F3 = \frac{-AP}{2.828427 \times B} \times \left( \frac{2.0 \times F3}{AC \times BTC(I)} \right) / BC \\
F3 = F3 \times DLOG\left( \frac{(ZV + 2.414 \times B)}{(ZV - 0.414 \times B)} \right) \\
PHI(I) = DEXP(F1 + F2 + F3) 

207 CONTINUE 
IF (NVLLH.EQ.0 OR ITAG.EQ.0) GO TO 810 

288 APX = ACX \times P / (10.73 \times T)^2. 
BX = BCX \times P / (10.73 \times T) 
A(1) = 1 
A(2) = BX - 1 
A(3) = APX - 3.0 \times BX^2 - 2.0 \times BX 
A(4) = BX^3 + BX^2 - APX \times BX 
CALL CUBEQN(A, Z, MTYPE) 
IF (MTYPE) 214, 215, 216

214 AMINI = Z(1) 
IF (AMINI.GT.Z(2) AND Z(2).GT.0) AMINI = Z(2) 
IF (AMINI.GT.Z(3) AND Z(3).GT.0) AMINI = Z(3) 
ZL = AMINI 
GO TO 217

215 ZL = Z(2) 
GO TO 217

216 ZL = Z(1) 
DO 218 I = 1, NCOMP
F1 = BTC(I) / BCX \times (ZL - 1.0) 
F2 = -DLOG(ZL - BX) 
F3 = 0.0 
DO 219 K = 1, NCOMP
F3 = F3 + XL(K) \times AY(K, I)

219 CONTINUE 
F3 = \frac{-APX}{(2.828427 \times BX) \times (2.0 \times F3 / ACX \times BTC(I) / BCX)} 
F3 = F3 \times DLOG\left( \frac{(ZL + 2.414 \times BX)}{(ZL - 0.414 \times BX)} \right) 
PHIL(I) = DEXP(F1 + F2 + F3)

218 CONTINUE
810 RETURN

C
END
C

*********************************************
SUBROUTINE YLIMIT(RLIMIT)
*********************************************

..... COPIED FROM W. R. PARRISH'S THESIS(BERKLEY)

THIS SUBROUTINE CALCULATES THE UPPER LIMIT OF 
INTEGRATION IN THE SMOOTH CELL LANGMUIR CONSTANT 
EXPRESION.

IMPLICIT DOUBLE PRECISION (A-H, O-Z)
COMMON /SIG/ SIGMA, EPS, RR, Z, A, T, RR2, Z2, RR3, Z3 
CA = A / RR 
CHECK = 0.0 
RCA = SIGMA / RR * 1.122462 
S = 1 - 0.98 * (SIGMA / (2 * (RR - A))) 
IF (S.LT.0.4) S = 0.4 
RCA6 = RCA ** 6 
RCA12 = RCA ** 12
DO 2 N=1,20
IF( S.GT.1..OR.S.LE.0.) GO TO 6
UM=1./(1.-S-CA)
UP=1./(1.+S-CA)
UM5=UM**5
UP5=UP**5
DA4=UM5+UP5
DA5=UM5*UM+UP5*UP
DB6=DA4+CA*DA5
UM11=UM**11
UP11=UP**11
DA10=UM11+UP11
DB12=DA10+CA*DA11
DB=RCA12*DB12-2.*RCA6*DB6
A10=UM11/UM-UP11/UP
A11=UM11-UP11
B12=A10/10. + CA*A11/11
A4=UM5/UM-UP5/UP
A5=UM5-UP5
B6=A4/4.+CA*A5/5.
B=RCA12*B12-2.*RCA6*B6
W=Z*EPS/(2.*S*T)*B
DWY=-W/S+Z*EPS*DB/(2.*S*T)
DS=S-(W-10.)/DWY
IF(ABS((DS-S)/DS).LT..01) GO TO 3
IF(DS.LE.0) CHECK=CHECK+1
IF(DS.LE.0) DS=S+1.05
IF(CHECK.GT.5) GO TO 6
2 S=DS
3 RLIMIT=S*RR
RETURN
6 CONTINUE
WRITE(6,100)SIGMA,EPS,A,RR,Z,T,S
100   FORMAT(' ','BLOW UP ON Y-LIMIT',7F10.5)
RETURN
END

******************************************************************************
REVISED SOLUBILITY SUBROUTINE
******************************************************************************

SUBROUTINE SOL7(JK,Y7,PHI7,P,T,X6)
******************************************************************************

THIS SUBROUTINE CALCULATES THE SOLUBILITIES OF THE GASES IN WATER USING
KRICEVSKY-KASARNOVSKY EXPRESSIONS FOR EACH GAS.

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION A(25),B(25),C(25),D(25)
DIMENSION VBAr(25),NCODE(25)
COMMON/NC/NCODE,NCOMP

P IS IN ATM. AND T IS IN K

DATA A/-15.826227,-18.400368,-18.057885,-20.958631,
A       -67.557,-22.150557,-20.108263,0.0,0.0,0.0
A       ,-868.764,0.0,0.0,-357.802,-14.283146,
C       -17.160634,-17.934347,-15.103508,-17.979226,
D       -336.76,-270.967,-877.845,-20.108263,
E       -20.108263,0.0/
C
DATA B/1559.0631,2410.4807,2627.6108,3109.3918,
A       9177.534,3407.2181,2739.7313,0.0,0.0,0.0
B       ,43323.6,0.0,0.0,13897.5,2050.3269,1915.144,
C       1933.381,2603.9795,2530.0405,16170.1,
D       15992.9,42051.0,2739.7313,2739.7313,0.0/
C
DATA C/0.0,0.0,0.0,0.0,0.0,0.072775,
A       0.0,0.0,0.0,0.0,0.0,0.0,
B       122.986,0.0,0.0,52.2871,0.0,0.0,
C       0.0,0.0,0.0,0.0,46.2117,0.0,
D       33.2892,125.018,0.0,0.0,0.0/
C
DATA D/1.0,1.0,1.0,1.0,1.0,760.0,
A       1.0,1.0,1.0,1.0,1.0,1.0,
B       0.0,1.0,0.0,-0.029836,1.0,0.0,
C       1.0,1.0,1.0,1.0,-0.00608793,1.0,
D       0.0260485,0.0,1.0,1.0,1.0/
C
DATA VBAR/32.0,32.0,60.0,13*32.0,
A       32.8,8*32.0/
C
AOR.JK.EQ.22)GO TO 10
AOR.JK.EQ.6.OR.JK.EQ.7)GO TO 20
XO=D(JK)*DEXP(A(JK)+B(JK)/T+C(JK)*T)
GO TO 30
10    XO=DEXP((A(JK)+B(JK)/T+C(JK)*DLOG(T)
A+AD(JK)*T)/1.987)
30    F=P*Y7*PHI7
X6=F*XO*DEXP(-1.0*VBAR(JK)*(P-1.0)/(82.06*T))
IF(X6.GT.0.05)GO TO 40
GO TO 50
40    CONTINUE
C
WRITE(6,200)JK,X6
X6=0.05
GO TO 50
C
WRITE(6,100)JK
20    X6=0.0
50    RETURN
100   FORMAT(1X,T20,' * * COMPONENT# ',I3,' NOT YET
A AVAILABLE IN SOL7 * * ')
200   FORMAT(1X,T20,' * * COMPONENT# ',I3,' HAS DEFAULTED
A TO X6 = 0.05 FROM X6 = ',E15.5,' * * ')
C
END
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XXIII. “Thermal Properties and Characterization of Methane Hydrates”

Eilis Rosenbaum (S) and Gerald Holder (F), University of Pittsburgh
with
Robert Warzinski (M), NETL
THERMAL PROPERTIES AND CHARACTERIZATION OF METHANE HYDRATES

by

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Submitted to the Graduate Faculty of

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Master of Science

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THERMAL PROPERTIES AND CHARACTERIZATION OF METHANE HYDRATES

Eilis Jill Rosenbaum, MS
University of Pittsburgh, 2003

Renewed interest in methane hydrates as a potential, unconventional energy source has prompted investigation into their thermal properties, which are necessary to determine heat flow through the hydrate for resource production.

In this investigation thermal property measurements have been made on unconsolidated pure methane hydrate samples formed in a high-pressure variable-volume viewcell (HVVC). Using a transient plane source (TPS) technique, a single measurement was used to simultaneously determine the thermal conductivity and thermal diffusivity of the methane hydrate inside the viewcell. A vessel was designed to contain the sample around the TPS for thermal property measurements while inside the HVVC. The vessel was successful in containing the sample during the hydrate formation experiments and its design made it possible to recover a methane hydrate sample, which was analyzed with Raman spectroscopy.

The striking quality of methane hydrate is that its thermal conductivity is much lower than ice, despite its structural similarities to ice. The thermal conductivity of pure methane hydrate for a temperature range of 264 K to 277 K and pressure range of 11.6 MPa to 13.0 MPa, respectively, can be described by \( k = (-0.0034 T + 1.2324) \) W/mK, where \( T \) is in Kelvin. The average of the thermal conductivity values within this range of temperatures and pressures is \( k = 0.30 \pm 0.02 \) W/mK. The sample was recovered and analyzed with Raman spectroscopy, confirming that the sample was pure hydrate.

The thermal diffusivity of methane hydrate has only been reported by one other investigator in preliminary experiments. The thermal diffusivity of methane hydrates determined in the work reported herein for a temperature range of 264 K to 277 K and pressure range of 11.6 MPa to 13.0 MPa, respectively, is \( \alpha = (2.59 \pm 0.16) \times 10^{-7} \) m\(^2\)/s. The thermal diffusivity can also be described by \( \alpha \times 10^7 = (0.0005 T + 2.4424) \) m\(^2\)/s where \( T \) is in Kelvin.
# TABLE OF CONTENTS

1 INTRODUCTION .......................................................................................................................... 1

2 LITERATURE REVIEW .................................................................................................................... 3

2.1 METHANE HYDRATE PROPERTIES ............................................................................................ 3

2.2 THERMAL PROPERTY MEASUREMENTS OF METHANE HYDRATES ........................................ 7

2.3 TRANSIENT PLANE SOURCE (TPS) TECHNIQUE ...................................................................... 12

3 EXPERIMENTAL ............................................................................................................................ 20

3.1 THERMAL PROPERTY MEASUREMENTS WITH THE TPS TECHNIQUE ...................................... 20

3.2 EXPERIMENTAL IMPROVEMENTS ............................................................................................. 26

3.3 EXPERIMENTAL SETUP .............................................................................................................. 27

3.3.1 High-Pressure Variable-Volume Viewcell (HVVC) ................................................................ 27

3.3.2 Transient Plane Source (TPS) Cup Assembly ........................................................................ 28

3.3.3 Environmental Chamber ...................................................................................................... 32

3.4 EXPERIMENTS ........................................................................................................................... 32

3.4.1 Experiment T20-006: Methane Hydrate Formation from Water and Methane With Visual Observation of Hydrate Formation and Dissociation ......................................................... 34

3.4.2 Experiment T20-009: Methane Hydrate Formation from Water Saturated Sand and Methane .... 36

3.4.3 Experiments T20-010 and T20-011: Thermal Property Measurements of Glycerol .................. 39

3.4.4 Experiment T20-014: Thermal Property Measurements of Water at Various Temperatures ...... 41

3.4.5 Experiment T20-015: Thermal Property Measurements of Hydrates Formed from Water and Methane 43

3.4.6 Experiment T20-016: Thermal Property Measurements of Hydrates Formed from Frost and Methane 45

3.4.7 Experiment T20-017: Thermal Property Measurements of Hydrates Formed from Water and Methane – The Cup Was Used Without the Cap ........................................................................ 47

3.4.8 Experiment T20-018: Thermal Property Measurements of Hydrates Formed from Water and Methane and Analysis with Raman .............................................................................. 50

4 DISCUSSION .................................................................................................................................. 63

5 CONCLUSIONS ................................................................................................................................ 67

6 FUTURE WORK ............................................................................................................................... 69

A DATA ACQUISITION AND ANALYSIS ........................................................................................... 72

A.1 NATIONAL INSTRUMENTS HARDWARE ..................................................................................... 72

A.2 DATA ANALYSIS PROGRAM (IN LABVIEW) .............................................................................. 75

B EQUATIONS AND CALCULATIONS ............................................................................................... 116

B.1 DERIVATION OF EQUATIONS USED IN THE DATA ANALYSIS .................................................. 116

B.1.1 $R_{ssn}$ Derivation .................................................................................................................. 116

B.1.2 $H(\tau)$ Values From Numerical Integration at Different $\tau$-Values ............................................. 117

B.2 RAMAN SPECTROSCOPY ANALYSIS ....................................................................................... 118
LIST OF TABLES

Table 3-1: Measured Thermal Property Data of Water (This Work) ..........................................................42
LIST OF FIGURES

Figure 2-1: Cavities in Gas Clathrate Hydrates (A.) Pentagonal Dodecahedron ($5^{12}$). (B.) Tetrakaidecahedron ($5^{12}6^2$). .......................................................... 3
Figure 2-2: Hydrate Crystal Unit Structure I (McMullan and Jeffrey, 1965; taken from Sloan [1]). .......................................................... 4
Figure 2-3: Temperature and pressure trace for formation of simple methane hydrates (from Sloan [1]). .......................................................... 5
Figure 2-4: Thermal conductivity history compiled by Asher [12] with recent measurements added. .......................................................... 9
Figure 3-1: Wheatstone bridge circuit, containing the TPS sensor. .......................................................... 20
Figure 3-2: Raw data collected and plotted using LabVIEW. .......................................................... 21
Figure 3-3: Resistance versus time data fit to a second order polynomial in the range of data $T = 2 \tau_v$ to $\frac{1}{2} \theta$. .......................................................... 22
Figure 3-4: $\Delta T$ versus $H(\tau)$ data fit to a straight line through the origin. .......................................................... 24
Figure 3-5: HVVC containing the TPS assembly. .......................................................... 28
Figure 3-6: Vishay Micro-Measurements precision strain gauge used for thermal property measurements. .......................................................... 29
Figure 3-9: (A.) Environmental chamber and computer system, (B.) HVVC mounted inside chamber. .......................................................... 31
Figure 3-10: Experiment T20-006, a typical pressure versus temperature trace of hydrate formation and dissociation. .......................................................... 35
Figure 3-11: Experiment T20-009. Post experiment picture of the CPVC tubing on top of the HVVC glass bottom. The water in the sand has already evaporated. .......................................................... 37
Figure 3-12: Experiment T20-009, formation of methane hydrates in sediments. .......................................................... 38
Figure 3-13: Experiment T20-009, post experiment picture showing the eruption of the sand mixture from the CPVC tubing. .......................................................... 39
Figure 3-14: Experiments T20-010 and T20-011, thermal conductivity of glycerol with literature values. .......................................................... 40
Figure 3-15: Thermal conductivity of water compared with literature values. .......................................................... 42
Figure 3-16: Experiment T20-015, cycle 1 down and up, cycle 2 down. .......................................................... 44
Figure 3-17: Experiment T20-016, cycles 1 up to 2 down. .......................................................... 45
Figure 3-18: Experiment T20-016, cycle 2 up. .......................................................... 46
Figure 3-19: Experiment T20-017, Pressure and temperature data with corresponding thermal conductivity measurements. .......................................................... 48
Figure 3-20: Experiment T20-018, cycle 1 up. .......................................................... 51
Figure 3-21: Experiment T20-018, cycle 2. .......................................................... 52
Figure 3-22: Experiment T20-018, cycle 3. .......................................................... 53
Figure 3-23: Experiment T20-018, cycles 4 and 5. .......................................................... 55
Figure 3-24: Experiment T20-018, cycles 1 up through 5 down with thermal conductivity values. .......................................................... 56
Figure 3-25: Experiment T20-018, cycles 1 up through 5 down with thermal diffusivity values. .......................................................... 57
Figure 3-26: Experiment T20-018, Thermal Conductivity and Thermal Diffusivity Data. .......................................................... 58
Figure 3-27: Hydrate in cup sleeve. The cup bottom was removed to view the hydrate sample and pictured above is the hydrate near the TPS. .......................................................... 59
Figure 3-28: Cup bottom shown with hydrate stuck on the TPS element. .......................................................... 60
Figure 3-29: Raman spectroscopy results. .......................................................... 61
Figure 3-30: The dissociated hydrate on the cup bottom. .......................................................... 62
Figure 4-1: Experiment T20-018, Thermal conductivity values from this work with literature values. .......................................................... 63
FIGURE 4-2: MODELS DEPICTING THE EFFECTIVE THERMAL CONDUCTIVITY FOR UNCONSOLIDATED METHANE HYDRATE [26, 27] .......................................................... 64
FIGURE 4-3: THERMAL CONDUCTIVITY OF METHANE HYDRATE FROM EXPERIMENTS T20-017 AND T20-018 ........ 65
FIGURE 4-4: EXPERIMENT T20-018, THERMAL DIFFUSIVITY DATA WITH LITERATURE DATA ................................. 66
FIGURE A-1: ELECTROMECHANICAL RELAY SWITCH USED TO INITIATE THERMAL PROPERTY MEASUREMENTS .... 73
FIGURE A-2: 8-CHANNEL ISOLATION AMPLIFIER, 10 KHZ BANDWIDTH .......................................................... 74
FIGURE A-3: TEMPERATURE SENSOR TERMINAL BLOCK .......................................................................................... 74
FIGURE A-4: FRONT PANEL OF THE LABVIEW DATA ANALYSIS PROGRAM .......................................................... 76
FIGURE A-5: LABVIEW BLOCK DIAGRAM OF THE DATA ANALYSIS PROGRAM ......................................................... 77
FIGURE A-6: HIERARCHY OF SUB-VI’S IN DATA ANALYSIS PROGRAM .......................................................... 78
FIGURE B-1: WHEATSTONE BRIDGE CIRCUIT, CONTAINING THE TPS SENSOR ....................................................... 116
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1 INTRODUCTION

With recent estimates of in situ gas hydrates in the ocean and permafrost regions there is renewed interest in hydrates because of their potential as an unconventional energy source. Interest in and studies of natural gas hydrates as a potential energy source date back to the mid-1960’s with the U.S.S.R.’s research of hydrate kinetics and thermodynamics [1]. Natural gas hydrates present an appealing resource of methane because energy obtained from the gas in the hydrate is fifteen times greater than the energy required to dissociate the hydrate for recovering the gas [1].

Gas production can be accomplished by creating a shift in the thermodynamic equilibrium of the hydrate [2]. Proposed gas recovery methods involve hydrate dissociation by three methods: thermal stimulation, depressurization, and inhibition [1, 2]. The rate of hydrate decomposition seems to be determined by the movement of a decomposition front which depends on the magnitude of heat flow through it [2]. If a temperature difference exists across the hydrate reserve, heat will flow from the hotter region to the cooler region via conduction. To model gas decomposition, knowledge of the heat flow through the sample must be determined which, therefore, requires knowing the thermal properties of the medium [2]. The thermal conductivity and thermal diffusivity are basic properties important in understanding the thermal behavior of the hydrate reservoir [3], however, the number of thermal property measurements reported is several orders of magnitude lower than that for phase equilibrium properties [1].

Further advances in hydrate research depends fundamentally on high-quality property data and laboratory exploration of the physics and chemistry that govern naturally occurring hydrates [4]. Measurements should also be made on samples inside the synthesis vessel. Because the thermal conductivity of an aggregate of sediment, water, and gas hydrate is a function of the individual phases, the concentration and distribution of those phases and, the nature of the interfaces between the phases, sample characterization is also essential.
In this work, a well developed and widely used method for thermal property measurements was employed. The transient plane source (TPS) technique, developed [5] and patented [6] by Gustafsson, allows the determination of both the thermal conductivity and thermal diffusivity from one measurement. This technique offers a non-invasive, quick, and reliable method of thermal property determination. Unlike past thermal property measurement methods, this technique can be used with small sample sizes and was adaptable, with minor modifications, to an existing experimental setup where methane hydrates have been successfully formed.

All components used in the setup of this system are commercially available. The experimental system has been updated using National Instruments components and a National Instruments programming system, LabVIEW, to automate thermal property measurements and data analysis for determining the thermal properties. Use of LabVIEW allows data acquisition and data analysis to be done coincidently during hydrate formation and dissociation experiments.
2 LITERATURE REVIEW

2.1 Methane Hydrate Properties

All natural gas hydrates form in one of three crystal structures (cubic structure I, cubic structure II, and hexagonal structure H) and, unlike ice which forms as a pure component, hydrates require guest molecules of the proper size to form. Methane hydrates form in cubic structure I which has large and small cavities. The large cage is a tetrakaidecahedron (14-sided) cavity, containing 12 pentagonal faces and 2 hexagonal faces ($5^{12}6^2$) (see Figure 2-1). The small cage is a pentagonal dodecahedron (12-sided) cavity which has twelve pentagonal faces ($5^{12}$) (see Figure 2-1). Hydrate crystal cell structure I is cubic with a body centered lattice. The small and large cages of Structure I are shown in Figure 2-2 where two complete $5^{12}6^2$ connect four $5^{12}$. [1]

![Figure 2-1: Cavities in Gas Clathrate Hydrates (a.) Pentagonal Dodecahedron ($5^{12}$). (b.) Tetrakaidecahedron ($5^{12}6^2$).](image)
Hydrates consist of about 85% water on a molecular basis, so many of their mechanical properties resemble those of ice Ih, however, their thermal expansion and thermal conductivity are significantly different than that of ice [1]. The thermal conductivity of hydrates is markedly lower than ice and close to that of water. The low thermal conductivity of hydrates is due to their lattice structure, where the water molecules are restricted from translation or rotation. Because they vibrate anharmonically about a fixed position, a mechanism for scattering of phonons is provided, which causes the thermal conductivity to be lower. A weak coupling between the guest and host lattice does not noticeably affect most structural thermodynamic and mechanical properties but does hinder the transport of heat.

In solids, heat transport and dissipation is accomplished via acoustic lattice vibrations. The methane molecule inside the hydrate cage rotates freely as was determined by neutron scattering experiments [7]. Though the methane is free to rotate, its coupled motion with the lattice vibrations dissipates heat transport of the crystal-like structure. This dissipation of heat caused by the host molecule thus causes the thermal conductivity to be lower.

In a constant volume pressure vessel containing liquid water and methane gas at sufficient pressure, the pressure is seen to decrease as the temperature is decreased until hydrate nucleation begins [1]. As hydrates nucleate, a rapid reduction in pressure is observed (see Figure 2-3).
pressure versus temperature of the dissociation line will retrace the pressure versus temperature of the formation line.

![Diagram of temperature and pressure trace for formation of simple methane hydrates (from Sloan [1]).](image)

**Figure 2-3**: Temperature and pressure trace for formation of simple methane hydrates (from Sloan [1]).

Hydrate from a two phase gas-water system has been hypothesized to occur in four stages [1]. The initial condition is where the pressure and temperature are favorable for hydrate formation but no gas molecules are yet dissolved in water. As gas dissolves, labile clusters form immediately. These labile clusters then agglomerate by sharing faces. When the size of the cluster agglomerates reaches a critical value, growth begins. When the critical cluster radius is reached, nucleation occurs. The induction time of methane hydrates is much longer than that of other gas hydrates, which has been measured to be longer than 24 hours. This sequence of steps continues to be a matter of some debate [8].

Hydrates form from gas and either water or ice at elevated pressures and low temperatures [1]. Nucleation from water is time-dependent with a high degree of metastability and a function of displacement from equilibrium, the state and history of the water, the composition of the gas,
the degree of agitation or turbulence, and the geometry of the system and surface area. Nucleation from solid ice occurs easier when the temperature is increased above the melting point. Melting ice provides a template for the formation of hydrates but once a protective film of hydrates forms at the surface, hydrate formation has been seen to diminish or cease.

Link et al [9] at the U.S. Department of Energy successfully formed methane hydrates from double-distilled water and methane in a high-pressure view cell with a high degree of vortex mixing. Hydrate was formed by pressurizing the cell with methane between 5.5 MPa and 13.8 MPa and dropping the temperature until hydrate formation was observed. In experiments to determine maximum methane uptake, methane was continually delivered to the cell to maintain a constant head pressure.

In experiments to study hydrate formation and dissociation, visual observation was made of hydrate crystals forming, agglomeration of the crystals, and the formation of a solid hydrate mass [9]. After formation of the solid hydrate mass, additional hydrate formation was observed with a decrease in the pressure with time as more free methane was incorporated into the crystal structure. Experiments were also performed using a surfactant. Additional hydrate could be formed because the formed hydrate was forced to the edges of the interfaces between water and gas, allowing the water-methane contact to be present longer, and the concentration of methane in the water to remain constant throughout formation. Using water containing 224 ppm of surfactant, the hydrate phase contained over 96% of the maximum theoretical amount of methane that would have been incorporated into hydrates if 100% of the water was converted to hydrate.

Waite et al from U.S. Geological Survey (USGS) [10] formed methane hydrate from granular ice in their thermal conductivity measurement device (thermal conductivity experiment described later). They started with granular ice (180 – 250 µm), or granular ice mixed with sediment in a methane pressurized vessel, and slowly heated the sample to form methane hydrates. They note that by creating hydrate from granular ice and sediment, a uniform mixture is obtained.

Once hydrate is formed and dissociated it has been seen that hydrates do not completely decompose but leave a partial structure which promotes hydrate formation more readily on subsequent cooling cycles. The residual structure of water is destroyed at temperatures greater than 28 °C [1]. In the work done by Link et al, this phenomenon was observed. With successive formations, the formation time decreased, which they attributed to possible microscopic hydrate
crystals that were still present in the solution at 15 °C. If present, the crystals would act like seeds for future hydrate formation. [9]

2.2 Thermal Property Measurements of Methane Hydrates

The number of thermal property measurements for natural gas hydrates are several orders of magnitude lower than those for phase equilibrium properties. A challenge in thermal property measurements lies in determination of the sample composition prior to measurement, which can be affected by hydrate decomposition when the apparatus is loaded with preformed hydrate [1]. Also a challenge is completely converting all of the water to hydrate and the ability to confirm this.

Sloan summarizes methods used thus far to determine thermal conductivity values of hydrates [1]. Stoll and Bryan [11] used a transient needle probe on propane hydrates, compacted after formation. A modified version of the needle probe was computerized, refined, and extended to short times and used by Asher [12] to measure the thermal conductivity of methane hydrates in sediments with an estimated accuracy of ± 8%. A steady-state method was used by Cook and Leaist [13] to measure the thermal conductivity of methane hydrates to within ± 12%. The thermal conductivity determined by Cook and Leaist was 0.45 W/mK at a temperature of 216.2 K. In this experiment, however, the sample was prepared and pressed externally and then introduced to the hot-plate cell of the apparatus. Sloan also notes that much remains to be explored in this area of hydrate research. Measurements reported by Sloan also indicate that neither the types of guest molecule nor the types of hydrate crystal significantly affect the thermal conductivity.

Ross and Anderson report thermal conductivity values for tetrahydrofuran using the transient hot-wire method [14]. Their results indicate that the thermal conductivity was proportional to temperature and not a function of pressure. In the range of temperatures from about 100 K to 250 K the thermal conductivity of tetrahydrofuran hydrate was about 0.47 W/mK to about 0.53 W/mK, respectively, showing a positive trend in the thermal conductivity with temperature, which they attribute to molecular disorder within the hydrate structure.

Cook and Leaist [13] measured the thermal conductivity of pressed samples of methane hydrate. To form the samples, powdered ice was loaded into a pressure vessel and ultrahigh
purity methane was condensed into the pressure vessel. Agitation of the sample was accomplished by rotating the vessel for several days, subjecting the sample to abrasion by rods contained within the vessel. The temperature was maintained at -13 °C to form the hydrate. The sample composition was \( \text{CH}_4 \cdot (5.7 \pm 0.8) \text{H}_2\text{O} \). After hydrate formation, the sample was removed and pressed into a disc for thermal conductivity measurements using the guarded hot-plate cell method. During the sample preparation some atmospheric water condensed in their sample. During thermal property measurements, the hydrate decomposed considerably. At the completion of the measurement, the methane hydrate content, determined by weight loss, was found to be 57 ± 5%.

Asher [12] used a needle probe to measure the thermal conductivity of methane hydrates in sediments. The hydrate formation cell was packed with sediment, saturated with water, and the needle probe was inserted. The cell was pressurized with methane up to 11.7 MPa (1700 psia). The temperature was lowered to 1 °C to form hydrates. They assumed complete formation when the pressure change approached zero. In order to verify that the sample was in fact hydrate and sediment and not ice in sediment, they measured the thermal conductivity above and below the ice point and concluded that it should be the same if the sediment was saturated with hydrate only. Their experimental system was calibrated with water and glycerin. The value he reports for methane hydrate in Ottawa sand is \( k = 2.75 \text{ W/mK at } T = 275 \text{ K} \). Other thermal conductivity values were displayed on a graph included in his thesis with no actual values reported. The graph compiled by Asher is in Figure 2-4 with other recent measurements included. The values reported by Asher show that hydrate in the sediments decrease the bulk thermal conductivity of the sample from that of water. The thermal conductivity of methane hydrates in sediment is about half of the thermal conductivity of ice in sediments.

Recent work done by Brian deMartin reports thermal conductivity values and thermal diffusivity values for methane hydrates and methane hydrates in Oklahoma 1 sand (~100%
Figure 2-4: Thermal conductivity history compiled by Asher [12] with recent measurements added.
quartz sand, density = 2,650 kg/m³, and grain size = 100 ± 50 µm) [15]. The thermal conductivity measurements were performed in the apparatus used for hydrate synthesis via the needle probe thermal conductivity method. Granular, sieved (180- to 250 µm) H₂O ice seed grains placed in a high pressure cylinder were pressurized with cooled methane to a pressure of 22 MPa. The sample was then heated to near the melting point of ice (271.5 K) to form methane hydrate. This method of hydrate formation is supposed to produce samples closest in properties to natural gas hydrates, even close in terms of stoichiometry. deMartin reports the thermal conductivity of a porous Structure I methane hydrate sample at 263 K and a confining pressure of about 28 MPa to be 0.32 ± 0.005 W/mK. The pure methane hydrate samples measured by deMartin were estimated to have a porosity of 28% to 33%, determined by knowing the hydrate volume and the volume of the sample vessel.

deMartin concludes from preliminary experiments that in sand, gas decreases the bulk thermal conductivity and hydrates act to increase the thermal conductivity from about 0.25 W/mK for a sand and gas mixture to about 0.82 W/mK for unconsolidated methane hydrate and sand mixtures [15]. He also found that the thermal conductivity of hydrate / sediment mixtures increased with the presence of methane hydrate. His explanation of this phenomenon is that the hydrate enhances grain to grain contact, thereby increasing heat flow through the sample.

The only other known measurements of thermal diffusivity were reported by deMartin using the modified Angstrom method [15]. The samples used to measure the thermal diffusivity were formed and compacted at USGS-Menlo Park, wrapped in aluminum foil, stored in liquid nitrogen and transported to Lawrence Livermore National Labs (LLNL) for the thermal diffusivity measurements. To make the measurements, the samples were drilled with two holes for inserting thermocouples. A wire at the center was used to apply a sinusoidal voltage to the samples and the temperature wave was monitored during the heating to determine the thermal diffusion of the sample. The thermal diffusivity was determined by knowing the phase difference between the two thermocouples, the period of the sinusoidal heat wave, and the radial distance between the two thermocouples.

The results reported by deMartin show that the thermal diffusivity rises with increasing pressure and falls with increasing temperature [15]. He also found that the presence of water ice affects the thermal diffusivity of the hydrate, and that the thermal diffusivity increases with increasing confining pressure. The character of the pressure dependence varied from sample to
sample. Because of problems in the experiment, thermal diffusivity values at a constant confining pressure of about 10 – 16 MPa, could only be made at temperatures between 148 K and 170 K. He reported thermal diffusivity values for temperatures of 150 K and 270 K at confining pressures of 0.1 MPa to 15 MPa as $\alpha = 4.5 \times 10^{-7}$ m$^2$/s and $\alpha = 4.2 \times 10^{-7}$ m$^2$/s, respectively. In his work the thermal diffusivity decreased with increasing temperature.

The most recently recorded methane hydrate thermal conductivity measurements were done by Waite et al at USGS [10]. They used a needle probe method as well, where the sample was formed and compacted around the needle probe in the thermal conductivity measurement chamber. They report values for ice Ih ($k = 2.12 \pm 0.015$ W/mK at $T = -10^\circ C$), pure methane hydrate ($k = 0.460 \pm 0.003$ W/mK at $T = -10^\circ C$ and $k = 0.454 \pm 8.14 \times 10^{-4}$ $T$ for a temperature range of $-30^\circ C$ to $-5^\circ C$), and a uniform mixture of 32 vol. % methane hydrate with 68 vol. % quartz sand ($k = 1.15 \pm 0.015$ W/mK at $-15^\circ C$). Before taking thermal conductivity measurements, the sample was compacted to reduce porosity in the sample until the thermal conductivity values ceased to change with increasing pressure. The hydrate samples were checked to ensure that all water in the sample was converted to hydrate by lowering the temperature to $-10^\circ C$ and checking for ice formation from any un-reacted water.

As evidenced above few thermal property measurements have been made on methane hydrates and the most recently reported thermal property values are in the developmental stages with little to no sample characterization reported. The values reported by Cook and Leaist were of samples made external to the actual thermal conductivity measuring device. Asher does not report values of pure methane hydrate and the samples he used are not well characterized in his thesis. deMartin has made significant progress with thermal property measurements and reports the only other known values of the thermal diffusivity of methane hydrates. USGS comes closest to reporting well characterized samples as well as measurements of consolidated methane hydrate samples. Much remains to be explored in the determination of the thermal properties of methane hydrates. Inherent is the challenge of sample characterization to ensure that the measurement can be correlated to the physical properties and composition of the sample.
2.3 Transient Plane Source (TPS) Technique

A technique has been developed and patented [6] by S. E. Gustafsson to determine the thermal diffusivity and thermal conductivity of a material by simultaneously heating the material with and recording the voltage change over a transient plane source (TPS) element [5]. The transient plane source (TPS) technique, transformed from the transient hot strip method, has been used for determining the thermal conductivity of a variety of materials in the range from 0.02 W/mK to 200 W/mK [16].

The TPS technique, unlike its predecessor, can be used for small sample sizes because its conducting pattern arrangement allows the total electric resistance of the TPS to be much higher than the hot strip [17]. Because the total time of the transient recording is based on the size of the TPS, the measurement time is also reduced.

The TPS element used and described by Gustafsson consisted of a pattern of a thin, electrically conducting material in a symmetric shape [5]. The conducting material is usually one with a well known or easily determined temperature coefficient of resistivity (TCR) that is relatively constant over a wide range of temperatures. The TCR of the conducting material is used to determine the temperature rise in the conducting material due to the electrical current pulse applied to the TPS during the transient heating.

Starting with Carslaw and Jaeger’s [18] point source solution to the thermal conductivity equation a solution can be found to describe the temperature increase in the sample. The temperature increase in an infinite solid due to a quantity of heat, \( Q \rho c \), instantaneously liberated at time, \( t' \) and at a point \((x', y', z')\), for an anisotropic material with principal thermal conductivities, \( k_1, k_2, k_3 \), along the directions of the x-, y-, z-axis, is given by:

\[
\Delta T(x, y, z, t) = \frac{Q(\rho C_p)^{3/2}}{8(\pi k_1 k_2 k_3)^{1/2} (t-t')^{3/2}} \exp \left\{ -\frac{\rho C_p}{4(t-t')} \left[ \frac{(x-x')^2}{k_1} + \frac{(y-y')^2}{k_2} + \frac{(z-z')^2}{k_3} \right] \right\} \tag{2-1}
\]

where \( \rho C_p \) is the specific heat capacity per unit volume. Accounting for the above assumptions, equation (2-1) satisfies the differential equation of conduction of heat.
Assuming that the conducting pattern is located in the $yz$ plane of a coordinate system and inside an infinite solid, the temperature increase, at point $y$, $z$ and time, $t$, due to an output power, $Q$, per unit area is [5 citing 18]:

$$
\Delta T(y, z, t) = \frac{1}{8\pi^{3/2}\rho C_p} \int_{0}^{t} \frac{1}{[\alpha(t-t')^{1/2}]^3} dt' \int_{A} Q(y', z', t') \exp \left\{ -\frac{[y-y']^2 + [z-z']^2}{4\alpha(t-t')} \right\} dy' dz', \quad (2-2)
$$

where $\alpha$ is the thermal diffusivity defined by:

$$
\alpha = \frac{k}{\rho C_p}, \quad (2-3)
$$

and $A$ is the total area of the conducting pattern.

To simplify the equation and for further convenience, the equation for the temperature increase is expressed as a function of $\tau$, defined as [5]:

$$
\tau = \left[ \frac{t}{\theta} \right]^\frac{1}{2}, \quad \theta = \frac{a^2}{\alpha}. \quad (2-4)
$$

$2a$ is the width of the conducting pattern. $\theta$ is the characteristic time of the measurement. $\Delta T(y, z, \tau)$ in terms of $\tau$, which results from a change of variable in equation (2-2), is:

$$
\Delta T(y, z, \tau) = \frac{1}{4\pi^{3/2}ak} \int_{0}^{\tau} \frac{1}{\sigma^2} d\sigma \int_{A} Q(y', z', t - \frac{\sigma^2 a^2}{\alpha}) \exp \left\{ -\frac{(y-y')^2 + (z-z')^2}{4\sigma^2 a^2} \right\} dy' dz'. \quad (2-5)
$$

To get the temperature rise in terms of $\tau$, $\alpha(t-t')$ was replaced by $\sigma^2 a^2$ to perform the integration [19].
The pattern of the TPS can be considered a series of “individual” strips. Defining the strip width as, $2D_p$, where $p$ represents a point on curve $P$, made up of points located at equal distances from the edges of the individual strips, the resistance increase due to a short element of an individual strip can be given as [5]:

$$dR = \rho_0 \left(1 + (TCR) \overline{\Delta T_p(\tau)}\right) \frac{1}{2D_p 2\nu} dr,$$

(2-6)

where $dr$ is defined as the displacement in the direction of the tangent to curve $P$, $\rho_0$ is the resistivity of the pattern material, and $2\nu$ is the constant thickness of the conducting pattern. The average temperature rise at each point, $p$, can then be expressed as [5]:

$$\overline{\Delta T_p(\tau)} = \frac{1}{2D_p} \int_{-D_p}^{D_p} \Delta T(y, z, \tau) dn,$$

(2-7)

Integration is performed for each point, $p$, in a direction $dn$ perpendicular to the tangent of the curve $P$ along the entire strip. $\Delta T(y, z, \tau)$ is given by equation (2-5).

The average temperature is related to the resistance through the following equation [5]:

$$R(t) = R_0 \left[1 + (TCR) \overline{\Delta T(\tau)}\right],$$

(2-8)

where $R_0$ is the initial resistance of the TPS before the power is supplied. The resistance across the TPS throughout the transient heating, $R(t)$, is calculated from voltage data collected during the transient heating. The temperature coefficient of resistivity ($TCR$) is known for the material of the conducting pattern, which allows the temperature rise to be calculated. The TCR is calculated by [20]:

$$TCR = \frac{1}{R(T)} \frac{\partial R(T)}{\partial T}.$$

(2-9)
The conducting pattern can be in any shape but generally in basic shapes for the ease of deriving equations to describe its temperature rise. Gustafsson presents equations for a “hot disk” configuration and a “hot square” configuration [5]. The conducting pattern can be produced by vapor deposition [5] and for the hot disk and hot square it is deposited in a “bifilar spiral” pattern resembling a disk or a serpentine pattern in the shape of a square, respectively.

Starting from equation (2-7) the average temperature increase can be given for the hot square pattern. Assuming that neither the square source nor the leads carrying the current would influence the temperature increase either as heat sources or heat sinks, and as a result, the output of power per unit area, $Q$ [W/m$^2$], is considered constant after time, $t_0$, the temperature increase in any point $(y, z)$ in the plane $x = 0$ can be given as [5]:

$$\Delta T(\tau) = \frac{P_0}{4\pi^{1/2}a_k} H(\tau),$$  \hspace{1cm} (2-10)

$$H(\tau) = \int_0^\tau \left\{ \text{erf} \left( \frac{1}{\nu} \sqrt{\frac{\nu}{\pi}} \left[ 1 - \exp \left( -\frac{1}{\nu^2} \right) \right] \right) \right\}^2 d\nu,$$  \hspace{1cm} (2-11)

$$\text{erf}x = \frac{2}{\pi^{1/2}} \int_0^x \exp(-\nu^2) d\nu.$$

$P_0$ is the constant output of power in the TPS element and assumed to be transferred to and consumed for heating the sample. The function $H(\tau)$ gives the temperature increase as a function of time [21] and can be approximated analytically or evaluated numerically. For $\tau$ values of about less than 0.3, equation (2-11) can be solved analytically [5].

Most commercially available TPS elements have thin insulating layers surrounding the conducting pattern for a sturdy sensing element that also allows measurements on electrically conducting materials. The equations given above for the temperature increase do not take into account these thin insulating layers above and below the conducting pattern and between the “strips” of the pattern. To include the effects of these layers, a good approximation can be established. By employing a numerical solution, integrals describing the theoretical expression can be solved [5].
Assuming that the strips are equally spaced and of equal width, the following can be defined: \(2n\) = number of strips, \(2d\) = width of each strip, \(2a\) = length of each strip, and \(2\delta\) = the distance between two strips. So that [5]:

\[
a = 2n(d + \delta) - \delta \quad (2-13)
\]

In the same manner as before, an expression for the temperature increase at point \((y, z)\) in the plane \(x = 0\) at time \(t\) due to one single strip, with number \(i\), is:

\[
\Delta T_i(y, z, t) = \frac{Q}{8\pi 1/2 C_p} \int_0^{t} \frac{dt'}{(\alpha(t-t')^{3/2}(2i-1)(d+\delta)-d} \exp\left(\frac{-(y-y')^2}{4\alpha(t-t')}\right) dy'
\]

\[
\times \int_{-a}^a \exp\left(\frac{-(z-z')^2}{4\alpha(t-t')}\right) dz'
\]

(2-14)

For the temperature increase, caused by all \(2n\) strips at the same point \((y, z)\) the expression is given as [5]:

\[
\Delta T_{2n}(y, z, t) = \sum_{i=1}^{n} \Delta T_i(y, z, t), \quad (2-15)
\]

where \(\Delta T_i(y, z, t)\) is given above.

The average temperature of one whole strip (with number \(i\)) is given as [5]:

\[
\overline{T_i(t)} = \frac{1}{4ad} \int_{(2i-1)(d+\delta)-d}^{(2i)(d+\delta)+d} dy \int_{-a}^a \Delta T_{2n}(y, z, t) dz . \quad (2-16)
\]

The average temperature, in terms of \(\tau\), taken over all the strips, becomes [5]:

16
\[ \Delta T(\tau) = \frac{1}{2n} \sum_{i=1-n}^{n} \Delta T_i(\tau), \] 

(2-17)

which can be rewritten in a useful form as [5]:

\[ \Delta T(\tau) = \frac{P_0}{4\pi^{1/2}ak} H_s(\tau). \] 

(2-18)

\( H_s(\tau) \) is a function of time only, but incorporates parameters of the source size and shape \((n, d, \text{and } \delta)\). After numerically evaluating the above equations, \( H_s(\tau) \) can be determined for different values of \( \tau \).

In the same manner, equations can be derived to describe the temperature rise in the hot disk. Although an exact solution is possible, Gustafsson gives two approximate solutions that he used in his work [5]. By assuming that the disk is made up of \( m \) number of concentric ring sources, the average temperature rise can be found from Carslaw and Jaeger’s ring source solution [18]. The average temperature rise can be approximated as:

\[ \Delta T(\tau) = \frac{P_0D_s(\tau)}{\pi^{3/2}ak}, \] 

(2-19)

where

\[ D_s(\tau) = \frac{1}{[m(m+1)]^{1/2}} \int_{0}^{\pi} \frac{1}{\sigma^2} \sum_{i=1}^{m} \sum_{j=1}^{m} i \exp \left( \frac{-i^2 + j^2}{4m^2 \sigma^2} \right) I_0 \left( \frac{li}{2m^2 \sigma^2} \right) d\sigma. \] 

(2-20)

\( P_0 \) is the total output of power, \( a \) is the radius of the disk, and \( I_0 \) is the modified Bessel function.

The second approximation assumes that the space between the concentric rings is infinitely small. The average temperature rise in this approximation is given as:

\[ \Delta T(\tau) = \frac{P_0D(\tau)}{\pi^{3/2}ak}, \] 

(2-21)
where

\[
D(\tau) = -\frac{1}{\sigma^2} \int_{0}^{1} d\sigma \int_{0}^{1} u \exp\left(-\frac{\left(u^2 + \nu^2\right)}{4\sigma^2}\right) I_0\left(\frac{u\nu}{2\sigma^2}\right) du d\nu .
\]

(2-22)

Through a detailed study, Gustafsson determined that the agreement between the two approximations was nearly perfect when a time correction was applied for \( \tau \) values larger than 0.1 and for more than 10 concentric rings \( (m \text{ greater than } 10) \) [5]. A correlation between the approximations and the ideal solution can also be made using a time correction. This close correlation between the approximate solutions and exact solution exists because the disturbances due to the space between the strips or rings in the conducting pattern are relaxing and disappearing very quickly at the beginning of the transient event. With a time correction, either of the approximations can be used to evaluate the thermal properties and the results will be close to those found using an exact solution [5].

As with the solution for the disk source, equation (2-11) can be used in conjunction with a time correction instead of solving for \( H_s(\tau) \). While equation (2-11) is for an infinite number of strips, it gives a good approximation to the actual solution for the square source.

For TPS elements covered with insulating layers, the thermal contact between the heating material and the sample is reduced. The result is seen at the beginning of the transient recording where the power \( Q(t) \) delivered to the sample is not constant. When a constant current is passed through the TPS element, the voltage drop across a Wheatstone bridge can be measured to determine the resistance variation across the element and therefore the temperature rise of the TPS element. The exact point where the power passing through the insulating layers is constant and is emitted to the sample is unknown and determination of which is influenced by a few factors. Non-ideal electrical components in the circuit will influence the start of the transient heating. The thermal resistance between the TPS element and the sample cause time delays between the power release in the element and delivery of the power to the sample [22].

Gustafsson et al derives a model to determine the actual start of the transient event and finds a time correction, \( t_c \). In his work he used a strip rather than a square or disk shaped source, but assumes that the strip is ideal with a variable output of power, all of which is delivered to the sample [22]. This means that any temperature difference between the two surfaces of the
insulating layer has become constant, though the mean temperature of the insulating layer itself will continue to increase throughout the transient heating. The thickness of the insulating layer should be much less than the width of the strip. Any disturbances at the beginning are assumed to dissipate quickly so that the power will become a constant value, $P_0$, after some time, $t_0$, after which the heat capacity of the insulating layer can be neglected. The time correction, $t_c$, and time zero, $t_0$, should be much less than the characteristic time, $\theta$, so that enough data exists for evaluation. Gustafsson et al uses a second order polynomial in $(t - t_c)^{1/2}$ to which the data is fit. In an iterative procedure, $t_c$ is determined by changing its value to maximize the fit of the data to the following polynomial [22]:

$$R = R_0 + A(t - t_c)^{1/2} + B(t - t_c).$$  \hspace{1cm} (2-23)

$A$ and $B$ are empirical constants, particular to and determined for each thermal property measurement. In Gustafsson’s work, $t_0$, was estimated as larger than $2t_c$.

All of the equations above assume that the material of interest surrounding the source is infinite. To make this assumption, it is sufficient if the material appears infinite to the source, so that the sample boundaries do not influence the thermal behavior of the sample. The probing depth, $\Delta_p$, is the region of the sample heated during the transient recording. The distance from the source to any point on the outer surface of the sample must be greater than [5, 17, 22]:

$$\Delta_p = \beta(\alpha t_{\text{max}})^{1/2},$$ \hspace{1cm} (2-24)

$t_{\text{max}}$ is the total time of the transient recording and must be at least 1.5 $\theta$, $\beta$ is a constant of the order of unity, which is chosen for the desired experimental accuracy [5]. Gustafsson defines this value as $\beta = 1.42$ [23]. For very precise work, $\beta$ can be chosen greater [17].
3 EXPERIMENTAL

3.1 Thermal Property Measurements with the TPS Technique

National Instrument’s hardware and LabVIEW software are used to control the thermal property measurements (see Appendix for component diagrams). An electromechanical relay switch (SCXI 1161) is used to apply the voltage from a dummy load to the Wheatstone bridge containing the TPS sensor (shown in Figure 3-1). A SCXI 1320 temperature sensor terminal block connects the signals from the bridge circuit to a SCXI 1120 isolation amplifier. LabVIEW virtual instruments (VI’s) acquire the data. The voltage difference across the bridge is measured with time using LabVIEW to collect the data. The voltage difference across the bridge will increase as the sensor is being heated. A plot of the voltage difference, $\Delta V$, versus time will show either an initial steep rise or fall, depending on the conditions of the bridge prior to measurement.

![Figure 3-1: Wheatstone bridge circuit, containing the TPS sensor.](image-url)
The actual bridge is located in the laboratory while the sensor is generally at a different initial temperature inside the environmental chamber; this initial temperature difference affects the initial state of the bridge. When the temperature of the TPS is lower than the rest of the bridge, a plot of $\Delta V$ versus time will show an initial drop, followed by a rise in $\Delta V$ as the sensor is being heated. Data points at the beginning, representative of systematic delays, are not used in the analysis. Figure 3-1 shows a typical data set where the voltage difference rises first, indicating that the sensor was initially at the same or greater temperature than the rest of the bridge. The shape of the curve gives useful information about the thermal nature of the sample and only this portion of the data is actually used in the analysis.

The voltage data, $\Delta V$ versus time, is used to calculate the resistance of the sensor during the transient heating through the following equation (derivation in appendix B.1):
\[ R_{\text{sen}} = R_{\text{ref}} \left[ \frac{1}{\frac{1}{2} - \frac{\Delta V}{V_{\text{tot}}}} - 1 \right]. \] (3-1)

\( R_{\text{ref}} \) is a constant at 50 \( \Omega \). \( \Delta V \) is the voltage difference across the bridge measured with time, and \( V_{\text{tot}} \) is the total voltage applied to the bridge from a power supply, which is also recorded during the measurement.

The power output to the sensor is calculated using the following equation:

\[ P = \frac{V_{\text{tot}}^2 R_{\text{sen}}}{\left[ R_{\text{sen}} + R_{\text{ref}} \right]^2}. \] (3-2)

When voltage is applied to the TPS element, the first points seen in the voltage rise are representative of the heat flow through the insulating layers of the TPS element. The exact time of when the heat flow actually penetrates to the test sample is unknown. Due to the time it takes for the heat flow to penetrate thermal barriers between the heated portion of the TPS element and the test sample, a time correction, \( t_c \), is applied to account for this delay [20].

Figure 3-3: Resistance versus time data fit to a second order polynomial in the range of data \( t = 2 t_c \) to \( \frac{1}{2} \theta \).
The data used to find the time correction, \( t_c \), is defined by the range of 2 \( t_c \) to \( \frac{1}{2} \theta \). \( \theta \) is a function of the thermal diffusivity, \( \alpha \) (equation (2-4)). Since \( \alpha \) is also a property to be determined, an initial guess of \( \alpha \) must be made in order to determine \( t_c \). \( t_c \) is changed to fit the resistance data (\( R_{sen} \)) versus time to a second order polynomial in \((t - t_c)^{1/2}\) given by equation (2-23) in the range of data mentioned above (see Figure 3-3).

The time correction, \( t_c \), is used to adjust the time data. The intercept, \( R_0 \), obtained from fitting the data to equation (2-23) is used to calculate the temperature rise of the TPS during the transient heating using equation (2-8).

The manufacturer of the TPS, Vishay Micro-Measurements, supplies equations to describe the behavior of the sensor and are given by following polynomial equations:

\[
T(R_{sen}) = A' + B'R_{sen} + C'R_{sen}^2 + D'R_{sen}^3 + E'R_{sen}^4 + F'R_{sen}^5 + G'R_{sen}^6, \quad (3-3)
\]

\[
R(T) = A + BT + CT^2 + DT^3 + ET^4 + FT^5 + GT^6, \quad (3-4)
\]

where the constants were determined for a temperature range of -195 °C to +260 °C.

The temperature coefficient of resistivity (TCR) is determined from equation (2-9), using the empirical equations above and used as:

\[
TCR = \frac{B + 2CT + 3DT^2 + 4ET^3 + 5FT^4 + 6GT^5}{A + BT + CT^2 + DT^3 + ET^4 + FT^5 + GT^6}. \quad (3-5)
\]

The temperature rise in the TPS can then be calculated by rearranging equation (2-8) as:

\[
\Delta T(\tau) = \frac{R_{sen} - R_0}{(TCR)R_0}, \quad (3-6)
\]

using the TCR calculated with equation (3-5) and the \( R_0 \) value obtained during the determination of \( t_c \).

As mentioned in section 2.3, an approximation of the function \( H_\alpha(\tau) \) can be made using a time correction and the function \( H(\tau) \) as was done in analyses utilizing the hot disk configuration.
of the TPS. An attempt was made at solving the equations needed to determine $H_s(\tau)$ but, even with the use of software designed to do numerical integration, the solution was difficult to determine. Because an approximate solution with a correction was seen to give good results [5], this was used in determining the thermal properties reported herein. In later work, if determined necessary, the “more” exact solution may be used. $H_s(\tau)$ takes into account the insulating created by the Kapton between the strips while $H(\tau)$ assumes that the conducting pattern is a solid square of nickel. Even $H_s(\tau)$ is partly an approximation (albeit a better one) since it treats the conducting pattern as strips.

An empirical formula was determined for values of $\tau$ ranging from 0 to 5. Equation (2-11) was solved numerically using Mathematica® (see appendix B.1.2 for the values) for the aforementioned values of $\tau$ and the constants of the polynomial were determined using Microsoft Excel. $H(\tau)$ values are calculated for the analysis with the following equation using $\tau$ values calculated with the corrected time:

$$H(\tau) = C_1 + C_2\tau^{1/2} + C_3\tau + C_4\tau^{3/2} + C_5\tau^2 + C_6\tau^3.$$  \hspace{1cm} (3-7)

![Figure 3-4: $\Delta T$ versus $H(\tau)$ data fit to a straight line through the origin.](image)
Through equation (2-18), a linear relationship exists between $H(\tau)$ and $\Delta T$. In an iterative process, the thermal diffusivity, $\alpha$, is changed to optimize the fit of $\Delta T$ versus $H(\tau)$ to a straight line through the origin using the numerical Golden Section method. $\alpha$ is chosen based on the value giving the lowest mean squared error (mse) of the data fit to the line. Figure 3-4 shows the best fit of the $\Delta T$ versus $H(\tau)$ data through the straight line. The slope of this line is used to calculate the thermal conductivity by rearranging equation (2-18) as:

$$k = \frac{P_{\text{ave}} s}{4\pi^{1/2} a_{1/2} (\text{slope})}.$$ \hspace{1cm} (3-8)

$P_{\text{ave}}$ is the average of the power calculated with equation (3-2). The half width of the sensor, $a$, is adjusted by a correction factor to account for the assumptions made in deriving the model used for analysis. The correction is applied as follows:

$$a_{1/2} = \frac{a}{\sqrt{\text{c.f.}}}.$$ \hspace{1cm} (3-9)

$2a$ is the nominal size of the conducting pattern of the TPS. A correction factor ($\text{c.f.}$) of 0.75 was used in the analysis, giving values for glycerol, water, and ice closest to literature values. The value represented by $s$ takes into account the fact that the TPS is not attached to a perfect insulator. Realistically, some of the power supplied to the TPS dissipates into the PVC backing. $s$ is between 1 and 2 depending on whether the TPS is surrounded on both sides by the sample of interest or if the sample contacts only one side of the TPS with a perfect insulator on the other, respectively. The $s$-value is determined by the following equation:

$$s = \frac{2 * k}{(k + k_{\text{PVC}})}.$$ \hspace{1cm} (3-10)

Since the thermal conductivity of the sample is used to determine $s$, a new value of thermal conductivity is calculated using the $s$-value, which is repeated until the old and new value of $k$ agree to within 0.000001 W/mK.
The information rich region of the data is used to determine the thermal diffusivity and here defined by where \( t = \frac{1}{2} \theta \) to \( 1\frac{1}{2} \theta \). Beginning data is eliminated because the temperature drop across the insulating layer is not yet constant, which is an assumption of the analysis developed above. After a certain time, the temperature increase of the TPS becomes nearly constant and no longer provides insight into the thermal behavior of the sample material and therefore data after \( 1\frac{1}{2} \theta \) is not used in the analysis.

Because the \( \alpha \)-value used to determine \( t_c \) was initially an approximation, the newly determined \( \alpha \)-value is used to determine \( t_c \) again as well as another \( \alpha \) - value. This process is repeated until the old and new values of \( \alpha \) agree to within \( 1 \times 10^{-10} \) m\(^2\)/s.

### 3.2 Experimental Improvements

Past measurement and data collection utilized a Keithley 2000 multimeter, a GPIB board to couple the Keithley to a laboratory computer, and LabVIEW for data acquisition, signal conditioning and file conversion. The TPS was part of the same Wheatstone bridge shown above but was connected to a manual switch. To take thermal property measurements during hydrate formation and dissociation, the experiments needed to be strategically planned so that someone was available to take the measurements during pertinent times of the experiment, which can span a week or more. This process was not only inconvenient but it limited the information that was attainable from the experiments to times when someone was available. Data collection was also limited to about 100 samples per second with the Keithley multimeter. To determine the thermal properties from the data collected, Microsoft Excel spreadsheets were used to process the data. Some portions of the data processing were automated with macros and Visual Basic but a majority of the data handling required user interaction. This was tedious and required a lot of time to obtain results. The Excel files, containing the relevant experimental data and calculated thermal properties were large and required a lot of storage space. While using Excel for data processing was somewhat sufficient for the size of the data files collected using the Keithley and GPIB board, the new capability to obtain 1000 samples or more per second using National Instruments components, made the files too large for Excel to handle. Recognizing these inadequacies, the system was redesigned and the data analysis program was rewritten in LabVIEW.
The current experimental system has been automated through National Instruments components. The data acquisition and data analysis described above are both accomplished using National Instrument’s software, LabVIEW. The modifications and improvements to the system have allowed measurement initiation and data collection to be automated. The number of measurements desired and the time between the measurements can be specified.

Only after the thermal properties are known, can changes and adjustments be made to the measurement such as increasing or decreasing the voltage supplied to the TPS, the frequency of the measurements, or the maximum required transient heating time. A program to process data immediately was, therefore, pertinent to efficient experimenting. The capabilities of LabVIEW will allow results from the measurements to be obtained right away and be used to adjust parameters to improve the next measurement.

3.3 Experimental Setup

3.3.1 High-Pressure Variable-Volume Viewcell (HVVC)

The HVVC, used for hydrate formation, has been described elsewhere [24] and used to form methane hydrates for thermal property measurements [25]. The HVVC is rated at 69 MPa (10,000 psig) at 25.0 °C, and has a working volume of 7 cm$^3$ to 38 cm$^3$. The internal piston can be used to change the pressure or volume inside the HVVC. The stainless-steel bottom, used in the thermal property measurement experiments, can be replaced with a glass or sapphire bottom to allow visual observation of the cell contents during an experiment. In this case, however, thermal property measurements cannot be made.

When performing thermal conductivity measurements in the HVVC, a small holding container with a transient plane source (TPS) element at the bottom is used to retain the sample around the TPS. Figure 3-5 shows the HVVC with the holding container. Some problems in the previous design included loss of sample, it was not detachable from the HVVC stainless steel base, and sample recovery was not possible.

During experiments, the pressure and temperature of the gas phase in the HVVC are monitored with a digital Heise gauge and platinum RTD probe, respectively.
3.3.2 Transient Plane Source (TPS) Cup Assembly

Thermal property measurements are made possible with a transient plane source (TPS) element attached to polyvinyl chloride (PVC) for support. The TPS element used in the experiments described is a commercially available precision strain gauge from Vishay Micro-Measurements Group, Inc. The TPS element is located at the bottom of a cup-like container (hereby referred to as “cup”) so that the sample to be measured is in good contact with the TPS element.
The TPS (Figure 3-6), approximately 3 mm², consists of a thin foil heater, made by depositing a narrow strip of high-purity nickel in a serpentine square pattern on a Kapton (polyimide) substrate. The exposed heater surface is coated with a thin film (0.03 mm) of Kapton, resulting in a robust, flexible heating element, which can be used on electrically conducting samples. The overall thickness of the gauge is less than 50 µm, with a working temperature range of about 78 K to 505 K. The TPS is part of a Wheatstone bridge whereby measuring the voltage difference across the bridge during a transient heating allows the temperature rise in the heating element to be calculated. The temperature rise history of the TPS, along with the temperature coefficient of resistivity (TCR) of the nickel, allows determination of the thermal properties of the sample in contact with the TPS.

In some preliminary experiments problems in the experimental setup were addressed with the redesigned cup assembly. During methane hydrate formation and dissociation experiments where thermal property measurements were taken, the old cup that was used did not contain the water when hydrates decomposed. After subsequent formation and dissociation cycles, the thermal conductivity values became lower and lower as sample was lost from the cup. Upon disassembly, it was seen that all of the sample was outside the cup. The lid was not secure enough to contain the sample. Power was supplied to the TPS via wires that ran through fittings.
and the viewcell bottom. Though the current experimental setup utilizes this same method of wiring, the old cup was directly connected to the wires. The cup was therefore attached to the viewcell bottom via the wires but was not secured to the viewcell bottom otherwise. Not only did this require cutting wires and soldering to replace the cup but the cup could easily tip while inserting and removing it from the viewcell. Accuracy was limited in weighing the sample because the viewcell bottom, fittings, and cup were all one entity. The sample could not be removed easily from the cup, especially without disturbing the sample and verification of the sample / TPS element contact was impossible. With these problems and inadequacies, the TPS / cup assembly was redesigned.

The redesigned cup allows for sample recovery when additional analysis is required or desired on the sample. It successfully contains the sample as well, which was one objective in its redesign. The cup bottom contains the TPS element and is removable from the cup sleeve for easy sample recovery and verification of the TPS contact with the sample. The cup lid can be pushed with the piston inside the HVVC to compact the hydrate sample, however this was not done in the work reported here. The cup is slipped inside the HVVC for experiments to allow thermal property measurements during hydrate formation and dissociation cycles.
Figure 3-7: (a.) Environmental chamber and computer system, (b.) HVVC mounted inside chamber.
3.3.3 Environmental Chamber

A Tenney Environmental T20S chamber houses the HVVC during experiments (Figure 3-7). With a 20 ft³, explosion-resistant interior, methane hydrate formation experiments can be carried out. The environmental chamber provides temperature control to within 0.1 K and can be programmed for temperature ramp cycles and soak intervals. ISCO syringe pumps are used to control the piston in the HVVC used for pressurizing the viewcell by adding or removing oil from behind the piston.

3.4 Experiments

For the experiments described below, water, purified by reverse osmosis and ion exchange to 18 MΩ-cm and methane, Matheson research grade (99.999%), were used to form methane hydrate unless otherwise noted.

In experiments involving thermal property measurements, the cup assembly with the TPS element was filled with water and placed inside the HVVC. The HVVC was pressurized using methane and, in some experiments, the piston. The temperature was cycled down and up at a rate of 1 K per hour to form and dissociate hydrates. During the temperature ramps, thermal property measurements were taken.

To obtain thermal property data, a small voltage (~ 1 V) was applied to the TPS element to raise the temperature of the sample about but not more than 1 K so that the sample was unaffected. During the transient heating, the voltage difference across the Wheatstone bridge was recorded at a rate of 1000 samples per second.

The pressure and temperature were recorded at a rate of 1 sample per minute. A plot of the pressure versus the temperature shows hydrate formation with a drop in the pressure and hydrate dissociation indicated by a sudden increase in the pressure. In all hydrate formation experiments, the hydrate dissociation correlated well with dissociation equilibrium data [1].

Initial experiments were done to make visual observations of the hydrate formation and dissociation since this is impossible when taking thermal property measurements. By better understanding the physical phenomenon that was occurring inside the HVVC and cup, experimental improvements could be made. In the first experiment described pure methane hydrates were formed and dissociated. A significant finding from this experiment was that the
cup needed to be redesigned since most of the sample was lost during the experiment. In the next experiment, methane hydrates were formed from a sand and water mixture. This was insightful to see how hydrate formed and dissociated in the pores created by the sand. The sample was not well contained in this experiment either and, with the observations made, the new cup was designed so that thermal property measurements could be made on hydrate and sediment samples as well.

After redesign and automation of the experimental setup and redesign of the cup, measurements were made on water, ice, and glycerol which all have well known thermal properties. Water and ice are also present during the formation and dissociation of methane hydrate so it was important to know these values so that when hydrate formed it could be distinguished. Glycerol is a good standard because it does not convect at room temperature and even at elevated temperatures. The problem encountered with glycerol, however, is that it hydrates quickly, giving falsely high thermal conductivity values for glycerol. Precautions were taken to ensure that the measurements of glycerol were taken on anhydrous and pure glycerol samples.

Two successive experiments were done to take thermal property measurements of methane hydrate using the new TPS cup assembly. In the first experiment methane hydrate was formed from water and methane, frost was used instead of water in the second experiment. In both experiments, the methane uptake was small as indicated by almost no change in pressure. Throughout both experiments the thermal conductivity values were either that of water or ice. The experiment starting first with a porous mixture of frost was done to reduce suspected limitations due to diffusion. In this experiment it is possible, however, that most of the frost sample melted even before pressurization with methane, thereby not enhancing diffusion.

The thermal property values are most influenced by the material closest to the TPS element and the thermal conductivity values obtained are indicative that hydrate did not form far enough down in the sample to influence the thermal conductivity. Since the new TPS cup assembly was successful in containing the sample, the surface area of exposed water or ice that could react with the methane was reduced and the depth of the sample was also greater.

It was suspected that hydrate was forming in the vent hole of the cup and preventing or reducing methane exposure to the water inside the cup. To rule out any limitations caused by the cup lid, it was left off during one experiment. It was only after successive cycles without
dissociating the hydrate, that significant hydrate formation was observed. The hydrate was not
dissociated until the last cycle upon which some of the sample was lost from the cup since it had
no lid. In this experiment the thermal properties of methane hydrates were successfully
measured.

The final experiment described below was successful in converting all of the water to
hydrate and thermal property measurements were taken of this pure methane hydrate sample.
The sample was recovered and Raman spectroscopy was performed on the sample to determine
the composition of the portion of the sample in contact with the TPS element.

3.4.1 Experiment T20-006: Methane Hydrate Formation from Water and Methane With
Visual Observation of Hydrate Formation and Dissociation

Because experiments involving thermal property measurements need to use the stainless
steel bottom of the HVVC instead of the glass bottom, the intent of this experiment was to make
visual observations of hydrate formation from methane and water and dissociation of the
methane hydrate.
Starting with 0.2546 g of water, placed in a cup made of CPVC tubing with a clear, plexiglass bottom and a PVC lid, hydrates were observed to form and dissociate both visually and from the pressure / temperature data. The cup rested on the glass bottom of the HVVC and activity inside the HVVC was monitored through the viewport by means of a remote video camera and borescope. The HVVC was pressurized with the piston and methane to about 13 MPa. Hydrate did not form in the cell until ice was observed visually, at a set point of 268 K (-5.0 °C). With subsequent temperature ramps, hydrate formation and dissociation was observed from the pressure / temperature data and visually through the HVVC bottom. By cycling between 278 K (5 °C) and 291 K (18 °C), cycles 5 through 8 show a typical pressure versus temperature trace of hydrate formation and dissociation. The hydrate dissociation equilibrium point of all four cycles corresponded well with literature data from Sloan [1]. Upon disassembly of the HVVC, no water could be seen in the cup, though water was on the viewcell bottom and

Figure 3-8: Experiment T20-006, A typical pressure versus temperature trace of hydrate formation and dissociation.
the bottom o-ring. Water loss was attributed to degassing, hydrate dissociation, and a poorly secured lid. Lack of water containment from this experiment prompted the redesign of the cup.

In Figure 3-8, the numbers correspond to the cycle which is herein defined by lowering the temperature and raising the temperature with the intent to form and dissociate hydrate, respectively. The pressure versus temperature profile is typical for hydrate formation and dissociation [1]. The dissociation of methane hydrates will follow the same path with subsequent cycles but, as seen in this experiment, the formation equilibrium varies.

This experiment was significant in making improvements to the experimental system, especially the cup which contains the sample. Because activity inside the cup was monitored during the experiment, the cause of sample loss from the cup was determined. Some water was lost from the cup during evacuation of the HVVC to remove air before the methane was introduced. It was also observed that the release of methane during hydrate dissociation caused sample loss from the cup. The cup lid needed to be redesigned to contain the sample but at the same time allow methane to contact the water inside the cup.

3.4.2 Experiment T20-009: Methane Hydrate Formation from Water Saturated Sand and Methane

Since observations of the HVVC contents cannot be made during experiments involving thermal property measurements, this experiment was performed to observe the formation and dissociation of methane hydrates in sediments, the first experiment of this work involving hydrate formation in sediments.

Sand from Lawrence Livermore National Labs was used to make a sand and water mixture. The density of the sand \( \rho_{\text{sand}} \) was determined to be \( 2.86 \pm 0.14 \text{ g/ml} \). The apparent density \( \rho_{\text{app}} \) of the sand was determined to be \( 1.7137 \text{ g/ml} \). The void fraction \( \Sigma \) of the sand was calculated as 0.401 by rearranging the following equation:

\[
\rho_{\text{app}} = \rho_{\text{air}} \Sigma + \rho_{\text{sand}} (1 - \Sigma).
\]

The mass of the water needed to completely saturate the sand was about 7 g. \( (6.9995 \text{ g. as calculated for 30.003 g. of sand}) \). The saturation of the sand was calculated as 99.97 %, though
water continued to evaporate from the mixture while it was outside the HVVC. Before placing the sample inside the HVVC, the mass of the mixture was 5.396 g.

A small piece of CPVC tubing was placed on the glass bottom of the HVVC with no bottom and no lid and filled with the mixture of sand and water as is seen in Figure 3-9. The activity inside the cell could then be observed through the viewport by means of a remote video camera and borescope. Some water migrated toward the bottom and seeped out onto the glass before inserting it into the viewcell.

The cell was pressurized with methane to about 7 MPa (1000 psig) then with the piston to 14.5 MPa (2087 psig).

During the first cycle problems occurred with a component of the National Instruments hardware. A replacement was obtained and used to record the pressure / temperature data. Hydrate dissociation was observed from the pressure versus temperature data.

The second cycle started at 293 K (20.2 °C). The temperature was lowered to a set point of 269 K (-4.0 °C) and soaked for an hour then ramped up to 293 K (20.0 °C). Hydrate formation was observed in the pressure / temperature data and visually through the viewport. The third and

Figure 3-9: Experiment T20-009. Post experiment picture of the CPVC tubing on top of the HVVC glass bottom. The water in the sand has already evaporated.
fourth cycles went from 293 K to 275 K (20.0 °C to 2 °C) then back to 293 K. A fifth cycle was done in the same temperature range to confirm the results of cycles 3 and 4.

Hydrate formation seemed to continue as the temperature was lowered. The presence of the sand seemed to alter consumption of gas by the water. Whereas the absence of sand produces an abrupt drop in pressure, the presence of sand showed a gradual uptake of the methane in most of the cycles (see Figure 3-10).

Upon dissociation, the equilibrium dissociation point for all cycles matched well with literature values [1]. As the temperature was increased to near the dissociation, decreases in the pressure indicated additional hydrate formation.

After taking the sample out of the cell, the sand mixture was highly porous and had been

---

**Figure 3-10**: Experiment T20-009, Formation of methane hydrates in sediments.
pushed out from the bottom and top of the CPVC tubing. This phenomenon probably occurred during hydrate dissociation as the gas was being released from the methane hydrate (see Figure 3-11). The voids extended throughout the sample indicating that hydrate had formed even in the center of the sand sediment.

3.4.3 Experiments T20-010 and T20-011: Thermal Property Measurements of Glycerol

After the last two experiments described, extensive changes were made to the experimental setup. The thermal property measurements were automated as described in section 3.2 and the TPS cup assembly was redesigned. To validate measurements with this new experimental setup, glycerol was used as a standard because of its high viscosity.
Anhydrous, 99.5% GC grade, glycerol containing less than 0.1% water was used to calibrate the TPS element and experimental system. Glycerol was placed in the thermal conductivity measurement cup and inserted into the HVVC with a silica gel drying packet and placed in the environmental chamber so that thermal conductivity measurements could be made at various temperatures. The silica gel packet was used to reduce hydration of the glycerol sample.

The thermal conductivity values of the glycerol were higher than most of the other literature values obtained at room temperature. One difficulty in determining the thermal properties of the sample from the data is determining when the power supplied to the TPS has penetrated to the sample. The range of data used in determining the thermal properties, itself influences the thermal property values obtained. Due to the insulating layers of the TPS element and systematic errors, the transient behavior in the $\Delta V$ versus time data at the very beginning

![Figure 3-12: Experiments T20-010 and T20-011, thermal conductivity of glycerol with literature values.](image-url)
will cause errors in the data analysis. Additionally, after a certain time the voltage difference across the bridge approaches a steady-state value and no longer gives useful information regarding the thermal properties of the sample (refer to section 3.1). This was one problem encountered when analyzing the data and may be the reason why the values vary so much and why the values are higher than expected.

It has not been determined whether the high thermal conductivity values are due to a numerical problem in the data analysis program or due to hydration of the glycerol sample, which would cause an increase in the thermal conductivity of the sample.

Figure 3-12 shows the thermal conductivity values obtained for glycerol from this work and literature values obtained by other investigators. Most of the thermal conductivity values obtained around room temperature are higher that the other reported literature values and in this work, the thermal conductivity was seen to increase with decreasing temperature. This trend with temperature has not been confirmed and could be due to a numerical problem in the data analysis.

3.4.4 Experiment T20-014: Thermal Property Measurements of Water at Various Temperatures

During the formation of methane hydrates, water and ice are also present at times. The thermal properties of liquid and solid water are also well known. This experiment was done to obtain thermal property values of water at various temperatures so that the presence of hydrate could be distinguished from that of the water and ice.

The water described above was boiled under vacuum at room temperature for about 10 minutes to remove most of the gas from the water. All subsequent experiments use this water as well. 7.65 mm (0.3012 inches, 1.563 g) of this water was placed in the cup and the cup was inserted into the HVVC. The HVVC was mounted in the environmental chamber so that thermal property measurements could be taken of the water at various temperatures. Thermal property measurements were taken at set points from 283 K down to 263 K (10 °C, 0 °C, -5 °C, -7 °C, and -10 °C) and given in Table 3-1.
Table 3-1: Measured Thermal Property Data of Water (This Work).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>State</th>
<th>Thermal Conductivity $k$ (W/mK)</th>
<th>Thermal Diffusivity $\alpha \times 10^7$ (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(297 K / 24 °C) 23.91 ± 0.07</td>
<td>Liquid</td>
<td>0.58 ± 0.01</td>
<td>1.98 ± 0.07</td>
</tr>
<tr>
<td>(283 K / 10 °C) 10.64 ± 0.17</td>
<td>Liquid</td>
<td>0.69 ± 0.01</td>
<td>1.74 ± 0.05</td>
</tr>
<tr>
<td>(273 K / 0 °C) 0.46 ± 0.01</td>
<td>Liquid</td>
<td>0.67 ± 0.02</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>(268 K /-5 °C) -4.28 ± 0.04</td>
<td>Liquid / Solid</td>
<td>0.69 ± 0.02</td>
<td>1.54 ± 0.06</td>
</tr>
<tr>
<td>(266 K / -7 °C) -6.29 ± 0.01</td>
<td>Solid</td>
<td>2.75 ± 0.20</td>
<td>4.25 ± 0.85</td>
</tr>
<tr>
<td>(263 K / -10 °C) -9.36 ± 0.03</td>
<td>Solid</td>
<td>3.36 ± 0.24</td>
<td>4.0 ± 0.2</td>
</tr>
</tbody>
</table>

Figure 3-13: Thermal conductivity of water compared with literature values.
At room temperature (23.91 ± 0.07 °C) and atmospheric pressure the thermal conductivity, $k$, of water was determined to be 0.584 ± 0.006 W/mK. The thermal conductivity of water was nearly constant with temperature as shown in Figure 3-13. When ice formed in the cup, the thermal conductivity rose greatly. The thermal conductivity of ice was determined to be 2.75 ± 0.20 W/mK and 3.36 ± 0.24 W/mK at -7 °C and -10 °C, respectively. The thermal conductivity value of ice at -10 °C is over one and a half times higher than other reported values for ice. Because the portion of the sample in contact with the TPS could not be examined during the measurement, the exact reason for this high value cannot be conclusively determined. It has been observed, however, from this work that trapped gasses in the ice cause unusually low thermal conductivity values of ice. The thermal conductivity values indicated whether ice or water was present in the cup since visual confirmation could not be made.

### 3.4.5 Experiment T20-015: Thermal Property Measurements of Hydrates Formed from Water and Methane

With the validated experimental setup, this experiment was performed so that thermal property measurements could be taken on a pure methane hydrate sample using the new TPS cup assembly.

Starting with 1.413 g. (6.92 mm) of water ($k = 0.63$ W/mK), the cell was pressurized with methane to cylinder pressure and then with the piston to about 13 MPa. The temperature was lowered to about 261 K (-12 °C) and raised to about 293 K (20 °C). Hydrate may have formed during this first cycle at around 267 K (-6.2 °C), where a slight drop in pressure occurred (Figure 3-14). Upon heating the sample beyond the dissociation equilibrium point, again, a very slight change (rise) in pressure seemed to indicate hydrate dissociation but so slight that hydrate presence could not be confirmed with the thermal property measurements. The temperature was again lowered to 261 K (-12 °C) and an estimated 7 % of the water was converted to hydrate based on about a 0.23 MPa (23 psi) pressure drop. Upon heating, hydrate dissociation was observed in the pressure / temperature data with a small rise in pressure around 291 K (17.5 °C), corresponding to literature data [1].
The thermal conductivity remained close to that of water (0.605 W/mK at 298 K, CRC Handbook) throughout the experiment, indicating that any hydrate formed in the cup was not near the TPS element. Because of the depth of the water in the cup, and the small surface area exposed to the methane, hydrate formation was limited by diffusion. The presence of some ice was indicated by a thermal conductivity of \( k = 1.46 \text{ W/mK} \) at \( T = 273.7 \text{ K} \) during the temperature increase of cycle 2. This value is low for ice but the measurement was taken above the freezing point. Liquid water may have been present near the TPS element. Thermal conductivity measurements were taken well below the freezing point of water but, as was seen in earlier experiments, it can be difficult to form ice from such pure water and at these temperatures. The thermal conductivity value obtained for ice was taken during the second cycle.

In Figure 3-14 the pressure versus temperature is shown along with the thermal conductivity values obtained during the experiment shown by the larger points as specified by

![Figure 3-14: Experiment T20-015, Cycle 1 down and up, Cycle 2 down](image-url)
the legend. Though it is apparent that any hydrate present in the cup did not form near the sensor, the thermal conductivity values were indicative of the contents of the cell. Note the high thermal conductivity value during the heating of cycle 2, indicating the presence of some ice near the sensor.

3.4.6 Experiment T20-016: Thermal Property Measurements of Hydrates Formed from Frost and Methane

![Diagram](image_url)

**Figure 3-15: Experiment T20-016, Cycles 1 up to 2 down.**

Since little hydrate formation was observed in experiment T20-015, this experiment was performed to enhance hydrate formation by starting with frost instead of water. In experiment T20-015, hydrate formation down to the TPS in the cup was thought to be limited by diffusion of the gas down to the water near the TPS. Hydrates have successfully been formed from granular ice and methane [10].
In this experiment, about 1.09 g. of frost, obtained from a freezer at about 203 K (-70 °C), was used to form methane hydrate. The thermal conductivity of the ice at the start of this experiment was 2.2 W/mK. The cell was pressurized with methane to about 8.8 MPa. After a few temperature ramps between 274 K and 271 K (1.0 °C and -2.0 °C), with no change in the thermal conductivity, the temperature was increased from a set point of 271 K to 282 K (-2.0 °C to 9.0 °C) and held for about 9 hours during which, additional hydrates formed. The temperature was increased further to a set point of 287 K (14.0 °C) and hydrate dissociation was observed in the pressure / temperature data by a slight increase in the pressure, corresponding with literature data [1] of the dissociation equilibrium. The thermal conductivity data indicated hydrate dissociation by a decrease during the dissociation (Figure 3-15).

The thermal conductivity values throughout the experiment were close to water, indicating (again) that the water converted to hydrate was not near the TPS. The decrease in thermal conductivity...
conductivity during hydrate dissociation was probably caused by the release of the gas (observed visually in experiments when the glass HVVC bottom was used) causing mixing in the sample, resulting in heat transport by convection. The gas released from hydrate dissociation may also have come close to the TPS, causing the decrease in the thermal conductivity. The temperature was decreased from a set point of 287 K to 271 K (14.0 °C to -2.0 °C) for cycle 2 down. Hydrate formation could not be detected from the pressure and temperature data and the thermal conductivity values were still near that of water.

The pressure of the system was increased with the piston to about 13.0 MPa from 8.8 MPa (Figure 3-16). The temperature was increased from a set point of 271 K to 287 K (-2.0 °C to 14.0 °C) at this elevated pressure, where it was held for 3 hours. The temperature was then increased to 291 K (18.0 °C). At both times in the experiment when the temperature was held for an extended period, a small amount of hydrate formed. During hydrate dissociation of cycle 2 the thermal conductivity decreased slightly, not nearly as much as the first cycle dissociation though.

Little hydrate formed according to the pressure and temperature data. Any hydrate that formed apparently was not close to the TPS according to the thermal property data, however, the thermal conductivity data did indicate the state of the sample and indicated hydrate dissociation.

3.4.7 Experiment T20-017: Thermal Property Measurements of Hydrates Formed from Water and Methane – The Cup Was Used Without the Cap

Because so little hydrate was observed to have formed in the preceding two experiments, the cap of the cup was left off in this experiment to determine if water was condensing in the vent hole of the cap and / or hydrates were forming in the hole, thus reducing or preventing the transfer of methane into the cup.

1.413 g. of water was used in the cup, corresponding to a depth of 6.86 mm (0.27 in.). The thermal conductivity of water at the start of the experiment was $k = 0.62 \pm 0.02$ W/mK. The cell was purged with methane, pressurized to bottle pressure with methane, then pressurized with the piston to about 13 MPa. The temperature was then lowered to a set point of 261 K (-12 °C) to first form ice. Ice formation was indicated by a rise in pressure as it expanded into a solid. Thermal property measurements were not possible at this temperature, however, because of physical limits set on the bridge. Therefore, ice formation could not be confirmed by the thermal
property data. Additionally, no hydrate was evident from the pressure / temperature data or thermal property measurements. The temperature was increased to a set point of 287 K (14 °C), right before the dissociation equilibrium point. During this heating, a small amount of hydrate formed once the temperature was near the melting point of ice, indicated by a slight drop in pressure starting around 273 K (0 °C). All of the pressure data for all cycles is shown in Figure 3-17 along with the corresponding thermal conductivity values.

For cycle 2, as the temperature was decreased to about 274.5 K (1.4 °C) more hydrate formed. The temperature was then raised to about 287 K (14.0 °C) and, even more hydrate formed just before the dissociation point. The temperature was lowered to 276 K, then increased to dissociate the hydrate for the third and final cycle.

It was seen from this experiment, that by not dissociating the hydrate with each cycle, hydrate formation was promoted with subsequent cooling. As seen in prior experiments, not
much hydrate formed during the first cycle. Subsequent cycles, however, promoted more hydrate formation.

Thermal conductivity values were only taken during the first and third cycles. During the first cycle, hydrate formation was indicated by the pressure / temperature data. The thermal conductivity values obtained, however, were indicative of water and at lower temperatures a combination of water and ice. Hydrate formation would begin at the top of the water (or ice) and be limited by diffusion. It can be assumed from the high thermal conductivity values that the measurements taken during cycle 1 were of water (or ice and water) rather than hydrate.

Thermal property measurements were taken during cycle 3 down and up. The $k$ values of cycle 3 down and up were almost the same. It appears from the pressure / temperature data and the nearly constant thermal conductivity values that all of the water was converted to hydrate. The thermal conductivity of cycle 3 up (before hydrate dissociation) in the temperature range of 276 K to 286 K was $k = 0.26 \pm 0.01 \text{ W/mK}$. A straight line fit through the thermal conductivity values of cycle 3 up can be described by the following equation, where $T$ is in Kelvin:

$$k = 0.0005T + 0.1058$$ (3-12)

During cycle 3 up, the thermal conductivity corresponded with the pressure / temperature data. Before the pressure / temperature data indicated dissociation, the thermal conductivity rose suddenly. The thermal conductivity was 0.262 W/mK then suddenly rose to 0.59 W/mK right before the pressure rose, indicating the start of hydrate dissociation. The higher value of thermal conductivity seems indicative of water which has a higher thermal conductivity than hydrate. During dissociation the thermal conductivity was determined to be 0.267 W/mK and after complete dissociation the thermal conductivity was 0.44 W/mK.

The rise in the thermal conductivity, indicating the start of dissociation, could be from convection occurring due to the release of gas or from water present near the TPS. The thermal conductivity value during dissociation could be low for a number of reasons. During dissociation, methane is being released from the hydrate causing mixing. The thermal property measurements are of the sample surrounding the TPS. Gases near the TPS would cause the thermal conductivity to be low. After dissociation the thermal conductivity was lower than typical values of water.
After taking the cup out of the HVVC, much of the water was found outside the cup. The water most likely came out of the cup during dissociation, which has been observed in other experiments when the cup lid could not retain the sample. Approximately 0.4 g of water remained in the cup corresponding to a depth of about 2.03 mm (0.08 in.) which is about half of the probing depth. Because the water depth in the cup was lower than the probing depth, the thermal conductivity values were influenced by the gas above the sample. The low thermal conductivity values obtained for the water of post dissociation can be attributed to the low depth of the water as well as bubbles observed in the water on the TPS after the experiment.

3.4.8 Experiment T20-018: Thermal Property Measurements of Hydrates Formed from Water and Methane and Analysis with Raman

This experiment was done to verify the thermal property values obtained from the last experiment and also to attempt recovering the sample for further analysis.

0.895 g. of water, a depth of 4.369 mm (0.172 in.), was placed in the cup with the cup lid secured. At room temperature (299.09 K, 25.94 °C) the thermal conductivity of the water under air at atmospheric pressure was $k = 0.53 \text{ W/mK}$. This thermal conductivity value is slightly lower than the literature values. Only one measurement of water at room temperature was taken in this experiment. Additionally, the depth of the water was close to the probing depth for a $\alpha$-value of $3.32 \times 10^{-7} \text{ m/s}^2$ determined at this temperature.

The temperature was lowered to 262.4 K (-10.8 °C, a set point of -12.0 °C) and held at this temperature for about 15 hours. The cell was pressurized with methane to bottle pressure then with the piston to about 12 MPa.
The temperature was then increased at 1 K per hour to about 275.9 K (2.7 °C) and was held at this temperature for about 5 ½ days. At about 272 K (-1 °C), hydrate formation was observed in the pressure / temperature data. More hydrate formation was observed while the temperature was held at 275.9 K (2.7 °C). The thermal conductivity data corresponded with the trend in the pressure / temperature data. As the pressure continued to drop at almost constant temperature, indicating hydrate formation, the thermal conductivity became lower with time as well. When the pressure ceased to fall and the thermal conductivity values remained about constant, the temperature was raised to a set point of 287 K (14 °C), near but before the dissociation point. The hydrate was not dissociated but rather held at 287 K (14 °C) till the pressure remained constant. The temperature was increased by half a degree then another half a degree so that the pressure and temperature were very near the dissociation point. Figure 3-18 shows the pressure

![Figure 3-18: Experiment T20-018, Cycle 1 up.](image-url)
and temperature data of the heating of cycle 1 and the corresponding thermal conductivity values versus temperature.

The temperature was lowered to 269.5 K (-3.7 °C) for cycle 2 then back to about 288 K (15 °C). No additional hydrate formation was observed in the pressure / temperature data, though the thermal conductivity was slightly lower than the first cycle thermal conductivity values (see Figure 3-19).

As the temperature was lowered to 262 K (-11 °C) in cycle 3, ice formation was observed in the pressure / temperature data with a rise in pressure as the water expanded into its solid state. The values of thermal conductivity, as taken during the cooling of cycle 3, were significant in two ways. The thermal conductivity indicated the formation of ice. The fact that the thermal conductivity value was close to ice indicates that water was near the sensor and not hydrate. The thermal conductivity right before ice formation was 0.708 W/mK and was 2.41 W/mK after ice formation was indicated in the pressure / temperature data.

The temperature was increased to a few degrees above the melting point of ice, 276 K, to

![Figure 3-19: Experiment T20-018, Cycle 2.](image-url)
form hydrate from the unconverted water. The temperature was then increased by 2 K. Around 272.7 K, more hydrate formed with an almost 0.2 MPa drop in pressure. Subsequent cooling, heating, and cooling (cycle 4 down, cycle 4 up, and cycle 5 down, respectively) with no apparent changes in pressure, indicated that all the water was converted to hydrate. The thermal conductivity corresponded with the indications of the pressure / temperature data. The thermal conductivity values, right before the drop in pressure of cycle 3 up, were between 1.87 and 1.98 W/mK. After hydrate formation was confirmed by the pressure / temperature data, the thermal conductivity dropped to 0.348 W/mK.

