line) and 318.69 K (red line).

Figure 4.8 – Ethane excess sorption versus equilibrium densities calculated from measured pressures of experiment 2 at 318.34 K. The vertical line describes the ethane’s critical density.

Experiments indicate that the excess sorption of ethane is more than one order of magnitude higher than that of methane. The higher sorption capacity for ethane was observed by Sakurovs et al. [61]. They proposed that the difference in sorption capacities of different gases on coals are related to their critical
Figure 4.9 – Ethane excess sorption versus equilibrium densities calculated from measured pressures of experiment 2 at 318.69 K. The vertical line describes the ethane’s critical density.

temperature. However, they reported slightly equal sorption capacities for ethane and carbon dioxide. By comparison of our results with the results of Khosrokhavar et al. [41], who measured CO$_2$ excess sorption in the same laboratory with the same sample type, it can be observed that the maximum excess sorption capacity of carbon dioxide is 3.5 times smaller than that of ethane. See however Sakurovs et al. that the ratio between the sorption capacities can be described by the ratio between the critical temperatures.
Table 4.2 – Equilibrium pressure of ethane in both experiments in each step

<table>
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<th>$T = 318.34$ K $^b$</th>
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<td>17.38325802</td>
<td>17.32422644</td>
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<tr>
<td>2</td>
<td>30.54390392</td>
<td>30.46830717</td>
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<tr>
<td>3</td>
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<td>39.86262358</td>
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<td>46.43835082</td>
<td>46.47199481</td>
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<tr>
<td>5</td>
<td>50.96523641</td>
<td>51.04170753</td>
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<tr>
<td>6</td>
<td>54.1392634</td>
<td>54.17223781</td>
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<tr>
<td>7</td>
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<td>56.39828345</td>
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<tr>
<td>8</td>
<td>58.04709754</td>
<td>58.07265343</td>
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<tr>
<td>9</td>
<td>59.3053346</td>
<td>59.36890624</td>
</tr>
<tr>
<td>10</td>
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<td>60.41101156</td>
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<tr>
<td>11</td>
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$^a$Experiment 1
$^b$Experiment 2
Summary

Regarding to the excess sorption measurement of methane at temperatures of 308 K, 318 K and 336 K and pressures up to 10 MPa and ethane measurements at temperature of 318 K and up to a pressure of 9 MPa on dried Belgian black shale sample by a precise manometric setup, the following remarks can be made:

- The manometric method is capable to measure the excess sorption of different gases on shale. Application of Monte Carlo simulation for the calculation of excess sorption values can show the experimental uncertainties in our calculations. The low values of error bars in each experimental step reveals the fact that our manometric setup possesses a high accuracy.

- The equilibration time depends on the type of the gas and the experimental temperature. In case of Helium or Argon, the equilibrium time was about one hour at all temperatures. This can be due to the fact that both of these gases are inert and their adsorption on the sample is considered to be zero. Therefore, the time it takes for the pressure to reach equilibrium is determined by the equilibrium temperature and the adiabatic compression of the gas. As the experiments with methane and ethane, the dependency to gas type and temperature was fully observable.

- Experiments on methane at different temperatures show a decrease in adsorption capacity at increasing the temperature. Therefore, the pressure for zero excess sorption decreases at increasing temperature. Moreover, at increasing temperature, the excess sorption isotherms become zero and subsequently negative values at lower pressures. We assert, it is due to (1) the overestimation of void volume by Helium and (2) the dependency of void volume to experimental temperature and the pressure. We could not observe any reaction during the measurement. In addition, the weight of the sample did not change during the measurement and the void volume before and after sorption/desorption experiments was the same. Therefore, we conclude that there is not any reaction and swelling in the sample.

- Experiments on ethane at 318 K and a pressure of 9 MPa show the higher sorption capacity of the shale for ethane than for methane. The ethane maximum excess sorption capacity of the shale is one order of magnitude higher than that of methane. Moreover, due to the constant sample weight and the void volume before and after experiments, we did not consider any reaction and/or swelling effects. Our results indicate that the pore accessibility and the polarizability of the adsorbate molecules cannot explain the sorption capacity of the shale for different gases comprehensively. As the methane and ethane molecules have the same kinematic diameter, but the sorption of ethane is higher than that of methane, and the carbon dioxide molecules have quadropole moment, but our sample has higher sorption capacity for ethane than that of carbon dioxide.