Thermal conductivity measurements taken right before and during hydrate formation were not possible to analyze. Right before the 0.2 MPa pressure drop, hydrate formation was indicated with the thermal conductivity data (voltage drop data). A slight drop in the pressure was indicated in the pressure / temperature trace about where hydrate formation occurred in cycle 2 up at about 272 K (-1 °C). The thermal conductivity data concurs in that the voltage drop

Figure 3-20: Experiment T20-018, Cycle 3.
data collected across the Wheatstone bridge did not show a smooth rise in $\Delta V$ with time (see Figure 3-20) when hydrate formation was starting. During hydrate formation, the $\Delta V$ data, again, did not show a smooth rise with time. The voltage data indicated activity inside the sample cup. In a sample where heat transfer is accomplished by conduction alone and without convection occurring, the plot of $\Delta V$ versus time rises smoothly and will eventually become almost level as the temperature rise becomes steady (refer to Figure 3-2).

During cycles 4 and 5, the thermal conductivity remained almost constant (see Figure 3-21). The pressure / temperature data during these cycles did not indicate any additional hydrate formation. The thermal conductivity values all decreased with increasing temperature. The behavior of the data can be described by the following equation for the temperature range of 264 K to 277 K ($T$ is in Kelvin):

$$k = -0.0034T + 1.2324$$  \hspace{1cm} (3-13)

The pressure data for all of the cycles with the corresponding thermal conductivity values versus temperature are included in Figure 3-22. With subsequent cycles, additional hydrate formed, indicated by a pressure drop. The thermal conductivity determined for cycles 1, 2, and 3 are near that of water and can be seen to drop with subsequent cycles. It was not until the heating of cycle 3 that significant hydrate formation was observed. The thermal conductivity values correspond well with the pressure / temperature data.

The thermal diffusivity was determined simultaneously with the thermal conductivity. The thermal diffusivity of water at room temperature was determined to be $\alpha = 3.32 \times 10^{-7} \text{ m}^2/\text{s}$. The diffusivity values dropped as more and more hydrate formed in the cup with subsequent cycles. The thermal diffusivity of ice was near that of the values obtained for cycles 1 and 2, which was determined to be water. The thermal diffusivity of ice was determined to be $\alpha = 1.39 \times 10^{-7} \text{ m}^2/\text{s}$ at 264.4 K. During cycle 3, when significant hydrate formation was observed from the pressure / temperature data, the thermal diffusivity right before formation was $\alpha = 0.51 \times 10^{-7} \text{ m}^2/\text{s}$ and rose to $2.25 \times 10^{-7} \text{ m}^2/\text{s}$ after formation. The thermal diffusivity for cycles 4 down, 4 up, and 5 down was determined to be $\alpha = (2.59 \pm 0.16) \times 10^{-7} \text{ m}^2/\text{s}$.
Figure 3-21: Experiment T20-018, Cycles 4 and 5.
Figure 3-22: Experiment T20-018, cycles 1 up through 5 down with thermal conductivity values.
Figure 3.23: Experiment T20-018, Cycles 1 up through 5 down with thermal diffusivity values.
Figure 3-24: Experiment T20-018, Thermal Conductivity and Thermal Diffusivity Data.
The temperature was lowered to a set point of 261 K (-12 °C) so that the sample could be recovered. The cup bottom was removed to recover the sample. The cup sleeve, containing the sample, was placed in liquid nitrogen so that it could be inspected and further analyzed. After taking the sample out of the liquid nitrogen, it was difficult to obtain a clear picture of the hydrate sample because of the evaporating liquid nitrogen. The picture shown in Figure 3-25 is a view of the hydrate that was in contact with the TPS element. The cup bottom, containing the TPS element, was removed to view the portion of the sample in contact with the TPS. The picture shows pores in the unconsolidated hydrate sample, which appeared almost snow-like. Because the sample was unconsolidated, any voids present in the sample would affect the thermal conductivity measurements.

Figure 3-25: Hydrate in cup sleeve. The cup bottom was removed to view the hydrate sample and pictured above is the hydrate near the TPS.
Figure 3-26 is a picture of the cup bottom after being placed in liquid nitrogen and exposure to the atmosphere. The TPS is covered with a portion of the hydrate sample as well as some frost formed from condensing water. Despite the fact that the sample was out of the liquid nitrogen for considerable amounts of time and at atmospheric pressure, the entire sample remained amazingly intact, though some water condensed and froze on the sample while taking pictures. The frost that formed on the hydrate sample and cup bottom can be seen in Figure 3-26.

Raman spectroscopy was performed on the recovered sample in the sleeve (see Figure 3-25). The sample was contained in the sleeve of the cup during testing. The Raman spectrum indicated a relatively pure sample of hydrate [1]. The results can be seen in Figure 3-27.
Large Cage:
Resonance Energy = 2902.4 cm$^{-1}$
FWHM = 7.28 cm$^{-1}$

Small Cage
Resonance Energy = 2914.2 cm$^{-1}$
FWHM = 4.68 cm$^{-1}$

Figure 3-27: Raman Spectroscopy Results.
After performing Raman spectroscopy on the sample, the sample was pushed out of the sleeve. The hydrate was dissociated at room temperature and atmospheric pressure. Figure 3-28 shows the water and gas of the dissociated hydrate that was stuck to the TPS element (see Figure 3-26). The bubbles usually found trapped in the water after dissociation are also seen in the picture.

Figure 3-28: The dissociated hydrate on the cup bottom.
The first few experiments performed enabled experimental improvements. The experiments where visual observations were made gave useful insight into redesigning the cup. After the cup was redesigned and the data collection and analysis was automated, a few more experiments prompted changes in the experimental procedure so that the final two experiments, T20-017 and T20-018 were successful in obtaining thermal property data of methane hydrates.

In experiment T20-017 the thermal conductivity and thermal diffusivity were determined for a methane hydrate sample formed in the new TPS cup. Verification of the sample

Figure 4-1: Experiment T20-018, Thermal conductivity values from this work with literature values.
composition was not done since the sample was dissociated and part of the water was lost during dissociation because of the absence of the cup lid during this experiment. The thermal property values were constant for the cooling and heating of the third (last) cycle, which seems to indicate that all of the water had converted to hydrate.

The thermal conductivity values obtained from experiment T20-018 during the fourth and fifth cycles, after complete conversion of the water to hydrate was confirmed, were low compared to other literature values. Most of the literature values shown in Figure 4-1 were of consolidated hydrate samples except for the values obtained by deMartin [15].

The thermal conductivity range obtained from experiment T20-018 of 0.264 W/mK to 0.338 W/mK corresponds to a void fraction of about 0.10 to about 0.25. Figure 4-2 shows the effective thermal conductivity of an unconsolidated methane hydrate sample [26]. Assuming a thermal conductivity value for a consolidated hydrate sample and the thermal conductivity of methane, the effective thermal conductivity at different void fractions is given by different models [27]. It seems reasonable that, after viewing the post-experiment pictures, the void fraction was not measured, but it is likely that the void fraction was close to the range indicated by the thermal conductivity values.

![Effective Thermal Conductivity for Unconsolidated Methane Hydrate](image)

**Figure 4-2:** Models depicting the effective thermal conductivity for unconsolidated methane hydrate [26, 27].
fraction in the sample of experiment T20-018 is between 0.10 and 0.25. The range of thermal conductivity values obtained for experiment T20-018 are indicated in Figure 4-2 by two horizontal lines. The only other reported thermal conductivity values on a porous methane hydrate sample were by deMartin [15]. The values deMartin reports were for pure methane hydrate samples with porosities between 28% and 33%, determined by knowing the hydrate volume and the volume of the sample vessel.

The thermal conductivity values obtained from Experiment T20-018 decrease with increasing temperature. Ross and Anderson report an increase in the thermal conductivity with increasing temperature for THF hydrate [14]. USGS reports decreasing thermal conductivity values with temperature [10]. Since few measurements exist, it has not been concluded what the dependence of the thermal conductivity on temperature is for methane hydrates.

Figure 4-3 displays the thermal conductivity values obtained for experiments T20-017 and T20-018. The values shown are of the last cycles in both experiments where the thermal conductivity values remained constant for subsequent cycles and the pressure / temperature data

![Thermal Conductivity of Methane Hydrate Obtained From Experiments T20-017 and T20-018](image)

**Figure 4-3:** Thermal Conductivity of methane hydrate from experiments T20-017 and T20-018.
did not indicate additional hydrate formation.

Only one other source reporting thermal diffusivity values was found. The thermal diffusivity values reported by deMartin are higher than the thermal diffusivity values reported here [15]. The values reported in deMartin’s thesis were of compressed, pre-stressed samples. In his work he found that thermal diffusivity rose with increasing confining pressure. Since increasing the confining pressure would essentially decrease pores in the hydrate sample, it seems reasonable that since the sample in this work is unconsolidated that the difference in the thermal diffusivities can be attributed to the difference in porosity.

Figure 4-4 displays the thermal diffusivity values obtained from this work along with the values reported by deMartin. Because of experimental problems in deMartin’s work, the other values he reports are at temperatures well below where measurements were taken in this work. One of his samples was also found to have ice in it and is also displayed in the figure as a straight line since his thermal diffusivity was described in terms of a straight line.

![Cycles 1-5 Thermal Diffusivity Data](image)

Figure 4-4: Experiment T20-018, Thermal diffusivity data with literature data.
5 CONCLUSIONS

The thermal conductivity and thermal diffusivity have been determined for an unconsolidated methane hydrate sample measured in the high-pressure vessel used to form the hydrate. Through experimental improvements, an automated, quick method has been developed to determine the thermal conductivity and thermal diffusivity of a sample of methane hydrate with a single measurement.

The cup designed to contain the sample around the TPS has proven to retain the sample during experiments. The interface between the sample and the TPS could be inspected by removing the cup bottom. The sample was also recovered during this experiment and additional Raman spectroscopy analysis was performed on the methane hydrate sample.

The experimental setup has been calibrated with substances of well investigated thermal properties. The thermal conductivity and thermal diffusivity of glycerol, water, and ice have been measured and compared with existing data of these substances.

In two experiments, the thermal properties have been determined for methane hydrates, though numerous insightful experiments were performed prior to these two successes. It must be noted that during the experiments performed, many thermal property measurements were possible throughout the process. The values for thermal conductivity and thermal diffusivity were validated through many measurements of the sample and the results are reproducible.

In all thermal property measurements, reported elsewhere and herein, the thermal conductivity of methane hydrate was found to be strikingly lower than ice by at least five times and lower than water by almost one and a half times, despite its structural similarities to ice. The thermal conductivity of methane hydrate in this work was determined to be $0.28 \pm 0.01 \text{ W/mK}$ for a temperature range of 276 K to 286 K in the pressure range 10.6 MPa to 11.4 MPa from experiment T20-017. In a similar experiment, experiment T20-018, where the sample was recovered and analyzed with Raman spectroscopy, the thermal conductivity decreased slightly with increasing temperature. The thermal conductivity for a temperature range of 264 K to 277
K and pressure range of 11.6 MPa to 13.0 MPa, respectively, can be described by $k = [-0.0034 \, T + 1.2324] \, \text{W/mK}$, where $T$ is in Kelvin. The average of the thermal conductivity values within this range of temperatures and pressures is $k = 0.30 \pm 0.02 \, \text{W/mK}$. The thermal conductivity values obtained from this investigation are lower than other reported values but seem reasonable if the porosity of our sample was between 10 % and 25 %, which seem valid given the visual observations of the sample recovered from the cup.

The thermal diffusivity of methane hydrates determined in this work from experiment T20-018 was $\alpha = [2.59 \pm 0.16] \times 10^{-7} \, \text{m}^2/\text{s}$. It can also be described by $\alpha = 0.0005 \, T + 2.4424 \, \text{m}^2/\text{s}$ where $T$ is in Kelvin. The aforementioned thermal diffusivity values were within the temperature range of 264 K to 277 K and pressure range of 11.6 MPa to 13.0 MPa, respectively.

Few measurements of the thermal conductivity of methane hydrates and even fewer measurements of the thermal diffusivity have been reported. The method developed in this work has proven successful, and reproducible so that many future experiments can be performed. Measurements are made within the synthesis vessel, which has made other reported values questionable. Because this measurement technique is fast, without altering the sample, and has now been automated, many measurements on the same sample are possible.
6 FUTURE WORK

From the insight of the experiments described in this report, many experiments remain to expand the knowledge of methane hydrates. Some objectives for future experiments and investigations include: measurements on compacted samples, measurements of methane hydrate and sediment mixtures of varying hydrate composition, utilizing gas mixtures containing other components of natural gas, sample characterization, the possible use of surfactants, and modeling to compliment experimental results.

As was seen with comparison to other literature values, the porosity of our methane hydrate affected the thermal conductivity making it lower than other reported values. To obtain more useful thermal property data, the sample will be compressed. Thermal property measurements will be made on the sample both pre and post-compression. In modeling of multi-component systems where gas, hydrate, liquid or solid water can exist, it is necessary to have thermal property data of consolidated hydrate.

Thermal conductivity values have been reported elsewhere for methane hydrates in sediment mixtures made from water / sand mixtures and ice / sand mixtures. This work has yet to complete thermal property measurements of hydrate / sediment measurements. Given the success of the current experimental setup thus far, measurements of hydrate / sediment mixtures can and will be performed in the very near future. Not only will the individual constituents of the mixtures need characterization (e.g. the composition of the sand, the size of the sand particles, and the voids created by the sand), but the mixture both pre and post experiment will need characterization. Because sample characterization is so important in determining the thermal properties, the cup designed in this work was a large focus in experimental improvement to allow for sample recovery.

Because these experiments are performed without any mixing, hydrate formation is limited by diffusion. Since the TPS element, measuring the thermal properties, is located at the bottom of the cup and methane is introduced to the top of the sample, it takes successive temperature
ramps to ensure that methane hydrate is formed down to the TPS. The use of surfactants could promote uniform hydrate formation and may even promote the hydrate to form on or near the TPS first.

No modeling has been reported in this work, which will be a very near future focus to compliment the experimental work. Modeling will serve to enhance the measurements and may lend insight for experimental improvements or directions.
APPENDIX
A DATA ACQUISITION AND ANALYSIS

A.1 National Instruments Hardware

The diagrams shown in this appendix are of National Instrument components used to automate the thermal property measurements. These components replaced a Keithley multimeter and manual switch of the previous experimental setup.

An electromechanical relay switch, SCXI-1161, shown in Figure A-1 is part of the Wheatstone bridge circuit and allows the current to flow through the Wheatstone bridge when prompted by the LabVIEW data acquisition program, allowing the experiments to be automated. The SCXI-1161 has eight independent, non-latching relays each with a normally closed (NC), normally open (NO), and common (COM) terminal. The relay can be controlled with National Instruments LabVIEW software.

The temperature sensor terminal block shown in Figure A-3 allows data collection of the voltage difference across the Wheatstone bridge, the voltage across the sensor, and the voltage across the reference resistor during the transient measurement. Each parameter to be measured is connected to a different channel on the temperature sensor terminal block and data collection is controlled by LabVIEW. The temperature sensor is plugged into a SCXI-1120 signal conditioning module. The SCXI-1120 diagram is shown in Figure A-2. The SCXI-1120 is an 8-channel isolated analog input module. The amplifiers can be configured using jumpers for input ranges from $\pm 2.5 \text{ mV}$ to $\pm 5 \text{ mV}$. 
Figure A-1: Electromechanical relay switch used to initiate thermal property measurements.
Figure A-2: 8-Channel isolation amplifier, 10 kHz bandwidth.

Figure A-3: Temperature sensor terminal block.
A.2 Data Analysis Program (In LabVIEW)

The data collected using the National Instruments components is analyzed using a program written in LabVIEW, a general-purpose programming system. LabVIEW is based on G programming, a graphical data flow programming language. The programs written in LabVIEW are referred to as virtual instruments (VIs) due to their appearance and operation which imitate actual instruments. LabVIEW offers a means for data acquisition, instrument control, data processing, and data storage. LabVIEW has an interactive user interface where inputs can be made and outputs displayed. This interface can simulate the panel of an actual instrument and is appropriately called the front panel. The actual code of the program is viewed and worked on in another window and the code is displayed in the form of a block diagram which is constructed in G.

The front panel of the data analysis program is shown in Figure A-4. The block diagram of the data analysis program is shown in Figure A-5 with the code displayed as sub-VIs and wires connecting the sub-VIs. The data analysis program is made up of many sub-routines referred to as sub-VIs. The calling hierarchy of these sub-VIs is shown in Figure A-6. What follows is the documentation of the data analysis program including the connector pane, showing the sub-VI inputs and outputs, and the block diagram of each sub-VI that makes up the data analysis program. Any hidden cases (i.e. true or false cases) are shown as separate blocks following the block diagram. The sub-VI documentation is listed in the hierarchical order of the data analysis program, shown in Figure A-6. The sub-VIs shown in the figure that have not been included in the documentation are the build-in sub-VIs included with the LabVIEW software package.
Data Analysis

Figure A-4: Front Panel of the LabVIEW Data Analysis Program.
Figure A-5: LabVIEW block diagram of the data analysis program.
Figure A-6: Hierarchy of sub-VI’s in data analysis program.
Choose Crop Point.vi

Connector Pane

Block Diagram
Conductivity.vi

Connector Pane

Front Panel

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81
Block Diagram
Delta Vo.vi

Connector Pane

Block Diagram
Diffusivity.vi

Connector Pane

Block Diagram
Diffusivity Solver.vi

Connector Pane

Front Panel

Diffusivity Parameters
- a [Diffusivity] (guess)
- lower bound: 1E-10
- upper bound: 1E-2
- tolerance: 1e-05
- range: 0.0
- accuracy: 0.001000

Slope
- R^2
- slope: 0.000000
- H(0.5 theta): 0.000000
- H(1.5 theta): 0.000000

Diffusivity Fit Range
- First: 0
- Last: 0

XY Graph
- x-axis: 0.000000
- y-axis: 0.000000

Data
- Data with Trendline
- Data without Trendline

Trendline
- Trendline

85
**H(tau) scalar.vi**

**Connector Pane**
- \( \text{tau} \rightarrow H(tau) \)

**Block Diagram**
- \( H(tau) = C_1 + C_2 t \alpha^{0.5} + C_3 t \alpha + C_4 t \alpha^{(3/2)} + C_5 t \alpha^2 + C_6 t \alpha^3; \)
- Details of coefficients and values:
  - \( C_1 = 0.0676466708963845 \)
  - \( C_2 = 2.886553632916120 \)
  - \( C_3 = 2.579668752457430 \)
  - \( C_4 = 0.815694278891507 \)
  - \( C_5 = -0.6356597307797302 \)
  - \( C_6 = 0.0316901007787064 \)

**corr-slope_HvsT.vi**

**Connector Pane**
- \( \text{diffusivity} \rightarrow 1/2 \)
- \( \Delta \text{tau} \rightarrow \theta \)
- \( \Delta \text{tau} \rightarrow \text{H(tau)} / \theta \)
- \( \text{H(tau)} \rightarrow \text{slope of DeltaT vs H} \)
- \( \text{R} \rightarrow 2 \)

**Block Diagram**
- Equations:
  - \( \Delta \text{tau} = \frac{\text{a} \cdot \text{a}}{\text{diff}} \)
  - \( \text{tau} = \sqrt{\text{a} / \theta} \)
  - \( \text{H(tau)} \rightarrow \text{slope of DeltaT vs H} \)
- Coefficients and values:
  - \( \text{a} = 1.0 \)
  - \( \theta = 1.0 \)
  - \( \text{H(tau)} = 1.0 \)
  - \( \text{R} = 2.0 \)
H(tau).vi

Connector Pane
\[ \tau \rightarrow H(\tau) \rightarrow H(\tau) \]

Block Diagram
\[
H = C_1 + C_2 \tau + C_3 \tau^2 + C_4 \tau^3 + C_5 \tau^4 + C_6 \tau^5;
\]
\[
\tau = 0.0676466708963845, 2.886553632916120, 0.81569278891507
\]
\[
C_1, C_2, C_3, C_4, C_5, C_6
\]

LinReg_origin.vi

Connector Pane
Slope through the origin?

Block Diagram
\[
Y = slope \times X + inte;
\]
\[
um = (Y \times Y) \times 2;
\]
\[
den = (Y - aveY) \times 2;
\]
\[
R^2
\]
Delta T vs H(tau) graph.vi

Connector Pane

Block Diagram
Graph Raw Data02.vi

Connector Pane

Block Diagram
1st derivative.vi

Connector Pane

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</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>dy/dx</td>
</tr>
</tbody>
</table>

Block Diagram

g1st derivative dy/dx
sensor half width.vi

Connector Pane
- Nominal Sensor Half-width
- Sensor Correction Factor

Block Diagram
- \( \text{ahalf} = \text{anom} \times 0.0254 / \sqrt{\text{cf}} \)
- \( \text{Sensor Correction Factor} \)

TCR & Delta T03.vi

Connector Pane
- Average Temperature
- \( R_{\text{sen},i} \)
- \( Ro \)
- Delta Temperature
- D T(t) input
- TCR
- TCR ave
- Rdiff
- error in (no error)
- error out
TCR.vi

Connector Pane
Temperature

Block Diagram
Coefficients from Vishay's web page
http://www.vishay.com/brandsmeasurements_group/guide/tn/tn506/506m.htm

Temperature [DBL]

4384157
0.250996
2.84985E-4

3.00807E-7
2.03720E-10
2.95460E-12
1.07663E-14
R(T).vi

Connector Pane

R(T) R(T)

Temperature

R(T)

Block Diagram
TCRave.vi

Connector Pane
Average Temperature

Block Diagram
Coefficients from Vishay's web page
http://www.vishay.com/brands/measurements_group/guide/tn/rf506/506m.htm
Power & Rsen.vi

Connector Pane

Ref (Reference)  power  Power
Vtot (Total Voltage)  Rsen  Rsen
Cropped Delta V

Block Diagram
Intermediate Calculations02.vi

Connector Pane

Block Diagram
Data Modification.vi

Connector Pane

Use Polynomial Fit Values
# of points to average
Adjust Data
Multiply time by:
Adjust Delta V
Multiply Delta V by:
error in (no error)
Time Data
Voltage Data
polynomial order

Block Diagram
Res_vs_tc_coeff.vi

Connector Pane

Block Diagram

Theta.vi

Connector Pane

Block Diagram
Retrieve Data.vi

Connector Pane

- file path
- error in (no error)
- Type of Data
- FILTER
- Duration
- voltage
- Polynomial Fit Values
- filename
- Raw Data
- stripped path
- mean temperature
- error out
- dt
- 4 channels
read and filter data2.vi

Connector Pane

- new file path
- mean temperature
- Polynomial Fit Values
- Y Array
- X Array
- dt
- voltage
- 4 channels
Block Diagram
B EQUATIONS AND CALCULATIONS

B.1 Derivation of Equations Used in the Data Analysis

B.1.1 \( R_{\text{sen}} \) Derivation

Figure B-1: Wheatstone bridge circuit, containing the TPS sensor.
\[ V_{\text{tot}} = IR_{\text{sen}} + IR_{\text{ref}} \]

\[ I = \frac{V_{\text{tot}}}{R_{\text{sen}} + R_{\text{ref}}} = \frac{V_{\text{ref}}}{R_{\text{ref}}} \]

\[ V_{\text{ref}} = \frac{V_{\text{tot}}}{2} - \Delta V \]

\[ R_{\text{sen}} = \frac{V_{\text{tot}} - IR_{\text{ref}}}{I} = \frac{V_{\text{tot}} - \frac{V_{\text{ref}}}{R_{\text{ref}}}}{\frac{V_{\text{ref}}}{R_{\text{ref}}}} = R_{\text{ref}} \left[ \frac{V_{\text{tot}} - V_{\text{ref}}}{V_{\text{ref}}} \right] = R_{\text{ref}} \left[ \frac{V_{\text{tot}} - \frac{V_{\text{ref}}}{R_{\text{ref}}} + \Delta V}{V_{\text{tot}}/2 - \Delta V} \right] \]

\[ R_{\text{sen}} = R_{\text{ref}} \left[ \frac{1}{\frac{\Delta V}{V_{\text{tot}}} - 1} \right] \]

(B.1)

### B.1.2 \( H(\tau) \) Values From Numerical Integration at Different \( \tau \)-Values

<table>
<thead>
<tr>
<th>( \tau )</th>
<th>( H(\tau) )</th>
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</table>
B.2 Raman Spectroscopy Analysis

The following analysis was performed by Christopher Matranga of US DOE National Energy Technology Laboratory.

The close up of the Methane Region was deconvoluted by a least squares fit of the experimental spectra to 2 lorentzian oscillators:

\[ I(\nu) = \sum_{q=1}^{2} \frac{A_q \Gamma_q}{(\nu-\nu_q)^2 + \Gamma_q} \]

\( A_q \) = Peak Height, \( \Gamma_q \) is the Half-Width Half Max, \( \nu_q \) is the resonance freq of the peak.

From the parameters on the fits the crystallographic hydration number and the occupancy of the large and small cages can be determined using:

1) \( \frac{I_L}{3I_s} = \frac{\theta_L}{\theta_s} \),
2) \( \Delta\mu_w^o = -\frac{RT}{23} \left[ 3 \ln(1-\theta_L) - (1-\theta_s) \right] \),
3) \( n_c = \frac{23}{3\theta_L + \theta_s} \)

\( \Delta\mu_w^o = 1297 \text{ J mol}^{-1} \), \( I_L \) & \( I_s \) are the integrated intensities from the deconvolution, \( \theta \) is the cage occupancy, \( n_c \) is the crystallographic hydration number.


From curve fits using Excel the frequency & full width half maximums (FWHM) for the peaks associated with the large & small cages are:

Large Cage:
Resonance Energy = 2902.4 cm\(^{-1}\)
FWHM = 7.28 cm\(^{-1}\)

Small Cage
Resonance Energy = 2914.2 cm\(^{-1}\)
FWHM = 4.68 cm\(^{-1}\)
REFERENCES
REFERENCES


[26] Models collected and developed by Dr. David Shaw, Geneva College, 3200 College Ave. 15010, and obtained through personal communication.

XXIV. “Temporary Storage of Sewage Overflow in Abandoned Underground Mines”

Larry Robelewski (S), Ronald Neufeld (F), University of Pittsburgh
with
Richard Hammack (M), NETL
Temporary Storage of Sewage Overflow in Abandoned Underground Mines

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Abstract

The discharge of untreated sewage during precipitation events is a significant source of pollution to our nation’s bodies of water. Pollutants from sewer overflows such as trash, sand and gritty material, organic pollutants, and biochemical oxygen demand (BOD) can all adversely affect the health of the aquatic community and can negatively impact water usage. In 1994, the EPA adopted a national policy to control and regulate the discharge of untreated sewage during precipitation events. The overall goal is bring wet weather sewage overflow discharge points into compliance with the requirements of the Clean Water Act and to minimize the impacts of sewage overflow discharges on water quality, aquatic biota, and human health. Solving this problem, however, will be expensive, with cost estimates ranging from $57 billion to over $100 billion.

One potentially less expensive alternative to this approach is to temporarily store the overflow sewage in abandoned underground mine voids. Such a system would work as follows:

- During precipitation events, potential overflow sewage (CSO/SSO) would be shunted into abandoned underground mine voids for temporary storage.
- When flows returned to normal, the stored sewage overflow would be pumped back out into the conveyance system and sent to the sewage treatment plant for treatment.
- While in mine storage, indigenous organisms (sulfate-reducing bacteria) would partially treat the sewage overflow.
- By-products of the sulfate reduction process would partially remediate any mine water contamination.

The research at NETL is focused on validating the proof of principle behind the sewage overflow mine storage concept. Specifically, it involves demonstrating the technology under actual mine conditions. A secondary aspect of the research entails investigation the biological aspects of the system.

Both batch and in-mine barrel testing is being conducted towards these goals. Batch test results show a relatively consistent substrate utilization rate of 0.0010 ± 0.0004 mg COD/L•SRB cell•day after a slight lag phase. Approximately 20% of the COD measured by the testing, however, turned out to be either inorganic or unable to be utilized by the sulfate-reducing bacteria. The data is currently being examined to determine applicable kinetic constants with respect to sewage-fed sulfate-reduction. In-mine barrel test data show that a sewage/mine water mixture of at least around 50/50 is required to achieve conditions necessary for sulfate-reduction to take place. At levels less than this figure (i.e. – more mine water, less sewage), environmental conditions such as oxidation/reduction potential are unfavorable.
Background:

In the United States, the discharge of untreated sewage during precipitation events is a significant source of pollution on our nation’s bodies of waters. This discharge is usually classified in two ways: combined sewer overflow (CSO) and sanitary sewer overflow (SSO). In combined sewer systems, both the sewage and the storm water flow through the same sewer mains to the sewage treatment plant. When the volume of flow is greater than the plant or conveyance system can handle, the “overflow” is diverted at various points in the collection system into local streams, rivers, or lakes. In separate sanitary sewer systems, the sewage is routed to the sewage treatment plant while the storm water is directed – via a separate storm sewer system – into nearly streams, rivers, and lakes. Due to physical characteristics of the system pipelines (joints, broken sections, etc.) and other causes (illegal connections, installation below groundwater levels, etc.), however, groundwater and storm water can infiltrate into the sanitary sewer system. When the flow is greater than the plant can handle, the “overflow” (SSO) is diverted into nearby receiving bodies of water.

Since the passage of the Clean Water Act in 1972, the construction of new combined sewer systems has been illegal. However, approximately 772 communities – mostly in the Northeast and Midwest – serving around 40 million people still employ combined sewer systems. (1) A 2001 EPA National Pollutant Discharge Elimination System (NPDES) files review found 859 CSO permits, which included descriptions of 9471 permitted outfalls nationwide (the number of SSOs remains unknown). (2) In Allegheny County (PA) alone, the Allegheny County Sanitation Authority (ALCOSAN) has 317 outfall structures, with over 50 identified as SSOs and the remaining 260+ classified as CSOs. (3)

These outfalls discharge large amounts of pollution into receiving waters during precipitation events. In 1993, the EPA reported individual CSOs discharged an average of 50-80 times a year, resulting in the delivery of approximately 1.2 trillion gallons of raw sewage, untreated industrial wastes, and storm water runoff into receiving waters nationwide each year. (2) Pollutants from sewer overflows such as trash and floatable debris, sand and gritty material, organic pollutants, biochemical oxygen demand (BOD), and pathogenic organisms all adversely affect the health of the aquatic community and can impact river usage. The EPA’s National Water Quality Inventory Report to Congress in 1995 lists CSO-caused pollution as a Top-12 cause of impairment to the nation’s estuaries, oceans, and the Great Lakes. (2)

In 1994, the EPA adopted a National CSO policy outlining 9 minimum steps to control and regulate CSO outflows. These controls aim to bring all wet weather CSO discharge points into compliance with the requirements of the Clean Water Act and to minimize the impacts of CSOs on water quality, aquatic biota, and human health. Consent decrees with appropriate sewage authorities to meet these standards have been or are being negotiated. (4) Similar guidelines for SSOs are currently under development. (5)
Resolving the sewage overflow problem will be costly. Estimates vary, depending upon the source, but the ballpark figures range from $57 billion to over $100 billion. Locally, ALCOSAN has estimated its proposed Regional Long-Term Wet Weather Control Concept Plan will cost over $3 billion, or approximately $6000 - $10,000 per household. (3)

Research Objectives:

Although many different methods for managing the CSO/SSO problem – such as sewer separation (separating sewage from storm water) and sewer rehabilitation (to reduce infiltration and flows) – have been attempted, the most common approaches for larger municipal systems incorporate some form of sewage storage, conveyance, and treatment at the sewage treatment plant. These schemes often involve the construction and operation of facilities to temporarily store overflow sewage and make up a sizable fraction of the projected cost for remediying the nationwide CSO/SSO problem. The ALCOSAN Regional Long-Term Wet Weather Control Concept Plan, for example, anticipates spending over $900 million to construct 10 swirl and 17 storage facilities to capture 85% of the combined sewer wet weather flow for treatment and to completely eliminate SSOs. (3)

One potential alternative to this approach is to temporarily store the overflow sewage in abandoned underground mine voids. In areas of the country that have been heavily mined (such as western Pennsylvania), abandoned mine voids are numerous and are apt to be situated near sewer mains. Costs connected with implementing such a concept – establishing connections between the mine voids and sewer mains, pumps, etc. – will likely be a fraction of those associated with the construction and operation of new storage facilities.

Ideally, such a system would work as follows:

- During precipitation events, potential overflow sewage (CSO/SSO) would be shunted into abandoned underground mine voids for temporary storage.
- When flows returned to normal, the stored sewage overflow would be pumped back out into the conveyance system and sent to the sewage treatment plant for treatment.
- While in mine storage, indigenous organisms (sulfate-reducing bacteria) would partially treat the sewage overflow.
- By-products of the sulfate reduction process would partially remediate any mine water contamination.

Many potential advantages exist with this proposal. In addition to likely cost savings due to limited capital expenses, the potential storage capacity within abandoned underground mines is large. Underground storage of sewage overflow is also aesthetically more acceptable to the above ground alternative. Naturally occurring sulfate-reducing bacteria (SRB) will partially treat both the sewage and existing mine
water. Possible disadvantages include potential groundwater contamination due to sewage leaching and possible methane and/or hydrogen sulfide accumulation.

The research at NETL is focused on validating the proof of principle behind the sewage overflow mine storage concept. Specifically, it involves demonstrating the technology under actual mine conditions. A secondary aspect of the research entails investigating the biological aspects of the system.

**Experimental Overview:**

Prior to actual experimentation, the necessary microorganisms (SRB) must be obtained and cultured. These microbes will be used as "seed stock" or inocula for batch experiments. In-mine barrel experimentation will rely on the indigenous microorganisms in the mine water and dilute sewage samples as their inocula.

Batch testing will be conducted in modified 2 L Erlenmeyer flasks to determine the kinetics of biodegradation of dilute sewage via biological desulphurization. The reactors will contain filtered sewage obtained from the primary clarifier of a local wastewater treatment plant, SRB inocula, and a sulfate source. The batch experiments will be executed at a temperature of approximately 10º C (50º F). Since mine temperatures – and groundwater temperatures – are usually a constant 10º - 13º C (50º - 55º F), the experimentation will yield kinetics more applicable to the operational concept. The batch test results are expected to produce a better understanding of the mechanics involved with sewage overflow mine storage.

In-mine barrel testing will be accomplished to demonstrate the proof of principle behind the sewage overflow mine storage concept. Several modified 55-gallon (210 L) High Density Poly Ethylene (HDPE) drums will serve as barrel reactors. The reactors will contain varying mixtures of highly diluted sanitary sewage taken from a heavily infiltrated sewer main in the Township of Upper St. Clair. Mine water will come from the Experimental Mine at the Bruceton Research Station and from selected AMD sites in the Chartiers Creek watershed. The barrel reactors will be placed within the Experimental Mine for the duration of the In-Mine Barrel Testing Phase.

**Results and Discussion:**

Microorganism inocula for the batch experiments were obtained from wetland sediments at several sites where sulfate reduction is known to take place. These samples underwent testing to see if: (1) viable SRB populations existed and (2) the resident SRB population could grow using sewage as its exclusive substrate and growth medium. Three samples met both criteria and were used as inocula for SRB cultivation. The cultivation occurred in a reactor vessel with dilute sewage employed as the sole substrate and growth medium.
Initial batch testing was started, but quickly terminated due to unforeseen interference problems with the Chemical Oxygen Demand (COD) tests. Changes were made to the sample preparation procedures that eliminated these interferences and a second series of batch tests were begun. These tests, however, also had to be prematurely terminated. Apparently, the sample preparation procedures changes created a new interference problem with the COD tests. Further changes were made and new sample preparation procedures were put into place (see Appendix). The method of COD determination was also changed from colorimetric to titration. These new modifications eliminated the interference problems and produced results more in line with expectations.

A third set of batch tests were then launched and, this time, acceptable COD data was obtained. Figures 1 - 3 show the substrate utilization for each of the batch reactors.

These figures show three distinct phases in the substrate utilization pattern. First, in two of the reactors, a noticeable lag time of approximately 5 days was detected. This same lag time (albeit somewhat longer) was also observed in the second (terminated) batch tests. Second a relatively linear region of constant substrate utilization was observed. Finally, a “plateau” region where substrate utilization ceased occurred at around 20-25 mg COD/L.

The lag phase was most likely created by one of two probable causes. First, many of the SRB in the initial inoculum could have been inactive or dormant. If this were the case, some period of time would be necessary for them to become active again. Second, the temperature difference between the cultivation and batch reactors could have temporarily “shocked” the SRB. Cultivation of the SRB occurred at a room temperature of approximately 20º C (≈ 68º F) while the batch testing took place at temperatures around 8º-10º C (46º-50º F). Some period of adjustment of the SRB to their new temperature environment might have been required.

The plateau region where substrate utilization ceased likewise had two probable sources. Several reduced and partially reduced inorganic species such as manganous manganese (Mn$^{2+}$) and nitrite (NO$_2^-$) are oxidized under COD test conditions and, thus, will exert a chemical oxygen demand. (6) Similarly, iron sulfide precipitate (FeS) will also cause a chemical oxygen demand. FeS was present in the batch reactors in noticeable quantities; furthermore, the sample preparation procedures remove ferrous iron from the COD sample through the precipitation of FeS. Although syringe filtering the sample through a 0.45µm nylon and glass filter should have removed the precipitate, it is possible some small particles of FeS escaped capture and, thus, exerted a chemical oxygen demand.

A second possible cause for the residual COD is that any remaining organic COD could not be utilized by the SRB. Sewage contains an olio of organic compounds and it is possible some of these compounds could not be consumed by the SRB present. For example, SRB cannot use natural polymers such as cellulose and hemicellulose as a substrate. (7,8) If these materials escaped capture by the syringe filter or were in soluble form, then they would exert a chemical oxygen demand that could not be utilized by the
SRB. It is most likely both of these situations contributed to the recalcitrant 20-25 mg COD/L observed in each of the batch reactors.

Between these two extremes, however, a relatively linear region of constant substrate utilization was observed. Normalized to the concentration of SRB present, the substrate utilization rate was roughly $0.0010 \pm 0.0004$ mg COD/L•SRB cell•day. This and other data are currently being scrutinized to determine the applicable kinetic constants.

In-mine barrel testing was also started, but a host of problems (i.e. - budgetary problems preventing the procurement of necessary supplies, mine access, mechanical problems) prevented more than one sample reading. Heavily infiltrated sewage from the Township of Upper St. Clair was delivered on 23 September 2003 and placed (in appropriate amounts) into the modified HDPE barrel reactors. Due to mechanical problems with the transportation equipment, the barrels were not transported into the mine until the week of 6 October 2003. Mine personnel filled the barrels to the mark with untreated mine water from the Bruceton Experimental and Safety Research Coal Mines. Access to the mine and barrel reactors, however, was unavailable until 20 October. By this time, approximately 3-4 weeks passed since the original delivery of the sewage.

Samples and readings of each barrel reactor were taken at this time and the results are found in Table 1 in the Appendix. This was the only sample taken from the barrel reactors due to the unavailability of testing supplies.

In spite of these setbacks, several observations from the (albeit – limited) data can be made. The first is that the overflow sewage/mine water mixture must be approximately 50/50 for favorable sulfate-reducing conditions to develop. The barrels containing less than an approximate 50/50 mixture (i.e. – more mine water than sewage) had highly oxidizing environments, with oxidation/reduction potentials (ORP) far above zero. Since SRB require an anoxic environment to affect sulfate-reduction (ORP $< \approx -100$ - -120 mV) (9,10), these conditions would not permit sulfate-reduction to transpire. Furthermore, the pH of these barrels is far below the 5 – 9.5 pH range Postgate reports that SRB are active in. (10) This information will be employed when conducting further barrel tests.

A second observation is that overflow sewage can effectively neutralize acidic mine waters with pH > 3.4 at volumetric ratios around 1:1. The overflow sewage contained a pH of 7.31 while the mine water had a pH of 3.38. When mixed in a roughly 50/50 ratio, however, the pH of the mixture became approximately 6.14-6.27 – an acceptable pH for discharge into the environment.

Further batch and in-mine barrel testing will commence upon receipt of ordered testing supplies.
APPENDIX
COD Sample Pre-Digestion Preparation Procedures

The following procedures were adopted to remove potential interferences with the COD testing caused by ferrous iron, free sulfides, and precipitated FeS:

1. An adequate amount of reactor sample ($\approx 30$ mL) is procured from the appropriate batch reactor.
2. Slightly higher than stoichiometric amounts of sodium sulfide ($\text{Na}_2\text{S}$) is added in a 50 mL volumetric flask. The stoichiometry is based on the original amount of ferrous sulfate ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$) added to the reactor at the onset of batch testing. The sulfide added will be slightly higher than the amount stoichiometrically necessary to remove all of the ferrous iron. The reactor sample is poured into the volumetric flask and mixed.
3. Slightly higher than stoichiometric concentrations of copper(II) sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) is added to the 50 mL beaker with a stirring bar. The stoichiometry is based on the original amount of sodium sulfide added in Step (2). The copper(II) added will be slightly higher than the amount stoichiometrically necessary to remove all of the sulfide. The sample from Step (2) is poured into the beaker and the ingredients mixed for a couple of minutes with the magnetic stirring bar.
4. After mixing, the beaker is removed from the magnetic stirring device and allowed to sit for several minutes. The copper/iron sulfides will precipitate to the bottom of the flask, leaving a relatively clear supernatant after several minutes of settling time.
5. The supernatant is syringe filtered through a 0.45 µm Diagger nylon and glass filter to remove any suspended precipitates.
6. The ferrous iron content of the filtered supernatant is checked with Quantofix Iron-100 Test Sticks for the Semi-Quantitative Determination of $\text{Fe}^{2+}/\text{Fe}^{3+}$. The ferrous iron content of the supernatant should read zero.
7. The filtered supernatant is now ready to undergo COD digestion. Two mL of this filtrate are pipetted into Hach Low Range COD Digestion vial. Triplicate digestions are done with each sample.
Figure 1

Substrate Utilization Curve – Batch Reactor #1
Figure 2

Substrate Utilization Curve – Batch Reactor #2
Figure 3

Substrate Utilization Curve – Batch Reactor 3
Table 1
Preliminary Results of Barrel Tests

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Note - The COD concentrations measured are filtered COD concentrations. A correction to remove inorganic COD (based upon the percentage of mine water in each barrel and the raw COD readings of the 100% mine water barrel) was implemented to yield the figures in the above table.
XXV. “Evaluation of the Biologically Catalyzed Treatment and Regeneration of NO\textsubscript{x} Scrubbing Process Water”

Robert Dilmore (S) and Ronald Neufeld (F) University of Pittsburgh
with
Richard Hammack (M), NETL
Evaluation of the Biologically Catalyzed Treatment and Regeneration of NOX Scrubbing Process Water

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ABSTRACT

This article summarizes preliminary findings related to biological treatment and regeneration of spent NOX scrubber solution. Included is a description of prototype-scale process, batch kinetic analyses used to model biologically catalyzed reduction reactions, and brief discussion of a proposed mechanism to selectively remove dissolved mercury from process waters.

BACKGROUND

Process Description
The process being evaluated involves the scrubbing of nitric oxide from the gas phase, biological treatment of spent scrubber solution and subsequent recycle of treated solution. The scrubbing of nitric oxide from the gas phase is based on the reaction of dissolved nitric oxide with ferrous ethylenediaminetetraacetic acid (Fe(II)EDTA2-) to form the reversible adduct NO•Fe(II)EDTA2-. The resulting spent scrubber solution is then treated biologically to remove the nitrosyl adduct (bound nitric oxide) from the ferrous EDTA and to reduce the oxidized ferric EDTA (Fe(III)EDTA-) to the ferrous form that is active for NOx scrubbing. In addition, the process water can be amended with limestone to make the scrubber function as a combined SOx/NOx scrubbing process. The scrubbing reactions of interest are as follows:

Scrubber Reactions.
In the process under consideration, NO is scrubbed from the gas phase using a solution of the chelate ferrous EDTA. The reaction between dissolved NO and this chelate is:

\[ \text{Fe(II)EDTA}^{2-} + \text{NO} \longrightarrow \text{NO} \cdot \text{Fe(II)EDTA}^{2-} \]  

(1)

NO is thus removed from bulk solution, allowing more NO to dissolve. Oxidation of a fraction of the ferrous EDTA to ferric EDTA will occur as a result of contact with oxygen in the flue gas, as described in Reaction 2.

\[ 2 \text{Fe(II)EDTA}^{2-} + \frac{1}{2} \text{O}_2 + 2 \text{H}^+ \rightarrow 2 \text{Fe(III)EDTA}^- + \text{H}_2\text{O} \]  

(2)

Nitric oxide will not form an adduct with the oxidized form of iron EDTA. An increase in ferric/ferrous ratio results in decreased NO solubility and scrubber efficiency.

Microbially-Catalyzed Reduction Reactions.
Biological treatment and regeneration of spent scrubber solution involves microbially-mediated reduction of Fe(III)EDTA^- and NO•Fe(II)EDTA2-. These reductions are coupled with the oxidation of ethanol, which also serves as the principle carbon source for new cell generation. The overall reduction reactions proceed as follows:

\[ \frac{1}{6} \text{CH}_3\text{CH}_2\text{OH} + \text{NO} \cdot \text{Fe(II)EDTA}^{2-} \longrightarrow \text{Fe(II)EDTA}^{2-} + \frac{1}{2} \text{N}_2 + \frac{1}{3} \text{CO}_2 + \frac{1}{2} \text{H}_2\text{O} \]  

(3)
Fe(III)EDTA$^-$ + 1/12 CH$_3$CH$_2$OH + ¼ H$_2$O $\rightarrow$ Fe(II)EDTA$^{2-}$ + 1/6 CO$_2$ + H$^+$  \hspace{1cm} (4)

**Kinetic Considerations**

Because these reactions are microbially mediated it is hypothesized that they behave according to the Michaelis-Menton, or Monod, expression for substrated limited growth. For example, in the case of microbially catalyzed Fe(III)EDTA reduction, the following rectangular hyperbolic expression is expected to describe reduction kinetics.

$$\frac{dS}{dt} = \frac{-kXS}{(K_s + S)}$$  \hspace{1cm} (5)

The biological reduction of Ferric EDTA is expected to be coupled with a proportional decrease in ethanol, the electron donor coupled to the microbially catalyzed reduction of ferric iron. Using the calculated yield coefficient and the specific growth rate, the maximum substrate utilization rate per unit biomass (k) can be calculated by:

$$k = \frac{\mu_m}{Y}$$  \hspace{1cm} (6)

**Mercury in Flue Gas**

Mercury that is released into the atmosphere as a result of combustion is deposited onto the land and into water bodies. There, it can be converted to methyl mercury under anaerobic conditions by sulfate reducing bacteria. Methyl mercury is readily absorbed into living organisms, and is biomagnified through the food chain, especially in aquatic systems. By this mechanism, methyl mercury can reach concentrations that are toxic to humans and other vertebrates.

In humans, low exposure to methyl mercury (greater than 0.1 µg/kg of body weight/day) is believed to cause neurological damage. Higher doses (0.1-0.5 µg/kg of body weight/day) have been shown to result in tremors, loss of motor function, and death in lab animals. Tragic events like the fish contamination and poisoning deaths of 439 at Minamata Bay, Japan and the death of Dr. Karen E. Wetterhahn, Professor of Chemistry at Dartmouth University, bring to our attention the extreme toxicity of methylated mercury.

The United States Environmental Protection Agency (US EPA) recently proposed regulation designed to curtail emission of mercury from coal fired utility boiler flue gas, the largest source of airborne anthropogenic mercury in the United States. Because it has a relatively low boiling point (357 °C), mercury present in coal is vaporized during combustion. Elemental mercury vapor in the flue gas is not soluble in aqueous streams and does not readily precipitate onto flyash particles. As a result, conventional APCDs do not remove elemental mercury from flue gas.

Most control technologies under development for mercury fall into two general categories: sorbent technologies and mercury oxidizing technologies. Sorbents are
typically either injected into the flue gas as a powder, or configured as a granular, packed, fixed-bed reactor. Sorbents that are currently being considered include activated carbon, sulfur impregnated activated carbon, sulfur impregnated activated alumina, cristobalite, and diatomaceous earth, among others. In many cases, mass transfer limitations prevent sufficient removal of elemental mercury through adsorption.

Oxidation of elemental mercury in flue gas is also under consideration. Several mechanisms for mercury oxidation are being studied, including: chlorine addition, corona discharge, and exposure to ultraviolet light. In addition, some work has been done on catalysis of oxidation reactions via titanium oxide, iron oxide, or copper oxide catalysts.

Unlike elemental mercury, oxidized mercury tends to adsorb onto fly ash or dissolve in wet scrubber solution and can be removed using conventional APCDs. As a result, oxidation of mercury in flue gas will result in increased concentration of mercury in fly ash, spent wet scrubber solutions, and gypsum product generated as a result of forced air oxidation. As the effort to curtail gaseous release of mercury from coal-fired utility boilers intensifies, the importance of considering fate and transport of mercury in solid and liquid process streams also increases.

APPARATUS & METHODS

Prototype Apparatus.
Process configuration and operation were investigated using a prototype scale apparatus consisting of a packed scrubbing tower (8.5” i.d., 21” bed height, 1” plastic pall ring packing), a 42.5 liter anaerobic reactor in upflow configuration, and a subsequent 20 liter slanted-plate solid/liquid separation unit. Synthetic flue gas was fed at flow rates of up to 40 liters per minute and NO concentration varying between 750 to 2500 parts per million (20 ºC, 1 atm). The bioreactor was inoculated with a blend of biomass from the anoxic denitrifying and anaerobic digestion stages of a municipal wastewater treatment plant. The reactor was operated for the first 50 days using an aqueous solution containing ferric EDTA and nitrate as the terminal electron acceptors. After a substantial population of denitrifying and iron-reducing bacteria was established, the absorption stage was introduced, and NO replaced nitrate as terminal electron acceptor. Figure 1 shows a simplified process schematic.
Reagent Preparation

Ferrous EDTA Preparation
A 0.045 M solution of ferrous EDTA was prepared using ferrous sulfate and electrophoresis grade tetrasodium EDTA added in equimolar concentrations to distilled water that was nitrogen purged to remove dissolved oxygen. Solution was prepared in a glove bag under anaerobic conditions in order to prevent introduction of dissolved oxygen and subsequent oxidation of ferrous EDTA to ferric EDTA. After preparation, the solution was stored in the dark and under anaerobic conditions in order to prevent chemical or photochemical oxidation of the ferrous iron in the chelate.

Preparation of NO-Fe(II)EDTA solution
NO is bubbled through the ferrous EDTA solution until full breakthrough (1019 ppm) of NO is observed in the sparging vessel effluent. The total mass of NO present in solution is determined by graphical integration of the plot of mass concentration scrubbed versus time. Concentration of NO-Fe(II)EDTA present in solution can then be calculated as the difference between the total NO absorbed and the previously calculated equilibrium concentration. The remaining concentration of ferrous EDTA present in solution without nitrosyl adduct was calculated as the difference between initial ferrous EDTA concentration (0.045 M) and the concentration of NO-Fe(II)EDTA. After this solution was prepared, it remained in a glove bag under N₂ positive pressure in order to avoid
oxidation of ferrous EDTA in solution. Batch tests were initiated within three hours as possible after NO-Fe(II)EDTA solution preparation.

**Ethanol/Nutrient Solution Preparation**

The nutrient solution used in prototype reactor and batch kinetic analyses was made up of 1.88 moles/liter of ethanol, 0.20539 moles/liter of ammonium chloride (NH₄Cl), and 0.01936 moles per liter of potassium phosphate (KH₂PO₄). Reverse osmosis distilled/deionized water was then used to bring the solution to volume. The carbon to nitrogen to phosphorus molar ratio of the nutrient solution being used in the reactor initially was 200:10.6:1. Nutrient solution was amended with a small concentration of a comprehensive trace element solution in order to ensure that concentrations of those elements were not limiting to cell growth and metabolic activity. One milliliter of a stock trace element solution was added to each liter of nutrient solution used in batch tests or continuous prototype-scale operation. The trace element solution contained (units of mg/l): FeCl₂·4H₂O (2000), H₃BO₃ (50), ZnCl₂ (50), CuCl₂·2H₂O (38), MnCl₂·2H₂O (500), (NH₄)₆Mo7O24·4H₂O (50), AlSO₄ (241.3), CoCl₂·6H₂O (2000), NiCl₂·6H₂O (92) and Na₂SeO₃·5H₂O (284). In addition, two milliliters of HCl was added to promote dissolution. The solution was buffered by addition of NaHCO₃ (5.4 g/l).

**Biomass preparation**

Seed inocula for batch analyses were taken from a prototype-scale upflow anaerobic sludge blanket (UASB) reactor. The UASB reactor functioned as the treatment and regeneration stage in a closed loop process used for the demonstration of a ferrous EDTA-based NO absorption column. Biomass was cultivated over a period of eight months with ethanol as the primary electron donor and NO-Fe(II)EDTA and Fe(III)EDTA as the primary electron acceptors. Bacteria were extracted using a syringe in order to minimize exposure to atmosphere. Samples were then centrifuged for 10 minutes at 4000 rpm at 4 °C, and the supernatant discarded. The remaining pellet of biomass was resuspended in a sterile 0.045 M solution of ferrous EDTA, and centrifuged as before. The supernatant was again discarded and the pellet of biomass was resuspended in a sterile 0.045 M solution of ferrous EDTA. After final centrifugation, the pellet of biomass was resuspended in a sterile 0.045 M ferrous EDTA solution. The inoculum suspension was then refrigerated (4 °C) overnight, providing time for biomass to exhaust any internal energy stores remaining from metabolism that initiated in the bioreactor. The resulting mixture was used as seed inoculum in batch experimentation. Duplicate inoculum samples (50 ml each) were analyzed for volatile suspended solids concentration.

**Analytical Methods**

**Ferric EDTA Concentration Determination**

Ferric EDTA concentration was determined by measuring and plotting absorbance values of standard solutions of varying ferric EDTA concentration, with constant total EDTA concentration. Absorbance at 477 nm was found to be proportional to the concentration.
of ferric EDTA. De-aerated solutions of 0.045 M ferrous and ferric EDTA were combined in several different volume ratios to generate solutions of varying ferric EDTA concentration but constant total iron EDTA concentration. These samples were analyzed spectrophotometrically to measure the absorbance response.

Figure 2. Results of spectrophotometric scans of iron EDTA solutions with varying ferric EDTA concentrations reveal a predictable absorbance peak at 477 nm.
Figure 3. There is a predictable increase in absorbance response (477 nm) with increasing ferric EDTA concentration in an 0.045 M Ferrous EDTA solution.

In addition to spectrophotometric analysis, samples were also analyzed using an electrochemical analyzer with rotating-disc electrode. Linear sweep and cyclic voltammetric methods were used. These electrochemical methods provide straightforward and theory grounded means of verifying the degree to which iron in solution is oxidized or reduced. Samples were analyzed using a platinum rotating disc working electrode, operated at 700 rpm, with a scanning rate of 50 mV/sec. Scans were carried out at 25°C with a Ag/AgCl reference electrode.
Cyclic Voltammograms for 0.045 M Iron EDTA solutions
(50 mV/sec, 700 rpm)

Figure 4. Illustration of the difference between positive voltage scans of 0.045 M ferrous and ferric EDTA solutions
Figure 5. Illustration of the increase in local current peak with increasing Ferric EDTA concentration (at a cathodic potential of -400 mV)

\[ y = 0.0148x + 6E-05 \]

\[ R^2 = 0.999 \]

Figure 6. Linear correlation between solution ferric EDTA concentration and current at -400 mV
**NO*Fe(II)EDTA Spectrophotometric Determination**

A spectrophotometric technique was employed for the measurement of [NO•Fe(II)EDTA$^{2-}$]. A standard curve was developed based on peak height of absorbance responses of samples of known NO•Fe(II)EDTA$^{2-}$ concentration. A 1:1 Fe(II)/EDTA ratio with a nitrosyl adduct exhibits peaks at wavelengths of 342, 433, and 633 nm. A peak at 433 nm shows the strongest differential absorbance, and was therefore used for quantitative determination of nitrosyl adduct concentration.

![Spectral scan of varying degrees of nitric oxide saturation of a 0.045 M solution of Fe(II)EDTA](image)

*Figure 7. Spectral scan of varying degrees of nitric oxide saturation of a 0.045 M solution of Fe(II)EDTA*

The absorbance response at 433 nm shows excellent correlation with the degree of NO saturation of the ferrous EDTA chelate (Figure 8).
Figure 8. Plot of absorbance at 433 nm vs. concentration of NOFe(II)EDTA

Total Suspended Solids, Volatile Suspended Solids, Ash Content
Samples taken from the reactor were centrifuged and the centrifugate was analyzed for total suspended solids, volatile suspended solids, and total non-volatile suspended solids (mineral ash) content according to procedure described in Standard Method 2540. Volatile suspended solid content is used as an approximation of total biomass concentration.

Quantitative analysis of ethanol and products of its oxidation
Quantitative analysis of ethanol and products of its oxidation was performed using a Hewlett Packard (HP) 5890A capillary gas chromatograph equipped with a split injector held at 200 °C, and a flame ionization detector. The column used for analysis was a 60m x 0.25 mm internal diameter fused silica capillary column coated with a 0.25 µm film of a cross-linked version of SP-1000® (commercially known as Nukol®). A helium carrier gas with an average linear velocity of 30 cm/sec at 50 °C was used. The column head pressure was maintained at 270 kPa. Approximate elution times for analytes of interest are 3.5 minutes for acetaldehyde, 6.5 minutes for ethanol, and 12.5 minutes for acetic acid. Detection limits are 5, 5, and 50 parts per million by volume, respectively with R² values of 0.999 for all analytes in the region between 1000 ppm and detection limit.
Figure 9. Plot of gas chromatograph integration area versus analyte concentration.

RESULTS AND DISCUSSION

Following is a brief discussion of preliminary results from batch analyses of the substrate limited kinetics of reduction of the nitrosyl adduct of ferrous EDTA, and reduction of ferric EDTA. In addition, issues related to the selective removal of mercury from the reactive process stream are considered.

**Batch Kinetic Tests - NO•Fe(II)EDTA²⁻**

The following figure shows representative kinetic batch test data collected for a 0.02 M solution of NO•Fe(II)EDTA²⁻ with a stoichiometric initial concentration of ethanol.
From the plot in Figure 10, the initial rate of NO reduction was determined. These experiments were carried out at several initial ethanol concentrations. It was observed that NO reduction rate increased with increasing ethanol concentration to a critical concentration above which the initial rate decreases (Figure 11).
Figure 11. These data suggest that relatively high (super-stoichiometric) concentrations of ethanol in solution will result in substrate inhibition of microbially-mediated reduction of NO•Fe(II)EDTA$^{2-}$.

Decreased rate of reduction of [NO•Fe(II)EDTA$^{2-}$] with increasing ethanol concentration above an initial ethanol concentration of 0.008 suggests substrate inhibition of microbially-mediated reduction. Kinetic coefficients were determined by plotting the double inverse of Figure 11 (a Lineweaver-Burke plot). The linear portion of the double inverse plot was used to determine Monod kinetic constants (y intercept being 1/k, and the slope being $K_S/k$) (Figure 12).
Figure 12. Lineweaver-Burke plot – inverse of reaction velocity as a function of inverse of initial substrate concentration is used to estimate kinetic constants.

As can be observed in Figure 12, the data fail to plot linearly at higher substrate concentrations. This increase in the inverse of the initial rate with decreasing inverse in initial substrate concentration is indicative of substrate inhibition. As a result, a modification to the Monod NO reduction rate expression must be made to properly account for the affect of substrate concentration on nitrosyl adduct reduction rate. Several models describing substrate limited growth with substrate inhibition have been described in the literature. One example that provides a fair approximation of empirically observed kinetics is the Haldane substrate inhibition equation:

\[
\nu = \frac{V_{\text{max}}[S_0]}{K_M + [S_0] \left(1 + \frac{S_0}{K_i}\right)}
\]  

(7)

Reduction of NO·Fe(II)EDTA$^{2-}$ was inhibited at super-stoichiometric concentrations of EtOH ($K_s = 0.00917027$ M EtOH, $k = 0.0091$ M NO/g VSS/l*hr, $K_i = 0.0047$ M EtOH).

Analysis by gas chromatograph shows that biogas composition is primarily nitrogen gas and carbon dioxide, verifying that NO reduction is carried out to completion (no $N_2O$ formation observed) and sulfate reduction/methanogenesis is minimal (Figure 12).
Figure 13. Prototype scale bioreactor gas composition

Similar data were collected during ferric EDTA reduction batch tests (see sample data in Figure 14). Batch tests showed that Fe(III)EDTA reduction proceeds according to the Monod kinetic expression for substrate limited growth ($K_s = 0.0172$ moles ETOH/l, $k = 0.0141$ M Fe(III)EDTA/g VSS/l*day) (Figure 15 and Figure 16). Figure 16 suggests that iron reducers may be inhibited at higher initial ethanol concentrations. Additional tests are being conducted to verify this trend.
Figure 14. In this representative data from a Fe(III)EDTA reduction batch test, COD consumption is coupled with Fe(III)EDTA reduction.

Figure 15. Plot of initial Fe(III)EDTA reduction rate as a function of initial substrate concentration with preliminary Monod fit.
Figure 16. Sample data showing Lineweiver-Burke Plot of Fe(III)EDTA reduction data

Possible Selective Precipitation of Hg
Initially, cultivation of a small SRB population in the mixed culture present in the bioreactor was seen as an opportunity to convert free mercury in solution to a highly insoluble metal sulfide precipitate. To that end, the prototype system was operated under the following conditions:

- Operated bioreactor at a lower oxidation reduction potential to promote a small amount of sulfate reduction (approximately -170 mV with standard hydrogen electrode)
- Maintained a low concentration of dissolved sulfide in solution (around three ppm)
- Maintain a low concentration of iron sulfide particulate that allows mercury capture through iron displacement
- Separate metal sulfide precipitate with biomass following anaerobic bioreactor

Maximum observed sulfide in bioreactor effluent was 7.22 mg/l, mean of 1.93 mg/l (n of 23, st.dev. 1.69 mg/l). During operation under NO reducing conditions, maximum observed aqueous sulfide concentration was 3.6 mg/liter, with a mean sulfide concentration of 1.84 mg/liter (n of 17, standard deviation of 1.3 mg/l). These concentrations of incidentally formed aqueous sulfide would be sufficient to promote the precipitation of essentially all oxidized mercury in solution.
However, literature review revealed that mercury sulfide will be methylated by active SRB. In the previously described configuration, it would be unadvisable to promote sulfate reducing conditions, since it will not be possible to sufficiently separate mercury sulfide precipitate from the sulfate reducing bacteria that are responsible both for sulfide production and methylation of mercury. As a result of this realization, preliminary consideration has been given to an alternative configuration that would allow formation of mercury sulfide while preventing contact between sulfide precipitate and SRB responsible for methylation. Characteristics of the alternative configuration include:

- Generation of iron sulfide in a small, high-rate sulfate reducing bireactor using sulfate and iron sources that are mercury free
- Introduction of biogenic FeS to a larger reactor where NO and Fe(III)EDTA reduction reactions occur.
- Removal of mercury from the active process stream through displacement of iron present as a sulfide
- Removal of iron sulfide precipitate with reactor biomass
- Chemical or thermal inactivation of bacteria in removed solids to prevent methylation
- Production of essentially mercury free gypsum product
- Configuration can be applied to most wet scrubbing processes

Batch tests were conducted using copper to determine the rate at which it would displace iron in an iron sulfide precipitate/biomass.

![Graph showing Cu(II) Concentration vs. time](image)

Figure 17. Rapid replacement of iron from iron sulfide using copper.

It was also demonstrated that in the presence of ferrous sulfide (FeS), more active divalent cations (copper was again used as a surrogate for mercury) rapidly replace the
iron in the sulfide complex. This serves as a useful physical/chemical mechanism by which mercury can be removed from spent scrubber solutions. However, methylation of the formed mercury sulfide remains a concern. In this situation, it would be necessary to inactivate the bacteria present in the precipitate through chemical or thermal treatment. A significant advantage of using FeS to remove Hg\(^{2+}\) through a chemical displacement (replacement) mechanism is that the Hg can be removed from solution without the process water ORP being as low as would be required by an active sulfate reducing reactor. Also, all sulfide present will be bound with a divalent metal molecule, and free dissolved sulfide would not rob iron from the metal chelate (as has been observed in sulfate reducing conditions).

**CONCLUSIONS**

Preliminary conclusions from the ongoing research include:

- Microbially-mediated Fe(III)EDTA\(^-\) reduction proceeds according to Monod kinetic model.
- Substrate inhibition was observed in the microbially-catalyzed reduction of the nitrosyl adduct of ferrous EDTA.
- Spectrophotometric method can be used to quantitatively determine Fe(III)EDTA\(^-\) and NO\(\cdot\)Fe(II)EDTA\(^2-\) concentrations in solution.
- Voltage-sweep electrochemical method can be used to quantitatively determine Fe(III)EDTA\(^-\) concentration.
- Selective removal of mercury should be possible if sufficient process configuration and control is implemented to prevent establishment of methylating conditions.

**FUTURE WORK**

Future investigation along these lines should include:

- Study of methylation rates in biologically active wet scrubber systems
- Evaluation of membrane separation technologies for separation of dissolved sulfide from sulfate reducing bacteria
- Evaluation of membrane filtration technologies for separation of fine suspended metal sulfide precipitate from spent scrubber process water
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XXVI. “Hydrogen Production via the High-Temperature, High-Pressure Homogenous Water-Gas Shift Reaction in a Membrane Reactor”

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HYDROGEN PRODUCTION VIA THE HIGH-TEMPERATURE, HIGH-
PRESSURE HOMOGENEOUS WATER-GAS SHIFT REACTION IN A
MEMBRANE REACTOR

Annual Report for the DOE – University Partnership Program
Period 08/02 to 08/03

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1. Introduction

Gasification of coal or any other carbon-based materials is considered to be the transition technology towards a Hydrogen Economy. The effluent stream from the gasifier is constituted primarily by a mixture of CO, CO\(_2\), \(H_2\) and \(H_2O\). The yield of hydrogen may be increased by reacting the CO with an excess of steam, i.e. via the *water-gas shift reaction* \((CO + H_2O \leftrightarrow CO_2 + H_2)\). In the current state of technology the high-temperature, high-pressure effluent stream is cooled down and sent to a high-temperature shift reactor (400\(^\circ\)C) followed by a low-temperature shift (250-300\(^\circ\)C). Although the water-gas shift reaction coupled directly to the gasifier would represent a more cost-efficient and straightforward process, the cooling down is essential due to the low equilibrium conversion of the water-gas shift reaction at high temperatures (>600\(^\circ\)C). This equilibrium limitation can be overcome, however, by using a hydrogen-selective membrane reactor were the continuous permeation of hydrogen would shift the reaction towards completion. Moreover, the high-temperature operation would eventually preclude the need of a catalyst, while the high-pressure would greatly enhance the flux of hydrogen through the membrane. The goal of this project is study the feasibility of this approach, namely to conduct the gas-phase water gas shift reaction in a membrane reactor at the temperature and pressure commonly encountered in industrial gasifiers. This project comprises two major areas: a) the study of the high-temperature, high-pressure, gas-phase kinetics of the reaction (a completely novel piece of work), and b) the study of the performance of the reaction when carried out in a membrane reactor at those conditions. This report will summarize briefly the results obtained until August 2003, as well as some of the key points to be tackled in the next year.
2. Accomplishments

- The first experimental study of the high-temperature, high-pressure kinetics of the gas-phase reverse water gas-shift reaction was conducted. The kinetics of the reaction were studied under ideal conditions, i.e. in the presence of an inert material, as well as in the presence of a representative construction material, i.e. Inconel® 600. The results have been presented in the meetings of the American Institute of Chemical Engineers and of the American Chemical Society. The work has found significant interest by third parties and a potential collaboration with industry to extend its scope is being explored. A journal paper will be published in the AIChE Journal (manuscript accepted for publication is included as Appendix).

- The first experimental study of the high-temperature, high-pressure forward water-gas-shift reaction is underway. Besides studying the reaction in quartz and Inconel® 600 reactors, the effect of potential membrane materials (Pd and PdCu alloys) was examined. The results are summarized in this report. Most of the information presented here was extracted from the draft of a journal paper that will be submitted for publication early next year. The draft has not yet been fully corrected and therefore the data should not be cited as definitive.

3. Experimental results on the forward Water-Gas Shift Reaction

3.1. Background and significance
The water-gas shift reaction, WGSR, Reaction 1, is well-known and used in industry as a means to increase the hydrogen yield in the production of hydrogen and/or to adjust the CO/H₂ ratio for Syngas applications.

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41 \text{ kJ/mol} \quad (1) \]

The WGSR is an equilibrium-limited reaction, with decreasing temperature favoring increased equilibrium conversion of carbon monoxide and steam to carbon dioxide and hydrogen. Therefore, the current industrial approach for the WGSR requires cooling the gasifier effluent stream before entering the “high-temperature” water-gas shift, WGS, reactor at 593-723K, which utilizes a packed bed of iron-based catalyst. The effluent from this reactor is usually fed to a “low-temperature” shift reactor at 473-523K, which employs a copper-based catalyst.

An alternative gasification plant concept studied by the US Department of Energy for the production of hydrogen in a Hydrogen Economy suggests to carry out the WGSR at high-temperature in a hydrogen-selective membrane reactor (Parsons, 2002). The gasifier effluent would be filtered and then introduced directly to the membrane reactor where the reaction and separation processes could be accomplished simultaneously. Unlike a conventional reactor, high conversions could be achieved at high temperature (despite the low value of the equilibrium constant) in a membrane reactor because the hydrogen partial pressure in the retentate would diminish as \( H_2 \) diffused through the
membrane into the permeate stream. The permeance of palladium-based membranes increases with temperature, therefore an increased membrane flux would result at elevated temperature. Moreover, the reaction rate of the homogeneous WGSR could be high enough that permeation through the membrane would limit reactor performance, thereby eliminating the need for the introduction of heterogeneous catalyst particles. The membrane reactor would produce a high-temperature, high-pressure retentate stream containing CO\textsubscript{2} and steam that could be sequestered after recovering heat and condensing water from the stream. The high-temperature, low-pressure, high-purity H\textsubscript{2} permeate stream would serve as an energy source.

The WGSR is reversible and the reaction rate of the reverse water-gas shift reaction, rWGSR, has been recently studied at elevated temperature and pressure in quartz and Inconel reactors (Bustamante et al., 2003). Graven and Long (1954) had previously conducted the only detailed studied of both low-pressure, high-temperature forward and reverse WGSR. Their rWGSR, rate constant values were somewhat larger than the reported in two later studies (Tingey, 1967; Kochubei and Moin, 1969); additionally, the difference in the energies of activation was much larger than the experimental error. Our recent paper on the rWGSR (Bustamante et al., 2003) addressed the discrepancies in the previous literature and showed that they could be related to the influence on the overall kinetics of an induction period where the concentration of the chain-carrier increases with time. However, no other complete studies on the low-pressure, high-temperature fWGSR are available in the open literature to determine whether the results published by Graven and Long on rate constant for the fWGSR might also be biased.
The forward reaction, fWGSR, is of more relevance to the design of post-gasifier membrane reactors than the reverse reaction, however. The heterogeneous fWGSR has been studied extensively (e.g. Newsome, 1980; Jianguo and Froment, 1989; Salmi and Hakkarainen, 1989; Keiski et al., 1993; Rhodes et al., 1995; Lund, 1996; Bunluesin et al., 1998; Li et al., 2000) at temperatures below 873 K. Studies of the homogeneous fWGSR at elevated temperatures, T>1073K, are uncommon due to the low equilibrium conversions attained in conventional reactors at those conditions. Some early investigations were performed, however, to explore the effect of the fWGSR in the oxidation of CO in the presence of water vapor (Hadman et al, 1932; Bradford, 1933; Long and Sykes, 1952).

Mechanism of the gas-phase fWGSR Bradford (1933) proposed a simple gas-phase mechanism for the WGSR. The mechanism, shown below for the fWGSR, is a chain reaction mechanism. Reaction 2 provides the chain initiation by the reaction of H\textsubscript{2}O with any gas-phase molecule (designated by M). Reactions 3 and 4 are the propagation steps, while reaction 5 is the termination step.

\[ H_2O + M \xrightarrow{k_1} H + OH + M \]  \hspace{1cm} (2)

\[ CO + OH \xleftarrow{k_2} \xrightarrow{k_1} H + CO_2 \]  \hspace{1cm} (3)

\[ H_2O + H \xleftarrow{k_3} \xrightarrow{k_1} OH + H_2 \]  \hspace{1cm} (4)

\[ H + OH + M \xrightarrow{k_4} M + H_2O \]  \hspace{1cm} (5)
The steady-state approximation for the concentration of the chain-carriers (H and OH) leads to the following expression for the rate of reaction, Equation 6, under the conditions of low conversions:

\[
    r = \frac{d[CO_2]}{dt} = \left[ \frac{k_1}{k_{-1}} k_2 k_3 \right]^{0.5} [CO]^{0.5} [H_2O] 
\]

(6)

The rate constant for the fWGSR is then (Equation 7),

\[
    k = \left( \frac{k_1}{k_{-1}} k_2 k_3 \right)^{0.5} 
\]

(7)

And the rate can be expressed as,

\[
    r = \frac{d[CO_2]}{dt} = k[CO]^{0.5} [H_2O] 
\]

(8)

An estimation of the energy of activation and pre-exponential factor, made by using in Equation 7 the values of \( k_1, k_{-1}, k_2, \) and \( k_3 \) reported in the GRI database (GRI, 2000), gives the values of 72.8 kcal/mol and 7.68E13 (cm\(^3\)/mol\()^{0.5} \) s\(^{-1} \), respectively. Experimental results from Graven and Long (1954) are 65.5 kcal/mol and 7.97E12 (cm\(^3\)/mol\()^{0.5} \) s\(^{-1} \), respectively, which yield rate constant values consistently greater than those obtained using the Bradford mechanism and GRI database, Figure 1. However, the value of the energy of activation appears to be in good agreement with the value obtained from the Bradford mechanism. An estimation of the pre-exponential factor and energy of activation from the results reported by Hadman and coworkers (1932), i.e. utilizing Eq. 8,
for the low-pressure, high-temperature (973-1073 K) fWGSR gives 2.22E14 (cm³/mol)⁰.⁵ s⁻¹ and 76.3 kcal/mol, respectively, giving rate constant values slightly lower than those predicted from the Bradford mechanism and GRI database rate constants; the energy of activation is also in good agreement with the value derived from the Bradford mechanism.

Figure 1. Arrhenius representations of the fWGSR rate constant presented in a literature correlation (Graven and Long, 1954), extracted from literature data (Haldman, 1932) and based on the Bradford mechanism combined with GRI database values for individual rate constants (GRI, 2000), Equation 6.

In view of the discrepancies of the previously reported rate constant values what could point out the importance of an induction period on the kinetics, the first objective of this investigation was to determine the high-temperature fWGSR at elevated temperatures and to assess the effect of the high-pressure on the rate constant. The effect of potential membrane materials (Pd and Pd-Cu alloys) on the reaction was then
determined. Finally, the impact of the reactor walls on the reaction was determined by carrying out the reaction in an Inconel® 600 reactor.

3. 2. Experimental

The experimental set-up has been described in detail elsewhere (Bustamante et al., 2003). The reactants were fed premixed to the reactor depicted in Figure 2. CFD modeling demonstrated that the reactor behaves like a laminar flow reactor, with small deviations from the ideal behavior, i.e. the average residence time was slightly lower than the expected from a tubular flow reactor (Bustamante et al., 2003). Typically, the reactor length was set at 19 mm, giving a volume of 1.8 cm$^3$; Figure 3 shows a schematic representation of the reactors. The volume of the annular space, providing the rapid heat-up of the reactants from 873K to the reaction temperature, was less than one-tenth of the reactor volume; no detectable reactant conversion occurred in that zone. (Control experiments with the quartz reactor had no detectable level of conversion at temperature lower than 973K.) The reaction pressure was controlled with a stainless steel Badger Research pressure control valve (PCV) employing a control loop with a pressure indicator (PI). The reaction temperature was controlled with a ceramic resistance heater using a control loop with a coaxially mounted, dual element type-K thermocouple (TI), which was placed approximately 3 mm from the reactor. The temperature profile inside the reactor was determined in control experiments flowing pure gases. Typically, a deviation of +/- 5K from the average temperature was observed; kinetic results were corrected to account for this factor.
Figure 2. Experimental set-up for the kinetic studies.

Figure 3. Inconel and Quartz reactors configuration. The actual reaction zone is shadowed.
Only CO and H₂O were fed to the reactor, i.e. no inert diluent gases were used. In the determination of the exponents of the rate expression, the partial pressure of one of the reactants was kept constant while the total pressure was varied. De-ionized liquid water, pumped by an ISCO 500D pump, was injected into a CO stream through a 0.004” ID tubing. Flowrate of CO (99.999%) was controlled with a Brooks 5850i mass flow controller. Tubing upstream and downstream the reactor was heated-up to about 150°C (423 K) in order to prevent condensation of water before the GC analysis. This temperature imposed a maximum to the partial pressure of steam in the high-pressure experiments; typically, the highest concentration of water under these conditions was 30%. An oxygen trap was located in the CO inlet line before the reactor to eliminate the pronounced catalytic influence of O₂ on the reaction. Argon was continually bubbled in the water reservoir to prevent diffusion of air into the water stream. The concentration of O₂ was below detectable limits for all the experiments.

A GC (HP-5890 II) equipped with a TCD detector was used to quantify all the components of the reactor effluent. A porous polymer (HaySep® D) was used as column packing and argon was employed as the carrier gas. The only detectable products in the quartz experiments were CO₂ and H₂. A CO₂/H₂ ratio greater than one (the ratio expected from the stoichiometry of the fWGSR, Reaction 1) was observed for most experiments in the quartz reactor, however. The CO₂/H₂ ratio at the reactor outlet was typically in the range of 1.1 – 1.4, but ratios as high as 1.9 were also observed. Formation of carbonaceous particles after the reaction suggested that the higher CO conversion could be attributed to the CO disproportionation or Boudouard reaction, reaction 9.
The build-up of carbon particles, which was observed to have some catalytic effect on the reaction, was minimized by flowing a 2% \( \text{O}_2/\text{Ar} \) after each experiment that were used to obtain conversion data for the fWGS reaction. The introduction of oxygen removed any traces of carbon that had deposited within the reactor via the formation of \( \text{CO}_2 \). In the experiments carried out in the Inconel® 600 reactor formation of methane, along with \( \text{CO}_2 \) and \( \text{H}_2 \), was observed and quantified.

Unless specified otherwise, the reaction rates were evaluated from the \( \text{H}_2\text{O} \) conversion, \( \text{H}_2\text{O} \) concentration and residence time. Given the high \( \text{CO}_2/\text{H}_2 \) ratio at the exit of the reactor, the use of CO conversion would over-predict the rate of reaction and rate constant. Once the CO and \( \text{H}_2\text{O} \) concentration exponents of the rate expression were elucidated, the rate constant was calculated using low-conversion data.

3.3. Results and discussion

Quartz reactor experiments

Low pressure experiments While studying the high-temperature, low-pressure fWGSR, it was critical to minimize the deposition of carbon inside the reactor. Figure 4 shows that if the reaction was conducted for a long period of time, a continuous increase of the rate of reaction was observed and significant deposits of carbon were detected throughout the reactor subsequent to the experiment. As illustrated in that figure, this effect was not significant until 10 hours had elapsed, after which the reaction rate
increased steadily. Hadman and coworkers (1932) reported a similar effect, although they attributed it to the reactor surface becoming active for the reaction. Further, Ingles (1952) showed that purified carbon (ash content, 0.15%) was active for the fWGSR and suggested that its role would be one of chain initiator for the gas-phase reaction. The carbon deposit inside the reactor was characterized by SEM-EDS and XRD analysis. SEM-EDS results did not detect any major heavy element on the sample (resolution for elements with molecular weight lower than carbon is very low, however) on the porous deposit. This carbon is most likely product of the Boudouard reaction, Reaction 8. This reaction is exothermic and consequently is favorable at moderately high temperatures (600-700°C). Visual inspection of the reactor revealed that the carbon deposits were predominantly located in the heating-up section of the reactor; the deposit found in the reactor could have been carried away by the gas flow. All the kinetic data used in the elucidation of the fWGSR rate expression presented hereafter were recorded during periods of less than 8 hours. Then an O₂/Ar mixture was fed to the system until no further CO₂ was detected, indicating that any carbon residue that had deposited was no longer present in the reactor. Carbon removal was periodically confirmed by visual inspection of the quartz reactor after the experiment. Although the inside of the reactor was clean, some residual carbon remained in the preheating section (temperature < 600°C). Model experiments did not show conversion at that low temperature, however. After switching back to the reactant mixture (CO/H₂O), two hours were permitted to elapse prior to recording data to ensure a complete sweep of O₂ from the reactor.
Figure 4. Increase of reaction rate with time on stream, fWGSR in a quartz reactor. Pressure, 0.101 MPa. Residence time, 0.22 s. Inlet composition, $y_{\text{CO}} = 0.85$, $y_{\text{H}_2\text{O}} = 0.15$, $y_{\text{CO}_2} = y_{\text{H}_2} = 0$. Only data collected during early times ($t<8$ hours) were used in kinetic study because they were considered to be unaffected by the accumulation of carbon.

The high-temperature, low-pressure fWGSR was conducted in a quartz reactor, Figure 3. The apparatus was designed primarily to collect high-pressure data representative of coal gasification conditions; therefore few low-pressure experiments were conducted. The exponents of the CO and water concentrations in the rate expression were assumed to be 0.5 and 1.0, respectively, (the exponents predicted in Equation 6) during the analysis of these low temperature experimental results. Rate constants were determined as a function of temperature, Figure 5. The scattering of the low-pressure rate constant data was primarily attributable to experimental fluctuations in maintaining a constant volumetric flowrate of low-pressure steam through the reactor. The rate constants appear to be similar to the low-pressure results reported by Graven and Long.
(1954), although the scatter of the low pressure data doesn’t allow for a correlation for the rate constant to be established.

Figure 5. Comparison of NETL low pressure fWGSR results with results of Graven and Long (1954) and with results obtained using Equation 7, which is based on the Bradford mechanism and individual reaction rate constants from the GRI database (GRI, 2000).

*High-pressure experiments* High-pressure experiments were conducted to confirm the exponent values of the rate expression. The best concentration exponents for CO and H$_2$O, as obtained from log-log plots of rate vs. concentration, were 0.49 and 0.97, respectively. These values were very close to the values of 0.5 and 1.0 associated with the Bradford mechanism, and the use of these exponent values provided a very good fit of our experimental results, as shown in Figures 6 and 7.
Figure 6. Rate expression exponent for CO. Temperature, 823°C. [H₂O] was kept constant to 0.021 mol/L while the total pressure was varied from 0.4 MPa to 1.6 MPa; residence times were in the range 0.5 – 2.5 s.

Figure 7. Rate expression exponent for H₂O. Temperature, 848°C. [CO] was kept constant at 0.097 mol/L while the total pressure was varied from 1.03 MPa to 1.24 MPa; residence times were in the range 1.3 – 2 s.
Having established the exponents of the CO and H$_2$O concentrations in the reaction rate expression, the temperature dependence of the rate constant value was determined between 1071 and 1121 K. The results are provided in Figure 8. The activation energy of the NETL correlation is 60.6 kcal/mol; 20% less than the value of 72.8 kcal/mol associated with the Bradford mechanism/GRI database correlation and 8.3% less than the value of 65.6 kcal/mol reported by Graven and Long. The rate constant values of the NETL high-pressure correlation, Figure 8, are intermediate to the Graven and Long correlation and the results obtained using Equation 7, reflecting that the pre-exponential constant of the NETL correlation is intermediate to the values of the other correlations.

---

Figure 8. High-temperature, high-pressure (1.6 MPa) fWGS in a quartz reactor. Except for pressure, conditions are similar to those in Figure 4.
In our previous study (Bustamante et al., 2003) on the kinetics of the high-temperature gas-phase RWGS we reported that our experimental energy of activation, as well as the value reported by Graven and Long (1954), were significantly lower than the predicted from the Bradford mechanism. The difference was traced to the induction period where the increasing concentration of chain carriers with time would invalidate the assumptions used in the derivation of the rate constant from the gas-phase mechanism. A similar behavior, i.e. an induction period that would lead to a wrong estimation of the energy of activation, could be expected from the fWGSR. Simulation of the gas-phase Bradford mechanism for the fWGSR, Equations 2 – 5, using a stiff numerical solver (ODE 23s, MatLAB®, maximum step size = 1E-04) confirmed that under our experimental conditions neither H nor OH would achieve their steady-state value (see figure 9). Moreover, if the concentration-time profiles obtained from the simulations are used to evaluate the rate constant under conditions similar to the experiments (i.e., inlet concentrations, reaction time, reaction rate exponents), the resultant energy of activation (Ea ~ 100 Kcal/mol) is larger and the rate constant lower than the corresponding values predicted from the mechanism. On the contrary, if the simulation is run under the constraint of inlet concentrations of H and OH close to their steady-state values, rate constants in excellent agreement with the derivation from the Bradford mechanism are predicted. This would point out to the absence of a significant induction period in our experiments, i.e. a relatively high inlet concentration of H and/or OH radicals. However, the simulation also showed that at the temperature and residence time present in the preheating section the formation of H and OH radicals from the gas-phase collisions of H2O, Reaction 2, is extremely low and exerts a negligible effect on the high-temperature reaction. The interaction with the quartz walls would not give rise to a high concentration
of radicals in the gas-phase because quartz acts a radical quencher under the experimental conditions studied here (Kondratjev and Ziskin, 1943; Bustamante et al., 2003). On the other hand, steam is known to adsorb on the loosely bound atoms in graphitic surfaces. Some early experimental work has suggested that the dissociation of the \( \text{H}_2\text{O} \) molecule in \( \text{H} \) and \( \text{OH} \) is an intermediate step in the reaction between carbon and steam (Long and Sykes, 1952). Indeed, Ingles (1952) found and enhancing effect when carrying out the reaction in the presence of pure carbon, the form of the rate expression being similar to the gas-phase reaction. He suggested that this enhancement was due to the role of carbon as a chain initiator. Moreover, the activation energy reported in that work (62 Kcal/mol) would suggest that the carbon deposited in our preheating section would be acting as a chain initiator.

Figure 9. Concentration profiles for \( \text{H} \) and \( \text{OH} \) species as a function of reaction time as obtained by numerical solution of the Bradford mechanism. Temperature (1173 K), pressure (16 atm), and inlet molar fractions (\( \gamma_{\text{CO},0} = 0.77 \), \( \gamma_{\text{H}_2\text{O},0} = 0.23 \)), were chosen to match the experimental conditions.
H₂O is an excellent collision partner (Baulch et al., 1992) for the gas-phase radical recombination reaction of H radicals to form H₂ molecules, Reaction 10, which constitutes the initiation step of the rWGSR.

\[ 2H + M \leftrightarrow H_2 + M \]  

(10)

A somewhat early onset of this reaction would result in an inhibitory effect due to the additional H-consuming reaction. To test for this possibility we added Reaction 10 to the Bradford mechanism. Figure 10 compares the expected conversions from the Bradford mechanism under the assumption of stationary-state, the results from the numerical solution of the mechanism (i.e. without any constraint), and the results from the mechanism with the addition of the gas-phase radical recombination reaction. The presence of the induction period is indicated by the shift of the conversion curve to higher reaction times. However, after relatively short reaction times, Reaction 10 begins to cause a considerable inhibition in the conversion. This effect may explain the lower value of our rate constant at high-pressure (e.g., higher conversions due to larger residence time and inlet concentrations) with respect to our low-pressure result as well as the lower slope (i.e. lower activation energy) in the high-pressure Arrhenius plot.
Figure 10. Effect of the radical recombination reaction $H + H + M \leftrightarrow H_2 + M$ on the fWGS reaction. The solid line represents the predictions of the Bradford mechanism under stationary-state conditions, while the dashed lines display the predictions from the numerical solution of the mechanism with and without considering the reaction $H + H + M \leftrightarrow H_2 + M$. Conditions are similar to Figure 9.

**Effect of Inconel® 600 surfaces on the fWGS reaction**

The fWGS reaction was conducted in an Inconel® 600 (approximate composition, 72% Ni, 17% Cr, 10% Fe) reactor to assess the potential impact that the walls of an industrial reactor might have in the gas-phase reaction at high-temperatures. There was a dramatic increase in the rate of reaction when the reaction takes place in an Inconel reactor, as shown in Figure 11. This trend is similar to that observed for the rWGS (Bustamante et al., 2003). For residence times of $0.5 - 1$ s at 0.101 MPa, equilibrium conversions are attained for temperatures as low as 700°C in the Inconel reactor. Conversions in the quartz reactor at comparable conditions were negligible. The relatively small number of
tests and the high levels of conversion attained during these experiments made it impractical to determine kinetic expressions for the fWGS reaction in an Inconel reactor. These results indicate that if the design of a membrane reactor with a metal shell incorporates reaction rates based on correlations obtained with quartz reactors, then the reaction rate will be underestimated and the reactor volume overestimated if any part of the membrane reactor is reaction-rate limited. Further, this catalytic effect may mitigate or eliminate the need to introduce a packed bed of heterogeneous catalyst particles into the reactor.

![Graph](image)

Figure 11. Low-pressure (0.1 MPa), high-temperature, gas-phase fWGSR in an Inconel® 600 reactor. Inlet composition, 77% CO – 23% H₂O. Residence time < 1s.

Methanation and Boudouard side reactions are present in the high-pressure fWGS reaction in the Inconel® 600 reactor. The amount of methane peaks around 700°C (Figure 12) which would suggest that methane is formed from the interaction of carbon
with the gas-phase mixture (i.e., H\textsubscript{2}). Effectively, Boudouard reaction is expected to be more significant at moderately-high temperatures where the trade-off between the high-rate and lower equilibrium conversions is more favorable. Additionally, SEM characterization of the carbonaceous residue showed the presence of finely dispersed nickel islands; this metal is known to catalyze both the water-gas shift reaction and the methanation.

Figure 12. Side reactions in the low-pressure water-gas shift reaction carried out in an Inconel® 600 reactor. Conditions are similar to those in Fig. 11.

**Water-gas shift reaction in the presence of Pd packing**

The quartz reactor was randomly packed with small palladium rods (3 mm length, 2 mm diameter). The reaction was carried out in conditions similar to the used in the quartz kinetic studies. Particularly, the O\textsubscript{2}/Ar treatment was carried out overnight to remove any carbon deposited on the reactor. Figure 13 compares the conversions in the
Pd-packed, quartz reactor to the predicted gas-phase and equilibrium conversions. With the fresh palladium packing a small increase in conversion is observed. However, after the standard overnight treatment with O$_2$/Ar, a significant increase in conversion was observed. The cycling between oxidizing (O$_2$/Ar) and reducing (CO/H$_2$O) environments appears to increase the conversions even further. This trend was also present in the high-pressure experiments (not shown) and could not be related to time on stream, i.e. continuous testing without O$_2$/Ar treatment brings no increase in conversion (Figure 13). Attempts to reverse the effect of oxygen on the palladium surface by treatment of the Pd-packing in the presence of hydrogen were unsuccessful. Surface chemistry characterization of the packing is currently underway.

![Graph](image)

**Figure 13.** Forward water-gas shift reaction in a Pd-packed, quartz reactor. Results are compared to the equilibrium conversions and the expected gas-phase conversions. 823°C, 1 atm, ? < 1s. Inlet concentration, 77% CO – 23% H$_2$O.
Water-gas shift reaction in the presence of PdCu packing

The forward water-gas shift reaction was also conducted in the presence of PdCu packing (80 wt% Pd, 20 wt% Cu), a sulfur-tolerant membrane material. Although conversions were larger in the presence of the PdCu packing than in the gas-phase reaction, no clear comparison can be made with the Pd packing. As it is shown in Figure 14, mass transfer limitations appear to play an important role under the experimental conditions studied. Indeed, due to the shape of the PdCu packing it could not be randomly distributed but was packed orderly, parallel to the direction of flow. This test will be repeated with randomly packed PdCu pellets with geometry similar to that of the Pd packing. However, it is clear that the O₂/Ar treatment also does enhance the conversions, similarly to what was observed with the Pd packing.

Figure 14. Forward water-gas-shift reaction in a PdCu packed, quartz reactor. Conditions are similar to Figure 13. O₂/Ar pretreatment only when indicated in the figure.
4. Future work

The water-gas shift reaction will be conducted in a membrane reactor at high temperature (900°C) and pressure (16 atm). Several reactor configurations will be explored: flat and tubular membranes. Although flat-disk membrane reactors do not optimize the surface/volume ratio, what appears to be a crucial aspect in view of the high reaction rate may cause the performance of the membrane reactor to be limited by the hydrogen permeation through the membrane, this type of reactors will facilitate the study of the effect of side reactions as well as of the effect of other gases (CO, CO\textsubscript{2}, H\textsubscript{2}O) on the permeation of hydrogen through the membrane. Pure palladium will be used in the initial tests and effort will be focused on the assembly of a thin-wall membrane reactor.

5. Literature Cited


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Appendix. Manuscript accepted for publication at the AIChe Journal
HIGH TEMPERATURE KINETICS OF THE HOMOGENEOUS REVERSE WATER-GAS SHIFT REACTION

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HIGH TEMPERATURE KINETICS OF THE HOMOGENEOUS REVERSE WATER-GAS SHIFT REACTION

ABSTRACT

The high-temperature rate of reaction of the homogeneous, reverse water-gas shift reaction (rWGSR) has been evaluated in quartz reactors with rapid feed pre-heating under low and high-pressure conditions. The form of the power-law rate expression was consistent with the Bradford mechanism. The Arrhenius expressions for the reaction rate constant corresponding to the empty reactor were in very good agreement with the low-pressure results of Graven and Long, but yielded rate constants roughly four times greater than those obtained in our packed reactor and those reported by Kochubei and Moin and by Tingey. Reactor geometry was not responsible for these differences because CFD simulations revealed similar residence time distributions and comparable conversions when the same kinetic expression was used to model the rWGSR in each reactor. Most likely, the empty NETL reactor and the Graven and Long reactor did not attain an invariant value of the concentration of the chain carrier (H) at low reaction times, which led to an overestimation of the rate constant. Conversions attained in an Inconel® 600 reactor operating at comparable conditions were approximately two orders-of-magnitude greater than those realized in the quartz reactor. This dramatic increase in conversion suggests that the Inconel® 600 surfaces, which were depleted of nickel during the reaction, catalyzed the rWGSR.
INTRODUCTION

The Water-Gas Shift Reaction

The water-gas shift reaction, Equation 1, is important as a method for further enhancing the yield of hydrogen from industrial processes such as the steam reforming of natural gas or the gasification of heavy carbonaceous materials. Syngas mixtures containing mostly hydrogen and carbon monoxide are typically generated at elevated temperatures via the conversion of natural gas, coal, bio-mass, petroleum and organic wastes (Wender, 1996). Steam is then added to the CO – H₂ feed mixture prior to being introduced to water-gas shift (WGS) reactors to convert the CO to CO₂ and additional H₂. However, thermodynamic equilibrium favors high conversion of CO and steam to hydrogen and carbon dioxide at low temperatures. Therefore, the water-gas shift reaction is commonly conducted at low temperature in the presence of catalysts that enhance the reaction rate.

\[
CO + H₂O \leftrightarrow CO₂ + H₂ \quad \Delta H = -41 \text{ kJ/mol} \quad (1)
\]

The water-gas shift reaction is reversible and several correlations for the equilibrium constant have been published (Moe, 1962; Benson, 1981; Babieri and DiMaio, 1997; Singh and Saraf, 1977). A simple temperature-dependent correlation (Moe, 1962) was used to estimate \(K_{eq}\) in this study.
\[ K_{eq} = \exp \left( -4.33 + \frac{4577.8}{T(K)} \right) \] (2)

There are numerous kinetic studies of the catalyzed forward water-gas shift reaction at temperatures up to 873 K (Newsome, 1980). Kinetic studies of the forward or reverse water-gas shift reaction at elevated temperatures (>873 K) are uncommon, however. This scarcity of data is probably attributable to the low equilibrium conversions of CO that can be achieved in conventional reactors operating in this temperature range. High conversions at elevated temperature can be achieved in a hydrogen-permeable membrane reactor, however (Enick et al., 2000). Further, extreme temperatures could enhance the kinetics to the extent that the reaction would proceed rapidly in the absence of heterogeneous catalysts. Therefore, an understanding of the forward and reverse reaction rates would be useful in the design of high temperature, hydrogen-permeable membrane reactors. The reverse water-gas shift reaction (rWGSR) is the focus of this investigation.

*The Reverse Water-Gas Shift Reaction*

Several investigations of the high temperature (>1148 K), low pressure (< 0.101 MPa), homogeneous, uncatalyzed rWGSR have been conducted. Power law correlations that comply with the Bradford mechanism (Bradford, 1933), a simple gas-phase chain-reaction model, have been used to model the rate of reaction. Although models based on a more comprehensive network of elementary steps, such as a model for the oxidation of \( \text{H}_2 \) and CO in sub- and supercritical water (Holgate and Tester, 1994), could be used to describe the reaction, we have found that such a network yields results nearly identical to
the Bradford mechanism. Therefore, the Bradford mechanism was considered to be an adequate representation of the rWGSR under the conditions studied.

The Bradford mechanism, provided below, employs M as any gas phase molecule:

\[
\begin{align*}
H_2 + M \xrightarrow{k_1} 2 \, H + M & \quad \text{Dissociation of hydrogen} \\
H + CO_2 \xleftrightarrow{k_2} CO + OH & \quad \text{Reaction between H and CO}_2 \\
OH + H_2 \xrightarrow{k_3} H_2O + H & \quad \text{Reaction between OH and H}_2 \\
M + 2H \xrightarrow{k_4} M + H_2 & \quad \text{Re-association of hydrogen}
\end{align*}
\] 

It has been shown (Graven and Long, 1954; Tingey, 1966) that the condition of low conversion (i.e. negligible effect of the opposing reaction) and the assumption of a stationary state for the concentrations of the intermediates (H and OH concentrations do not change significantly with respect to time) leads to the following rate expression, Equation 7,

\[
r = \frac{d[CO]}{dt} = \left[ \frac{k_i}{k_{-1}} \right]^{0.3} k_2 [H_2]^{0.5} [CO_2]
\] 

Accordingly, the rate constant for the rWGSR may be expressed as shown in Equation 8.
\[ k = \left[ \frac{k_1}{k_{-1}} \right]^{0.5} k_2 \] (8)

Therefore, the expression for the rate of reaction in terms of \( k \) becomes,

\[ r = \frac{d[CO]}{dt} = k[H_2]^{0.5}[CO_2] \] (9)

The temperature-dependence of the rate constant, \( k \), is described by the Arrhenius equation

\[ k = k_0 e^{-\frac{E_A}{RT}} \] (10)

Most prior investigations of the homogeneous rWGSR at elevated temperature have employed power law models that are consistent with Equations 9 and 10. The activation energy and pre-exponential constant associated with each of these studies are summarized in Table 1. Graven and Long (1954) studied the rWGSR in the temperature range 1148-1323 K. CO\(_2\) and H\(_2\) were introduced to the reactor along with the N\(_2\) diluent gas to control partial pressures. Their cylindrical quartz reactor (3.4 cm diameter, 6.4 cm length) featured tangential feed and withdrawal lines (1.5 mm ID). They reported that the reaction occurred rapidly in the gas phase without any heterogeneous contribution from the quartz surfaces. Tingey's reactor (Tingey, 1966) consisted of a cylindrical quartz tube (3.3 cm ID, 27.1 cm length) that contained a co-axial quartz insert (2.2 cm ID, 21.0 cm length), resulting in a long annular flow section that was preceded and followed by short cylindrical sections (3.3 cm ID, 6.1 cm combined length). Coaxial capillary tubing served
as feed and effluent channels for the reactor. Kochubei and Moin (1969) designed empty quartz reactors (ID ranging from 0.6 – 6.5 cm) that employed a static mixer to mix the pre-heated hydrogen and carbon dioxide. The effluent gases were withdrawn from a capillary tube (1.5 mm ID) extending in the same axial direction as the cylinder, but located along the outside edge of the reactor. Tingey (1966) and Kochubei and Moin (1969) published results that were in very good agreement, with both obtaining lower values for the rate of reaction than Graven and Long (1954). Tingey suggested that the higher reaction rate reported by Graven and Long (1954) may have been caused by traces of oxygen in their feed stream that acted as a homogeneous catalyst, but was unable to substantiate this claim.

The values of the rate constant, $k$, for the low-pressure rWGSR are presented as a function of inverse absolute temperature over the 1123 – 1223 K in Figure 1. The pre-exponential constant and activation energy of each correlation is listed in Table 1. The prediction of the Karim and Mohindra (1974) model of the water-gas shift reaction as twelve, simple, reversible, intermediate reaction steps involving nine species at temperatures up to 2500 K which used kinetic data available at the time is also presented. Given the disagreement among these reported values, our first objective was to investigate the rWGSR kinetics at low-pressure conditions in quartz reactors. The rWGSR kinetics were then determined in a pressure-equilibrated quartz reactor that enabled the reaction to be conducted at elevated pressures similar to those attained in a gasifier. Finally, the rWGSR was conducted in an Inconel® 600 vessel at low- and high-pressure conditions in order to assess the catalytic influence of the metal reactor wall on the reaction rate. The reactors were designed to be analogous to the industrial application:
rapid heating of a hydrogen and carbon dioxide gas mixture followed by introduction to
the quartz or Inconel® 600 reactor. In all cases, only the reacting gases, CO₂ and H₂, were
introduced to the reactor. Gas phase partial pressures were adjusted by varying both total
pressure and feed composition.

**EXPERIMENTAL**

**rWGSR Apparatus**

The Hydrogen Membrane Test Unit Number 1 (HMT-1) at the US DOE National
Energy Technology Laboratory (NETL) was designed to attain high-pressure (up to 3.0
MPa), high-temperature (up to 1198 K) conditions in Inconel® 600 or quartz reactors,
Figure 2. The reaction pressure was controlled with a stainless steel Badger Research
pressure control valve (PCV) employing a control loop with a pressure indicator (PI). The
reaction temperature was controlled with a ceramic resistance heater using a control loop
with a coaxially mounted, dual element type-K thermocouple (TI), which was placed
approximately 3 mm from the reactor. An Iconic Genesis process control program
provided the process control for the unit. It was not possible to place a thermocouple
inside the reactor to monitor the outlet temperature due to the catalytic effect of the metal.
The existence of a temperature profile, however, was verified with hydrogen or carbon
dioxide flowing through the system. Under typical low-pressure experimental conditions,
the temperature within the reaction zone varied by ±8 K along its length from the average
temperature that was used in the evaluation of the data.
**Reactor Feed**

The flow rates of the feed gases, $\text{H}_2$ and $\text{CO}_2$ (99.999%) were controlled with Brooks 5850i mass flow controllers (FCVs) and verified with a soapfilm flow meter. Kinetic studies were conducted using either an equimolar feed mixture introduced to the reactor over a range of flow rates or feed mixtures in which the concentration of one reactant was held constant while the concentration of the other was varied. Partial pressures were established by adjusting feed gas composition and total pressure; no inert diluent gases were employed. An oxygen trap was located before the reactor to eliminate the pronounced catalytic influence of $\text{O}_2$ on the reaction. Concentrations of oxygen in the feed remained below the gas chromatograph detection limit of 1 ppm.

The reactants were premixed and then fed to the quartz reactor through quartz tubing and a narrow annulus with a volume of 0.2 cm$^3$, approximately one tenth that of the reaction zone volume. The gases were rapidly heated from 873 K to the reaction temperature as they passed through the annulus (annular gap = 0.13 mm). Control experiments indicated that no conversion of the $\text{CO}_2$ in the quartz reactor was detectable for reaction temperatures below 873 K.

**Reaction Zone**

A pressure-equilibrated quartz reactor or Inconel® 600 reactor was accommodated in the HMT-1 unit. The geometry of these reactors is illustrated in Figure 3 and the dimensions of the reaction zone are provided in Table 2. When the quartz reactor was operated at elevated pressure, a pressure equalization fluid, $\text{CO}_2$, was maintained at the same pressure as the reacting gases within the reactor to prevent stresses across the
reactor walls. The pre-heated feed gases entered the reaction zone and flowed upward toward the top of the narrow inner tube that led to the reaction zone exit. Residence times of 0.3 - 0.5 s were chosen for the reactions conducted in the quartz reactor at low pressure. This yielded conversions of 0.1 - 0.8 %, which were great enough to assure accurate calculation of conversion. Residence times of 2-10 s were realized at high-pressure conditions because of the increased gas density. Comparable residence times were selected when the Inconel® 600 reactor was used.

The reacting gases then flowed downward through the inner tube and exited the reaction zone. The reaction products were rapidly cooled to 873 K as they flowed toward the reactor effluent line. The temperature of the tubing was maintained at 573 - 673 K, which was hot enough to prevent condensation of water produced by the rWGSR but cold enough to prevent further conversion of the reactants.

**Effluent Gas Stream**

The effluent of the reactor was analyzed with a gas chromatograph equipped with a TCD detector. Argon was used as carrier gas. The GC column, HayeSep® D (porous polymer), allowed the separation and quantification of H₂, CO, CO₂ and H₂O in the range of concentrations of interest. Concentrations of oxygen in the product remained below the detection limit of 1 ppm. Reaction rates were evaluated from the CO₂ conversion, CO₂ concentration and residence time. Rates calculated from H₂ were found to be identical. Once the CO₂ and H₂ concentration exponents of the rate expression were elucidated, the
rate constant was calculated from the rate value by using the integrated form of a PFR reactor design equation (Fogler, 1999).

**Computational Fluid Dynamics Numerical Simulations**

The steady-state flow of the gases through the empty quartz reactor used in this study was modeled using Computational Fluid Dynamics (CFD). Similar computations were also performed for the reactors described by Graven and Long (1954), Tingey (1966), and Kochubei and Moin (1969). The objective of these computations was to determine whether the reactor geometry could have influenced the kinetic results. Mixing within the reactor was assessed using residence time distribution plots that were determined by simulating the effluent concentration of a gas (hydrogen) that was pulsed into the feed stream (nitrogen). Additionally, the rWGSR was modeled in each reactor under the same conditions of temperature, pressure, residence time, and rate constant expression to elucidate the effect of the non-ideal flow on the kinetic results. A commercial CFD software (Fluent, 2003), was used for all the numerical simulations.

*Flow Field*

The geometries were generated and meshed by using Gambit 2.0 software (Fluent). Axisymmetric two-dimensional geometries that incorporated a mesh of quads were used for the NETL quartz reactor and the Tingey (1966) reactor. Three-dimensional geometries that incorporated a mesh of hexahedral/tetrahedral hybrid grids were used for the Graven and Long (1954) reactor and the Kochubei and Moin (1969) reactor. Finer
grids were applied at the reactor inlet, reactor outlet and near the reactor walls in all cases.

The governing equations that were solved in order to describe the flow of gas through the isothermal reactors consisted of the continuity equation and the Navier-Stokes equations. The continuity equation can be expressed in the following form:

\[
\frac{\partial \rho}{\partial t} + \nabla (\rho \vec{v}) = 0
\]  

(11)

where \( \rho \) is the density, \( t \) is time, and \( \vec{v} \) is the velocity vector. The conservation of momentum equation is described as:

\[
\frac{\partial}{\partial t} (\rho \vec{v}) + \nabla (\rho \vec{v} \cdot \vec{v}) = -\nabla p + \nabla (\bar{\tau})
\]  

(12)

where \( p \) is the pressure and \( \bar{\tau} \) is the stress tensor given by

\[
\bar{\tau} = \mu \left[ (\nabla \vec{v} + \nabla \vec{v}^T) - \frac{2}{3} \nabla \bar{I} \right]
\]  

(13)

where \( \mu \) is the molecular viscosity, \( \bar{I} \) is the unit tensor, the superscript \( T \) means transposed matrix, and the second term on the right hand side is the effect of volume
dilation. Because the flow is laminar in the reactors, no turbulence model has been included.

For steady-state calculations, the time derivative terms vanished. The governing equations were discretized by using a control-volume technique in which the algebraic equations were integrated on each control volume, yielding discrete equations that conserved each quantity on a control-volume basis. Second order upwind schemes were used for spacial discretizations. The solutions were converged quickly and the residuals were kept under 1.0E-06.

Simulation of a Tracer Input

This simulation is an unsteady-state calculation, therefore time derivative terms were included. A first order implicit method was applied to discretize the governing equations. In this simulation, the species transport scalar equations were solved in order to trace the evolution of the species. The species transport scalar equation can be written in the following form:

\[
\frac{\partial}{\partial t} (\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + R_i + S_i
\]  

(14)

where \( Y_i \) is the local mass fraction of species \( i \), \( \vec{J}_i \) is the diffusion flux of species \( i \), \( R_i \) is the net rate of production of species \( i \) by chemical reaction, and \( S_i \) is the rate of reaction by addition from the dispersed phase plus any user-defined source.
The diffusion flux of species $i$ was formulated as:

$$\tilde{J}_i = \rho D_{i,m} \nabla Y_i$$  \hspace{1cm} (15)$$

where $D_{i,m}$ is the diffusion coefficient for species $i$.

The two components used in the tracer simulation were non-reactive, therefore the last two terms in the species transport equation, Equation 14, were neglected. The flow rate at the inlet of the reactor was calculated corresponding to a residence time of 0.5 s. The inlet conditions were specified as to simulate a pulse of hydrogen into a stream of nitrogen flowing to the reactor:

$t \leq 0$ s and $t > 0.01$ s, only N$_2$ flows into the reactor.

$0 < t \leq 0.01$ s, a pulse of dilute H$_2$ (mole fraction = 0.01) is introduced.

*Simulation of the conversions inside the reactor*

When reactions are involved, the net source of chemical species $i$ due to reaction $R_i$ in the species transport scalar equation can be computed as the sum of the reaction source over the $N_r$ reactions that the species participate in:

$$R_i = M_{w,i} \sum_{r=1}^{N_r} \hat{R}_{i,r}$$  \hspace{1cm} (16)$$
where $M_{w,i}$ is the molecular weight of species $i$, $N_r$ is the number of the reactions, and

$\dot{R}_{i,r}$ is the molar rate of creation/destuction of species $i$ in reaction.

The molar rate of creation/destuction of species $i$ in reaction $r$ is given by

$$\dot{R}_{i,r} = (\nu_{i,r}^r - \nu_{i,r}^-)(k_f \prod_{j=1}^{N_r} [C_{j,r}]^{\eta_{j,r}^r} - k_b \prod_{j=1}^{N_r} [C_{j,r}]^{\eta_{j,r}^-})$$  \hspace{1cm} (17)

where

$\nu_{i,r}^r = $ stoichiometric coefficient for reactant $i$ in reaction $r$

$\nu_{i,r}^- = $ stoichiometric coefficient for product $i$ in reaction $r$

$N_r = $ number of chemical species in reaction $r$

$C_{j,r} = $ molar concentration of reactant and product species $j$ in reaction $r$ (kgmol/m$^3$)

$\eta_{j,r}^r = $ forward rate exponent for each reactant and product species $j$ in reaction $r$

$\eta_{j,r}^- = $ backward rate exponent for each reactant and product species $j$ in reaction $r$

For the low conversions observed in our study, the rate of reaction can be expressed as Equation 9. The parameters for the rate constant, Equation 10, were evaluated by determining the temperature dependence of Equation 8 using values available from the up-dated and comprehensive kinetic GRI database (GRI-MECH 3.0, 2000) for each of the elementary reactions. The resultant parameters were $k_0 = 3.52E+11$ (m$^3$/mol)$^{0.5}$ s$^{-1}$ and $E_a = 3.27E+05$ (J/mol). The residence time was set at 0.5 second for a stoichiometric feed of hydrogen and carbon dioxide.
RESULTS AND DISCUSSION

Low-pressure rWGSR in a quartz reactor

Equimolar feeds of CO₂ and H₂ were introduced at a total pressure of 0.101 MPa to the empty NETL quartz reactor that is illustrated in Figure 3. The power law exponents of the H₂ and CO₂ were assumed to be 0.5 and 1.0, respectively. The Arrhenius representation of the reaction rate data for this low-pressure rWGSR over the 1148 – 1198 K temperature range is found in Figure 4. Table 1 provides the corresponding activation energy and pre-exponential constant.

The NETL rWGS reaction rate constant was approximately 20% greater than that reported by Graven and Long (1954) as illustrated in Figure 4. The activation energy of 53.1 ± 0.9 kcal/mol [222.2 ± 3.9 kJ/mol] was slightly less than the value of 56 kcal/mol [234.3 kJ/mol] reported by Graven and Long. The measured reaction rate constant values were roughly four times greater than those reported by Tingey (1966) and Kochubei and Moin (1969), however, as shown in Figures 1 and 4 and Table 1. Thus, our low-pressure results for the empty reactor exhibited closest agreement with the results of Graven and Long (1954).

High-pressure rWGSR in a quartz reactor

Equimolar feeds of CO₂ and H₂ were introduced at a total pressure of 1.6 MPa to the NETL empty quartz reactor. A separate stream of a pressure equalization fluid, CO₂, was also maintained at 1.6 MPa in the space between the outer surface of the quartz reactor and the inner wall of the Inconel® 600 pressure vessel. The power law exponents of the
H₂ and CO₂ were determined to 0.5 and 1.0, respectively (see Figure 5 and 6). The results are summarized in Figure 4 and Table 1. The activation energy of 52.2 ± 1.2 kcal/mol [218.4 ± 5.1 kJ/mol] was slightly smaller than the low-pressure result of 53.1 ± 0.9 kcal/mol [222.2 ± 3.9 kJ/mol] and the reaction rate constant slightly less than that reported by Graven and Long. Thus, our high-pressure results for the empty reactor were also in good agreement with the Graven and Long (1954) finding.

**Effect of reactor geometry on quartz reactor results**

An attempt was made to determine the cause of the differences between the low-pressure rate constant correlations illustrated in Figures 1 and 4. Tingey (1966) suggested the relatively high reaction rate constant values reported by Graven and Long (1954) may have been caused by oxygen in their feed stream, but our rate constants derived from the empty quartz reactor were comparable to those of Graven and Long and no detectable amounts of O₂ were found in the CO₂ or H₂ feed streams or the pre-mixed feed stream. Therefore, CFD calculations were performed to determine if the reactor geometry could have influenced the kinetic results. Comparisons of the flow patterns of a non-reacting gas, the residence time distributions of a non-reacting mixture, and the conversion of the rWGSR under identical conditions were made for the NETL empty quartz reactor and the Graven and Long (1954), Kochubei and Moin (1969), and Tingey (1966) reactors.

*Flow Patterns and Residence Time Distributions* In each representation of the flow patterns within the reactor, Figures 7 – 10, the length of the vector is proportional to the velocity of the particle at the origin of the vector. The direction of the vector indicates the
direction in which the fluid located at the origin of the vector is moving. In some cases, as noted in the figure legends, portions of the reactor in which the fluid is moving at extremely high velocity are represented by a white field (rather than a group of extremely long vectors) to avoid cluttering the figure.

The NETL quartz reactor was characterized by upward flow through the large annular gap within the reaction zone followed by a flow reversal at the top of the reactor. The gas then flowed vertically downward through the inner tube. There is a very small stagnant zone above the exiting port. This is manifested in the tailing of the Residence Time Distribution, RTD, plot, Figure 11, which exhibits a distribution broader than that expected for a laminar flow reactor with axial dispersion (Fogler, 1999).

The tangential feed and withdrawal of the Graven and Long reactor induced circular flow that formed vortices within the reactor as shown by the velocity vectors along the edge of the two xy-planes in Figure 8. The performance of this reactor is very similar to an ideal CSTR as the RTD shows (Figure 12).

The Tingey reactor also had very high sweep efficiency, Figure 9. Small recirculation zones formed at the entrance of the annular section of the reactor, but the majority of the reactor volume was retained in this annular section where the reactor performed like a tubular laminar flow reactor. The flow of gases out of the annulus and toward the product port had small stagnant zones along the surfaces and no re-circulation zones. The RTD plot, Figure 11, is representative of a laminar flow reactor with dispersion, being very close to the ideal PFR behavior.
The flow field of the Kochubei and Moin reactor, Figure 10, was similar to a laminar flow reactor. It exhibited high sweep efficiency and had no significant recirculation or stagnant zones, Figure 10. However, the broader RTD and its displacement towards lower times (Figure 11) confirms the channeling observed in the flow field at the bottom part of the reactor (Figure 10). There is a small effect of the stagnant zone as well, observed in the tailing of the RTD. It was assumed that the static mixer on the left-hand side of the reaction zone mixed the CO$_2$ and H$_2$ feed streams perfectly and instantly as they entered the reactor zone.

Despite the almost ideal behavior observed in the reactors used by Graven and Long (1954) and Tingey (1966), there was a four-fold difference in the reaction rate constants reported for these investigators suggesting that the discrepancy was not related to the geometry of the reactor.

*Conversions of the rWGSR* The influence of reactor geometry on the kinetics results was also determined by modeling the rWGSR in each reactor. The rate of reaction was determined from Equation 9. The rate constant was obtained from Equation 8 using the values reported in the GRI database (GRI-Mech 3.0, 2000). The reaction conditions were 1173 K, 0.1 MPa, equimolar feed of CO$_2$ and H$_2$ and a residence time of 0.5 seconds. The results, shown in Table 3, indicate that the outlet concentrations were within 7% of one another, confirming that the reactor geometry was not responsible for the differences observed in the reported reaction rate expressions.
Effect of pressure on the quartz reactor results

Because all prior studies had been confined to ambient pressure conditions and there was a slight difference between the NETL low-pressure and high-pressure results, the effect of elevated pressure conditions employed in this study on the reaction kinetics was considered. The low-pressure experimental results of Tingey (1966) and Kochubei and Moin (1969) are in excellent agreement with the value obtained from the Bradford mechanism by using the values for the rate constant of the elementary steps reported in the GRI database (GRI-Mech 3.0, 2000) in Equation 8: $k_1$, $k_{-1}$ and $k_2$, the rate constants of the initiation (Eq. 3) step, termination (Eq. 6) step, and forward reaction of Equation 4, respectively. Although Reaction 4 is known to display pressure-dependence (Bierman et al, 1978; Fulle et al, 1996; Troe, 1998) with the rate constant being proportional to the total pressure, the pressure dependence is very weak (less than 10%) under the temperature range of interest in this study. Therefore, the very small difference between our low-pressure and high-pressure results was probably due to experimental uncertainties rather than changes in the reaction mechanism. Further, the difference of the NETL results and the Kochubei and Moin (1969) and Tingey (1967) results cannot be attributed to the pressure difference.

Effect of H and OH Not Being at Stationary State Conditions within the Reactor

The concentration of H and OH radicals within the reactor may not have been invariant as was assumed in the derivation of the expression for the overall rate constant, Equation 4. This effect was addressed to some extent in the prior investigations of the low-pressure rWGSR. Graven and Long (1954) noted an induction period for the
rWGSR, a common feature in chain-reaction chemistry. Kochubei and Moin (1969) kept the H\textsubscript{2} stream at the reaction temperature for a time long enough (15 - 1000 s) to achieve a stationary state concentration of H (i.e., the equilibrium concentration from the H\textsubscript{2} dissociation (Eq. 3 and 6)) before mixing it with CO\textsubscript{2} at the reactor inlet. Tingey (1966) stated that the geometry of the reactor was changed to minimize the observed induction period, which was attributed to heating and cooling times as well as the time to achieve invariant concentrations of H and OH radicals within the reactor.

The possibility of changing concentrations of H and OH under our experimental conditions of rapid feed heating and mixing at the reactor entrance was studied using ChemKin® (Chemkin® is a software for solving complex chemical kinetics problems. We used the application Creslaf, which models laminar, chemically reaction boundary layer flow in a tubular channel. The thermodynamic and transport data of all the species have either been calculated or collected from different available web libraries.) The NETL empty quartz reactor, Figure 7, was modeled with a tubular laminar flow reactor of comparable dimensions (1 cm diameter, 1.6 cm long). The residence time of the simulations was maintained at values similar to the observed in the experiments by adjusting the volumetric flowrate. The elementary steps of the Bradford gas-phase mechanism were used as the input for ChemKin® and rate constant values were taken from the GRI database. Figure 13 shows the molar fraction of H as a function of the distance along the reactor. The simulation results indicate that the NETL results may have been influenced by the non-stationary state concentration of H, which would vary significantly along the first fourth (0 - 0.4 cm) of the NETL reactor (1.6 cm total length). In the temperature range corresponding to our experiments, 1148 - 1198 K, the steady-
state concentration of H was attained only at the latter section of the reactor, confirming that the initial transient period of [H] and [OH] values must be accounted for in determining the actual rate parameters of the reaction.

The Bradford mechanism was solved numerically to determine whether this induction period might have a significant effect on the overall reaction at low conversions. Stiff integrators (ODE23s from MatLab®) were used to solve the concentration-time profiles for each one of the six species involved in the reaction mechanism. This simulation describes the reaction as it would take place in an ideal isobaric and isothermal (i.e. constant density) batch reactor. Values of the individual rate constants were taken from the GRI database. Figure 14 shows the concentration profile of H as a function of reaction time at 1250 K and 1.6 MPa, confirming the results from the ChemKin® simulation. The simulation was run until a H₂ conversion of 10% was obtained, which was low enough to minimize the effect of the opposite reaction. There was a continuous increase in [H] until the stationary state value was achieved at time greater than 0.5 s (conversion at t = 0.5 s is 1.86 %), suggesting that the period during which [H] changes plays a significant role in the gas-phase kinetics, especially for low reaction times/conversions.

The reaction rate expression derived from the Bradford mechanism is:

\[
\frac{d[CO]}{dt} = k_2[CO_2][H] - k_{-2}[CO][OH]
\] (18)
Equation 18 reduces to Equation 7 under steady-state concentrations of \( H \) and \( OH \). The second term on the right hand side can be neglected for the early stages of the reaction because the concentration of \( CO \) is close to zero, \( k_2 \) and \( k_2 \) are of the same order of magnitude, and \( [OH] \) is several orders of magnitude smaller than \( [H] \). The reaction rate can therefore be simplified to the expression below, Equation 19.

\[
 r = \frac{d[CO]}{dt} = k_2[CO_2][H] 
\]  

(19)

From Equation 19 and Figure 14, it can be concluded that as the reaction commences, the rate of reaction increases (rather than decreases) with residence time because the increase in \( [H] \) is more significant than the decrease in \( [CO_2] \). Once an invariant concentration of \( [H] \) is attained, however, the rate of reaction decreases with residence time as \( CO_2 \) is depleted.

If the reaction rate data is collected during this initial period and analyzed using Equation 9, (the rate expression obtained under the assumption of stationary \([H]\)) the rate constant will be given by Equation 20 (obtained from combining Equations 9 and 19). This rate constant will be an apparent rate constant rather than the effective rate constant of the rWGS (Equation 9).

\[
k = k_2 \frac{[H]}{[H_2]^{1/2}}
\]  

(20)

The effect of the changing concentrations of \( H \) and \( OH \) on the magnitude of the reaction rate constant was determined for conditions of 1250 K and 0.1 MPa to provide
an indication of the significance of the non-stationary state condition on the interpretation of the results. The reaction rate constant was determined using (a) Equation 20 and [H] and [H₂] values from the simulation during the initial non-stationary period (e.g., t < 0.5 s in Figure 14), (b) results from the simulation when stationary [H] is imposed at the beginning of the reaction (i.e., inlet [H] is the equilibrium value at that temperature), (c) results directly from the simulation of the Bradford mechanism where the simulation is allowed to run long enough for both the non-stationary state and stationary state regimes to be manifest, i.e. until stationary-state is achieved (the rate constant was determined by linear regression from runs varying the inlet [H₂] and [CO₂]), (d) NETL experimental correlation for the rate constant obtained by analyzing our experimental rate data with Equation 9, (e) the GRI data in Equation 8, (f) the correlation of Tingey (1966), and (g) the correlation of Kochubei and Moin (1969). Results are presented in Table 4. The simulation results that account for the changing concentrations of H and OH, entry (c), are of the same order of magnitude as our experimental results, entry (d), suggesting that if [H] varies during an experiment but this change is not accounted for (i.e. equation 9 is used to solve for k), then the k values will overestimate the effective rate constant. This is a likely cause for the discrepancies between the data reported in this study and that of Tingey (1966) and Kochubei and Moin (1969). The presence of the non stationary period where [H] has not yet attained its equilibrium value might also explain the results of Graven and Long, whose rate constant values lie between our correlation and the predicted value from the steady-state Bradford expression, Equation 8.

An attempt to further verify that the presence of a non-stationary state regime at the reactor inlet caused an overestimation of the reaction rate constant was then made. It is
well known that quartz surfaces act as radical quenchers for reactions involving H radicals. This would cause an increase in the rate of the chain termination, via the additional wall reaction. Simulations of the intrinsic kinetics (MatLab®) suggested that such an increase would bring the [H] to a stationary state earlier during the reaction. However, the value of the stationary [H] is lower than the predicted from the purely gas-phase reaction. This should render an energy of activation similar to the Bradford value, but with a smaller pre-exponential value. Such a possibility was studied using simulations (ChemKin®) and an experiment with a quartz-packed quartz reactor. The temperatures were chosen in the interval where surface reactions appear to have some effect on the rWGSR, i.e. 1073 - 1123 K (Kochubei and Moin, 1969; Tingey, 1966).

We attempted to track the radical quenching effect by adding the surface reactions suggested in the work of Aghalayam (Aghalayam et al., 1998). However, the kinetic parameters available, i.e. the sticking coefficient, only provide an upper bound for the effect of radical quenching. Consequently, the simulation predicted a large inhibition in the rate of reaction even at high temperature (>1148 K) where such inhibition has not been observed experimentally (Graven and Long, 1954; Kochubei and Moin, 1969). Therefore, no reliable estimation could be obtained from these calculations.

Figure 15 presents the experimental results from the quartz reactor packed with small cylinders of quartz, Table 2, that increased the quartz surface area by a factor of three. Our correlation was extrapolated to the 1123 - 1223 K temperature range to facilitate the comparison with our previous empty reactor results. CFD simulations of this packed reactor, in which the packing was modeled as porous media, yielded flow patterns
nearly identical to those shown in Figure 7. The rate constant for the quartz-packed quartz reactor was similar to the results of Tingey (1966) and Kochubei and Moin (1969). The corresponding values of the pre-exponential constant and the energy of activation are reported in Table 1. This observation appears to corroborate the hypothesis that the suppression or minimization of the period of the reaction where \( [H] \) increases considerably, brought by the radical-quenching effect of the quartz surface at moderate temperature, prevents an over-estimation of the rate constant. However, we could not reconcile the observation of Kochubei and Moin (1969) of a small enhancement in the reaction rate brought by the addition of quartz packing. The high inlet \( [H] \) in the work of Kochubei and Moin would reduce the impact of the radical quenching, however. Further, the removal of \( H \) radicals from the gas-phase could eventually drive the chain initiation step towards the production of \( H \), decreasing the concentration of \( H_2 \).

**Low-pressure rWGSR in an Inconel reactor**

Rates of reactions in quartz vessels provide an understanding of the intrinsic kinetics of the rWGSR. Industrial application of this technology will occur in vessels where the reacting gases will be exposed to the metal surfaces within the reactor. Therefore, the catalytic wall effects on the rate of reaction were evaluated for empty and packed Inconel® 600 reactors at 1173 K and 0.1 MPa using an equimolar feed of \( CO_2 \) and \( H_2 \). Conversions were very high (10-40%), given the short residence time (< 0.5 s) and the equilibrium limitation of 55%, as shown in Figure 16. These levels of conversion were approximately two orders of magnitude greater than those observed using the quartz reactor, which were less than 0.1% under the same experimental conditions. This result
implied that the metal walls of the Inconel® 600 reactor catalyzed the reaction. An increase in the Inconel surface area was achieved by packing the reactor with Inconel rings. As shown in Figure 16, the conversions were twice that observed with the empty Inconel reactor.

**High-pressure reverse water gas shift reaction in an Inconel reactor**

The rWGSR was also conducted at high-pressure conditions in an Inconel reactor over a wide temperature range using equimolar feeds of CO₂ and H₂. Longer residence times were employed (8-10 sec) because of the increase in gas density and limitations on the maximum flow rate of the reactor effluent. The high-pressure results from the Inconel reactor experiments are presented in Figure 17 along with experimental results obtained using the empty quartz reactor. The rate of reaction in the Inconel reactor was significantly greater than that obtained in the quartz reactor, especially at low temperature. Near-equilibrium conversions were attained at temperatures greater than 873 K in the Inconel reactor. These results confirm the observations obtained at low-pressure conditions, Figure 16; Inconel® 600 surfaces catalyze the rWGSR. Levels of conversion were so high that accurate kinetic expressions could not be derived for the reverse WGS reaction in an Inconel reactor. Although a residence time of 10 s was used in this study, the residence time needed to achieve this level of conversion may have been substantially less, especially at higher temperature.

Both the low-pressure and high-pressure results indicated that the Inconel® 600 catalyzed the rWGSR. Two rings of the Inconel® 600 packing (72% Ni, 17% Cr, and 10% Fe) were analyzed using a scanning electron microscope equipped with an energy
dispersive X-ray detector (SEM-EDS) before and after their use in the lowpressure reactor, Figures 18 (a) and 18 (b), respectively. Significant loss of Ni and/or enrichment of Cr occurred in the Inconel surface after exposure of the Inconel to the rWGSR environment. (The Al, Si, and Ti detected in the rings reflect the composition of the Inconel® 600; the source of the Ca is not known but could be due to surface contamination.) A likely cause of Ni loss is the so-called “metal dusting”. This type of corrosion is characterized by mass loss due to the formation of carbon deposits in H₂-CO-H₂O environments in the temperature range 673-1073 K. The carbon diffuses into the metal and the nickel migrates to the surface forming small pure-nickel particles. Inconel® 600 has been reported to be susceptible to this kind of attack (Klower et al., 1998). Evidence to this effect was gathered in our experiments: a considerable amount of coke was removed from the reactor and SEM-EDS analysis confirmed the presence of small Ni particles dispersed in the coke. The formation of carbon deposits may be attributable to the Boudouard reaction (Eq. 21), due to the somewhat large CO concentrations present in the system. This reaction is known to occur in the temperature range 673 - 1173 K.

\[ 2CO \leftrightarrow C + CO_2 \]  (21)

Although the mass loss in Inconel® 600 associated with “metal dusting” is more considerable than for other high-Ni alloys, the damage appears to be more superficial (Baker et al., 2002). However, other materials should be considered for the long-term operation of the moderate-high temperature, high-pressure WGSR.

Another side reaction, formation of methane, was observed in the Inconel reactor. The concentration of methane at the outlet of the reactor exhibited temperature
dependence reaching a maximum value at 1023 K, as shown in Figure 19. Methane formation in a CO-CO\textsubscript{2}-H\textsubscript{2}-H\textsubscript{2}O system is possible via reactions 22 – 25. With our experimental data it is not possible to determine which one of those reactions is the main contributor to the formation of methane. However, the fact that the CO/H\textsubscript{2}O ratio decreases and the CO\textsubscript{2}/H\textsubscript{2} ratio increases noticeably at 1023 K suggests that reaction 22 and/or 24 are playing an important role in the process. Removal of H\textsubscript{2} from the system led to complete suppression of methane formation.

\[
CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (22)
\]

\[
CO_2 + 2H_2 \leftrightarrow CH_4 + 2H_2O \quad (23)
\]

\[
2CO + 2H_2 \leftrightarrow CO_2 + CH_4 \quad (24)
\]

\[
C + 2H_2 \leftrightarrow CH_4 \quad (25)
\]

**Conclusions**

The rate of reaction of the homogeneous, reverse water-gas shift reaction has been evaluated in an empty quartz reactor at elevated temperature (1148-1198 K), low pressure (0.1 MPa) conditions in the absence of a diluent gas. The power-law rate expression employed exponent values of 1.0 and 0.5 for CO\textsubscript{2} and H\textsubscript{2}, respectively. The reaction rate was characterized by an activation energy of 53 kcal/mol [222 kJ/mol] and a pre-exponential constant of 9.83E08 L\textsuperscript{0.5}mol\textsuperscript{-0.5}s\textsuperscript{-1}. This result was consistent with the previously published, low-pressure rate expression of Graven and Long, but the resulting rates were roughly four times greater than reaction rates obtained in our quartz-packed
reactor (energy of activation and pre-exponential constant were 356 kJ/mol and 3.0E14 L^{0.5}\text{mol}^{0.5}\text{s}^{-1}, respectively) and rates reported by Tingey and by Kochubei and Moin. CFD simulation results indicated that differences in reactor geometry were not responsible for these differences. Further, oxygen, which is known to catalyze the reverse WGS reaction, was maintained at a concentration of less than 1 ppm in our reactor. The importance of an initial induction period in which the concentration of the chain carriers increases steadily with time was confirmed and the discrepancies between the different studies could be related to this effect. The simple gas-phase mechanism proposed by Bradford was found to satisfactorily describe the reaction. The presence of packing at moderate-high temperature reduced the effect of the induction period by achieving the stationary state quicker due to the H radical quenching in the quartz surface.

A pressure-equilibrated quartz reactor was also used to study the homogeneous rate of reaction for the first time at high temperature, high-pressure conditions (up to 1.6 MPa). The results yielded an activation energy of 52 kcal/mol [218 kJ/mol] and a pre-exponential constant of 5.39E08 L^{0.5}\text{mol}^{0.5}\text{s}^{-1}. The rate constant correlated by the low-pressure and high-pressure Arrhenius expressions were in good agreement over the 1148 – 1198 K temperature range, indicating there was no significant effect of elevated pressure on the rate constant.

Conversions attained in an Inconel® 600 reactor at 1173 K and 0.101 MPa were approximately two orders-of-magnitude greater than those attained in the quartz reactor for residence times of 0.1 – 0.5 seconds. A dramatic increase in the reaction rate was also observed when the Inconel® 600 reactor was operated at high pressure, with near-
equilibrium conversions realized at temperatures as low as 873 K for residence times of 8-10 s. This increase in conversion suggested that the Inconel® 600 surfaces catalyzed the rWGSR. Therefore, the use of intrinsic kinetic results based on quartz reactors in the design of a reverse WGS Inconel® 600 reactor will lead to overestimates of the volume required to attain a specified level of conversion. Further, the depletion of nickel from the Inconel® 600 reactor surfaces indicates that metal dusting is an issue that needs to be addressed in an Inconel® 600 reactor for the moderate-high temperature rWGSR.

Acknowledgements

We would like to acknowledge the operational and maintenance contributions of the Parsons engineering technicians, including Ronald Hirsch, Jeremy Brannen, Ray Rokicki, Russ Miller, Brian Neel, Michael Ditillo, and Bruce Blednick. This work was sponsored through the “Transportation Fuels and Chemicals”, “Gasification Technologies”, and “Hydrogen, Fuel Cells, and Infrastructure” programs within the U.S. Department of Energy. F.B. wishes to acknowledge Universidad de Antioquia for granting a leave of absence to pursue his doctoral degree.
Literature Cited


Notation

\[ C_{j,r} = \text{Molar concentration of reactant and product species } j \text{ in reaction, mol/m}^3. \]

\[ D_{i,m} = \text{Diffusion coefficient for species } i, \text{ m}^2/\text{s}. \]

\[ E_a = \text{Energy of Activation, kJ/mol.} \]

\[ k = \text{Rate constant of the overall rWGSR, } (\text{L/mol})^{0.5} \text{ s}^{-1}. \]

\[ K_{eq} = \text{Equilibrium constant of the forward WGSR.} \]

\[ k_i = \text{Rate constant of elementary reaction } i \text{ (i = 1, -1, 2, -2, 3, -3), } [\text{(cm}^3/\text{mol})^{\gamma_i} \text{ s}^{-1}]; \gamma \text{ depends on the reaction} \]

\[ k_0 = \text{Pre-exponential factor, } [\text{(L/mol)}^{\gamma_0} \text{ s}^{-1}] \text{ or } [\text{(cm}^3/\text{mol})^{\gamma_1} \text{ s}^{-1}]; \gamma \text{ depends on the reaction} \]

\[ I = \text{Unit tensor} \]

\[ \vec{J}_i = \text{Diffusive flux of species } i, \text{ mol m}^2 \text{ s}^{-1} \]

\[ [M] = \text{Molar concentration of species } M, [\text{mol/L}] \text{ or } [\text{mol/m}^3]. \]

\[ M_{w,i} = \text{Molecular weight of species } i, \text{ kgmol/kg} \]

\[ N_R = \text{Number of the reactions} \]

\[ N_r = \text{Number of chemical species in reaction } r \]

\[ p = \text{Pressure, MPa} \]

\[ R_i = \text{Rate of production of species } i \text{ by chemical reaction, mol m}^3 \text{ s}^{-1} \]

\[ \dot{R}_{i,r} = \text{Molar rate of creation/destruction of species } i \text{ in reaction, mol m}^3 \text{ s}^{-1} \]

\[ r = \text{Reaction rate, [mol L}^{-1} \text{ s}^{-1}] \]

\[ S_i = \text{Rate of reaction by addition from the dispersed phase plus any user-defined source, mol m}^3 \text{ s}^{-1}. \]
T = Absolute temperature, K
\( t \) = Time, s
\( \bar{v} \) = Velocity vector, m/s
\( Y_i \) = Local mass fraction of species \( i \)

**Greek letters**

\( \Delta H \) = Heat of reaction, kJ/mol
\( \gamma \) = Global reaction order
\( \rho \) = Density, Kg/m\(^3\)
\( \bar{\tau} \) is the stress tensor
\( \mu \) = Molecular viscosity, Pa s

\( \nu_{i,r}^{'} \) = Stoichiometric coefficient for reactant \( i \) in reaction \( r \)
\( \nu_{i,r}^{''} \) = Stoichiometric coefficient for product \( i \) in reaction \( r \)

\( \eta_{j,r}^{'} \) = Forward rate exponent for each reactant and product species \( j \) in reaction \( r \)
\( \eta_{j,r}^{''} \) = Backward rate exponent for each reactant and product species \( j \) in reaction \( r \)

**Superscript**

\( T \) = Transposed matrix
Table 1. Kinetic expressions for the \( \text{r} \text{WGSR in quartz reactors.} \)

\[
r = k[H_2]^\alpha[CO_2]^\beta = k_0 \exp(-E_a/RT)[H_2]^\alpha[CO_2]^\beta, \quad R = 8.3145 \times 10^{-3} \text{kJ/mol} \cdot \text{K};
\]

<table>
<thead>
<tr>
<th>Reference</th>
<th>( T ) K</th>
<th>( P ) MPa</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( E_a ) kJ/mol</th>
<th>( k_0 ) (L/mol)(^{\alpha+\beta-1}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graven and Long (1954)</td>
<td>1148-1323</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>234.3</td>
<td>2.9 \times 10^{7}</td>
</tr>
<tr>
<td>Kochubei and Moin (1969)</td>
<td>1023-1523</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>326.4</td>
<td>6.4 \times 10^{12}</td>
</tr>
<tr>
<td>Tingey (1966)</td>
<td>1073-1323</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>318.0</td>
<td>1.2 \times 10^{13}</td>
</tr>
<tr>
<td>Tingey (1966)</td>
<td>673-1073</td>
<td>0.1</td>
<td>0.333</td>
<td>1.0</td>
<td>164.2</td>
<td>7.6 \times 10^{11}</td>
</tr>
<tr>
<td>Kam and Mohindra (1974)</td>
<td>&lt;2500</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>397.5</td>
<td>2.3 \times 10^{16}</td>
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<tr>
<td>NETL empty reactor (this work)</td>
<td>1148-1198</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>222.2 \pm 3.9</td>
<td>1.09 \times 10^{7}</td>
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<td>NETL empty reactor (this work)</td>
<td>1148-1198</td>
<td>1.6</td>
<td>0.5</td>
<td>1.0</td>
<td>218.4 \pm 5.1</td>
<td>5.99 \times 10^{9}</td>
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<tr>
<td>NETL packed reactor (this work)</td>
<td>1063-1138</td>
<td>1.6</td>
<td>0.5</td>
<td>1.0</td>
<td>355.6 \pm 1.5</td>
<td>3.0 \times 10^{14}</td>
</tr>
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</table>
Table 2. Dimensions of the reaction zone of the NETL quartz and Inconel® 600 reactors.

<table>
<thead>
<tr>
<th></th>
<th>Quartz with Tube*</th>
<th>Inconel With Tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Height (cm)</td>
<td>1.9</td>
<td>2.54</td>
</tr>
<tr>
<td>Reactor ID (cm)</td>
<td>1.1</td>
<td>1.35</td>
</tr>
<tr>
<td>Inner Tube Height (cm)</td>
<td>1.4</td>
<td>1.91</td>
</tr>
<tr>
<td>Inner Tube ID (mm)</td>
<td>1.85</td>
<td>2.87</td>
</tr>
<tr>
<td>Inner Tube OD (mm)</td>
<td>3.85</td>
<td>4.14</td>
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<tr>
<td>Annular Gap, reactor (mm)</td>
<td>3.57</td>
<td>4.66</td>
</tr>
<tr>
<td>Volume (cm$^3$)</td>
<td>1.81</td>
<td>3.38</td>
</tr>
</tbody>
</table>

* Quartz packing (small rods, 2 mm diameter, 3 mm long) was added to the quartz reactor in some experiments.
Table 3. CFD conversions of the four reactors assuming identical operating conditions and rate of reaction. Conditions: 1173 K, 0.1 MPa, residence time 0.5 s, inlet molar fractions of CO$_2$ and H$_2$ are 0.5.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>CO$_2$ conversion, %</th>
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<tbody>
<tr>
<td>Graven and Long (1954)</td>
<td>0.0990</td>
</tr>
<tr>
<td>Tingey (1967)</td>
<td>0.1017</td>
</tr>
<tr>
<td>Kochubei and Moin (1969)</td>
<td>0.0990</td>
</tr>
<tr>
<td>NETL (this work)</td>
<td>0.1053</td>
</tr>
</tbody>
</table>
Table 4. Estimation of $k$ Values at 1250 K and atmospheric pressure. $\gamma$ is the global reaction order.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$K$ (cm$^3$/mol)$^{\gamma-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Non-stationary [H]</td>
<td>325</td>
</tr>
<tr>
<td>b Mixed, non-stationary and stationary [H]</td>
<td>79</td>
</tr>
<tr>
<td>c Stationary [H]</td>
<td>7.1</td>
</tr>
<tr>
<td>d NETL</td>
<td>44</td>
</tr>
<tr>
<td>e GRI, stationary [H]</td>
<td>7.3</td>
</tr>
<tr>
<td>f Tingey (1967)</td>
<td>9.1</td>
</tr>
<tr>
<td>g Kochubei and Moin (1969)</td>
<td>9.0</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Figure 1. Arrhenius representations of rate constant expressions for the reverse WGS reaction obtained using a quartz reactor, \( r = k[\text{CO}_2][\text{H}_2]^{0.5}, k \ [\text{L}^{0.5}\text{mol}^{0.5}\text{s}^{-1}] \); results of previously published literature.

Figure 2. Schematic of HMT-1 unit. FCV – Flow Control Valve. PCV – Pressure Control Valve. PI – Pressure Indicator. GC - Gas Chromatograph. TI – Temperature Indicator.

Figure 3. Details of the quartz (a) and Inconel® 600 (b) reactors.

Figure 4. Arrhenius representations of rate constant expressions for the reverse low and high-pressure WGS reaction obtained at NETL using the quartz reactor, \( r = k[\text{CO}_2][\text{H}_2]^{0.5}, k \ [\text{L}^{0.5}\text{mol}^{0.5}\text{s}^{-1}] \). Graven and Long low pressure correlation (Graven and Long, 1954) -dotted line- provided for reference.

Figure 5. Dependence of the rate on the concentration of \( \text{CO}_2 \). Partial pressure of \( \text{H}_2 \) was maintained at 0.8 MPa. All experiments were performed at 1173 K. Residence time = 1.92 ± 0.15 s based on swept volume.

Figure 6. Dependence of the rate on the concentration of \( \text{H}_2 \). Partial pressure of \( \text{CO}_2 \) was maintained at 0.8 MPa. All experiments were performed at 1173 K. Residence time = 1.85 ± 0.08 s based on swept volume.

Figure 7. Flow field in NETL quartz reactors; axisymmetric; feed from narrow annulus along the perimeter of the bottom of the reactor; reactor with product withdrawal from the co-axial tube.

Figure 8. Graven and Long; non-axisymmetric cylindrical reactor; tangential feed entering at the top, right hand corner of the xz plane; tangential withdrawal of products through narrow tube at the bottom left hand corner of the xz plane; the 2 circular xy cross-sections are 1/3 and 2/3 of the way up the reactor in the z-direction.

Figure 9. Tingey reactor; axisymmetric; enlargement of feed and product sections provided; white rectangle is a solid quartz cylinder; white flow field in feed section is high velocity flow field.

Figure 10. Kochubei and Moin; non-axisymmetric cylindrical reactor; axial feed along entire cross-section on the left-hand side of the reactor; product withdrawn through a narrow tube at the bottom right corner of the xz plane; white field in the center of the xz plane is a thermocouple; velocity vectors on a xy circular plane normal near the right-hand side of the reactor also shown; white field in this plane near the bottom corresponds to high fluid velocity near the exit tube.

Figure 11. Residence Time Distribution plots for the (a) Tingey (1966), (b) Kochubei and Moin (1969) and (c) NETL reactors. Nominal residence time is 0.5 s. Ideal case (PFR) reactor is included as comparison.
Figure 12. Residence Time Distribution plots. Graven and Long (1954) reactor.

Figure 13. ChemKin® simulation of the rWGS in a tubular reactor. Inlet molar flowrates: \( \text{CO}_2 = \text{H}_2 = 50 \text{ sccm} \). Reactor diameter, 1 cm. Pressure, 1.6 MPa.

Figure 14. Concentration – time profile for H species. \([\text{CO}_2]_0 = [\text{H}_2]_0\), \([\text{CO}]_0 = [\text{H}_2\text{O}]_0 = 0\), 1250 K, 1.6 MPa, final conversion is 10%.

Figure 15. Arrhenius representation of rate constant for the high-pressure (1.6 MPa) reverse WGS reaction in the quartz packing reactor, \( r = k[\text{CO}_2][\text{H}_2]^{0.5}, k \left[ \text{L}^{0.5} \text{mol}^{-0.5} \text{s}^{-1} \right] \). The actual data points are represented by open diamonds, while the solid line represents their extrapolation to higher temperatures.

Figure 16. Reverse water-gas shift reaction in an Inconel® 600 reactor. 1173 K, 0.101 MPa, \([\text{H}_2]_0 = [\text{CO}_2]_0\). Equilibrium conversion at these conditions is 55%.

Figure 17. Reverse water-gas shift reaction in an Inconel® 600 reactor. 1.6 MPa, \([\text{H}_2]_0 = [\text{CO}_2]_0\). Conversions in the quartz reactor were estimated with our high-pressure kinetic results. Residence times were 8-10 s.

Figure 18. SEM-EDS for Inconel® 600 rings before (a) and after (b) exposure to reverse WGSR environment.

Figure 19. Side reactions in the WGS in an Inconel® 600 reactor. Formation of methane as a function of temperature. 1.6 MPa, \([\text{H}_2]_0 = [\text{CO}_2]_0\). Residence times were 8-10 s.
Figure 1. Arrhenius representations of rate constant expressions for the reverse WGS reaction obtained using a quartz reactor, \( r = k[\text{CO}_2][\text{H}_2]^{0.5} \), \( k \ [L^{0.5} \text{mol}^{0.5} \text{s}^{-1}] \); results of previously published literature.
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Figure 3. Details of the quartz (a) and Inconel® 600 (b) reactors.
Figure 4. Arrhenius representations of rate constant expressions for the reverse low and high-pressure WGS reaction obtained at NETL using the quartz reactor, \( r = k[\text{CO}_2][\text{H}_2]^{0.5} \), \( k [\text{L}^{0.5} \text{mol}^{0.5} \text{s}^{-1}] \). Graven and Long low pressure correlation (Graven and Long, 1954) -dotted line- provided for reference.
Figure 5. Dependence of the rate on the concentration of CO₂. Partial pressure of H₂ was maintained at 0.8 MPa. All experiments were performed at 1173 K. Residence time = 1.92 ± 0.15 s based on swept volume.
Figure 6. Dependence of the rate on the concentration of $\text{H}_2$. Partial pressure of $\text{CO}_2$ was maintained at 0.8 MPa. All experiments were performed at 1173 K. Residence time = $1.85 \pm 0.08$ s based on swept volume.
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Figure 12. Residence Time Distribution plots. Graven and Long (1954) reactor.
Figure 13. ChemKin® simulation of the rWGS in a tubular reactor. Inlet molar flowrates: CO$_2$ = H$_2$ = 50 sccm. Reactor diameter, 1 cm. Pressure, 16 MPa.
Figure 14. Concentration – time profile for H species. $[\text{CO}_2]_0=[\text{H}_2]_0$, $[\text{CO}]_0=[\text{H}_2\text{O}]_0 = 0$, 1250 K, 1.6 MPa, final conversion is 10%. 
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XXVII.  “Simulations of Adsorptions and Phase Transitions”

Wei Shi (S) and Karl Johnson (F), University of Pittsburgh
with
Brad Bockrath (M), NETL
SIMULATIONS OF ADSORPTIONS AND PHASE TRANSITIONS

by

Wei Shi

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MA, Chemical Engineering, East China University of Science and Technology, 1996

Submitted to the Graduate Faculty of

the School of Engineering in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

University of Pittsburgh

2003
This dissertation was presented

by

Wei Shi

It was defended on

May 5, 2003

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Dissertation Director: J. Karl Johnson, Associate Professor, Chemical and Petroleum Engineering
ABSTRACT

SIMULATIONS OF ADSORPTION AND PHASE TRANSITIONS

Wei Shi, PhD
University of Pittsburgh, 2003

The objective of this thesis is to develop simulation tools that will allow us to study many phenomena from a molecular level. The topics covered in this thesis include bulk phase transitions, phase transitions in adsorbed fluids, and the application of single-walled carbon nanotubes as a gas storage media.

Multiple histogram reweighting and mixed-field finite-size scaling techniques have been developed to calculate the phase diagram for classical and quantum fluids in bulk and adsorbed phases. We show, for the first time, that capillary condensation shows a crossover of the effective exponent for the width of the coexistence curve from 2-D Ising-like (1/8) farther away from the critical point to mean-field (1/2) near the critical point. The first prewetting transitions clearly observed from simulation of quantum fluids are presented. The experimental wetting temperature of 19.1 K is reproduced from the simulation with a modified potential. Hydrogen adsorbing on a 15 Å thick film of Rb on Au gives a wetting temperature of about 1 K less than H$_2$ on pure Rb. This prediction should be observable from experiments.

Hydrogen adsorption onto single walled carbon nanotube bundles has been performed from computer simulations and compared with the experiments. We study the effect of CO$_2$ oxidation of the nanotubes on adsorption. Isotherms computed with a standard graphitic potential give remarkably good agreement with the experimentally measured isotherms before activation with
CO$_2$. The effect of activation is modeled by independently increasing the nanotube spacing and the solid-fluid interaction potential. It is found that only a combination of increased nanotube spacing and increased solid-fluid potential gives rough agreement with experiments.

Gases such as CH$_4$, Xe, and Ar have been studied on both the homogeneous (same tube diameter) and heterogeneous (different tube diameters) closed single-walled carbon nanotube bundles constructed from the basin-hopping method. Experimental gas adsorption data on SWNT bundles have previously been analyzed in terms of an over-simplified model of homogeneous nanotubes packed into perfect arrays. This analysis has led to the general conclusion that gases do not adsorb inside interstitial channels of homogeneous nanotube bundles. Our analysis overturns the current paradigm of gas adsorption on SWNTs by showing that adsorption inside interstices of heterogeneous SWNT bundles is vitally important to accurately describing these materials.
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td>1.0 OVERVIEW</td>
<td>1</td>
</tr>
<tr>
<td>2.0 HISTOGRAM REWEIGHTING AND FINITE-SIZE SCALING STUDY</td>
<td>6</td>
</tr>
<tr>
<td>2.1 INTRODUCTION</td>
<td>6</td>
</tr>
<tr>
<td>2.2 THEORY</td>
<td>9</td>
</tr>
<tr>
<td>2.2.1 Histogram reweighting</td>
<td>9</td>
</tr>
<tr>
<td>2.2.2 Finite-size scaling</td>
<td>15</td>
</tr>
<tr>
<td>2.3 SIMULATION DETAILS</td>
<td>19</td>
</tr>
<tr>
<td>2.3.1 Vapor-liquid equilibrium</td>
<td>20</td>
</tr>
<tr>
<td>2.3.2 Finite-size scaling</td>
<td>20</td>
</tr>
<tr>
<td>2.4 RESULTS AND DISCUSSION</td>
<td>21</td>
</tr>
<tr>
<td>2.4.1 The LRC fluid</td>
<td>21</td>
</tr>
<tr>
<td>2.4.2 The TR and TS fluids</td>
<td>23</td>
</tr>
<tr>
<td>2.4.3 Summary of critical constants</td>
<td>24</td>
</tr>
<tr>
<td>2.5 CONCLUSIONS</td>
<td>25</td>
</tr>
</tbody>
</table>
6.0 CHEMICAL ACTIVATION OF CARBON NANOTUBES .......... 89
  6.1 INTRODUCTION ........................................... 89
  6.2 EXPERIMENTAL METHODS ................................. 91
  6.3 SIMULATION METHODS .................................... 97
  6.4 RESULTS AND DISCUSSION ............................... 100
  6.5 SIMULATION RESULTS .................................... 109
  6.6 CONCLUSIONS ............................................ 113

7.0 GAS INTO INTERSTITIAL ................................. 115
  7.1 INTRODUCTION ........................................... 115
  7.2 SIMULATION DETAILS ................................... 116
  7.3 RESULTS .................................................. 118
  7.4 CONCLUSIONS ............................................ 125

8.0 ADSORPTION ONTO CLOSED NANOTUBE BUNDLES .......... 126
  8.1 INTRODUCTION ........................................... 126
  8.2 THEORETICAL CALCULATIONS ............................ 127
  8.3 RESULTS .................................................. 130
    8.3.1 Results for CH₄ ........................................ 133
    8.3.2 Results for Ar ........................................ 140
    8.3.3 Results for Xe ........................................ 140
  8.4 CONCLUSION ............................................. 146

9.0 FUTURE WORK ............................................. 147
  9.1 FUTURE WORK ............................................. 147

BIBLIOGRAPHY ................................................ 149
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# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table No.</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Saturation densities computed from the EOS and Hill’s method</td>
</tr>
<tr>
<td>2.2</td>
<td>Comparison between Hill’s method and the equal area construction.</td>
</tr>
<tr>
<td>2.3</td>
<td>Critical properties of the LJ fluids</td>
</tr>
<tr>
<td>3.1</td>
<td>Ratios of the grand canonical partition function</td>
</tr>
<tr>
<td>3.2</td>
<td>Reduced wetting temperature and prewetting critical temperature</td>
</tr>
<tr>
<td>5.1</td>
<td>Well depths, wetting temperatures, and prewetting critical points</td>
</tr>
<tr>
<td>6.1</td>
<td>Classes of nanotube bundles</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>The $\mu^<em>-\rho^</em>$ isotherms for LRC at $T^* = 1.15$</td>
<td>12</td>
</tr>
<tr>
<td>2.2</td>
<td>The $\mu^<em>-\rho^</em>$ isotherms for LRC at $T^* = 1.27$</td>
<td>13</td>
</tr>
<tr>
<td>2.3</td>
<td>Hill’s method for calculation of the saturation chemical potential</td>
<td>14</td>
</tr>
<tr>
<td>2.4</td>
<td>The apparent $T_c^*(L)$, plotted as a function of $L^{-(\theta+1)/\nu}$</td>
<td>27</td>
</tr>
<tr>
<td>2.5</td>
<td>The apparent $(\beta\mu)_c(L)$, plotted as a function of $L^{-(\theta+1)/\nu}$</td>
<td>28</td>
</tr>
<tr>
<td>2.6</td>
<td>Isotherms for two temperatures and two different system sizes</td>
<td>28</td>
</tr>
<tr>
<td>2.7</td>
<td>Coexistence densities for LRC</td>
<td>29</td>
</tr>
<tr>
<td>2.8</td>
<td>The phase diagram for the LRC fluid with a cutoff of $5.0\sigma$</td>
<td>30</td>
</tr>
<tr>
<td>2.9</td>
<td>A plot of $T^<em>-\mu^</em>$ at coexistence for $r_c^* = 2.5$ and $5.0$</td>
<td>31</td>
</tr>
<tr>
<td>2.10</td>
<td>The density versus chemical potential isotherms</td>
<td>32</td>
</tr>
<tr>
<td>2.11</td>
<td>The phase diagrams for the TR and TS fluids with $r_c^* = 2.5$</td>
<td>33</td>
</tr>
<tr>
<td>2.12</td>
<td>The phase diagrams for the TR and TS fluids with a cutoff of $r_c^* = 3.5$</td>
<td>34</td>
</tr>
<tr>
<td>2.13</td>
<td>The phase diagrams for the LRC and TR fluids with $r_c^* = 5.0$</td>
<td>35</td>
</tr>
<tr>
<td>3.1</td>
<td>Isotherms for $T^* = 0.7$ and $0.6$</td>
<td>43</td>
</tr>
<tr>
<td>3.2</td>
<td>The $T^<em>-\rho^</em>$ phase diagram for capillary condensation</td>
<td>45</td>
</tr>
<tr>
<td>3.3</td>
<td>Scaled width of the coexistence data</td>
<td>46</td>
</tr>
<tr>
<td>3.4</td>
<td>Isotherms for $T^* = 0.83$, $0.88$ and $1.0$</td>
<td>49</td>
</tr>
<tr>
<td>3.5</td>
<td>Density probability distribution at $T^* = 0.83$ and $\mu^* = -3.801$</td>
<td>50</td>
</tr>
<tr>
<td>3.6</td>
<td>Local density profiles at $T^* = 0.83$</td>
<td>51</td>
</tr>
<tr>
<td>3.7</td>
<td>Local density profiles at $T^* = 0.88$</td>
<td>52</td>
</tr>
<tr>
<td>3.8</td>
<td>A plot of $\Delta\mu^* = \mu_{sat}^* - \mu_{pw}^*$ as a function of temperature</td>
<td>53</td>
</tr>
</tbody>
</table>
1.0 OVERVIEW

The equilibrium thermophysical properties and phase behavior of pure fluids and their mixtures is of central importance to many technological and scientific fields, for example, in designing separation processes for the chemicals, petroleum, pharmaceutical, and many other industries. Understanding the metabolism in living systems also requires a knowledge of the equilibrium properties of fluids. Numerous experiments have been performed to map out various phase transitions and obtain parameters for empirically or theoretically based models. However, experimental measurements are very time consuming and expensive. Empirical models are only valid over the range of conditions for which experimental data have been used for obtaining the model parameters. Even theoretically based models have limited predictive abilities for conditions and systems different from the ones for which they were designed\(^1\). I still remember the painful experience I went through when I tried to design a distillation tower during a undergraduate class. There were so many equations and parameters I had to choose with caution in order to obtain an accurate design.

Molecular-based simulations are an increasing important alternative to experimental measurements and theoretical techniques for obtaining properties of fluids and materials. By comparing the simulations with the experiments, the accuracy of the interaction potentials between particles can be assessed. Once the interaction potential is known, the properties at any condition can in principle be obtained through simulations. Using the same interaction potential as used in a theory, the accuracy of the theory can be evaluated. The power of the simulations lies in the ability to predict properties at any set of conditions, which can be verified from experiments. In the past few decades molecular simulation techniques have become powerful tools for studying phase transitions in fluids and solids, for predicting thermodynamics and transport properties of fluids, for aiding the interpretation of experimental measurements, for design of new materials, and for directing experimental studies.

Several books and review articles on the subject of simulation methods have appeared in recent years\(^2-6\). Readers seeking a more thorough discussion of the methodological aspects pertaining to a
particular simulation technique are therefore referred to the respective works described in the books and the review articles. We here present a simple review of several important methods. Monte Carlo methods or molecular dynamics methods are available to calculate the equilibrium properties of materials. Monte Carlo methods are based on generating a chain of configurations in phase space in terms of Boltzmann distribution. Some properties, such as pressure, enthalpy, etc. can be calculated as the ensemble average of the configuration chain. Compared with Monte Carlo methods, molecular dynamics methods generate the configuration chain by solving Newton’s equations of motion with some kinds of numerical method. Dynamical properties, such as transport coefficients, which can not be obtained through Monte Carlo methods, can be obtained through molecular dynamics. Monte Carlo methods have proved to be more efficient than molecular dynamics for studying phase transitions although molecular dynamics is useful for obtaining the interfacial properties.

Many kinds of Monte Carlo methods have been used to calculate phase transitions. These methods can be divided into two categories, namely direct and indirect. By in direct, we mean that the phase transition can be directly identified from a single simulation. This includes Gibbs Ensemble Mote Carlo (GEMC)\textsuperscript{8,9}, etc. Gibbs ensemble has been widely used for simulation of fluid-phase equilibrium. GEMC is performed by carrying out a simulation simultaneously in two or more boxes at the same temperature. Each box represents distinct phases that coexist at a phase transition. The conditions for phase equilibrium, namely equality of pressure, temperature, and chemical potential of each component, are satisfied by exchanges of volume and the particles between the boxes. Chemical potential does not need to be calculated since the equality in chemical potential is implicitly satisfied by exchange of the particles. However, molecules must be transfered from one box to another. Hence, this method is not efficient at high densities, or as the complexity of the structure of the molecules increases. This problem can be partially alleviated with the configurational bias method\textsuperscript{10}. GEMC is less accurate than the multiple histogram reweighting technique described below\textsuperscript{11–13}. By indirect, we mean that the phase transitions can not be identified directly from the simulations. Data are collected during the simulation and post-processing of the data is performed to compute the phase equilibrium. Indirect methods include the $NPT$ plus test particle method\textsuperscript{14},
Grand canonical Monte Carlo, semigrand ensemble\textsuperscript{15}, the Gibbs-Duhem integration method\textsuperscript{16,17}, multiple histogram reweighting, etc. Grand canonical Monte Carlo method is widely used in the construction of isotherms of adsorption. Particles have to be deleted or created in the box during the simulation. This method will encounter the same problem as the GEMC does. The semigrand method is especially useful for studying mixtures. However, this technique is only efficient when the components under study are similar in both size and shape since the successful identity exchange in the simulation will be very low if the components are very dissimilar. The \textit{NPT} plus test particle method is based on calculations of the chemical potentials for a number of state points. A phase coexistence point is determined at the intersection of the vapor and liquid branches of the chemical potential versus pressure diagram. Obviously, it requires many calculation to get one point of equilibrium. The Gibbs-Duhem integration is performed by numerically calculating a differential equation from a series of simulations. An Initial condition (one equilibrium point) is needed. One drawback of this method is that the error in the numerical integration may accumulate and propagate. The basic idea of histogram reweighting is that the microcanonical partition function is independent of temperature, chemical potential, etc. A global microcanonical partition function can be constructed from histograms in terms of the energy and number of particles collected during simulations at a series of different conditions. The phase diagram can then be obtained using the equal area criterion for the distribution curve of number of particles for the vapor and liquid sides. By combining with mixed-field finite size scaling, the critical point can be accurately identified. Overlap in the energy and particle number distributions between two neighboring state points are required in multiple histogram reweighting. Hence, enough points have to be run before multiple histogram reweighting can be used. This problem may be alleviated by using parallel tempering\textsuperscript{18}. Many methods have been developed to model polymeric molecules. The expanded ensemble method is such an example\textsuperscript{5}. The basic idea of the expanded ensemble is similar to parallel tempering. Both these two methods construct a series of different states. There are two main kinds of difference between these two methods:
1. The expanded ensemble is commonly used in canonical ensemble to measure the chemical potential of polymeric molecules. Hence, all the states must be the same temperature and volume. The parallel tempering method is widely used in the Grand canonical ensemble. The only constraint is that all the states must have the same volume.

2. Prefactor weights are needed for all states in the expanded ensemble to assure that all the states are visited with approximately the same frequency. An iterative process is used to obtain these weights. All the prefactor weights are set to unity in the parallel tempering method. Hence, it is more difficult to implement the expanded ensemble method than to use the parallel tempering method.

All of the methods mentioned above are intrinsically subject to finite size effects. This problem becomes more serious near the critical point. When the state point is close to the critical point, the long range fluctuations are suppressed by the finite size of the simulation box. Mixed-field finite size scaling has been developed\textsuperscript{19,20} to calculate the critical parameters for an infinite system from the apparent critical parameters for finite sized systems.

Adsorption is another very important topic, governing processes such as water purification, gas separation, pollution prevention, and heterogeneous catalysis. Recently, hydrogen adsorption onto carbon nanotubes has attracted much attention\textsuperscript{21--27}. Interest in hydrogen as a fuel has grown dramatically since 1990\textsuperscript{21} due to the fact that hydrogen is non-polluting, forming water as a harmless combustion byproduct. There are currently four methods of storing H\textsubscript{2}. These are: (1) compression, (2) liquefaction, (3) metal hydrides and (4) adsorption. None of these methods are currently suitable for on-board storage for fuel cell vehicles because none meets the DOE volumetric and gravimetric targets. Carbon nanotube based materials have been proposed as effective hydrogen sorbents because of their large theoretical surface areas and binding energies.

Many experiments for hydrogen adsorption onto carbon nanotube bundles have been performed. Claims of high values of hydrogen adsorption have been made in reports of investigations at low
temperature,\textsuperscript{22} room temperature\textsuperscript{23,24} and even higher temperatures\textsuperscript{28}. Other experimental studies have found very limited uptake of hydrogen\textsuperscript{25–27}. The reason for the difference is still unknown. These variations in the experiments may be in part due to differences in the way the SWNT samples were prepared or pretreated. To accurately understand the adsorption sites in the nanotube bundles is fundamental for the carbon nanotubes to be optimized as adsorbents. Many experiments to identify the adsorption sites onto single-walled carbon nanotubes (SWNTs)\textsuperscript{29–43} have been performed. It is interesting to note that many researchers are still arguing whether or not gases can penetrate into the interstitial region of the nanotube bundles.

Molecular simulations can help resolve the above questions about adsorption onto carbon nanotubes. By comparing simulations with experiments, we can deduce the molecular level phenomena that give rise to experimentally observed quantities. This is one of the main objectives we will address in this thesis.

This thesis is composed of eight main chapters aside from this introduction. Chapter 2 is related to the histogram reweighting and finite size scaling techniques used to study the effects of different potentials, such as truncated and long-range corrected potentials on the vapor-liquid phase diagram. This problem is important to know since in the adsorption study, the truncated potential is always used. Chapter 2 has been published in \textit{Fluid Phase Equilibria}\textsuperscript{44}. Chapter 3 deals with the extension of multiple histogram reweighting to phase transitions in adsorption. This material has been published in \textit{Molecular Physics}\textsuperscript{45}. Chapters 4 and 5 deal with the phase transition of path integral fluids and the wetting of these fluids on metals. Chapter 6 presents experimental and simulation studies on H\textsubscript{2} adsorption on SWNTs. The experimental work was performed at NETL by Smith and coworkers. This material has been published in \textit{the Journal Physical Chemistry B}\textsuperscript{46}. Chapters 7 and 8 present simulations on adsorption of various gases on closed nanotube bundles. Chapter 7 has been submitted to \textit{Physical Review Letters}\textsuperscript{47}. Chapter 9 presents suggestions for future work.
2.0 HISTOGRAM REWEIGHTING AND FINITE-SIZE SCALING STUDY OF THE LENNARD-JONES FLUIDS

2.1 Introduction

The Lennard-Jones (LJ) potential has been one of the most widely used functions for approximating the physics of simple nonpolar molecules. Both theory and simulations have been used to compute the properties of the LJ fluid and solid. The popularity of the LJ model is due more to its convenient mathematical form than to its accuracy in representing the properties of real fluids. For example, it is known that the LJ potential cannot be used to accurately represent the Ar potential energy surface.

The full LJ potential is given by

\[ \phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \]  

(2-1)

where \( \epsilon \) is the well depth of the potential and \( \sigma \) is the diameter of the atom, or the location at which the potential crosses zero, and \( r \) is the center to center distance between the LJ atoms. In computer simulations and many theories it is common to approximate thermodynamic (infinitely large) systems with finite-size systems that employ periodic boundary conditions. The LJ potential is often said to be short-ranged because the attractive tail decays as \( r^{-6} \). However, for any finite system size the potential is not rigorously zero at a distance of half the box length where the potential is typically truncated. There are basically three approaches for dealing with the long-range tail of the LJ potential. The first option is to truncate the potential and add an approximate correction term for the tail. This is the long-range corrected (LRC) fluid model that is commonly used for studies involving isotropic fluids and solids.

\[ \text{This chapter is reprinted from reference}^{44} \]
The second option is to truncate the potential at some distance, \( r_c \), and ignore the tail corrections. This is the truncated model (TR),

\[
\phi_{\text{TR}}(r) = \begin{cases} 
\phi(r) & r \leq r_c \\
0 & r > r_c
\end{cases}.
\]

(2-2)

Molecular simulation studies of anisotropic or inhomogeneous systems, such as simulations of adsorption, interfaces, and surface tension typically use this method, although methods have recently been developed to include tail corrections for surface tension calculations.\(^{49,50}\)

The third possibility is to use a truncated and shifted potential that goes smoothly to zero at some finite value of \( r \). This method is often used in molecular dynamics studies. The truncated and shifted (TS) potential is given by

\[
\phi_{\text{TS}}(r) = \begin{cases} 
\phi(r) - \phi(r_c) & r \leq r_c \\
0 & r > r_c
\end{cases}.
\]

(2-3)

A shifted-force potential has been developed for MD simulations,\(^{51}\) but we will not consider that potential in this work. All three of these potentials (LRC, TR, TS) are used in both theoretical and simulation studies of fluids. It is therefore important to understand the phase behavior and the critical parameters of each of these fluids. A knowledge of how the properties change with the value of the cutoff is needed for comparing with experimental results or extrapolating to the full potential case.

In this paper we present a study of the critical parameters and phase diagrams of the LRC, TR, and TS LJ fluids as a function of the potential cutoff distance. Mixed-field finite-size scaling\(^{19,20}\) is used to obtain estimates of the critical constants for each of the three potential models in the thermodynamic limit. Multiple histogram reweighting\(^{11-13}\) is used to compute the phase diagrams. The multiple histogram reweighting technique is more precise and more efficient for computing phase diagrams than the widely used Gibbs Ensemble method.\(^{8,9}\)

Mon and Binder proposed a way to calculate the critical temperature of infinite systems from a series of apparent critical temperatures using a classical power law. The critical temperature for the 2-D lattice gas was obtained.\(^{52}\) Panagiotopoulos\(^{53}\) obtained values of the reduced critical
temperature, $T^*_c$, and reduced critical density, $\rho^*_c$, for the LJ truncated potential by fitting the coexistence data estimated from Gibbs Ensemble Monte Carlo at sub-critical temperatures to the Ising-like scaling law. In keeping with common practice, we define the reduced temperature as $T^* = kT/\epsilon$, where $k$ is the Boltzmann constant and $T$ is the absolute temperature. The reduced density is defined as $\rho^* = N\sigma^3/V$, where $N$ is the number of atoms and $V$ is the total volume.

Panagiotopoulos observed crossover from mean field to Ising-like behavior for 2-D, but not 3-D fluids. The disadvantage of this approach is that there is no rigorous way of deciding how many data near the critical point should be discarded from the parameter fitting to the scaling law. Smit calculated the critical point for the LRC and TS potentials by fitting coexistence data from Gibbs ensemble simulations to the scaling law and the law of rectilinear diameters. His results were $T^*_{cLRC} = 1.316(6)$, $\rho^*_{cLRC} = 0.304(6)$ for the LRC potential and $T^*_{cTS} = 1.085(5)$, $\rho^*_{cTS} = 0.317(6)$ for the TS potential with $r_c = 2.5\sigma$, where the number in parentheses represents the uncertainty in the last digit. Lotfi et al. used the NPT plus test particle method to predict $T^*_{cLRC} = 1.310$, $\rho^*_{cLRC} = 0.314$ for the LRC fluid by correlating the resulting bubble and dew densities. Caillol performed a finite-size scaling study for the LRC potential in the grand canonical ensemble with hyper-spherical boundary conditions. Results from the predictions were $T^*_{cLRC} = 1.326(2)$ and $\rho^*_{cLRC} = 0.316(2)$.

Wilding used finite-size scaling to estimate the critical constants in the thermodynamic limit. The critical temperature, chemical potential, and the field-mixing parameter can be tuned to satisfy the universal ordering operator distribution, $\hat{p}_M^*(x)$, assuming that the LJ fluid belongs to the same universality class as the Ising model. Apparent critical constants for a series of different system sizes were determined. The apparent critical constants are system size dependent due to corrections to scaling, energy operator asymmetry, and field mixing. The critical parameters at infinite volume can be obtained by extrapolating finite volume values to infinite volume using the proper scaling coordinates.

Wilding used the histogram reweighting technique to facilitate the prediction of critical constants and calculation of vapor-liquid equilibrium (VLE). The histogram reweighting technique was introduced by Ferrenberg and Swendsen. The essence of the method is that a single simulation
can give information about the properties of nearby state points. They developed a method of combining histograms from multiple simulations to greatly improve the statistics and extend the range of applicability of the method. This histogram reweighting method has been used to compute the phase diagrams and free energies of various fluids, but without applying finite-size scaling corrections.\textsuperscript{57–60} Wilding\textsuperscript{20} combined multiple histogram reweighting with mixed-field finite-size scaling to compute the critical constants for the TR LJ fluid truncated at $r_c = 2.5\sigma$. His results were $T_c^* = 1.1876(3)$ and $\rho_c^* = 0.3197(4)$. Potoń and coworkers\textsuperscript{56,61,62} also applied the same techniques to the LRC fluid and to LJ mixtures. They obtained $T_c^* = 1.3120(7)$, $\rho_c^* = 0.316(1)$ for the LRC fluid. The same methods have been applied to critical phenomena in polymer blends.\textsuperscript{5,63–66}

We note that Yan and de Pablo have developed a method they call hyper-parallel tempering for computing phase transitions.\textsuperscript{18} This method can also be combined with mixed-field finite-size scaling to compute critical properties extrapolated to the thermodynamic limit. The advantage of hyper-parallel tempering is that it is much more efficient at exploring phase-space than other methods.

\subsection*{2.2 Theory}

In this section we provide a brief overview of the multiple histogram reweighting and the mixed-field finite-size scaling methods and describe the use of the two methods to compute vapor liquid equilibrium phase diagrams.