The excess sorption isotherms presented for ethane and methane in this work can be used to develop a model to describe the adsorption behavior of these gases on Belgian black shale. Moreover, they can be used to estimate the gas in place in the shale.
References


REFERENCES


REFERENCES


REFERENCES


REFERENCES


The Monte Carlo simulation for calculation of methane excess sorption is presented in this section. For calculation of densities from pressure and temperature, another function with Span-Wagner equation of state of methane is called in this code. All the files can be found in the attached CD to this report.

```matlab
% Conducts Monte Carlo simulation for methane excess sorption
% OUTPUT
% output - 1st column: equilibrium pressure [bar]
% - 2nd column: excess sorption [mmol/g]
% - 3rd column: error bars [mmol/g]
% INPUTS
% volratio - ratio of void volume to reference volume []
% stdev - Standard deviation of the volume ratio
% p_fill - pressure of filling (column matrix) [bar]
% p_eq - equilibrium pressure (column matrix) [bar]
% w - weight of sample [g]
% T - Temperature of the experiment [K]

function output = montecarlo_methane(volratio, stdev, p_fill, p_eq, w, T)

nexp=size(p_eq,1);

n = 250;
montecarloexc = zeros(nexp, n);
mexc = zeros(nexp+1,1);
for i=1:n

% Randomizing Pressures
error1 = norminv(rand(nexp,1), 0, 0.01);
p_fill_rnd = p_fill + error1;
error2 = norminv(rand(nexp,1),0,0.01);
p_eq_rnd = p_eq + error2;

% Randomizing Temperature
error3 = norminv(rand(nexp,1),0,0.02);
T_rnd = error3 + T;

% Density calculation by SpanWagner EOS for methane
for k=1:nexp

% Measurement densities
rho_fill(k,1) = rho_Spanwagner_CH4(p_fill(k),T);
rho_eq(k,1)= rho_Spanwagner_CH4(p_eq(k),T);
```

% Randomized densities
rho_fill_rnd(k,1) = rho_Spanwagner_CH4(p_fill_rnd(k), T_rnd(k));
rho_eq_rnd(k,1) = rho_Spanwagner_CH4(p_eq_rnd(k), T_rnd(k));
end

% Randomizing reference cell volume
vref0 = 3.524;
error4 = norminv(rand(nexp,1), 0, 0.007);
ref = vref0 + error4;

% Randomizing volume ratio matrix
error5 = norminv(rand(1,n), 0, stdev);;
volratio_rnd = volratio + error5;

% Define matrix of equilibrium densities in step N-1
rho_eq_nminus1_rnd = [0; rho_eq_rnd(1:nexp-1)];

% Excess sorption calculation with Monte Carlo
for j=1:nexp
mexc(j+1) = mexc(j) + (rho_fill_rnd(j) - rho_eq_rnd(j))*vref(j) +
(rho_eq_nminus1_rnd(j) - rho_eq_rnd(j))*vref(j)*volratio_rnd(i);
montecarloexc(j,i) = mexc(j+1);
end
end

% Transpose
montecarloexc = montecarloexc';

% Sort every column ascending
montecarloexc = sort(montecarloexc,1);

% Regression
x = 1/(n*2):1/n:(2*(n-1)+1)/(n*2);
x = x';
xinv = norminv(x, 0, 1);
a = zeros(1,nexp);
b = zeros(1,nexp);
c = round(nexp/2);
for i=1:nexp
p = polyfit(xinv, montecarloexc(1:n,i),1);
a(i) = p(1);
b(i) = p(2);
figure(i);
subplot(2,c,i);
hold on;
plot(xinv,montecarloexc(1:n,i),'s');
plot(xinv,xinv*a(i)+b(i),'.r');
title{i};
grid on;
end

% Divide excess sorption quantities and error values by mass
aw = a/(w);
bw = b/w;

% Calculation of excess sorption without error analysis
rho_eq_nminus1 = [0; rho_eq(1:nexp-1)];
mexc_m = zeros(nexp+1,1);
for j=1:nexp
    mexc_m(j+1) = mexc_m(j) + (rho_fill(j) - rho_eq(j))*vref0 + ... 
    (rho_eq_nminus1(j) - rho_eq(j))*vref0*volratio;
end

% Adding [0,0] point to the graph
p_eq_p=[0;p_eq(:,1)];
bw_p=[0,bw(1,:)];
aw_p=[0,aw(1,:)];

% Plotting
figure(2);
errorbar(p_eq_p,bw_p,aw_p,aw_p,'r.','LineWidth',2);
hold on;
plot(p_eq_p,bw_p,'k','LineWidth',2);
hold on;
plot(p_eq_p,mexc_m(1:nexp+1)/w,:bo');
hleg1=legend('Error bars with a Monte Carlo simulation', ...  
'Monte Carlo error analysis','Excess sorption measurement');
set(hleg1,'Location','NorthWest');
grid on;
grid minor;
xlabel('Equilibrium Pressure [bar]');
ylabel('Cumulative Excess Sorption [mmol/g]');

% Outputs
output = zeros(nexp+1,3);
output(:,1) = p_eq_p;
output(:,2) = bw_p;
output(:,3) = aw_p;

Answers='Answers.xlsx';
xlswrite(Answers,output);
end
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<th>Year</th>
<th>Authors</th>
<th>Title</th>
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<td>Cao, Y. / Eikemo, B. / Helmig, R.</td>
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<td>Strohmer, V.</td>
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