\subsection*{2.2.1 Histogram Reweighting}

We have collected histogram data for fluctuations in energy and particle number from grand canonical Monte Carlo (GCMC) simulations. As the GCMC simulation proceeds, the potential energy and the number of particles are recorded in a two-dimensional histogram $H(U_N, N)$, where
$U_N$ is the configurational energy of the $N$ particle system. The grand partition function can be written as

$$
\Xi(\mu, V, T) = \sum_N \sum_{U_N} \exp[N\beta \mu - \beta U_N]\Omega(N, V, U_N)
$$

$$
= \sum_N \sum_{U_N} C H(U_N, N),
$$

(2-4)

where $\beta = 1/kT$, $\Omega(N, V, U_N)$ is the microcanonical partition function, and $C$ is a simulation-specific constant. The probability of observing the system in a given state point is

$$
P(U_N, N; \beta, \mu) = \frac{H(U_N, N)}{N} \exp[(N\beta \mu) - \beta U_N]\Omega(N, V, U_N)
$$

$$
= \frac{\Xi(\mu, V, T)}{N},
$$

(2-5)

where $N$ is defined as $N = \sum_N \sum_{U_N} H(U_N, N)$. In this work we use a modified chemical potential $\mu$ defined by

$$
\mu = \mu^f - kT \ln \Lambda^3,
$$

(2-6)

where $\mu^f$ is the full chemical potential and $\Lambda$ is the thermal de Broglie wavelength. Note that $\Omega(N, V, U_N)$ is independent of $T$ and $\mu$, so that simulations at different values of $T$, $\mu$, but the same $V$ all provide estimates of the same $\Omega$. Ferrenberg and Swendsen$^{12,13}$ proposed a method for combining multiple histograms in a way that minimizes the global error in the estimate of $\Omega(N, V, U_N)$. Using this procedure, one can show that the normalized joint probability distribution is given by

$$
P(U_N, N; \beta, \mu) = \sum_{j=1}^{K} H_j(N, U_N) \exp(-\beta U_N + \beta \mu N)
$$

$$
= \sum_{j=1}^{K} N_j \exp(-\beta_j U_N + \beta_j \mu_j N) \Xi(\mu, T, V) / \Xi(\mu_j, T_j, V),
$$

(2-7)

where $K$ is the number of histograms combined. The above equation assumes that the histogram data are collected from configurations that are essentially uncorrelated from one another. This means that $g_n = 1$ in Eq. (3) of ref.$^{12}$. If we set $\beta = \beta_i$ and $\mu = \mu_i$ in Eq. (2-7) where $i$ denotes one of the $K$ state points then we can sum Eq. (2-7) over all $U_N$ and $N$ to obtain

$$
1 = \sum_{N} \sum_{U_N} \frac{\sum_{j=1}^{K} H_j(N, U_N) \exp(-\beta_i U_N + \beta_i \mu_i N)}{\sum_{j=1}^{K} N_j \exp(-\beta_j U_N + \beta_j \mu_j N)} \Xi(\mu_i, T_i, V) / \Xi(\mu_j, T_j, V).
$$

(2-8)
Equation (2-8) can be used to estimate a value for each of the \( K - 1 \) independent ratios, \( \Xi_i/\Xi_j \), where \( \Xi_j = \Xi(\mu_j, T_j, V) \). There are \( K \) equations given by Eq. (2-8), one for each of the \( K \) state points. The values of \( \Xi_i/\Xi_j \) are obtained from a least squares fit. Values for each of the \( \Xi_j \)s may be estimated by arbitrarily specifying the value of \( \Xi \) at one of the \( K \) state points, then all the other \( \Xi_j \)s can be calculated from Eq. (2-8). Note that values of \( \Xi \) so calculated can only be determined to within a multiplicative constant. The ensemble average of some property \( X \) at \( \mu, V \) and \( T \) is given by

\[
\langle X \rangle_{\mu, V; T} = \sum_N \sum_{U_N} P(U_N, N; \beta, \mu) X(N, V, U_N) \\
= \frac{\sum_N \sum_{U_N} X(N, V, U_N) \Omega(N, V, U_N) \exp(-\beta U_N + \beta \mu N)}{\sum_N \sum_{U_N} \Omega(N, V, U_N) \exp(-\beta U_N + \beta \mu N)}, \tag{2-9}
\]

where

\[
\Omega(N, V, U_N) = \frac{\sum_{j=1}^K H_j(N, U_N)}{\sum_{j=1}^K N_j \exp(-\beta_j U_N + \beta_j \mu_j N)/\Xi(\mu_j, T_j, V)}. \tag{2-10}
\]

The pressure is given by

\[
PV = kT \ln \Xi, \tag{2-11}
\]

where \( \Xi \) can be obtained from Eq. (2-8) once all the \( \Xi_j \)s are known. Vapor-liquid equilibrium can then be determined by solving Eq. (2-11) for the chemical potential that gives the same pressure for both phases at the same \( T \). This can be accomplished by combining a limited number of histograms on each side of the phase diagram to form separate equations of state for the vapor and liquid branches. Several state points from the vapor side are combined to form an expression for \( \Xi^V \) for the vapor according to Eq. (2-8). Likewise, \( \Xi^L \) for the liquid branch is obtained by combining liquid and liquid-like state points. If the volume is constant for all the simulations then the equality of coexisting pressures implies the coexistence chemical potential, \( \mu^{\text{sat}} \), can be obtained by adjusting \( \mu \) so that

\[
\Xi^L(\mu^{\text{sat}}, T, V) = \Xi^V(\mu^{\text{sat}}, T, V), \tag{2-12}
\]

One can only determine the ratio of partition functions at two different states from Eq. (2-8). The absolute value of the partition function can be computed by extrapolation to low density.\(^{56}\)
However, the absolute value is not needed for computing VLE as long as the expressions for $\Xi$ on each side of the phase envelop are referenced to the same arbitrary constant. In this case the constant in Eq. (2-8) can be eliminated from Eq. (2-12). Hence, we use the least squares solution to Eq. (2-8) for all $K$ state points, referenced to a single constant, as the solutions for $\Xi^L$ and $\Xi^V$. The values of $\langle N \rangle$ for each phase can be obtained from Eq. (2-9). The coexistence density is given by $\langle N \rangle / V$. We designate this method for computing coexistence value of $\mu$ and $\rho$ as the EOS method, because we utilize the equation of state (EOS) through Eq. (2-11). We believe this to be the first time that this method has been used. There is some ambiguity as to how many state points to include in the expressions for $\Xi^L$ and $\Xi^V$. Clearly, including all $K$ state points would give a single isotherm with only trivial solutions to Eq. (2-12). The EOS method is shown graphically in Figs. 2.1 and 2.2 for the LRC fluid with a total of 14 state points. The solid lines

![Figure 2.1: The $\mu^*-\rho^*$ isotherms for the LRC fluid with $r_c^* = 2.5$ and $V^* = 1331$ at $T^* = 1.15$. The solid line is computed from multiple histogram reweighting of all 14 state points. The dotted lines are vapor (lower) and liquid (upper) isotherms constructed from nine state points in each phase, and containing four common state points. The dashed lines are vapor (lower) and liquid (upper) isotherms constructed from four state points in each branch.](image-url)
in these figures are isotherms generated by combining all 14 state points. The dashed lines are obtained by combining four state points on each side of the phase diagram for $\Xi^L$ and $\Xi^V$. The dotted lines are the results of combining nine state points, including four common points, in the expressions for $\Xi^L$ and $\Xi^V$. For $T^* = 1.15$ (Figure 2.1) there are no differences in the coexistence properties computed from either the four or nine histogram expressions. At the higher temperature of $T^* = 1.27$ (Figure 2.2) the four histogram expressions yield accurate saturated densities, while the expressions constructed from nine histograms give unreasonable densities, although the value of $\mu^{\text{sat}}$ is still accurate. The validity of the EOS method relies on an accurate extrapolation of the densities into the beginning of the metastable region for both the liquid and vapor branches. This is also a requirement of Hill’s method for computing phase transitions for small systems.\textsuperscript{67}

In all calculations of the EOS method we have used four state points each to construct $\Xi^L$ and $\Xi^V$ because this number of state points was found to give reliable extrapolation to the metastable region for all cases.
We have also used Hill’s method\textsuperscript{67} combined with the density distribution to calculate VLE. The two requirements for the validity of Hill’s method are that the system is not too small and that the temperature is not too close to criticality. There does not appear to be any quantitative measure for these requirements. The procedure for finding the coexistent chemical potential in our implementation of Hill’s method goes as follows. The $\mu$--$\rho$ isotherm near the transition region from vapor to liquid is first plotted. Linear extrapolation approximation of both the vapor and liquid branches is then performed. A vertical line is drawn that connects the extrapolated isotherms such that this line is bisected by the $\mu$--$\rho$ isotherm. In other words, the $\mu$--$\rho$ isotherm computed from multiple histogram reweighting passes through the midpoint of the vertical line. See Figure 2.3 for an example of this procedure. The value of the chemical potential that defines this vertical line is the coexistence chemical potential. If the exact extrapolation into the metastable region were known
then Hill’s method would yield the coexistence densities. Since we use linear extrapolation we need to use a more accurate method to compute the densities. We therefore compute the density distribution at the chemical potential obtained from Hill’s method. The number distribution, \( P(N) = \sum_{U_N} P(U_N, N; \beta, \mu) \), gives two distinct peaks, corresponding to the liquid and vapor states at subcritical temperatures. We have found that chemical potentials from Hill’s method produce curves with approximately equal area under each peak, as required for equilibrium from the equal area criterion.\(^5\) The agreement between Hill’s method and the equal area construction will be explored in more detail in Sec. 2.4. The coexistence densities are the weight averaged densities in each of the two regions. The position of each of the peaks also gives estimates of the coexistence densities. The procedure for calculating the coexistence chemical potential in Hill’s method can be automated by fitting lines to the liquid and vapor branches in the linear region of the curve. A one dimensional search is performed to find the vertical line whose mid-point is intersected by the \( \mu - \rho \) curve.

As stated above, we use linear extrapolation from the liquid and vapor branches into the metastable region. This gives very accurate estimates of \( \mu_{\text{sat}} \), although the extrapolation is not accurate at higher temperatures. An accurate extrapolation into the metastable region can be obtained by using the EOS method described above. Using \( \Xi^L \) and \( \Xi^V \) to extrapolate into the metastable region with Hill’s method is essentially a graphical implementation of the EOS method.

2.2.2 Finite-Size Scaling

The finite-size scaling technique (FSS) holds that the coarse-grained properties of systems near the critical point are universal. A prerequisite for universality is that the system size \( L \), where \( L \) is the box length, must be sufficiently large. The properties depend on the specific combination of \( L \) and the scaling field, which measures the deviations from criticality. At criticality, the joint
distribution \( p_L(M, E) \) exhibits scaling behavior of the form

\[
p_L(M, E) \simeq \Lambda_M^+ \Lambda_E^+ \tilde{p}_{M,E}(\Lambda_M^+ \delta M, \Lambda_E^+ \delta E) .
\]  

(2-13)

Near criticality,

\[
p_L(M, E) \simeq \Lambda_M^+ \Lambda_E^+ \tilde{p}_{M,E}(\Lambda_M^+ \delta M, \Lambda_E^+ \delta E, \Lambda_M h, \Lambda_E \tau) ,
\]  

(2-14)

where \( \tau \) and \( h \) are used to describe how far away the state point is from criticality. We introduce Eq. (2-14) because the universal distribution function \( \tilde{p}_{M}(x) \) is obtained from the integration of Eq. (2-14) with respect to energy \( E \) and then by setting \( h = 0 \) and \( \tau = 0 \) at criticality. The parameters in Eq. (2-13) and (2-14) are defined in the following equations,

\[
\Lambda_E = \alpha_E L^{1/\nu} ,
\]  

(2-15)

\[
\Lambda_M = \alpha_M L^{d-\beta/\nu} ,
\]  

(2-16)

\[
\Lambda_M \Lambda_M^+ = \Lambda_E \Lambda_E^+ = L^d ,
\]  

(2-17)

\[
\delta M \equiv M - \langle M \rangle_c ,
\]  

(2-18)

\[
\delta E \equiv E - \langle E \rangle_c ,
\]  

(2-19)

\[
\mathcal{M} = \frac{\rho^* - su^*}{1 - sr} ,
\]  

(2-20)

\[
\mathcal{E} = \frac{u^* - r \rho^*}{1 - sr} ,
\]  

(2-21)

where \( s \) and \( r \) are the mixed-field parameters, \( u^* = U_N/(eV^*) \), where \( V^* = V/\sigma^3 \), \( d, \beta \) and \( \nu \) are universal constants and \( \alpha_M \) and \( \alpha_E \) are system related constants. Equation (2-13) is only valid in the limit of large \( L \). For small system sizes, one must consider \( L \)-dependent corrections to scaling.
This means that the apparent critical constants for small systems are $L$-dependent. The infinite volume critical constants can be extrapolated from results of finite systems plotted against the appropriate coordinate.\textsuperscript{19,20} For example, the critical temperature scaling law is

$$T_c^*(\infty) - T_c^*(L) \propto L^{-(\theta+1)/\nu},$$  \hspace{1cm} (2-22)

where $T_c^*(\infty)$ is the reduced critical temperature in the thermodynamic limit, while, $T_c^*(L)$ is the reduced apparent critical temperature for the system size with box length of $L$, and $\theta$ is a universal constant.

Several histogram reweighting simulations near the critical point must be performed and combined in order to compute the apparent critical temperature with sufficient accuracy. This means that we must have an initial estimate for the critical point before collecting the histograms. This can be accomplished by performing histogram collection simulations over a range of temperatures and chemical potentials in order to estimate the phase diagram from either Hill’s method or the EOS method. The coexistence data away from the critical region are then fitted to the Ising form power law to obtain estimates for $T_c$ and $\rho_c$. The power law expression is given by

$$\rho_\pm^* - \rho_c^* = a|T^* - T_c^*|^{\beta} \pm b|T^* - T_c^*|^{\beta},$$  \hspace{1cm} (2-23)

where $\rho_+$ is the liquid density and $\rho_-$ is the vapor density, and $\beta$ is the critical exponent. Values of the parameters $a, b, T_c^*$, and $\rho_c^*$ are adjusted simultaneously to obtain the best fit to the data. An estimate of $\mu_c$ is then obtained from Hill’s method by constructing the $\mu-\rho$ isotherm for the estimated $T_c$ with multiple histogram reweighting from Eq. (2-9). Two other temperatures, one on either side of the estimated critical temperature, are chosen and the corresponding coexistence chemical potentials are computed from Hill’s method for those temperatures. Although Hill’s method is not strictly valid near the critical point, it is used to provide an estimate of the coexistence chemical potential. Our calculations show that this estimate is quite close to the infinite volume critical chemical potential. Histograms are collected at each of these three state points. The histograms are then combined according to Eq. (2-8) and an estimate of the global microcanonical
partition function is obtained from Eq. (2-10). The probability distribution of $\mathcal{M}$ is mapped onto $x$, where

$$x = \frac{\mathcal{M} - \langle \mathcal{M} \rangle}{\sqrt{\langle \mathcal{M}^2 \rangle - \langle \mathcal{M} \rangle^2}}.$$  \hspace{1cm} (2-24)

This definition results in $x$ having unit variance. The apparent critical constants are obtained by adjusting $T_c$, $\mu_c$ and $s$ such that $p_L(x)$ collapses onto the universal distribution $\tilde{p}_\mathcal{M}(x)$. We have used the BFGS method\(^6\) to find the optimal values of the critical constants. It is important to have good initial guesses for $T_c$, $\mu_c$ and $s$ to ensure the convergence of the method. The process for finding $T_c$, $\mu_c$ and $s$ is outlined as follows:

1. An initial guess for $T_c(L)$ is taken from the fit to the power law.

2. An initial guess for $\mu_c(L)$ is found by iteration starting from the value of $\mu_c(L)$ from Hill’s method. The probability $P(U_N, N; \beta, \mu)$ is computed from Eq. (2-7), with the values of $\Xi(\mu_j, T_j, V)$ calculated from Eq. (2-8) using the three histograms collected at the state points identified above. The normalized probability $P(N)$ is obtained from $P(U_N, N; \beta, \mu)$ with

$$P(N) = \sum_{U_N} P(U_N, N; \beta, \mu).$$

The density distribution, $P(\rho) = P(N)$, is plotted and the chemical potential is adjusted by trial and error until a double-peaked distribution with approximately equal peak heights is obtained.\(^2\)

3. An initial guess for $s$ is chosen, keeping $r = -1.0$. The values of $\mathcal{M}$ are computed from Eq. (2-20) for all non-zero values of $P(U_N, N; \beta, \mu)$. A table containing $\mathcal{M}$ and $P(U_N, N; \beta, \mu)$ sorted by $\mathcal{M}$ is created and the minimum and maximum values of $\mathcal{M}$ corresponding to non-zero probability are identified. The probability of $\mathcal{M}$, $P(\mathcal{M})$, is computed by summing $P(U_N, N)$ over all values of $(U_N, N)$ corresponding to the same (discrete) value of $\mathcal{M}$. In our calculations, we divide the range of $\mathcal{M}$ into 90 intervals with the interval width given by

$$\Delta \mathcal{M} = \frac{(\mathcal{M}_{\text{max}} - \mathcal{M}_{\text{min}})}{90},$$  \hspace{1cm} (2-25)
where $M_{\text{max}}$ and $M_{\text{min}}$ are the maximum and minimum values of $M$ corresponding to nonzero values of $P(M)$. The density distribution of $x$, $p_L(x)$, is obtained through

$$p_L(x) = \frac{P(M)}{\Delta M} \sqrt{\langle M^2 \rangle - \langle M \rangle^2}.$$  \hspace{1cm} (2-26)

The value of $s$ is tuned until $p_L(x)$ is qualitatively (visually) similar to the universal distribution $\bar{p}_M(x)$. We have found that the value of $s$ is typically close to $-0.035$.

4. If $p_L(x)$ does not qualitatively collapse onto $\bar{p}_M(x)$ in Step 3 then one chooses a new initial guess for $T_c(L)$ and returns to Step 2.

5. The initial guesses for $T_c(L)$, $\mu_c(L)$ and $s$ from the above steps are input to the BFGS method and the output values are taken as the best estimates for the system size dependent critical parameters. The objective function used in the BFGS method is the sum of the square of the difference between $p_L(x)$ and $\bar{p}_M(x)$ on the 91 discrete points defined by $\Delta M$.

### 2.3 Simulation Details

We have performed separate sets of GCMC histogram simulations for estimating the saturated liquid and vapor densities and for computing the apparent critical constants. A single Monte Carlo (MC) move consisted of either an attempt to displace, create, or destroy an atom. The probability of making a displacement was set to 0.5, and the probability of attempting to create or destroy an atom was set to 0.25. The displacement acceptance ratio was adjusted during equilibration to be close to 0.4.
2.3.1 Vapor-Liquid Equilibrium

The VLE calculations for the LRC fluid were performed for values of the reduced cutoff, $r_c^* = r_c/\sigma$, of 2.5 and 5.0. Reduced volumes, $V^* = V/\sigma^3$, of 270, 540, and 1331 were used. Vapor-liquid equilibrium densities were computed for the $r_c^* = 5.0$ LRC fluid for $V^* = 1331$. Cutoff values of 2.5, 3.5, and 5.0 were used for the TR fluid. The volumes used in the simulations were 729, 729, and 1331, respectively. Vapor-liquid equilibrium for the TS fluid was computed for $r_c^* = 2.5$ and 3.5, with $V^* = 729$ in both cases. In all the simulations for VLE calculations the systems were equilibrated for at least $5 \times 10^6$ MC moves, and data collection was carried out for $5 \times 10^6$ MC moves. Production runs were divided into 10 subblocks for estimation of the variance.

2.3.2 Finite-Size Scaling

The simulations for use in FSS calculations required much longer runs to collect histograms of the accuracy required by the FSS method. The production runs lasted a total of $10^8$ to $10^9$ MC moves, depending on the system size. A linked cell neighbor list was used for simulations of the larger systems ($L > 3r_c$). The cell lists were regenerated only after successful deletion steps. For displacements and creation steps the lists were directly updated rather than being regenerated. The reduced volumes used for simulations of the TR fluid with a cutoff of $2.5\sigma$ are $V^* = 422, 729, 1000, 1331, 1953$ and $3375$. Two independent sets of simulations were performed for each volume, giving two independent estimates of the apparent critical properties. The standard deviations (error bars in Figs. 2.4 and 2.5) were estimated from the two independent estimates of the critical properties.

The uncertainty in the intercept (i.e., $T_c$ or $(\beta\mu)_c$) was computed from the uncertainty in the individual values of the data as described in 69. The critical density and standard deviation at the thermodynamic limit was simply taken as the average of the apparent critical densities because the apparent critical density was essentially independent of system size.
Table 2.1: Saturation densities computed from the EOS and Hill’s method (see text for details). Data are for the LRC fluid with \( r_c^* = 2.5 \) and \( V^* = 1331 \). The percent difference is calculated relative to Hill’s method. The percent average absolute deviation is denoted as %AAD. The uncertainties of the coexistence densities from the EOS method are estimated from three sets of independent calculations for a smaller system size \((V^* = 270)\).

<table>
<thead>
<tr>
<th>( T^* )</th>
<th>( \rho^*_V ) EOS</th>
<th>( \rho^*_V ) Hill’s Method</th>
<th>% difference</th>
<th>( \rho^*_l ) EOS</th>
<th>( \rho^*_l ) Hill’s Method</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15</td>
<td>0.0726(4)</td>
<td>0.0726</td>
<td>0</td>
<td>0.608(3)</td>
<td>0.608</td>
<td>0</td>
</tr>
<tr>
<td>1.16</td>
<td>0.0769(4)</td>
<td>0.0769</td>
<td>0</td>
<td>0.601(3)</td>
<td>0.601</td>
<td>0</td>
</tr>
<tr>
<td>1.17</td>
<td>0.0816(5)</td>
<td>0.0816</td>
<td>0</td>
<td>0.594(3)</td>
<td>0.594</td>
<td>0</td>
</tr>
<tr>
<td>1.18</td>
<td>0.0866(5)</td>
<td>0.0866</td>
<td>0</td>
<td>0.587(4)</td>
<td>0.587</td>
<td>0</td>
</tr>
<tr>
<td>1.19</td>
<td>0.0920(6)</td>
<td>0.0920</td>
<td>0</td>
<td>0.578(4)</td>
<td>0.578</td>
<td>0</td>
</tr>
<tr>
<td>1.20</td>
<td>0.0978(9)</td>
<td>0.0978</td>
<td>0</td>
<td>0.569(4)</td>
<td>0.569</td>
<td>0</td>
</tr>
<tr>
<td>1.21</td>
<td>0.1039(9)</td>
<td>0.104</td>
<td>0.1</td>
<td>0.559(5)</td>
<td>0.559</td>
<td>0</td>
</tr>
<tr>
<td>1.22</td>
<td>0.110(1)</td>
<td>0.111</td>
<td>0.9</td>
<td>0.548(6)</td>
<td>0.548</td>
<td>0</td>
</tr>
<tr>
<td>1.23</td>
<td>0.117(2)</td>
<td>0.118</td>
<td>0.8</td>
<td>0.537(7)</td>
<td>0.537</td>
<td>0</td>
</tr>
<tr>
<td>1.2405</td>
<td>0.124(3)</td>
<td>0.126</td>
<td>1.6</td>
<td>0.526(8)</td>
<td>0.525</td>
<td>0.2</td>
</tr>
<tr>
<td>1.25</td>
<td>0.131(5)</td>
<td>0.134</td>
<td>2.2</td>
<td>0.516(10)</td>
<td>0.515</td>
<td>0.2</td>
</tr>
<tr>
<td>1.2603</td>
<td>0.138(6)</td>
<td>0.143</td>
<td>3.5</td>
<td>0.505(13)</td>
<td>0.502</td>
<td>0.6</td>
</tr>
<tr>
<td>1.27</td>
<td>0.144(9)</td>
<td>0.153</td>
<td>5.9</td>
<td>0.496(16)</td>
<td>0.488</td>
<td>1.6</td>
</tr>
<tr>
<td>%AAD</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
</tbody>
</table>

The volume sizes for the TR and TS fluids with cutoffs of 3.5 \( \sigma \) were 729, 1405, 2000, and 2800. The volumes for the TR and LRC fluids with cutoffs of 5.0 \( \sigma \) were chosen to be 1331, 1953, and 3375. For the TS fluid with a cutoff of 2.5 \( \sigma \) the volumes were 729, 1000, 1331, 1953, and 3375. For the LRC fluid with a cutoff of 2.5 \( \sigma \) the volumes were 729, 1000, 1331, and 1953.

2.4 Results and Discussion

2.4.1 the LRC Fluid

The results of VLE calculations from the EOS method and Hill’s method are shown in Table 2.1. The data are for \( V^* = 1331 \). The EOS partition functions were constructed by combining four state points in each phase. The saturated densities computed from these two methods are in excellent agreement. The error estimates for the EOS method were computed from the standard deviations.
Table 2.2: Comparison between the reduced saturation chemical potentials $\mu^{\text{sat}}$ and densities computed from Hill's method and the equal area construction. The state points are for the LRC fluid with a cutoff of 2.5 $\sigma$ and reduced volume of 1331.

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\mu^{\text{sat}}$</th>
<th>$\rho_e$</th>
<th>$\rho_i^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hill’s Method</td>
<td>Equal Area</td>
<td>Hill’s Method</td>
<td>Equal Area</td>
</tr>
<tr>
<td>1.15</td>
<td>$-3.684358$</td>
<td>$-3.684357$</td>
<td>0.072569</td>
</tr>
<tr>
<td>1.18</td>
<td>$-3.659204$</td>
<td>$-3.659207$</td>
<td>0.086633</td>
</tr>
<tr>
<td>1.23</td>
<td>$-3.621868$</td>
<td>$-3.621879$</td>
<td>0.117536</td>
</tr>
</tbody>
</table>

from three independent sets of simulations at a smaller volume ($V^* = 270$). This assumes that the error in the EOS method is roughly constant in going from $V^* = 270$ to 1331.

We calculated the saturation chemical potential $\mu^{\text{sat}}$ from the equal area construction using the bisection method for three different temperatures. We started the iteration with an initial guess for $\mu^{\text{sat}}$ from Hill’s method (truncated to four decimal places). The values of $\mu^{\text{sat}}$ from Hill’s method and the equal area construction are compared in Table 2.2.

The bisection method typically converged to five decimal places within ten iterations. We have also computed the saturation densities from the value of $\mu^{\text{sat}}$ from both Hill’s method (combined with the density distribution) and the equal area construction. The results are shown in Table 2.2. The difference between the saturated densities from the two methods is smaller than the statistical uncertainty in the data. Hence, we choose to use Hill’s method because it has the advantage of giving good estimates even for small systems fairly near the critical point where the density distributions overlap and the equal area construction is difficult to implement.

Several $\mu^*-\rho^*$ isotherms for the LRC fluid with $r_c^* = 2.5$ are plotted in Figure 2.6, where $\mu^* = \mu/\epsilon$. Results for two different temperatures, $T^* = 1.16$ and 1.25, and volumes $V^* = 270$ and 540 are presented. The effect of volume on the equilibrium chemical potential was found to be very small at both temperatures. For a temperature of $T^* = 1.16$, $V^* = 270$ gave a saturation chemical potential of $\mu^* = -3.6735$, while $V^* = 540$ resulted in $\mu^* = -3.6736$. For $T^* = 1.25$, the values of $\mu^*$ at saturation are $-3.6074$ and $-3.6070$ for $V^* = 270$ and 540, respectively.

We have estimated the critical constants by fitting the coexistence data for $V^* = 1331$ at low temperature (1.15–1.26) to the power law using the 3-D Ising critical exponent $\beta = 0.3258$ (This
\( \beta \) is not to be confused with the reciprocal temperature, as in Eq. (2-4)). This gave \( T_c^* = 1.3119 \), \( \rho_c^* = 0.316 \). Finite-size scaling was then used to calculate the critical constants using this estimated \( T_c^* \) as an initial guess. The results are \( T_c^*(\infty) = 1.3241(9) \), \( \rho_c^*(\infty) = 0.3165(7) \). The coexistence densities were calculated from Hill’s method. We have used \( T_c^*(\infty) \) and \( \rho_c^*(\infty) \) in conjunction with the power law expression of Eq. (2-23) to correlate the VLE surface treating \( a \) and \( b \) as the only adjustable parameters. In this paper, data from the six lowest temperatures were used to fit the values of \( a \) and \( b \) in each case. The phase diagram generated from Eq. (2-23) for the LRC fluid with \( r_c^* = 2.5 \) is shown in Figure (2.7). The effect of changing the cutoff from 2.5\( \sigma \) to 5.0\( \sigma \) on the coexistence properties of the LRC fluid is shown in Figs. 2.8-2.9. From Figure (2.8) we see that the coexistence densities for \( r_c^* = 2.5 \) and \( r_c^* = 5.0 \) at \( V^* = 1331 \) are in very close agreement over the entire temperature range. Figures 2.10 and 2.9 demonstrate that there is a systematic difference in the values of the the saturation chemical potentials for the LRC fluids with \( r_c^* = 2.5 \) and 5.0, both at \( V^* = 1331 \). The values of \( \mu^* \) at saturation are uniformly higher for \( r_c^* = 5.0 \) compared with \( r_c^* = 2.5 \) over the entire temperature range. The average shift is about 0.0043. The reason for this is not apparent.

2.4.2 the TR and TS Fluids

We have performed detailed calculations of the TR fluid with a cutoff of 2.5\( \sigma \). The results are shown in Figs. 2.4 and 2.5. The extrapolated value of \( T_c^*(\infty) \) is 1.1879(4) and \( (\beta\mu)_c(\infty) \) is \(-2.777(1) \). These values are in excellent agreement with \( T_c^*(\infty) = 1.1876(3) \) and \( (\beta\mu)_c(\infty) = -2.778(2) \) from Wilding.\(^{20} \) We have found that \( \rho_c^*(L) \) varies weakly with system size. The arithmetic average of \( \rho_c^*(L) \) was used to approximate \( \rho_c^*(\infty) \), giving a value of 0.3201, which is very close to 0.3197(4) from Wilding.\(^{20} \) The field mixing parameter \( s \) was around \(-0.035 \), which is reasonably close to Wilding’s value of \(-0.0275 \), converted to the reduced units used in this paper.

The phase diagrams for the TR and TS fluids with \( r_c^* = 2.5 \) were generated in the same way as for the LRC fluid and are plotted in Figure 2.11. The phase diagrams for the TR and TS fluids
Table 2.3: Critical properties of the LJ fluids considered in this work. Critical constants estimated from the power law, Eq. (2-23), are denoted by PL. Finite-size scaling was used to compute the properties denoted by FSS.

<table>
<thead>
<tr>
<th>Type</th>
<th>$T_c^*(\infty)$</th>
<th>$\rho_c^*(\infty)$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>LRC 2.5</td>
<td>1.3241(9)</td>
<td>0.3165(7)</td>
<td>this work [FSS]</td>
</tr>
<tr>
<td>LRC 5.0</td>
<td>1.3145(2)</td>
<td>0.316(1)</td>
<td>this work [FSS]</td>
</tr>
<tr>
<td>LRC</td>
<td>1.3120(7)</td>
<td>0.316(1)</td>
<td>Potoff et al. [FSS]</td>
</tr>
<tr>
<td>LRC</td>
<td>1.326(2)</td>
<td>0.316(2)</td>
<td>Caillol 55</td>
</tr>
<tr>
<td>LRC</td>
<td>1.310</td>
<td>0.314</td>
<td>Lotfi 14</td>
</tr>
<tr>
<td>LRC</td>
<td>1.316(6)</td>
<td>0.304(6)</td>
<td>Smit 54</td>
</tr>
<tr>
<td>TR 2.5</td>
<td>1.1879(4)</td>
<td>0.3201(4)</td>
<td>this work [FSS]</td>
</tr>
<tr>
<td>TR 3.5</td>
<td>1.2647(4)</td>
<td>0.3164(4)</td>
<td>this work [FSS]</td>
</tr>
<tr>
<td>TR 5.0</td>
<td>1.2963(1)</td>
<td>0.3161(8)</td>
<td>this work [FSS]</td>
</tr>
<tr>
<td>TS 2.5</td>
<td>1.0795(2)</td>
<td>0.3211(5)</td>
<td>this work [FSS]</td>
</tr>
<tr>
<td>TS 3.5</td>
<td>1.2211(9)</td>
<td>0.3183(5)</td>
<td>this work [FSS]</td>
</tr>
</tbody>
</table>

with $r_c^* = 3.5$ are plotted in Figure 2.12.

### 2.4.3 Summary of Critical Constants

Values of $T_c^*(\infty)$ and $\rho_c^*(\infty)$ from this work and previous simulations are summarized in Table 2.3.

The critical temperature for the TR fluid is about 10% larger than that for the TS fluid when both have $r_c^* = 2.5$. When $r_c^*$ is increased to 3.5 the difference in critical temperature is reduced to 3.6%. We are specifically interested in comparing the properties of the LRC fluid with the truncated fluid. The reason for our interest is that in many simulations of inhomogeneous fluids (e.g., adsorption) the TR fluid is used as an approximation to the LRC fluid since it is more difficult to apply the long range corrections for an inhomogeneous fluid. One would therefore like to know what value of the cut off would give a phase diagram that is “similar” to that of the LRC fluid.
We compare the LRC and TR fluid, both with \( r_c^* = 5.0 \). The critical temperature for the LRC fluid is 1.3145(2) while that for the TR fluid is 1.2963(1). This is a decrease of 1.4% in \( T_c^* \). The phase diagrams for these two fluids are plotted in Figure 2.13. The average absolute deviation in the coexistence densities between the LRC and TR fluids is about 0.8% and 1% for the vapor and liquid, respectively (using the LRC fluid as the reference). These are the magnitudes of the errors one would expect to incur by using the TR, \( r_c^* = 5.0 \) fluid to represent the LRC fluid.

The value of \( T_c^*(\infty) \) for the LRC fluid with a cutoff of 5.0\( \sigma \) is closer to that reported by Potoff \textsuperscript{56} than for 2.5\( \sigma \). In Potoff’s calculation, the cutoff distance is not actually fixed, but increases with the system size. Hence, we expect the larger cutoff to be in better agreement with Potoff’s calculation. The value of \( T_c^*(\infty) \) for the LRC fluid with a cutoff of 2.5\( \sigma \) is about 0.7% larger than that for 5.0\( \sigma \) and they are both close to Smit’s calculation given the range of uncertainties.\textsuperscript{54}

The critical constants for the TR fluid with a cutoff of 2.5\( \sigma \) are in excellent agreement with those from Wilding.\textsuperscript{20} They are also consistent with those from Potoff.\textsuperscript{56} The estimate of critical constants for TS fluid with a cutoff of 2.5\( \sigma \) is close to Smit’s results.\textsuperscript{54}

Predictions of \( T_c^* \) from the power law (Eq. (2-23)) are different from those using FSS. The power law critical temperatures are uniformly higher than the values of \( T_c^* \) from FSS. The difference is less than 2% in each case (see Table 2.3). The FSS method is more accurate, but the scaling law can provide estimation of the critical point around which histograms are collected when FSS is used to calculate the critical constants for infinite volume.

### 2.5 Conclusions

We have developed a new method for computing VLE from multiple histogram reweighting. We call this the EOS method because the expressions for the equation of state are constructed separately for the liquid and vapor branches from the histograms. We have used the EOS approach,
Hill’s method, and equal area construction to compute VLE. All three methods are in very good agreement.

The difference in $T_c^*(\infty)$ between the TR and TS fluids decreases from 10% to 3.6% as the cutoff distance increases from $2.5\sigma$ to $3.5\sigma$. The critical temperature for the LRC fluid is 1.4% larger than $T_c^*(\infty)$ for the TR potential with $r_c^* = 5.0$. The absolute average deviations in the saturation densities for the LRC and TR fluids with cutoffs of $5.0\sigma$ are 0.8% and 1% for the vapor and liquid, respectively. This indicates that the TR fluid with $r_c^* = 5.0$ is a reasonable approximation to the LRC fluid, giving quantitative agreement within a few percent at temperatures well below the critical point.

It is commonly assumed that the properties of the LRC fluid are not sensitive to the value of the cutoff for $r_c^* \geq 2.5$. This appears to be true for saturated vapor and liquid densities. However, the values of $\mu$ at vapor-liquid coexistence for the LRC fluid are systematically shifted to larger values as the reduced cutoff distance increases from 2.5 to 5.0. The reason for the shift in $\mu^{\text{sat}}$ with $r_c^*$ is not known. The infinite volume critical temperature for $r_c^* = 2.5$ is about 0.7% larger than that for $r_c^* = 5.0$. 


Figure 2.4: The apparent $T^*_{c}(L)$, plotted as a function of $L^{-(\theta+1)/\nu}$, with $\theta = 0.54$ and $\nu = 0.629$. The estimated value of $T^*_c(\infty)$ from extrapolation to infinite volume of the least squares fit to the data yields 1.1879(4).
Figure 2.5: The apparent \((\beta \mu)_c(L)\), plotted as a function of \(L^{-(\theta+1)/\nu}\) as in Figure 2.4. The estimated value of \((\beta \mu)_c(\infty)\) is \(-2.777(1)\).

Figure 2.6: Isotherms for two temperatures and two different system sizes for the LRC fluid with a cutoff of \(2.5\sigma\).
Figure 2.7: Coexistence densities for the LRC fluid with a cutoff of $2.5\sigma$ and a volume of $V^* = 1331$. The line is a fit to Eq. (2-23) using the critical point and the coexistence densities in the range $1.15 \leq T \leq 1.20$. The filled circle is the critical point extrapolated from finite-size scaling. The coexistence densities were obtained from Hill’s method. Also shown ($\triangleright$) are the results of Conrad and de Pablo for the LRC fluid.\textsuperscript{60}
Figure 2.8: The phase diagram for the LRC fluid with a cutoff of 5.0σ (squares). The finite-size corrected critical point for $r_c^* = 5.0$ is shown as the filled square. The line is a fit to Eq. (2-23) using the critical point and the coexistence densities in the range $1.16 \leq T \leq 1.21$. The coexistence densities for $r_c^* = 2.5σ$ (pluses) are also included. The system volume was $V^* = 1331$ in both cases.
Figure 2.9: A plot of $T^* - \mu^*$ at coexistence for $r^*_c = 2.5$ (pluses) and 5.0 (squares), both at $V^* = 1331$. The lines are drawn as a guide to the eye. The value of $\mu^{\text{sat}}$ increases with increasing cutoff.
Figure 2.10: The density versus chemical potential isotherms for $r_c^* = 2.5$ (solid line) and 5.0 (dashed line), both for $V^* = 1331$, and $T^* = 1.17$. 
Figure 2.11: The phase diagrams for the TR and TS fluids with $r_c^* = 2.5$ and $V^* = 729$. The open circles (TR) and diamonds (TS) are computed from Hill’s method. The filled symbols are the critical constants extrapolated from finite-size scaling. The lines are fits to the low temperature data and the critical points according to Eq. (2-23). The coexistence data for the TR fluid from Wilding$^{20}$ ($\triangle$) and the TS fluid from Smit$^{54}$ ($\triangledown$) are included for comparison.
Figure 2.12: The phase diagrams for the TR and TS fluids with a cutoff of $r_c^* = 3.5$ and a volume of $V^* = 729$. The data for the TR fluid are shown as open circles, and the data for the TS fluid are denoted by the open diamonds. The infinite volume critical constants are shown as filled symbols. The lines are fits of the critical constants and VLE data away from criticality to Eq. (2.23).
Figure 2.13: The phase diagrams for the LRC (open squares) and TR (open circles) fluids with $r_c^* = 5.0$ and $V^* = 1331$. The finite-size scaling corrected critical constants are shown as filled symbols. The lines are fits of the critical constants and VLE data away from criticality to Eq. (2-23).
3.0 PHASE TRANSITIONS OF ADSORBED FLUIDS COMPUTED FROM MULTIPLE HISTOGRAM REWEIGHTING

3.1 Introduction

Confined fluids are known to exhibit a rich variety of phase transitions that are absent in bulk fluids. Perhaps three of the most interesting phenomena are capillary condensation, prewetting transitions, and layering transitions. Each of these transitions have previously been studied in some detail through the use of a variety of computer simulation techniques. Different simulation methods are often required to characterize these different phenomena; for example grand potential or Gibbs ensemble calculations are needed to locate capillary condensation. Prewetting transitions are often located by plotting the isotherms and density profiles from grand canonical Monte Carlo or isothermal-isobaric Monte Carlo simulations. Layering transitions have been observed from grand canonical Monte Carlo simulations coupled with grand potential calculations.

In this paper we demonstrate that multiple histogram reweighting (MHR) can be an accurate and efficient tool for studying phase transitions in confined fluids. The MHR method has been shown to be useful for studying the phase behavior of bulk fluids, but has not been widely used for studying the properties of confined fluids.

Gelb and Gubbins have applied the histogram reweighting technique to study the phase diagram of a simple binary liquid mixture in the semi-grand canonical ensemble. They used single histogram reweighting to estimate the biasing potential needed for barrier crossing. Escobedo and de Pablo have studied the secondary transition for a 12-6 Lennard-Jones fluid in a composite large-sphere matrix with histogram reweighting analysis. Recently, Potoff and Siepmann have calculated the effect of branching on the fluid phase behavior of alkane monolayers using histogram reweighting with the finite-size scaling technique.

\[\text{This chapter is reprinted from reference 45}\]
Capillary condensation occurs when a fluid is strongly adsorbed in a micropore below the capillary condensation critical temperature. The transition is characterized by a gas condensing to a liquid-like state that entirely fills the pore space at a bulk pressure less than the saturation value. Grand canonical Monte Carlo (GCMC) simulations are typically used to construct the adsorption isotherms for the prediction of capillary condensation. Peterson and Gubbins calculated the grand potential through integration of isotherms and paths of constant chemical potential in order to compute the equilibrium chemical potential for capillary condensation. In a completely different approach, Heffelfinger et al. used quenched molecular dynamics to study capillary condensation in cylindrical pores. The chemical potentials of the gas-like and liquid-like regions were computed from the potential distribution theorem for inhomogeneous fluids. Some prior knowledge of the phase behavior is required to implement this approach, because the overall density must be chosen such that the system is in the unstable region when quenched. Panagiotopoulos extended the Gibbs ensemble Monte Carlo method for the prediction of adsorption and capillary condensation. The coexistence densities of gas-like and liquid-like phases in equilibrium inside a pore can be obtained through a single pore-pore calculation. However, a series of pore-fluid calculations are then needed to construct the isotherm.

The existence of wetting transitions was first predicted in 1977 independently by Cahn and Ebner and Saam. It was predicted that a gas that weakly adsorbs onto a solid surface will exhibit nonwetting behavior at low temperature and may undergo a first order transition to wetting behavior at a higher temperature $T_w$. By nonwetting we mean that the thickness of a film adsorbed on a surface remains finite at all pressures below the saturation vapor pressure; by wetting we mean that the film thickness diverges as the saturation pressure is approached. Prewetting occurs when there is a first order transition from a thin-film to a thick-film adsorbed on the surface. The prewetting transition terminates at the critical prewetting temperature. Finn and Monson were the first to observe the existence of a prewetting transition through molecular simulation. They used isothermal-isobaric Monte Carlo to identify the prewetting transition by observing the jump in adsorption on an isotherm associated with the thin- to thick-film transition. Large
fluctuations in the coverage typically accompany prewetting transitions, making precise location of the transition a difficult task. For this reason, later work by Fan and Monson\textsuperscript{86} utilized calculation of the surface tensions in the thin- and thick-films in order to locate the prewetting transition more precisely. Experiments and simulations by Mistura \textit{et al.}\textsuperscript{87} recently demonstrated that Ar on solid CO$_2$ actually exhibits triple-point wetting rather than prewetting as predicted by Monson and coworkers. The reason for this discrepancy is that the potential models used in the simulations\textsuperscript{76,86} do not accurately represent the potential surface of the real Ar-CO$_2$ system. More realistic solid-fluid potential models\textsuperscript{87} are more strongly attractive than the potential used by Monson \textit{et al.} We note that grand canonical Monte Carlo simulations have been used to study prewetting transitions for a variety of other systems\textsuperscript{88,89}.

Thick films adsorbing on a substrate can either grow continuously or in a stepwise fashion. If the growth is stepwise, then each layer grows by a succession of first-order layering transitions at pressures lower than the bulk saturation pressure\textsuperscript{90}. Layering transitions of simple fluids and lower alkanes on graphite have been studied extensively through experimental techniques\textsuperscript{91}. Iwamatsu has shown that layering transitions can be expected to occur for systems that exhibit both incomplete and complete wetting\textsuperscript{92}. For wetting growth the thickness of the film increases to infinity as the bulk saturation pressure is approached. If the wetting is incomplete then a transition from incomplete wetting to wetting will occur as the temperature is increased. Layering transitions will persist to $T_w$ if $T_w < T_R$ where $T_R$ is the bulk roughening transition\textsuperscript{93}. If $T_w > T_R$ then a thin-film to thick-film prewetting transition precedes divergence of the film thickness. Each of the layers terminates at a layer critical point temperature, $T_c(m)$, where $m$ is the number of layers in the film. It has been found that $T_c(m)$ can approach the triple point either from above\textsuperscript{93} or below\textsuperscript{94} with increasing $m$.

In this paper we demonstrate that MHR can be applied accurately and efficiently to compute capillary condensation, prewetting transitions, and layering transitions. Histograms for a given system can be combined in order to compute isotherms at any of the conditions spanned by the simulations. The location of phase transitions can be accurately computed through the equal area
criterion\textsuperscript{44} without resorting to computation of the grand potential\textsuperscript{72,73}. The precision of MHR allows us to observe crossover in the critical exponents for capillary condensation. This is difficult to accomplish through a series of isolated simulations. In this paper, we use MHR to construct estimates for the capillary condensation, wetting temperature and prewetting critical temperatures, and to find layering transition pressures for propane on graphite.

### 3.2 Theory and Methods

The basic idea of MHR is that histograms collected from a number of independent simulations may be combined to construct an estimate for the partition function\textsuperscript{11–13}. The multiple histogram reweighting technique can be used to accurately calculate phase diagrams of bulk fluids\textsuperscript{4,5,44,77,78}. This method allows the calculation of equilibrium properties over a range of conditions from a relatively small number of state points. The phase diagrams from histogram reweighting can be very accurate\textsuperscript{4}. The coexistence densities and saturation chemical potential can be calculated through the use of the equal area criterion and Hill’s method\textsuperscript{44}.

Sufficient overlap between histograms of adjacent state points is necessary in order to implement the MHR technique. We here describe one method for checking for the extent of overlap between pairs of state points. The grand canonical partition function can be written as

\[
\Xi(\mu, V, T) = \sum_N \sum_{U_N} \exp[N\beta\mu - \beta U_N] \Omega(N, V, U_N)
\]

\[
= \sum_N \sum_{U_N} CH(U_N, N),
\]

(3-1)

where \(\beta = 1/kT\), \(k\) is the Boltzmann constant, \(T\) is the absolute temperature, \(\Omega(N, V, U_N)\) is the microcanonical partition function, \(C\) is a simulation-specific constant, and \(H(U_N, N)\) is the two dimensional histogram of configurational energy, \(U_N\), and number of molecules, \(N\), collected during the simulation. The configurational chemical potential, \(\mu\), is defined by

\[
\mu = \mu^f - kT \ln \Lambda^3 + kT \ln(q_{\text{int}}),
\]

(3-2)
where $\mu^f$ is the full chemical potential, $\Lambda$ is the thermal de Broglie wavelength, and $q_{\text{int}}$ is the intramolecular partition function, accounting for density independent terms such as rotational and vibrational Hamiltonians. The grand canonical partition function for a different state point with configurational chemical potential $\mu'$, and temperature $T'$ can be estimated by single histogram reweighting

$$
\Xi(\mu', V, T') = \sum_N \sum_{U_N} \exp[N \beta' \mu' - \beta' U_N] \Omega(N, V, U_N) \\
= \sum_N \sum_{U_N} \exp[N (\beta' \mu' - \beta \mu) - (\beta' - \beta) U_N] H_{\mu, V, T}(U_N, N) C,
$$

(3-3)

where $H_{\mu, V, T}(U_N, N)$ is the histogram collected at $(\mu, V, T)$. The ratio of the grand canonical partition functions between these two state points based on the histogram collected at $(\mu, V, T)$ is computed through

$$
\frac{\Xi(\mu', V, T')}{\Xi(\mu, V, T)} = \frac{\sum_N \sum_{U_N} \exp[N (\beta' \mu' - \beta \mu) - (\beta' - \beta) U_N] H_{\mu, V, T}(N, U_N)}{\sum_N \sum_{U_N} H_{\mu, V, T}(U_N, N)}.
$$

(3-4)

Likewise, one may collect histogram data at the state point defined by $(\mu', V, T')$ and extrapolate to $(\mu, V, T)$. The ratio of these two partition functions can be expressed by interchanging $\mu$ with $\mu'$ and $T$ with $T'$ in Eq. (3-4). In the thermodynamic limit the following equation must be satisfied,

$$
\frac{\Xi(\mu', V, T')}{\Xi(\mu, V, T)} \times \frac{\Xi(\mu, V, T)}{\Xi(\mu', V, T')} = 1.
$$

(3-5)

We use Eq. (3-5) to check the extent of overlap between histograms by performing relatively short GCMC simulations at each state point. Not all of the fluctuations in energy and particle number accessible to the state points in the thermodynamic limit can be observed in a finite simulation. Consequently, Eq. (3-5) will not be exactly satisfied for state points extrapolated from histogram reweighting, but should be approximately satisfied within some tolerance

$$
\frac{\Xi(\mu', V, T')}{\Xi(\mu, V, T)} \bigg|_{\text{HR}} \times \frac{\Xi(\mu, V, T)}{\Xi(\mu', V, T')} \bigg|_{\text{HR}} = 1 \pm \delta,
$$

(3-6)

where the subscript HR indicates that the partition function in the numerator has been extrapolated from histogram reweighting. We have found that $\delta = 0.65$, that is, values of the left hand side of Eq. (3-6) between 0.35 and 1.65, indicate sufficient overlap of the two state points. We have
used this method to select the state points to simulate in longer production runs. We denote this procedure to check the overlap as the single histogram reweighting method (SHR). Note that Eq. (3-6) is not symmetric with respect to inversion because we stipulate that the extrapolated partition functions are always in the numerator.

Details of our implementation of the multiple histogram reweighting technique are described elsewhere\textsuperscript{44}. The ratios of the $\Xi$s for several state points were obtained from multiple histogram reweighting and compared with the values calculated from Eq. (3-4) in order to verify that the degree of overlap between adjacent state points was sufficient. Single histogram reweighting from Eq. (3-6) and MHR were used to analyze the histograms. The results are presented in Table 3.1. The values computed from MHR are based on a combination of 30 histograms. The values of the ratios $\Xi_2/\Xi_1$ between 10 pairs of state points as calculated from SHR and MHR are tabulated in Table 3.1. The good agreement between the two methods indicates that a value of $\delta \leq 0.65$ in Eq. (3-6) is indicative of histograms with sufficient overlap.

### 3.3 Capillary Condensation

In this section we present results of MHR for capillary condensation. The potential model used to investigate capillary condensation is the same as that used by Jiang \textit{et al.}\textsuperscript{73}, namely, methane adsorbing in a graphite slit-like pore of width $H = 5\sigma$, where $\sigma$ is the Lennard-Jones (LJ) diameter of a methane molecule. The fluid particles in the slit pore interact with each other via the truncated and shifted (TS) LJ potential

$$
\phi_{TS}(r) = \begin{cases} 
\phi(r) - \phi(r_c) & r \leq r_c \\
0 & r > r_c 
\end{cases},
$$

where $\phi(r)$ is the full LJ potential given by

$$
\phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right],
$$

\text{Eq. (3-7)}
where $\epsilon$ is the well depth and $\sigma$ is the molecular diameter. The value of the cutoff was $2.5\sigma$ as used in ref.\textsuperscript{73}. The solid-fluid interactions are represented by the 10-4-3 solid-fluid potential\textsuperscript{95,96}

$$
\phi_{sf}(z) = 2\pi\rho_s\epsilon_{sf}\sigma_{sf}^2 \Delta \left\{ \frac{2}{5} \left( \frac{\sigma_{sf}}{z} \right)^{10} - \left( \frac{\sigma_{sf}}{z} \right)^4 - \left( \frac{\sigma_{sf}^4}{3\Delta (0.61\Delta + z)^3} \right) \right\},
$$

(3-9)

where $z$ is the distance between a fluid particle and a solid surface, $\Delta$ is the separation between the individual graphene planes, and $\rho_s$ is the solid density. The cross-parameters $\sigma_{sf}$ and $\epsilon_{sf}$ were calculated from the Lorentz-Berthelot combining rules. The parameters were taken from refs.\textsuperscript{95,96}. They are $\sigma_{sf} = 0.381$ nm, $\epsilon_{sf}/k = 148.1$ K, $\sigma_{ss} = 0.340$ nm, $\epsilon_{ss}/k = 28.0$ K, $\Delta = 0.335$ nm, and $\rho_s = 114$ nm$^{-3}$. For a given slit pore of width $H$, the external potential experienced by a fluid molecule at $z$ is given by $\phi_{ext}(z) = \phi_{sf}(z) + \phi_{sf}(H - z)$.

The volume of the unit cell was fixed at 900$\sigma^3$ with a separation of 5$\sigma$ between the two opposite adsorbent surfaces. The lateral dimensions of the box were equal in the $x$ and $y$ directions. Periodic boundary conditions in the $x$ and $y$ directions were employed. We used $7 \times 10^7$ trials to achieve equilibrium and $7 \times 10^7$ moves for data collection. Histograms were collected every 14 moves. Standard reduced units were used with the reduced temperature given by $T^* = kT/\epsilon$ and the reduced density $\rho^* = \rho\sigma^3$. The reduced chemical potential is $\mu^* = \mu/\epsilon$.

We combined 30 histograms in the reduced temperature region from 0.6 to 0.9. Two representative isotherms are plotted in Fig. 3.1. As a general test of the accuracy of the MHR isotherms we have also plotted state points calculated directly from GCMC simulations in Fig. 3.1. We show data from simulations that were included in generating MHR isotherms and also data from state points that were not used to construct the histograms in the MHR. The differences between densities obtained from multiple histogram reweighting and those from GCMC simulations are small. The average densities obtained from 19 GCMC simulations not included in multiple histogram reweighting, were compared with densities from multiple histogram reweighting. The isotherms examined were $T^* = 0.9, 0.85, 0.825, 0.8, 0.7,$ and $0.6$. The average absolute error in the densities between GCMC and MHR is $3 \times 10^{-3}$. The maximum and minimum absolute errors are $7 \times 10^{-3}$.
Figure 3.1: Isotherms for $T^* = 0.7$ (solid line) and $0.6$ (dashed line) from multiple histogram reweighting for methane adsorption in a graphitic slit pore of width $5\sigma$. Data from individual GCMC simulations that were (○) and were not (□) included in the MHR calculations are shown.
and $2 \times 10^{-4}$, respectively. Many of the values from MHR agree with those from the simulations within the uncertainty of the simulations.

For $T^* = 0.7$, the values of the coexistence densities computed from MHR are 0.358 and 0.631 for the vapor-like and liquid-like branches, respectively, and the capillary condensation coexistence chemical potential $\mu^*_{cc}$ is $-5.978$. These data are in excellent agreement with the values from Jiang et al.\cite{73}, who reported densities of 0.36 and 0.627 for the vapor-like and liquid-like branches, respectively, and $\mu^*_{cc} = -5.93$. Jiang et al. located the coexistence points by calculating the grand potentials in each branch. The equilibrium transition occurs when the grand potentials in each phase are equal\cite{72}, whereas adsorption and desorption isotherms are plagued by metastability-induced hysteresis.

The lowest temperatures where histograms were collected were 0.6 and 0.65 for the vapor-like and liquid-like sides, respectively. The $T^* = 0.6$ isotherm was generated by extrapolating the histograms at higher temperatures and lower densities in order to generate the liquid-like branch of the isotherms. This is possible because fluctuations recorded at higher temperatures and lower densities sample some of the microstates important at lower temperatures and higher densities, giving a physically realistic extrapolation. The reliability of the extrapolation is confirmed by the agreement between the MHR isotherm and the two simulation points (not included in the histograms) on the liquid-like branch shown in Figure 3.1. The values of coexistence densities from MHR are 0.360 and 0.692 for the vapor-like and liquid-like branches, respectively. These values are very close to those of 0.36 and 0.68 from Jiang et al.\cite{73}. The MHR isotherm gives $\mu^*_{cc} = -6.309$, which is in good agreement with the value computed from grand potential calculations of $-6.32$\cite{73}.

The coexistence densities in the reduced temperature region from 0.68 to 0.76 were fitted to the scaling law and rectilinear law\cite{54}.

$$\frac{\rho^*_l + \rho^*_v}{2} = \rho^*_c + A(T^* - T^*_c)$$  \hspace{1cm} (3-10)

$$\rho^*_l - \rho^*_v = B(T^*_c - T^*)^{\beta_c}$$  \hspace{1cm} (3-11)
where $\rho^*_l$ and $\rho^*_v$ are the reduced coexistence densities for the liquid-like and vapor-like branches, respectively, $T^*_c$ and $\rho^*_c$ are the reduced critical temperature and density, $\beta_c$ is the critical exponent, $A$ and $B$ are fitting parameters. Regression of the MHR equilibrium data to Eqns. (3-10) and (3-11) gave $T^*_c = 0.77$, $\rho^*_c = 0.482$, and $\beta_c = 0.119$. The fitted value of $\beta_c$ is reasonably close to the value of 0.125 (1/8) for the 2-D Ising universality class. The data calculated from MHR and the fitting are shown in Figure 3.2.

![Figure 3.2](image_url)

Figure 3.2: The $T^*-\rho^*$ phase diagram for capillary condensation of methane in a graphitic slit pore. The filled circles are the coexistence data calculated from the equal area criterion. The filled diamond is the critical point estimated from fitting the coexistence data to the rectilinear and scaling laws, Eqns. (3-10)-(3-11). The solid line is the fit to the data. The squares are the rectilinear diameters. The dashed line is shown as a guide to the eye.

The crossover of the effective exponent from 2-D Ising-like (1/8) away from the critical point to the mean-field value (1/2) in the immediate vicinity of the critical point can be observed clearly in Figure 3.3. These results reveal the 2-D behavior of capillary condensation. As Mon and Binder
Figure 3.3: Scaled width of the coexistence data versus reduced temperatures for the capillary condensation of methane in a graphitic slit pore. The 2-D Ising exponent of $\beta_c = 1/8$ is shown as $\bullet$ and $\circ$ denotes the mean-field value of $\beta_c = 1/2$. 

(Δρ $^{1/\beta_c}$) versus $T^*$
have pointed out\textsuperscript{52}, one expects the observed exponents to correspond to the correct universality class when the correlation length is much less than the simulation box length. This is indeed the case for low temperatures, corresponding to $T^* < 0.74$ for the system represented in Figure 3.3. At temperatures near the capillary condensation critical point the correlation length becomes large compared with the box length and the fluid then conforms to mean field behavior due to the suppression of critical fluctuations. Figure 3.3 is, to the best of our knowledge, the first observation of crossover for capillary condensation.

3.4 Prewetting

In this section we present details and results of our MHR calculations for a system that exhibits a prewetting transition. We have investigated the same system studied by Monson and coworkers, namely, Ar adsorbing on a solid CO\textsubscript{2} surface\textsuperscript{76,86,98}. Their simulations were performed for a fluid interacting through the truncated LJ potential,

$$\phi_{TR}(r) = \begin{cases} \phi(r) & r \leq r_c \\ 0 & r > r_c \end{cases},$$

(3-12)

where $\phi(r)$ is the full LJ potential given by Eq. (3-8) and $r_c$ is $2.5\sigma$. The fluid-solid interaction at the adsorbing wall is given by the LJ 9-3 potential,

$$\phi_w(z) = \frac{2\pi}{3} \rho_w \sigma_w^3 \epsilon_w \left[ \frac{2}{15} \left( \frac{\sigma_w}{z} \right)^9 - \left( \frac{\sigma_w}{z} \right)^3 \right],$$

(3-13)

with $\sigma_w = 0.3727$ nm, $\epsilon_w/k = 153$ K, $\rho_w \sigma_w^3 = 0.988$, and $z$ is the distance between the fluid and the adsorbing wall. The opposite wall was chosen to be reflecting. The parameters for the fluid-fluid interactions are $\epsilon/k = 119.8$ K, and $\sigma = 0.340$ nm.

Monson and coworkers\textsuperscript{76,86,98} reported isotherms between $T^* = 0.83$ and 1.0 for pressures up to saturation. Their estimate for the reduced wetting temperature is $T_{w}^* = 0.84 \pm 0.01$ and the reduced prewetting critical temperature estimate is $T_{pwc}^* = 0.94 \pm 0.02$. They observed a prewetting
transition at $T^* = 0.88$ from their simulations, but no prewetting transitions at $T^* = 0.83$ and $T^* = 0.80$.

In this work we have chosen the volume of the unit cell for the Ar/CO$_2$ model system to be $1620\sigma^3$ with $H = 20\sigma$. Periodic boundary conditions were applied in the $x$ and $y$ directions. We used $10^7$ steps for equilibration followed by an additional $10^8$ steps for data collection. Histograms were collected at every step. We collected and combined 30 histograms in the temperature region from 0.8 to 1.05. We compute the total, not excess adsorption in this work. Note that the equal area criterion can be used with the total adsorption to find prewetting transitions. The bulk density term adds a constant to both the thin and thick films at a fixed $T^*$ and $\mu^*$. This constant cancels out when computing the difference between the areas of the probability density distributions. The ability to use total instead of excess adsorption isotherms is an advantage because the procedure for computing excess adsorption in a simulation is somewhat ambiguous. Several isotherms computed from MHR are shown in Figure 3.4, along with results from GCMC simulations. The differences between densities obtained from GCMC simulations and MHR are typically smaller than the errors in the simulations. Prewetting is associated with the first S-shaped rise in coverage in Figure 3.4 for $T^* = 0.83$ and 0.88. The second rise and plateau are associated with box filling close to the bulk saturation point. The prewetting transition exhibits considerable rounding due to finite-size effects; hence it is difficult to tell if there is a first order transition from the shape of the isotherm. The coexistence densities and chemical potentials were computed from the equal area criterion as for capillary condensation. Hill’s method was used to get an initial estimate for the value of the coexistence chemical potential. The existence of two distinct peaks with equal areas in the density probability is sufficient to identify the transition as first order. The density probability distribution at $T^* = 0.83$ and $\mu^* = -3.801$ is shown in Figure 3.5.

We also obtained a two peak equal area density distribution for $T^* = 0.80$. This is significant because Monson and coworkers did not observed prewetting transitions at these temperatures. At these low temperatures, the prewetting transition pressure is closer to the saturation pressure than
Figure 3.4: Isotherms for $T^* = 0.83$ (solid line), 0.88 (dashed line), and 1.0 (long dashed line) from multiple histogram reweighting for Ar adsorption on solid CO$_2$. Data from individual GCMC simulations that were ($\circ$) and were not ($\square$) included in the MHR calculations are shown.
Figure 3.5: Density probability distribution for the same system as Figure 3.4 at $T^* = 0.83$ and $\mu^* = -3.801$. 
at higher temperatures, making identification of the prewetting transition especially difficult from standard simulations. However, MHR allows relatively easy identification of prewetting transitions, even very near the saturation pressure.

The prewetting transitions seen on the $T^* = 0.83$ and 0.88 isotherms can also be characterized by the local density profiles, shown in Figs. 3.6 and 3.7. We note that density profiles cannot be computed from MHR because we have not collected histograms of $\rho(z)$ as a function of $U_N, N$.

Referring to Figure 3.6, we observe that adsorption is limited to a thin layer on the surface for $\mu^* < -3.8$. For $\mu^* \geq -3.8$ the adsorption abruptly changes to multiple layers that appear to grow continuously as the chemical potential is increased. This behavior is indicative of a prewetting

![Figure 3.6: Local density profiles obtained from GCMC simulations for the same system as Figure 3.4. Profiles are for $\mu^* = -3.9$ (solid line), $-3.81$ (dotted line), $-3.8$ (dashed line), $-3.78$ (long dashed), and $-3.77$ (dot-dashed) at $T^* = 0.83$.](image)
Figure 3.7: Local density profiles obtained from GCMC simulations for the same system as Figure 3.4. Profiles are for $\mu^* = -3.85$ (solid line), $-3.8$ (dotted line), $-3.76$ (dashed line), $-3.75$ (long dashed), and $-3.73$ (dot-dashed) at $T^* = 0.88$. 
transition occurring. The coexistence chemical potential at this temperature calculated from the equal area criterion is $-3.801$, in agreement with the local density profiles in Figure 3.6. Similar behavior can be seen in Figure 3.7, where the thin- to thick-film transition occurs between $\mu^* = -3.76$ and $-3.75$. The coexistence chemical potential calculated from MHR is about $-3.75$, in agreement with the local density profiles.

We have computed the saturation chemical potential ($\mu_{sat}^*$) for the bulk phase vapor-liquid transition from $T^* = 0.8$ up to the apparent critical point from MHR of the bulk fluid. The values of the prewetting transition chemical potentials ($\mu_{pw}^*$) were computed over $0.8 \leq T^* \leq 0.88$ from which $\Delta \mu^* = \mu_{sat}^* - \mu_{pw}^*$ was computed. The plot of $\Delta \mu^*$ vs. $T^*$ is shown in Figure 3.8.

![Figure 3.8: A plot of $\Delta \mu^* = \mu_{sat}^* - \mu_{pw}^*$ as a function of temperature for the same system as in Figure 3.4. Filled circles are computed from MHR. Also shown are the fits to the data to the power law form (solid line), and linear form (long dashed).](image-url)
Theoretical predictions indicate that $\Delta \mu^* \propto (T^* - T_{w}^{*})^{3/2}$\textsuperscript{102}. Hence, a plot of $\Delta \mu^*$ vs. $T^*$ can be used to identify the wetting temperature by extrapolating the curve to $\Delta \mu^* = 0$\textsuperscript{103}. The solid line in Figure 3.8 is the result of a power law fit to the data using an exponent of $3/2$. However, inspection of simulation data reveals that they lie on a straight line with a correlation coefficient of 0.9994. The estimates of $T_{w}^{*}$ from the power law and linear fits are 0.53 and 0.623, respectively.

The prewetting line for this system was computed\textsuperscript{104,105} in order to compare with data from ref.\textsuperscript{76}. The density of the gas in equilibrium with the adsorbed phase at the prewetting point was computed by
\begin{equation}
\rho_{pw}^* = \rho_{sat}^* \exp \left( \frac{\mu_{pw}^* - \mu_{sat}^*}{T^*} \right),
\end{equation}
where $\rho_{pw}^*$ and $\rho_{sat}^*$ are the reduced bulk densities for gas at the prewetting transition and vapor-liquid saturation, respectively. This assumes that the bulk gas is ideal in the calculation. The results are shown in Figure 3.9.

The prewetting transition densities at $T^* = 0.85, 0.87$ and 0.88 are 0.0146, 0.0170 and 0.0183, respectively. These results agree well with values reported by Finn and Monson\textsuperscript{76}. We fitted the prewetting line and the saturated vapor line to two separate polynomials. The solid and long dashed lines are the results from the fitting. The value of $T_{w}^{*}$ was estimated by extrapolating the two lines to where they intersect. This gave $T_{w}^{*} = 0.69$. We note that it has been predicted from theory that the prewetting and bulk saturation lines should meet tangentially\textsuperscript{76,104–106}. Therefore, extrapolation of the two polynomials is not only unreliable, but also theoretically not justified. Nevertheless, the estimate of $T_{w}^{*} = 0.69$ is in reasonable agreement with $T_{w}^{*} = 0.62$ obtained from linear extrapolation of $\Delta \mu^*$ vs. $T^*$.

The reduced wetting and critical prewetting temperatures estimated for the Ar/CO$_2$ system or similar systems are given in Table 3.2. Note that many of the calculations employed density functional theory, which is not expected to give results identical to simulations given the approximations of the theory. From comparison with the previous estimates of $T_{w}^{*}$, we conclude that the power law extrapolation of the $\Delta \mu^*-T^*$ curve is not accurate. We believe that $T_{w}^{*}$ for this system is probably
Figure 3.9: The temperature–density phase diagram for the same system as in Figure 3.4. The circles are the densities of the bulk gas in equilibrium with the adsorbed fluid at the prewetting transition points calculated from MHR. The squares are the vapor side of the bulk vapor-liquid phase diagram computed from MHR of the bulk fluid. The solid line and the dashed line are polynomial fits to the data. The two lines intersect at $T^* = 0.69$. 
close to our estimates from linear $\Delta \mu^*-T^*$ extrapolation and extrapolation of the prewetting line, $T_w^* \sim 0.69$. The estimate of Finn and Monson of $T_w^* = 0.84$ is undoubtedly too high given that we definitely observe a prewetting transition at $T^* = 0.8$.

The relative ratios, $P_{wet}/P_{sat}$, are plotted in Figure 3.10.

![Figure 3.10: The ratio of the prewetting transition pressure to the saturation pressure for the same system as in Figure 3.4.](image)

The ratio was computed from $P_{wet}/P_{sat} = \exp(\frac{\mu_{pw}^*-\mu_{sat}^*}{T^*})$, where $P_{wet}$ and $P_{sat}$ are the pressures at the prewetting transition and saturation, $\mu_{pw}^*$ and $\mu_{sat}^*$ are the reduced chemical potentials calculated from MHR the with the equal area criterion. Ideal gas behavior was assumed in the calculation. As expected, the ratio decreases with temperature. The value at $T = 0.88$ is 85.5%, close to 87.9% calculated by Finn and Monson.  

56
The density probability distributions at $T^* = 0.92$ for $-3.72 \leq \mu^* \leq -3.66$ are shown in Figure 3.11(a). The isotherm is shown in Figure 3.11(b). It is difficult to tell from the isotherm whether or not there is a prewetting transition at this temperature (Figure 3.11(b)). However, the density probability distributions are definitive proof that $T^* = 0.92$ is above the prewetting critical point because the equal area criterion cannot be satisfied for any choice of $\mu^*$ (Figure 3.11(a)). Probability distributions at $T^* = 0.91$ and 0.9 are somewhat ambiguous. They show two peaks that are in the process of merging. From these observations we estimate that $T^*_{pwc}$ is close to 0.92. This value is in reasonable agreement with other estimates (see Table 3.2). We note that an accurate estimate of $T^*_{pwc}$ would require a finite-size scaling analysis, which is beyond the scope of this work.
3.5 Layering Transition

In this section we present our MHR predictions for the 1-2 layering transition of propane on the basal plane of graphite. Propane was modeled as a three site united atom molecule using the potential model of Lustig and Steele\textsuperscript{107}. The potential parameters for this model are the LJ parameters $\epsilon$ and $\sigma$, the bond lengths of the isosceles triangular framework $\delta$, and the bond angle $\theta$. The values of the potential parameters are $\epsilon/k = 119.57$ K, $\sigma = 3.527$ Å, $\delta = 2.16$ Å, and $\theta = 90^\circ$. We note that there are several united atom propane models available in the literature\textsuperscript{108–111}. We adopted this model because of its accuracy in predicting the $PVT$ properties and internal energies of pure propane and the good agreement between experimental and simulated adsorption isotherms for propane on graphite\textsuperscript{112}. The graphite surface was modeled as a smooth basal plane using the 10-4-3 potential given by Eq. (3-9).

The volume of the simulation box for histogram collection calculations was set to $1000\sigma^3$. Periodic boundary conditions and minimum image conventions were applied in the $x$ and $y$ directions of the simulation box. The lateral dimensions of the simulation box were equal in $x$ and $y$ directions. One wall of the simulation box was chosen as the adsorbing surface and the opposite wall was chosen to be purely repulsive to keep the molecules in the box. The separation between the two walls was fixed at $H = 10\sigma$ so that the influence of the repulsive wall on the adsorption properties was negligible. The site-site interaction cutoff distance was $3.5\sigma$ and no long range corrections were applied. Each simulation was equilibrated for $5\times10^7$ moves, after which histogram data were collected for another $5\times10^7$ moves. We collected histograms spanning coverages ranging from a monolayer ($5.9\mu\text{mol m}^{-2}$) to a complete bilayer ($14.2\mu\text{mol m}^{-2}$) at a temperature of 130 K. We chose this temperature because it appears to be above the critical layering transition temperature, which allowed sampling of all coverages spanning the 1-2 layering transition. Additional histograms were collected at temperatures down to 100 K, but only sampling a few state points in the monolayer or bilayer regime. A total of 53 histograms from different state points were collected.
An independent series of GCMC simulations were performed (without collecting histograms) for a larger system size with a volume of $4250\sigma^3$ and $H = 20\sigma^{112}$. The isotherms predicted from MHR for the smaller volume are compared with GCMC simulations in Figs. 3.12 and 3.13.

![Graph showing isotherm comparison](image)

**Figure 3.12**: The $T = 100$ K isotherm (solid line) for propane adsorption on graphite predicted from MHR for a small system size (volume = $1000\sigma^3$) compared with GCMC simulations for a larger system volume of $4250\sigma^3$ (circles).

We observe that the MHR calculations on the small system size give a very reasonable representation of the behavior of the larger system size. The layering transitions occur at close to the same pressures, although there is some difference in the coverages, which may be due to finite size effects. The 1-2 layering transition observed from the GCMC simulations does not appear to be very sharp. In contrast to simple fluids like methane on graphite$^{113}$ that show very sharp layering transitions, the propane/graphite system is complicated by orientational changes of the propane in...
Figure 3.13: The $T = 110$ K isotherm (solid line) for propane adsorption on graphite predicted from MHR for a small system size (volume = $1000\sigma^3$) compared with GCMC simulations for a larger system volume of $4250\sigma^3$ (circles).
the first layer. The orientational changes allow an increase in coverage in the first layer after the monolayer is apparently “full” and also promotes adsorption in the second layer. Density distributions from MHR at 100 K show two regions that are not well separated. This may be indicative of system size effects. We have previously observed that vapor-liquid density distributions for bulk fluids start to merge for subcritical temperatures, when the system size is small.

The value of the critical layering transition temperature is often of interest. In principle, one can estimate the location of the critical layering transition temperature by the disappearance of two distinct peaks in the density distribution. However, the lack of distinct peaks is not a necessary condition for supercriticality, since two peaks in the density probability distribution may be observed for temperatures slightly greater than the apparent critical temperature. A rigorous estimate of the critical layering transition temperature would require finite-size scaling analysis. An additional problem for this system is that the density distributions at subcritical temperatures are not well separated to begin with. Nevertheless, we have estimated $T_c(2)$ to be around 120 K for the propane/graphite system. This value is very close to the experimental result for ethane on graphite of $T_c(2) = 120.8 \pm 0.3$ K. It is somewhat surprising that $T_c(2)$ is so similar for ethane and propane. This may be due to inaccuracies in the potential models used in these simulations or perhaps due to the orientational transitions in the propane monolayer. Additional simulations for ethane adsorption would be useful for understanding the similarities and differences in these systems.

3.6 Conclusion

The multiple histogram reweighting technique has been used to study capillary condensation, prewetting transitions, and layering transitions. The critical capillary condensation temperature and density are estimated to be $T^*_c = 0.77$ and $\rho^*_c = 0.482$ for methane adsorption in a graphitic slit pore of width $H = 5\sigma$. Crossover of the effective exponent value from 2-D Ising-like to mean-field
occurs for capillary condensation. To our knowledge, crossover for capillary condensation has not previously been observed. The precision and abundance of the coexistence data generated from MHR were crucial factors in the successful observation of crossover. Adsorption of Ar on solid CO$_2$ using the potential models of Finn and Monson shows prewetting transitions at temperatures lower than previously observed. The reduced wetting temperature is estimated to be around 0.69 from the extrapolation of the prewetting transition line and the saturated vapor line. The reduced critical prewetting temperature is about 0.92 as estimated from the disappearance of two distinct peaks in the density probability distribution. Layering transitions were computed from MHR for propane adsorbing on graphite. The transition pressures are in good agreement with previous simulations for larger system sizes, indicating that MHR calculations for small system sizes can be useful for predicting the behavior of larger systems. We estimate $T_c(2) \sim 120$ K based on the merging of the density probability distributions.

We have demonstrated that MHR can be a useful tool for computing the properties of adsorbed fluids, especially when one is interested in investigating phase transitions. There are, however, drawbacks to MHR that we should mention. Efficiency in collecting histograms decreases dramatically with decreasing temperature and increasing volume. It is advisable to use the smallest simulation box size that is possible when performing MHR. The reasons for this are two fold: (1) The overlap between neighboring states becomes smaller as the system size increases, necessitating a larger number of simulations to span the same temperature range. (2) Longer simulations are required to capture the increased number of microstates available in larger systems. We have used standard Metropolis Monte Carlo in our work. Efficiency gains could be made by implementing biasing methods that would increase the width of the density and energy distributions sampled in a single simulation. However, it is clear that MHR is not a very efficient method if large system sizes are needed. Another drawback of the MHR method is that there is no clear way to estimate the precise critical temperature for a transition without resorting to finite-size scaling methods. The disappearance of two peaks in the density distribution is a sufficient but not necessary condition for a system being in the supercritical region. The double peaked distribution is known to persist.
to temperatures that are slightly supercritical\textsuperscript{114}, so that absence of the two peaks can only serve as an upper bound measure of the critical point.
Table 3.1: Ratios of the grand canonical partition function computed from single histogram reweighting (SHR) and multiple histogram reweighting (MHR). The calculation is for methane adsorption in graphitic slit pore.

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<th>$T_1^*$</th>
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<th>$T_2^*$</th>
<th>$\mu_2^*$</th>
<th>SHR</th>
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<th>$\frac{g_{\mu_2}}{g_{\mu_1}}$</th>
<th>MHR</th>
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<td>0.9</td>
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Table 3.2: Reduced wetting temperature ($T_{w}^*$) and reduced prewetting critical temperature ($T_{pwc}^*$) for Ar on CO$_2$ and Ne on Mg.

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<th>$T_{pwc}^*$</th>
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<td>Tarazona and Evans$^{116}$</td>
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<td>0.988</td>
</tr>
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<td>Meister and Kroll$^{117}$</td>
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<td>Finn and Monson$^{76}$</td>
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<tr>
<td>Sokolowski and Fischer$^{118}$</td>
<td>0.975 ± 0.025</td>
<td>...</td>
</tr>
<tr>
<td>Bojan et al.$^{119}$</td>
<td>0.65</td>
<td>0.88 ± 0.03</td>
</tr>
<tr>
<td>This work</td>
<td>0.69</td>
<td>0.92</td>
</tr>
</tbody>
</table>
4.0 MULTIPLE HISTOGRAM REWEIGHTING APPLIED TO PATH INTEGRAL FLUIDS

4.1 Introduction

It is well known that the thermophysical properties of light molecules at low temperatures can be dramatically altered by quantum mechanical effects. These effects have their origin in the wave-particle duality of matter and are manifest when the thermal de Broglie wavelength is similar to the spacing between molecules. An example of quantum effects on the thermodynamic properties of fluids can be seen by comparing the critical temperatures of H\textsubscript{2} with “classical” H\textsubscript{2}, i.e., a hypothetical hydrogen with the exact same intermolecular potential, but with a high mass so that no quantum effects are manifest. Real H\textsubscript{2} has a critical temperature of about 33 K, while “classical” H\textsubscript{2} has a critical temperature of about 44 K,\textsuperscript{120} showing that quantum effects are profound for phase equilibrium properties.

Until recently, no simulation methods existed for directly computing the phase equilibrium properties of strongly quantum fluids. By strongly quantum, we mean fluids for which the Wigner-Kirkwood expansion does not converge within the first two terms. Such fluids are most commonly simulated using the path integral formalism of Feynman.\textsuperscript{121} Wang and coworkers developed the first direct method for computing phase equilibria within the path integral formalism by extending the Gibbs ensemble method.\textsuperscript{120,122} They also developed an extension of the grand canonical Monte Carlo technique for path integral fluids.\textsuperscript{123} Nevertheless, until multiple histogram reweighting (MHR)\textsuperscript{11–13} has not been applied to path integral fluids. This is because the MHR technique cannot be directly applied to the Hamiltonian used in the path integral formalism. The MHR technique is very efficient and accurate for computing phase transitions of classical fluids\textsuperscript{4,5,44,45,77,78,81} and is especially useful in cases where it is important to locate the coexistence point with high precision. An example of such a case is the study of prewetting and wetting transitions. For H\textsubscript{2} adsorbing on Rb the prewetting transition occurs at about 99.2% of the saturation pressure at
19.91 K. The uncertainties in the saturation chemical potential computed from Gibbs Ensemble simulations of quantum fluids give rise to errors in the saturation pressures of several percent. In contrast, the saturation pressure for classical fluids can be computed from MHR to within a fraction of a percent.  

In this study, we have successfully extended the MHR technique to path integral fluids and have calculated phase diagrams of hydrogen isotopes. We have used the Silvera-Goldman potential to compute properties of H₂ and D₂ with different potential cutoffs. The saturation chemical potentials have been used to study the wetting behavior of H₂ on Rb with MHR. The importance of this work is that the method of dealing with the microcanonical partition function can be extended to other kinds of Hamiltonians. The key is to split the Hamiltonian in a suitable way such that the microcanonical partition function is independent of temperature.

### 4.2 Theory

The basic equation for the MHR method applied to classical fluids is that the microcanonical partition function, \( \Omega_c \), is independent of temperature. I.e.,

\[
\Omega_c(N, V, U_{\text{tot}}, T_i) = \Omega_c(N, V, U_{\text{tot}}, T_j) \neq f(T), \tag{4-1}
\]

where \( N \) is the number of the particles, \( V \) is the volume of the simulation cell, \( U_{\text{tot}} \) is the total configurational potential energy, \( T_i \) and \( T_j \) are two different temperatures. Obviously, \( \Omega_c \) with indices of \( N \), and \( U_{\text{tot}} \) will be constant if the volume is the same for different state points. However, this is not true for path integral fluids, i.e,

\[
\Omega(N, V, U_{\text{tot}}, T_i) \neq \Omega(N, V, U_{\text{tot}}, T_j). \tag{4-2}
\]

For path integral fluids, the total potential energy is given by

\[
U_{\text{tot}} = U_{\text{ext}} + U_{\text{int}}. \tag{4-3}
\]
The external potential is given by

\[ U^\text{ext} = \frac{1}{P} \sum_{\alpha=1}^{P} \sum_{i<j}^{N} V(r_{ij}^\alpha), \quad (4-4) \]

where \( P \) is the number of beads in the polymer, \( N \) is the total number of molecules, \( V(r_{ij}^\alpha) \) is the pair potential between bead \( \alpha \) on molecule \( i \) and bead \( \alpha \) on molecule \( j \). Note that \( V(r_{ij}^\alpha) \) only depends on the positions of the molecules and therefore \( U^\text{ext} \) is independent of temperature. \( U^\text{int} \) is in the form of a harmonic potential given by

\[ U^\text{int} = \frac{P m}{2 \beta^2} \sum_{\alpha=1}^{P} \sum_{i=1}^{N} (r_{i}^\alpha - r_{i}^{\alpha+1})^2, \quad (4-5) \]

where \( r_{i}^\alpha \) is the position of bead \( \alpha \) on ring \( i \), \( m \) is the mass of the quantum molecule, \( \beta = 1/kT \), \( k \) is the Boltzmann constant. When \( \alpha = P, \alpha + 1 = 1 \) as required for a ring polymer. Note that \( U^\text{int} \) depends on temperature and hence \( U^\text{tot} \) is a function of temperature and positions of the beads. This implies that the microcanonical partition function, \( \Omega(N,V,U^\text{tot}) \), is an implicit function of temperature.

It is clear that new indices for the microcanonical partition function, \( \Omega \), are needed in order to obtain a temperature independent \( \Omega \). The new indices are chosen to be \( N, V, U_1, U_2 \), where \( U_1 \) and \( U_2 \) are given by

\[ U_1 = U^\text{ext}, \quad (4-6) \]

and

\[ U_2 = U^\text{int} \beta^2 \]

\[ = \frac{P m}{2} \sum_{\alpha=1}^{P} \sum_{i=1}^{N} (r_{i}^\alpha - r_{i}^{\alpha+1})^2. \quad (4-7) \]

The microcanonical partition function will be temperature independent provided that the number of beads, \( P \), is constant. The \( \Omega \) described by the new indices can be written as

\[ \Omega(N,V,U_1,U_2) \neq f(T). \quad (4-8) \]

The grand canonical partition function for path integral fluids in the context of the new indices is given by

\[ \Xi(\mu,V,T) = \sum_{N} \sum_{U_1} \sum_{U_2} \Omega(N,V,U_1,U_2) \frac{\exp[-\beta U^\text{tot} + N \beta \mu]}{\Lambda^{3N(P-1)}}, \quad (4-9) \]
where $\Xi(\mu, V, T)$ is the grand canonical partition function at $\mu$ and $T$, $\mu$ is the configurational chemical potential defined by $\mu = \mu^f - kT \ln \Lambda^3$, $\Lambda$ is the thermal de Broglie wavelength, $\mu^f$ is the full chemical potential and $U^{\text{tot}}$ is the total potential energy given by Eq. (4-3).

Using the same procedure for the derivation of multiple histogram reweighting for classical fluids $^{11-13,44}$, we obtained the formula for multiple histogram reweighting for path integral fluids. The microcanonical partition function is given by

$$
\Omega(N, U_1, U_2) = \frac{\sum_j H_j(N, U_1, U_2)}{\sum_j N_j \exp \left(-\beta_j U^{\text{tot}}_j + \beta_j \mu_j N \right) / (\Xi_j^{3N(P-1)})},
$$

where $j$ denotes the $j$th state points at temperature $T_j$, and chemical potential $\mu_j$. $H_j(N, V, U_1, U_2)$ is the histogram collected at the $j$th state point in terms of $N$, $U_1$, and $U_2$, and

$$
N_j = \sum_N \sum_{U_1} \sum_{U_2} H_j(N, V, U_1, U_2).
$$

The grand canonical partition function at $\mu$ and $T$ is given by Eq. (4-9). The ensemble average of any property $X$ at $\mu$, $V$ and $T$ is given by

$$
\langle X \rangle_{\mu, V, T} = \frac{\sum_N \sum_{U_1} \sum_{U_2} \Omega(N, V, U_1, U_2) X(N, U_1, U_2) \exp \left[-\beta U^{\text{tot}} + N \beta \mu \right] / (\Xi^{3N(P-1)})}{\Xi(\mu, V, T)}.
$$

The extension of the above MHR technique for pure path integral fluids to path integral mixtures is very simple. All that needs to be changed are the indices for the microcanonical partition function. For a binary mixture, the indices for the microcanonical partition function are $N_1$, $N_2$, $U_{21}$, $U_{22}$, $U_1$, and $U_2$, where $N_1$ and $N_2$ are the number of species 1 and 2, respectively, $U_{21}$ and $U_{22}$ are the internal energies divided by temperature given by Eq. (4-7) of the species 1 and 2, $U_1$ and $U_2$ are the total external energies given by Eq. (4-6) for the species 1 and 2.

To test the above algorithm, we have run three sets of $NVT$ simulations with $N = 108$, the reduced volume, $V = 222$ and temperatures of 45 K, 50 K, and 55 K. The number of beads $P$ is set to be 10. The number of histogram observations is $6.25 \times 10^6$. The histograms at these three temperatures are combined and used to predict the thermodynamical properties at 47 K. The total potential energy of Eq. (4-3) and the internal energy of Eq. (4-5) per particle are 16.31 and 19.05,
respectively, as predicted from the MHR technique. A simulation was run at 47 K giving values of the total and internal energies per particle of $16.32 \pm 0.02$ and $19.07 \pm 0.02$, respectively. The results from the MHR calculation agree with those from direct simulation. This agreement between the simulation and the MHR calculation verifies the algorithm.

### 4.3 Simulation Details

Molecular simulations were performed using path integral grand canonical Monte Carlo. The fluid interactions were modeled with the Silvera-Goldman potential, which is accurate for both $\text{H}_2$ and $\text{D}_2$. The number of beads was set to 40 for $\text{H}_2$ and 20 for $\text{D}_2$ in the simulations. For $\text{H}_2$, the cutoff for both the long-ranged corrected (LRC) and truncated (TR) potentials was set to 15 Å. The volumes are chosen to be $27.1 \text{ nm}^3$. We used $6 \times 10^5$ steps to collect the data with $2 \times 10^5$ steps for equilibration. For LRC $\text{H}_2$, 57 state points in the temperature range between 25 K and 36 K both on the gas and liquid sides were chosen. For TR $\text{H}_2$, 84 state points covering the temperature range of 19 K and 36 K were used. The cutoff for LRC $\text{D}_2$ was chosen to be $9 \text{ Å}^3$. The volume of the simulation is chosen to be $19 \text{ nm}^3$. The number of steps is $3.2 \times 10^5$ to collect the data following $2 \times 10^5$ steps for equilibration. Fifty five state points between 31 K and 41 K were performed. Some liquid state points had to be as close as 0.25 K in temperatures to obtain good overlap between the neighboring state points.

We also studied the adsorption of $\text{H}_2$ on the Rb surface using MHR. The truncated potential was used for the adsorbate-adsorbate interaction. The adsorbate-adsorbent interaction was calculated with the empirical 9-3 potential,

$$V(z) = \frac{4C_3^3}{27D^2z^9} - \frac{C_3}{z^3},$$  \hspace{1cm} (4-13)$$

The parameters of $C_3$ and $D$ are $2420 \text{ K Å}^3$ and $44 \text{ K}$, respectively. The simulation cell was a cube with a volume of $27.1 \text{ nm}^3$. A total of 33 state points were run to cover temperature range from 28 K to 32 K.
Since the microcanonical partition function is described by three indices, the histograms are collected in a table list. The instantaneous values of \(N\), \(U_1\), and \(U_2\) are recorded in the table during the production run. The raw data in the table were then sorted in terms of \(N\) followed by concatenation of the table with the same indices of \(N\), \(U_1\), and \(U_2\). The table was first sorted because it is very time consuming to concatenate the table list. Our calculation showed that sorting of the table saved a good deal of time. After the histograms were processed as specified as above, they were combined to estimate the grand canonical partition function from Eq. (4-9).

The isotherms were calculated from Eq. (4-12). The saturation chemical potential was estimated from Hill’s method\(^{14,67}\). The equal area criterion was applied to calculate the coexistence chemical potential and coexistence densities by constructing the density probability distribution\(^{44,45}\).

### 4.4 Results

The coexistence densities for the LRC and TR \(\text{H}_2\) potentials are shown in Figure 4.1. The coexistence densities for the TR \(\text{H}_2\) were fitted to the scaling law and rectilinear law. The critical temperature and critical density from the fitting are about 32.5 K and 32.2 kg/m\(^3\), respectively. These values are close to the experimental values of 32.976 K and 31.4285 kg/m\(^3\) for para-hydrogen, 33.180 K and 31.4285 kg/m\(^3\) for normal hydrogen\(^{126}\). The coexistence densities for LRC \(\text{H}_2\) are close to those for TR \(\text{H}_2\). The difference in the coexistence densities between TR and LRC is small. The average absolute deviation (ADD) for the coexistence densities was calculated as

\[
AAD\% = \frac{\sum_{i=1}^{N} \left| \frac{\rho_{\text{TR}}^{i} - \rho_{\text{LRC}}^{i}}{\rho_{\text{LRC}}^{i}} \right|}{N},
\]

where \(N\) is the number of points for comparison, and \(\rho_{\text{TR}}\), \(\rho_{\text{LRC}}\) denote the coexistence densities for TR and LRC \(\text{H}_2\), respectively. The values for AAD between LRC and TR \(\text{H}_2\) of the vapor and liquid sides are 6.9% and 1.1%, respectively. The values for ADD between TR and LRC classical Lennard-Jones (LJ) fluids both with a cutoff of 5\(\sigma\) are 0.8% and 1% for the vapor and
Figure 4.1: The $T-\rho$ phase diagram for the TR H$_2$ with a cutoff of 15 Å calculated from multiple histogram reweighting (MHR). The line is a fit of the data to the scaling law and rectilinear law. The open square is an estimate of the the critical point based on the fit. Also shown are the coexistence data (filled right triangles) of the long range corrected H$_2$ with a cutoff of 15 Å calculated from MHR.
Figure 4.2: The $T$–$\rho$ phase diagram of long range corrected H$_2$ with a cutoff of 15 Å computed from multiple histogram reweighting. The filled right triangles are the coexistence data. The solid lines are calculated from the equation of state. The circles are Gibbs ensemble data from$^{127}$. 
liquid branches, respectively\textsuperscript{44}. The coexistence densities for LRC H\textsubscript{2} are shown in Figure 4.2. The results from MHR calculation agree very well with those from equation of state and Gibbs ensemble calculations. Note that the results from the MHR calculations are not smooth on the liquid side. This is also the case for the TR H\textsubscript{2} phase diagram calculated from MHR shown in Figure 4.1. We attribute this to runs that are not sufficiently long to collect accurate histograms for liquid-like state points. Runs that are too short will result in density distributions that are not smooth, as shown in Figure 4.3. These rough density distributions give rise to uncertainty in the coexistence densities and hence scatter in the phase envelop.

![Graph](image)

Figure 4.3: The density distribution with equal area under two peaks. This is for D\textsubscript{2} with a cutoff of 9 Å at 33 K.

A plot of $\mu_{\text{sat}}/T$ versus $1/T$ is shown in Figure 4.4. The data are very close to being linear, with correlation coefficients of $x$ and $y$ for the TR and LRC potentials to be very close to 1.0. The
linearity of the data make it possible to interpolate and even extrapolate (over a limited range) $\mu_{\text{sat}}$ with a high degree of confidence.

Figure 4.4: The $T-\mu/T$ phase diagrams of the truncated and long range corrected H$_2$ both with cutoffs of 15 Å. The filled circles corresponds to truncated H$_2$. The open squares corresponds to long range corrected H$_2$. The lines are the linear fitting to the data.

The coexistence densities for LRC D$_2$ with a cutoff of 9 Å are shown in Figure 4.5. The coexistence densities are are fitted to the scaling law and rectilinear law. The critical temperature and density from the fitting are about 37.9 K and 71.1 kg/m$^3$, respectively. The value of critical temperature for D$_2$ from the experiment is 38.2 K, close to that from the calculation. The coexistence densities computed from MHR agree with those from experiments$^{126}$ and Gibbs ensemble simulations$^{127}$. The AAD between MHR and Gibbs ensemble for the vapor and liquid branches are
Figure 4.5: The $T-\rho$ phase diagram of long range corrected D$_2$ with 9 Å. The filled circles are calculated from multiple histogram reweighting (MHR). The solid line is the fitting of the coexistence data computed from MHR to the scaling law and rectilinear law. The unfilled circle denotes the critical point from the fitting. The squares are from the experiment$^{126}$. Also shown are the results (crosses) calculated from Gibbs ensemble simulations.
5.2% and 1.6%, respectively. It is common within Gibbs ensemble simulation to allow the potential cutoffs in the two boxes to fluctuate in response to volume moves during the simulation. For example, at 32 K, the average cutoffs are 12 Å and 16.5 Å for the liquid and vapor branches, respectively. The results from MHR calculation are for 9 Å. This may attribute slightly to the difference in the coexistence densities between MHR and Gibbs ensemble. The values of ADD between MHR and the experiment are 6% and 2% for the vapor and liquid branches, respectively.

An additional 50 sets of simulations were run for LRC D$_2$ to estimate the uncertainty from MHR. Histograms were collected for $3.2 \times 10^5$ steps, with simulations starting from different initial configurations for the previous set of 55 state points. There are 19 state points out of the 50 sets different from all of the 55 sets. The left 31 state points out of the 50 sets have the same temperature and chemical potential as those of 55 sets do. The uncertainties of the coexistence densities computed from the two sets of data are in the third decimal places for both the liquid and vapor densities. The uncertainties of the saturation chemical potentials are also typically in the third decimal places.

We have previously shown that MHR can be used to accurately identify wetting transitions in classical simulations. Here we present similar calculations for quantum fluids. The isotherms for H$_2$ adsorption on the Rb surface are shown in Figure 4.6. The isotherms at 28 K and 29 K clearly indicate nonwetting since the amount adsorbed is finite even past the saturation chemical potential. The isotherms at 31 K and 32 K are continuous, indicating complete wetting. A jump on the isotherm at 30 K can be observed when the chemical potential is close to that of the saturation chemical potential. A density distribution of Figure 4.7 shows two peaks. Although the curves are not smooth and the two peaks are not well separated, the equal area construction does indicate a first order phase transition between a thin and thick film. The roughness of the density distribution may be attributed to insufficiently long runs for collecting histograms. The fact that the peaks are not well separated is attributed to the temperature being close to the bulk critical temperature. The jump in the isotherm corresponds to a prewetting transition. The wetting temperature is hence estimated to be 29.5 K. This value is much higher than the wetting temperature of 20 K computed
Figure 4.6: The isotherms calculated from multiple histogram reweighting calculations for the 9-3 potential.
Figure 4.7: The number density distribution at 30 K. Note that we can see two peaks although the two peaks are not well separated.
from the simple theory\textsuperscript{125}. The critical prewetting critical temperature is estimated to be 31 K. The wetting temperature from experiment is 19.10 K\textsuperscript{103}. The discrepancy between experiments and simulations can be attributed to errors in the solid-fluid potential, as discussed in the next chapter.

4.5 Conclusions

We have extended the multiple histogram reweighting technique to path integral fluids for both bulk and inhomogeneous fluids. The phase diagrams of both TR and LRC H\textsubscript{2} with a cutoff of 15 Å, LRC D\textsubscript{2} with a cutoff of 9 Å were calculated. The average absolute deviations for the the coexistence density between LRC and TR H\textsubscript{2} are 6.9\% and 1.1\%, respectively, for the vapor and liquid branches. This is considerably larger than for classical fluids. The wetting temperature for H\textsubscript{2} adsorption onto Rb surface with the 9-3 model potential is estimated to be 29.5 K,

The disadvantage of MHR technique for path integral fluids is that many more state points are needed compared with classical fluids. This is due to the number of beads needed to accurately describe H\textsubscript{2} and D\textsubscript{2}, making the overlap in \textit{U\textsubscript{1}} and \textit{U\textsubscript{2}} rather poor. The number of state points may be reduced by employing the multicanonical ensemble technique\textsuperscript{128}.
5.0 WETTING TRANSITIONS OF HYDROGEN AND DEUTERIUM ON THE SURFACE OF ALKALI METALS

5.1 Introduction

Consider a fluid near a solid surface at pressure $P$ and temperature $T$ (below the liquid-vapor critical temperature $T_c$). When $P$ is equal to the saturated vapor pressure ($P_{svp}$), an adsorbed liquid film may exhibit either one of two possible behaviors: spreading across the surface or beading up to form a droplet. These possibilities are called wetting (or complete wetting) and nonwetting (or incomplete wetting), respectively. This distinction is compatible with Young’s equation for the contact angle (which vanishes in the wetting case) and thus the behavior of a given system can, in principle, be derived from the $T$-dependence of three surface tensions (gas-solid, liquid-solid and gas-liquid). Some 25 years ago, scenarios of thermodynamic transitions between wetting and nonwetting were predicted by Cahn$^{83}$ and Ebner and Saam$^{84}$. Subsequently, such wetting transitions have been observed experimentally for both isotopes of He and for hydrogen on Rb and Cs, for Ne on Rb, and for Hg on sapphire and Ta. Similar transitions have been predicted to occur for other adsorption systems (e.g. Ne/Mg and Ar, Kr and Xe on alkali metal surfaces)$^{103,129-138}$. The common feature of all of these systems is the existence of a very weakly attractive adsorption potential; the well-depth ($D$) of the gas-surface interaction $V(z)$ is less than, or of the order of, the well-depth ($\varepsilon$) of the intermolecular potential of the adsorbing fluid.

These wetting transitions have been studied by a variety of general theoretical models, including lattice-gas, density functionals, and classical Monte Carlo simulations$^{76,102,139-142}$. To date, remarkably, there has been no quantum simulation exhibiting a wetting transition$^{143}$, even though the quantum fluids He and H$_2$ are paradigms of this transition$^{144}$. Moreover, the only classical simulation study pertinent to any experimentally observed wetting transition (Ne/Rb) is difficult to compare with the data because of uncertainties arising from the proximity (within 1%) of the wetting transition temperature $T_w$ to $T_c$$^{131,140}$ and neglect of quantum effects in the simulations$^{120}$. 
This lack of theoretical analysis for systems studied in the laboratory leaves open many questions, e.g., how reliable are the adsorption potentials and theoretical models used to predict the transition? What is the detailed nature of the thin-to-thick film wetting transition? Can simulations accurately predict other systems which will exhibit prewetting transitions?

In the absence of exact calculations for experimentally relevant systems, an alternative approach to predicting $T_w$ has been posited, a so-called “simple model”\(^1\). In that model, the thin-to-thick film transition is predicted to occur when the surface tension “price” of forming two interfaces becomes equal to the free energy reduction due to the integrated fluid-surface attraction. Estimates of these terms lead to an implicit relation for the wetting temperature:

$$
\sigma_{lg} = -\frac{1}{2} \rho_0 \int_{z_{min}}^{\infty} V(z) dz,
$$

where $\sigma_{lg}$ is the bulk liquid-vapor surface tension and $\rho_0$ is the bulk fluid number density, both at $T_w$, and the integral extends from the minimum of the potential to infinity. Some evidence implies that this model works surprisingly well in predicting $T_w$ of classical gases, except in cases of the least attractive interactions\(^2\). However, no comparison between “exact” calculations, this model, and experimental data has ever been made. Such calculations are therefore needed in order to further test this model and theoretical calculations of the adsorption potential. This paper presents evidence relevant to these open questions by comparing wetting transition data with results of path integral grand canonical Monte Carlo simulations for the hydrogen isotopes. This simulation method is exact, in principle, assuming that the interaction potentials are correct.

### 5.2 Theory and Simulation Details

Molecular simulations were performed using path integral grand canonical Monte Carlo\(^3\,\,4\). The fluid interactions were modeled with the Silvera-Goldman potential\(^5\), which is accurate for
both $H_2$ and $D_2^{120,123,146}$. The saturation properties of the bulk fluids were computed from multiple histogram reweighting (MHR)$^{11,12}$ adapted for path integral Hamiltonians$^{146}$.

A number of different potentials for $H_2/Rb$ were considered, four of which appear in Figure 5.1. The *ab initio* potential of Chizmeshya et al. (CCZ)$^{137}$ was derived from a Hartee-Fock repulsion and a damped van der Waals (vdw) dispersion term$^{147}$. The resulting potential was found to fit the following expression:

$$V(z) = V_0(1 + \alpha z)e^{-\alpha z} - f_2(\beta(z)(z - z_{vdw}))\frac{C_{vdw}}{(z - z_{vdw})^3}, \quad (5-2)$$

where $z$ is the distance between the adsorbate the jellium boundary of the metal, $f_2$ is a damping function given by $f_2(x) = 1 - e^{-x}(1 + x + x^2/2)$, $\beta(z)$ is given as $\beta(z) = \alpha^2 z/(1 + \alpha z)$, $V_0$, $\alpha$, $C_{vdw}$ and $z_{vdw}$ are the four parameters of the potential. We have also used an empirical 9-3 potential,
which was used by Cheng et al.\textsuperscript{125} to compute the wetting temperature for H\textsubscript{2} on Rb from the simple model.

The CCZ parameters for H\textsubscript{2}/Rb are \( V_0 = 0.274 \) eV, \( \alpha = 1.769 \) Å\(^{-1}\), \( C_{vdw} = 0.297 \) eV Å\(^2\), and \( z_{vdw} = 0.246 \) Å. This potential is characterized by a well-depth ratio \( D/\epsilon \approx 1.26 \).

## 5.3 Results

The simple model predicts a \( T_w \) of 22.7 K\textsuperscript{137} for the CCZ potential and a value of 22 K for the 9-3 potential. The simulations discussed below indicate that \( T_w = 25.5 \pm 0.5 \) K for the CCZ potential and 29.5±0.5 K for the 9-3 potential. This finding was unexpected because the 9-3 potential has a substantially larger well depth than the CCZ potential, which would be expected to result in a lower \( T_w \). This is reflected in the predictions from the “simple model” (see Table 5.1). However, the simulations show that the broader potential well of the CCZ potential more than compensates for the smaller value of \( D \) compared with the 9-3 potential. This sensitivity to the shape of the potential does not appear to be adequately captured in the “simple model”. Figure 5.2 presents simulation results for the film density, obtained with the CCZ potential, at 25 K and 26 K. At 25 K, only a thin film forms at all \( P < P_{svp} \), indicating nonwetting. Note that due to metastability the adsorption is very small even at a pressure a little higher than \( P_{svp} \). The thermodynamic excess coverage (the integrated excess of the film density relative to the vapor density) is minuscule, about \( \sim 15\% \) of

<table>
<thead>
<tr>
<th>Potential Model</th>
<th>( D ) (K)</th>
<th>( T_w ) (K)</th>
<th>( T_{pwc} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-3</td>
<td>44</td>
<td>29.5 (22)</td>
<td>31</td>
</tr>
<tr>
<td>CCZ</td>
<td>41</td>
<td>25.5 (22.7)</td>
<td>30</td>
</tr>
<tr>
<td>0.9 ( V_0 )</td>
<td>45</td>
<td>22.5 (20.3)</td>
<td>28</td>
</tr>
<tr>
<td>1.1 ( C_{vdw} )</td>
<td>49</td>
<td>18.5 (19)</td>
<td>25.5</td>
</tr>
<tr>
<td>0.9 ( V_0 ), 1.08 ( C_{vdw} )</td>
<td>53</td>
<td>17.5 (18.6)</td>
<td>24.5</td>
</tr>
</tbody>
</table>
Figure 5.2: The local density profiles for the original CCZ potential\textsuperscript{137} at 25 and 26 K. The relative pressure, $P/P_{\text{svp}}$, at which the calculations were performed are indicated by the numbers on the graph.
the close-packed monolayer coverage. The simulation results for the film at 26 K manifest quite different behavior, characteristic of a prewetting transition. Below 98% of $P_{svp}$, a thin film forms. At $P/P_{svp} = 0.98$, however, there is a factor of 8 jump in the excess coverage. Further increases in $P$ toward $P_{svp}$ yield an ever thickening film, i.e., wetting behavior. Thus, the CCZ potential yields a first order wetting transition, with a wetting temperature somewhere between these two values of $T$, i.e., $T_w = 25.5 \pm 0.5$ K. This value is significantly higher than the experimentally measured value of $T_w = 19.10 \pm 0.06$ K. The discrepancy implies that the assumed $V(z)$ is too weakly attractive, which we address below. We have empirically adjusted $V(z)$ to bring the $T_w$ prediction into agreement with experiment by making changes to $C_{vdw}$ and $V_0$. Some results are shown in Table 5.1.

These results (and others, not tabulated) indicate the sensitivity of the wetting behavior to the potential parameters, especially the vdw coefficient. For example, for H$_2$ on Rb a 10% increase in $C_{vdw}$ (1.1$C_{vdw}$) leads to a 27% decrease in $T_w$, whereas a 10% decrease in $V_0$ (0.9$V_0$) gives a 12% decrease in $T_w$. Of the potentials we have examined, 1.1$C_{vdw}$ gives the best agreement with experiments. The simple model consistently underestimates the wetting temperature by a few Kelvin, or about 10% for most of the potentials in Table 5.1. This finding is consistent with that obtained from classical simulations, which show a similar systematic discrepancy. This semiquantitative consistency is better than what might be expected with such a primitive model!

Comparison of calculated and experimental $T_w$ values implies that the CCZ potential is not sufficiently attractive to explain the H$_2$/Rb data. We have made additional comparisons to test the generality of this conclusion. One comparison involves the adsorption of D$_2$ on Rb. This is a fairly stringent test of the new potential and its relation to the experiments, which were carried out in the same laboratory in which the H$_2$/Rb data were taken. We have used the potential in best agreement with H$_2$/Rb experimental data, i.e., 1.1$C_{vdw}$, for these simulations. The result is that the simulation yields $T_w = 29 \pm 0.5$ K, in excellent agreement with the experimental value of 28.9 $\pm$ 0.3 K. This agreement improves our confidence in the new potential, which should be virtually identical for the two isotopes (differing only in very small effects of the 1% difference in
the isotopes' polarizabilities). We have also studied H₂ wetting on a similar system, H₂/Cs. The potential well-depth for H₂/Cs was found by Chizmeshya et al. to be some 5% smaller than that for H₂/Rb. The simple model predicts a $T_w \sim 23$ K, which is higher than the experimental value of $20.57 \pm 0.05$ K of Ross et al. We have simulated this system with the $1.1C_{\text{vdw}}$ potential, assuming that the error in the ab initio potential is systematic. The resulting wetting temperature for this system is $19.5 \pm 0.5$ K which is slightly lower than the experimental result. The agreement for the three relevant systems that have been studied experimentally encourages our confidence in the both the revised potential and the experiments. The comparison is particularly meaningful because the experiments were performed in different laboratories, using quite distinct methods of surface preparation.

We have computed $T_w$ of H₂ on Au coated with Rb, a system not yet studied experimentally. The potential for this system is given by $V_{\text{Rb/Au}}(z) = V(z) - \frac{\delta c}{(z+d)^3}$, where $\delta c = 474$ meV Å$^3$ is the difference of the $C_{\text{vdw}}$ between Au and Rb, $d$ is the film thickness of Rb, set to 15 Å in this case, and $V(z)$ is given by Eq. (5-2) with the parameter for H₂/Rb using $1.1C_{\text{vdw}}$. The potentials for H₂ interacting with a pure Rb surface and a 15 Å film of Rb on Au are plotted in the inset of Figure 5.1. Note that the potentials are nearly identical, with the Rb/Au potential being about 1 K deeper at the minimum. $T_w$ for H₂ on a 15 Å film of Rb on Au is $17.5 \pm 0.5$ K, about 1 K lower than the pure Rb case. The lowering of $T_w$ has been observed for $^4$He on Cs films of various thicknesses. At 20 K the relative prewetting transition pressure, $P_w/P_{\text{svp}}$, is 0.93 for the Rb on Au substrate, while for the pure Rb substrate $P_w/P_{\text{svp}} = 0.97$, a decrease of about 4%. The $P_w/P_{\text{svp}}$ at 21 K also differ by about 4%. These differences in $T_w$ and $P_w/P_{\text{svp}}$ should be large enough to detect experimentally. The simple theory predicts that the wetting temperature shifts in proportion to $\delta c$, with a resulting shift of 0.9 K for a Rb film thickness of 15 Å. This is consistent with the simulation result. The surprisingly large shift is indicative of the extreme sensitivity of the wetting transition behavior to the long range interaction, as implied by Eq. (5-1). It is possible to experimentally construct such a film of Rb on Au and to measure the wetting properties to test these predictions.
5.4 Discussion and Conclusion

We address briefly the intriguing question: why does the theoretical CCZ potential underestimate the gas-surface attraction by $\sim 10\%$? Possible explanations include the contribution of the $\text{H}_2$ quadrupole interaction with its image (omitted from CCZ), uncertainty about the image plane’s position, the form of the damping function, and the need for a more careful treatment of the electron gas, including hybridization with the adsorbate states$^{151}$. Here, we consider the contributions of two independent quadrupole-related terms. The first is the permanent quadrupole moment’s orientation-dependent interaction with its image, which has been evaluated elsewhere for similar problems$^{152}$. The resulting energy is small: just 0.2 K (compared to a well depth of 41 K). The other term is the fluctuating quadrupole moment of the molecule interacting with its image in the metal. Using the theory of Jiang et al. to evaluate this quantity, we obtain an attractive energy of 2.0 K for an $\text{H}_2$ molecule at its equilibrium position on Rb$^{153}$. This represents a 5\% contribution to the well depth, too small to explain the discrepancy manifested in $T_w$. Thus, the adsorption potential remains an open problem.

Finally, we comment on the decade-long evolution of our understanding of this problem. A theoretical potential was proposed in 1993, from which the simple model predicted a wetting temperature $\sim 22$ K for $\text{H}_2$/Rb, close to the experimental value of 19 K$^{125}$. This agreement was a fortuitous consequence, we now believe, of a systematic error inherent in the simple model (explained above) and a systematic error in the potential used at that time. These two errors shifted the prediction of $T_w$ in opposite directions, so that their effects approximately canceled, resulting in nominal agreement with experiment. In that initial study, the uncertainty in the well depth of the potential was reported to be 40\%. The more recent CCZ potential employs better justified methods and approximations than the 1993 study and has a smaller estimated uncertainty, $\sim 25\%$. However, the good agreement of 1993 between experiment and theory has been lost, leaving unanswered questions about the origin of the remaining discrepancy. The present study indicates how wetting transition data can be utilized to test and refine theoretical adsorption potentials. Com-
plementary experimental investigations, such as gas-surface scattering measurements and a test of the predicted shift in $T_w$ for the Rb/Au compound substrate, would provide additional assessments of predictions based on these new potentials.
6.0 CHEMICAL ACTIVATION OF SINGLE-WALLED CARBON NANOTUBES FOR HYDROGEN ADSORPTION

In this chapter, we report the isotherms of hydrogen adsorption onto single carbon nanotube bundles. The data have been compared with the experiments. All the experimental work are done by M. R. Smith, Jr., E. W. Bittner, and B. C. Bockrath.

6.1 Introduction

The unique porosity of single walled carbon nanotubes (SWNTs) has prompted considerable interest in their gas adsorption properties. The present need for better materials for hydrogen storage has led to much of the interest in this direction. Several reviews of this rapidly growing area have appeared.\textsuperscript{21,154,155} Among the various reports are claims that significant amounts of hydrogen are taken up by SWNTs. Claims of high values of hydrogen adsorption have been made in reports of investigations at low temperature,\textsuperscript{22} room temperature\textsuperscript{23,24} and even higher temperatures.\textsuperscript{28} In contrast, most theoretical calculations of hydrogen adsorption have given considerably lower estimates.\textsuperscript{156–166} These results may indicate that physisorption on pure nanotubes may not be an effective method of storing hydrogen. Other experimental studies have found very limited uptake of hydrogen,\textsuperscript{25–27} in agreement with simulations. However, variations in the experiments may be due to differences in the way the SWNT samples were prepared or pretreated.

Chemical activation is one option for improving adsorption characteristics. Although it has a long history of application in carbon chemistry, its potential for use with the recently synthesized carbon nano-structures is just beginning to become evident.\textsuperscript{167,168} It has been shown that Xe adsorption on SWNTs is dramatically affected by the pretreatment procedure.\textsuperscript{169} Eklund and coworkers have shown that the hydrogen uptake on nanotubes at low temperatures can be increased radically by activation of the nanotube samples.\textsuperscript{168}

\textsuperscript{1}This chapter is reprinted from reference 46
In the work described below, we have used a tapered element oscillating mass analyzer (TEOM) to obtain isotherms for hydrogen adsorption on SWNTs at 25 °C over the range of pressure from one to 48 bar. This instrumental method is based on measurement of the weight change observed as a function of the applied hydrogen pressure in a flow-through system. The application of this instrument to determine adsorption isotherms has been recently demonstrated in the case of light alkanes (methane – butane) on silicalite.\textsuperscript{170} In the work reported below, samples of SWNTs were used as-received and after various pretreatments. The most remarkable results were obtained using a simple activation procedure based on partial oxidation using carbon dioxide at 600 °C. The adsorption of excess hydrogen increased markedly after SWNTs were activated by this procedure. Activated samples were found to adsorb 1.2 wt\% hydrogen at 48 bar and 25 °C. Details of the activation procedure are described in a recent paper.\textsuperscript{171} Characterization of the surfaces of the same raw and purified nanotubes as used in this work has been made by a pulse adsorption technique using the TEOM.\textsuperscript{172}

We also present molecular simulations as a means of identifying possible reasons for the observed increase in adsorption in the samples that have been activated by CO\textsubscript{2} oxidation. Theoretical calculations of hydrogen adsorption on SWNTs have been performed using various methods.\textsuperscript{156–166} With few exceptions, these studies indicate only modest uptake of hydrogen at room temperature and moderate pressures. \textit{Ab initio} simulations that indicate the potential for higher uptake are subject to substantial error because the description of the H\textsubscript{2}-nanotube interaction within the tight-binding or density functional approximations is not expected to be accurate for physisorption.\textsuperscript{173–177}

All of the theoretical studies performed so far have been carried out on SWNT samples that are, by necessity, idealized in some ways. Some of the studies consider only single isolated nanotubes. Other studies assume idealized nanotube bundles composed of perfect hexagonal or square arrays of identical nanotubes, all of the same diameter and chirality. In reality, experimentally produced SWNT bundles are composed of nanotubes of different diameters and chiralities.\textsuperscript{178–182} While nanotubes pack into a hexagonal array, the packing is not expected to be perfect because of the
distribution of nanotube diameters in a bundle. At least some nanotube samples have a significant number of defects that may contain carbonyl or other oxygenated groups. Nanotube bundles are also not perfectly straight. There is curvature over length scales of hundreds of nanometers, allowing nanotube bundles to cross one another, leading to complex secondary structures. The external surfaces of the SWNT bundles are also complicated by the presence of amorphous carbon and catalytic metals. All of these factors make exact modeling of real SWNT bundles a very difficult task. In addition, the exact form of the nanotube-hydrogen potential is unknown and could only be computed accurately from very high-level electronic structure methods that include electron correlation (e.g., coupled cluster or configuration interaction); such calculations are impractical for SWNTs because of the large number of atoms involved. It is also not known exactly how the presence of defects changes the interaction potential. Activation processes, such as the one used in this study to improve hydrogen uptake, further complicate the description of the nanotube samples by adding unknown chemical and topological changes to the underlying structure. Previous simulations have accounted for defects in an approximate way by including point dipoles or point charges. Size heterogeneity in different bundles has been modeled by picking nanotube diameters randomly from a given size distribution. In this study we examine the effect of the nanotube diameter distribution and packing on hydrogen uptake. We also vary the nanotube-hydrogen interaction potential by arbitrarily increasing the potential well depth to mimic the effect of chemical activation.

6.2 Experimental Methods

A block diagram of the experimental apparatus including the TEOM Series 1500 Pulse Mass Analyzer (Rupprecht and Patashnick Co.) is given in Figure 6.1.
The TEOM Series 1500 is a flow-through microbalance that detects mass changes by an inertial system. It was initially used to study coke deposition on zeolite catalysts, and has since found general application for following mass changes in a variety of chemical systems including a recent study of the adsorption isotherms of light hydrocarbons on zeolites. It employs a tapered glass element to measure mass changes. The element consists of a hollow glass tube that leads the gas stream through a cylindrical sample bed, diameter 4 mm, height 6 mm, located at its lower end. Samples were packed into the bed between “Astro quartz” wool plugs and retained there by a ventilated, gold-plated metal cap. Gas streams were controlled using a manifold that included mass flow controllers and a back-pressure regulator. Instrument control and data recording were managed through a PC. The control system allowed the programmed selection of the gases, their flow rates, system pressure and temperature, and other functions. Two gas streams were supplied to the instrument; one passes through the sample in the packed bed (reactive gas) and the other sweeps the volume outside the sample bed (purge gas). The tapered-element was enclosed within a heated stainless steel pressure vessel. The instrument is capable of operating from ambient temperature to 700 °C and from ambient pressure to 48 bar. The combined flow of both gas streams is sampled at the exit port by a capillary tube that serves as a transfer line to a quadrupole mass spectrometer.

The operating principle of the instrument is based on the relationship between changes in the mass of the sample bed to changes in the frequency of oscillation of the tapered element. The element is stimulated to vibrate at its natural frequency by a mechanical system. The frequency of oscillation is measured by an optical system through two ports in the pressure vessel. Mass changes are determined by the following equation:

$$\Delta m = \frac{k}{\frac{1}{f_1} - \frac{1}{f_2}},$$

where $f_1$ and $f_2$ represent the frequencies observed at two different loadings, and $k$ is an empirically determined constant. The instrument was equilibrated at the isotherm temperature and flow conditions in order to determine the value of $k$. The frequency of the empty reactor was measured without the retaining cap in place, then the procedure was repeated with the cap in place. The constant was calculated using the known mass of the cap.
Figure 6.1: Block diagram of the Rupprecht and Patashnick TEOM 1500 and associated hardware.
The mass changes observed in the instrument as the pressure is varied result from both changes in density of the free gas within the oscillating element and the change in the amount of gas adsorbed by the sample. To obtain the isotherm of the excess adsorbed gas, the amount due to the change in density of the free gas must be subtracted from the total. The values due to the free gas density changes were obtained from experiments with the reactor empty. In this case, the observed mass change increased in a nearly linear fashion with pressure. Measurements were then taken with a sample in place under exactly the same conditions. Isotherms were generated by subtracting the mass change found with the empty reactor from the corresponding value found with the packed reactor for each step in pressure. A correction was applied to the empty reactor data to account for the volume occupied by the sample (see calculations below).

In a typical experiment, a sample of 30-50 mg was packed into the bed between 20-40 mg of quartz wool used as plugs. The bed was flushed with dry helium or nitrogen, then heated to 200 °C for at least two hours. After the signal from the mass spectrometer indicated that the release of small amounts of water and oxygen was complete, the sample was cooled to 25 °C and both reactant and purge gases were switched to hydrogen at a flow rate from 10-50 cc/min. Hydrogen was used as both purge and reactant gas in all experiments reported here to eliminate possible instrumental artifacts that may arise due to back-mixing of a dissimilar purge gas into the packed bed.

The pressure program was only begun after all of the inert gas had been swept from the reactor by hydrogen as indicated by the response of the mass spectrometer sampling the exit stream. Then the pressure was taken from ambient to 48 bar in seven steps. It was held constant for 10–20 minutes after each increment. At the end of the ascending program the pressure was returned to ambient using 1.4 bar decrements to avoid expelling the sample from the bed. The entire program was then repeated several times. Note that in these experiments, the origin of the pressure/mass change data is ambient pressure. Thus, isotherms refer to the increment in hydrogen adsorption above that already taken up at one atmosphere.
As noted above, a correction was applied to account for the portion of the free gas volume in the packed bed that is occupied by the sample and quartz wool. The correction was made by multiplying the mass changes for the empty reactor by the ratio of the free volume for the packed to that of the empty reactor. The total free volume sensed by the oscillating element was determined by applying the ideal gas law to the variation of the measured mass of the empty reactor when the hydrogen pressure was increased from ambient to 48 bar. The error in the specific volume from assuming ideal gas behavior at 48 bar and room temperature is about 3%. The volume of the sample was calculated from the mass of carbon in the sample and the theoretical density. The correction factor found using these values had a relatively small effect on the calculated amount of adsorbed hydrogen because the measured free volume of the reactor element is roughly an order of magnitude larger than the volume occupied by the sample. The mass change assigned to excess hydrogen was expressed as weight percent of gas adsorbed based on the total mass of carbon in the sample. The later was determined by thermal gravimetric analysis (TGA). Atomic adsorption spectroscopy was used to verify the identity of the residual catalytic metals recovered after the TGA analysis.

The weight percent of excess H$_2$ adsorbed is given by

$$wt\% = 100 \frac{\Delta m_s - V_{corr} \Delta m_E}{f_cm_{ads} - \Delta m_{ads}},$$

(6-2)

where $\Delta m_s$ is the mass change for the packed bed after change to pressure $P_i$, $V_{corr}$ is the volume correction factor ($\sim$0.977) to account for the volume occupied by the sample, $\Delta m_E$ is the corresponding mass change in the empty reactor on reaching $P_i$, $f_c$ is the fraction of SWNT sample that is carbon, $m_{ads}$ is the mass of the SWNT sample, and $\Delta m_{ads}$ is the weight lost after pyrolysis at either 200 or 700 °C.

The values used for each mass change were averages of from 80 to 160 data points taken over the 10-20 minute interval after a plateau was reached following each pressure step. Points in the isotherms are averages of 2-13 individual determinations of excess hydrogen for each pressure. The most extensively measured sample was calculated from 7 cycles of pressure up and down made
over 12 days. Data were taken from the 20 min plateaus at each step of the seven programs up in pressure and the 10 min plateaus of six programs down. The last depressurization failed and was not included. Sample standard deviations for the average of the 13 values for each point in the isotherm were between 0.03 and 0.11 wt%, being smaller at lower pressures. No trends were apparent over time nor differences noted for pressurizing or depressurizing sequences. One set of values for wt% H$_2$ (reaching 1.54 wt% at 48 bar) was tested for rejection using updated values for Dixon’s $Q$ test. The resulting $Q_{\text{EXP}} = 0.72$ indicated rejection at the 99% confidence interval and this set was therefore not incorporated in the isotherm in Figure 6.2. The remaining set of 12 values for each pressure has standard deviations between 0.02-0.03 wt% for each point.

![Adsorption isotherms for hydrogen on “Raw Material” Rice SWNTs after CO$_2$ oxidation (sample A). Sample B is derived from A after heating at 700 °C in H$_2$. Sample C consists of “Purified” Rice nanotubes after CO$_2$ Oxidation. Sample D is sample C after heating at 700 °C in He. The lines are drawn to guide the eye.](image_url)

Figure 6.2: Adsorption isotherms for hydrogen on “Raw Material” Rice SWNTs after CO$_2$ oxidation (sample A). Sample B is derived from A after heating at 700 °C in H$_2$. Sample C consists of “Purified” Rice nanotubes after CO$_2$ Oxidation. Sample D is sample C after heating at 700 °C in He. The lines are drawn to guide the eye.
Nanotubes were purchased from Tubes@Rice in two grades. “Raw Material Grade” was obtained as a solid, fibrous, mat. It was subjected to light grinding to make it easier to load into the sample cell. Grinding was performed by agitation for 4-8 min. in a small agate ball mill (Wiggle Bug, Brinkman Instruments). “Purified Grade” was purchased as a suspension in toluene. Typically 10-15 mL of the suspension was withdrawn from the bulk sample and evaporated in a stream of dry nitrogen at ambient temperature. When toluene was no longer evident, the sample was further dried at 140 °C for up to a week. Activated nanotubes were prepared by partial oxidation in a tube furnace held at 600 °C using a stream of CO₂ and argon at about a 50/50 ratio. Details are given in another paper.¹⁷¹ A sample of activated carbon (G-32 H, 4 × 10 mesh, Süd Chemie Inc.) was used to compare with the nanotube samples. The hydrogen, nitrogen, and carbon dioxide isotherms of this sample have been determined independently at this laboratory by a volumetric technique.¹⁸⁷ Hydrogen was “Extra Dry” grade (> 99.9%) from Matheson Tri-Gas. Helium and nitrogen were Matheson Tri-Gas UHP grade. The gases were further dried by passage through a Matheson Gas Purifier Cartridge Type 452 (4A molecular sieve).

6.3 Simulation Methods

Adsorption isotherms were computed from grand canonical Monte Carlo (GCMC) simulations.² The Silvera-Goldman potential¹²⁴ was used to describe the H₂-H₂ interactions. This potential has been shown to be accurate for computing equilibrium bulk properties over a very wide range of temperatures and pressures.¹²⁰ The H₂-nanotube interaction was taken as a pair-wise summation over H₂-C interactions computed from the Crowell-Brown potential.¹⁸⁸ This type of potential has been shown to reproduce experimental H₂-graphite adsorption isotherms and isosteric heats at low temperatures.¹⁸⁹ The solid-fluid potential used in the simulations is actually an integrated potential form so that a single polynomial function was fitted to the H₂-exohedral (outside) nanotube interactions and a second polynomial was used for the H₂-endohedral (inside) nanotube interactions.
Thus, each type of nanotube was described by two polynomial functions. We have constructed several different types of SWNT bundles in order to study the effects of diameter heterogeneity and packing effects on hydrogen uptake. We have constructed bundles by choosing nanotubes of various diameters from a given diameter distribution to mimic experimental distributions. We have also developed bundles based on an arbitrary diameter distribution for comparison with results from the experimental distributions. The bundles were packed by placing the first nanotube in the bundle at the center of the cell. The next nanotube was placed at a random position far enough away so as to ensure no overlap with the existing nanotube. The nanotube was then brought in a straight line toward the center of the box until the van der Waals (vdW) gap between the first and second nanotubes achieved some pre-specified value. The vdW gap is defined as the shortest distance between the walls of adjacent nanotubes, as measured from atom-center to atom-center. Subsequent nanotubes were added in a similar fashion to the second, except that the tube is brought in until its vdW gap with any other tube in the bundle reaches the specified value. The simulation box is a rectangular parallelepiped with a height (z-direction) of 34 Å and equal x and y dimensions. Periodic boundary conditions were applied in all three directions. The x and y dimensions were large enough to eliminate nearest neighbor interactions with tubes or hydrogen in the periodic images in order to mimic isolated SWNT bundles. Typical values of the width of the simulations box were between 100 Å and 250 Å, depending on the size of the bundle. A sample nanotube bundle is shown in Figure 6.3. The bundle contains 45 nanotubes and corresponds to bundle type a in Table 6.1.

Typical GCMC moves were attempted randomly with probabilities of 0.4 for displacements and 0.3 each for creation and deletion. The systems were first equilibrated for $5 \times 10^6$ steps, followed by $10^7$ steps for data collection. Adsorption isotherms were computed for five different classes of

<table>
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<th>Bundle ID</th>
<th>Num. of tubes</th>
<th>(8,8)</th>
<th>(9,9)</th>
<th>(10,10)</th>
<th>(11,11)</th>
<th>(12,12)</th>
<th>Average diameter (Å)</th>
</tr>
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<tr>
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<td>10</td>
<td>25</td>
<td>5</td>
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</tr>
<tr>
<td>b</td>
<td>100</td>
<td>6</td>
<td>29</td>
<td>35</td>
<td>28</td>
<td>2</td>
<td>13.44</td>
</tr>
<tr>
<td>c</td>
<td>50</td>
<td>3</td>
<td>14</td>
<td>18</td>
<td>14</td>
<td>1</td>
<td>13.45</td>
</tr>
<tr>
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<td>20</td>
<td>0</td>
<td>4</td>
<td>14</td>
<td>2</td>
<td>0</td>
<td>13.42</td>
</tr>
<tr>
<td>e</td>
<td>50</td>
<td>0</td>
<td>10</td>
<td>35</td>
<td>5</td>
<td>0</td>
<td>13.42</td>
</tr>
</tbody>
</table>
Figure 6.3: Sample nanotube bundle used in the molecular simulation. This bundle contains 45 nanotubes with diameters drawn randomly from a distribution similar to that observed in experiments (sample a in Table 6.1).
nanotube bundles shown in Table 6.1. The bundles contain from 20 to 100 nanotubes. Samples a – c are constructed to mimic two different diameter distributions observed in the experiment.\textsuperscript{181} Samples d and e were constructed from an arbitrary diameter distribution. Samples b and c have almost the same diameter distribution. Sample c contains half as many nanotubes as sample b. Samples d and e have exactly the same diameter distribution, with sample e having 2.5 times as many nanotubes as sample b.

From two to ten different realizations of each bundle were constructed by starting the construction procedure outlined above with different random number seeds. Adsorption isotherms were computed for each of the realizations and the averages were reported. The differences in adsorption on different bundle realizations for a specified diameter distribution were typically on the order of the uncertainties in the simulations. To be consistent with the experiment, the excess adsorption is calculated as

\[ \text{wt\%} = 100 \frac{(N_{\text{H}_2,P} - N_{\text{H}_2,P}^{\text{rep}}) - (N_{\text{H}_2,1} - N_{\text{H}_2,1}^{\text{rep}})}{6N_C}, \]  

(6-3)

where \( N_{\text{H}_2,P} \) is the number of adsorbed \( \text{H}_2 \) molecules in the simulation cell at pressure \( P \), \( N_{\text{H}_2,P}^{\text{rep}} \) is the number of \( \text{H}_2 \) molecules at pressure \( P \) in the cell when the attractive part of the potential between \( \text{H}_2 \) and nanotube is turned off, \( N_{\text{H}_2,1} \) and \( N_{\text{H}_2,1}^{\text{rep}} \) are the corresponding values at the reference pressure, i.e., 1 atm, \( N_C \) is the number of carbon atoms in the simulation cell. The excess adsorption defined in Eq. (6-3) is directly comparable to those from the experiments defined in Eq. (6-2). Note that this definition of the excess adsorption is different from that typically used because of the reference to one atmosphere rather than to vacuum.

### 6.4 Results and Discussion

Figure 6.4 contains the mass data used as a basis for the hydrogen isotherms described below. Curve A is the record of the mass changes for the packed reactor, and curve B is that for the empty reactor. Both mass curves closely follow the pressure curves (not shown). The initial spike found
Figure 6.4: Mass versus time as the $\text{H}_2$ pressure increases in steps of about 7 bar from one to 48 bar. Curve A is a 29 mg sample of purified Rice nanotubes after $\text{CO}_2$ oxidation and B is for the empty reactor.
at the leading edge of each pressure step is due to an overrun of the set point by the back-pressure regulator. The mass change curve for the packed reactor reaches a new plateau after each pressure change and remains constant. This behavior is consistent with a physisorption process without a significant kinetic barrier. Separate experiments were made to test whether slow adsorption might take place over time scales much longer than the 20 min intervals used here. No measurable mass changes were found even when the initially formed plateau was extended for 28 hours at 48 bar. A very similar pattern was found for the depressurization data. These results for the kinetics of hydrogen adsorption and those reported on a different set of SWNTs of somewhat larger diameter are distinctly different. In the later case, six hours was required for the pressure to equilibrate during the volumetric measurement made at room temperature, indicative of a significant kinetic barrier. No such barrier was found in any of the adsorption results given here.

The adsorption isotherm for hydrogen on an activated carbon is given in Figure 6.5 curve A. The isotherm is nearly linear up to the limit of pressure for these measurements, reaching a value of 0.66 wt% at 48 bar. Isotherms for hydrogen and other gases up to about 19 bar have recently been determined by a volumetric technique on this same lot of activated carbon. Comparison of the two sets of data reveals the value measured volumetrically at room temperature and 14 bar is 1.2 moles/kg, while the corresponding point from the TEOM at 25 °C is 1.04 moles/kg. There is reasonable agreement between the values obtained by the two different techniques. Note that the TEOM and volumetric methods have different reference points. The TEOM technique measures the increment in hydrogen adsorbed above 1 atmosphere [see Eq. (6-2)], while the volumetric technique begins the measurement of excess adsorption after the sample chamber has been evacuated. Given that the amount adsorbed at 1 atm is only about 0.01 wt%, the observed differences between the TEOM and the volumetric method cannot be attributed to the difference in reference points.

Two isotherms for a sample of “Raw Material” SWNTs from Rice are also shown in Fig 6.5. Curve B was taken after the sample had been heated in situ to 200 °C under a flow of helium, then cooled before the isotherm experiment was begun. Curve C was obtained in a subsequent experiment after the sample had been heated in a similar manner but to 700 °C. Pyrolysis at
Figure 6.5: Hydrogen isotherms for activated carbon (A) and “Raw Material” as-produced Rice nanotubes after treatment at 200 °C (B) and 700 °C (C) in flowing helium. The lines are drawn to guide the eye.
700 °C reduced the affinity of the sample for hydrogen by a significant amount. (The apparently anomalous value at 41 bar for curve C was due to the influence of one of only two values determined under these conditions for this sample.)

Evidence that the pyrolysis of the raw material resulted in considerable loss of functional groups was provided by the in-line mass spectrometer used to monitor the exit gases throughout the course of heating to 700 °C. Hydrogen, methane, and carbon oxides were detected as the temperature increased. After the sample had returned to 25 °C, the TEOM measured a weight loss of 13.2 mg, or 23.2% of the sample weight. Data in Figure 6.5 are based on total mass of non-metals and have been corrected for loss of mass to allow direct comparison of the samples.

In comparison to the sample of activated carbon (curve A), the “Raw Material” nanotube samples have at best roughly one half the storage capacity under the same pressure. Again, the saturation loading of either the fresh or the pyrolyzed samples has not been reached at the highest pressure used here, although curve B seems to show some curvature not apparent in curve A.

Adsorption isotherms on “Purified” nanotubes obtained from Tubes@Rice are shown in Figure 6.6. These tubes have undergone oxidation by reflux in 2.6 M nitric acid for 12 hours. The oxidation is reported to selectively remove amorphous carbon, leaving behind a greater proportion of nanotubes in the sample. The samples were represented as containing greater than 90% SWNT. The relative amount of the residual metal catalyst left in the sample increases as well. Presumably an overlay of graphitic carbon protects these particles from removal by oxidation. The metal content of the sample used here was determined by complete combustion using TGA in combination with atomic adsorption spectroscopy of residual oxides. The metals content was 8.8 wt% and the spectroscopy confirmed the presence of nickel and cobalt. The isotherms given in Figure 6.6 were normalized on the basis of total carbon content to obtain a more useful comparison, but were not adjusted for the fraction purported to be SWNT.

Isotherms A and B in Figure 6.6 were taken sequentially using the same protocol as employed for raw material above. To a first approximation, the amounts of hydrogen adsorbed by the purified
Figure 6.6: Comparison of adsorption isotherms of hydrogen on “Purified” Rice tubes: Sample A was heated at 200 °C in He. Sample B is sample A heated at 700 °C in He. Sample C is sample B after removal and milling in air. Sample D is sample C treated at 700 °C in H₂. The lines are drawn to guide the eye.
nanotubes and the raw material are similar. This result is contrary to the simple expectation that the purified material should adsorb a greater amount of hydrogen per sample weight because of its higher nanotube content. Heating to 700 °C in flowing He led to a modest increase in hydrogen adsorption as shown by comparing curves A and B. Perhaps it is more significant that the slope over this nearly linear region of the isotherm has increased after pyrolysis. Thus, the difference between the two may well increase at hydrogen pressures above those used here.

The mass spectra of the gases produced during pyrolysis were similar to those seen with the raw material and consistent with the loss of carboxyl and other oxygen containing functionalities. The mass loss following pyrolysis was 12.7% and may be compared with the value of 23.2 wt% found with the raw material. The functional groups responsible for this weight loss were likely introduced during the oxidative purification with nitric acid. Further evidence of their connection to the adsorption properties of the SWNTs was provided by a separate experiment in which another sample was carried through five cycles of pyrolysis at 700 °C over several days. The isotherms found before and after the first pyrolysis are nearly identical to A and B given in Figure 6.6. However, repetition of the initial pyrolysis had little further effect on the storage capacity or the slope of the isotherms. The relative amounts of the products from pyrolysis detected by the mass spectrometer were much reduced after the first cycle. Thus, the sample is chemically stable to 700 °C after the first pyrolysis cycle and no evidence for further annealing of the physical structure is found in the isotherms.

As mentioned in the Experimental section, these nanotube samples are difficult to pack into a small bed because their fibrous nature resists compaction. A mild mechanical milling procedure renders them much more amenable to packing. To determine whether this procedure has an effect on the adsorption properties, the sample was removed after isotherm B in Figure 6.6 was completed, milled by agitation in a small ball mill, and repacked in the bed. Milling the sample in air in this way decreased its adsorption capacity slightly (curve C). This loss was mostly restored (curve D) when the sample was again pyrolyzed, this time in flowing H₂. Thus, the effects seem more related to the oxidative consequences of milling in air rather than the milling itself. Mild ball milling in air
introduces oxygen containing functional groups into the nanotubes as evident from the evolution of CO and CO\textsubscript{2} observed in the mass spectrum on heating to 700 °C. In view of the small change, the issue was not pursued further.

Activation of the nanotube samples took place in two steps. The first step was conducted by partial oxidation of a roughly 200 mg sample of nanotubes in a tube furnace under a stream of CO\textsubscript{2} at about 600 °C. Burn out during the initial oxidative procedure removed about 37 wt% of the purified nanotube sample. In the case of the raw material, about 21% of the weight was removed during CO\textsubscript{2} oxidation. TEM images taken before and after the reaction with CO\textsubscript{2} show that in the case of the purified grade material the rope-like structures are left intact.\textsuperscript{171} It is unexpected that a larger fraction of the purified sample would oxidize in the CO\textsubscript{2} treatment than for the raw material. This may be a result of the damage done to the nanotubes during the purification procedure.\textsuperscript{190}

A marked improvement in the amount of hydrogen adsorbed was obtained for both the raw material and the purified tubes (Figure 6.2, curves A and C) after the first step. The amount adsorbed at 48 bar has increased from 0.29 to 0.89 wt% for the raw material and from 0.23 to 0.64 wt% for the purified material. The second step of activation was accomplished in the TEOM by heating the oxidized tubes to 700 °C in a flow of He or H\textsubscript{2}. This induced further weight loss. For example, the oxidized raw material lost an additional 20% when pyrolyzed under H\textsubscript{2} at 700 °C. The pyrolysis lead to a further increase in hydrogen adsorption. The cumulative effect of the two steps is a significant increase in hydrogen storage capacity (Figure 6.2, curves B and D). Values of 1.16 wt% (“Purified”) and 1.2 wt% (“Raw Material”) were reached at 48 bar.

The data in hand do not permit an assignment of hydrogen adsorption capacity to particular fractions of carbon such as those identified by TGA for example. Thus, if the material removed by CO\textsubscript{2} oxidation had been relatively inert toward hydrogen adsorption the remaining material would show a corresponding increase in percent adsorption. Removal of this dilution effect could account for increases of 16% for the raw material and 59% for the purified material, but that is far short of the more than three-fold increase actually found. Instead, the large magnitude of the increase points toward a form of chemical activation.
It is reasonable to assume that this activation for adsorption may occur by opening the internal surfaces of tubular structures by oxidative destruction of part of the tube wall. In fact, evidence has been presented for thinning and opening of multi-walled tubes by partial oxidation with CO$_2$ at 850 °C, a somewhat higher temperature than used here.$^{167}$ The potential benefit created by removing tube end-caps and thus enhancing gas storage properties through the use of this method has been claimed in a patent, although no adsorption data were given.$^{191}$ Another study has demonstrated that opening the sidewalls of SWNTs by a combined cycle of oxidation and pyrolysis enhances the kinetics of xenon adsorption.$^{184}$ In this case, oxidation was accomplished with ozone, and the pyrolytic removal of the carboxylic groups so created was performed at the same temperature as used here, 700 °C. The maximum in the observed rate of xenon adsorption was found after a considerable percentage of the carbon had been etched away.

Parallels exist with the result reported here. The activation by CO$_2$ is likewise an oxidation. Because it is carried out at 600 °C it is simultaneously a pyrolysis, thus combining oxidation/pyrolysis cycle in one step. It also removes a considerable fraction of the carbon in the sample. The adsorption isotherms measure a thermodynamic property and we are unable to detect evidence for kinetic limitations in any case. However, TPD experiments described in the xenon adsorption work show that the majority of the sites that are more accessible after oxidation also desorb xenon at higher temperatures, implying deeper potential wells.$^{184}$ On the other hand, comparison of our data with computer simulation results (see below) indicate that in this case the increase in adsorption cannot be ascribed to opening of entry ports to the nanotubes alone.

It should be noted that pyrolysis of purified tubes results in a modest increase in hydrogen storage (Figure 6.6), but in the case of “Raw Material” SWNTs it results in a decrease of smaller magnitude (Figure 6.5). This result is puzzling, but we note that in the first case an oxidation using nitric acid was done to generate purified material before the pyrolysis was carried out. In the later case, pyrolysis was applied without prior oxidation. Annealing of the rope-like structures of nanotubes at elevated temperatures has been reported and must be considered as another potential side effect of pyrolysis. Annealing may reduce the amount of interstitial volume in bundles of the
raw material. The differences seen in Figure 6.5 are rather small, and would be in concert with the expectation that the relative amount of hydrogen taken up in the interstitial spaces is a small part of the total. Thus, the contradictory trends in adsorption may be the result of the dominance of an annealing effect in the case of raw nanotubes and the opening of additional porosity in the case of the purified nanotubes.

### 6.5 Simulation Results

We have computed H$_2$ adsorption isotherms on each of the nanotube bundles listed in Table 6.1. The isotherms on the different bundles are in quantitative agreement with one another. This is an important result because it indicates that the simulation results are not strongly dependent on the details of the bundle geometry or even the nanotube size distribution within the bundle. This insensitivity to the details of the geometry was unexpected. The excess adsorption isotherms are plotted in Figure 6.7. Results from simulations on bundle samples b, c, and e from Table 6.1 are plotted along with experimental data for purified nanotubes before being subjected to CO$_2$ oxidation (curve B from Figure 6.6). Adsorption isotherms from simulations on other bundles are very similar and are not shown for the sake of clarity. The agreement between the simulation and experimental isotherms is striking. Assuming that the solid-fluid interaction potential is accurate, the remarkable agreement between simulations and experiments indicates that the samples before CO$_2$ oxidation can be considered to be mainly composed of nanotube bundles (once the weight of the metal has been subtracted) and that amorphous carbon present in the sample and pore blocking functional groups do not severely inhibit hydrogen adsorption. On the other hand, it could be that the assumed H$_2$-nanotube interaction potential is too weak and that the adsorption is attenuated in the experiment due to pore blocking or unopened nanotubes to a degree that gives fortuitous agreement with simulations. Given the insensitivity of the computed adsorption isotherms to the
Figure 6.7: Adsorption isotherms computed from simulations for several of the bundles listed in Table 6.1. The experimental data for a sample of purified nanotubes heat treated to 700 °C, (sample B from Figure 6.6) are shown for comparison. The lines are drawn to guide the eye.
bundle size and nanotube diameter distribution, we cannot deduce anything about the experimental nanotube bundle geometry from the agreement between the simulations and experiments.

We next examine the possible causes for the dramatic increase in adsorption observed after CO$_2$ oxidation and subsequent heat treatment. The oxidation treatment will likely etch holes in the nanotubes and deposit oxygen-containing functional groups at these defect sites. We therefore hypothesize that the increase in adsorption capacity may be due to an enhancement of the solid-fluid potential (as a result of the introduction of polar functional groups), or due to an increase in the available volume (from holes etched in the tubes), or to a combination of these. We test this hypothesis by arbitrarily increasing the gap between the nanotubes, or increasing the strength of the solid-fluid potential, or a combination of both increasing the gap and the strength of the interaction potential. This procedure is only a first order approach to modeling the effects of CO$_2$ oxidation. Simulations of nanotubes with side-wall holes and explicit functional groups will be part of a future study. The optimal vdW gap for a perfect SWNT array is about 6.4 Å for maximizing the excess volume adsorbed at moderate pressures. This is double the experimentally measured gap in as-produced nanotube bundles. Our simulations (not shown) indicate that increasing the vdW gap alone is not sufficient to reproduce the magnitude of the increase in adsorption observed after CO$_2$ oxidation and subsequent heat treatment of the nanotube samples. The solid-fluid potential $V_{sf}$ was increased by simply multiplying the potential by an arbitrary factor. Thus, $1.5V_{sf}$ means that the potential has been increased by 50%. Isotherms computed from bundles with various values of the vdW gap and $V_{sf}$ multipliers are shown in Figure 6.8. The experimental data for H$_2$ adsorption on the CO$_2$ oxidized and heat treated purified nanotubes (sample D from Figure 6.2) are plotted as circles in Figure 6.8. Simulations show that increasing the interaction potential while holding the vdW gap fixed at 3.2 Å produces a curve that is substantially concave downward and hence cannot match both the low and high pressure regions of the experimental data, which are approximately linear in pressure. This indicates that the mechanism for increasing the adsorption in experiments cannot be described by a simple increase in the solid-fluid potential. An adsorption isotherm on a bundle with a vdW gap of 6.4 Å and a potential of $1.3V_{sf}$ is represented by the up
Figure 6.8: Adsorption isotherms computed from simulations with increased gap spacing and enhanced solid-fluid attractive potentials. All the simulations are for bundles containing 45 nanotubes with a diameter distribution given by sample a, from Table 6.1. Experimental data from Figure 6.2 sample D are shown as circles. The up triangles denote the results for a bundle with the vdW gap increased to 6.4 Å and the solid-fluid potential increased by 30%. The down triangles represent data for a bundle with a vdW gap of 6.4 Å and the potential increased by 50%. The stars are for a vdW gap of 12 Å and a potential increased by 50%. The lines are drawn to guide the eye.
triangles in Figure 6.8. These simulation data agree well with the experiments at low pressures but
under-predict the amount adsorbed at high pressures. If a potential of 1.5\(V_{sf}\) is used with a gap of
6.4 Å (down triangles) then the simulations and experiments agree at high pressure but not at low
pressure. If we increase the vdW gap further the curvature of the simulation data decreases. The
simulations for a vdW gap of 12 Å and 1.5 \(V_{sf}\) are shown as stars in Figure 6.8. This value of the
vdW gap is unrealistically large and yet still gives an isotherm that is slightly concave downward.
This indicates that no physically reasonable values of the vdW gap and interaction potential can be
found that can accurately reproduce the shape of the experimental isotherms observed on samples
that have been oxidized with CO\(_2\). The simulated isotherms are all curved and tend to approach
a plateau region at higher pressures, while the experimental isotherms are all approximately linear
or concave upward in coverage at all pressures studied. However, reasonable qualitative agreement
between experiments and simulations is achieved for 1.5 \(V_{sf}\) and a vdW of 12 Å. All of the isotherms
shown in Figure 6.8 were computed from nanotube bundles of type a from Table 6.1. Calculations
for nanotube bundles from sample b are similar to those shown for sample a and are not shown for
clarity.

### 6.6 Conclusions

The hydrogen adsorption properties of SWNTs have been investigated using a TEOM to deter-
mine mass changes on exposure of the samples of up to 48 bar pressure. The rates of adsorption
and desorption are apparently fast and indicative of physisorption. The isotherms are still ascend-
ing at the upper pressure limit of the instrument and it is clear that the saturation loading of
these materials is not defined by these experiments. The raw and purified SWNTs samples do
not adsorb as much hydrogen as a typical sample of activated carbon under similar conditions.
Most importantly, we have shown that a simple, controlled oxidation with CO\(_2\) activates SWNTs
for adsorption of hydrogen. A roughly three-fold increase in the amount of hydrogen adsorbed
is observed at the highest pressures. Up to 1.2 wt% hydrogen was observed in the best case. Molecular simulations have been performed to compute the adsorption isotherms of hydrogen on finite size nanotube bundles that are composed of nanotubes of various diameters. The size of the bundles studied ranged from 20 to 100 tubes drawn from three different diameter distributions. Adsorption isotherms from simulations on the various bundles are all in relatively good agreement with one another. The amount of hydrogen adsorbed at these conditions does not appear to be a strong function of the size of the bundle or the diameter distribution for the samples studied here. Remarkably good agreement is seen between the simulations and experimental isotherms on nanotube samples before activation. This implies that the solid-fluid potential for the nanotubes before activation is fairly accurate and that the endohedral sites are available for adsorption on these samples. It is also possible that the agreement between simulations and experiments is fortuitous and that the unactivated samples do not adsorb H\textsubscript{2} inside the nanotubes, although this scenario seems unlikely. Adsorption isotherms on nanotube bundles with larger free volumes and stronger solid-fluid attractive potentials were computed to evaluate if these factors could explain the observed increase in H\textsubscript{2} uptake capacity after activation. It was found that a bundle with a vDW gap of 12 Å and a potential increased by 50% agrees fairly well with the experimental data, although the shape of the simulated and experimental isotherms differs. Given that the size of the vDW gap and the increase in the potential are both too large to be physically reasonable we conclude that the increase in adsorption upon activation is not solely due to increased free volume and solid-fluid potential enhancement. Hence, standard physisorption potentials do not adequately describe the activated nanotube samples. However, chemisorption cannot make a significant contribution to the experimental isotherms because the process is completely reversible and adsorption and desorption kinetics are too fast to be described by chemisorption.

This work shows that activation of SWNT samples can profoundly impact the adsorption of H\textsubscript{2}. Understanding the process will ultimately help optimize the activation, further enhancing the adsorption capacity.
7.0 GAS ADSORPTION ON HETEROGENEOUS SINGLE-WALLED CARBON NANOTUBE BUNDLES

7.1 Introduction

The adsorption of gases on single-walled carbon nanotubes (SWNTs) has been of great interest for the past several years due to the unique structural properties of SWNTs. There are four types of adsorption sites on SWNT bundles: inside the nanotubes (endohedral), interstitial channels (where three or more tubes meet), external groove sites (where two tubes meet on the surface of the bundle), and the external surface of individual tubes.\textsuperscript{163,192} One-dimensional (1-d) and quasi-1-d phases are possible for gases adsorbed on SWNT bundles.\textsuperscript{32,33,193–195} As-prepared SWNTs are capped, making endohedral adsorption unlikely to occur to any significant extent. Many careful experimental studies of gas adsorption on closed SWNT bundles have been performed, yielding adsorption isotherms, binding energies, and isosteric heats of adsorption ($q_{st}$).\textsuperscript{29–42,196–199} Several of these studies have focused on determining where gases are adsorbed on SWNT bundles. The theoretical analysis of the data assumed SWNT bundles composed of homogeneous (all the same diameter) nanotubes, perfectly aligned on a 2-d hexagonal lattice. This is also the case for almost all simulations of adsorption on SWNTs.\textsuperscript{156,160,162–164,192,200–202} Interpretation of the experimental data in terms of this idealized model of SWNT bundles has lead to the conclusion that gases do not adsorb in the interstitial channels (ICs) of bundles.\textsuperscript{35} Theory, based on homogeneous bundles, predicts that small molecules such as H$_2$, He, and Ne will adsorb in the ICs, but that larger molecules, such as CH$_4$, Ar, and Xe, are too large to enter the ICs.\textsuperscript{192} In reality, nanotube bundles are not homogeneous; they contain a distribution of different nanotube diameters (heterogeneous).\textsuperscript{178–182} Here we present molecular simulations of adsorption on both heterogeneous and homogeneous SWNT bundles. We compare our simulations to previous experimental $q_{st}$ data for adsorption of CH$_4$,\textsuperscript{30,31,34,37}, Xe\textsuperscript{31,36,39,42} and Ar\textsuperscript{36,40} onto SWNT bundles. These data are found to be in excellent agreement when the coverage dependence of $q_{st}$ is considered. We show, for the first time, that low coverage
\( q_{st} \) values from experiments strongly indicate that gases as large as Xe can easily adsorb in the interstitial channels formed by packing defects in heterogeneous bundles.

### 7.2 Simulation Details

We have generated both homogeneous and heterogeneous SWNT bundles containing from 45 to 100 tubes. The tube diameters in the heterogeneous bundles were chosen to resemble the diameter distributions measured in experiments. Homogeneous bundles were constructed of (10,10) SWNTs. The initial positions of the nanotubes were chosen randomly with the constraint that none of the tubes overlap. The tubes were held rigid and geometries were optimized using the basin-hopping method. Sample optimized homogeneous and heterogeneous bundles, each containing 45 nanotubes, are shown in Figure 7.1. Optimization of homogeneous bundles results in packing of the tubes into perfect 2-d hexagonal lattices, while optimized heterogeneous bundles always contain multiple packing defects that give comparatively large ICs. This is a key result. It shows that the basin-hopping method is capable of finding near-global minima for tube packing, as is evident from the hexagonal packing of homogeneous bundles. It also indicates that heterogeneous bundles, such as those produced in current experiments, must contain a number of packing defects that give rise to relatively large ICs. The heterogeneous bundle in Figure 7.1 contains 10 (8,8), 25 (9,9), 5 (10,10), and 5 (11,11) nanotubes. This gives an average diameter of 12.4 Å and a standard deviation of 1.2 Å, which is much smaller than the 2 Å standard deviation calculated from detailed analysis of the types of SWNT bundles used in the experiments. We therefore expect our models to exhibit fewer defects than real SWNT bundles.

We have performed grand canonical Monte Carlo (GCMC) simulations to study the adsorption of CH\(_4\), Xe, and Ar onto bundles of closed-ended SWNTs. The Lennard-Jones (LJ) potential was used to model fluid-fluid and solid-fluid interactions. The parameters are \( \sigma_x = 3.4, 3.81, 3.4, 4.1 \) Å and \( \epsilon_x = 28, 148.1, 120, 221 \) K, for \( x = C, CH_4, Ar, \) and Xe, respectively. Lorentz-
Figure 7.1: Sample of heterogeneous (left) and homogeneous (right) bundles optimized by the basin-hopping technique. The blue spheres represent CH$_4$ adsorbed in equilibrium with a bulk phase at 159.88 K and 0.05 bar.
Berthelot combining rules were applied and the parameter values were taken from the literature. Binding energies for the gases on graphite from the potentials (experiments) are 11.4 (12.2), 9.1 (9.2), and 15.2 (15.6) kJ mol$^{-1}$ for CH$_4$, Ar, and Xe, respectively. The experimental data were reported by Vidali et al. The excellent agreement between the potential models and the experimental data indicate that these parameters are a good first approximation to the fluid-nanotube interaction potential. Our molecular simulations confirm the assumption that CH$_4$, Ar, and Xe do not adsorb into the ICs of homogeneous bundles (see Figure 7.1). Simulations also show that all heterogeneous bundles we have constructed contain large ICs at packing defect sites that do allow adsorption of all three probe molecules. For example, CH$_4$ is shown to adsorb in four interstitial defect sites in the left hand panel of Figure 7.1, while no interstitial adsorption is found for the homogeneous bundle on the right hand side.

7.3 Results

Experimental and simulation $q_{st}$ data for CH$_4$ are plotted in Figure 7.2. The coverage (mol CH$_4$/mol C) was computed from the known weight of the sorbent and an estimated purity of 60%. The inset shows the low coverage region. This low coverage region has been assigned to adsorption into the groove sites of SWNT bundles. The simulation data show that groove site adsorption on homogeneous tubes (squares in Figure 7.2) gives $q_{st}$ about 40% lower than values from experiments. In contrast, $q_{st}$ for simulations on heterogeneous bundles are in good qualitative and quantitative agreement with experiments. The diamonds in Figure 7.2 are for a heterogeneous bundle containing 45 nanotubes that has a larger number of packing defects than the bundle shown in Figure 7.1. The more defective bundle was generated by making only a few optimization steps in the basin-hopping method. Simulations for a number of different heterogeneous nanotube bundles all have $q_{st}$ values at low coverage that agree quite well with the experimental data. The low coverage isosteric heats result from adsorption in the interstitial defect channels of the bundles, where the
Figure 7.2: Isosteric heats of adsorption for CH$_4$ from experiments$^{34,37}$ (circles) and simulations. The diamonds (squares) are for adsorption onto heterogeneous (homogeneous) bundles. The triangles are for a homogeneous bundle with the solid-fluid potential increased by 45%. All bundles contain 45 nanotubes. The simulations were performed at 159.88 K. The inset shows $q_{st}$ at low coverage. The lines are drawn as a guide to the eye. The estimated error bars are about the size of the symbols.
adsorption potential is the highest. More highly optimized bundles contain fewer such defects per
bundle, resulting in a narrower low coverage plateau region than observed in experiments. We
also observe a large low-coverage plateau region for larger bundles. Simulations on heterogeneous
bundles containing 100 nanotubes give similarly good quantitative agreement with the experimental
$q_{st}$ values. This indicates that either the bundles in the SWNTs used in the experiments contain
more tubes than previously estimated\textsuperscript{31,178} or more defects than our highly optimized bundles. The
larger number of defects in real bundles may be due to the larger standard deviation of nanotube
diameters observed in real bundles.\textsuperscript{178}

One might argue that the nanotube-gas (solid-fluid) interaction potential is not accurately
known and that $q_{st}$ for homogeneous bundles could be brought into agreement with experimental
data by adjusting the solid-fluid potential. We have manually increased the solid-fluid potential
to bring the low coverage $q_{st}$ from simulations on homogeneous bundles into agreement with ex-
periment. We found that the magnitude of the potential must be increased by 45\% to match
experiments in the low coverage region. Isosteric heat data for this system are shown as triangles
in Figure 7.2. As can be seen from the inset, the agreement at low coverage is excellent. How-
ever, at high coverage, corresponding to complete monolayer formation on the external surface of
the nanotubes, the simulated $q_{st}$ values are at least 25\% too high compared with experiments.
Only when the coverage reaches the multilayer do $q_{st}$ values from these simulations agree with the
monolayer values from experiments. In contrast, the monolayer heats from both homogeneous and
heterogeneous bundles are in fairly good agreement with experiments, although the simulations are
consistently lower than experiments. This analysis suggests that the assumed solid-fluid potential
is relatively accurate and that only adsorption onto heterogeneous bundles, including interstitial
adsorption, is consistent with experimental data.

The plot of $q_{st}$ versus coverage for heterogeneous bundles shows a plateau region at low coverage
responding to adsorption in ICs and some groove sites. At high coverage another plateau is
observed that corresponds to adsorption on external surface sites, near monolayer completion.
This is in qualitative agreement with the experimental data from Migone \textit{et al.},\textsuperscript{34,37} although more
experimental data are needed to identify these regions with certainty. Muris et al.\textsuperscript{30} identify two steps in experimental isotherms of CH\textsubscript{4} adsorption on closed nanotubes, one corresponding to low coverage and another to high coverage. They estimate $q_{st} = 18.3 \pm 1$ and $11.2 \pm 0.5$ kJ mol\textsuperscript{-1} for low and high coverage, respectively. Talapatra and Migone\textsuperscript{37} point out that the low coverage data from Muris et al. corresponds to the intermediate coverage range of their data, or around 0.01 CH\textsubscript{4}/C (mol/mol) in Figure 7.2. Thus, these data are in reasonable agreement with both the experimental data of Talapatra and Migone\textsuperscript{37} and also our simulation data. The high coverage datum from Muris and coworkers is likewise in good agreement with the highest coverage region in Figure 7.2 for simulations on heterogeneous bundles and experimental data. Thus, $q_{st}$ values computed from adsorption on heterogeneous bundles are in good agreement with all available experimental data, while simulations on homogeneous nanotubes are not consistent with the data.

The simulation data in Figure 7.2 were calculated at a temperature of 159.88 K, corresponding to one of the isotherms used in the experiments. While $q_{st}$ is usually assumed to be independent of temperature,\textsuperscript{209} our simulations show that $q_{st}$ values computed at 110 K are typically about 5-10\% larger than at 159.88 K. Data from both temperatures are in reasonably good agreement with experimental values, which were derived from isotherms over a range of temperatures.

$q_{st}$ for Ar on closed SWNT bundles has been reported by Wilson et al. over a range of coverages.\textsuperscript{40} No purity is given for the nanotubes used in this experiment. We have assumed a purity of 60\%, the same as in the studies of Migone et al.,\textsuperscript{39,208} because the nanotubes in each of these studies were obtained from the same source. The isosteric heats for Ar from simulations and experiments\textsuperscript{40} are plotted in Figure 7.3. The experimental data (circles) were derived from isotherms at average temperatures around 90 K. The simulation data were collected at 90 K. We see from Figure 7.3 that the data for heterogeneous bundles (diamonds) are in qualitative agreement with experiments. The experimental data are shifted to larger abscissa values compared with the simulation results; if the experimental $x$ values are multiplied by a factor of 0.6 then nearly perfect agreement results between experiment and simulation. The values of $q_{st}$ from simulations on homogeneous bundles (squares) are not in good agreement with the experimental data. However, experimental data for much lower
Figure 7.3: Experimental\textsuperscript{40} and simulated $q_{st}$ for Ar on SWNT bundles. Symbols have the same meaning as in Figure 7.2.
coverages (near zero loading) are needed to unambiguously resolve the major difference between homogeneous and heterogeneous bundles. The simulations on heterogeneous bundles predict that the isosteric heat increases dramatically at the lowest coverage due to adsorption into defect ICs. This should be observable in experiments at higher temperatures where it is possible to achieve lower coverages.

Ar adsorption isotherms between 60 and 87 K have been measured by Talapatra and Migone. They report \( q_{st} = 13.2 \text{ kJ mol}^{-1} \) for the groove phase, which is about 2 kJ mol\(^{-1}\) lower than the lowest coverage data of Wilson et al. in Figure 7.3, but in excellent agreement with a coverage of about 0.025 mol Ar/mol C and also in good agreement with the simulation data corresponding to filling of the groove phase, which occurs at about 0.005 and 0.015 for homogeneous and heterogeneous tubes, respectively.

The heat of adsorption or binding energy of Xe on closed SWNT bundles has been determined experimentally by at least three different groups. Only one of these groups reported \( q_{st} \) as a function of coverage. These data are plotted in Figure 7.4 along with simulation results. The main graph contains data from simulations on homogeneous (squares) and heterogeneous (diamonds) bundles. These data were collected at 110.6 K at coverages up to complete monolayer formation on the external surface of the tubes. The experimental data (circles) are from isotherms over a range of temperatures from 210 to 295 K at very low coverage. The inset is for the low coverage range and includes simulations for heterogeneous nanotubes at 210 K. Note that the high temperature simulation data are qualitatively different from the low temperature data, although the two sets only differ by about 10%. At low temperatures the Xe molecules are much more likely to become trapped in the lowest energy sites, which at this loading are the defect ICs, giving a larger variance in \( q_{st} \) as high energy sites fill first, followed by lower energy sites. At the higher temperature, adsorbates tend to sample many different sites, averaging out the energy differences between the sites. Note that this gives better agreement with the experimental data, which were collected at higher temperatures. Other studies report binding energies at low coverage\(^{35,42}\) and \( q_{st} \) at high coverage. Talapatra et al.\(^{35}\) report a binding energy of -27 kJ mol\(^{-1}\) based on isotherms

123
Figure 7.4: Xenon $q_{st}$ from experiments$^{39}$ (circles) and simulations on homogeneous (squares) and heterogeneous (diamonds) bundles at 110.6 K. The inset shows the low coverage region along with simulations on a heterogeneous bundle at 210 K (triangles).
from 220 to 295 K. This is in excellent agreement with the binding energy measured from thermal desorption spectroscopy of 27 kJ mol\(^{-1}\) at around 100 K.\(^{42}\) Using the formula \(q_{st} = -\epsilon + \alpha kT\) where \(\epsilon\) is the binding energy, \(\alpha = 0.5\) for 2-d systems and 2 for 1-d systems,\(^{40}\) we find \(q_{st} = 29\) and 30.5 kJ mol\(^{-1}\) at 110.6 and 210 K, respectively. These values are in very good agreement with our low coverage simulation data for heterogeneous bundles. Note that the simulations for homogeneous bundles give values of \(q_{st}\) that are too low compared with experiments by about 25-30%. Muris and coworkers measured \(q_{st} = 15.7\) kJ mol\(^{-1}\) and Talapatra and Migone\(^{36}\) reported \(q_{st} = 16.6\) kJ mol\(^{-1}\) for coverages corresponding to full monolayer completion. These values are in reasonably good agreement with simulations on both the homogeneous and heterogeneous bundles near monolayer completion. This is to be expected, since the external surface of the nanotubes are not sensitive to the diameter distribution or packing defects in the bundles.

### 7.4 Conclusions

In summary, \(q_{st}\) for CH\(_4\) and Xe on closed SWNT bundles from different experimental groups\(^{30,31,34,37,39,42}\) are shown to be in remarkable agreement with each other when the coverage dependence of \(q_{st}\) is considered. These data, along with data for Ar,\(^{40}\) agree very well with simulation data of adsorption on heterogeneous nanotube bundles over the entire range of coverage. The low coverage region is dominated by adsorption in the interstitial channels of heterogeneous bundles, whereas homogeneous bundles do not allow adsorption of these gases into the ICs. The overall agreement between simulations and experiments clearly indicates that gases do adsorb in the ICs that result from packing defects in real nanotube bundles.
8.0 ADSORPTION ONTO CLOSED NANOTUBE BUNDLES:
THEORETICAL CALCULATIONS AND COMPARISON WITH THE EXPERIMENT

8.1 Introduction

There has been a great deal of recent interest in adsorption of gases on single walled carbon nanotubes (SWNTs) both experimentally\textsuperscript{22–28,30–43,46,169,197–199,210} and theoretically.\textsuperscript{46,156,160,162–164,192,200–202} Many of these studies have focused on identifying potential adsorption sites. Experimentally produced SWNTs are known to form bundles containing 10s to 100s of individual tubes.\textsuperscript{178–182} The bundles contain tubes with a distribution of diameters, depending on the methods used to produce the SWNTs. The tubes are observed to pack into hexagonal lattices when they form bundles, with gaps between the tubes of about 3.2 Å,\textsuperscript{211} slightly smaller than the gap between layers of graphite. There is little direct experimental evidence that the nanotube diameter heterogeneity causes packing defects in the bundles. Most of the theoretical calculations to date have assumed that nanotubes in the bundles have identical diameters (homogeneous) and are packed in perfect 2-d hexagonal arrays.\textsuperscript{156,160,162–164,192,200–202} This simple model is also invoked by many experimentalists to interpret experimental data.\textsuperscript{36,38,40,42} We have shown in our previous paper\textsuperscript{47} that SWNT bundles composed of heterogeneous nanotubes with diameter distributions similar to those observed in experiments always exhibit packing defects. Moreover, these defects result in large interstitial channels that allow adsorption of gases as large as Xe, and perhaps larger gases. This finding contradicts the interpretation of previous experimental data, reportedly showing that gases do not adsorb in interstices of SWNT bundles.\textsuperscript{36,37} We have shown that experimental isosteric heat of adsorption at low coverage is a very sensitive indicator of interstitial adsorption and that these data are very consistent with adsorption into interstices of heterogeneous bundles.\textsuperscript{47}

In our modeling we assume that nanotubes are straight, rigid, and parallel to each other. Dilation of the bundle induced by adsorption into the ICs\textsuperscript{212} and thermal vibrations of tubes
themselves\textsuperscript{213} are ignored. We also ignore the atomic corrugation of the nanotubes by integrating over the individual atoms in the nanotube to produce a smooth potential.\textsuperscript{46,160} This is a reasonable assumption given that the corrugation in the solid-fluid potential is only a few Kelvin.\textsuperscript{214}

8.2 Theoretical Calculations

The interaction potentials between tubes are required to construct realistic models of nanotube bundles. By considering the periodicity of the tube, the averaged smoothed potential between two parallel tubes with indices \((n_1 p, n_1 p)\) and \((n_2 p, n_2 p)\) is given by

\[
\langle u(r) \rangle = \frac{\int_{0}^{\theta_{1\text{max}}} d\theta_1 \int_{0}^{\theta_{2\text{max}}} d\theta_2 \int_{0}^{Z_{uc}} dz_1 \int_{0}^{Z_{uc}} dz_2 u(r, \theta_1, \theta_2, z_1, z_2)}{\theta_{1\text{max}} \theta_{2\text{max}} Z_{uc}}
\]

\[
= \frac{\int_{0}^{\theta_{1\text{max}}} d\theta_1 \int_{0}^{\theta_{2\text{max}}} d\theta_2 \int_{0}^{Z_{uc}} dz_2 u(r, \theta_1, \theta_2, z_2)}{\theta_{1\text{max}} \theta_{2\text{max}} Z_{uc}},
\] (8-1)

where \(r\) is the distance between the centers of the two tubes, \(\theta_{1\text{max}} = 2\pi/n_1 p\), \(\theta_{2\text{max}} = 2\pi/n_2 p\), \(\theta_1\) and \(\theta_2\) are the rotational angles of tube 1 and tube 2 around their respective \(z\) axes, \(z_2\) is the displacement in \(z\) direction of tube 2, \(Z_{uc}\) is the length for the unit cell of the tubes, \(u(r, \theta_1, \theta_2, z_2)\) is the interaction between the two tubes. The interaction energy depends on the length of the two tubes. In our calculations, tube 1 is one unit cell in length, and tube 2 contains an effective infinite number of unit cells. Equation (8-1) is derived from the following related equations,

\[
\int_{0}^{Z_{uc}} dz_2 \int_{0}^{\theta_{1\text{max}}} d\theta_1 \int_{0}^{\theta_{2\text{max}}} d\theta_2 u(r, \theta_1, \theta_2, z_1 = 0, z_2) =
\]

\[
\int_{z}^{z+Z_{uc}} dz_2 \int_{0}^{\theta_{1\text{max}}} d\theta_1 \int_{0}^{\theta_{2\text{max}}} d\theta_2 u(r, \theta_1, \theta_2, z_1 = z, z_2) =
\]

\[
\int_{0}^{Z_{uc}} dz_2 \int_{0}^{\theta_{1\text{max}}} d\theta_1 \int_{0}^{\theta_{2\text{max}}} d\theta_2 u(r, \theta_1, \theta_2, z_1 = z, z_2).
\] (8-2)

The pair-wise summation over all carbon-carbon atoms in the system is represented by \(u(r, \theta_1, \theta_2, z_2)\). The Lennard-Jones (LJ) potential for carbon is used. In the computation, tube 2 is set to 20 unit cells in height. This height is found to be large enough such that the contribution to the interaction energy due to carbon atoms beyond 20 unit cells is negligible. Tube 1 with one unit cell is fixed
to be in the center of a cubic box as a reference tube. The minimum image convention is used in $z$ direction when the interaction between carbon atoms in tube 1 and tube 2 is calculated. Gaussian numerical integration is used. The values of $\langle u(r) \rangle$ are fitted to a polynomial with 15 terms. The fitting procedure has been described elsewhere. The effective values of $\sigma$ and $\epsilon/k$ for carbon atom are set to be 3.47 Å and 28 K. The equilibrium distance between two closest carbon atoms in two neighboring tubes is calculated as $d_{eq} = r_{eq} - R(1) - R(2)$, where $r_{eq}$ corresponds to the well depth of $\langle u(r) \rangle$ between the two tubes, $R(1)$ and $R(2)$ are the tube radius of tube 1 and tube 2, respectively. The values of $d_{eq}$ for 15 sets of combinations between (8,8) tube and (12,12) tube have been computed. Those values are between 3.199 and 3.205 Å, very close to 3.2 Å, a value observed from the experiment. Note that the effective value of 3.47 Å was chosen to match the value of 3.2 Å for $d_{eq}$. When the interaction between nanotube and adsorbate is calculated, the values of $\sigma$ and $\epsilon/k$ for carbon are set to be 3.4 Å and 28 K. The adsorbate-nanotube interaction was taken as a pair-wise summation over adsorbate-carbon interactions. The parameters and the calculations have been described elsewhere.

The final smoothed nanotube potential should be independent of which tube is chosen as the reference. This is indeed the case for the interaction potential given by Eq. (8-1) when the potential is expressed on a per length basis. We have calculated the interaction potential between (8,8) and (12,12) tubes with the (8,8) and (12,12) tubes to be the reference tube, respectively. The differences in all the potential energies are negligibly small.

The basin-hopping method was used to construct both the heterogeneous and homogeneous bundles once the tube-tube interaction is obtained. This technique can be applied to locate the global minimum energy with a high probability as well as many local minimum energy structures for difficult clusters. The algorithm is outlined as below:

1. The initial configuration for all the tube centers is generated. This is done by randomly choosing the $(x,y)$ coordinates of each tube center in a square box such that there is no overlap between the tubes. The size of the box in the calculation is typically set to be
between 150 Å and 300 Å depending on the size of bundle. The box is used to prevent the evaporation of the tubes from the bundle. Note that two neighboring tubes should not be too close. The van der Waals gap between two neighboring tube is set to be between 4 to 6 Å in the initial configuration.

2. Find the local minimum starting with the configuration from Step 1. This is done by the BFGS method.68

3. Randomly move the centers of all tubes in both $x$ and $y$ directions. Periodic boundary conditions are used in both $x$ and $y$ directions.

4. Find the local minimum of this new configuration as in Step 2.

5. Accept the new structure with probability of $\min[1, \exp(-\beta \delta U)]$. The value for $\delta U$ is the difference in energy between Step 4 and Step 2. The value of $T$ is chosen to be about 0.8 of the value of the potential well depth in the calculation.

During the calculation, the maximum displacement of a single tube used in Step 3 is adjusted such that 50% of the trial configurations are accepted. Note that in conventional Monte Carlo, the step size is adjusted only during equilibration. During the production run, the maximum displacement is fixed to satisfy detailed balance. However, there is no such constraint in the basin-hopping method. We have checked the code by performing optimization of three dimensional Lennard-Jones clusters. We obtained exactly the same results as reported in reference.203 The number of step to implement the basin-hopping calculation for the nanotube bundle was set to $4 \times 10^5$. The lowest energy in every run was typically found in several thousands steps. Note that this lowest energy may be not the true lowest energy, but a local minimum energy.

Once the nanotube bundle structure with a local minimum energy for both the homogeneous and heterogeneous bundles were constructed, isotherms and isosteric heat of adsorption were computed from grand canonical Monte Carlo (GCMC) simulations on these bundles. The calculation details were described elsewhere.46,47 The height of the simulation box was typically set to 10 $\sigma$, where $\sigma$
is the Lennard-Jones parameter for the gases. When the coverage was small at low pressures, the height of the box was increased to between 100 and 5000 $\sigma$ such that the amount adsorbed had a magnitude of tens of gas atoms to make the calculations statistically reasonable. The length and the width of the simulation box were set to be equal to each other. The values were between 150 and 250 Å. To improve the efficiency of the simulation, the corrected volume in the calculation was defined as $V_{\text{box}} - V_{\text{tubes}}$, where $V_{\text{box}}$ and $V_{\text{tubes}}$ are the volumes of the simulation box and the summation of all tubes in the bundle, respectively. We have verified that this works. When an attempt is made to create a particle in a box, it is repeated until the position for the particle is found to be outside of all the tubes in the bundle. The number of attempted steps are set to $10^8$ and $10^7$ for the production and equilibration runs, respectively.

8.3 Results

We have constructed homogeneous bundles with 25, 45, 70, and 100 (10,10) tubes, and heterogeneous bundles with 45 and 100 tubes. The diameter distributions in the heterogeneous bundles were chosen to resemble those measured from the experiment.$^{181}$ The heterogeneous bundles with 45 tubes contain 10 (8,8), 25 (9,9), 5 (10,10), and 5 (11,11) tubes. The average of the diameter and the diameter standard deviation for this heterogeneous bundle is 12.36 Å and 1.18 Å, respectively. The heterogeneous bundle with 100 tubes contains 6 (8,8), 29 (9,9), 35 (10,10), 28 (11,11), and 2 (12,12) tubes. The average of the diameter and the diameter standard deviation for this bundle is 13.44 Å and 1.28 Å, respectively. Note that the values for the diameter standard deviation of the above two samples we chose are far less than the experimental value of 2 Å.$^{178}$ The nanotube materials with a standard deviation of 2 Å$^{178}$ have been used by many experimental groups.$^{30,40}$ This implies that the heterogeneous bundles in our calculations will have fewer ICs than the real bundles.
We have optimized every bundle starting from 10 different initial configurations. For the homogeneous bundles with 25 tubes, we got the same “lowest” minimum energy from two different initial configurations. These two “lowest” minimum energies converged to the eighth decimal place. The structures corresponding to these two “lowest” minimum energies look identical. This strongly indicates that the true “global” minimum has been found for this homogeneous bundle. For the homogeneous bundles containing 45, 70, and 100 tubes, we have not found the same “lowest” minimum energy from 10 sets of optimizations. For the 45 and 70 homogeneous bundles, Optimization always resulted in packing of the tubes into perfect 2-d hexagonal lattices. For the 100 tube bundles, Four sets of optimization gave perfect 2-d packing, the other six sets presented imperfect packing with packing defects inside the bundle. A single (10,10) tube can be fitted into the defects. This means that these six geometries are not close to the global minimum energy point. For the heterogeneous bundles with 45 and 100 tubes, we always obtained imperfect packing with defects inside the bundles. Some interstitial channels (ICs) (defects) are large enough to accommodate gas adsorption. Two examples of heterogeneous bundles are shown in Figure 8.1. The left bundle is obtained during 1000 steps of optimization. The right one is optimized only with one step. The left one seems to be more structured and has fewer ICs than the right one does. The interaction potential energy for the left is about 8% less than that for the right.

The nearest distance between two neighboring carbon atoms on the two neighboring tubes was computed for many of the optimized homogeneous and the heterogeneous bundles. For the homogeneous bundles, all the nearest neighbor distance were found to be between 3.2015 and 3.2027 Å, close to the equilibrium value of 3.2 Å. For the heterogeneous bundles, many of the nearest neighbor distance were less than 3.2 Å. For example, the right one in Figure 8.1 has 52 sets of neighboring tubes with the nearest distances between 3.05 and 3.2 Å. The right one has about 90 sets of neighboring tubes totally.
Figure 8.1: Figure for two heterogeneous bundles both with 45 tubes.
8.3.1 Results for CH$_4$

Isotherms from simulations and the experiment at 159.88 K are shown in Figure 8.2. This is the

Figure 8.2: Isotherms from simulations and experiment for CH$_4$ at 159.88 K. Both the circles and triangles correspond to heterogeneous bundles with 45 tubes. The bundle (circles) has been less optimized than that (triangles). The diamonds are for a heterogeneous bundle with 100 tubes. The filled squares are from the experiment.$^{34}$ Also shown are open squares for a homogeneous bundle with 45 (10,10) tubes.

low coverage region used in the experiment$^{34}$ to compute the binding energy. The snap shots from simulations on the heterogeneous bundles in this region indicate that most of the gas molecules are adsorbed into the ICs region with only very few molecules adsorbed on the groove sites. Not all of the groove sites of the homogeneous bundle have gas adsorbed molecules in this low coverage region. The difference in the amount adsorbed between the homogeneous and heterogeneous bundles can be
seen clearly at this low coverage region. The amount adsorbed reported in the experiment is about 100 times larger than that on the homogeneous bundle. In contrast, the amount is only about 2 to 6 times of that onto the heterogeneous bundles for most of the pressures. The less optimized bundle with 45 tubes (circles), corresponding to the the bundle on the right in Figure 8.1, gives the highest adsorption capacity. We expect that realistic bundles with larger diameter standard deviation will exhibit higher adsorption capacity than the heterogeneous bundles used here. Isotherms at 194.68 K (not shown) also show the same behavior. The amount adsorbed from the experiment is about 6 times higher than those on the heterogeneous bundles, 50 times higher than those on the homogeneous bundles. It can thus be concluded that the heterogeneous bundles give isotherms more close to the experiment than the homogeneous bundles do for CH$_4$.

Isotherms in the temperature range between 69 and 195 K have been measured in the experiment to calculate the isosteric heats at low, intermediate, and monolayer coverage regions.$^{34,37}$ Three temperatures of 110, 159.88, and 194.68 K have been chosen to study the temperature effect on the isosteric heat of adsorption. The results are shown in Figure 8.3. The isosteric heat at 110K clearly shows a wide plateau region with a adsorption between 0.00264 and 0.00907 mol(CH$_4$)/mol(C). This region roughly corresponds to filling of the groove sites. It is interesting to note that the isosteric heat ($q_{st}$) at point “a” at 110 K is about 18% higher than that at point “b” at 159.88 K. The amount adsorbed at these two points are very close to each other. The amount adsorbed for “a” is 0.00907, a little higher than the value of 0.00889 for point “b”. The difference in $q_{st}$ is partially due to the sites where the gases are adsorbed. A snap shot for “a” shows that the ICs and the groove sites have almost been filled. Almost no adsorption occurs on the outside surface of the bundle. In contrast, about 20 out of 218 gas molecules are adsorbed onto the outside surface of the bundle for point “b”. The outside surface is less attractive than the groove sites and the ICs. This gives a corresponding lower $q_{st}$ value. This results in the overall $q_{st}$ for point “b” being smaller than point “a”. In both the low and the high coverage regions, the variance in $q_{st}$ is typically less than 10% for different temperatures. The snap shots in the low coverage region for 110 K show that the adsorption occurs only in two strong ICs when the amount adsorbed is less than
Figure 8.3: The temperature effect on isosteric heat for CH$_4$. All the simulations are performed on the same highly optimized heterogeneous bundle with 45 tubes. The diamonds and the open circles are for 159.88 K and 110 K, respectively. Also shown in the inset is the experimental data (filled circles)\(^{37}\) and results from simulations at 194.68 K (triangles) at low coverages. The lines are drawn as a guide to the eye.
Actually, the adsorption mainly occurs in only one IC. The linear density is increased in this IC when chemical potential (pressure) is increased. The isosteric heat is hence increased due to the interaction between adsorbate molecules. When the pressure is increased further beyond the amount adsorbed of 0.000516, the snap shots show that gas molecules will be adsorbed into ICs with smaller binding energies. This leads to a decrease in $q_{st}$. The isosteric heat for 194.68 K at low coverage show qualitatively different behavior from that for 110 K. This is because the temperature of 194.68 K is high enough to allow molecules to sample many different binding energy sites, such as different ICs and groove sites, even at low coverages. The temperature effect on the isosteric heat for the homogeneous bundle (not shown here) at low coverage is also studied. The difference in $q_{st}$ is about 9% between 159.88 and 194.68 K. Note that the heterogeneous bundle in Figure 8.3 is highly optimized and hence it shows small plateau region at low coverage.

The effect of bundles of different sizes and different structures on the $q_{st}$ is shown in Fig 8.4. The difference in $q_{st}$ on the heterogeneous bundles at the low and the outside surface regions is typically less than 10%. The bundles with a larger number of tubes that are less optimized give results that are closer to the experimental results over the whole region. At low coverage, the less optimized and larger bundles show wider plateau region than the smaller, highly optimized bundles. This is due to the larger number of defects in those bundles.

One may wonder if there is a substantial difference between groove sites on homogeneous and heterogeneous bundles. The difference in adsorption capacity on the groove sites and the outside surface between the homogeneous and heterogeneous bundles has been studied. For a heterogeneous bundle (the left one in Figure 8.1), four ICs inside the bundle and one channel on the outside of the bundle enclosed by three neighboring tubes (the low left side) are excluded for adsorption. The isosteric heat and isotherms are shown in Figure 8.5 and Figure 8.6, respectively. The results on the homogeneous and heterogeneous bundles are very close to each other if the ICs for the heterogeneous bundles are excluded for adsorption. At the highest coverage, the difference between homogeneous and heterogeneous bundles is 6% for $q_{st}$, and at the highest pressure the difference in coverage is 2%. This strongly indicates that the adsorption capacity for groove sites and the outside surface
Figure 8.4: The bundle effect on isosteric heat of adsorption for \( \text{CH}_4 \). All the simulations are performed at 159.88 K. The diamonds are for a bundle highly optimized than that for stars. Both these two heterogeneous bundles have 45 tubes. The open circles and the pluses (shown in inset) both are heterogeneous bundles with 100 tubes. The circles are for a bundle a little highly optimized than that for the pluses. Also shown are the experimental data (filled circles).\(^{34,37}\) The lines are shown as a guide to the eye.
Figure 8.5: The isosteric heats at 159.88 K for CH$_4$ on the homogeneous and heterogeneous bundles excluding ICs adsorption. The diamonds are for a heterogeneous bundle with four ICs inside the bundle and one channel outside of the bundle excluded from adsorption. The squares are for a homogeneous bundle. The lines are drawn as a guide to the eye.
Figure 8.6: The isotherms at 159.88 K for CH$_4$ on the homogeneous and heterogeneous bundles excluding ICs adsorption. The diamonds and the squares have the same meaning as in Fig. 8.5. The lines are drawn as a guide to the eye.
is fairly insensitive to the size heterogeneity of the tubes in the bundles. Many simulations have been performed for CH$_4$ onto homogeneous 45 tube bundles with different optimized structures, homogeneous bundles with 25 and 70, and 100 tubes. At low coverage, the amount adsorbed per groove sites, and the isosteric heat are almost the same onto all those homogeneous bundles. This is expected since the adsorption capacity of the groove sites are insensitive to the detailed structure of the bundles.

8.3.2 Results for Ar

The effect of different bundles on the isosteric heat for Ar is shown in Figure 8.7. The difference in the isosteric heat on different heterogeneous bundles at low and the monolayer coverage regions is less than 10%. The experimental values are consistent with each other on the outside surfaces. However, there are some differences in the intermediate coverage region. This is in part due to Ar adsorbing on different sites even at the same coverage.

8.3.3 Results for Xe

Isotherms at 250 K for Xe are shown in Figure 8.8. Note that this temperature of 250 K and pressure range correspond to the low coverage region. Isotherms are measured in this low coverage range to calculate the isosteric heat of adsorption and the binding energy from the experiment. The simulation onto a heterogeneous bundle shows that the gas molecules are adsorbed mainly into the ICs with only a few molecules on the groove sites in this low coverage region. For the homogeneous bundle, only a few groove sites hold a small number of molecules. The rest of groove sites are empty. The amount adsorbed at this low coverage region clearly shows the difference in amount adsorbed between the homogeneous and heterogeneous bundles. The results on the heterogeneous bundle are very close to the experiment. In contrast, the homogeneous bundle gives amount about 30 times less than that from the experiment. Two other sets of isotherms at 210
Figure 8.7: The effect of different bundles on isosteric heat for Ar. All the simulations were performed at 90 K. The stars are for a bundle less optimized than that corresponds to the diamonds. Both the stars and the diamonds are for heterogeneous bundles with 45 tubes. The triangles are for a heterogeneous bundle with 100 tubes. Also shown are the experimental results from two different groups (circles—⁴⁰ squares—⁴³). The lines are drawn as a guide to the eye.
Figure 8.8: Isotherms at 250 K for Xe. The stars are for a heterogeneous bundle with 45 tubes, corresponding to the right bundle in Figure 8.1. The squares are for a homogeneous bundle with 45 tubes. Also shown are the experimental data from\textsuperscript{39} (filled circles).
K and 295 K (not shown here) also show the same behavior. The heterogeneous bundle typically gives amounts adsorbed about 50% less than experiments. However, the amount adsorbed on the homogeneous bundle is typically 10 to 30 times less than that from the experiments. The isotherms at these three temperatures verify again that the heterogeneous bundles give better agreement with the experiments than the homogeneous bundles do in the amount adsorbed.

Isotherms at 150 K are shown in Figure 8.9. Note that in the pressure region of the experiment,

![Figure 8.9: Isotherms at 150 K for Xe. The stars are for a heterogeneous bundle with 45 tubes corresponding to the right one in Figure 8.1. The triangles are for an heterogeneous bundle with 45 tubes more highly optimized than that for the stars. The squares are for a homogeneous bundle with 45 tubes. Also shown are the experimental data (filled circles) from\textsuperscript{39}.](image)

Xe molecules have already filled all the accessible ICs region of the heterogeneous bundles. The two steps observed from the experiment corresponding to the groove site and outside surface filling
can not be resolved very clearly from the isotherms on both the heterogeneous and homogeneous
bundles. The step corresponding to filling of the ICs can not be resolved. This is partially due
to the small number of defects in the heterogeneous bundles. The experimental data lie between
two heterogeneous bundles. The amount adsorbed onto the homogeneous bundle is systematically
smaller than the experiment.

Migone and coworkers\textsuperscript{39} have concluded that Xe can not adsorb into ICs by calculating the
ratio of the heights for the two steps. One significant drawback in their argument is that they
count all the ICs region in a bundle when they assume that ICs can adsorb Xe. This assumption
is not correct. Only a few ICs in the bundle are accessible for adsorption of Xe.

The temperature effect on $q_{st}$ for both the homogeneous and heterogeneous bundles up to
monolayer coverage region is shown in Figure 8.10 for Xe. The temperature range between 112
and 150 K has been used in the experiment\textsuperscript{36} to measure the isosteric heat for the outside surface
of the bundle and the second layer. The difference in $q_{st}$ is typically less than 10\% for both the
homogeneous and heterogeneous bundles at the low and monolayer coverage regions. The isosteric
heat for the monolayer region from the experiment\textsuperscript{36} is 16.5 kJ/mol, consistent with the values
from the simulations on both the heterogeneous and homogeneous bundles. This is expected since
the adsorption capacities of the outside surface of the homogeneous and heterogeneous bundles
are very close to each other as has been shown for CH\textsubscript{4} (see Figure 8.5). Simulations have also
been performed onto a heterogeneous bundle with a different detailed structure at 110.6 K (not
shown here). The isosteric heats in the low and outside surface regions are close to the values in
Figure 8.10 for the heterogeneous bundles. The difference is typically less than 6\%. The isosteric
heat of adsorption at low coverage is calculated from isotherms at temperatures between 210 K and
295 K.\textsuperscript{39}
Figure 8.10: The temperature effect on isosteric heat for Xe. All the bundles have 45 tubes. The squares and the diamonds are for the same homogeneous bundle. The diamonds correspond to a temperature of 110.6 K. While, the squares are for 150 K. The open circles and the stars are for the same heterogeneous bundle. The open circles are for 150 K. While, the stars are for 110.6 K. Also shown are the isosteric heats from the experiments at low coverage (filled circles). The inset shows the data at low coverage.
8.4 Conclusion

Isotherms at low coverage region onto heterogeneous bundles are typically about 2–6 times less than those from the experiment for CH$_4$ and close to the experimental value for Xe at all the temperatures. In contrast, the amount adsorbed from the experiment are typically 30-50 times larger than those on homogeneous bundles. The isotherms at low coverage indicate that adsorption into ICs of heterogeneous bundle does occur. In the high coverage region, the isotherms from both the heterogeneous and homogeneous bundles are very similar although the isotherms onto homogeneous bundles are systematically less than those onto heterogeneous bundles. This is due to the small number of accessible ICs in the heterogeneous bundle.

The adsorption capacity for the groove sites and outside surfaces of heterogeneous bundles are very close to those of the homogeneous ones. This implies that the adsorption capacity for these two kinds of adsorption sites are comparatively insensitive to the detailed bundle structures.

Temperature effects for isosteric heat of adsorption have been studied for Ar, Xe, and CH$_4$. The difference in the low and high coverage is typically less than 10%. The large difference in isosteric heat at the intermediate coverage region is due to adsorbates occupying different binding energy sites at different temperatures.

The binding energy sites for heterogeneous bundles can roughly be divided into three parts, i.e., the IC’s, the groove sites, and the outside surface. The isosteric heats for CH$_4$ are $\sim 25$ kJ/mol, 16 kJ/mol, and 11 kJ/mol, respectively for the ICs, groove sites, and outside surface. The values of $q_{st}$ for Ar are $\sim 19$ kJ/mol, 13 kJ/mol, and 10 kJ/mol respectively; for Xe are 32 kJ/mol, 21 kJ/mol, and 17 kJ/mol, respectively.
9.0 FUTURE WORK

9.1 Future Work

We have shown some results in chapters 7 and 8. Some future work for these two chapters is proposed.

1. Migone and coworkers have identified the steps on the isotherms by computing the isothermal compressibility of $dN/dP$, where $N$ and $P$ are the amount adsorbed and the pressure, respectively\textsuperscript{29,36,39}. These steps correspond to the binding sites with almost the same binding energies. The peaks on the curve of $dN/dP$ versus $P$ or $N$ correspond to the jumps on the isotherm. It is difficult to directly observe a jump from the isotherms since the transition regions are somewhat rounded (See Figure 8.9). Note that the isothermal compressibility is closely related with $dN/d\mu = \frac{(\langle N^2 \rangle - \langle N \rangle^2)}{kT}$, where $\mu$ is the chemical potential and $T$ is the temperature. The transitions will be able to be located from simulations by computing these statistical fluctuations. However, many simulations have to be implemented in order to locate the transition accurately since one has to find a peak on a curve of $dN/d\mu$ versus $\mu$ or $N$. This problem can be alleviated by using multiple histogram reweighting. Only several simulations are needed to generate the full curve. The multiple histogram reweighting can also be used to calculate the heat capacity.

2. Some tubes may be open even in the claimed closed nanotube bundles\textsuperscript{42}. Several initial calculations have been performed onto open homogeneous (10,10) tube bundles. It is shown that methane is first adsorbed inside the tubes at low pressures (low coverages). The isosteric heat at low coverage is 17.87 kJ mol\textsuperscript{-1}. This value is about 15\% higher than the value of 15.6 kJ mol\textsuperscript{-1} for the groove site, 26\% lower than the experimental value of 24 kJ mol\textsuperscript{-1}\textsuperscript{215}. This implies that only the interstitial adsorption can interpret the high isosteric heat at low coverages from the experiment. However, it is still important to know the effect of open
tubes in the claimed closed bundles on the isosteric heats of adsorption and the isotherms. For example, how is the isosteric heat curve being changed by the open tubes in the bundles, especially at low coverage. The amount adsorbed will be increased after some tubes are open. An interesting question is how the transition steps on the isotherm is changed. This will affect the transition pressure, which has been measured from the experiments, for example by Muris et al.\textsuperscript{30,31}.

3. Several kind of gases, such as He, Ne, H\textsubscript{2}, and D\textsubscript{2} have been studied in nanotube bundles\textsuperscript{32,35,40,216}. These light molecules will exhibit quantum effects at low temperatures typically used in the experiment. Path integral calculations are needed to compare with experiments. The specific surface area of nanotube bundle is fundamental for it to be used as gas adsorbents. Migone and coworkers have reported that the surface areas measured from Ne and Xe for a sample of closed nanotube bundle are very close to each other. Both values are about 40 m\textsuperscript{2}/g. The specific surface area may be computed from the simulations and compared with the experiments. Several simulations have been reported to calculate the BET surface area\textsuperscript{217–219}. 
BIBLIOGRAPHY


[144] We note that Faccin et al. studied this transition with a finite T density functional method.

[145] This method has previously been used in an attempt to locate a prewetting transition for H2 on Rb but the results were inconclusive.


XXVIII. “Adsorption of CF$_4$ on Single Walled Carbon Nanotubes and Adsorption of CO on the Ag (110) Surface”

Liang Chen (S) and Karl Johnson (F), University of Pittsburgh
with
Brad Bockrath (M), NETL
First Principles Computational Chemistry
Studies of Microwave Processing and
Trapped CO$_2$ in Carbon Nanotubes

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Department of Chemical Engineering
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Advisor:  J. Karl Johnson

NETL mentor: Kurt Rothenberger
Contents

Part I: First Principles Computational Chemistry Studies of Microwave Processing ................................................................. 3

Adhesion, bonding and catalytic property of Co/WC surface .......... 3

Part II: Trapped CO2 on Carbon Nanotubes .............................. 7

Simulation Methods .................................................................................................................. 7

Simulation results and discussion: .......................................................... 9
Part I: First Principles Computational Chemistry Studies of Microwave Processing

Adhesion, bonding and catalytic property of Co/WC surface

Tungsten Carbide is an important material for catalysis and fuel cell electrodes. However, very little is known about the fundamental processes on WC. Experimental work has shown that microwave processing of materials such as tungsten carbide with cobalt produce functional materials with much higher strength and corrosion resistance than thermal and pressure treated materials. Experiments show that the electric and magnetic fields play different roles in the processing of materials. However, there is little fundamental understanding of the underlying physics of microwave processing. It is not known exactly how or why microwave processed materials possess better properties.

The goal of this project is to provide insight into the basic atomic processes of diffusion in materials such as W/Co/C and how these processes are affected by electric and magnetic fields. This project employs ab initio density functional theory and electrodynamic modeling as initial computational techniques to model these effects. Specifically, NETL University Partnership Program (UPP) student Dennis Chen is computing the adhesion energy for tungsten-cobalt interfaces. He is also computing the catalytic properties of the W(111) and WC(001) surfaces. He is using density functional theory to perform the calculations. The catalytic studies are focusing on the adsorption, diffusion and dissociation of carbon monoxide on W and WC surfaces.

During this year, first principles density functionally theory has been used to compute the structural and energetic properties of the WC/Co interfacial systems. Using pure W systems as reference materials, we have examined the system size effects of limiting the size of the super cell used to model the bulk material. We have employed accurate gradient corrected density functional theory, specifically the PW91 functional with ultrasoft pseudopotentials and revised PBE functional with projector augmented wave (PAW) potentials in our calculations. Details of the calculations are given below.

We have studied the Co(001)/WC(001) interface. Considering the high temperature during sintering process, the Co phase was taken as FCC. The WC phase was first taken to be cubic (β phase). The Co(001)/WC(0001) interface is modeled in a symmetric super cell containing 1 WC slab and 2 Co slabs. A 3 layer slab of WC (001) is placed between two five-layer slabs of Co(111) (Figure 1.1). The free Co surfaces of Cobalt slabs are separated by 10Å of vacuum. Some previous study and our test work indicated that asymmetric super cell induces a spurious dipole moment, which may bring error to the calculated forces and energies. The lattice constant of WC was kept fixed, and that of Cobalt was stretched to match the structure. During the calculation, the middle layer or WC slab was fixed, while all of the remaining atoms were allowed to relax. Four possible configurations were considered (Figure 1.2).
In the calculation, the plane wave energy cutoff was set to 287eV. The Brillouin zones were sampled with 6x6x1 k-point grids. Using this super cell, the work of separation and interfacial energy were calculated. The work of separation is defined as the work required to separate the interface into two free surfaces, which can be expressed as:

\[ W_{sp} = (E_1 + E_2 - E_{12})/2A \]

\( E_{12} \) is the total energy of the interface system, \( E_1 \) and \( E_2 \) are energies of the separate slabs. \( A \) is the area of the computational super cell in the plane of the surface.

Interfacial energy is the work required to create the interface from the bulk materials. It is expressed as:

\[ IE = (E_{12} - E_{1,\text{bulk}} - E_{2,\text{bulk}})/2A \]

Here, \( E_{1,\text{bulk}} \) and \( E_{2,\text{bulk}} \) are energies of the bulk materials.

The results are presented in table 1.1: the previous non-vacuum super cell calculation results are represented in the parenthesis.

### Table 1.1: Work of Separation and Interfacial Energy:

<table>
<thead>
<tr>
<th>Interface</th>
<th>( W_{sp} ) (J/m²)</th>
<th>( IE ) (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.26 (5.24)</td>
<td>-0.58 (-0.61)</td>
</tr>
<tr>
<td>2</td>
<td>2.39 (2.46)</td>
<td>2.43 (2.50)</td>
</tr>
<tr>
<td>3</td>
<td>3.44 (3.52)</td>
<td>0.30 (0.32)</td>
</tr>
<tr>
<td>4</td>
<td>3.36 (3.46)</td>
<td>0.19 (0.22)</td>
</tr>
</tbody>
</table>

It is found that the symmetric vacuum included super cell is another reasonable assumption of the interface as well as the non-vacuum super cell which we have used before.

We have also done the calculation of CO adsorption on W(111) surface to study the catalytic properties of W related materials. We compared these results (using larger super cell and more sample k-points) with our previous calculation (Table 1.2).

### Table 2.2: Calculated Binding Energy and Vibrational Frequency of CO Adsorbed on W(111) Surface

<table>
<thead>
<tr>
<th>One fold</th>
<th>Shallow 3 fold</th>
<th>Deep 3 fold</th>
<th>2 fold</th>
<th>Laying down</th>
</tr>
</thead>
<tbody>
<tr>
<td>2x1 cell</td>
<td>1.47</td>
<td>1.62</td>
<td>0.89</td>
<td>2.01</td>
</tr>
</tbody>
</table>
It was found:

1.) The coverage (0.25ML to 0.5ML) affects binding energy very much (the CO…CO lateral repulsion may not be neglected.)

2.) The 2x1 super cell is not enough to converge the binding energy. And in the ongoing diffusion and dissociation calculation, 2x2 super cell is required.

3.) Revised PBE functional gives better binding energy and frequency comparing to PW91 functional.

In summary, we have verified the accuracy of the calculation method. We have then computed the relaxation of several interfacial systems. We have computed the relaxed geometry, work of separation, and interfacial energies for different WC/Co systems. This work is a crucial first step toward understanding why microwave processed WC/Co materials are much stronger and have sharper interfaces than corresponding thermally treated materials.

<table>
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<td>1774</td>
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Figure 1.1: Diagram of layering assumptions at WC/Co Interface. (a) is the non-vacuum super cell (b) is the symmetric vacuum included super cell.
Part II: Trapped CO₂ on Carbon Nanotubes

Simulation Methods

We have modeled two different scenarios in our simulations. In the first case we model CO₂ molecules that are trapped inside the interior of individual SWNTs and in the interstitial regions of SWNT bundles. In this scenario the number of molecules in the simulation is fixed (canonical, or $NVT$ ensemble). In the second case we consider an open system where CO₂ is allowed to adsorb onto the external and internal surfaces of SWNT bundles from the bulk gas phase. The number of molecules in the adsorption simulations fluctuates (grand canonical or $\mu VT$ ensemble). The scenario is meant to
model the experiments involving trapped CO$_2$, whereas the $\muVT$ simulations mimic CO$_2$ dosing experiments. Canonical ensemble simulations were carried out by first performing grand canonical Monte Carlo (GCMC) simulations$^1$ to achieve a desired fixed coverage, after which the system was allowed to equilibrate and data were taken in the $NVT$ ensemble. The GCMC algorithm consists of three types of moves, namely, translation and rotation of a single molecule, creation of a new molecule, and deletion of an existing molecule. Moves were attempted randomly with probability 20% for translation/rotation and 40% each for creation and deletion. The $NVT$ simulations consist of translation/rotation moves only. Simulations were typically equilibrated for $10^7$ moves, followed by data taking for $5 \times 10^6$ moves. The maximum displacement step size was adjusted during equilibration to achieve approximately a 40% acceptance ratio for combined translation and rotation moves. The CO$_2$-CO$_2$ interaction was described by the Harris-Yung potential model$^2$, which employs three Lennard-Jones (LJ) sites and charges centered at each atom. The sites were held rigid (no bond vibration or bending allowed). Lorentz-Berthelot combining rules were used for the cross interactions. The LJ potential parameters are given in Table 2.1 where $\sigma$ is the atomic diameter in Å and $\epsilon$ is the potential well depth such that $\epsilon/k$ is in units of K, where $k$ is the Boltzmann constant. The charge on the carbon atom is $q_c = +0.6645e$ with the charge on the oxygen given by $q_O = -q_c/2$. The C-O bond length is 1.161 Å. The interaction potential between CO$_2$ and the nanotubes was taken as cross interactions between the LJ atoms of CO$_2$ and the C atoms of a graphene sheet, wrapped into a carbon nanotube. The graphite LJ parameters from Steele$^3$ were used for these calculations, with parameters shown in Table 2.1. The use of classical potentials to model the nanotube-fluid interactions precludes the modeling of electronic effects, such as the differences between metallic and non-metallic nanotubes. However, this type of potential has been shown to be accurate for modeling the adsorption of simple fluids, such as methane, adsorbed in bundles of carbon nanotubes$^4$. The solid-fluid potential used in the simulation was smoothed by integrating over the positions of all the carbon atoms in the nanotube. The resulting integrated potential is solely a function of the distance $r$ from the center of the
nanotube. The smoothed potential was fitted to separate polynomials for endohedral (internal) and exohedral (external) adsorption for each LJ atom type (i.e., different polynomial coefficients for carbon-carbon and for oxygen-carbon interactions).

Three different nanotube bundles were considered in this work. Two bundles were constructed by randomly placing nanotubes of various diameters in a box and then optimizing the spacing between the nanotubes as described by Simonyan and Johnson\textsuperscript{5} to mimic the vacuum heated sample. Each of these two bundles contained 18 nanotubes. The numbers of each type of nanotube in each bundle are given in Table 2.2. Bundles 1 and 2 are representative of heterogeneous bundles, i.e., bundles with a heterogeneous distribution of nanotube diameters. Bundle 3 is a homogeneous bundle containing 9 (10,10) nanotubes packed into a perfect 3×3 array. This bundle is used to mimic the untreated nanotube samples because we only allow adsorption on the external surface (including grooves) of the bundle. We use a homogeneous bundle as a model for an unopened nanotubes bundle because previous work has shown that adsorption on the external surface of homogeneous and heterogeneous bundles is virtually identical\textsuperscript{6}. Periodic boundary conditions were applied in all three directions. The $x$ and $y$ dimensions were large enough to eliminate the nearest neighbor interactions between periodic images in order to mimic isolated SWNT bundles.

**Simulation results and discussion:**

We model CO\textsubscript{2} trapped in the interior of SWNTs and in the interstitial channels of nanotube bundles in order to examine possible causes for the temperature dependence of the IR peaks. For the vacuum heated samples, the CO\textsubscript{2} molecules are trapped in the interior and interstitial sites; thus we use a heterogeneous bundle in the calculations since GCMC simulations indicate that CO\textsubscript{2} does not adsorb in the interstitial channels of close-packed homogeneous nanotubes. We have computed the potential energy distribution for CO\textsubscript{2} trapped inside heterogeneous nanotube bundles (bundles 1 and 2) at endohedral and interstitial sites at a constant coverage as a function of temperature. Figures 2.1(a) and 2.1(b) present the results for endohedral and interstitial sites,
respectively. At low temperatures, CO$_2$ molecules are practically trapped in the sites with the highest binding energies, as seen by the sharply peaked potential energy distribution. As the temperature increases, the CO$_2$ molecules move more freely in phase space and have a much larger probability of occupying sites with lower binding energy, which results in broader peaks with increasing temperature as shown in figure 2.1. If we assume that the IR shift is roughly proportional to the binding energy, then the broadening and decrease of the 2330cm$^{-1}$ and 2340cm$^{-1}$ peaks can be understood as the result of CO$_2$ molecules escaping from a tightly bound solid-like adsorbed phase to a freer, gas-like phase that is much less strongly bound to the surface. This change of state can be seen more clearly in figure 2.2, which shows the densities profiles inside a (10,10) nanotube at the same coverage as in figure 2.1. The lowest temperature the CO$_2$ molecules are mostly packed against the walls of the nanotube, shown as the first peak on the right in figure 2.2. The smaller second peak on the right arises from configurations where the CO$_2$ molecules are closely packed together in such a way that some molecules are not parallel with the nanotube’s axis, thus shifting their center of mass out slightly from the tube wall. This orientational ordering is due to quadrupole-quadrupole interactions and will be discussed in more detail later. There is also a small peak for CO$_2$ molecules in the center of the tube shown by the peak at $r=0$ for 100 K. This annular CO$_2$ occurs because the molecules form solid-like clusters rather than showing uniform density down the length of the tube. As the temperature increases the structure disappears; the density next to the wall decreases and the second and third peaks disappear. At very high temperatures the fluid is almost uniformly distributed across the radius of the nanotube, indicating a gas phase confined within the tube.

Note the presence of a large gap in energy distributions between 100 and 200 K in figure 2.1(a). This feature is indicative of a phase transition from a condensed phase of CO$_2$ to a gas-like phase inside the nanotube. There is no such energy gap for CO$_2$ in the interstitial sites because the interstitial channels are more strongly confined and more closely correspond to a true 1-dimensional system (i.e., no first order phase transitions). The interior of a (10,10) nanotube is large enough to exhibit quasi-2-dimensional
Figure 2.3 presents the results for CO$_2$ adsorption isotherms on the closed perfect bundle (bundle 3 in Table 2.2) at temperatures ranging from 77 to 100 K. No molecules were allowed to adsorb inside the nanotubes during the simulation. These simulation results should be compared with experimental data for CO$_2$ adsorption on untreated SWNT bundles. We assume that untreated nanotubes are either unopened or have internal and interstitial adsorption sites blocked by residual functional groups. Hence, we expect only groove site and external surface adsorption for these untreated nanotubes. Other simulations have shown that adsorption of simple gases on groove sites and external surfaces of homogeneous and heterogeneous bundles are virtually identical. Therefore, we have used homogeneous bundles to examine adsorption of CO$_2$ in the groove sites in order to simplify the simulations. The coverage in this and subsequent figures is expressed in units of CO$_2$ molecules/carbon atom in the nanotubes.

The isotherms in figure 2.3 each contain two plateaus. Each plateau corresponds to the filling of a certain type of site on the exterior of the nanotube bundle. Groove site filling corresponds to the first plateau in the isotherms shown in figure 2.3. Analysis of simulation snapshots shows that quadrupole-quadrupole interactions force CO$_2$ molecules to form a T-shaped 1-dimension chain in the groove, as shown in Figure 2.4. Analysis of simulation snapshots at lower pressures show that a low density adsorbed phase forms first, where the CO$_2$ molecules are well separated and have their axes aligned with the groove axis in order to maximize their van der Waals interactions with the tubes making up the groove. As the pressure increases the distance between the CO$_2$ molecules in a single groove gets smaller and the molecules experience competing effects of repulsive quadrupole-quadrupole interactions and attractive dispersion interactions between a pair of CO$_2$ molecules. Roughly speaking, at close packing every other CO$_2$ molecule rotates up with its molecular axis perpendicular to the direction of the groove in order to make the quadrupole-quadrupole interactions attractive. This behavior is shown for a snapshot from a simulation at 90 K in Figure 2.4. Snapshots from isotherms at 77 and 100 K also show this behavior for loadings.
corresponding to groove site filling.

The second plateau appearing on each of the isotherms in figure 2.4 corresponds to the formation of a monolayer film. These films begin to form at about $10^{-7}$, $3 \times 10^{-5}$, and $6 \times 10^{-4}$ torr at 77, 90, and 100 K, respectively. A contour density plot showing a close up of the bundle surface is shown in Figure 2.5. The top panel corresponds to the monolayer plateau region. However, the entire surface of the bundle is not actually covered. Heterogeneity in the coverage is due to nanotubes at the corners of the bundle having a slightly different potential energy surface than nanotubes midway along the edge. This heterogeneity is in contrast with the work of Cole et al. who used a model of a periodic slab of nanotubes, so that any nanotube was exactly equivalent to any other one on the surface. The type of model used by Cole and coworkers gives sharp transitions similar to layering transitions on graphite. Our results show that even a perfect homogeneous bundle introduces enough heterogeneity into the problem to make the transitions appear continuous rather than first order. A bilayer film begins to form past the second plateau regions on each of the isotherms shown in figure 2.3. The density contours are shown in figure 2.4 in the lower panel. Note that the bilayer begins to form over the groove site first. Examination of various simulation snapshots and density contour plots (not shown) indicates that the bilayer begins to form well before the entire surface of the bundle is covered with a monolayer. In general, tubes on the corners of the bundle have sub-monomolecular coverage, whereas tubes away from corners have complete monolayer coverage. This means that experimentally observed vibrational spectra are not expected to show distinct changes with increased exposure. The spectra should gradually broaden and shift as the coverage increases. This is precisely what is observed in the experiments. We note that we do not observe a clear second-layer groove phase or three-stripe phase as observed by Cole et al. We believe that this is due to our using a small finite bundle rather than an infinite row of nanotubes.

We next consider adsorption of CO$_2$ on interstitial and internal sites of a heterogeneous nanotube bundle. Results of GCMC simulations on bundle 1 (see Table 2.2) are plotted in Figure 2.6. Note that at low pressures (see the inset to Figure 2.6) the
interstitial sites fill first, followed by adsorption inside the nanotubes. This qualitatively matches the experimental observations from dosing CO$_2$ on the heated nanotubes. The 2340 cm$^{-1}$ mode, which we assign to interstitial adsorption, is seen to fill first, followed by growth of the 2330 cm$^{-1}$ mode (assigned to internal adsorption). The quantitative differences may stem from the fact that in the experimental situation only a small fraction of the interstitial sites and nanotubes are opened enough to allow gas adsorption.

Table 2.1: Lennard-Jones potential parameters for CO$_2$ and for the carbons in nanotubes.

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<th>Atom</th>
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Table 2.2: Classes of Nanotube bundles studied in the molecular simulations in this work

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<th>Number of (9,9) tubes</th>
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<td>9</td>
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Figure 2.1: Potential energy distributions as a function of temperature for (a) CO$_2$ trapped in the interior of a (10,10) nanotube and (b) CO$_2$ trapped in the interstitial regions of a heterogeneous nanotube bundle.
Figure 2.2: Density profiles for CO$_2$ trapped inside a (10,10) nanotube at constant coverage of 0.16 molecules per Angstrom as a function of temperature.
Figure 2.3: Adsorption isotherm for CO₂ on a closed perfect bundle of 9 (10,10) nanotubes.
Figure 2.4: (top) Snapshot of CO$_2$ adsorption in a single groove site on a closed perfect bundle of 9 (10,10) nanotubes at 90 K and 3×10$^{-6}$ Torr. Snapshots at other temperatures display similar structures at groove filling. Red spheres are oxygen atoms, blue spheres represent carbon in CO$_2$, and gray spheres represent carbon in the nanotubes. (bottom) Snapshot of CO$_2$ adsorption in an interstitial site of bundle 1. The carbons in the nanotubes are shown in wire frame to make the adsorbed CO$_2$ molecules visible. Most of the tubes in the bundle have been excluded from the figure for clarity.
Figure 2.5: Density contours for CO$_2$ adsorbed on the external surface of a perfect bundle of (10, 10) nanotubes. The bundle contains 9 nanotubes placed on a hexagonal array. Two groove sites are shown, along with the surface of the central tube and half of the surfaces of the neighboring tubes. The central tube is located in the center of the edge of the nanotubes bundle. The upper panel corresponds to a coverage of 0.055 molecule/carbon atom and the lower panel to a coverage of 0.1 molecule/carbon atom. Individual nanotubes are represented as dashed lines.
Figure 2.6: Adsorption isotherm at 77 K on a heterogeneous bundle. The inset shows the low pressure region. Note that gas initially adsorbs in the interstitial channels formed by nanotube packing defects, then into the open nanotubes.

5 Simonyan, V.; Johnson J.K.; in preparation
6 W. Shi and J. K. Johnson, in preparation
7 Shi & Johnson, to be published
XXIX. “Environmentally Relevant Adsorption on Carbonaceous Surface Studied by Optical Differential Reflectance and Temperature Programmed Desorption”

SeokJoon Kwon (S) and Radisav Vidić (F), University of Pittsburgh

with

Brad Bockrath (M), NETL
ENVIRONMENTALLY RELEVANT ADSORPTION ON CARBONACEOUS SURFACES
STUDIED BY OPTICAL DIFFERENTIAL REFLECTANCE AND TEMPERATURE
PROGRAMMED DESORPTION

by

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Submitted to the Graduate Faculty of
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Doctor of Philosophy

University of Pittsburgh
2002
This dissertation was presented

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It was defended on

May 9, 2002

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Ronald D. Neufeld, Professor, Department of Civil and Environmental Engineering

Dissertation Director: Radisav D. Vidić, Associate Professor, Department of Civil and Environmental Engineering
ABSTRACT

ENVIRONMENTALLY RELEVANT ADSORPTION ON CARBONACEOUS SURFACES STUDIED BY OPTICAL DIFFERENTIAL REFLECTANCE AND TEMPERATURE PROGRAMMED DESORPTION

Seokjoon Kwon, Ph.D.

University of Pittsburgh, 2002

This study evaluated the application of a versatile optical technique to study the adsorption and desorption of model adsorbates representative of volatile polar (acetone) and non-polar (propane) organic compounds on a model carbonaceous surface under ultra high vacuum (UHV) conditions. The results showed the strong correlation between optical differential reflectance (ODR) and adsorbate coverage determined by temperature programmed desorption (TPD). The ODR technique was found to be a powerful tool to investigate surface adsorption and desorption from UHV to high pressure conditions.

The effects of chemical functionality and surface morphology on the adsorption/desorption behavior of acetone, propane and mercury were investigated for two model carbonaceous surfaces, namely air-cleaved highly oriented pyrolytic graphite (HOPG) and plasma-oxidized HOPG. Oxygen-containing functional groups exist on both air-cleaved and plasma-oxidized HOPG. They can be removed by thermal treatment (> 500 K). The presence of these groups almost completely suppresses propane adsorption at 90 K and removal of these groups leads to a dramatic increase in adsorption capacity. The amount of acetone adsorbed is independent of surface heat treatment and depends only on total exposure. The effect of
morphological heterogeneity is evident for plasma-oxidized HOPG as this substrate provides
greater surface area, as well as higher energy binding sites. Mercury adsorption at 100 K on
HOPG surfaces with and without chemical functionalities and topological heterogeneity created
by plasma oxidation occurs through physisorption. The removal of chemical functionalities from
HOPG surface enhances mercury physisorption. Plasma oxidation of HOPG provides additional
surface area for mercury adsorption. Mercury adsorption by activated carbon at atmospheric
pressure occurs through two distinct mechanisms, physisorption below 348 K and chemisorption
above 348 K. No significant impact of oxygen functionalities was observed in the chemisorption
region.

The key findings of this study open the possibility to apply scientific information
obtained from studies with simple surfaces like HOPG under ideal conditions (UHV) to
industrial sorbents under realistic process conditions. HOPG surfaces can be modified
chemically and topologically by plasma oxidation to simulate key features of activated carbon
adsorbents.

**DESCRIPTORS**

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TABLE OF CONTENTS

ABSTRACT ................................................................................................................................... iii

ACKNOWLEDGEMENTS ............................................................................................................ ii

TABLE OF CONTENTS ............................................................................................................... iv

LIST OF FIGURES ...................................................................................................................... vii

1.0 INTRODUCTION ....................................................................................................................1

2.0 LITERATURE REVIEW .........................................................................................................5
  2.1 Mercury Emission and Control Technologies ........................................................................5
  2.2 Chemical and Morphological Heterogeneity of the Carbon Surface ...................................9
  2.3 Optical Surface Probes ........................................................................................................13
  2.4 Temperature Programmed Desorption (TPD) .....................................................................16
  2.5 Kinetics of Adsorption and Desorption on Solid Surfaces ..................................................18
     2.5.1 Langmuir Adsorption Kinetics .....................................................................................18
     2.5.2 Desorption Kinetics ....................................................................................................19
  2.6 Research Objectives and Outline .......................................................................................21

3.0 MATERIALS AND METHODS ...........................................................................................24
  3.1 Ultra High Vacuum Apparatus ............................................................................................24
  3.2 Sample Preparation and Adsorbates ....................................................................................26
     3.2.1 Highly Oriented Pyrolytic Graphite (HOPG) ...............................................................26
     3.2.2 O2 Plasma Treated HOPG ..........................................................................................27
     3.2.3 Adsorbates ................................................................................................................28
  3.3 Temperature Programmed Desorption (TPD) Experiment ....................................................28
  3.4 Optical Differential Reflectance (ODR) Experiment ..............................................................29
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>Atomic Force Microscope (AFM) Imaging</td>
<td>31</td>
</tr>
<tr>
<td>3.6</td>
<td>Activated Carbon Based Fixed-Bed Adsorption</td>
<td>33</td>
</tr>
<tr>
<td>3.6.1</td>
<td>Activated Carbon</td>
<td>33</td>
</tr>
<tr>
<td>3.6.2</td>
<td>Fixed-bed Adsorption Experiments for Gas Phase Mercury Uptake</td>
<td>33</td>
</tr>
<tr>
<td>3.6.3</td>
<td>AAS Calibration</td>
<td>36</td>
</tr>
<tr>
<td>4.0</td>
<td>RESULTS AND DISCUSSION</td>
<td>39</td>
</tr>
<tr>
<td>4.1</td>
<td>A combined Study Using TPD and ODR Techniques: Acetone Adsorption and</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Desorption on HOPG Surface</td>
<td></td>
</tr>
<tr>
<td>4.1.1</td>
<td>Temperature Programmed Desorption (TPD)</td>
<td>39</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Optical Differential Reflectance (ODR)</td>
<td>42</td>
</tr>
<tr>
<td>4.2</td>
<td>ODR Investigation of Reversible and Irreversible Adsorption and Desorption: Propane Adsorption and Desorption on HOPG</td>
<td>46</td>
</tr>
<tr>
<td>4.3</td>
<td>The Effects of Surface Functional Groups on Adsorption and Desorption of Acetone on Carbonaceous Surfaces</td>
<td>52</td>
</tr>
<tr>
<td>4.4</td>
<td>The Effects of Surface Functional Groups and Topological Heterogeneity on Propane Adsorption and Desorption on Carbonaceous Surface</td>
<td>59</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Adsorption /Desorption on Air-Cleaved HOPG (a-HOPG)</td>
<td>60</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Adsorption/Desorption on Plasma-oxidized HOPG (p-HOPG)</td>
<td>62</td>
</tr>
<tr>
<td>4.5</td>
<td>Adsorption and Desorption of Mercury on Model (HOPG) and Real (activated carbon) Carbonaceous Surfaces</td>
<td>66</td>
</tr>
<tr>
<td>4.5.1</td>
<td>UHV studies with HOPG</td>
<td>66</td>
</tr>
<tr>
<td>4.5.2</td>
<td>Fixed-bed Adsorption Studies with Activated Carbon</td>
<td>70</td>
</tr>
<tr>
<td>5.0</td>
<td>SUMMARY AND CONCLUSIONS</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>Task 1</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Task 2</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>Task 3</td>
<td>76</td>
</tr>
<tr>
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<td>77</td>
</tr>
<tr>
<td></td>
<td>Task 5</td>
<td>78</td>
</tr>
<tr>
<td>5.1</td>
<td>Significance of the Study</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>APPENDIX</td>
<td>88</td>
</tr>
<tr>
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<td>------------------------------------------------------------------------</td>
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<td>A1. Propane Heat of Vaporization (at 100 K) Calculation</td>
<td>88</td>
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<tr>
<td>A2. Acetone Heat of Sublimation (at 130 K) Calculation</td>
<td>89</td>
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<td>A3. Mercury Heat of Sublimation (at 200 K) Calculation</td>
<td>90</td>
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<td>A4. Properties of Adsorbates</td>
<td>91</td>
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</tr>
<tr>
<td>FIGURES</td>
<td>104</td>
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LIST OF FIGURES

Figure 2-1. Normalized difference in p-polarized reflectivity for a 5 Å layer of acetone on HOPG ($\varepsilon_3 = 5.04 + 8.4$) and Cu ($\varepsilon_3 = -13.33 + 1.24$) as a function of the angle of incidence at $\lambda = 655$ nm. The lines are prediction from equation 4-2. ................................................................. 105

Figure 2-2. Coordinate system describing the polarization state of light. ............................................... 106

Figure 2-3. Schematic view of various carbon materials. ........................................................................ 107

Figure 3-1. Schematic of the UHV chamber and gas handling unit. ...................................................... 108

Figure 3-2. Schematic of the dual sample mount: (a) side view and (b) front view. ......................... 109

Figure 3-3. Structure of HOPG. HOPG is a relatively new form of high purity carbon consisting of planes of well-defined honeycomb structure. ................................................................. 110

Figure 3-4. Schematic of O$_2$ plasma system. ......................................................................................... 111

Figure 3-5. Experimental procedure for TPD experiments. .......................................................... 112

Figure 3-6. Optical differential reflectance (ODR) System. ............................................................. 113

Figure 3-7. Schematic view of AFM imaging. ....................................................................................... 114

Figure 3-8. AFM images for (a) virgin HOPG, (b) and (c) O$_2$ plasma oxidized HOPG for 20 min (d) for 90 min. Graphs under the images show cross sectional in height. ............................. 115

Figure 3-9. Setup of the fixed-bed adsorber. ......................................................................................... 116

Figure 3-10. Experimental system for fixed-bed breakthrough tests. .............................................. 117

Figure 4-1. TPD spectra for acetone on HOPG at 91 K (temperature ramp at 2.5 K/sec) ............. 118

Figure 4-2. Integrated area of monolayer and bilayer of TPD features. The dotted lines are model fits assuming that adsorption follows Langmuir kinetics. .................................................. 119

Figure 4-3. Schematic of the proposed growth model (Volmer-Weber) of acetone on graphite at 91 K. ........................................................................................................................................ 120

Figure 4-4. Intensity of s and p-polarized light reflected from HOPG as a function of exposure induced by acetone adsorption at $1.2 \times 10^{-7}$ torr and 91 K. ................................................................. 121
Figure 4-5. ODR signal as a function of acetone exposure at 91 K................................. 122

Figure 4-6. Correlation between ODR and TPD experiments for acetone adsorption on graphite. The solid line is a linear fit of experimental data ($R^2=0.995$)............................................. 123

Figure 4-7. (a) Background ODR signal for a clean surface (b) ODR signal during thermal desorption for a surface containing pre-adsorbed acetone.................................................. 124

Figure 4-8. $d(\text{ODR})/dT$ and TPD spectra as a function of temperature for graphite initially exposed acetone at 19L....................................................................................................... 125

Figure 4-9. Schematic view of the three layer model. Each layer is described by its dielectric constant ($\varepsilon_i$). $d$ is the adsorbate overlayer thickness, $\phi$ is the angle of incidence ...................... 126

Figure 4-10. ODR signal and TPD area resulting from adsorption of propane on graphite at 100 K as a function of exposure (a) and the correlation between ODR and TPD (b). .............. 127

Figure 4-11. Propane adsorption on graphite at 90 K : ODR as a function of propane pressure ................................................................................................................................. 128

Figure 4-12. Propane adsorption on graphite at (a) 90 and (b) 95, 100 and 105 K determined from ODR and molecular simulation as a function of propane pressure$^{(112)}$ ...................... 129

Figure 4-13. TPD of propane adsorption on HOPG at 90 K (temperature ramp at 2.5 K/sec) .. 130

Figure 4-14. Plots of the ln P versus $1/T$. This approach reveals that the bilayer heat of adsorption of propane on graphite is $23 \pm 2$ kJ/mol.......................................................... 131

Figure 4-15. Evolution of masses 16, 18, 28 and 44 amu during initial heat treatment of air-cleaved HOPG to different temperatures. Data for 16, 18 and 44 amu in the 1323 K scan are multiplied by 10 to aid in viewing................................................................. 132

Figure 4-16. TPD spectra of acetone on HOPG after heat treatment at various temperatures. Note that identical vertical scales are used for all figures except for 473 K. ....................... 133

Figure 4-17. Area of each individual TPD peak. Areas were obtained by the deconvolution of TPD spectra for 25 L exposure.......................................................... 134

Figure 4-18. Total area of TPD spectra for 25 L and 5 L exposure as a function of heat treatment temperature. .................................................................................................................. 135

Figure 4-19. Experimental (symbols) and simulated (lines) TPD of acetone monolayer. The insert (a) shows the fitting using conventional pre-exponential factor ($10^{13}$ sec$^{-1}$) for 7 L exposure and insert (b) shows a fitting trial with zero order for 3 L exposure................. 136
Figure 4-20. Acetone TPD for 7L exposure at different heating rates. The insert shows a graph of \( \ln(\beta/Tp^2) \) versus \( 1/Tp \) ................................................................. 137

Figure 4-21. TPD spectra at 29 m/e (propane) for air-cleaved HOPG after heat treatment at various temperatures. Note that identical vertical scales are used for all figures. Data for 473 K are multiplied by 10 to aid in viewing ................................................................. 138

Figure 4-22. TPD areas for propane at 25 L exposure as a function of heat treatment temperature for air-cleaved and plasma-oxidized HOPG ................................................................. 139

Figure 4-23. Evolution of masses 16, 18, 28 and 44 amu during initial heat treatment of plasma oxidized HOPG to different temperatures. Data for 16, 18 and 44 amu in the 1323 K scan are multiplied by 10 to aid in viewing ................................. 140

Figure 4-24. TPD spectra for propane after 1173 K heat treatment for (a) air-cleaved HOPG (b) \( O_2 \) plasma-oxidized HOPG. The same arbitrary units are used in both figures to facilitate comparison ................................................................. 141

Figure 4-25. TPD area of propane for air-cleaved and plasma-oxidized HOPG after 1173 K heat treatment ........................................................................................................................................ 142

Figure 4-26. Quantitative analysis of high temperature TPD peak of propane from plasma oxidized HOPG. (a) Coverage dependant first order simulation and (b) average heat of adsorption for both low and high temperature peak ................................................................................................. 143

Figure 4-27. TPD spectra of mercury on air cleaved HOPG that was previously heated at (a) 473 K and (b) 1273 K .................................................................................................................. 144

Figure 4-28. Modeling of TPD spectrum of mercury at 20 L exposure using coverage dependant first order desorption kinetics(\( \alpha=0.003 \)) ...................................................................................... 145

Figure 4-29. TPD area as a function of mercury exposure for air-cleaved HOPG ................. 146

Figure 4-30. TPD spectra of mercury on (a) plasma-oxidized HOPG for 20 min and (b) plasma-oxidized HOPG for 90 min. Note that both HOPG samples were pretreated at 1273 K and that identical scales are used for both figures ................................................................. 147

Figure 4-31. TPD area as a function of mercury exposure for air-cleaved and 20 min (p-20-HOPG) and 90 min (p-90-HOPG) sample after 1273 K heat treatment ................................. 148

Figure 4-32. Impact of temperature on mercury breakthrough from a fixed bed adsorber at influent mercury concentrations of (a) 70 \( \mu \)g/m\(^3\) and (b) 1120 \( \mu \)g/m\(^3\) ......................................................... 149

Figure 4-33. Mercury uptake capacity as a function of equilibrium pressure, \( P_e \) at different adsorption temperatures (lines represent linear regression fit to experimental data) .... 150
Figure 4-34. Equilibrium pressure at 200 µHg/gAC as a function of 1/T. Line (a) represents a linear fit to adsorption data collected below 348 K and line (b) is a linear fit to adsorption data collected above 348 K.

Figure 4-35. Impact of sample pretreatment on elemental mercury breakthrough from a fixed bed adsorber operated at (a) 293 K and (b) 423 K with influent mercury concentration of 70 µg/m³.
1.0 INTRODUCTION

Environmental control agencies, researchers and the general public are concerned about the increasing mobilization and release of trace elements to the environment from fossil fuel burning and other combustion processes such as municipal waste combustion (MWCs) and hazardous waste incineration due to their impact on human health and the environment in general. Of 189 hazardous air pollutants listed in Title III of the Clean Air Act Amendments (CAAA) of 1990, mercury is a trace element of special concern because of its high volatility that allows transfer into the flue gas stream during coal combustion. Existing pollution control technologies, such as wet scrubbers and fabric filters, are not capable of adequately controlling gas-phase mercury emissions. Once emitted to the environment, mercury can be deposited locally or globally to create a long-term contamination problem.\(^{1-4}\) There is a lot of evidence in the literature about the high toxicity of mercury to plants and animals through bioaccumulation and food chain transport. Thus, strict control of mercury emissions from municipal waste combustors (MWCs) and Coal-Fired Power Plants (CFPPs) is required.\(^{4,5}\)

Mercury adsorption on carbonaceous surfaces, such as activated carbon, is the most common approach for mercury removal from various sources. It can be implemented as fixed-bed granular activated carbon (GAC) adsorbers or powdered activated carbon (PAC) injection systems.

However, although the carbon-based adsorption technology has been used for air pollution control and has attracted much experimental and theoretical interest in the past decades as well as more recently (consideration of adsorption on carbon surfaces has been extended to new carbonaceous materials, such as carbon nanotubes), there is still a lack of fundamental
understanding of the physics and chemistry of carbonaceous surfaces related to adsorption/desorption kinetics, sorbent capacity, and interference of other components in the gas mixture.

While various factors can influence mercury adsorption and removal, the most important factor is probably the sorbent type and its associated properties. It should be noted that sorbent properties, that allow a given sorbent to effectively adsorb mercury, are not well understood. Specific functional groups present on the good mercury sorbents have not been identified. In addition, the mercury adsorption mechanisms on activated carbon are not well understood. Also, variations in the physical properties of a given sorbent such as size, shape, effective surface area, and porosity can affect adsorption effectiveness.

High surface area nanoporous carbon materials, such as activated carbon, are characterized by high chemical and morphological heterogeneity. These characteristics affect their adsorption capacity, kinetics, and catalytic activity.\(^6,\ 7\) Therefore, understanding the chemistry and physics of carbonaceous surfaces may enable optimization of their function and usefulness.\(^8\) For example, oxidation of activated carbon by nitric acid creates acidic groups on the surface, thereby hindering alkane adsorption.\(^9\) It is also well known that activated carbon surfaces chemisorb oxygen at low temperature, forming oxygen-containing functional groups.\(^10\) The oxygen-containing functional groups, removed by outgassing above 500 K, can either enhance or reduce the adsorption capacity of microporous carbon depending on the specific adsorbate\(^11,\ 12\) The presence of functional groups also modifies other carbon properties. For example, when activated carbon is used as a support for Pt catalysts, the dispersion of Pt increases as the concentration of oxygen functional groups on the carbon surface increases\(^13\) because of electrostatic interactions.\(^14,\ 15\) The high surface area provided by morphological
heterogeneity is one feature that makes carbonaceous materials useful for adsorption purposes. In general, higher surface area provides more adsorption sites leading to higher adsorption capacity.\(^{(16)}\) However, the role of the morphological heterogeneity of carbon surfaces is not clearly understood and is still a subject of intense study.\(^{(17-20)}\)

Environmental engineers are faced with the lack of fundamental understanding of molecular interactions in complex mixtures and at the mineral, organic, and biological interfaces that characterize environmental systems. This is particularly troubling because many of the techniques and associated methods for data interpretation have been developed to study well defined systems, e.g., single crystals under ideal conditions (ultra high vacuum). However, the application of these tools to environmental samples is very challenging due to their amorphous, complex, and multiple natures. Therefore, the objectives of this study are to investigate chemical functional groups and topological heterogeneity related issues on adsorption through fundamental studies of adsorption and desorption of a model adsorbent representative of volatile polar (acetone), non-polar (propane) organic compounds and vapor phase elemental mercury on a model carbonaceous surface (HOPG, highly oriented pyrolytic graphite), in an ultra high vacuum (UHV) apparatus.

Many environmental phenomena involving carbonaceous surfaces occur under conditions where standard UHV surface science techniques cannot be applied, e.g., atmospheric pressure. Therefore, the optical differential reflectance (ODR) technique was investigated as an in-situ, real time surface analysis approach. It was assessed by comparison of its sensitivity to adsorption and desorption from carbonaceous surfaces with temperature programmed desorption (TPD). The results showed that the strong correlation between ODR, determined in real time, and relative surface coverage determined a posteriori by TPD for metal systems could be extended to
carbonaceous surfaces. By combining these techniques, a new experimental methodology was developed with a potential to be used for many environmental phenomena involving carbonaceous and other adsorptive surfaces.

This study also describes the effects of surface functional groups and topological heterogeneity on adsorption and desorption using air cleaved HOPG and O$_2$ plasma treated HOPG as model surfaces. The study suggests an integrated approach that may provide a better understanding of adsorption processes and reveal approaches for sorbent optimization. A long-term goal of the study is to design more efficient and cost-effective sorbents for mercury control through the basic understanding of the mercury adsorption process.
2.0 LITERATURE REVIEW

2.1 Mercury Emission and Control Technologies

Mercury emission sources are commonly categorized into natural and anthropogenic sources. Total vapor phase mercury emitted from combined natural sources, such as oceans, can be as high as 2000 ton/year.\(^{(21)}\) Lindberg et al.\(^{(22)}\) estimated that the total global anthropogenic mercury emissions range from 2000 to 4000 tons/year which represents 30 to 55 % of global mercury emissions. While most other trace elements emitted from human sources (e.g., Co, Fe, and Se) can likely be removed by common air control devices such as electrostatic precipitator (ESP) or fabric filters (bag house)\(^{(23)}\), mercury remains mostly in the gaseous form and easily escapes into the air through these control devices.

Combustion of fossil fuels to produce electricity and heat is one of the major anthropogenic sources of mercury emissions. While the US electric utility industry uses three major fossil fuels, normally coal, fuel oil and natural gas, 35 % of the global atmospheric emission of mercury occurs from coal combustion.\(^{(24)}\) Chu and Porcella have estimated that 89 tons/year of mercury is emitted to the atmosphere from US coal-fired power plants (CFPPs) in 1990.\(^{(25)}\) US EPA estimated that about 300 ton/year of mercury was emitted from anthropogenic sources in the U.S. in 1990, with 30 % of total mercury emissions coming from coal fired power plants (CFPPs).\(^{(26)}\)

Hospital/medical/infectious waste incineration is a common unit operation used for medical waste disposal in the United States and worldwide. The US EPA reported that about 2,300 medical waste incinerators (annual operation rate: \(37.6 \times 10^5\) ton/year) were in operation
and more than 65 ton/year of mercury was emitted from those incinerators in 1995 in the United States.\(^{27,28}\)

Although coal fired power plants represent the main combustion source of mercury listed by the US EPA,\(^{29}\) mercury concentrations in flue gases from municipal waste combustors are much higher than those from CFPPs. Several studies reported that the flue gases from municipal waste combustors have 1 to 3 orders of magnitude higher mercury concentrations than those from CFPPs.\(^{30-32}\) One of the major mercury containing products burned in municipal waste combustors (MWCs) are household batteries. Based of 1989 estimates, approximately 600 tons of mercury in household batteries was added to municipal solid waste and their separation would result in 80% reduction of mercury emissions.\(^{33}\) Other significant mercury inputs into MWCs are paper industry, ferrous food cans, and electronic devices including mercury lamps.\(^{33}\)

Cement manufacturing and smelting and refining of metals belong among minor sources of mercury emission.\(^{33-36}\) Pai et al.\(^{28}\) estimated that cement production industries emitted about 5 ton/year of mercury during 1990.

While studies to control trace elements have focused largely on the destruction and removal efficiency of incinerators for hazardous organic compounds and on the particulate removal efficiencies of air pollution control systems, attention has recently focused on the potential risks related to stack emissions of carcinogenic compounds and toxic metals. As part of these efforts, many countries have set limits for the emission of hazardous air pollutants. The EEC (European Economic Community) is restricting mercury emissions from municipal waste combustors to 50 µg/m\(^3\).\(^{37}\) In the United States, most states have limits for mercury emissions in a range of 100 – 130 µg/m\(^3\).\(^{37}\) However, the regulations governing mercury emission will probably require lower limits than current regulation.
Activated carbon adsorption has been the most common approach for mercury removal from air. It can be implemented as fixed-bed granular activated carbon (GAC) adsorbers or powdered activated carbon (PAC) injection systems. There are numerous studies in the literature and field works on the capacity of activated carbon to adsorb mercury from flue gas streams under a variety of process conditions.\(^\text{(37-39)}\) In this study, the adsorption capacity of activated carbon was found to depend on its surface area, temperature, mercury concentration and speciation, etc. Generally, a high portion of oxidized mercury, high sorbent surface area and low temperature represent favorable conditions for high mercury removal.\(^\text{(37-39)}\) Other flue gas components, such as sulfur dioxide, water vapor\(^\text{(37)}\), oxygen and HCl\(^\text{(40)}\), can also affect the saturation capacity and the time needed to reach the saturation capacity for gas-phase elemental mercury. However, mercury removal by virgin activated carbon adsorption showed limited success especially in the case of very high temperatures and short contact times.\(^\text{(41-43)}\)

In recent years, chemically modified novel activated carbon sorbents have been developed for mercury removal. While the mechanisms of mercury uptake for these sorbents are not fully understood, orders of magnitude increases in mercury adsorption capacities compared to virgin activated carbons were exhibited.\(^\text{(44)}\)

Numerous studies tested the effect of sulfur impregnation on activated carbon on mercury removal capacity using fixed bed system.\(^\text{(16, 44-46)}\) It was found that the removal capacity drastically increased with sulfur impregnation because of mercury chemisorption as compared to physisorption mechanisms that predominate for virgin carbons and lower temperatures. However, a high concentration of sulfur on activated carbon does not always guarantee higher mercury removal efficiency. Otani \emph{et al.}\(^\text{(16)}\) reported that if impregnated sulfur blocked accessible pores, resulting in significant reduction of the surface area of activated carbon, mercury
adsorption efficiency could decrease even at higher sulfur content. Kwon and Vidic (46) and Liu et al. (40) also discovered that the uniform distribution of short linear chains of sulfur allotropes ($S_2$ and $S_4$) on activated carbon obtained from elemental sulfur at high temperature (600 °C) showed much higher mercury adsorption capacity compared to those produced by $H_2S$ oxidation at lower temperature (150 °C). These studies concluded that the sulfur impregnation temperature, which dictates the predominant sulfur allotropes on carbon, the sorbent surface area remaining after impregnation, and the pore size distribution strongly affected mercury removal efficiency by impregnated sorbents.

Karatza et al. (47) studied adsorption of mercuric chloride on activated carbon and on $Na_2S$ impregnated carbon. This study showed that impregnation with $Na_2S$ enhanced the adsorption capacity of activated carbon for $HgCl_2$, especially at 150 °C. It was also suggested that 18.7% $Na_2S$ on activated carbon doubled in mercury chloride adsorption capacity compared to activated carbon impregnated with 7.8% $Na_2S$. However, the adsorption isotherm data indicated that adsorption on $Na_2S$ impregnated activated carbon did not occur via a chemical reaction of $HgCl_2$ with $Na_2S$, but that impregnation with $Na_2S$ increased the number of active sites.

Powdered sorbent e.g., powdered activated carbon (PAC)) injection systems have been developed as a cost effective means of mercury removal from flue gas since they can be combined with existing particulate control facilities. The PAC injection technique involves the injection of PAC into the flue gas stream after which mercury loaded sorbent particles are collected in downstream particulate control devices, such as ESPs and baghouses. The efficiency of activated carbon injection in capturing vapor phase mercury is dependent on activated carbon properties, flue gas composition, temperature, type of fuel used, and sorbent injection rate (42, 45). However, these studies show numerous discrepancies in the results, which suggests that factors
influencing mercury removal are very complex. A fundamental understanding of the adsorption mechanisms under well defined conditions is essential in order to elucidate the role of each factor and advance the future of this control technology.

2.2 Chemical and Morphological Heterogeneity of the Carbon Surface

High surface area nanoporous carbon materials (e.g., activated carbon) are characterized by a great degree of chemical and morphological heterogeneity. These characteristics affect their adsorption capacity, kinetics, and catalytic activity.\(^6\,7\)

It has long been known that oxygen-containing functional groups, that normally exist on a variety of carbon surfaces, play important roles in the adsorption of organic and inorganic compounds or catalytic reactions occurring on the carbon surface. It is also well known that activated carbon chemisorbs oxygen at low temperatures (e.g., at room temperature and atmospheric pressure), thereby forming oxygen-containing functional groups.\(^10\) It has been suggested that the major oxygen-containing compounds on activated carbon surface are carbonyl-, phenolic-, lactonic- or carboxyl type functionalities.\(^48\) In spite of the importance of carbonaceous materials, the understanding of the role of the chemical and morphological characteristics for the carbon surface in terms of surface related properties (e.g., adsorption, catalysis) is less developed compared to the understanding of other materials.

There are numerous studies in the literature on the impact of surface chemical functional groups, both naturally occurring or artificially introduced, on the capacity of carbon surfaces to adsorb organic or inorganic adsorbates under a variety of process conditions. The oxygen-containing functional groups, that can be removed by outgassing above 500 K, can either
enhance or reduce the adsorption capacity of microporous carbon depending on the specific adsorbate.\(^{11, 12}\) Mangun et al.\(^{49}\) concluded that the activated carbon fiber (ACF) adsorption capacity for sulfur dioxide (SO\(_2\)), the principal cause of acid rain, is highly dependent on the amount of nitrogen containing functional groups. The introduction of nitrogen containing functionalities by ammonia treatment of ACF significantly enhanced the amount of SO\(_2\) adsorption by suppressing the catalytic reaction between oxygen chemisorbed on the surface and SO\(_2\). Swiatkowski and Goworek\(^{50}\) treated activated carbon with O\(_3\), H\(_2\)O\(_2\) and H\(_2\)SO\(_4\) and showed that the formation of oxygen functional groups on the activated carbon surface enhanced the adsorption capacity of activated carbon for volatile organic compounds (C\(_6\)H\(_6\)).

The existence of chemical functional groups can also have negative impact on the adsorption capacity of carbon-based sorbents. Bandosz et al. found that oxidation of activated carbon by nitric acid creates acidic groups on the surface and hinders alkane adsorption.\(^{9}\) The negative impact of functional groups was reported in the study of xenon adsorption in single walled carbon nanotubes (SWNTs).\(^{51, 52}\) Thermal treatment above 600 K leads to desorption of oxygen- and hydrogen- containing functional groups, which are believed to block the entry ports of the nanotubes without changing the basic tubular structure of the nanotubes. The removal of these functional groups enhances the capacity of carbon nanotubes for xenon adsorption as well as the uptake efficiency.\(^{53}\)

Chemical functional groups on carbon surfaces also affect the adsorptive efficiency of inorganic adsorbates. Jia and Thomas\(^{54}\) introduced various types of oxygen containing functional groups onto coconut shell-based activated carbon via nitric acid oxidation and tested its adsorptive capacity for cadmium ions. Although some phenol and quinone groups were formed by nitric acid treatment, carboxylic acid groups were the main compounds created by this
treatment. Cadmium adsorption was enhanced by the introduction of these functional groups. Removal of these acidic functional groups by thermal treatment resulted in significant deterioration in adsorptive capacity for Cd$^{2+}$.

Toles et al.$^{(48)}$ quantified surface functional groups on a nutshell-based granular activated carbon by titration with bases of different ionization potentials after air oxidation and showed that copper (Cu$^{2+}$) uptake appears to be directly correlated with the amount of oxygen containing functional groups in liquid phase. The correlation of the amount of oxygen containing functional groups with copper uptake was especially true for carbonyl groups as well as ionizable groups such as carboxylic acids and lactones.

The high surface area provided by morphological heterogeneity is one of the major features that makes carbonaceous materials useful for adsorption purposes. In general, higher surface area provides more adsorption sites leading to higher adsorption capacity for both organic and inorganic adsorbates.$^{(16)}$ Chiang et al.$^{(55)}$ investigated the effects of carbon treatment with inorganic salts, for example by Mg(NO$_3$)$_2$, on physical characteristics and adsorption efficiency for acetic acid. Significant variation in pore volume and diameter was observed when the initial pore diameter was less than 7 Å because activation with Mg(NO$_3$)$_2$ reduced both the surface area and pore diameter of activated carbon. As a result, the adsorption capacity for acetic acid was lowered. However, regeneration of activated carbon at 400 $^\circ$C restored high acetic acid adsorption capacity by opening the micropores and increasing the surface area.

Morphological heterogeneity of carbon surfaces also affects the adsorptive efficiency for inorganic adsorbates. In the fixed-bed study with six activated carbons, Krishnan et al.$^{(37)}$ observed an increase in gas phase elemental mercury adsorption with an increase in surface area and suggested that the total sorbent surface area is directly related to the adsorption capacity. Hsi
et al.\textsuperscript{(56)} suggested that the higher percentage of micropores leads to more effective elemental mercury uptake by activated carbon if other chemical and structural parameters are the same.

However, there are numerous conflicting reports in the literature on the effect of chemical and morphological characteristics of carbon surface on adsorption.\textsuperscript{(17-20, 57, 58)} Several studies argued that oxygen containing functional groups introduced by nitric acid oxidation weakened the capacity of activated carbon for SO\textsubscript{2} uptake,\textsuperscript{(59)} while others suggested that the treatment of activated carbon with nitric acid enhanced SO\textsubscript{2} adsorption and its oxidation to SO\textsubscript{3}.\textsuperscript{(12, 60)} It was reported that there is no strong correlation between SO\textsubscript{2} adsorption capacity and activated char surface area.\textsuperscript{(57)} However, Davini suggested that surface area is the key physical parameter determining adsorptive capacity of activated carbon for SO\textsubscript{2},\textsuperscript{(19)} while Daley et al. reported that the pore size and volume are more important than surface area.\textsuperscript{(20)} There are also conflicting arguments on the effect of pore size distribution (importance of micropores versus the transport pores) on SO\textsubscript{2} adsorption capacity of carbon.\textsuperscript{(17, 18)} Therefore, the role of the morphological heterogeneity of carbon surfaces is not clearly understood and is still an object of intense study. It should be an important subject to study.

Unequivocal characterization of the chemical properties of carbon surfaces lags behind that of other surfaces due to the complexity of carbon surfaces compared to many other materials. Understanding the chemistry and physics of carbonaceous surfaces may enable optimization of their function and usefulness.\textsuperscript{(8)}
2.3 Optical Surface Probes

It is known that when molecules adsorb on metal surfaces this changes the optical response of the surface.\(^{(61)}\) These changes can be utilized to investigate molecule-surface processes, e.g., adsorption. In the study of surfaces, there are a number of advantages of optical techniques compared with conventional surface probes, such as ion and electron spectroscopy and temperature programmed desorption spectroscopy (TDS). Optical techniques are surface sensitive, \textit{in-situ}, and non-destructive methods to investigate surface processes.\(^{(62)}\) Optical techniques are useful over a wide range of ambient conditions, can be extremely sensitive and offer real-time detection.\(^{(63-65)}\)

A number of different optical techniques have been developed to study surfaces. For example, infrared (IR) spectroscopy is widely applied to investigate adsorbates on both metal and semiconductor surfaces.\(^{(66)}\) However, it is not typically resistive to metal adsorbates such as mercury.

Adsorbate induced non-resonant reflectivity changes can probe adsorbate coverage on metal surfaces quantitatively. Optical differential reflectance (ODR) is an optical technique that has been applied to investigate adsorption and desorption on surfaces, resulting in estimation of coverage from optically determined film thickness.\(^{(65, 67)}\) This technique uses the small change induced in the reflectivity when a molecule adsorbs onto the surface.\(^{(68, 69)}\)

ODR has been used to investigate adsorption and desorption kinetics of a chemisorbed species, CO, on a metal surface, Cu(100), at visible wavelengths (632 nm) under ultra high vacuum (UHV) conditions.\(^{(61)}\) ODR is sensitive to chemisorption,\(^{(61)}\) and, in favorable cases, physisorption on metal surface.\(^{(61)}\) Chemisorption causes a much greater ODR signal change due
to adsorbate-induced perturbation of electronic structure of the metal surface. It is also reported that the utilization of ODR technique to study surface kinetics must rely on the correlation of the reflectivity changes with coverage. A good correlation between reflectivity change from adsorbate coverage and relative coverage estimated by temperature programmed desorption was demonstrated.\(^{(68)}\)

ODR enabled adsorbate coverage measurements during the adsorption/desorption of physisorbed species on a metal surface.\(^{(63)}\) Wong and Zhu\(^{(63)}\) investigated the adsorption and desorption of Xe on Ni surface and found that the ODR signal increased almost linearly with the surface coverage of Xe. The ODR signals can be described by a three-layer model with the known dielectric responses of the surface layer.

ODR can be used over a broad spectral range. It has been shown that chemisorption of H on W (100) results in an optical reflectance change attributed to an adsorbate induced electronic resonance in the infrared (IR) region.\(^{(70)}\) Subsequent studies have demonstrated the presence of nonresonant reflectivity change in the IR and visible region for other chemisorbed systems, such as CO on Pt(111)\(^{(67)}\), and NO on Cu(111).\(^{(71)}\)

ODR has been employed to investigate diffusion on metal surfaces.\(^{(72)}\) Xiao et al.\(^{(72)}\) revealed that diffraction of reflected light is sensitive for the diffusion of adsorbed CO molecules on Ni surface with much higher signal-to-noise ratio than second harmonic generation.\(^{(73)}\) In summary, ODR measures the change of light intensity reflected from a surface induced by adsorption and desorption and is a simple and versatile surface sensitive probe.

In this study, ODR was used in order to monitor adsorption and/or desorption of polar and non-polar organics and metals on carbonaceous surfaces. One significance of the ODR study is the ability to observe adsorption and desorption with real time resolution. The details of how
reflectivity changes when a new layer is deposited on a planar surface under UHV condition will be described in Section 4.1.2.

In order to establish the utility of the ODR technique for carbonaceous surfaces, the calculation of the angular dependent sensitivity change for monolayer of acetone adsorbed on two different surfaces is illustrated in Figure 2-1. The conventional three-layer model was applied for this calculation (see Section 4.1.2). The y-axis in Figure 2-1 is the normalized change of surface reflectivity as a function of the angle of incidence of light (x-axis). The light approaching and reflected from surface can be divided into two components, p- (electric field in the plane of incidence) and s-(electric field perpendicular to the plane of incidence) polarized light. (Figure 2-2) As the angle of incidence increases, the reflectivity of p-polarized light for HOPG changes for more than either s-polarized light for HOPG or p-polarized light for copper. The reflectivity change of p-polarized light induced by physisorbed acetone on HOPG (Figure 2-1) is over an order of magnitude higher than for Cu at an incident angle of 75 degrees. Based on the model calculation in Figure 2-1, and given that the noise of the laser source is about 0.0005 in $\Delta R/R$ units, ODR can be applied with sub-monolayer sensitivity (i.e. < 0.01 ML) for physisorption systems on carbonaceous surfaces. In addition, the intensity change from s-polarized light is almost negligible, which suggests that it can be used as a reference signal for the experiments. Therefore, from the prediction of the reflectivity change from HOPG with a model polar organic compound it should be possible to use the ODR technique to study carbonaceous surfaces with greater sensitivity than metal surfaces.
2.4 Temperature Programmed Desorption (TPD)

Temperature programmed desorption (TPD) spectroscopy is one of the most widely used analytical techniques in ultra high vacuum (UHV) surface science.\(^{(74)}\) In a typical TPD experiment, gas molecules are adsorbed on the clean surface by backfilling the UHV chamber to a fixed pressure for a fixed time at a known surface temperature.(Fig 3-5) The chamber is then evacuated back to UHV conditions followed by programmed heating of the surface with continuous monitoring of desorbed molecules by a quadrupole mass spectrometer (QMS).

TPD is a simple method to monitor the thermal evolution of the adsorbate layer into the gas phase and to determine the binding energy between adsorbate and surface\(^{(75)}\). The reaction order and sticking coefficient, i.e., the probability that a gas molecule hitting a surface will remain adsorbed, can be deduced from a series of desorption spectra with different initial doses. TPD can also provide information about the kinetics of adsorption and desorption, directly or indirectly. The relative amount of adsorbed molecules is determined by integrating the desorption signal. Computer fitting using proper adsorption models can be used to determine the desorption parameters.\(^{(76)}\)

TPD was developed in the late 1940's, and has been extensively used to characterize energetics and surface stoichiometry for adsorbates on various surfaces.\(^{(77)}\) For instance, using TPD experiments to study desorption of ethers and alcohols from a-CNx, amorphous hydrogenated carbon, surfaces as a model for the interaction of perfluoropolyalkyl (PFPE) lubricant with surface of magnetic storage devices, Paserba et al. measured the desorption energy and suggested that the hydrogen bond with a-CNx increased as a result of fluorination of the adsorbate.\(^{(78)}\) TPD has been used to study oxide formation on tungsten surfaces at high
temperature, e.g., > 1200 K. At low coverage on tungsten surface, oxygen mainly desorbed as oxygen atoms with first order kinetics. However, as oxygen coverage increased, oxygen desorbed as the oxide (WO$_x$). This study also found that the sticking probability of oxygen is highly dependent on surface temperature and coverage.

TPD can be combined with other techniques. With the aid of molecular simulation and FTIR, Kuznetsova et al. described how the adsorption capacity of single walled carbon nanotubes (SWCNs) for Xe increases after removal of chemical functional groups on SWCNs. In this study, TPD revealed that thermal treatment above 500 K leads to desorption of oxygen- and hydrogen-containing functional groups and the removal of these functional groups enhances the capacity of carbon nanotubes for xenon adsorption as well as the uptake efficiency. However, TPD is limited in its ability to identify the microscopic nature of the adsorption site mechanism of Xe on nanotubes. Molecular simulations suggest that Xe molecules adsorb into the tubular structure of the nanotubes by opening the entry ports of the nanotubes that are blocked by chemical functionalities.

Although TPD was developed to study adsorbate-surface interactions in UHV, it also can be utilized in atmospheric pressure if the desorbing species of interest can be detected. Otake and Jenkins applied TPD to estimate the amount of chemical functional groups on activated carbon surfaces. Li et al. performed TPD experiments after adsorption of elemental mercury on activated carbon samples and provided evidence that chemisorption predominates over physisorption for mercury adsorption on moisture-containing activated carbon samples. However, TPD under atmospheric pressure is limited to the estimate of the energetics of adsorption or desorption due to difficulty of initial exposure estimation and high background contribution, etc. Another disadvantage of TPD is that it destroys adsorbed layer. In spite of
numerous limitations, however, a great deal of information can be obtained about surface processes using the TPD technique.

2.5 Kinetics of Adsorption and Desorption on Solid Surfaces

The fundamental description of adsorption and desorption kinetics is presented in this section for the development of specific models used to analyze experimental results in later sections.

2.5.1 Langmuir Adsorption Kinetics

The Langmuir adsorption model provides a simple picture of adsorption at low pressure and is applicable in many situations of gas adsorption on surfaces.\(^{84}\) Basic assumptions of the Langmuir model are; 1) the adsorption probability depends on the number of available sites; 2) no mechanism exists for lateral transport of impinging gas in a weakly bound state; 3) all molecules bind to identical sites, 4) no multilayer formation, and 5) adsorbate configuration on the surface is completely random.\(^{85}\) The Langmuir adsorption model is described by the following equation;

\[
\theta(L) = \theta_s [1 - EXP (-kL / \theta_s )]
\]  

\[(2-2)\]
where \( \theta \) is the surface coverage, \( L \) is the exposure in Langmuir (1L is the exposure for 1 sec at \( 10^{-6} \) torr), \( k \) is the rate constant for adsorption and \( \theta_s \) is the saturation coverage \(^{85} \). The surface coverage is defined by:

\[
\theta = \frac{\text{Number of occupied adsorption sites}}{\text{Total number of adsorption sites}}
\]  

(2-3)

Relative surface coverage can be extracted by integrating the area of the peaks in a TPD spectrum. The major feature of this model is the coverage dependence the sticking coefficient. The sticking coefficient describes the probability that a gas molecule hitting the surface site will remain adsorbed.

### 2.5.2 Desorption Kinetics

In a TPD experiment, the partial pressure increase caused by desorbing species during heating of a surface contains a great deal of information about the desorption process, e.g., activation energy, reaction order. The thermal desorption rate can be interpreted by an Arrhenius formula, the so-called Polanyi-Wigner equation, which assumes that the desorption rate constant, \( k_d \), is independent of surface coverage, as follows \(^{75, 77} \):

\[
- \frac{d \theta}{dt} = k_d \theta^n = v \theta^n \exp \left( - \frac{E_d (1 + \alpha \theta)}{RT} \right)
\]  

(2-4)
where, \(-d\theta/dt\) is the rate of desorption, \(k_d\) is the desorption rate constant, \(\theta\) is the surface coverage, \(T\) is the temperature, \(t\) is the time, \(v\) is the pre-exponential factor of desorption, and \(n\) is the reaction order. \(\alpha\) is intermolecular interaction which positives number indicates attractive reaction and negative indicates repulsive reaction. \(E_d\) and \(R\) are the desorption activation energy and ideal gas law constant, respectively.

A wide variety of different procedures have been developed for the evaluation of the desorption parameters associated with this formula. Leading edge analysis, developed by Habenschaden and Kůpper (86), is frequently used for the interpretation of TPD peaks, especially for zero order desorption (\(n = 0\)). Zero order desorption occurs when the desorption rate is independent of coverage, resulting in the same initial desorption rate (leading edge) for different exposures and a sharp drop at the maximum desorption rate (77). This method uses a plot of Equation 2-4 (\(\ln (d\theta/dT)\) versus \(1/T\)), which yields a straight line with \(-E_d/R\) as the slope and \(n\ln\theta + \ln v\) as the intercept. The activation energy (\(E_d\)) can be easily determined from the value of the slope.

In the case when intermolecular interactions are important, the desorption rate parameters will change as a function of coverage. While various approaches are available to determine the desorption reaction order (87, 88), this study uses a simple approximation method developed by Redhead (89) to describe the first order desorption detected by TPD. Redhead developed the relationship between the temperature of maximum desorption rate (\(T_m\)) and activation energy from the differentiation of Equation 2-4 when \(n = 1\). The final equation is given as follows:

\[
E = RT_p (\ln (vT_p/\beta)-3.64) \quad (2-5)
\]
where, $T_p$ is the temperature at which the maximum desorption rate is achieved and $\beta$ is the heating rate ($dT/dt$). A value for $\nu$ must be chosen to determine the activation energy value, which is the energy needed to desorb adsorbed species, with the usual choice between $10^{10}$ and $10^{20}$/sec.$^{(90)}$ However, since the deviations in activation energy values are within 1.5% for $\nu/\beta$ in the range between $10^8$ and $10^{13}/K^{-1}$, this approach may be used for the first order desorption.$^{(89)}$

In addition to this simple approach, more sophisticated analysis, e.g., line shape calculation is performed.

### 2.6 Research Objectives and Outline

The overall goal of this study is to understand the physics and chemistry involved in mercury adsorption on carbonaceous surfaces and to optimize the adsorption process and operating conditions for cost effective mercury uptake. In order to investigate the fundamentals of mercury uptake by carbonaceous surfaces, graphite was employed as a model sorbent and a new sub-monolayer sensitive optical surface probe (ODR) was combined with conventional thermal desorption technique in ultra high vacuum condition. In light of significant interest in mercury adsorption on carbonaceous sorbents, a series of investigations was undertaken. It was necessary to establish that the optical probe is a reasonable tool to study adsorption on carbonaceous surfaces by developing a correlation between the new optical probe (ODR) and a conventional vacuum technique (TPD) for the adsorption/desorption of a model polar organic gas (acetone) on graphite. ODR and TPD experiments and analysis will also elucidate adsorption/desorption kinetics of acetone on graphite, relative surface coverage and adsorbed layer thickness in real time.
One of the advantages of optical techniques over TPD is the practical application under high pressures and reversible reaction conditions. Therefore, a series of ODR experiments was conducted at different surface temperatures to investigate propane adsorption behavior on graphite of pressures ranging from UHV to over $10^{-4}$ torr. The aim of this part of study was to demonstrate the versatility of the ODR technique under the condition where TPD cannot be used. Furthermore, these tests evaluated the possibility to study mercury adsorption in the gas mixture by documenting the performance of ODR experiments for propane adsorption and desorption on HOPG surface under pressures that are much higher than UHV and approach atmospheric conditions.

The surface of activated carbon is characterized by high morphological heterogeneity and different chemical functionalities. Therefore, the direct extension of adsorption/desorption results obtained for the relatively well-ordered graphite surface with very little chemical functionality to highly non-uniform activated carbon may lead to serious errors in developing practical carbonaceous sorbents. The adsorption and desorption of model adsorbates representative of polar (acetone) and non-polar (propane) organic compounds and metals (elemental mercury) on model carbonaceous surfaces (Air cleaved as well as plasma oxidized HOPG) were performed to elucidate the effects of chemical functional groups and surface morphology on adsorption/desorption behavior. A dynamic mercury adsorption experiments was also conducted with activated carbon (BPL) in fixed-bed reactor in order to compare with the findings of UHV studies.

Figure 2-3 shows a diagram of various carbon materials in terms of chemical and topological heterogeneity. Graphite represents a carbon material which contains very low chemical and topological heterogeneity while activated carbon is very high in chemical and
topological heterogeneity. This study represents an important step in trying to overcome vast differences in chemical and topological heterogeneity between a simple surface like HOPG and a complex industrial sorbent like activated carbon. In order to overcome the differences between HOPG and activated carbon, the mercury breakthrough experiments were conducted and the energetics of mercury adsorption from chemically and topologically modified HOPG in the UHV conditions and from activated carbon in atmospheric conditions. Virgin HOPG is assumed to contain no chemical or topological heterogeneity. Creating pits in this homogeneous surface and decorating the edge atoms with typical oxygen functionalities (e.g., carboxyl, carbonyl, etc.) would impart some of the features that are known to exist on activated carbon.\(^{(10, 91, 92)}\) On the other hand, there is very little that can be done to alter topological heterogeneity of activated carbon in a controlled fashion. However, outgassing at elevated temperatures would remove most of the oxygen functionalities on this industrial sorbent with minor changes in surface area, pore structure or pore size distribution.\(^{(93)}\)

While there is still a significant void space on Figure 2-3, it should be possible to fill it at least partially through careful selection and modification of other carbonaceous surfaces like carbon molecular sieves, activated carbon fibers, carbon nanotubes, etc. This study represents the first steps in filling that space in an effort to understand fundamental aspects of elemental mercury adsorption by carbonaceous sorbents.
3.0 MATERIALS AND METHODS

3.1 Ultra High Vacuum Apparatus

A custom-made stainless steel UHV chamber, shown in Figure 3-1, was used for all the experiments in this study. The UHV conditions are achieved by a 350 L/sec turbo molecular pump (Leybold, Model: Turbvac350, Export, PA) backed by a mechanical pump (Leybold, Model D16-B, Export, PA). The base pressure of $5 \times 10^{-10}$ torr can be accomplished after over 72 hours of chamber bakeout at around 200 °C and appropriate degassing of all equipment in the chamber.

The number of molecules with molecular weight $M$ hitting a unit surface area per unit time, denoted as $f$, is given in practical units (P in torr and T in K) as \(^{(89)}\):

$$f (cm^{-2} sec^{-1}) = \frac{3.51 \times 10^{22} P}{\sqrt{TM}} \quad (3.1)$$

In order to evaluate the base pressure contribution to surface coverage, one can consider a surface in contact with gas at a pressure of $1 \times 10^{-6}$ torr for one second, which is one Langmuir (L) exposure. If $N_2$ is used as the adsorbing gas then a 1L exposure means will produce one monolayer assuming 100% sticking probability. However, if the pressure is maintained at $5 \times 10^{-10}$ torr, about 85 min of exposure with $N_2$ at room temperature is required to achieve the same conditions assuming a typical surface coverage of $10^{15}$ cm\(^{-2}\) and assuming that each $N_2$ molecule sticks to the surface. Therefore, $5 \times 10^{-10}$ torr of base pressure is suitable to study the surface adsorption and desorption.
The chamber was equipped with a Bayard-Alpert type (nude) ion gauge (Kurt J Lesker, Model: G8130) and a quadrupole mass spectrometer (QMS, AccuQuad300, Stanford Research System, Sunnyvale, CA) to measure total and partial pressure in the chamber. While the ion gauge filament is exposed to the chamber space, the QMS probe arm is sealed by a stainless steel shield with 0.1 in diameter aperture. The shield opening could be repeatedly located to within <1 mm of the sample and retracted about 20 mm by a movable vice. This configuration ensures the collection of molecules from sample alone and allows for sample rotation and adsorbate exposure.\(^{(94, 95)}\) The chamber is equipped with several view ports to allow the laser light access and observation of the sample inside the chamber.

A schematic view of the sample mount is depicted in Figure 3-2. A dual sample holder is mounted on a copper (OFHC) block welded on a stainless steel liquid nitrogen reservoir. The sample holder can be rotated around the \(z\)-axis by a sample manipulator (MDC, model RMTG-275, Hayward, CA) for placing the sample to an appropriate position. Two copper supports are fitted on both sides of the block and electronically isolated in order to allow independent heating of each sample. Samples are mounted on the sample holder with Ta support plates to which a thermocouple tip is welded.

The sample can be heated resistively up to 1300 K with a linear ramping control and cooled to 87 K with liquid nitrogen. A bundle of copper wires is attached to the copper supports to provide electric power. The sample temperature is measured by a chromel-alumel (K-type) thermocouple. Adsorbate exposure is accomplished by backfilling the chamber via a leak valve (Duniway Co., Model VLVE-1000, Mountain View, CA) from the gas reservoir attached to the chamber. The gas reservoir, including stainless steel gas lines and connections, is also pumped.
by a mechanical pump and baked out to get rid of impurities such as water vapor and previously used gas.

The constant temperature ramping rate, typically 2.5 K/sec, is accomplished by a 40 amp-power supply (Kepco, KS DC power supply, Flushing, NY) controlled by a computer with LabView interface (Version 5.0, National Instruments, Austin, TX). Total and partial pressure, sample temperature and laser signal can be monitored via a computer equipped with an A/D board (PCI1200, National Instruments, Austin, TX) and controlled by a customized LabView program.

3.2 Sample Preparation and Adsorbates

3.2.1 Highly Oriented Pyrolytic Graphite (HOPG)

HOPG is a relatively new form of high purity carbon, consisting of a well-defined honeycomb structure of carbon as shown in Figure 3-3. The substrate used in the study was a 10 × 10 × 2 mm HOPG sample (Grade SPI-1, SPI Supplies, West Chester, PA) and a 12 × 12 × 2 mm HOPG sample (Grade ZYA, Advanced Ceramics, Lakewood, OH). A 2 mm – thick HOPG was sliced with a razor blade into several thin (0.5 mm) samples for installation in the chamber or O2 plasma treatment. After air cleaving with adhesive tape to remove the topmost layers of the HOPG surface and expose a fresh surface of basal plane graphite to air, the HOPG was mounted on the sample support. Two mounting holes (Dia =1/16 inch) were drilled in each HOPG samples using clean tools sonicated in 100 % acetone. Atomic force microscope (AFM) images of the sample were taken at atmospheric pressure prior to installation into the chamber.
After the chamber bakeout, the samples were typically annealed at 1000 K overnight for acetone TPD and ODR experiments. For the experiments investigating chemical functional effects, both air cleaved and O\textsubscript{2} plasma treated samples were subjected to the routine bakeout procedure and annealed to the desired temperature before experiments. This annealing procedure removes possible contamination adsorbed from the background or introduced during sample preparation\(^{(94, 95)}\).

### 3.2.2 O\textsubscript{2} Plasma Treated HOPG

In order to investigate the effects of surface morphology on adsorption and desorption, HOPG samples were treated in oxygen plasma to create defects and pores in this ideal surface. Figure 3-4 illustrates the treatment scheme. A raw HOPG sample on a glass slide was placed in the plasma generator (March Instruments Inc., Model March Plasmod). The pressure was lowered to $5 \times 10^{-3}$ mbar by a mechanical pump. During pumping, high-grade oxygen gas was introduced into the generator through a flow controller (March Instruments Inc., Model GCM 250, Concord, CA) to achieve the pressure of 1 mbar. Oxygen pressure was maintained for several minutes to ensure that the oxygen gas filled the entire generator. The plasma flux was provided for 20 and 90 minutes at the power of 100 W. After the treatment, the sample was transferred to a clean plastic container to avoid damage or contamination. The treated sample was examined by AFM prior to installation. The topological surface modification will be discussed in Section 3-5.
3.2.3 Adsorbates

Acetone used in this study was research grade and was degassed by freeze–pump–thaw cycle before dosing. A 195 K temperature bath, which lowers the temperature below the freezing point of acetone \( (T_{\text{melt}} = 239 \, \text{K}) \), was prepared with dry ice and acetone\(^{96}\).

Propane was commercially available research grade and was used as supplied.

The gas phase mercury was generated from a mercury permeation cell (VICI Metrons Inc. Santa Clara, CA) and was prepared by the same freeze–pump–thaw cycle as for acetone. Since mercury vapor pressure is not high enough to achieve reasonable dosing pressure, the mercury reservoir and gas lines were heated at about 100 °C by a customized heating oven to increase the vapor pressure of mercury.

3.3 Temperature Programmed Desorption (TPD) Experiment

A clean surface exposed to a gas at fixed pressure and constant surface temperature for a fixed time duration provides the initial condition. During the desorption cycle as the temperature is increased at a constant rate and the mass spectrometer is used to detect the type and the amount of species desorbing from the surface. Figure 3-5 describes the steps in a TPD experiment.

TPD experiments always began with cooling the samples to below 90 K using liquid N\(_2\). After the sample was positioned to face the QMS, the QMS shield opening was brought close to the sample (< 1mm). The sample was then initially heated at 5 K/sec to a desired temperature depending on the purpose of the experiment and gas species that evolved from the surface were
monitored by the QMS. The gas compounds monitored in this initial phase are at 16 atomic mass unit (amu), at 18 amu, at 28 amu and at 44 amu. This most likely corresponds to CH₄, H₂O, CO and CO₂. Once the sample reached the desired temperature, it was cooled back to 90 K as fast as possible and the shield was retracted to allow dosing. The sample was typically held around 90 K during dosing. Once the exposure (L) reached the desired value, the QMS shield opening was brought close to the sample surface. The sample was heated at a known rate (typically at 2.5 K/sec) while monitoring the sample temperature and partial pressure of adsorbates as a function of time. Once the sample reached the desired temperature (typically 373 K) the heating was stopped and the sample was cooled back to 90 K for subsequent TPD experiments. The resulting QMS signals at 43 amu for acetone, 29 amu for propane and 201 amu for mercury integrated over the desorption temperature range provide the relative amount of adsorbate loaded on the sample surface during the adsorption phase.

3.4 Optical Differential Reflectance (ODR) Experiment

The optical set-up for measuring the ODR signal induced by surface adsorption and desorption is illustrated in Figure 3-6. The laser light, via a polarizer and half waveplate, enters the chamber through a viewport to the sample. The reflected light is divided into two components and two photodiodes measure the intensity of the light. The light source for optical differential reflectance is a low-cost laser pointer (Marlin P. Johnson & Assoc. INC, model #8689-LZ, Lake Park, FL), which is operated at the maximum output power of 5 mW with the wavelength of 655 nm. The laser beam passes through a polarizer (Lambda Research Optics, INC. model ppb-2506u-248, Costa Mesa, CA) and half wave plate (Lambda Research Optics,
INC. model WP-10QC-M, Costa Mesa, CA) on a rotatable mount to adjust the relative intensity of p- and s- polarized light incident to the sample. The polarized laser beam is introduced to the sample via a viewport and reflected at an angle of about $65 \pm 2^\circ$, for acetone, and $70 \pm 2^\circ$, for propane experiments, off the sample housed within a UHV chamber. The reflected light is divided into p- and s- polarized light via a polarizing beam splitter (Coherent, model 44-4703, Santa Clara, CA). Each polarized light intensity component is measured separately by commercially available photodiodes (Thermolabs, model DET-110). For a typical ODR experiment, the cycle started by first cooling the sample and then cleaning it by heating to over 1000 K. The sample is then brought to a desired temperature (typically 90 K) and the intensities of reflected p- and s- polarized light were equalized by adjusting the half wave plate. The monitoring of ODR signal, temperature and pressure as a function of time was performed while dosing the adsorbate gas. After completing the desired exposure (L), the temperature was ramped to about 373 K for desorption, while still monitoring all three signals. As soon as the desired temperature was reached, the heating was stopped and the signals were saved. The experimentally measured normalized ODR signal change is reported as $\Delta R/R$, which is defined by equation (3-2)

$$\frac{\Delta R}{2R} = \frac{I_p - I_s}{I_p + I_s}$$

(3-2)

where, R is the total reflectivity of clean surface and $\Delta R$ is the reflectivity change due to adsorption or desorption. The customized unit for reporting the ODR signal change is either % or relative arbitrary units. $\Delta R/R$ is a complex function of the incident angle, as well as the optical
properties of the adsorbate and substrate. \(^{(61, 97-99)}\) \(I_p\) and \(I_s\) indicate the intensity of p- and s-polarized light reflected from the substrate surface, respectively. Both these quantities are linearly related to the reflectivity: 
\[
I_s = R_s I_{os}, \quad I_p = R_p I_{op},
\]
where \(I_{os}\) and \(I_{op}\) are the intensity of p- and s- polarized light incident on the surface and \(R_s\) and \(R_p\) are the reflectivity of s- and p-polarized light, respectively. The p-polarized light is the "signal" and the s-polarized light is used as the "reference" due to the fact that adsorbate-induced reflectivity changes depend on polarization, with p-polarized light being far more sensitive than s-polarized light to the presence of adsorbates.\(^{(68)}\) This subtraction scheme cancels drift and noise caused by the fluctuations of laser intensity and mechanical instabilities that are polarization independent thereby, maximizing the signal to noise ratio. A sensitivity of 0.04 % (\(\Delta R/R\)) over the time of a single experiment is achieved even with base intensity drift and fluctuations as large as 4 %.

### 3.5 Atomic Force Microscope (AFM) Imaging

Invented in mid 1980’s by Binning et. al. \(^{(100)}\), atomic force microscopy (AFM) has provided unprecedented microscopic details about a variety of different systems,\(^{(101)}\) such as metal electrodes, semiconductors, insulators and biological systems in different environments, such as air, liquid and ultra high vacuum (UHV).

AFM (Pico SPM, Molecular Imaging, Phoenix, AZ) involves, as shown in Figure 3-7, a sharp probe on a cantilever brought into proximity to the surface. A piezoelectric tube is used to control the position of the cantilever (or the sample, depending on the particular instrument) in three dimensions with nanometer precision. The repulsive or attractive interaction between the probe and surface causes the deflection of the cantilever. The deflection of the cantilever is
detected by the movement of laser beam reflected from the top of the cantilever. In contact mode, the most common mode of AFM, the feedback loop attempts to maintain the same deflection while the piezoelectric is scanning the surface line by line. The height signal is recorded at each point on the (x,y) coordinate plane and a topographic plot can therefore be constructed.

Contact mode AFM images were acquired with a Molecular Imaging PicoSPM system (Pico SPM, Molecular Imaging, Phoenix, AZ). Silicon Nitride tips with curvature radius of 10-20 nm and cantilevers with spring constant 0.06-0.12N/m were selected for imaging.

Both raw and plasma oxidized HOPG have been examined by Atomic Force Microscopy (AFM) and Figure 3-8 shows AFM images for virgin and 20 min and 90 min plasma oxidized HOPG. 20 min oxygen plasma treatment provides a significant amount of pits and defects on the graphite surface, which are shown as darker spots on the image, while the air cleaved HOPG reveals a clean and flat surface except for a few steps (0.5~2.5 nm high). The defects on 20 min plasma treated HOPG vary from ~10 to ~200 nm in diameter, and from ~1 to ~10 nm in depth. Longer exposure time to plasma oxidation does not lead to essential changes of HOPG morphology except that pits become wider and deeper. The surface modification by plasma oxidation was fairly reproducible. Two AFM images on Figure 3-8 (b and c) compare two HOPG surfaces after 20 min plasma oxidation on different days under identical treatment conditions and show very similar distributions of defect sites with similar width and depth. Figure 3-8 (d) illustrates an HOPG sample following 90 min plasma oxidation. Defects increased in diameter from ~100 to 500 nm and in depth from ~50 to 200 nm, which is commonly observed morphological change of HOPG surface with plasma oxidation.\(^{(102)}\)
It can be concluded that plasma treatment results in the formation of a morphologically heterogeneous HOPG surface distinct from the topologically homogeneous virgin or air-cleaved HOPG surface.

3.6 Activated Carbon Based Fixed-Bed Adsorption

3.6.1 Activated Carbon

A bituminous coal-based carbon (BPL) was used in this study. BPL is supplied by the manufacturer (Calgon Carbon Co, Pittsburgh, PA) in 12×30 U.S. Mesh size. 60×80 U.S. Mesh size was produced by pulverizing the carbon and sieving to a desired range. The carbon was washed in deionized water to eliminate fines and impurities. Prior to its use, the carbon samples were dried at room temperature and stored in a dessicator. In order to investigate surface water effect, the stored activated carbon sample was heated to 150 °C for 2 hours and cooled to room temperature under nitrogen atmosphere. The sample was heated to 1173 K overnight and cooled to room temperature under nitrogen atmosphere to study the effects of chemical functional groups on mercury uptake.

3.6.2 Fixed-bed Adsorption Experiments for Gas Phase Mercury Uptake

Fixed-bed adsorption experiments were conducted to determine mercury uptake by activated carbon under various mercury inlet concentration and adsorption temperatures. Based
on the breakthrough curves, the adsorption dynamics for various adsorbents could be analyzed both qualitatively and quantitatively.

Adsorber experiments were performed using a quarter inch diameter stainless steel column charged with 100 mg of sorbent. This set-up was found to induce relatively small pressure drop (< 5%) across the bed.

Figure 3-9 illustrates schematic view of the fixed-bed reactor. In order to support the 100 mg of 60 × 80 U.S Mesh size adsorbent, a 170 U.S Mesh size stainless steel sieve was installed on top of a 10 Mesh size stainless steel sieve that served as structural support. The adsorber was always operated in a down flow mode to minimize the potential for bed fluidization.

A schematic representation of the experimental setup of activated carbon fixed bed adsorption is shown in Figure 3-10. The adsorber was placed in a laboratory oven (Cole Parmer, Model 05015, Cole Parmer Instrument Company, Niles, IL) to control the adsorption temperature. In order to allow efficient heating of the influent gas, 4 ft of coiled Teflon tubing was installed in the oven prior to the adsorber inlet. Two feet of Teflon tubing was placed downstream of the adsorber inside the oven and two feet of Teflon tubing was used outside the oven.

Carrier gas was supplied through a regulating valve (Precision Scientific, Chicago, IL) connected to the nitrogen tank to control the flowrate in the system. The drier was placed downstream of the nitrogen tank to remove the existing moisture content that may influence generation and purity of vapor-phase mercury injected from the mercury permeation device.

Prior to the start of an adsorption experiment, clean nitrogen was passed through the AAS during a one-hour warm-up period. Once the intensity and energy level in AAS was stabilized
auto-zero button was pushed to set a zero point. At this time, the mercury permeation device was introduced on-line and the oil bath temperature adjusted to a desired level. The gas flowrate was adjusted to 1 l/min and the system was allowed to stabilize for a period of two hours. The absorbance reading on the AAS was recorded, and the adsorber was placed on-line and time set to zero.

The absorbance reading from the adsorber effluent was initially recorded every 0.5 minutes with increasing time intervals depending on the rate of mercury breakthrough. Since most adsorber runs didn’t last longer than 10 hours, the AAS was turned off when the system reached 100% breakthrough. The next day when the AAS was turned on, it was first re-zeroed by diverting the adsorber effluent away from the AAS quartz cell using a 3-way valve, and supplying clean nitrogen from an auxiliary nitrogen source.

Mercury breakthrough from fixed-bed adsorber is depicted in Figure 4.32 as the ratio of mercury effluent concentration ($C_e$) to influent concentration ($C_o$) as adsorber run progressed in time. The lower values of $C_e/C_o$ represents better mercury adsorption by sorbents and $C_e/C_o = 1.0$ indicates that the adsorption column reached 100% mercury adsorption capacity of the sorbent and no more mercury adsorption will occur. After obtaining the mercury breakthrough profile, the adsorptive capacity of the sorbent was calculated by integrating the area above the breakthrough curve using the following equation:

$$Hg\text{ Adsorbed} = \int_{V_o}^{V_f} (C_o - C) dV \quad (3-2)$$

where, $C_o = \text{adsorber influent concentration (µg/m}^3\text{)}$

$C = \text{adsorber influent concentration (µg/m}^3\text{)}$

$V = \text{Volume of mercury laden gas (m}^3\text{)}$
3.6.3 AAS Calibration

It is essential to properly calibrate the AAS so that the absorbance reading from the AAS can be correlated to the concentration of elemental mercury passing through the quartz cell. The AAS used in this study was calibrated based on the EPA Method 7470 (Mercury in liquid Waste, Manual Cold Vapor Technique)\(^{(103)}\) and the study performed by Shendrikar et al.\(^{(104)}\) Prior to the commencement of the AAS calibration, mercury trapping impinger solution was produced to collect vapor-phase mercury samples in order to calibrate the atomic absorption spectrophotometer (AAS) and to determine the concentrations of total mercury vapor in the gas stream. The impinger solution used for absorbing the vapor-phase mercury was prepared using 1.5 % potassium permanganate (KMnO\(_4\), Fisher Scientific, Pittsburgh, PA) in 10 % (3.6N) sulfuric acid (Fisher Scientific, Pittsburgh, PA) as described by Shendrikar et al.\(^{(104)}\) The 10 % (3.6N) sulfuric acid solution was prepared by diluting the 36 N sulfuric acid with deionized water. Due to the instability of the impinger solution in the presence of light, all glassware was covered with aluminum foil and the impinger solution was always prepared within 10 hours of its use.

The optimum setting of the monochrometer wavelength of the AAS was 253.7 nm and the slit was adjusted to 0.1 mm. The hollow cathode lamp and quartz cell were positioned to maximize the energy level of the detector. In the calibration process, 1 l/min of a steady-state stream of gas-phase mercury was passed through the AAS quartz cell and trapped in an impinger solution.

Two 250 ml gas trapping impingers with coarse glass stones (Corning Inc. Horseheads, NY) were arranged in series downstream of the AAS quartz cell. The neck of the impinger
cylinders and all the connections were sealed with Teflon tape to secure the ground glass joints and avoid potential leakage of mercury from the impinger train. A three-way valve placed upstream of the impinger train was installed to bypass the impingers and vent the gas stream prior to the commencement of the impinger run. After preparation of the impingers, which were filled with impinger solution and sealed tightly, the three way valve was turned so that the gas stream passed through the impinger solution and a rotameter. The impinger run proceeded for 1 hour, while the absorbance reading detected by the AAS and flowrate of the gas stream were recorded at 5-minute intervals.

The impingers were taken off-line after 1 hour and 100 ml of the impinger solution from each bottle was transferred into a 120 ml-volumetric flask. 10 ml of concentrated hydrochloric acid (aqua regia) was used to collect any mercury that condensed on the walls of the impinger cylinders. Since the concentration of mercury in the first impinger solution may be very high, it usually required dilution with fresh impinger solution to reach the linear range of the liquid-phase calibration curve. The second impinger typically did not require dilution. 100ml of the diluted impinger solutions was transferred to 150 ml PTFE bottle and 15 ml of a solution containing 12 % hydroxlyamine sulfate and 12 % sodium chloride in DI water was added to each bottle to prevent interference of permanganate with mercury analysis by cold-vapor AAS. The PTFE bottles were mixed vigorously, vented to release extra gas generated by the addition of reducing solution, and kept for liquid-phase analysis. A standard mercury solution was prepared by spiking clean impinger solution with a given volume of 1000µg/l mercury atomic absorption standard (Aldrich Chemical Company, Milwaukee, WI). Four standard solutions prepared by serial dilution and one blank solution were used to generate liquid-phase calibration curve in the concentration range of 1 to 31 µg/l. After completing cold vapor mercury analysis to determine
the mass of mercury trapped in the impinger train, the concentration of the gas-phase mercury corresponding to the AAS absorption reading was determined using the following equation:

\[ C_{\text{Hg}} = \frac{M}{Q \times t} \]  

(3-3)

Where

- \( C_{\text{Hg}} \) = concentration of gas-phase mercury (\( \mu \text{g/m}^3 \))
- \( M \) = mass of mercury in the impinger train (\( \mu \text{g} \))
- \( t \) = time of impinger run (min)
- \( Q \) = gas flowrate (l/min)

Once the AAS was calibrated, a simpler method was used for AAS spot check and accuracy of the system using Jerome Calibration Vessel (Arizona Instrument Corporation, Phoenix, AZ), a thermos bottle containing liquid mercury capped with a rubber stopper. This rubber stopper contained a narrow slit through which a syringe was inserted to extract a given volume of mercury vapor from the thermos maintained at room temperature. The mercury vapor from the thermos was injected into a hollow quartz cell of the AAS through a rubber septum. Since the concentration of vapor-phase mercury at a given temperature in the thermos can be calculated from the table supplied by manufacturer, the mercury concentration in the quartz cell can be easily calculated. The calibration curve obtained using this method corresponded very well (within 1%) to one obtained by the impinger technique.
4.0 RESULTS AND DISCUSSION

4.1 A combined Study Using TPD and ODR Techniques: Acetone Adsorption and Desorption on HOPG Surface

This study reports the adsorption and desorption of a model adsorbent representative of a volatile polar organic compound (acetone) on a model carbonaceous surface (HOPG). Many environmental phenomena involving carbonaceous surfaces occur under conditions where standard UHV surface science techniques cannot be applied, e.g., atmospheric pressure. ODR and TPD experiments were performed to show that the strong correlation between ODR, determined in real time, and relative surface coverage, determined a posteriori by TPD, could be extended from metal surfaces to carbonaceous surfaces. Thus, it was established that ODR could be used quantitatively to determine coverage on carbonaceous surface under conditions where TPD cannot be employed. Acetone was chosen as the first adsorbate because it represents polar organics, it is easy to handle (e.g. dosing, fast pumping) and analyze, and there are numerous literature references regarding adsorption of acetone on a variety of surfaces.

4.1.1 Temperature Programmed Desorption (TPD)

The results of TPD experiments for 1000 K treated HOPG surfaces dosed with increasing acetone exposures are shown in the Figure 4-1, where the partial pressure of acetone (QMS signal) is plotted as a function of sample temperature. The area under each curve is proportional to the amount of acetone retained by the sample surface during the adsorption phase (surface
coverage). Each peak in the TPD spectra corresponds to the temperature of maximum desorption rate. In the lowest exposure data, until 7.5 L, only one peak is seen at 160-170 K. For exposures >7.5 L, two peaks are seen at 154-158 K and 160-165 K, respectively. For 15 Langmuir exposure, three peaks can clearly be seen at around 145 K, 156 K, and 164 K, respectively. The three characteristic peaks are still present at higher exposure with the lowest temperature peak growing the most. The high temperature peaks are located between 160 K to 170 K for all exposures.

Each TPD feature is associated with molecules desorbing from different surface layers in agreement with a literature report for acetone desorption from a graphitic layer on Pt(111). The highest temperature peak (160-170 K) represents desorption from the monolayer. The second TPD peak (154-158 K) is associated with desorption from the bilayer. The lowest temperature TPD peak (at about 145 K) represents desorption from the multilayer. Figure 4-2 illustrates the growth of the TPD area of the monolayer and bilayer peaks calculated by the best fit for each individual peak (deconvolution). The dotted lines are the fitting curves assuming that adsorption follows Langmuir kinetics. The bilayer peak begins to grow after the first layer has reached about two thirds of its saturation coverage. The similarity of the slopes of the Langmuir fits for both monolayer and bilayer indicates that the sticking probabilities of acetone on the HOPG surface and on the monolayer are similar, because the slope of the TPD signal as a function of acetone exposure represent the sticking probability. The appearance of the multilayer peak in the TPD spectra (Figure 4-1), at about 13 L, indicates the point at which molecules begin to adsorb on the bilayer. Again, the multilayer peak appears before the bilayer feature has saturated. The data in Figure 4-2 indicate that the monolayer is about 80% complete and the bilayer is about 55% complete when the multilayer appears.
The data clearly suggest that the adsorbates grow according to a Volmer-Weber mechanism rather than a layer by layer mode, as discussed below.\textsuperscript{107} Figure 4-3 illustrates the adsorption sequence for the proposed Volmer-Weber adsorption sequence. At low exposure, acetone molecules adsorb directly on the surface, in a monolayer state. The appearance of a second peak before the monolayer state is completely saturated suggests that, in addition to molecules binding on the HOPG surface, acetone molecules begin to bind to the monolayer, thereby creating a bilayer. As the bilayer feature grows, the monolayer feature continues to increase, though more slowly, indicating that there are still monolayer surface sites to be filled. The absolute coverage at which the bilayer and multilayer features appear can be estimated, in principle, from optical difference reflectance as discussed below.

The activation energy of desorption from the monolayer, bilayer and multilayer states can be estimated, as described by Witman et at.\textsuperscript{108} For example, the thermal desorption spectra of the acetone multilayer state are described by a zero order rate law, because of the observed invariance of the leading edge of the TPD spectra to changes in the coverage of the adsorbate.\textsuperscript{79} The activation energy for desorption can be calculated by fitting the Equation 2-3 (\(\ln (d\theta/dT)\) versus \(1/T\)) to Arrhenius plot of with \(n=0\). The activation energy for desorption of the acetone multilayer from graphite was determined to be \(31 \pm 2\) kJ/mol. The activation energy of the multilayer of acetone on HOPG is in agreement with the sublimation energy of acetone, 31 kJ/mol.\textsuperscript{96, 109} Therefore, it can be concluded that multilayer growth of acetone on graphite is independent of substrate adsorbate interaction and that bulk molecular interactions dominate the behavior of this system because TPD spectra follows a common leading edge (zero order) and a good agreement of the activation energy and the sublimation energy means substrate adsorbate interaction is almost negligible.
4.1.2 Optical Differential Reflectance (ODR)

ODR experiments were performed by continuous exposure at $1.2 \times 10^{-7}$ torr of acetone pressure with the HOPG sample at 91 K. Figure 4-4 shows the intensity change of p- and s-polarized light reflected from HOPG as a function of exposure. As the exposure increases, the intensity of p-polarized light increases while the s-polarized light intensity remains constant. The data clearly indicate that p-polarized light is much more sensitive to adsorption than s-polarized light. This confirms the use of p-polarized light as a "signal" and s-polarized light as a "reference".

Using equation 3-2, the ODR signal is plotted as a function of acetone exposure in Figure 4-5. The near linearity of the ODR with exposure suggests that overall acetone adsorption on graphite does not follow simple Langmuir adsorption kinetics because no saturation of signal can be observed. However, the individual monolayer and bilayer states do follow Langmuir adsorption kinetics as discussed with Figure 4-2. As can be seen in Figure 4-5, ODR signal increases linearly until about 7 L exposure (dashed line) at which point the bilayer has begun to grow and the slope of the ODR (solid line) becomes steeper. Even though the number of available sites for adsorption on graphite decreases as the coverage increases, the actual adsorption surface area increases since the acetone layers themselves provide sites for acetone adsorption (see Figure 4-3). Such behavior explains why the slope of the ODR signal and TPD area grow faster at higher coverage rather than saturating once the bilayer appears. The model for acetone adsorption on graphite in Figure 4-3 illustrates how the surface area available for adsorption can increase as adsorption occurs.
In order to validate ODR as a quantitative technique for adsorption analysis, the optical reflectivity change should correlate with coverage as determined from TPD. A plot of the ODR signal as a function of the integrated TPD area is shown in Figure 4-6. The linear correlation between the two signals is very good with $R^2$ of 0.995. The correlation of the ODR signal and the TPD area clearly demonstrates that ODR measures the surface coverage change induced by adsorption.

The reflectivity change can also probe the surface coverage during thermal desorption. Figure 4-7 (b) shows the ODR signal as the temperature of a surface previously exposed to 19 L of acetone is increased. There is a sharp drop of the ODR signal induced by acetone desorption. The magnitude of ODR signal decrease was similar to the ODR increase (about 1 %) during adsorption. The temperature at which the signal drop occurs corresponds to the temperature range at which desorption is observed in the TPD experiment. Because the light reflectivity can be changed as surface temperature changes, temperature-dependant reflectivity changes of the substrate itself must be accounted for. Therefore, it is essential to perform a background reflectivity scan as a function of temperature without adsorbate dosing to correct for such effects (Figure 4-7 (a)). This procedure also corrects for possible sample motion that might occur during heating due to different thermal expansion of different materials. By subtracting the temperature induced reflectivity change of the adsorbate-covered substrate from that of the clean substrate, the adsorbate induced ODR signal can be isolated.

TPD spectra measure the rate of desorption as a function of temperature ($d\theta/dT$).

Given the linear relation between the coverage and ODR signal (ODR signal $\propto$ coverage ($\theta$)), the derivative of the ODR signal with respect to temperature, $d(ODR)/dT$, during desorption should be proportional to the rate of desorption. Thus, the rate of change of the ODR signal with
temperature should correlate with the TPD spectrum (dθ/dT). Figure 4-8 shows the comparison of the d(ΔR/R)/dT signal during the thermal desorption with the TPD spectrum for a surface dosed with 20 L of acetone. Good agreement of desorption peak location between the two curves provides additional evidence for the linearity of the ODR signal with coverage on carbonaceous surfaces. While the TPD clearly has better sensitivity, it can be expected that a more sophisticated modulation scheme could significantly improve the signal-to-noise ratio of the ODR measurement. TPD often detects molecules desorbed from surfaces other than actual sample. However, the ODR can isolate signal contributions from the sample support or other surfaces because it measures the light intensity directly from the sample surface. The ODR technique clearly demonstrates the ability to probe surface coverage changes on a carbonaceous surface in-situ and in real time.

The reflectivity change, ΔR = R(θ)-R(θ=0), induced by adsorption/desorption of a physisorbed species can be described by a three-layer model, as shown in Figure 4-9.(69) Figure 4-9 shows a schematic view of the three-layer model. The interface between the layers is considered planar. As acetone does not visible absorb light, the reflectivity change can be described by the following equation when the dielectric constant for the ambient media ε₁, and for adsorbate layer, ε₂, are real numbers, ε₃ is a complex number and |ε₃| ≫ 1,(69)

\[
\Delta R_s \frac{R_s}{\lambda} = \frac{8 \pi d \cos \phi}{\lambda} \text{Im} \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_1 - \varepsilon_3} \right) \tag{4-1}
\]

\[
\frac{\Delta R_p}{R_p} = \frac{8 \pi d \cos \phi}{\lambda} \text{Im} \left[ \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 - \varepsilon_3} \left( \frac{1 - \varepsilon_1 / \varepsilon_3 (\varepsilon_2 + \varepsilon_3) \sin^2 \phi}{1 - (\varepsilon_3 / \varepsilon_1)(\varepsilon_1 + \varepsilon_3) \sin^2 \phi} \right) \right] \tag{4-2}
\]
where $d$ is the adsorbate overlayer thickness, $\text{Im}$ represents imaginary part, $\phi$ is the angle of incidence, and $\lambda$ is the probe wavelength. $R_{p,s}(\theta=0)$ and $R_{p,s}(\theta\neq0)$ refer to the reflectivity of the clean and adsorbate covered surface for $p$- and $s$-polarized light, respectively. These equations suggest that $p$-polarized light is more sensitive to an adsorbate than $s$-polarized light. This was confirmed experimentally; $s$-polarized light exhibited almost no intensity changes during adsorption (Figure 4-4).

The acetone overlayer “thickness” for 7L exposure, the point at which the bilayer begins to grow, can be estimated using this model assuming that graphite, in a first approximation, is an optically isotropic substrate. Using the following dielectric constants, 1.846 for acetone and 5.0 + i8.4 for the substrate (graphite), the ODR signal (0.35 %) in Figure 4-5 corresponds to a "thickness" of $5 \pm 2 \text{Å}$. The overlayer "thickness" at which the multilayer begins to grow is calculated from the ODR signal (0.65 %) for 13 L exposure to be $10 \pm 3 \text{Å}$. Errors in the film thickness estimation originate from the ODR noise and the accuracy of the incident angle measurement. The ODR “thickness” compares favorably to the thickness for a single layer estimated from the molecular simulation study that indicates that the locus of the first layer lies at about $3.5 \text{Å}$ above the graphite, that of the second layer is located at $7 \text{Å}$ above the surface, and the third at $10.5 \text{Å}$.
4.2 ODR Investigation of Reversible and Irreversible Adsorption and Desorption: Propane Adsorption and Desorption on HOPG

Although temperature programmed desorption (TPD) is the most widely used surface analysis technique, there are several limitations due to the fact for example that the adsorption process must be irreversible. An *in-situ* surface probe may be needed to investigate reversible processes. The aim of the study is to demonstrate the ability of the ODR technique to monitor adsorption in situations where the TPD technique cannot be used. Propane adsorption on raw graphite (HOPG) was performed while the graphite surface was kept at 90, 95, 100, 105 and 110 K after heat cleaning at over 1270 K. The experimental results are supported by Monte-Carlo Simulations. A detailed description of the simulation study is discussed elsewhere. Propane was chosen as the adsorbate because it is a representative of non-polar organics and lower hydrocarbons that have received significant research attention. However, through literature review, no experimental work has been done on the adsorption behavior of propane on graphite at low temperatures and vacuum pressure.

Both TPD and ODR experiments for propane adsorption were performed on HOPG. The TPD method has been used extensively for studying both chemisorption and physisorption and is considered to be very accurate for determining relative coverage. The ODR method, however, is not as widely used, especially for physisorption systems. In order to validate ODR as a quantitative technique the optical reflectivity change should correlate with coverage as determined from TPD. TPD area has been shown to be proportional to the surface coverage. Figure 4-10, a plot of the ODR signal and TPD area as a function of a common exposure, shows a good agreement between these techniques. Both the ODR signal and TPD area saturate at
around 8 Langmuir. The excellent correlation of the ODR signal and the TPD area indicates that ODR accurately measures the surface coverage change induced by monolayer adsorption. Excellent correlation between ODR and TPD measurements also indicates that the TPD spectra are free from contributions due to desorption from other surfaces in the chamber because ODR only probes a small area (<1 mm$^2$) in the center of the HOPG sample.\(^{(113)}\)

The ODR measurements were performed to determine the reversibility of bilayer formation. The ODR signal change as a function of propane pressure at 90 K is provided in Figure 4-11. The different symbols on the figure describe the sequence of propane pressure adjustment and its adjustment direction (increase or decrease). The propane pressure was initially increased from UHV to about $5 \times 10^{-6}$ torr (triangles) and then reduced to below $10^{-7}$ torr (squares). Finally, the propane pressure was increased to above $5 \times 10^{-5}$ torr while the ODR signal was recorded. The initial signal growth in the lower pressure region, up to $2 \times 10^{-7}$ torr, in Figure 4-11, suggests monolayer adsorption, as verified by TPD and simulations. The signal in the submonolayer regime does not represent an equilibrium condition. The coverage increases with increasing time as the pressure is increased from UHV to about $10^{-7}$ torr. Hence, the initial rise in coverage shown in Figure 4-11 reflects the kinetics of the dosing process. It can be assumed that the signal increase for propane pressures between $3 \times 10^{-6}$ torr and $5 \times 10^{-6}$ torr is induced by bilayer formation. The reversibility of bilayer formation can be clearly seen from the ODR signal decrease to the monolayer ODR signal level when the pressure is reduced to under $1 \times 10^{-7}$ torr. However, the ODR signal remained at the level induced by the monolayer formation, although the propane pressure was reduced below the pressure at which monolayer formation occurred. Such behavior suggests that the propane monolayer adsorption is not reversible on the time scale of our measurements at 90 K. Bilayer formation is only observed above a critical
pressure of about $3 \times 10^{-6}$ torr. Surface coverage increases when the rate of molecular adsorption is greater than the rate of desorption. The bilayer formation occurs at pressures over $3 \times 10^{-6}$ torr, when the total flux of propane molecules is $6.31 \times 10^{14}$ cm$^{-2}$ sec$^{-1}$ as calculated at room temperature by the kinetic theory.$^{(114)}$ Multilayer condensation is observed at over $1 \times 10^{-5}$ torr of propane total pressure (circles). Multilayer formation is also reversible, as the ODR signal returned to the monolayer coverage when the pressure was brought back below $1 \times 10^{-5}$ torr (not shown here).

Propane isotherms at about 91, 95, 100, 105, and 110 K were obtained in our experimental study. A distinct bilayer transition (apparently first order) was observed for the experiments at 105 K and below. No layering transition was observed in the 110 K experiment because the pressure was not high enough. The pressures at which the bilayer begins to form were found to be about $2.4 \times 10^{-6}$, $2.3 \times 10^{-5}$, $7 \times 10^{-5}$, and $2.4 \times 10^{-4}$ torr, for 91, 95, 100, and 105 K, respectively. These transition pressures are average values from several runs. The estimated uncertainty in the absolute pressure at which the bilayer forms is about 30%, while the uncertainty in the relative temperature is about 1 K. In order to compare the adsorption behavior of propane on HOPG at different surface temperatures, ODR experiments were performed at 90 K, 100 K and 105 K along with data from GCMC simulations and the results are plotted as a function of propane pressure in Figure 4-12. The observation of the formation of the bilayer and multilayer was enabled by the use of ODR. Although temperature programmed desorption (TPD) is a widely used surface analysis technique, it is not suitable to observe the states that are reversibly populated, i.e., states that require high ambient pressure to be observed. The reduction in pressure required to perform TPD de-populates bilayer and multilayer states, hence the absence of the corresponding peaks in TPD spectra on Figure 4-13.
Figure 4-12 describes the adsorption isotherm data for propane on HOPG at 91 K determined from experiments and simulations. The experimental adsorption loadings were measured in arbitrary units and converted to $\mu$mol/m$^2$ by matching the monolayer loading with the simulation data. Because the relative adsorbed amount measured experimentally are accurate, the good agreement between experiments and simulations for the second layer loadings indicate that simulations accurately predict relative coverages in the first and second layers. The position of the first to second layer transition on the pressure axis determined from experiments and simulations are in remarkable agreement. The agreement, however, is probably fortuitous because of the experimental difficulty in measuring the absolute pressure accurately. Furthermore, transition pressures are very sensitive to substrate temperature. While relative temperature is accurate to about one degree K, absolute temperature is measured less accurately. It was not possible to observe a transition from zero loading to the first layer in any of the simulations. Virtually complete monolayer coverage at the lowest pressures simulated (about $2 \times 10^{-8}$ torr) is obtained, indicating that the 0-1 transition must occur at pressures lower than $2 \times 10^{-8}$ torr. The apparent 0-1 layering transition seen in the experimental data (e.g., Figure 4-12 (a) and (b)) is the result of kinetic effects. The pressure in the UHV chamber was rapidly increased before the monolayer had a chance to form completely and the experimental data below the monolayer coverage in Figure 4-12 (a) do not reflect true equilibrium. The kinetic nature of the ODR data can also be inferred from the data in Figure 4-11, which shows that the first layer remains intact upon reduction of the pressure. Indeed, we find that the first layer cannot be removed over a reasonable time by evacuating the chamber; the substrate must be heated to remove the first layer (see Figure 4-13). These data reflect the dynamic nature of adsorption.
experiments, i.e., it takes a finite time to form a monolayer at a fixed pressure. The simulations, however, reflect equilibrium (or metastable) conditions.

Experimental data for $T = 95, 100, 105$ K and simulation isotherms for $T = 100$ and 105 K are shown in Figure 4-12 (b). The 1-2 layering transition pressures at 100 and 105 K from simulation and experiment do not agree as well as in the 91 K case, but they are in good qualitative accordance. The relative coverages in the first and second layer are in excellent agreement.

As noted above, the desorption of the second layer of propane is reversible, i.e., it can be achieved by lowering the pressure, whereas the monolayer must be heated to be removed. The fact that monolayer desorption is an activated process means that we can use TPD to probe the energetics. We used the equation (2-4) to calculate the activation energy of desorption from TPD experiments\(^{(89, 108)}\)

A series of TPD spectra for propane dosed at 90 K on HOPG are shown in Figure 4-13. A single peak appears around 115 K. The propane TPD spectra grow with a common leading edge and abrupt trailing edge, indicating zero order desorption.\(^{(75)}\) Using zero order desorption kinetics, the activation energy for desorption of propane on HOPG is estimated to be $30 \pm 2$ kJ/mol (Figure inserts). The uncertainties arise in part from the accuracy of temperature measurements. The heat of vaporization of propane at its normal boiling point (230.9 K) is 19.04 kJ/mol,\(^{(96)}\) while integration of the heat capacity yields a value of 24 kJ/mol for the heat of vaporization at 100 K.\(^{(96, 115)}\) This is smaller than the calculated activation energy and is consistent with the strong solid-fluid interaction for adsorbed propane. There is no evidence in the TPD spectra of bilayer or multilayer formation under present experimental conditions.
The isosteric heat of adsorption can be obtained from the following relationship, the Clausius-Clapeyron equation \(^{(84)}\)

\[
\frac{d(\ln P)}{d(1/T)} = -\frac{\Delta H}{R}
\]  

(4-3)

Where \(\Delta H\) is the heat of adsorption, \(T\) is the temperature at which the layer formation occurs, \(P\) is the pressure and \(R\) is the ideal gas law constant (8.314 kJ/mol). Plots of \(\ln P\) as a function of reciprocal absolute temperature at constant coverage are called adsorption isosteres and the isosteric heat of adsorption is determined by their slopes. Experiments performed at five temperatures (91, 95, 100, 105 and 110 K) allow determination of \(\Delta H\). The average pressure where the second layer just begins to form at each temperature was used to construct a single isostere. For experiments at 110 K second layer formation was not observed at pressures up to \(2 \times 10^{-4}\) torr, consistent with the simulations showing that the second layer forms at a pressure of about \(5 \times 10^{-4}\) torr. The isosteres procedure can be applied to the isotherms calculated from simulations and a value of \(\Delta H\) can be obtained.

The heat of adsorption computed from experimental and simulation data are plotted in Figure 4-14. The experimental values in Figure 4-14 represent the average of several isotherm measurements and the error bars were estimated based on the scatter in the experimental data. The values of isosteric heat at bilayer formation determined from experimental and simulation data are in excellent agreement. The experimentally determined value of \(\Delta H\) is \(23 \pm 2\) kJ/mol. The isotherms computed from Monte-Carlo simulation agree well quantitatively with ODR experimental results in terms of the location of pressure at which bilayer of propane occurs. In addition, molecular simulations estimated heat of adsorption of propane bilayer of \(24 \pm 1\) kJ/mol,
which is in good agreement with experimental data. Therefore, this study clearly showed that ODR is suitable for investigating reversible adsorption phenomena in real time and over a wide pressure range.

4.3 The Effects of Surface Functional Groups on Adsorption and Desorption of Acetone on Carbonaceous Surfaces

A series of experiments was designed to probe the role of surface chemical heterogeneity on the adsorption process on carbonaceous surfaces. The objective of this study was to investigate the role of air-formed surface chemical functional groups on a model carbonaceous surfaces (HOPG, highly oriented pyrolytic graphite) on the adsorption and desorption of acetone as a representative of polar organic compounds.

The gas evolution profiles as a function of temperature during surface heat treatment of a-HOPG are displayed in Figure 4-15. Heat treatment clearly leads to desorption of 16, 18, 28 and 44 atomic mass unit (amu) containing species, probably H$_2$O, CO and CO$_2$ related compounds, at temperatures above 500 K. It can be seen from Figure 4-15 that there is no re-appearance of these features in the ~24 hours that elapse between each successive heat treatment. The gas evolution only starts at temperatures higher than previous day’s maximum treatment temperature. This result can be compared to the study of thermal desorption of spectroscopy of the heterogeneous surface of activated carbon.$^{(116)}$ It was found that the decomposition of the surface oxides on carbon, yielding CO and CO$_2$, occurs at temperatures above 520 K and that outgassing above 1273 K is required to remove essentially all functional groups. In order to
verify that gas desorption during heat treatment originated from the HOPG samples and not other parts of the sample holder, control experiments were performed where the air-cleaved HOPG sample was replaced by a gold coated Ta sample (10×10×0.05 mm). Heat treatment to over 873 K resulted in no significant gas desorption.

TPD spectra for surfaces dosed at around 120 K with increasing acetone exposures after the desired heat treatment are shown in Figure 4-16, where the partial pressure of acetone (QMS signal at 43 m/e) is plotted as a function of the sample temperature. For all exposures after 473 K heat treatment, a single desorption peak, with a common leading edge, appears at around 130 K (Figure 4-16 (a)).

For 673 K heat treatment (Figure 4-16 (b)), the TPD spectra at the lowest exposure, until 5 L, consist of only one peak at around 155 K. For exposures above 5 L, two peaks are seen at about 147 K and 155 K. For 7 L exposure, three peaks can clearly be seen at around 137 K, 147 K, and 155 K. Each TPD peak is likely associated with molecules desorbing from different surface layers.\(^{111}\) The highest temperature peak for the TPD spectra after 673 K heat treatment (150-155 K) represents desorption from the monolayer, i.e. acetone bound to HOPG surface.\(^{61, 105}\) The second TPD peak (around 147 K) is associated with desorption from the bilayer.\(^{105}\) The lowest temperature TPD peak (at about 137 K) represents desorption from the multilayer.\(^{61, 105}\) These three characteristic peaks are also present at higher exposures. The two high temperature peaks saturate while the lowest temperature peak grows with increasing exposure.

TPD spectra after 873 K heat treatment (Figure 4-16 (c)) shows the same three peaks at temperature identical to those in TPD spectra after 673 K heat treatment. The acetone exposure required for monolayer peak saturation, as well as the magnitude of this peak, increases as the heat treatment temperature increases. It can be seen in Figure 4-16 that the monolayer saturates
at 5L for 673 K, between 7 and 10L for 873 K and around 10L for 1073 K and greater heat treatments, respectively. The saturation exposure for the bilayer also increases as the temperature of the heat treatment increases.

Essentially identical results to those reported herein were obtained using an HOPG sample manufactured by a different company (Grade ZYA, Advanced Ceramics Co). Heat treatment leads to similar gas evolution profiles as shown in Fig 4-15. The acetone TPD spectra were almost identical to those shown in Fig 4-16. Exposure of HOPG samples treated to 1323 K to ambient laboratory air results in the regeneration of oxygen functionalities and TPD behavior similar to that depicted in Figures 4-15 and 4-16 is observed. This suggests that the experimental observations reflect intrinsic properties of HOPG, rather than contamination of the HOPG surface during production or preparation.\(^{117}\)

The evolution of each feature observed in the acetone TPD (Figure 4-16) was investigated by deconvolution of the TPD spectra, the separation of each individual peak by curve fitting. The integrated TPD area for each layer corresponds to the relative amount of acetone molecules adsorbed at 25 L exposure and is plotted as a function of heat treatment temperature in Fig 4-17. As can be seen in Figure 4-16, both the monolayer and bilayer are almost saturated at 25 L in all cases. As the sample is treated at higher temperature, the amount of acetone adsorbed directly on the HOPG surface (monolayer) increases as well as the amount adsorbed on the monolayer of acetone (bilayer). Both features appear to level off for heat treatment above 1000 K.

The results shown in Figures 4-16 and 4-17 suggest that the removal of the surface functional groups from HOPG by heat treatment creates a surface that is representative of a clean HOPG surface for acetone adsorption. The TPD spectra are then almost identical to acetone TPD
from a single graphitic layer grown on Pt(111).\(^{(105)}\) The higher temperature associated with the monolayer feature suggests that acetone molecules bind more tightly on the clean HOPG surface than on the functional groups that are initially present on the air cleaved surface. The saturation of the monolayer adsorption uptake of acetone, Figure 4-17, for outgassing temperatures above 1000 K suggests that a heat treatment temperature of at least 1000 K is needed to remove functional groups from the surface and prepare a clean HOPG surface.

It is unlikely that HOPG offers “entry ports” for acetone molecules since intercalation, the adsorption of adsorbate into the layers of HOPG, is unlikely given the size of the molecule and the pressures employed in this investigation. Furthermore, intercalation of acetone molecules should not result in saturation of all HOPG layers with such low acetone exposures, less than 15 L after 1273 K heat treatment. The similarity of TPD spectra for heat treatment above 1000 K (Figure 4-16 (d) and 4-16 (e)) and those from a previous study involving desorption of acetone from a monolayer of graphitic carbon grown on a Pt(111) surface,\(^{(105)}\) further supports the hypothesis that acetone molecules do not intercalate into HOPG layers, because a monolayer of graphitic carbon on Pt does not offer any layers for intercalation.

To investigate possible changes in acetone uptake capacity as a function of heat treatment temperature, the total TPD area at 25 L acetone exposure is shown in Figure 4-18. In spite of the changes in the area for each individual TPD feature, the total TPD area at constant exposure remains approximately constant for all heat treatments. This indicates that the sticking probability of acetone on clean HOPG and HOPG decorated with air-formed functional groups is similar. The contribution from each individual TPD peak changes with the removal of functional groups, while the overall adsorption remains constant. On the other hand, the TPD area for low exposure (e.g., 5 L) decreases, by almost a factor of two, as the pre-treatment temperature
increases (inset in Figure 4). Such behavior clearly demonstrates that the sticking probability of acetone on functionalities or an acetone layer already present on the HOPG surface is higher than on a functional group-free HOPG surface.

Previous studies documented quite different behavior for adsorption of a non-polar organic, propane, on HOPG following heat treatment. In the case of propane, the initial uptake capacity was very low. Heat treatment to over 1270 K increased the total adsorption capacity on HOPG by over an order of magnitude. This indicates that the air-formed functional groups on HOPG interact more favorably with polar adsorbate compared to non-polar adsorbates. The higher adsorption capacity of carbonaceous surfaces for polar organic molecules (acetone) than non-polar (propane) is consistent with reports that air-formed functional groups are also polar, e.g., carboxyl group. The presence of polar oxygen-containing functional groups is not completely unexpected because carbonaceous surfaces exposed to ambient conditions typically contain the kind of functionalities encountered in this study. However, it is surprising for HOPG, which is believed to contain very little functionality.

The energy of acetone desorption from the clean HOPG surface (monolayer of acetone) can be determined through the analysis of the desorption rate (-dθ/dT), which is commonly described by Equation (2-4). Figure 4-19 shows both experimental and simulated TPD for acetone exposure from 1L to 7L. The best fits of Equation (2-4) to experimental data shown in Fig 4-19 are obtained with n = 1, a pre-exponential factor of $10^{20\pm1.5}$ sec$^{-1}$, an activation energy of $55.5 \pm 3.0$ kJ/mol and intermolecular interaction parameter of 0.045 monolayer$^{-1}$ for the acetone monolayer on the clean HOPG surface. The pre-exponential factor obtained from this fit is much higher than the usually assumed value of $10^{13}$ sec$^{-1}$. However, the use of a $10^{13}$ sec$^{-1}$ pre-exponential factor in the TPD peak simulation procedure failed to achieved reasonable fits of
experimental TPD data, as shown in insert (a) on Fig 4-19. The $10^{-13}$ sec$^{-1}$ pre-exponential factor results in a TPD peak twice as broad as that observed experimentally. One may claim that the monolayer of acetone grows with zero order due to similar leading edge of TPD spectra at different exposures. However, the fitting using zero order reaction fails to predict the tailing feature of the experimental data as shown in insert (b) on Fig 4-19.

The desorption parameters for the second layer (bilayer) can also be estimated using coverage dependant first order simulation. Monolayer and bilayer peaks are separated by deconvolution and are fitted separately using the same simulation procedure as that employed for acetone monolayer. The best fits to experimental data were obtained with $n = 1$, a pre-exponential factor of $10^{21.6 \pm 1.5}$ sec$^{-1}$, an activation energy of $51.5 \pm 3.0$ kJ/mol and an intermolecular interaction parameter of 0.004 for the acetone bilayer on the clean HOPG surface.

Thermal desorption spectra of acetone multilayer state are usually described by a zero order rate law because of the observed invariance of the leading edge of the TPD spectra to changes in the initial coverage of the adsorbate and a sharp drop after reaching maximum desorption rate.$^{(77)}$ The activation energy for desorption can be calculated by fitting the intensity profile to Equation (2-4) with $n = 0$ and $\alpha = 0$. The activation energy for desorption of acetone multilayer from graphite was determined using this procedure to be $31 \pm 2$ kJ/mol This is in agreement with the sublimation energy of acetone, $31$ kJ/mol.$^{(96, 109, 119)}$ The excellent agreement between the multilayer desorption energy determined in this study and the bulk enthalpy of sublimation suggests that relative sample temperature readings are quite accurate ($\pm 2$ K) and that the adsorbate is pure. The results obtained in this study can be compared to the TPD spectra of other polar organic adsorbates (alcohols and ethers) on HOPG, which showed first order monolayer and zero order multilayer desorption peaks.$^{(120, 121)}$
In addition to using the simulation method described above to assess the desorption parameters, acetone TPD experiments were performed using different heating rates at 7L acetone exposure to independently determine acetone desorption parameters.\(^{(89)}\) Figure 4-20 illustrates how the TPD peak amplitude grows and the peak location shifts to higher temperature as the heating rate increases. These experiments allow the determination of the pre-exponential factor and activation energy using Redhead first order kinetics, described by Equation (4-4).\(^{(89)}\)

\[
\frac{E_d}{RT_p^2} = \left(\frac{\nu}{\beta}\right) \exp\left( -\frac{E_d}{RT_p} \right) 
\]

(4-4)

where, \(T_p\) represents temperature where the maximum desorption rate occurs.

The Equation (4-4) can be transformed to Equation (4-5) to allow direct estimation of exponential factor and activation energy.\(^{(75, 102)}\)

\[
\nu = \beta \frac{E_d}{RT_p^2} \exp\left( \frac{E_d}{RT_p} \right) 
\]

(4-5)

The procedure for the determination of activation energy and pre-exponential factor involves plotting \(\ln(\beta/T_p^2)\) versus \(1/T_p\). This yields a straight line with a slope of \(-E_d/R\), as shown in the insert on Figure 4-20. A linear regression performed on the data yielded activation energy of \(57.7 \pm 2.5\, \text{kJ/mol}\) for 7 L and \(54.9 \pm 2.5\, \text{kJ/mol}\) for 3 L, and a common pre-exponential factor of \(10^{19\pm1}\, \text{sec}^{-1}\). Both methods for the analysis of acetone desorption kinetics parameters resulted in very similar values for the activation energy and pre-exponential factor, which gives confidence in the data reported here. The pre-exponential factor obtained from both simulation and experimental methods is much higher than the typical value of \(10^{-13}\, \text{1/sec}\) assumed in TPD.
analysis. However, the high pre-exponential factor for organics on HOPG surface can be found in a study which investigated desorption kinetics of n-alkanes (n > 5) from HOPG. This study also compared pre-exponential factor estimated by first order simulation and experiments using variable temperature ramping rate in TPD studies and showed high values of ν in the range from $10^{19}$ to $10^{20}$ sec$^{-1}$.

### 4.4 The Effects of Surface Functional Groups and Topological Heterogeneity on Propane Adsorption and Desorption on Carbonaceous Surface

This section discusses the adsorption and desorption of a model adsorbent representative of non-polar organic compounds (propane) on model carbonaceous surfaces. Both raw and plasma oxidized HOPG were used to investigate the effects of chemical functional groups and surface morphology on the adsorption/desorption behavior of propane. Considering that industrial sorbents like activated carbon contain chemical functionalities as well as topological surface roughness, understanding the role of these heterogeneities on adsorption and desorption is extremely important in terms of producing “better sorbents” for a given purpose. By introducing chemical and morphological heterogeneity on homogenous HOPG surface, this approach can provide a better understanding of the adsorption/desorption characteristics of carbonaceous surfaces used in practice (e.g., activated carbon that contains high chemical and morphological heterogeneity).
4.4.1 Adsorption/Desorption on Air-Cleaved HOPG (a-HOPG)

A series of TPD spectra for propane dosed at 90 K on air-cleaved HOPG following heat treatment to various temperatures is shown in Figure 4-21. A peak appears around 115 K in all cases and saturates at 3L for 673 K, 7L for 873 K and 8L for 1073 K and higher heat treatments, respectively. The TPD peak for air-cleaved HOPG treated at 473 K is barely detectable even when multiplied by 10 on this scale. As the heat treatment temperature increases, the propane TPD desorption peak height increases at equivalent exposure levels.

Figure 4-22 illustrates the integrated TPD areas, corresponding to the relative amount of propane molecules adsorbed at 25 L exposure for air-cleaved HOPG and plasma-oxidized HOPG, as a function of the heat treatment temperature. A 25 L exposure results in saturation for all heat treatments reported here. The results depicted in Figure 4-15 suggest that oxygen-containing functional groups exist on the air-cleaved HOPG surface and that they are removed by thermal treatment. The results shown in Figures 4-21 and 4-22 suggest that the removal of these functional groups increases the number of accessible adsorption sites for propane molecules. The results also suggest that propane, a non-polar organic, has an unfavorable interaction with the naturally existing polar functional groups on air-cleaved HOPG prior to heat treatment. The saturation of the adsorption uptake seen in Figure 4-22 for outgassing temperatures above 1173 K suggests that heat treatment at $T \geq 1173$ K is needed to clean the air-cleaved HOPG surface for alkane adsorption.

Exposure to laboratory air for 24 hours results in the reappearance on HOPG of similar types and quantities of functional groups as those that have been removed by heat treatment of air-cleaved HOPG. This is revealed by the observation that the surface capacity for propane
adsorption is initially low and that heating to 1273 K results in evolution of the same fragments as observed from air cleaved HOPG, resulting in, once again, a factor of 20 increase in propane adsorption capacity. This behavior suggests that these oxygen-containing surface functionalities result from the interaction of the freshly cleaved or vacuum heat treated surface with air.

Interestingly, qualitatively similar behavior was seen in the study of xenon adsorption on carbon nanotubes.\(^{(52, 53)}\) Thermal treatment over 600 K leads to the desorption, of oxygen containing functional groups, which are believed to block the entry ports of the nanotubes, without change of the molecular structure of the nanotubes. The removal of the blocking functional groups enhances the capacity of the carbon nanotubes for xenon uptake.\(^{(53)}\)

Propane TPD spectra grow with a common leading edge for all heat treatments, indicating zero order desorption\(^{(75)}\). Using zero order desorption kinetics, the activation energy for propane desorption on HOPG is estimated to be 30 ± 2 kJ/mol, which represents a reasonable agreement with another study of n-alkane adsorption on HOPG\(^{(76)}\). Uncertainties in the estimation of activated energy arise in part from the accuracy of temperature measurements. The location of the thermocouple in this experimental system is restricted by the fact that it cannot be spot-welded to HOPG. The calculated activation energy is about 25 % greater than the heat of vaporization of propane of 23.9 kJ/mol at 100 K as shown in appendix.\(^{(96, 115)}\)

The observations that the shape of the TPD spectra does not change with heat treatment temperature, the increasing propane uptake subsequent to each heat treatment temperature, and the invariance of the activation energy with each heat treatment step verifies that little adsorption occurs at 90 K at sites blocked by chemical functional groups. It is very likely that chemical functional groups on HOPG are polar species (e.g., quinone, carbonyl or carboxylic acid) and that adsorption of a non-
polar organic (e.g., propane) is hindered by their presence on the surface. This is consistent with the well-known immiscibility of polar and non-polar solvents, e.g., oil and water.

The magnitude of the desorption energy suggests that the interaction between propane and the clean HOPG surface is greater than the interaction between propane molecules. There is no evidence of bilayer or multilayer formation under the present experimental conditions, because ambient pressures in excess of $10^{-6}$ torr are necessary for propane bilayer formation at 90 K.\(^\text{(112)}\)

The propane adsorption capacity increase of air-cleaved HOPG after high temperature heat treatment is highly reproducible from sample to sample. During thermal treatment to 1050 K of air-cleaved HOPG from Advanced Ceramics, the desorption of gases containing 16, 18, 28 and 44 amu fragments was also observed in similar temperature regions to those evolved from the HOPG sample supplied by SPI. TPD experiments using air-cleaved HOPG from Advanced Ceramics also verify that HOPG has almost no propane adsorption capacity after 473 K heat treatment and that its ability to adsorb propane increased by over an order of magnitude after heat treatment to 1050 K.

4.4.2 Adsorption/Desorption on Plasma-oxidized HOPG (p-HOPG)

An important objective of this study was to understand the role of chemical and topological heterogeneity on adsorption and desorption on carbonaceous surfaces. In order to introduce defect sites and etch pits on HOPG, an air-cleaved HOPG sample was subjected to plasma treatment at controlled oxygen pressure. It has been shown previously that high temperature oxidation in air creates low density ($< 1\%$ by surface area) of monolayer deep etch
pits at existing defects of HOPG, while maintaining the flatness of the graphite surface\textsuperscript{(102, 122-125)}. Plasma oxidation, however, creates mechanical damage on initially flat surface that augments pre-existing defect sites\textsuperscript{(102)}. Plasma oxidation etches the surface, resulting in highly roughened surfaces confirmed by our AFM images\textsuperscript{(102)}.

Similar features to those shown in Figure 4-15 evolve during the heat treatment of plasma-oxidized HOPG as shown in Figure 4-23. Exposure of plasma-oxidized HOPG to air for about 24 hours results in essentially complete recovery of these features while the amount of the desorption of each detected gas compound and their peak location is varies somewhat. This suggests that the oxygen-containing groups do not result from impurities incorporated during sample preparation or manufacture.

The effects of surface morphology on adsorption are depicted in Figure 4-24, which compares TPD spectra from air-cleaved and plasma-treated HOPG at low propane exposure (<3L) after heat treatment at 1173 K. TPD spectra for air-cleaved HOPG below 3 L propane exposure consist of a single peak with a leading common edge. On the other hand, for plasma-oxidized HOPG, it consists of two peaks, at around 120 K and 175 K, which both grow together with propane exposure. The growth of the lower temperature peak with exposure resembles that observed for the air-cleaved HOPG except that the peak height is about a factor of 5 lower. The higher temperature peak shifts to lower temperatures with increasing exposure.

It is reasonable to assume that the TPD spectra observed on p-HOPG are a consequence of the defects generated by plasma treatment. These defects provide adsorption sites with stronger binding energy as indicated by the higher temperature peak. These sites do not exist on air cleaved HOPG. The downward shift in peak temperature with increasing exposure suggests sequential filling of the defect sites, with the higher binding energy sites being filled first. This
behavior also suggests significant mobility of adsorbed species enabling them to sample all the sites. In addition, the TPD areas for plasma-oxidized HOPG are always greater than those for the air-cleaved HOPG under identical exposure conditions, as shown in Figure 4-25. Hence, the capacity for propane adsorption on plasma-oxidized HOPG is greater than that for air-cleaved HOPG. Plasma-oxidized HOPG has pits that are several tens of layers deep, thereby providing access to many more graphite layers than air-cleaved HOPG. Control experiments with a gold coated Ta sample indicate that the quantity of propane desorbed from a gold-coated Ta sample is similar to that desorbed from the heat-treated air-cleaved HOPG. These results suggest that no propane intercalation occurs under the experimental condition used in this study. The pits would provide access to many more layers than air cleaved HOPG. Therefore, the observed increase in uptake capacity of plasma-oxidized HOPG of about 50% is most likely associated with the increased surface area provided by the topologically heterogeneous plasma-oxidized HOPG sample.

The energy of propane desorption from the clean HOPG surface for high temperature peak can be determined through the analysis of the desorption rate (-dθ/dT), which is commonly described by Equation (4-6)\(^{(76)}\)

\[
-\frac{d\theta}{dT} = \frac{\nu}{\beta} \theta^n \exp\left(-\frac{E_d (1 + \alpha \theta)}{RT}\right)
\]

(4-6)

where, \(\nu\) is the pre-exponential factor, \(\theta\) is the adsorbate coverage, \(\beta\) is temperature ramping rate \((dT/dt)\), \(n\) is the order of the desorption process, and \(E_d\) is the activation energy for desorption at zero coverage.\(^{(76)}\) The variable \(\alpha\) is an intermolecular interaction parameter. Positive values of \(\alpha\)
reflect attractive intermolecular interactions and negative values of $\alpha$ reveal repulsive intermolecular interactions.

After numerous trials to generate a reasonable fit of experimental data, it was decided that a simple first order kinetics never describes this high temperature peak properly because of significant surface heterogeneity caused by plasma oxidation. It was therefore decided to insert a pseudo-parameter ($\gamma \theta^2$) into the $(1+\alpha \theta)$ term to better model the coverage dependence of the activation energy for desorption and to improve the quality of the fit, as follows,

$$- \frac{d \theta}{dT} = \frac{v}{\beta} \theta^n \exp \left( - \frac{E_d (1 + \alpha \theta + \gamma \theta^2)}{RT} \right)$$

(4-7)

The lineshape simulation of the high temperature propane peak and average heat of adsorption for both low and high temperature peak are shown in Figure 4-26. The main purpose of this phenomenological analysis is to demonstrate that the average binding energy of propane from defect sites created by plasma oxidation is higher than that from basal plane of HOPG and that there is considerable heterogeneity in the sites generated by plasma oxidation.

As shown in Figure 4-25, the TPD areas for plasma-oxidized HOPG are always greater than those for the air-cleaved HOPG under identical exposure conditions. Hence, the capacity for propane adsorption on plasma-oxidized HOPG is greater than that for air-cleaved HOPG. As discussed earlier, the observed increase in uptake capacity of plasma-oxidized HOPG of about 50% is most likely associated with the increased surface area provided by the topologically heterogeneous plasma-oxidized HOPG sample.
4.5 Adsorption and Desorption of Mercury on Model (HOPG) and Real (activated carbon) Carbonaceous Surfaces

This section compares adsorption and desorption of gas-phase elemental mercury on real and model carbonaceous surfaces. The investigation of elemental mercury adsorption is carried out using both highly oriented pyrolytic graphite (HOPG) as a model carbonaceous surface in well-controlled UHV condition and coal based activated carbon (BPL) in fixed bed conditions. It is clear that there are major differences between graphite and other carbonaceous sorbents with regards to inorganic impurities (ash content) and morphology. Therefore, attempts will be made to modify the pore structure and chemical heterogeneity (surface functional groups) of HOPG to capture the essential features of porous carbon because most researchers believe that these are the key surface properties influencing adsorption and catalysis by carbonaceous sorbents. Carefully selected thermal and chemical modifications of graphite and other sorbents would aim to delineate the importance of these surface properties in both adsorption and catalysis. (See Figure 2-3)

4.5.1 UHV studies with HOPG

A series of TPD experiments were carried out to investigate the impact of oxygen-containing functional groups on mercury adsorption and desorption from chemically modified HOPG surface. Figure 4-27 shows a series of TPD spectra for mercury dosed at 100 K on air cleaved HOPG sample following heat treatment to 473 K and 1273 K. A mercury TPD desorption peak appears around 200 K in both cases. It increases in height and width with an
increase in exposure levels. The peak did not saturate up to 20 L exposure and its location tends to shift to higher temperature with an increase in exposure.

The energy of mercury desorption from HOPG can be determined through the analysis of the desorption rate \( -\frac{d\theta}{dT} \), which is commonly described by Equation (102)\(^{(4-4)}\). Figure 4-28 is one example showing experimental and simulated TPD peaks for mercury exposure at 20L for a 1273 K treated a-HOPG sample. The best fit of Equation (4-4) to all experimental data shown on Figure 4-28 was obtained using 1st order kinetics, a pre-exponential factor of \( 10^{18\pm1} \) sec\(^{-1}\), an average heat of adsorption of \( 82 \pm 3 \) kJ/mol and an intermolecular interaction parameter of 0.003. Uncertainties arise in part from the accuracy of temperature measurements because location of the thermocouple in the experimental system is restricted by the fact that it cannot be spot-welded to HOPG. The calculated activation energy is only about 25 % greater than the heat of sublimation of mercury of 64.3 kJ/mol at 200 K.\(^{(96, 115)}\) It can be concluded that mercury adsorption on HOPG under the experimental conditions used in this study occurs exclusively through physisorption.\(^{(127)}\)

Figure 4-29 illustrates the integrated TPD areas, which correspond to the relative amount of adsorbed mercury, as a function of mercury exposure for both air cleaved HOPG samples. These results indicate that the heat treatment of HOPG at 1273 K causes some increase in the amount of mercury adsorbed under the experimental conditions used in this study. Previous studies demonstrated that heat treatment of HOPG leads to desorption of oxygen containing functional groups at temperatures above 500 K and that there is no re-appearance of these functionalities over a 24 hour period that elapses between successive heat treatments in UHV condition.\(^{(117)}\) Similar behavior was demonstrated earlier for graphitized carbon fiber\(^{(128)}\) and activated carbon\(^{(116)}\), which demonstrated that outgassing above 1273 K is required to remove
essentially all functional groups. Therefore, it can be concluded that the increase in mercury adsorptive capacity of HOPG after 1273 K heat treatment was caused by the removal of chemical functionalities from the surface. Similar behavior was observed for the adsorption of propane on HOPG\textsuperscript{111} and xenon on single wall carbon nanotubes.\textsuperscript{52, 53} Propane, a non-polar organic, has unfavorable interactions with functional groups that exist on air-cleaved HOPG. Heating to 1273 K removed these functionalities and resulted in over an order of magnitude increase in propane adsorption capacity. The degree of the increase in mercury adsorption capacity upon heating HOPG to 1273 K was significantly lower than that observed for propane indicating stronger interaction between surface functional groups and non-polar organic molecules than metallic atoms.

An important objective of this study was to understand the role of topological heterogeneity on adsorption and desorption on HOPG under UHV conditions. In order to introduce defect sites and etch pits on HOPG, an air-cleaved HOPG sample was subjected to plasma treatment at controlled oxygen pressure. It has been shown that high temperature oxidation in air creates low density (< 1\% by surface area) of monolayer deep etch pits at existing defects of HOPG, while maintaining the flatness of the graphite surface.\textsuperscript{102, 122, 123, 129} Plasma oxidation, however, creates mechanical damage on initially flat surfaces that augments pre-existing defect sites.\textsuperscript{102} Plasma oxidation etches the surface, resulting in highly roughened surfaces as confirmed by AFM measurements.\textsuperscript{102} As shown in Figure 3-8, the air-cleaved HOPG (Figure 3-8 (a)) shows a clean and flat surface except for a few steps of ~2.5 nm height. A significant density of defects (dark spots in Fig 3-8 (b) and (c)) is observed on the 20 min plasma-oxidized HOPG surface (20-p-HOPG). Most defects are around 100 nm in diameter, and from ~1 to ~10 nm in depth. Plasma oxidation clearly results in the formation of topologically
heterogeneous surface distinct from the topologically homogeneous air-cleaved surface. Longer exposure to plasma oxidation does not lead to essential changes in the morphology of HOPG samples. Figure 3-8 (d) illustrates an increase in defect diameter (from ~100 to 500 nm) and depth (from ~ 50 to 200 nm) following 90 min plasma oxidation (90-p-HOPG), a commonly observed behavior.\(^{102}\)

The 20 min plasma-oxidized HOPG and 90 min plasma-oxidized HOPG samples were subjected to heat treatment at 1273 K before mercury exposure to ensure that they contain no chemical functionalities and that only the impact of topological heterogeneity on mercury uptake is studied. Figure 4-30 shows a series of TPD spectra for mercury dosed at 100 K on plasma oxidized HOPG, while Figure 4-31 compares relative amounts of mercury adsorbed on virgin and plasma oxidized samples.

The impact of topological heterogeneity on elemental mercury adsorption can be evaluated by comparing TPD spectra for 1273 K treated a-HOPG (Figure 4-27 (b)) to those shown in Figure 4-30. The changes in the TPD spectra resulting from the difference in topology caused by plasma oxidation are minimal. There is no evidence that the defect sites caused by plasma treatment created new adsorption sites for mercury under the experimental condition used in this study because all desorption peaks appear at almost identical temperature. In addition, the heat of adsorption on plasma-oxidized samples, which was also estimated using coverage dependant first order kinetics, is within the error range of the heat of adsorption determined for air cleaved HOPG sample. As shown in Figures 4-30 and 4-31, the mercury adsorption capacity of HOPG increased after 20 min plasma oxidation, but no significant increase in the capacity was observed with further plasma oxidation. Therefore, it can be concluded that defect sites created by plasma oxidation only provided additional surface area for mercury adsorption.
On the other hand, the adsorption of an organic adsorbate (propane) was drastically different for air-cleaved and plasma-oxidized HOPG.\textsuperscript{(117)} Plasma-created defects provided adsorption sites with stronger binding energy and faster adsorption kinetics for propane molecules as indicated by the appearance of the high temperature peak, the sequence of peak growth in a TPD spectra, and additional adsorption capacity.

The fact that there is no further increase in mercury adsorptive capacity with 90-p-HOPG sample over 20-p-HOPG sample also suggest that micro-pores are more important for mercury adsorption than meso- or macropores since after 20 min plasma oxidation of HOPG surface already produced defects with meso- and macro-sized ones and 90 min plasma oxidation just expanded existing defect site in size and depth.\textsuperscript{(125)} It is well known that plasma oxidation initially attacks the pristine HOPG surface (basal plane) and that longer treatment leads to further expansion of initial defects.\textsuperscript{(102)} As shown in Figure 3-8, 90 min plasma oxidation simply enlarged all smaller defects created on HOPG after 20 min treatment. However, even for a 20 min plasma oxidized sample, most of the defects are approximately 100 nm in diameter and fall in the mesopore region as classified by IUPAC, which explains limited increase in capacity for 20-p-HOPG over a-HOPG.

4.5.2 Fixed-bed Adsorption Studies with Activated Carbon

Breakthrough of elemental mercury from an adsorber charged with outgassed BPL carbon measured at different adsorption temperatures and influent mercury concentrations of 70 and 1120 µg/m\textsuperscript{3} are shown in Figure 4-32. It can be seen that mercury uptake increases with a decrease in the reaction temperature, which follows the well-documented impact of temperature
on adsorption. Breakthrough studies with influent mercury concentrations of 540 and 780 µg/m³ were also performed in this study (data not shown here). Mercury uptake as a function of equilibrium vapor pressure at 100% breakthrough, that was estimated by integrating the breakthrough curves at different bed temperatures, is shown in Figure 4-33. It can be observed that the mercury adsorptive capacity increases linearly with an increase in influent mercury concentration for all adsorption temperatures, which suggests mercury adsorption on activated carbon occurs in Henry's law region under the experimental conditions used in this study. Such behavior can be explained by the fact that the highest mercury concentration used in breakthrough experiments was less than 5% of the vapor pressure at that temperature. In that case, mercury atoms are isolated from their neighbors and the equilibrium relationship between the gas phase and adsorbed phase concentration is linear.

The relationship between the mercury equilibrium pressure and the reaction temperature at constant coverage can be approximated by the Clausius-Clapeyron equation given in equation 4-3. Figure 4-34 depicts adsorption equilibrium data in the form of lnP versus 1/T for constant coverage of 200 µg/g at different adsorption temperatures investigated in this study. It is quite obvious that the experimental data point to two distinct regions with 348 K as the common point. Linear fit to data collected below 348 K is obtained with the heat of adsorption of 97 ± 5 kJ/mol while the data collected above 348 K revealed the heat of adsorption of 579 ± 25 kJ/mol. Compared to the heat of vaporization of mercury at 298 K of 64.3 kJ/mol, it is clear that mercury adsorption on activated carbon below 348 K is accomplished through physisorption, while the reaction temperatures above 348 K promote chemisorption. These findings are supported by previous studies which suggested that mercury adsorption by activated carbon occurs through a combination of chemisorption and physisorption at ambient temperature and
that chemisorption predominates at higher temperatures.\(^{(37, 130)}\) The heat of adsorption of mercury on activated carbon at low temperatures (below 348 K) is in reasonable agreement with the value of \(82 \pm 3 \text{ kJ/mol}\) estimated from the TPD studies with HOPG at UHV conditions. It can, therefore, be concluded that UHV studies with simple model carbonaceous surface can be used to investigate mercury adsorption on activated carbon in the physisorption region.

The data presented in Figures 4-27 and 4-29 demonstrated extremely limited impact of chemical functional groups on mercury uptake by HOPG. The impact of activated carbon surface chemistry on mercury uptake was studied using fixed-bed adsorption experiments with different samples of BPL activated carbon. Mercury breakthrough was measured for virgin (as received) BPL carbon and BPL carbon that was outgassed at 423 K (BPL-423) and 1173 K (BPL-1173). The heat treatment at 423 K was chosen because the water present on the carbon surface can be removed by this low temperature treatment without changing or damaging morphological structure of activated carbon\(^{(131)}\) or removing the significant amount of oxygen containing functional groups that are normally stable up to 473 K.\(^{(10)}\) The heat treatment at 1173 K was chosen to completely remove oxygen-containing functional groups from the carbon surface.\(^{(93)}\)

Figure 4-35 compares mercury breakthrough at 293 and 423 K from fixed-bed adsorbers charged with different BPL samples using influent mercury concentration of 70 \(\mu\text{g/m}^3\). The operating temperatures of 293 and 423 K were selected based on the findings shown in Figure 4-34 to facilitate physisorption and chemisorption mechanisms for mercury uptake, respectively. Breakthrough profiles on Figures 4-35 (a) and (b) suggest that the virgin BPL sample with original moisture content had the highest mercury adsorption capacity among the samples tested in this study. This observation agrees with the findings of Li et al.,\(^{(83)}\) who also suggested that the surface water content of a carbon-based sorbent significantly enhances mercury uptake.
However, the water content was less significant for mercury uptake in chemisorption region because water is vaporized and removed from the carbon surface during the adsorption experiment at high bed temperatures. Figure 4-35 (a) also shows that mercury uptake capacity in a physisorption region increases by about 25 % as a result of the removal of surface functional groups by outgassing at 1123 K. Possible explanation for such behavior is that these functional groups restrict access of mercury molecules to micro pores that are very important for physisorption as demonstrated in studies with plasma-oxidized HOPG. On the other hand, removal of surface functionalities has an adverse impact on mercury uptake by chemisorption as shown in Figure 4-35 (b). Such behavior was expected because oxygen containing functional groups are important chemisorption sites for elemental mercury.\(^{132}\)

The key findings of this study open the possibility to apply scientific information obtained from the studies with simple surfaces like HOPG under ideal conditions (UHV) to industrial sorbents process conditions. HOPG surface can be modified chemically and topologically by plasma oxidation to simulate key features of activated carbon adsorbents. A good agreement between the heats of adsorption determined from TPD studies under UHV conditions and breakthrough experiments at atmospheric pressure validates the proposed approach to bridge the traditional pressure gap in surface science.
5.0 SUMMARY AND CONCLUSIONS

This study investigated adsorption and desorption of model adsorbents representative of polar (acetone) and non-polar (propane) organic compounds and metallic (elemental mercury) compounds on a model carbonaceous surface (HOPG) under ultra high vacuum (UHV) conditions. Optical differential reflectance (ODR) technique was proven to be a powerful tool to investigate surface adsorption and desorption under the conditions where the temperature programmed desorption (TPD) technique can not be used, e.g., high pressure or reversible adsorption. The results showed a strong correlation between ODR determined in real time and a conventional surface science probe like TPD. This study also evaluated the effects of surface functional groups and topological heterogeneity on adsorption and desorption using and plasma oxidized HOPG as model carbonaceous surfaces. The key tasks that have been accomplished in this study include:

1. Demonstrate the utility of ODR technique for surface science studies on carbonaceous surfaces by comparison with conventional methods like TPD. This task was accomplished using acetone as a model adsorbate.

2. Establish the superiority of ODR technique over TPD to study reversible adsorption on HOPG using propane as a model adsorbate.

3. Determine the impact of oxygen containing functional groups on HOPG on adsorption and desorption of polar (acetone) organic compounds.

4. Establish the methodology to study the impact of chemical and topological heterogeneity (presence of pores) on adsorption/desorption on carbonaceous surfaces. This task was
accomplished using virgin and plasma-oxidized HOPG and propane as model adsorbent-adsorbate system.

5. Attempt to bridge the traditional pressure gap in surface science and extend the findings from UHV studies to industrial applications. This task was accomplished by studying mercury adsorption on model (HOPG) and real (activated carbon) carbonaceous surfaces under UHV and atmospheric pressure. The discussion that follows represents a summary of the accomplishments for each task of this study.

**Task 1**

Optical differential reflectance (ODR) and temperature programmed desorption (TPD) were combined to investigate adsorption and desorption of a volatile polar organic compound (acetone) on a semi-metal surface (highly oriented pyrolytic graphite, HOPG) under ultra high vacuum (UHV) conditions. The ODR change induced by adsorption/desorption was shown to correlate with relative coverage as determined by TPD experiments. TPD spectra revealed the existence of monolayer, bilayer and multilayer adsorption states with coverage dependent binding energies, reflecting inter-adsorbate interactions. Absolute acetone coverage was estimated from ODR experiments and adsorption was found to follow Volmer-Weber rather than layer-by-layer growth mode. ODR showed a great promise to monitor sub-monolayer coverage of organic compounds on carbonaceous surfaces.
**Task 2**

Propane adsorption and desorption on HOPG was studied to demonstrate the ability of the ODR technique in situations where the TPD technique cannot be used. Experiments were carried out for surface temperatures from 90 K to 110 K and pressures from ultra high vacuum up to $10^{-4}$ torr. The results showed that propane adsorbs in a layer-by-layer fashion. The reversibility of bilayer (and multilayer) formation can be clearly seen from the ODR signal increase and decrease caused by increases and decreases in propane pressure, while the monolayer of propane is formed regardless of propane pressure. The ODR method is able to dynamically follow the adsorption process as a function of time over a wide pressure range. The TPD measurements provide an estimate of the binding energy of propane monolayer on HOPG of $30 \pm 2$ kJ/mol. ODR measurements were used to estimate the heat of adsorption at incipient second layer formation of $23 \pm 2$ kJ/mol. The layer-by-layer formation feature can be observed by molecular simulations, showing a good agreement in the heat of adsorption for bilayer. This study clearly showed that ODR is suitable for investigating adsorption phenomena in real time and over a wide pressure range.

**Task 3**

Oxygen-containing functional groups that exist on both air-cleaved HOPG and plasma-oxidized HOPG can be removed by thermal treatment at over 500 K. Once these functional groups are removed, there is little re-adsorption occurring in UHV conditions. TPD results revealed a high temperature acetone desorption peak, which cannot be observed before significant amount of chemical functionalities are removed from HOPG surface. Thus, the
removal of oxygen containing functional groups on HOPG surfaces provides access for a polar organic adsorbate to a clean carbonaceous surface. These results suggest that carbonaceous surfaces should be thermally treated at temperatures above 1000 K to provide access to a non-functionalized surface. However, carbon sorbents may not need high temperature treatment for adsorption of polar organics, depending on the adsorption temperature. The energetics of acetone desorption from clean HOPG surface were estimated using both TPD simulation and variable heating rate experiments. The heat of adsorption of acetone using coverage dependant first order kinetics was estimated to be $55.5 \pm 3.0$ kJ/mol and $51.5 \pm 3.0$ kJ/mol for monolayer and bilayer, respectively. The thermal desorption spectra of acetone multilayer state are usually described by a zero order rate law. The activation energy for desorption of the acetone multilayer from graphite was determined using this procedure to be $31 \pm 2$ kJ/mol.

**Task 4**

The effects of chemical functional groups and surface morphology on the adsorption/desorption behavior of a model non-polar organic adsorbent (propane) on model carbonaceous surfaces: air-cleaved highly oriented pyrolytic graphite (HOPG) and plasma-oxidized HOPG, were investigated using temperature programmed desorption (TPD). The presence of oxygen functional groups almost completely suppresses propane adsorption at 90 K. However, these groups can be removed from both air-cleaved and plasma-oxidized HOPG by thermal treatment ($> 500$ K), leading to more than an order of magnitude increase in adsorption capacity. Oxygen related surface functional groups exist on HOPG surface. They apparently block available adsorption sites for non-polar organics. Heat treatment can remove existing functional groups to make these adsorption sites more accessible. It is essential for both air-
cleaved HOPG and plasma-oxidized HOPG to be outgassed at over 1273 K for all the adsorption sites to be chemically accessible for propane molecules.

Plasma oxidation, however, creates mechanical damage on initially flat surface that augments pre-existing defect sites which vary from ~10 to ~200 nm in diameter, and from ~1 to ~10 nm in depth. These defects serve as additional adsorption sites with stronger binding energy as indicated by the appearance of high temperature TPD features that do not exist on air-cleaved HOPG. The downward shift in peak temperature with increasing exposure suggests sequential filling of the defect sites, with the higher binding energy sites being filled first. In addition, the TPD areas for plasma-oxidized HOPG are always greater than those for the air-cleaved HOPG under identical exposure conditions. The effect of morphological heterogeneity is evident for plasma-oxidized HOPG as this substrate provides greater surface area available for adsorption as well as higher energy binding sites. It can be concluded that HOPG surface can be modified chemically and topologically by plasma oxidation to simulate key features of activated carbon adsorbents. The key findings of this study open the possibility to apply scientific information obtained from the studies with simple surfaces like HOPG under ideal conditions (UHV) to industrial sorbents and realistic process conditions.

**Task 5**

Temperature programmed desorption (TPD) with a model carbonaceous material (highly oriented pyrolytic graphite, HOPG) under ultra-high vacuum (UHV) conditions and fixed bed adsorption by activated carbon (BPL) at atmospheric conditions were combined to investigate the effects of chemical and morphological heterogeneities on mercury adsorption by
carbonaceous surfaces in an attempt to bridge the traditional pressure gap between UHV and atmospheric conditions in surface science. TPD results showed that mercury adsorption at 100 K onto HOPG surfaces, with and without chemical functional groups and topological heterogeneity created by plasma oxidation, occurs through physisorption. The removal of oxygen containing functional groups from HOPG surface slightly enhances mercury physisorption. Plasma oxidation of HOPG provides additional surface area for mercury adsorption. However, the pits created by plasma oxidation are more than 100 nm in diameter and do not simulate microporosity that predominates in activated carbons.

Mercury adsorption by activated carbon at atmospheric pressure occurs through two distinct mechanisms. Physisorption governs mercury adsorption at temperatures below 348 K while chemisorption predominates at adsorption temperatures above 348 K. The presence of water on activated carbon surface enhances mercury uptake by both physisorption and chemisorption. While oxygen-containing functional groups reduce mercury physisorption by blocking access to the micropores, no significant impact of oxygen functionalities was observed in the chemisorption region.

Overall, an optical technique (ODR) was proven to be a versatile tool to investigate surface adsorption and desorption under the conditions where TPD technique cannot be used due to high pressure or reversible adsorption. Surface chemical functional groups, which exist on HOPG surface, exert significant impact on the adsorption and desorption of polar and non-polar organics, but not so much for metallic species. Creating defects by plasma treatment of HOPG and adsorption/desorption studies under UHV conditions provides a great opportunity to understand the fundamental aspects of adsorption/desorption on high surface area carbonaceous materials (e.g., the impact of chemical and/or topological heterogeneity). A good agreement
between TPD studies under UHV conditions and breakthrough experiments at atmospheric pressure validates the proposed approach to bridge the traditional pressure gap in surface science.

5.1 Significance of the Study

This study demonstrated that in the presence of oxygen containing functional groups and topological heterogeneity (pores or defects) on carbonaceous surfaces, the adsorption capacity can vary significantly depending on the characteristics of the adsorbate. Experimental results showed that the removal of oxygen functional groups from HOPG surfaces leads to significant increase in adsorption capacity for propane. It can therefore be concluded that oxygen containing functional groups exhibit adverse impact on the uptake of non-polar organic adsorbates. One practical implication of this finding is that activated carbon manufacturers may find it beneficial to take necessary steps to prevent excessive oxidation of the carbon surface during the manufacturing process (e.g., reduce the oxygen content of the activation agent) if that adsorbent is to be used for the control or recovery of non-polar organic compounds.

On the other hand, removal of oxygen-containing functional groups from HOPG resulted in a slight increase in the adsorption capacity for mercury that can serve as a representative of metallic vapors. Furthermore, the removal of oxygen containing functional groups from HOPG resulted in higher energy binding sites on these carbonaceous surfaces for the adsorption of polar organic compounds (i.e., acetone), while the total adsorption capacity for these compounds remained unchanged regardless of the presence or absence of these groups. Therefore, it can be suggested that carbon sorbents that will be used for the uptake of metallic compounds, most notably, mercury, and polar organic compounds may not require special steps to prevent
excessive oxidation during manufacturing and should not be subjected to high temperature cleaning procedure (i.e., outgassing) as a pretreatment step. On the other hand, high temperature heat treatment may be one way to remove oxygen containing functional groups from the adsorbent surface to enhance its uptake efficiency for non-polar organic compounds.

This study also showed that the UHV studies with air-cleaved HOPG could be used to obtain fundamental insight into the adsorption processes occurring on high surface area carbonaceous materials (e.g., activated carbon) operated in physisorption region and under more realistic pressures (i.e., atmospheric). This extremely important finding is for the first time advanced by the results of this study and is supported by the fact that similar binding energies were obtained for mercury adsorption on HOPG operated under UHV conditions and commercially available activated carbon operated at lower adsorption temperatures (i.e., below 348 K). It is likely that the development of future adsorbent materials will take advantage of UHV studies because they allows precise determination and accurate understanding of adsorption processes on a molecular level. Such understanding will be crucial if we were to develop highly specialized adsorbents and take full advantage of new carbonaceous materials (e.g., nanotubes, nanofibers, etc.) that are currently quite expensive and should be used only for high value-added application (separation of valuable products like proteins, medications, noble metals, etc.)

Plasma oxidation is the experimental method that was deployed in this study in order to create adsorbents with high surface area to be able to study the impact of surface heterogeneity on adsorption process and offer a better approximation for industrial sorbents like activated carbon. However, the plasma treatment utilized in this study created mostly large pores (> 10 nm) that are representative of meso- and macropores in activated carbons. Therefore, the pores
created during a 20-min plasma treatment only provide additional surface area for the adsorption of propane and mercury. While these large pores resulted in only about 10% increase in mercury uptake, propane adsorption was enhanced by over an order of magnitude and even the propane binding energy increased due to the introduction of this surface heterogeneity.

Therefore, it could be concluded that the relatively large pores (> mesopore) existing in carbon materials are not as significant in mercury adsorption as the smaller pores (micropore), which can be explained by capillary condensation that is facilitated in the pores whose size is on the same order of magnitude as the adsorbate molecule. Microporosity should be promoted during sorbent manufacturing (e.g., higher degree of burnout, more aggressive activating agent) in order to optimize particular sorbent for mercury removal.

This study also showed that mercury adsorption by activated carbon at atmospheric pressure and by HOPG at the UHV conditions occurs through two distinct mechanisms. Physisorption, which is typically considered reversible and results from low-level non-specific van der Waals forces, governs mercury adsorption at temperatures below 348 K. On the other hand, chemisorption, which is typically considered irreversible and results from high energy covalent bonds, predominates at adsorption temperatures above 348 K. Based on these findings, it can be concluded that any sorbent removing mercury from a contaminated air stream using a physisorption mechanism will not be a good long-term solution for mercury control because these weak bonds between mercury and adsorbent surface can be easily broken leading to mercury leaching into the environment. Such outcome is particularly undesirable in the case of mercury because there is no known mechanisms that leads to mercury degradation, while a well-known methylation process leads to the creation of highly toxic methyl mercury forms.
The presence of water on activated carbon and HOPG surface enhances mercury uptake by both physisorption and chemisorption. While oxygen-containing functional groups reduce mercury physisorption on activated carbon by blocking access to the micropores, no significant impact of oxygen functionalities was observed in the chemisorption region.

This study suggests that the high temperature (over 900 °C) treatment of carbon substrate provides only about 10 % increase of the mercury uptake capacity, thus treatment at high temperature of carbon substrate may not be a cost effective method for both low and high temperature flue gas conditions. The optimization of pore size distribution or finding favorable chemical functional groups should be much better approach to obtain a cost effective carbon adsorbent for mercury removal.
6.0 SUGGESTIONS FOR FUTURE WORK

Environmental engineering is faced with the lack of fundamental understanding of molecular interactions in the complex mixtures and at the mineral, organic, and biological interfaces that characterize environmental systems. This is particularly troubling because many of the techniques and associated methods for data interpretation have been developed to study well defined systems, e.g. single crystal under ideal conditions (ultra high vacuum). However, the application of these tools to environmental samples is very challenging due to their amorphous, complex, and multiple nature.

From the results of current study, it is clear that a linear optical differential reflection technique can be used to monitor adsorption of organic and metallic adsorbates. It can be suggested that improvement of the sensitivity of ODR is needed so that the differential ODR signal as a function of temperature in the desorption can be used in place of QMS for doing TPD at high pressure. It was also demonstrated that UHV studies using chemically and morphologically modified HOPG as a model carbon surface could be a possible approach to investigate the roles of chemical complexes and carbon morphological structure on mercury uptake. However, the role of chemical functional groups and morphological structure for efficient uptake of various other pollutants has not yet been determined. Therefore, the identification of the exact functional groups on carbonaceous surface and the investigation of the role of those functional groups should be followed.

Future studies may focus on extending adsorption study with model carbonaceous surface under UHV conditions using strategy that combines multiple techniques to fully characterize the many components of environmental samples. For instance, nano-scale carbon materials, such as
nanotubes or nano-carbon fibers, have attracted huge attention for controlling organic or inorganic gas and liquid phase pollutants by adsorption. In order to provide insight into environmental phenomena of these systems, experimental studies will be required. This work can be based on experimental analytical methodologies that I have used and developed through my research. However, in order to understand these phenomena more quantitatively, one should apply more advanced surface science approaches, such as scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRAS), etc.

It is well known that the performance of sulfur-impregnated activated carbons for mercury uptake is strongly related to physical and chemical properties of both the sulfur and carbon. However, in order to gain a better understanding of mercury uptake, it is important to incorporate information on the micro–structure and surface chemistry of the carbon. It is also important to expand molecular-level insight into adsorption, dissociation, and subsequent impregnation of sulfur containing compounds on carbonaceous surface. This work may offer the potential to understand the formation of HgS inside the carbon and the basic science underlying the adsorption of mercury on sulfur impregnated activated carbon.

The presence of a particular combination of gas constituents in the carrier gas, especially those that can affect the performance of carbonaceous adsorbents, (i.e., SO₂, NO and water) may also have some impacts on the carbon surface. Carbon may selectively adsorb certain gases, which could change the surface of that carbon. Furthermore, these gas molecules may compete for active sites with mercury. It may be very helpful to investigate this effect on selective adsorption on a microscopic level to explain findings from pilot scale column tests in terms of surface chemistry.
Novel carbon materials such as carbon nanotubes and activated carbon fiber have potential uses in selective adsorption of toxic species and selective catalysts or catalytic supports, since these carbon materials have distinct advantages over the activated carbon sorbents used industrially due to their abilities of modification on the molecular level to adsorb or transport specific classes of molecules. One may be able to extend the experimental approach used in this study to a study of the essential physics of the interactions on these nanoporous carbonaceous surfaces.
APPENDIX
A1. Propane Heat of Vaporization (at 100 K)

- Calculation of heat of vaporization of propane at 100 K

\[ \Delta H_{vap}(231K) \]

\[ \text{Propane (liquid) at 231 K} \rightarrow \text{Propane (gas) at 231 K} \]

\[ \text{Heat (Y)} \]

\[ \text{Propane (liquid) at 100 K} \rightarrow \text{Propane (gas) at 100 K} \]

\[ \Delta H_{sub}(100K) \]

- \( \Delta H_{vap}(231K) \) = Propane heat of vaporization at 231 K = 19.04 kJ/mol \(^{(96)}\)

- Energy needed to heat liquid propane from 100 K to 231 K

\[ Y = \int_{100}^{231} C_p[\text{propane (l)}]dT = \int_{100}^{231} [59.642 + 0.32831T - 0.0015377T^2 + (3.6539 \times 10^{-6})T^3]dT \]

\[ = 11.6 \text{ kJ/mol} \]

\( C_p[\text{propane (l)}] \) = Heat capacity of liquid propane \(^{(115)}\)

- Energy needed to cool vapor propane from 231 K to 100 K

\[ Z = \int_{231}^{100} C_p[\text{propane (g)}]dT \]

\[ = \int_{231}^{100} [28.277 + 0.116T + 0.00019597 T^2 - (2.3271 \times 10^{-7})T^3 + (6.8669 \times 10^{-11})T^4]dT \]

\[ = -6.81 \text{ kJ/mol} \]

\( C_p[\text{propane (g)}] \) = Heat capacity of vapor propane \(^{(115)}\)

The heat of vaporization of propane at 100 K = \( \Delta H_{vap}(231K) + Y + Z \)

\[ = 19.04 + 11.64 - 6.81 \]

\[ = 23.87 \text{ kJ/mol} \]
A2. Acetone Heat of Sublimation (at 130 K) Calculation

- **Calculation of heat of sublimation of acetone at 130 K**

\[ \Delta H_{\text{sub}}(130K) = \Delta H_{\text{fus}}(179K) + X + \Delta H_{\text{vap}}(329K) + Y + Z \]

\[ = 5.69 + 4.31 + 18.13 + 29.1 - 12.95 \quad = 44.28 \text{ kJ/mol} \]
A3. Mercury Heat of Sublimation (at 200 K) Calculation

- Schematic view for the calculation of heat of sublimation of mercury at 200 K

- $\Delta H_{\text{ fus}}(234\text{K}) = \text{Mercury heat of fusion at 234 K: 2.3 kJ/mol}^{(96)}$

- $\Delta H_{\text{ vap}}(629\text{K}) = \text{Mercury heat of vaporization at 629 K = 59.11 kJ/mol}^{(96)}$

- $X = \int_{200}^{234} C_p[\text{mercury (s)}] \, dT = \int_{200}^{234} [21.905 + 0.023673 + 0.00001707 \, T^2] \, dT$

- Energy needed to heat solid mercury from 200 K to 234 K

  $C_p[\text{mercury(s)}] = \text{Heat capacity of solid Hg}^{(115)}$

- Energy needed to heat liquid mercury from 234 K to 629 K

  $Y = 59.11 + \int_{234}^{629} C_p[\text{mercury(l)}] \, dT$

  $= 59.11 + \int_{234}^{629} [30.388 - 0.01098T + (9.4412 \times 10^{-6})T^2 + (6.7418 \times 10^{-10})T^3] \, dT$

  $= 10.9$

  $C_p[\text{mercury(l)}] = \text{Heat capacity of liquid Hg}^{(115)}$

- Energy needed to cool vapor mercury from 629 K to 200 K

  $Z = \int_{629}^{200} C_p[\text{mercury(g)}] \, dT$

  $= \int_{629}^{200} [20.79 - 0.00001831T^2 + (2.3525 \times 10^{-8})T^2 - (1.0144 \times 10^{-11})T^3 + (1.3685 \times 10^{-15})T^4] \, dT$

  $= -8.92 \text{ kJ/mol}$

  $C_p[\text{mercury(g)}] = \text{Heat capacity of vapor Hg}^{(115)}$

- The heat of sublimation of mercury at 200 K

  $= X + \Delta H_{\text{ fus}}(234\text{K}) + \Delta H_{\text{ vap}}(629\text{K}) + Y + Z = 0.95 + 2.3 + 59.11 + 10.9 - 8.92$

  $= 64.34 \text{ kJ/mol}$
A4. Properties of Adsorbates

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<th>Mercury (Hg)</th>
<th>Acetone (C\textsubscript{3}H\textsubscript{6}O)</th>
<th>Propane (C\textsubscript{3}H\textsubscript{8})</th>
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<tr>
<td><strong>Molecular weight (g/mol)</strong></td>
<td>200.59\textsuperscript{(96)}</td>
<td>58\textsuperscript{(96)}</td>
<td>44.1\textsuperscript{(96)}</td>
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<td><strong>Boiling point (T\textsubscript{b},K)</strong></td>
<td>629.73\textsuperscript{(96)}</td>
<td>329\textsuperscript{(96)}</td>
<td>230.9\textsuperscript{(96)}</td>
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<td><strong>Melting point (T\textsubscript{m},K)</strong></td>
<td>234.17\textsuperscript{(96)}</td>
<td>229\textsuperscript{(96)}</td>
<td>83.3\textsuperscript{(96)}</td>
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<tr>
<td><strong>Refractive index</strong></td>
<td>1.91\textsuperscript{+i} 5.15 at 619.9 nm\textsuperscript{(133)}</td>
<td>1.36 at 589 nm\textsuperscript{(96)}</td>
<td>1.4745 at 589 nm\textsuperscript{(96)}</td>
</tr>
<tr>
<td><strong>Triple point (K)</strong></td>
<td>234.17\textsuperscript{(96)}</td>
<td>229\textsuperscript{(96)}</td>
<td>83.3\textsuperscript{(96)}</td>
</tr>
<tr>
<td><strong>Critical point (K)</strong></td>
<td>1750\textsuperscript{(96)}</td>
<td>508\textsuperscript{(96)}</td>
<td>369.83\textsuperscript{(96)}</td>
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<td><strong>Density (g/cm\textsuperscript{3})</strong></td>
<td>13.53 at 20 °C\textsuperscript{(96)}</td>
<td>0.7899 at 20 °C\textsuperscript{(96)}</td>
<td>0.493 at 25 °C\textsuperscript{(96)}</td>
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<tr>
<td><strong>Heat capacity (J/mol-K)</strong></td>
<td></td>
<td></td>
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<tr>
<td>Sol</td>
<td>28.196 \textsuperscript{at 228K\textsuperscript{(115)}}</td>
<td>93.32 \textsuperscript{at 178 K\textsuperscript{(115)}}</td>
<td>52.32\textsuperscript{(126)} \textsuperscript{at 84 K}</td>
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<td>Liq</td>
<td>27.87 \textsuperscript{at 298K\textsuperscript{(96)}}</td>
<td>127.53 \textsuperscript{at 298K\textsuperscript{(115)}}</td>
<td>117.67 \textsuperscript{at 298K\textsuperscript{(115)}}</td>
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<td>Gas</td>
<td>20.79 \textsuperscript{at 298K\textsuperscript{(96)}}</td>
<td>80.32 \textsuperscript{at 329K\textsuperscript{(115)}}</td>
<td>62.86 \textsuperscript{at 230.9K\textsuperscript{(11)}}</td>
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<td><strong>Heat of vaporization (kJ/mol)</strong></td>
<td>59.11 \textsuperscript{at T\textsubscript{b}\textsuperscript{(96)}}</td>
<td>28.31 \textsuperscript{at T\textsubscript{b}\textsuperscript{(96)}}</td>
<td>19.04 \textsuperscript{at T\textsubscript{b}\textsuperscript{(96)}}</td>
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<td><strong>Heat of fusion (kJ/mol)</strong></td>
<td>2.3 \textsuperscript{at T\textsubscript{m}\textsuperscript{(96)}}</td>
<td>5.69 \textsuperscript{at T\textsubscript{m}\textsuperscript{(96)}}</td>
<td>3.53 \textsuperscript{at T\textsubscript{m}\textsuperscript{(96)}}</td>
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BIBLIOGRAPHY


98


FIGURES
Figure 2-1. Normalized difference in p-polarized reflectivity for a 5 Å layer of acetone on HOPG ($\varepsilon_3 = 5.04 + i 8.4$) and Cu ($\varepsilon_3 = -13.33 + i 1.24$) as a function of the angle of incidence at $\lambda = 655$ nm. The lines are prediction from equation 4-2.
Figure 2-2. Coordinate system describing the polarization state of light.
Figure 2-3. Schematic view of various carbon materials
Figure 3-1. Schematic of the UHV chamber and gas handling unit
Figure 3-2. Schematic of the dual sample mount: (a) side view and (b) front view.
Figure 3-3. Structure of HOPG. HOPG is a relatively new form of high purity carbon consisting of planes of well-defined honeycomb structure.
Figure 3-4. Schematic of O$_2$ plasma system
Figure 3-5. Experimental procedure for TPD experiments
Figure 3-6. Optical differential reflectance (ODR) System
Figure 3-7. Schematic view of AFM imaging
Figure 3-8. AFM images for (a) virgin HOPG, (b) and (c) O2 plasma oxidized HOPG for 20 min (d) for 90 min. Graphs under the images show cross sectional in height
Figure 3-9. Setup of the fixed-bed adsorber
Figure 3-10. Experimental system for fixed-bed breakthrough tests
Figure 4.1. TPD spectra for acetone on HOPG at 91 K (temperature ramp at 2.5 K/sec)
Figure 4-2. Integrated area of monolayer and bilayer of TPD features. The dotted lines are model fits assuming that adsorption follows Langmuir kinetics.
Figure 4-3. Schematic of the proposed growth model (Volmer-Weber) of acetone on graphite at 91 K.
Figure 4-4. Intensity of s and p-polarized light reflected from HOPG as a function of exposure induced by acetone adsorption at $1.2 \times 10^{-7}$ torr and 91 K.
Figure 4-5. ODR signal as a function of acetone exposure at 91 K
Figure 4-6. Correlation between ODR and TPD experiments for acetone adsorption on graphite. The solid line is a linear fit of experimental data ($R^2 = 0.995$)
Figure 4-7. (a) Background ODR signal for a clean surface (b) ODR signal during thermal desorption for a surface containing pre-adsorbed acetone
Figure 4-8. $\frac{d(ODR)}{dT}$ and TPD spectra as a function of temperature for graphite initially exposed acetone at 19L.
Figure 4-9. Schematic view of the three layer model. Each layer is described by its dielectric constant ($\varepsilon_i$). $d$ is the adsorbate overlayer thickness, $\phi$ is the angle of incidence.
Figure 4-10. ODR signal and TPD area resulting from adsorption of propane on graphite at 100 K as a function of exposure (a) and the correlation between ODR and TPD (b).
Figure 4-11. Propane adsorption on graphite at 90 K: ODR as a function of propane pressure.
Figure 4-12. Propane adsorption on graphite at (a) 90 and (b) 95, 100 and 105 K determined from ODR and molecular simulation as a function of propane pressure.\(^{(112)}\)
Figure 4-13. TPD of propane adsorption on HOPG at 90 K (temperature ramp at 2.5 K/sec)
Figure 4-14. Plots of the ln P versus 1/T. This approach reveals that the bilayer heat of adsorption of propane on graphite is $23 \pm 2$ kJ/mol.
Figure 4-15. Evolution of masses 16, 18, 28 and 44 amu during initial heat treatment of air-cleaved HOPG to different temperatures. Data for 16, 18 and 44 amu in the 1323 K scan are multiplied by 10 to aid in viewing
Figure 4-16. TPD spectra of acetone on HOPG after heat treatment at various temperatures. Note that identical vertical scales are used for all figures except for 473 K.
Figure 4-17. Area of each individual TPD peak. Areas were obtained by the deconvolution of TPD spectra for 25 L exposure.
Figure 4-18. Total area of TPD spectra for 25 L and 5 L exposure as a function of heat treatment temperature.
Figure 4-19. Experimental (symbols) and simulated (lines) TPD of acetone monolayer. The insert (a) shows the fitting using conventional pre-exponential factor ($10^{13}$ sec$^{-1}$) for 7 L exposure and insert (b) shows a fitting trial with zero order for 3 L exposure.
Figure 4-20. Acetone TPD for 7L exposure at different heating rates. The insert shows a graph of \( \ln(\beta/T_p^2) \) versus \( 1/T_p \).
Figure 4-21. TPD spectra at 29 m/e (propane) for air-cleaved HOPG after heat treatment at various temperatures. Note that identical vertical scales are used for all figures. Data for 473 K are multiplied by 10 to aid in viewing.
Figure 4-22. TPD areas for propane at 25 L exposure as a function of heat treatment temperature for air-cleaved and plasma-oxidized HOPG.
Figure 4-23. Evolution of masses 16, 18, 28 and 44 amu during initial heat treatment of plasma oxidized HOPG to different temperatures. Data for 16, 18 and 44 amu in the 1323 K scan are multiplied by 10 to aid in viewing.
Figure 4-24. TPD spectra for propane after 1173 K heat treatment for (a) air-cleaved HOPG (b) O₂ plasma-oxidized HOPG. The same arbitrary units are used in both figures to facilitate comparison.
Figure 4-25. TPD area of propane for air-cleaved and plasma-oxidized HOPG after 1173 K heat treatment.
Figure 4-26. Quantitative analysis of high temperature TPD peak of propane from plasma oxidized HOPG. (a) Coverage dependant first order simulation and (b) average heat of adsorption for both low and high temperature peak.
Figure 4-27. TPD spectra of mercury on air cleaved HOPG that was previously heated at (a) 473 K and (b) 1273 K
Figure 4-28. Modeling of TPD spectrum of mercury at 20 L exposure using coverage dependent first order desorption kinetics ($\alpha=0.003$)
Figure 4-29. TPD area as a function of mercury exposure for air-cleaved HOPG
Figure 4-30. TPD spectra of mercury on (a) plasma-oxidized HOPG for 20 min and (b) plasma-oxidized HOPG for 90 min. Note that both HOPG samples were pretreated at 1273 K and that identical scales are used for both figures.
Figure 4-31. TPD area as a function of mercury exposure for air-cleaved and 20 min (p-20-HOPG) and 90 min (p-90-HOPG) sample after 1273 K heat treatment.
Figure 4-32. Impact of temperature on mercury breakthrough from a fixed bed adsorber at influent mercury concentrations of (a) 70 µg/m$^3$ and (b) 1120 µg/m$^3$.
Figure 4-33. Mercury uptake capacity as a function of equilibrium pressure, $P_e$ at different adsorption temperatures (lines represent linear regression fit to experimental data)
Figure 4-34. Equilibrium pressure at 200 µgHg/gAC as a function of 1/T. Line (a) represents a linear fit to adsorption data collected below 348 K and line (b) is a linear fit to adsorption data collected above 348 K.
Figure 4-35. Impact of sample pretreatment on elemental mercury breakthrough from a fixed bed adsorber operated at (a) 293 K and (b) 423 K with influent mercury concentration of 70 µg/m³.
XXX. “Delineating the Subsurface: Using Geophysics to Identify Groundwater Flow Paths Applied in a Carbonate Aquifer”

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DELINEATING THE SUBSURFACE:
USING SURFACE GEOPHYSICS TO IDENTIFY
GROUNDWATER FLOW PATHS IN A CARBONATE AQUIFER

by

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Abstract
Pollution and alteration of surface and subsurface hydrology increasingly threaten karst areas. In order to protect these fragile and dynamic watersheds, efficient diagnostic methods must be adapted for use in complex karst settings. While application of surface geophysical techniques to karst problems is not new, its use to delineate possible flow paths of clean water is. This study examines stream loss in a small tributary of the Youghiogheny River known as Hoyes Run in Garrett County, Maryland. The stream bounds the pit of the Deep Creek limestone quarry, operated by Keystone Lime Company. During low flow, the stream abruptly terminates in a swallet, leaving approximately 100 m of dry bed. Two other zones of loss were located during periods of higher flow. Multiple resistivity profiles using the SuperSting™ Resistivity System were generated along the zone of stream loss. Dye trace using fluorescein™ confirmed the flow path of water from the stream into the quarry. Geologic examination of the area reveals several sizable known caves developed in the same limestone sequence [Greenbrier Formation, Loyalhanna Member (Ml)]; however, there are no known cave entrances in the immediate vicinity. Borehole confirmation is slated before remediation measures are executed. The study suggests that surface geophysics coupled with hydrologic and geologic analysis can locate possible flow paths for groundwater in a karst aquifer, even in the absence of obvious karst surface expression.
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TABLE OF CONTENTS

List of Tables
List of Figures
List of Appendices

Chapter

1 Introduction
   1.1 Purpose and Scope
   1.2 Location, Historical Use and Geologic Setting of Study Area
   1.3 Previous Use of Geophysics in Karst Studies

2 Methods
   2.1 Overview of Geophysical Applications
      2.1.1 Electrical Resistivity
      2.1.2 Electromagnetic Conductivity
      2.1.3 Ground Penetrating Radar
   2.2 Data Interpretation
      2.2.1 Data Processing
      2.2.2 Interpretation
      2.2.3 Data Correlation
   2.3 Hydrologic and Geologic Analysis
      2.3.1 Dye Trace
      2.3.2 Sedimentary and Structural Geology
      2.3.3 Fracture Analysis
      2.3.4 Regional Speleogenesis
   2.4 Borehole Drilling

3 Discussion of Results
   3.1 Stream loss location and interpretation
   3.2 Location of cavities
   3.3 Defining likely groundwater flow path

4 Conclusions and Further Study

References
INTRODUCTION:

Dry quarrying is a common approach to removing viable materials for aggregate production. As many of these rock units occur at or below the water table, in order to extract these resources, significant amounts of groundwater must be pumped from the active quarrying location. In a karst aquifer this process can have unpredictable results.

The objective of this study was to apply several methods of surface geophysical analysis to a stream loss problem near a limestone quarry, ultimately to distinguish between solution cavities containing air, sediment and water in order to best delineate groundwater flow paths. This information was instrumental in designing a remediation approach to correct or alleviate significant surface water impacts directly resulting from dry quarrying practice. Chiefly, the loss of the entire volume of Hoyes Run, a previously pristine trout stream with neutral pH and low sediment load, was being lost in a swallet that had developed in the streambed. Quarry management hoped that once the groundwater flow path was determined, a grouting solution could be enacted which would restore the stream and reduce energy expenditure associated with dewatering activities, while simultaneously improving the quality of water in the downstream portion beyond the swallet.

The selected study area is in the Sang Run quadrangle in Garrett County, Maryland. The quarry (known as Deep Creek) is leased by Keystone Lime. It is situated on a knob that is bordered on the southeast by Hoyes Run, a small tributary of the Youghiogheny River. The geology of the area, as described by Brezinski, is a very gently dipping sedimentary series of Mississippian age consisting of various limestone, dolostone, sandstone and shale units. The basal unit exposed in the quarry is the Loyalhanna member of the Greenbrier series. There is some evidence, however,
that the Burgoon Sandstone of the Purslane formation is now exposed at the quarry floor. The
quarriers refer it to as the “blue sand” while the Loyalhanna is referred to as the “blue lime.”
The region is fluviokarstic, with minimal karst surface expression. There is no evidence of
sinkholes per se, although springs do appear in the area in both the Deer Valley and Loyalhanna
Limestone members.

John Friend Cave is developed in the Loyalhanna Limestone, and occurs northwest of the quarry
at the base of Gap Hill. It is the only known cave in the area to have significant passage
development and appears to be hydrologically unrelated to the drainage system surrounding the
quarry. This is due to the fact that the topography is the geomorphological result of a gently
plunging irregular domal structure such that Ginseng Hill occurs on the northwest limb of the
fold while the quarry is situated on the southwestern plunge, or slightly closer to the axis.
Therefore Ginseng Run functions as a surface, and most likely a subsurface, drainage divide
isolating John Friend Cave from any groundwater associated with the Hoyes Run area.

The channel of Hoyes Run exposes the Loyalhanna limestone (Ml) in its bed for several hundred
meters until a red calcareous mudstone functioning as a cap for the Loyalhanna member contains
the entire volume. There is evidence that the previous quarry operators, Gaylord Fuel, made
attempts to repair several locations of bottom and lateral streambank volume loss. These efforts
included placement of brattice cloth and crushed fines, or larger gravel and geotextile, cement fill
and occlusion with sediment and stream gravels. There is, however, no record as to whether or
not these efforts were successful.

Stream loss was reactivated when Keystone Lime dewatered the mine pit after the quarry was
left dormant between lessees. It appears as though changes in sedimentation during that time
resulted in variable loss of flow into several swallets and lateral bank zones. This became pronounced upon dewatering of the quarry. A sizeable swallet was noted in the center of a small, structurally controlled meander. Over the course of the study, a total of three additional loss zones were detected. These zones were dynamic, often opening and closing with respect to changes in stream volume and sediment load. The protracted drought conditions in the region beginning in 1998 and continuing through the study period (summer, 2002) exacerbated this effect, where Garrett County experienced as much as a 30% shortfall in precipitation. Often areas where vortices over stream loss locations were detected during high flow later showed evidence of having silted shut. Reactivating these features simply required removal of debris from the target.

Although surface geophysics have been used extensively in carbonate bedrock areas, they have traditionally been limited to detection of cavities that are air or sediment filled, or sinkholes. By using a combination of traditional geology and hydrology, coupled with the application of surface geophysics, an analysis of the results indicated notable signal response characteristic that were quite different from location to location.

Geophysical studies of karst have generally not emphasized detection of indirect indicators of deeper conduits, or mapping of recharge features, such as soil pipes or filled collapse features overlying active karst conduits. (Ahmed, p. 26) Combined methods of electromagnetics (EM) and GPR were used by Benson and La Fountain (1984) to identify soil piping and deep cavity detection with some success. Cooper and Ballard (1988) used microgravity, spontaneous potential, various downhole methods, sonar, resistivity, and ground penetrating radar over known targets with varying success.
Most methods of comparison have focused on identifying sinkholes; however, Chamberlain, et. al (2000) successfully utilized ground penetrating radar (GPR) to delineate sediment-filled caves that were appropriate for archaeological excavation. They compared the findings of a GPR survey to a resistivity survey in the same location. While they did not find a correlation between shallow-surface anomalies detected by resistivity and deep anomalies detected by GPR, they determined that the presence of high resistance solid limestone close to the ground surface masked the effects of any structures located at depth. Although there is a strong correlation between the resistivity of limestone and natural water in residence in a limestone aquifer, when employed in the vertical dipole mode, EM measurements are capable of detecting dissolution enlarged joints (Yuhr, et.al, 1993).

It appears from the literature that success in karstic terrains is dependant upon the method selected and its appropriateness to the subsurface conditions. While an homogenous medium may be an ideal circumstance for effective results from GPR, 2-D resistivity may provide poor results. Similiarly, 2-D resistivity is much more successful in identifying shallow features, even when a clay-rich layer is present which would otherwise negate the radar signal of GPR.

4.1 Data Interpretation
   4.1.1 Data Processing
   4.1.2 Interpretation
   4.1.3 Data Correlation
4.2 Hydrologic and Geologic Analysis
   4.2.1 Dye Trace
   4.2.2 Sedimentary and Structural Geology
   4.2.3 Fracture Analysis
   4.2.4 Regional Speleogenesis
4.3 Borehole Drilling
METHODS:

An initial site evaluation was completed to assess the geology and characterize the stream loss. A number of maps, quarry records and verbal reports from the quarry operator were included in the subsequent plan to conduct geophysical activities. An analysis of the joint sets was conducted, along with stream and spring assessment in the region to better plan a dye trace.

Geophysics:

A variety of geophysical methods and types of equipment were assessed. The following units were selected for the initial phase of the study:

- **Ground Penetrating Radar (GPR)** – GSSI SIR 2000 unit utilizing 400 MHz and 200 MHz antennae
- **Terrain (Electromagnetic) Conductivity (EM)** – Geonics EM-31 conductivity unit in both horizontal and vertical dipole mode at 5 m intervals
- **Resistivity (2-D)** – Advanced Geosciences Sting/Swift Resistivity unit using 2 m electrode spacing on 56 electrode array, single-line deployment using dipole-dipole method.

Ground Penetrating Radar

From Keary & Brooks p. 225
Ground-penetrating radar (GPR) is a technique of imaging the subsurface at high resolution. Although analogous in some ways to the seismic methods, the propagation of radar waves through a medium is controlled by its electrical properties at high frequencies.

GPR is a non-destructive technique and can consequently be applied in urban and sensitive environments. GPR has many geological applications, such as imaging shallow soil and rock structure at high resolution, locating buried channels and mapping the water table. It also has several non-geological uses such as in archaeology for the location of buried walls or cavities, and in forensic investigations, for the location of recently-disturbed ground where a burial has taken place.

GPR is similar in its principle to seismic reflection profiling and sonar surveying. A short radar pulse in the frequency band of 10-1000 MHz is introduced into the ground. Radar velocities are controlled by the dielectric constant (relative permittivity) and conductivity of the subsurface.

**Terrain (EM) Conductivity**

Electromagenetic (EM) surveying methods make use of the response of the ground to the propagation of electromagenetic fields, which are composed of an alternating electric intensity and magnetizing force. Primary electromagnetic fields may be generated by passing alternating current through a small coil made up of many turns of wire or through a large loop of wire. The response of the ground is the generation of secondary electromagnetic fields and the resultant fields may be detecting by the alternating currents that they induce to flow in a receiver coil by the process of electromagnetic induction.

The primary electromagnetic field travels from the transmitter coil to the receiver coil via paths both above and below the surface. Where the subsurface is homogenous there is no difference between the fields propagated above the surface and through the ground other than a slight
reduction in amplitude of the latter with respect to the former. However, in the presence of a conducting body the magnetic component of the electromagnetic field penetrating the ground induces alternating currents, or eddy currents, to flow in the conductor. The eddy currents generate their own secondary electromagnetic field which travels to the receiver. The receiver then responds to the resultant of the arriving primary and secondary fields so that the response differs in both phase and amplitude from the response to the primary field alone. These differences between the transmitted and received electromagnetic field reveal the presence of the conductor and provide information on its geometry and electrical properties.

An electromagnetic can penetrate a medium based on the fields frequency and the medium's electrical conductivity through which it is propagating. This results in the equation:

\[
d = \frac{503.8}{\sqrt{\sigma f}}
\]

Where \(d\) = depth of penetration (in meters)
\(\sigma\) = conductivity of the ground in S m\(^{-1}\)
\(f\) = frequency of the field in Hz

Therefore the depth of penetration increases as a function of a decrease in both the electromagnetic field and the conductivity of the ground.

A phase measuring system (known as a slingram or twin-coil) is an efficient way to measure the difference in phase of electromagnetic waves. This difference results from a series of sinusoidal electromagnetic waves each with a wavelength \(2\pi\), and one lags behind the other. The resulting relationship can be represented by a phase angle \(\theta\) which corresponds to the angular separation of the waveforms.

A primary field travels directly from a transmitter to a receiver above the ground and suffers no modification other than a small reduction in amplitude caused by a geometric spreading. As the
primary field penetrates the ground it is reduced in amplitude to greater extent but remains in phase with the surface primary. The primary field induces an alternating voltage in a subsurface conductor with the same frequency as the primary but with a phase lag of $\pi/2$.

The electrical properties of a conductor cause additional phase lag which can be measured by the receiver. The net effect is that the secondary field produced by the conductor lags behind the primary field of the transmitter, resulting in an angle $\phi$ which can be measured, allowing for separation of the real or measured secondary field in the horizontal from the imaginary or quadrature phase of its vertical component.

Fieldwork is simple and requires a small crew of 2-3 people. The spacing and orientation of the coils is critical as a small percentage error in spacing can produce appreciable error in phase measurement. The coils must also be kept accurately horizontal or vertical and coplanar as small relative tilts can produce substantial errors. The required accuracy of spacing and orientation is difficult to maintain with large spacing and over uneven terrain.

**Resistivity**

The resistivity of a material is defined as the resistance in ohms between the opposite faces of a unit cube of the material. For a conducting cylinder of resistance $\delta R$, length $\delta L$ and cross-sectional area $\delta A$, the resistivity $\rho$ is given by:

$$\rho = \frac{\delta R \delta A}{\delta L}$$

The SI unit of resistivity is the ohm-meter. Resistivity is one of the most variable physical properties. Most rock forming minerals are insulators, and electrical current carried through a rock is mostly a function of pore water. Thus, most rocks conduct electricity by electrolytic
rather than electronic processes. This property suggests that the resistivity (or inversely, the conductivity) of a rock unit is dictated by porosity or the presence of fractures – any means by which water may be contained within the rock unit. It is, therefore, impossible to determine what type of rock produces a certain electrical response. In a homogeneous body, resistivity should be constant and independent of both electrode spacing and surface location. However, when subsurface in-homogeneities exist the resistivity will vary with the relative positions of the electrodes. Any computed value is then known as the apparent resistivity ($\rho_a$) such that

$$\rho = \frac{2\pi \Delta V}{I \{(1/r_A - 1/r_B)-(1/R_A - 1/R_B)\}}$$

delta V - change in potential
I is the current
$\rho$ is the resistivity
$r$ represents the distance associated with the potential gradient
$R$ represents the electrode separation distance

In homogenous ground the depth of current penetration increases as the separation of the current electrodes is increased. Therefore, a percentage of current as represented by figure 8.5 shows that $L$ – electrode spacing, dictates $Z$ (depth of penetration).

Vertical electrical sounding (VES) data from several soundings can be presented in the form of a pseudo-section and it is now possible to invert the data into a full two-dimensional geoelectric model rather than a sequence of discrete, uni-dimensional geo-electric sections. This technique is known as electrical imaging or tomography.

Resistivity surveys are limited by the following:

1) Interpretations are ambiguous and must be correlated with secondary methods. Assessment of geologic controls is necessary to discriminate between valid alternative interpretations of the resistivity data.
2) Interpretation is limited to simple structural configurations. Any deviations from these simple situations may be impossible to interpret.

3) Topography and the effects of near-surface resistivity variations can mask the effects of deeper variations.

4) The depth of penetration of the method is limited by the maximum electrical power that can be introduced into the ground and by the physical difficulties of laying out long lengths of cable. Practical depth is limited to about 1 km, and detail is sacrificed with deeper penetration. However, realistic limits to depth are dictated by geology and signal response.

Specs on equipment for all methods will be found in Appendix

**DYE TRACE**

Planning a dye trace is slightly more complex than selecting an input and output location for the dye. Initially, a target must be selected for dye placement. A sinkhole (swallet) during high to moderate flow conditions is most suitable. Then, any and all locations downstream of the input, including springs, seeps, other stream junctions, etc. must be evaluated for monitoring purposes. At least one week before the dye trace, a dye receptor should be placed at each selected location. After 1-2 days and up to one week) it should be checked for background fluorescence – the presence of any fluorescent materials normally occurring in the water can affect the final trace. After background fluorescence has been measured, the formal dye trace can be initiated. An appropriate volume of fluorescein (recommended) should be mixed and injected directly to the selected site. The normal estimate for “appropriate volume” of fluorescein is 1 lb/gallon of water/mile of travel. (NOTE: if another dye is selected this volume calculation does not apply.)
DISCUSSION:

Karst areas typically have complex groundwater hydrology which is more closely approximated by surface water processes than most groundwater models. Any alteration of groundwater dynamics can significantly impact drainage, infiltration and hydraulic head. A system previously dominated by diffuse flow can quickly become dominated by conduit flow. Once altered, dramatic surface impacts, including sinkhole development and loss of surface water, can result. Natural variations in precipitation can dramatically enhance these problems. Property damage, well loss, spring and seep formation, and reactivation of sediment transport mechanisms can occur.

If the water table is above the level of the sediment-transporting solution cavities, sediment movement is very inefficient. Further, wet sediments are more cohesive than dry sediments and have less tendency to move. If the water table is lowered because of mine or quarry pumping or from over pumping an aquifer, hydraulic gradients are increased and instead of a water-filled cave system, there may be a flowing stream, which is much more efficient at sediment transport. (White 1988).

It is estimated that up to 25% of the world's surface is underlain by karst formations. Therefore, it is not uncommon for an area with no known caves, and not exhibiting classic karst features (sinkholes, springs, etc.) to nevertheless contain significant solution passage and subsequent turbulent karst hydrology. In most karst regions, the accessible caves represent a few percentage points or less of the total conduit system (White, p. 61). A considerable effort has been made to develop geophysical methods to detect cavernous terrain beneath a soil mantle (White, p. 372).
It is a challenge to find methods which would make it possible to detect underground stream channels and to determine the velocity of stream flow and the origin of springs (Frohlich, 1972).

In Maryland, the Greenbrier formation is subdivided into four members. The basal member, The Loyalhanna Limestone, is overlain by the Deer Valley Limestone, which is overlain by an interval of predominately red clastic rocks…herein designated the Savage Dam Member, and topped by the upper member, the Wymps Gap Limestone which is in turn overlain by the Mauch Chunk Formation. (Brezinski – p. 21) The uppermost layers of the Loyalhanna, near the contact with the Deer Valley Member, typically consist of either a tan argillaceous dolomitic siltstone or a red calcareous siltstone 0.5 to 6.0 inches in thickness. This thin interval usually allows easy separation of the Loyalhanna from the Deer Valley Members. It is evident at the stream level in outcrop, and is known to the quarriers as the “red binder.”

The Loyalhanna Limestone (Ml) is the principal unit of interest at the Deep Creek Quarry. It is known to the quarriers as the “blue lime” where it has a distinctly blue/grey appearance, often arenaceous and argillaceous. It is a carbonate unit with a high quartz sand content, often exceeding 50%. This has given rise to a great deal of debate to both the origin, as well as the name, of the Loyalhanna member. It is interesting to note that a survey completed by Highland Engineering and Survey Inc. in May 1996 designates the Loyalhanna Limestone as separate from the overlying Greenbrier Series.

Throughout the Mid-Atlantic region, the Loyalhanna Limestone is known as a cave-developing unit. Garrett County is no exception. John Friend Cave (Friends Saltpeter Cave), which is owned by the Nature Conservancy, is a prominent and highly visited single-passage cave that is
developed in the Loyalhanna Limestone. It occurs less than one mile from the quarry site, but is hydrologically separated from it by Ginseng Run, a small tributary of the Youghiogheny River. Ginseng Run has been used as a model for comparative research with Hoyes Run by the Maryland Department of Natural Resources. Ongoing estimates of trout populations have shown significant decrease in Hoyes Run, while they have stayed the same or increased in Gap Run. This has factored strongly into the desire to remediate the conditions existing at Hoyes Run.

Structural controls on the area are dominated by Appalachian Mountain orogenic events. The quarry is situated on what was previously a small, unnamed knob just southeast of Ginseng Hill and about two miles southeast of the town of McHenry. The knob as shown on topographic maps effectively no longer exists due to the quarry activity where the top of the hill has been removed as overburden, and displaced around the quarry pit. The permitted area is situated at approximately 79°23′05″; 39°33′15″.

This knob is located on the structural feature known as the Accident Dome. This is actually a slightly southwesterly plunging anticlinal feature that trends northeast towards Pennsylvania. Its trend is parallel to other major structural features of the region, including the Castleman Basin and the Deer Park Anticline. The quarry occurs along the axis of this fold. Because of the plunge of the knob, Hoyes Run has formed as a tributary of the Youghiogheny River, rather than flowing towards the adjacent watershed of the Castleman River. Generally, Hoyes Run tends to flow southwest almost along the axis of this feature, in contrast to the tributaries to its north, which all appear to flow more towards the west, the most direct down-dip route to the Youghiogheny River.

The study area surrounding Hoyes Run and the Deep Creek quarry is an excellent example of this dramatic impact. Aggregate production is a growing industry that often has the unfortunate
byproduct of surface impacts in this fluviokarstic environment. A near total loss of stream volume occurs in a small swallet in the middle of the streambed. Other zones of loss occur upstream and downstream but none with such dramatic results. Restoring the natural hydraulic gradient is the most natural way to restore the stream to its original condition; however, due to the necessity to continue aggregate production at this site, a repair to prevent flow loss is instead being considered.

A literature search was completed to assess which geophysical methods of delineating subsurface hydrology and structural features might be most appropriate in a carbonate aquifer. Wilson and Beck (1988) applied multiple methods to delineating sinkhole hazards in a mantled karst. While no method was ideal, their assessment of surface geophysical methods in this application was favorable. Based on this available research and prior demonstrated effectiveness, GPR, Terrain (electromagnetic) conductivity (EM) and resistivity were selected for this study. Additionally, the availability of equipment, relative ease of use and surface penetrating characteristics were all weighed in making this decision.

After an initial field evaluation, a linear traverse was selected that would best incorporate known stream loss zones, and include as much of the floodplain as possible. This line was utilized for each geophysical survey as a basis for comparison of techniques and determination of best means for additional studies.

Upon visual inspection, the most prominent zone of stream loss was located. The entire stream volume was being lost into a swallet in the center of the streambed. Approximately 100 m of the
bed downstream was dry due to this pirated stream. The stream was once again flowing where the quarry’s sedimentation pond discharges at an overflow pipe back into the stream bed. The addition of this water, as well as other surface runoff results in a significant increase in stream volume downstream.

A resistivity survey using dipole-dipole method at 3 m spacing indicated several anomalous areas of increased resistivity. Stream loss was confirmed at the known swallet, coinciding at approximately 70 m. However, a second zone was noted at approximately 87 m. A visual inspection of the area confirmed that the stream was entering a small swallet in the stream bank at an area where the lower limestone unit contacted the upper redbed which was functioning as a confining unit for the Loyalhanna Limestone.

EM data indicated subtle variations of several millisiemens per meter (mS/m) in the vertical and horizontal dipole modes (depth of penetration 4m and 6.5m, respectively). This correlated with resistive areas at 70m at the known swallet, and suggested air-filled void space at depth. This survey, however, failed to detect the second zone of stream loss. This was attributed to the sensitivity of the instrument at the selected location, which was several meters on the opposite bank from the area of interest. It is also possible that the loss zone was temporarily occluded by sediment due to consistent higher flow. The likelihood of a cavity occluded by clay fill was less likely as the anomaly was recorded as resistive, suggesting that it was air filled. It is likely that clay or water would have produced a more conductive signal.

Evaluation with ground penetrating radar (GPR) correlated with the location of the primary anomaly (swallet) at 70 m, but also failed to detect the secondary loss zone. It did, however, detect an area of stream loss that was previously not recorded. The loss occurred at a prominent outcrop of limestone bedrock at approximately 63 m, and appeared to have been treated with
cement to prevent water loss. Although this zone had been visually examined on several occasions, no apparent loss had been noted. Visual inspection after GPR indicated a small amount of disturbed sediment disappearing into a void in the bedrock.

It is of interest that the electrical methods both confirmed resistive anomalies at approximately 25-30 feet (9-10 m) below the surface, while in this study GPR data did not quantify the depth of the anomaly, only indicating its presence.

Upon completion of the comparative methods along the selected traverse, the results ranged from subtle definition of anomalies (GPR and EM) to well-defined spatially (resistivity). It was determined on this basis to utilize resistivity for future studies.

A second resistivity line was completed approximately 30 m north of the first line, and approximately 8m higher in elevation. This traverse was selected because it represented an intermediate contour midway between the stream and the quarry pit. The dipole-dipole survey was completed using a 2m spacing with a 56 electrode array. Data inversion revealed several negative values which were discarded in further processing. Overall the error rate of the survey was low, with RMS error of ~5-8%. This profile revealed two very large anomalous features which appeared to represent solution cavities. The pinnacled karst bedrock was evident, and was buried under a large volume of relatively homogenous and conductive overburden that had been moved to the area as part of quarry operation. This highly resistive anomalies had subtly different signal response such that the easternmost anomaly appeared extremely resistive, suggesting air filled void, while the larger anomaly seemed slightly more conductive towards its center, suggesting residual clay fill. These characteristics are being interpreted as two parallel
passages which may or may not be hydrologically connected. However, the easternmost cavity appears to be communicating water from the stream to the quarry pit as it has likely been flushed of all sediment fill which appears to remain in the larger void.

Of course, geophysical results to not yield to a simple or unique interpretation. It is necessary to confirm these assertions with drilling to determine the actual subsurface conditions.

Cavities, both sediment filled, had been developed, and then subsequently lined with crystals (dogtooth spar and calcite lining) during a period of time that they intersected the water table (characteristic of vadose/phreatic interface) and at some later date, were both occluded by sediments that washed into the cavities.

These were located when the quarry moved their highwall. Repeated charges failed to produce rock fracture. Upon inspection it was noted that a large solutional fissure was widened. Manual digging and the use of a backhoe revealed two sizeable cavities, occurring along joint trends and both measuring approximately 1-3m in width and as much as 7m in depth. Their linear extent could not be determined as unfortunately very little remained after the quarriers were done with them!

This confirmed the likelihood of additional solutional passages occurring in the same Ml formation at roughly the same elevation (which those on the 2nd profile appeared to). Confirming the groundwater flow path along geologic strike from the stream to the quarry pit was required to determine if these cavities were pirating the stream, taking it to the artificial water table as efficiently as the karst system would permit it. A dye trace was proposed to determine if this was indeed so.
DYE TRACE

During a period of high stream volume, a dye trace utilizing fluorescein (tm?) dye was conducted to verify the suspected surface and groundwater interaction. After obtaining permission from Garrett County Department of Health as well as Maryland Department of Natural Resources, a protocol established by the EPA and adopted by the NSS was adapted for use at the site. Due to the poorly accessible location of the resurgent water, a number of methods were attempted at the collection point. It was finally determined that the best approach was to utilize more dye than calculated for, and to place dye receptors immediately beneath the cascade, in the quarry pond. A device consisting of fishing bobbers and high strength polyester rope was constructed and mounted in the pond at the base of the transfer pipe from the pit pump (see picture). Based on the calculation (put in calculation here) a total of $\frac{1}{2}$ lb of fluoro dye was utilized. This amount, while greater than the calculated amount, was selected so that dilution could be minimized and a visual trace could be conducted. Fluoroscein dye was mixed according to the calculation below with water from the stream. Due to extremely low temperatures, mixing was incomplete as Fluoroscein is not very soluble at low temperatures. Due to flashy stream conditions, a background fluorescence study could not be conducted; therefore, an additional trap was placed upstream, approximately 5 m away from the dye injection to assess background fluorescence. Dye traps were placed as noted and the mixed dye was injected directly into the main swallet utilizing an 8” piece of 4” diameter PVC conduit. This encouraged most of the dye to enter the swallet, with only a small amount being swept downstream with the current. Due to weather conditions, dye traps were not changed until the third day following dye injection. Traps were collected according to protocol, and field analyzed for the presence of fluorescein. A total of 4 of the six traps located in the quarry pond tested strongly positive for fluorescein, while one trap
was accidentally cross-contaminated by the technician. A second trap was intentionally cross-contaminated for comparison with all traps, resulting in a distinct contamination spot, but an overall weakly positive fluorescence.

The control trap (1) was negative for presence of fluoro, as was trap 2 at the settling pond overflow valve. However, trap 3 located at the pump pipe outlet was moderately positive, indicating that dilution of the dye did occur, but not significantly enough to result in a negative trace. The presence of dye at this location confirmed the validity of the positive results from the quarry pit, as the only transport mechanism for water into this location was, indeed, from the quarry pit itself.

**FURTHER STUDY:**

Treatment plans include possible grouting with urethane/combustion byproduct slurry, or introduction of geotextile for containment purposes. A secondary geophysical survey will be completed after remediation efforts to assess their efficacy. If continued stream gauging or geophysical assessment notes volume loss, culverting of recalcitrant areas may be necessary.

**CONCLUSIONS:**

While all selected geophysical methods were able to detect known and unknown anomalous stream loss, electrical methods (especially resistivity) seemed best able to characterize the extent
and depth of these variations. However, ease of use of the EM-31, coupled with its correlation to other methods, makes it an excellent choice for use in initial characterization of a similar condition. However, in the inhomogeneous, highly stratified environment of this study, resistivity proved far superior in characterizing suspected targets.
Appendix – Stratigraphy

From Brezinski – Locality #17

Section of Gaylord Fuel Company quarry 2 miles southeast of McHenry, Garrett County, Longitude 79 23’05”: Latitude 39 33’15”. Base of section is the Loyalhanna Member of the Greenbrier Formation.

Thickness (feet)

Greenbrier Formation

Loyalhanna Member
- 15.0 Light-gray, dense limestone with a few thin layers of tan dolomite at top.

Deer Valley Member
- 12.0 Greenish-gray, thin-bedded, shaly limestone
- 2.0 Light-gray, ripple-laminated, sandy limestone

Savage Dam Member
- 6.0 Reddish-brown mudstone.
- 5.0 Light-gray, cross-bedded, medium-to coarse-grained, calcareous sandstone containing corals and brachiopods, and exhibiting herringbone cross-bedding. Grades up into tan, dolomitic siltstone.
- 6.0 Greenish-gray, calcareous, platy siltstone.
- 5.0 Greenish-gray mudstone.
- 2.0 Tan, calcareous, fine-grained sandstone.
- 3.0 Red-brown siltstone.
- 1.0 Red-brown claystone.
- 1.0 Red-brown siltstone.
- 2.0 Red-brown mudstone.
- 1.0 Reddish-brown claystone with carbonate nodules.
- 7.0 Red-brown mudstone.
- 8.0 Reddish-brown, silty, argillaceous sandstone.
- 4.0 Red-brown mudstone.
- 2.0 Interbedded, white, medium-grained sandstone and green-gray and red shale.
- 1.0 Reddish-brown, argillaceous sandstone.
- 0.8 Red-brown, silty mudstone.
- 2.0 Light-gray-green, shaly, sandy limestone.
- 0.3 Greenish-gray shale.

Wymps Gap Member
- 2.0 Greenish-gray, nodular-bedded, sandy limestone.
- 0.35 Red and green mottled shale.
- 3.0 Thinly interbedded, light-gray limestone and tan shale.
- 0.5 Greenish-gray claystone.
- 3.0 Thinly-bedded, dark-gray, fetid limestone with shaly laminae. Contains Composita, Anthracospirifer, and bryozoans.
- 4.0 Medium-to dark-gray, medium-bedded, fetid limestone containing Anthracospirifer, Composita, and Diaphragmus.
- 2.0 Greenish-gray claystone with thin beds of argillaceous limestone.
4.0 Dark-gray, thick-bedded, argillaceous lime wackestone, containing Anthracospirifer, Marinia, bryozoans, crinoids and pyrite.

Appendix

Dye Receptor instructions:

Using household fiberglass screen replacement (one roll makes approximately 65 traps) cut 4” x 9” rectangles as shown:

```
fold into three segments, in a “Z” shape to create two small pockets.
fill one pocket with folded cotton pad (must be unbleached cotton)
staple the unit on three sides, leaving the top open
fill the second pocket with approximately 1 tsp. of coconut activated charcoal (optional)
staple the remaining side shut to seal completely
```

Storage: Dye receptors can be stored in a light and airtight container for several months.
Activated charcoal loses its adsorptive properties after being exposed to air for a period of time.

This procedure can be modified if activated charcoal is not being used. Simply make screen segment 4”x7”, fold in half and place cotton pad inside, stapling all around to seal.

NOTE: Cotton pads and activated charcoal MUST be handled in separate circumstances from any dye materials to prevent cross contamination! Always wash hands or use rubber gloves when handling dye receptors!

Dye Trap Protocol:

All dye traps must be handled with surgical (latex) gloves!
Traps should be changed daily during working hours.

For traps located in stream flow, approach from downstream. Remove the trap from the support. Place the trap in a plastic (Ziploc) bag. Label the bag with project name, location, date and time, initials of collector. Place the sealed bag in the cooler and close the cooler until it is well sealed.

Use clean gloves to handle new traps. Place a new trap on each support.

Traps must remain sealed in plastic bags, and in cooler to prevent air or light from reaching them. Cooler should be stored in refrigerator to prevent mold growth on traps. (Note: if cooler will not fit in refrigerator, closed cardboard box is acceptable).

Try to maintain traps in chronological order. Note on bag if dye trap was in water for more than one day.

A spreadsheet with location name, number, date and description is included. Please try to note any important information such as stream conditions, weather conditions, condition of trap when retrieved, any unusual situation (e.g. trap not in water, trap not located, etc.) (see figure)
<table>
<thead>
<tr>
<th>Location #</th>
<th>Location (Description)</th>
<th>Date</th>
<th>Time</th>
<th>Weather/Stream Conditions</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
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</table>
XXXI. “The Effect of Coatings on the Durability of Metallic Materials for Interconnects in Solid Oxide Fuel Cells”

Scot Laney (S), Gerald Meier (F) and Frederick Pettit (F), University of Pittsburgh with
Christopher Johnson (M), NETL
University/NETL Student Partnership Program Annual Report

The Effect of Coatings on the Durability of Metallic Materials for Interconnects in Solid Oxide Fuel Cells

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Report Date: November 24, 2003
ABSTRACT

The NETL Fellowship awarded to Mr. Scot Laney started in September 2002. This report summarizes the status of Mr. Laney’s research and indicates how it fits into the overall research effort of the group directed by Professors Pettit and Meier, which is conducting a study directed at improving the durability of interconnect materials for solid oxide fuel cells (SOFCs). The NETL Fellowship is being used to enhance this research by supporting Mr. Laney in conducting his Ph. D research in the Department of Materials Science at the University of Pittsburgh. The topic of his research is “The Effect of Coatings on the Durability of Metallic Materials for Interconnects in Solid oxide Fuel Cells”. Mr. Laney is being supervised by Professors Pettit and Meier and Dr. Christopher Johnson, NETL-Morgantown, is serving as his NETL Mentor.

The overall research program of the Pittsburgh group has three thrusts. The first is to develop mechanism-based evaluation procedures for the durability of interconnect materials and to use these procedures to study and modify a group of alloys, which have already been identified as candidate interconnect materials.

The second thrust is to investigate the fundamental aspects of the thermo-mechanical aspects of SOFC interconnects. This will involve “Stress Measurement by X-ray Diffraction” and “Indentation Testing of Interface Adhesion” and development of “Accelerated Testing Procedures”. This part of the research is being carried out in collaboration with Professor J. L. Beuth in the Mechanical Engineering Department at Carnegie Mellon University.

The third thrust is to investigate the potential for the application of “new” metallic materials as interconnect materials. These will include materials based on pure nickel, materials based on the “Invar” concept, and coated materials to optimize properties in both the anode and cathode gases.

Part of this research is being funded by NETL through a SECA grant, which had a September 30, 2002 start date. The grant is supporting one graduate student at the University of Pittsburgh and one at Carnegie Mellon University. One undergraduate Senior Design Project is being supported each year at the University of Pittsburgh. Mr Laney’s fellowship research on coatings is being conducted in parallel with the efforts on the SECA grant and constitutes an extension of the three research thrusts, mentioned above. He is studying the effect of several chromite coatings on the oxidation behavior of ferritic stainless steel interconnect alloys. This involves both the oxidation kinetics and the volatilization of CrO₃ from the oxidized surfaces. He is measuring the stresses in the chromite coatings using x-ray diffraction and studying the adhesion of the coatings using an indentation technique. He is collaborating closely with students supported by the SECA grant and with Dr. Johnson at NETL.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title Page</td>
<td>1</td>
</tr>
<tr>
<td>Abstract</td>
<td>2</td>
</tr>
<tr>
<td>Table Of Contents</td>
<td>3</td>
</tr>
<tr>
<td>List of Graphical Materials</td>
<td>4</td>
</tr>
<tr>
<td>Introduction</td>
<td>5</td>
</tr>
<tr>
<td>Experimental</td>
<td>10</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>10</td>
</tr>
<tr>
<td>Conclusion</td>
<td>13</td>
</tr>
<tr>
<td>References</td>
<td>14</td>
</tr>
</tbody>
</table>
LIST OF GRAPHICAL MATERIALS

Figure 1  Long term cyclic oxidation data for three chromia-forming alloys in air at 982°C from Ref. 2.

Figure 2.  Vapor species diagram for the Cr-O system at 1250 K from Ref. 5.

Figure 3.  Effect of CO₂ on the isothermal oxidation rates of Fe-Cr alloys Ref. 16.

Figure 4  Cross-sections of a specimen of LaCrO₃ Coated T446 Stainless Steel (~0.5µm coating thickness) before and after exposure to air at 900°C.

Figure 5  SEM images after indentation of La₀.₈Sr₀.₂CrO₃ coating on E-BRITE, AL 453 and AL 29-4C in the as-processed state.

Figure 6  SEM images after indentation of LaCrO₃ Coating on Inconel and SS 446 in the as-processed state.

Figure 7  Comparison of indentation images from as-processed and exposed chromite coated specimens.
INTRODUCTION

Current Status of Metallic Interconnect Materials for Solid Oxide Fuel cells

A number of studies have been conducted on potential metallic interconnect materials, particularly with regard to their stability in the cathode and anode gases. Virtually all of these materials form chromia scales in both gases.

Cathode Gas
The cathode gas provides the oxidant for the cell and will generally consist of air. England and Vircar [1] oxidized thin foils of the commercial Ni-base alloys Inconel 625, Inconel 718, Hastelloy X, and Haynes 230 in air under isothermal conditions at temperatures between 800 and 1100°C. All the alloys formed scales consisting essentially of chromia and the apparent parabolic rate constants varied over nearly two orders of magnitude e.g. between $4 \times 10^{-12}$ and $10^{-10}$ g$^2$/cm$^4$h at 800°C. Such isothermal data are of limited value in selecting materials for applications in which the temperature is cycled. Figure 1 shows data for a similar group of chromia-forming alloys [2] which exhibit a wide range of behavior under thermal cycling conditions. These data also illustrate an important point that extrapolation of short term test data to long term behavior is difficult: after 180 days ($\approx$ 4000 h) there are no apparent differences in the oxidation kinetics of the three alloys whereas at longer times profound differences develop. Clearly, oxidation testing must be done under cyclic conditions and a mechanism-based accelerated testing protocol is needed for interconnects in SOFCs.

![Figure 1](image.png)

Figure 1 Long term cyclic oxidation data for three chromia forming alloys in air at 982°C from Ref. 2.
Quadakkers et al [3] have studied chromium-based alloys since they have lower coefficients of thermal expansion than the nickel based alloys. The addition of a Y\textsubscript{2}O\textsubscript{3} dispersion improved the mechanical strength and lowered the oxidation rates of the alloys. (The mechanisms for the reactive element, e.g. Y, Ce, La, effects on oxidation behavior will be discussed separately below.) A significant problem with Cr (and chromia-forming alloys) which has been recognized for many years [4] is the reactive evaporation of chromia scales. This is a particular problem in the cathode gas since the CrO\textsubscript{3} partial pressure increases with oxygen partial pressure, as illustrated in Figure 2 [5]. The volatile species are reduced at electrochemically active sites on the cathode during SOFC operation, which inhibits the required oxygen reduction [6]. Analysis of the Cr vapor species [7] indicates water contents above about 0.1% in air result in partial pressures of CrO\textsubscript{2}(OH)\textsubscript{2} which exceed the partial pressure of CrO\textsubscript{3}. Thus, maintaining the cathode gas as dry as possible is desirable. **Notwithstanding, the issue of evaporation of Cr-containing species must be addressed.**

Quadakkers et al [8, 9] have studied the behavior of ferritic stainless steels as interconnect materials since they have a good thermal expansion match with typical ceramic components of SOFCs. Model alloys have been developed based on the philosophy of:

i. Using La additions to slow the growth rate of the chromia scale and improve the adherence of the scale to the alloy.

ii. Making additions of Ti and Mn to form spinels on the chromia scale to reduce CrO\textsubscript{3} evaporation.

iii. Maintaining Al and Si levels as low as possible to prevent the formation of electrically insulating alumina or silica layers.

(The last point is quite important in that many commercial Fe- and Ni-base alloys, which are nominally chromia-formers, contain sufficient Al and/or Si so that, under certain exposure conditions, alumina or silica can form between the chromia layer and the alloy.)

Coatings of La\textsubscript{0.9}Sr\textsubscript{0.1}CrO\textsubscript{3} have also been applied to ferritic alloys to limit CrO\textsubscript{3} evaporation [10]. The potential for coatings to limit CrO\textsubscript{3} evaporation is a major focus of Mr. Laney’s Ph. D. research.

**The ferritic alloys have suitable potential to justify studies to optimize their properties as SOFC interconnects. Coatings are believed to offer the best approach to this optimization.**
Figure 2. Vapor species diagram for the Cr-O system at 1250 K from Ref. 5.

**Anode Gas**

The anode gas consists of the fuel (typically hydrogen or hydrocarbons) and the products of combustion (water vapor and, possibly, CO and CO$_2$). England and Vircar [11] oxidized thin foils of the commercial Ni-base alloys Inconel 625, Inconel 718, Hastelloy X, and Haynes 230 in hydrogen, which was saturated with water at 40°C under isothermal conditions at temperatures between 700 and 1100°C. The growth rate of the chromia scales at 800°C were higher than those observed in air [1] for the same alloys and the electrical resistance of the scale was higher than for those formed in air.

Quadakkers et al [12-14] have studied pure Cr and yttria-dispersed Cr at 950 and 1000°C in Ar/H$_2$/H$_2$O mixtures. They too observed larger mass gains in H$_2$/H$_2$O mixtures but correctly point out that this is the result of mass losses from CrO$_3$ evaporation in air, which are minimal at the reduced oxygen partial pressures in H$_2$/H$_2$O mixtures. One rather surprising result of this study was that the chromia scales were substantially more adherent when formed in H$_2$/H$_2$O mixtures than in dry air. It is well documented that spallation of alumina scales is accelerated by water vapor [15] so these results for chromia are in need of further study.
The chromia scales formed on ferritic stainless steels in simulated anode gas at 800°C were found to be thinner than those formed in air [8,9].

If hydrocarbons, e.g., natural gas, are used in place of hydrogen as the fuel in an SOFC, the presence of carbon can result in additional reactions with the interconnect materials. In stainless steels and superalloys carbon results in the formation of carbides based on chromium and other alloying elements. Excessive carburization can result in the removal from solution of protective elements such as chromium. This can seriously reduce the corrosion resistance of the component, particularly at grain boundaries. This is illustrated in Figure 3 [16]. The oxidation of Fe-15Cr is very slow in pure O2 because it forms a continuous chromia film. However, in CO2 the oxidation rate is rapid because the Cr is tied up as carbides and a scale of iron oxides forms even though the oxygen partial pressure is low.

If the hydrocarbons are injected directly into the cell, carbon deposition can occur. If deposition does not occur conditions are set up which can allow a very serious, often catastrophic, form of degradation known as metal dusting [17, 18]. In this reaction, the carbon activity in the gas must be greater than unity and it appears that the carbon from the atmosphere gas species dissolves into the metal faster than it can nucleate as soot on the metal surface. This produces high carbon activities in the metal and leads to the growth of metastable carbides, which subsequently decompose to a powdery product. These reactions occur typically in the temperature range 450-800°C.

Much of the work on the dusting attack of alloys has been carried out on nickel and iron based stainless systems similar to those used in reforming reactions where the phenomenon is a significant problem [17 –21]. The reaction is also dangerous in that it can lead to the perforation of tubes and thin sheets very rapidly, within a few hours, and it is found generally where metal components are in contact with gases which are typically CO-H2 mixtures or atmospheres containing organic gases. Because the carbon activity of the atmosphere exceeds unity and because of the difficulty in nucleating graphite on the metal surface, without a catalyst, it is possible for metastable carbides of the type M3C and M23C6 to form. These metastable carbides later decompose to metal and carbon. Thus, the corrosion products of metal dusting attack are powdery mixtures of fine metal powder and carbon. The alloy is quite uniformly attacked in the case of low alloy steels, but involves pitting in the cases of alloy steels and nickel based alloys.

Metal dusting of iron proceeds in five stages. (1) carbon dissolves in the metal to a degree of supersaturation. (2) cementite precipitates at the metal surface and in grain boundaries. (3) graphite deposits from the atmosphere on to the cementite. (4) the cementite begins to decompose forming graphite and metal particles. (5) further graphite deposition proceeds, catalyzed by the metal particles. Similar mechanisms are thought to be valid for low alloy steels.

In the case of alloys that contain high concentrations of chromium, a protective scale is formed of chromium oxides. Where this scale fails locally, the dusting sequence can proceed. This results in the formation of a pitted surface, beginning with small pits which widen to larger hemispherical sites with time. It is feasible that, if the chromia scale could be made more stable, the alloy would show improved resistance to metal dusting. It should be recognized, however, that this increased resistance is not stable and that failure would be swift, once the sequence of dusting is begun. Pure chromium and chromium-based alloys have been found to be quite resistant to metal dusting [21].
There is a clear need to evaluate potential interconnect materials for their susceptibility to carburization and metal dusting and to determine the effects of water vapor on the oxidation kinetics and oxide properties.

Figure 3. Effect of CO$_2$ on the isothermal oxidation rates of Fe-Cr alloys Ref. 16.
EXPERIMENTAL

Specimen Procurement
Specimens of three alloys, which are potential interconnect materials, have been obtained. These are the ferritic stainless steels: E-brite 26-1, AL453, and Crofer22 APU. In addition, specimens of Ebrite 26-1 and AL453, which are coated with LaCrO₃, have been provided by Pacific Northwest National Laboratory. Dr. Johnson at NETL Morgantown has provided both magnetron sputtered films of LaCrO₃ on Inconel and 446 Stainless Steel. Subsequently he will provide La₁₋ₓCaₓCrO₃ on both substrates. Study of these coated specimens is the focus of Mr. Laney’s research.

Preliminary Experiments
The microstructures of the as-received metallic specimens were characterized by optical microscopy (OM) and scanning electron microscopy (SEM).
Specimens of E-brite 26-1, AL453, and Crofer22 APU were exposed to air (cathode gas) under thermal cycling conditions at temperatures of 700 and 900°C. The specimens were also exposed to air, which contains 10% water vapor, to ascertain the effect of moisture on the degradation of the protective oxides.
Mr. Laney collaborated with a Senior Project student on these preliminary experiments and is now focussing his research on the coated alloys. This involves studies of both the oxidation kinetics and the volatilization of CrO₃ from the oxidized surfaces. He will also measure the stresses in the chromite coatings using x-ray diffraction and is studying the adhesion of the coatings using an indentation technique. He is collaborating closely with the students supported by the SECA grant and with Dr. Johnson at NETL.

RESULTS AND DISCUSSION

Chromite Coated Specimens
Figure 4 shows cross-sections of a specimen of LaCrO₃ Coated T446 Stainless Steel (~0.5µm coating thickness) before and after exposure to air at 900°C. A chromia layer formed under the chromite coating. However, examination of the uncoated side of the specimen (also shown in Figure 4) revealed a much thicker chromia layer. This indicates that the coating has provided some retardation in the transport of oxygen to the substrate. More importantly this indicates the coating should also be a barrier to CrO₃ evaporation. Similar results were also obtained with La₀.₈Sr₀.₂CrO₃ Coated E-Brite (~5µm coating thickness).
Figure 4 Cross-sections of a specimen of LaCrO$_3$ Coated T446 Stainless Steel (~0.5µm coating thickness) before and after exposure to air at 900°C.

The concept of indentation testing can be applied to a wide range of brittle coating/ductile substrate SOFC systems. As part of this project, a first round of indentation tests have been performed on the chromite coated specimens, where the debonding layer consists of the chromite coating and any chromia scale that may have grown under the coating due to thermal exposure. The specific coating systems studied are 1) a La$_{0.8}$Sr$_{0.2}$CrO$_3$ coating on E-BRITE, AL 453 or AL 29-4C from PNNL and 2) a LaCrO$_3$ Coating on Inconel or SS 446 from Drexel and NETL. Of interest is how the addition of a chromite coating might add to the stored energy acting to drive chromia scale spallation, and how the effect of the coating on chromia scale growth and evaporation rates during exposure will affect spallation resistance (by also changing the stored energy in the chromia layer).

Figures 5 and 6 show SEM images from indentation of these two types of coatings in the as-processed state (with no chromia scale between the coating and alloy). In the as-processed state, the results for each type of coating are consistent, and roughly independent of the alloy the coatings were deposited upon. The La$_{0.8}$Sr$_{0.2}$CrO$_3$ coating consistently showed some susceptibility to debonding; however, the radial extent of the debonding is not large. In contrast, the LaCrO$_3$ coating did not debond at all, though some radial tensile cracks were seen in the coating deposited onto Inconel, suggesting that the coating itself may be brittle. This difference in behavior may be due to the difference in thickness for the two coatings. The La$_{0.8}$Sr$_{0.2}$CrO$_3$ coatings were each on the order of 5 µm thick. The LaCrO$_3$ coatings were each less than 1 µm thick.
Figure 5 SEM images after indentation of La$_{0.8}$Sr$_{0.2}$CrO$_3$ coating on E-BRITE, AL 453 and AL 29-4C in the as-processed state.

Figure 6 SEM images after indentation of LaCrO$_3$ Coating on Inconel and SS 446 in the as-processed state.

Figure 7 provides a comparison of two of the five coating systems from figures 5 and 6 (one with an La$_{0.8}$Sr$_{0.2}$CrO$_3$ coating and one with an LaCrO$_3$ coating) in the as-processed state and after thermal exposure for 100 hours at 900°C. It is clear that thermal exposure has resulted in both types of coating systems becoming more susceptible to debonding. The La$_{0.8}$Sr$_{0.2}$CrO$_3$ on E-BRITE system now exhibits more complete debonding than was exhibited in the as-processed state, though the radial extent of the debonding is still not large. The LaCrO$_3$ on SS 446 system is now experiencing some flaking of the coating from the substrate, in contrast to the lack of debonding in the as-processed state. These results are consistent with an increase in debonded coating thickness caused by chromia scale growth beneath the chromite coatings. SEM/EDS analysis of the debonded portions of the exposed specimens confirms that the debonding has exposed the bare metal in both coating systems. Exposed flakes of chromia have also been found in the debonded portions of the coating, which is consistent with the results in Figure 4.
CONCLUSION

Mr. Laney’s research on coatings to improve the durability and effectiveness of metallic interconnects for SOFCs is proceeding well. Experiments have been conducted on the effect of oxidation on the coated alloys and the adherence of the coatings. Experiments on the effect of the coatings in reducing CrO$_3$ evaporation will be initiated in the near future.
REFERENCES

XXXII. “A Modeling Study of CO₂ Sequestration Using a Compositional Reservoir Simulator”

Ajitabh Kumar (S), Gary Pope (F), University of Texas – Austin
with
Duane Smith (M), NETL
A Modeling Study of CO2 Sequestration
Using a Compositional Reservoir Simulator

Final Report

September 1, 2002 -
August 2003

Gary A. Pope and Ajitabh Kumar

December 2003

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Abstract

The goal of this research is to use a compositional reservoir simulator to better understand and quantify the chemical and physical phenomena associated with the injection and geological storage of supercritical CO₂ in aquifers. More particularly, the goal was to quantitatively assess two key features of the process: the effect of the increase in brine density due to dissolved CO₂, and the effect of geochemical reactions. The former might be exploited to store significant quantities of dissolved CO₂ within the aqueous phase, avoiding problems with escape of CO₂ in the gas phase. The latter offers the possibility of an additional sink for CO₂ via mineralization. In addition to these two mechanisms, the storage of supercritical CO₂ as residual gas emerged in this study as a very significant issue meriting further investigation. This was a scoping study to calculate the magnitude of these three CO₂ sinks by considering mass transfer under realistic physical conditions. The latter conditions include movement of the CO₂-rich gas phase and dissolved CO₂ plume after injection is halted and the consequent mixing of brines of widely varying CO₂ concentrations. Based on our simulations, we hypothesize that the ultimate storage modes of CO₂ are a residual CO₂-rich gas phase and as CO₂-saturated brine. The gravity-driven movement of mobile gas after injection is halted is the basis for this hypothesis. This movement brings the CO₂ into contact with unsaturated water, causing more dissolution into brine, and leaves behind a residual gas saturation. The key question becomes the time required to reach this state. This will depend strongly on petrophysical parameters of the aquifer, particularly the residual gas saturation. A critical operational factor is whether the mobile gas phase reaches the upper seal of the aquifer, at which point it may travel for extremely long distances. Simulations indicate that injecting the supercritical CO₂ in the lower half of the aquifer is likely to prevent this situation. A substantial fraction of injected CO₂ (~75%) exists in the residual gas and brine at the end of a 50 year injection period. The fraction of CO₂ in a mobile gas phase decreases to small values (~5%) within a few centuries. For the cases studied, mineralization (conversion of dissolved CO₂ into carbonate minerals) occurs over a much longer time scale, on the order of 10⁴ years. However, if the rate of gravity-driven gas movement is sufficiently small, mineralization could play a significant role in immobilizing injected CO₂.
Table of Contents

Abstract.............................................................................................................................................. iii
Table of Contents.......................................................................................................................... iv
List(s) of Graphical Materials
 Figures............................................................................................................................................... v
 Tables................................................................................................................................................ vi
Introduction........................................................................................................................................ 1
Executive Summary...................................................................................................................... 3
Experimental..................................................................................................................................... 4
Results and Discussion................................................................................................................... 4
Conclusions....................................................................................................................................... 38
References......................................................................................................................................... 39
List(s) of Graphical Materials

Figures

Figure 1  Effect of brine salinity on CO2 solubility in the aqueous phase at 60°C (140°F).......................... 4
Figure 2  Effect of CO2 on brine density at 122°F and 5830 psi........................................................... 6
Figure 3  Density of CO2-saturated aqueous solutions at temperatures between 50°C and 100°C........ 6
Figure 4  Schematic of aquifer and well locations.............................................................................. 9
Figure 5  Water-gas relative permeability curves.............................................................................. 9
Figure 6  Gas saturation at 10 years (vertical slice through the injection well in X-Z direction).......... 10
Figure 7  Gas saturation at 1000 years (vertical slice through the injection well in X-Z direction)...... 10
Figure 8  Aqueous phase density in lb/cu ft at 1000 years (vertical slice through the injection well in X-Z direction)........................................................................................................... 11
Figure 9  Effect of permeability on the distribution of CO2 between phases at 1000 years............. 11
Figure 10 Effect of vertical to horizontal permeability ratio on the distribution of CO2 between phases at 1000 years.................................................................................................................... 15
Figure 11 Effect of residual gas saturation on the distribution of CO2 between phases at 1000 years 15
Figure 12 Effect of salinity on the distribution of CO2 between phases at 1000 years....................... 16
Figure 13 Effect of temperature on the distribution of CO2 between phases at 1000 years................. 16
Figure 14 Effect of aquifer dip on the distribution of CO2 between phases at 1000 years.................. 17
Figure 15 Water-gas relative permeability curves with hysteresis..................................................... 19
Figure 16 Gas saturation at 50 years (vertical slice through the injection well in X-Z direction)........ 20
Figure 17 Gas saturation at 1000 years (vertical slice through the injection well in X-Z direction).... 20
Figure 18 Gas saturation at 100,000 years (vertical slice through the injection well in X-Z direction). 21
Figure 19 Gas saturation at 1000 years for a brine salinity of 100 ppm and kv/kh=0.001. Brine density is 60.18 lb/ft³ (with CO2) and 61.81 lb/ft³ (without CO2).................................................. 21
Figure 20 Gas saturation at 1000 years for a brine salinity of 200,000 ppm and kv/kh = 0.001. Brine density is 70.57 lb/ft³ (with CO2) and 68.98 lb/ft³ (without CO2)......................................... 22
Figure 21 Gas saturation at 1000 years for a brine salinity of 100 ppm and kv/kh = 0.1. Brine density is 60.18 lb/ft³ (with CO2) and 61.81 lb/ft³ (without CO2).................................................. 22
Figure 22 Gas saturation at 1000 years for a brine salinity of 200,000 ppm and kv/kh = 0.1. Brine density is 70.57 lb/ft³ (with CO2) and 68.98 lb/ft³ (without CO2)........................................ 23
Figure 23 Effect of gravity-driven fluid migration on the distribution of CO2 between phases after injection for 50 years.............................................................................................................. 23
Figure 24 Effect of average aquifer properties (stochastic realizations) on the distribution of CO2 between phases....................................................................................................................... 24
Figure 25 Effect of Dykstra-Parsons coefficient on the distribution of CO2 between phases............. 24
Figure 26 Gas saturation at 1000 years in a layered aquifer with high permeability at the top of the injection interval.............................................................................................................. 25
Figure 27 Schematic of 1D flow field used for simulations that account for mineralization.............. 26
Figure 28 Relative permeability curves used for simulations that account for mineralization......... 27
Figure 29 Gas and aqueous concentrations...................................................................................... 29
Figure 30 Mineralization of injected CO2....................................................................................... 29
Figure 31 Concentration history of anorthite and calcite.................................................................. 30
Figure 32 Molar change profiles for anorthite and calcite at 10000 years........................................ 31
Figure 33 Gas saturation profiles with time.................................................................................... 32
Figure 34 Comparison of gas saturation profiles at 10000 years. (1) CO2 injection only for 10 years and shut in, (2) same amount of CO2 injection accompanied with water, (3) same CO2 injection for 10 years, then water injection for 10 years.............................................. 32
Figure 35 Porosity profile of Case 3 at 10000 years.......................................................................... 33
Figure 36 Comparison of calcite precipitation histories for Case 3 and 4. Case 4 has 10 times more initial anorthite than Case 3............................................................... 36
Tables

Table 1  Experimental Data for CO2-Solubility in Brine ................................................................. 5
Table 2  Simulation Input for Base Case Simulation ........................................................................ 8
Table 3  Summary of Simulations Made for Sensitivity Analysis ..................................................... 12
Table 4  Aqueous Reactions ............................................................................................................ 27
Table 5  Properties of Mineral Reactions ........................................................................................ 27
Table 6  Initial Concentrations for Aqueous Components ............................................................... 28
Table 7  Mineral Properties ............................................................................................................ 28
Table 8  Distribution of Injected CO2 for Test Cases at 10000 Years ................................................ 33
Introduction

This is the final report of a scoping study involving modeling and simulation of a prototypical CO₂ storage project in a deep saline aquifer. CMG's GEM simulator was used in this study. CO₂ solubility, brine density and brine viscosity models have been calibrated against experimental data as a function of salinity, temperature and pressure. Base case simulations were conducted for aquifer storage times of 1000 years. Some simulations were continued for up to 100,000 years. Because the goal was to determine feasibility of CO₂ storage in dissolved (aqueous phase), residual gas and solid (mineralization) forms, an injection stream of pure supercritical CO₂ was assumed for the base case.

The principal geochemical driver accompanying storage is the acidification of the brine resulting from dissociation of dissolved CO₂. Low pH brine in turn induces a wide range of reactions with host minerals in the formation. An obvious example is the dissolution of carbonate cements. Other reactions are analogous to weathering, in which the acid extracts cations from aluminosilicates (feldspars, clays, etc.). On the one hand these reactions buffer the acidification, but on the other the released cations may form relatively insoluble carbonate precipitates such as siderite. The competition between these reactions will determine the potential for additional storage, and the balance is likely to be time dependent as the approach to equilibrium will involve transport time scales (convection, dispersion/diffusion) as well as the kinetics (interphase mass transfer, dissolution, precipitation).

It is imperative to solve the geochemistry problem simultaneously with the flow and transport equations described above. Brine acidification requires mass transfer from the CO₂-rich gas phase to the aqueous phase, and contact between these phases has been shown to be a complicated function of time depending on the aquifer heterogeneity, especially after CO₂ injection ceases and buoyancy forces can substantially rearrange the fluid distribution. The latter period will involve the mixing of very different brine compositions, ranging from isolated volumes of residual aqueous phase saturated with CO₂ to original formation brine. We conducted two- and three-dimensional simulations with fully coupled reactive flow and transport in a wide variety of heterogeneous aquifers both to better understand and predict behavior and to determine whether simpler models (e.g. one-dimensional flow of saturated brine or time evolution of batch chemistry) can adequately represent the net additional CO₂ storage capacity. Some reactive minerals may be distributed in the aquifer in thin layers or otherwise heterogeneous in such as way as to make very fine-grid simulations necessary. In extreme cases, some upscaling of the reactive transport may be necessary.

Storage via mineralization

The supercritical CO₂ injection into deep aquifers in sedimentary basins represents a large potential for CO₂ disposal because of the large volume of available pore spaces (Bachu et al., 1994). The basic idea is that by injecting CO₂ into deep, low permeability aquifers in a sedimentary basin, both the dissolved and the gas phase CO₂ will travel with the natural velocity of formation water. This CO₂-rich fluid will react with the minerals present in the aquifer and consume the injected CO₂ into the secondary minerals. For long time scales, CO₂ will be permanently trapped in the subsurface as a form of carbonate minerals (Hichon et al., 1996; Gunter et al., 1997).

Siliciclastic aquifers were predicted to have the best potential for the mineral trapping of CO₂ compared to carbonate aquifers (Gunter et al., 1997). Depending on whether the basic aluminosilicate minerals, such as feldspars, zeolites, illites, chlorites and smectites, contain an alkali or alkaline earth cation, two types of CO₂ trappings can be considered. Na/K-bearing minerals result in the development of bicarbonate brines. Fe/Ca/Mg-bearing minerals result in the precipitation of siderite, calcite or dolomite. Gunter et al. (1997) presented that both cases show a substantial amount of trapping and immobilization of CO₂. They performed an experimental and numerical study on CO₂-trapping reactions in the Glaucnonic Sandstone aquifer, which is a typical sandstone aquifer from the Alberta Basin. Their study indicated that geochemical trapping of CO₂ is slow, on the order of tens to hundreds of years, but fast.
enough to form effective CO$_2$ traps compared to the fluid flow in aquifers. They also suggested that the aquifer porosity and permeability reduction by the carbonate mineral precipitation is expected to be small. Thousands of years of reactions with basic minerals in aquifers may trap over 90% of the injected CO$_2$. 
Executive Summary

The goal of this research was to use a compositional reservoir simulator to better understand and quantify the chemical and physical phenomena associated with the storage of carbon dioxide (CO₂) in aquifers. Our focus was upon evaluating conditions conducive to permanent trapping of the CO₂. Three modes of trapping emerge: dissolution of CO₂ into brine, a residual saturation of a portion of CO₂ phase and its retention by capillary forces and precipitation of carbonate minerals. The remainder of the injected supercritical CO₂ would exist as a mobile phase, at any point of time, which could conceivably escape from the aquifer if the integrity of the geological seal overlying the aquifer were to be breached or it might get dissolved into brine as time passes. Several processes, primarily the gravity-driven flow that occurs after CO₂ injection, cause mobile gas to be converted to immobile or trapped forms. The critical question becomes the time required for this conversion to occur. The petrophysical properties of the aquifer, notably residual gas saturation and relative permeability including hysteresis, strongly influence this time. A compositional simulator was used for this study after tuning the Peng-Robinson equation-of-state to fit available experimental data on the solubility of CO₂ in brine and the density of brine as a function of CO₂ concentration in the brine, brine salinity, temperature and pressure. Because this is a generic study of CO₂ injection into deep, saline aquifers rather than the study of a specific aquifer, the goal was to select representative characteristics for the aquifer that would serve our purpose of understanding the potential for CO₂ storage in immobile forms with little or no tendency to escape from the aquifer. There are of course many arbitrary decisions involved setting up such a base case model, so a sensitivity study was done where many of the most important parameters were varied over a wide range. Nevertheless, the base case is very important and a great deal of thought and discussion went into it including discussions with geologists with the Bureau of Economic Geology at the University of Texas at Austin. Parameter selection was based in part on our experience with the preliminary study completed by Vikas (2002) and other literature and more than 30 years of reservoir engineering experience by two of us.

Simulations of CO₂ storage for 1000 years were done to study the impact of several of the most important parameters on the process. The parameters studied include mean aquifer permeability, the ratio of vertical to horizontal permeability, residual gas saturation, salinity, pressure, dip, temperature, Dykstra-Parson coefficient, hysteresis of relative permeability curves, and correlation of porosity, permeability and residual gas saturation. A simple layered permeability model was used for the base case simulation. Subsequent studies used geostatistical realizations of correlated permeability fields.

One of the most significant conclusions to emerge was that the effect of residual gas on CO₂ storage can be very large and has the potential to significantly impact the strategy used to store CO₂ in aquifers. Therefore, its magnitude and variation merit further study. This form of immobile storage may actually turn out to be more significant than storage in brine and minerals. The concerns about CO₂ escape pathways would certainly be reduced if all or almost all of the CO₂ were to be stored in the form of residual gas, dense brine and minerals. A limited but representative set of mineral reactions was considered that included dissolution of anorthite and glauconite and precipitation of calcite, siderite and kaolinite. The carbonic acid-driven attack of anorthite and glauconite releases calcium and iron cations, respectively, which can precipitate with carbonate anions in the brine. At typical aquifer temperatures, the characteristic time scale for the dissolution reactions is on the order of 10,000 yrs. Thus mineralization makes only a small contribution to the permanent trapping of CO₂ during the 1000 year span of our base case simulations. Over longer times, mineralization is limited only by the amount of divalent cation initially present in the aquifer minerals.

These simulations provide important guidance towards strategies for promoting the storage of all or almost all of the CO₂ in immobile forms so that its escape from the aquifer is unlikely and not as sensitive to possible geological escape pathways as it would be if stored in a mobile gas form. Well placement and completion play a key role in this strategy.
Experimental

This project does not include an experimental component.

Results and Discussion

Because this is a generic study of CO₂ storage in deep, saline aquifers rather than the study of a specific aquifer, the goal was to select representative characteristics for the aquifer as a base case for a systematic simulation study. Once established, the base case was used to conduct a sensitivity study in which many of the most important parameters were varied over a wide range. This in turns provides insight into the potential for CO₂ storage in immobile forms with minimal tendency to escape from the aquifer.

The calibration of the fluid property models with experimental data is a very important first step in establishing the input to the simulator for this or any similar engineering problem. The properties include the solubility of CO₂ in brine, the brine density and the brine viscosity. All of these depend on temperature, pressure and salinity. The brine density and viscosity also depend on the CO₂ concentration. An extensive literature search was made to find the best sources of experimental data. These data were then used to tune the Peng-Robinson equation-of-state for CO₂ solubility and density and the Pedersen correlation for brine viscosity. Flash calculations are done in the compositional simulator each time step to calculate the phase behavior of the CO₂ and H₂O mixtures in each grid block as well as the density of both the gas and aqueous phases. The binary interaction parameter between the CO₂ and H₂O was adjusted to fit the CO₂ solubility data and the volume shift parameter for H₂O was adjusted to fit the aqueous phase density. The computed curves for CO₂ solubility as a function of salinity and pressure are shown in Fig. 1 and compared with experimental data points. Similar plots were made at temperatures ranging from 20 to 100 °C, so this is just one of many comparisons that were made with experimental data to verify that the equation-of-state was accurately representing the experimental data. A linear correlation of the binary interaction coefficient with temperature and salinity was developed based upon the solubility data from 20 to 100 °C and from 0 to 350,000 ppm salinity (NaCl).

Figure 1  Effect of brine salinity on CO₂ solubility in the aqueous phase at 60 C (140 °F).
Solubility data for CO₂ in brine are available from Rumpf et al. (1994), Shagiakhmetov et al. (1982) and Teng et al. (1998). These sources were preferred over others as they give similar trends over a wide range of temperature and salinity [Table 1].

<table>
<thead>
<tr>
<th>Source</th>
<th>Temperature Range, °F</th>
<th>Pressure Range, psia</th>
<th>Salinity Range, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rumpf et al.</td>
<td>104-319</td>
<td>100-1400</td>
<td>230,000-350,000</td>
</tr>
<tr>
<td>Shagiakhmetov et al.</td>
<td>120-302</td>
<td>1450-5800</td>
<td>0</td>
</tr>
<tr>
<td>Teng et al.</td>
<td>40-69</td>
<td>930-4280</td>
<td>0-31,000</td>
</tr>
</tbody>
</table>

Density data for pure water was taken from Wagner et al. (2002). This source was preferred over others because it is based on the IAPWS-95 formulation adopted by International Association for the Properties of Water and Steam (IAPWS). Density data for pure brine have been taken from Simonson et al. (1994) for a wide range of temperature (77-477 °F), pressure (1030-5830 psi) and salinity (30,000-300,000 ppm of NaCl). Unfortunately, there are very few experimental data in the temperature and pressure range of interest for the density of brine saturated with CO₂. Parkinson et al. (1969) give density values for CO₂-H₂O mixtures for pressures less than 500 psia and temperatures less than 105 °F. Teng et al. (1998) give density values of CO₂-brine mixtures for temperatures less than 68 °F. Data from Hnedkovsky et al. (1996) was used to verify density trends. Data from Nighswander et al. (1989) was not used because it shows a reverse trend for the variation of brine density upon CO₂ dissolution.

Those few density data that could be found were used to develop a correlation for the volume shift parameter of H₂O used in the Peng-Robinson EOS over the same range of temperature and salinity. Figure 2 shows an example of the predicted density of both brine and brine saturated with CO₂ as a function of salinity at 60 °C (140 °F) and 5830 psia. The density of brine saturated with CO₂ is greater than brine without CO₂ and this is favorable for CO₂ storage. However, the differences are very small and uncertain and decrease as salinity increases.
Temperature has a considerable effect on the density of CO$_2$-saturated aqueous solutions. Some experimental data are available from King et al. (2003) and Hnedkovsky et al. (1996) relating the partial molar volumes of the CO$_2$-saturated aqueous solutions with temperature at different pressures. The partial molar volumes corresponding to 50°C to 100°C at 20 MPa (2900 psi) pressure were converted to CO$_2$-saturated aqueous solution densities as shown in Fig. 3 below.
The densities calculated using the Peng-Robinson equation-of-state are also included in Fig. 3. The values are close to experimental values within the temperature range of 50°C to 100°C. As the temperature increases, the density of the CO₂-saturated aqueous solutions decreases.

The input parameters for the base case simulation are summarized in Table 2. The simulated aquifer is 53,000 ft long, 53000, wide and 1000 ft thick. Constant pressure wells are used along all boundaries to model an open aquifer. The injection well is in the center of the aquifer as shown in Fig. 4. The relative permeability curves are shown in Fig. 5. Pure supercritical CO₂ is injected in a well into the aquifer for ten years. The injection well is then shut in, and the simulation continues with only density differences driving the flow. The total simulation time is 1000 years. Figure 6 shows the gas saturation profile at 10 years for a vertical X-Z cross-section through the injection well. Figure 7 shows the same profile after 1000 years. These simulations were done with CMG’s GEM simulator.
Table 2  Simulation Input for Base Case Simulation

<table>
<thead>
<tr>
<th>Aquifer Properties</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Length, ft</td>
<td>53000</td>
</tr>
<tr>
<td>Width, ft</td>
<td>53000</td>
</tr>
<tr>
<td>Thickness, ft</td>
<td>1000</td>
</tr>
<tr>
<td>Depth at top of formation at injection well, ft</td>
<td>5300</td>
</tr>
<tr>
<td>Temperature, °F</td>
<td>140</td>
</tr>
<tr>
<td>Initial Pressure, psia</td>
<td>2265</td>
</tr>
<tr>
<td>Dip, degree</td>
<td>1</td>
</tr>
<tr>
<td>Salinity, ppm</td>
<td>100000</td>
</tr>
<tr>
<td>Dykstra-Parsons Coefficient</td>
<td>0.7</td>
</tr>
<tr>
<td>Horizontal to vertical permeability ratio</td>
<td>0.001</td>
</tr>
<tr>
<td>Mean Permeability, md</td>
<td>100</td>
</tr>
<tr>
<td>Horizontal Permeabilities of Each Layer*, md</td>
<td></td>
</tr>
<tr>
<td>Layers 1-4</td>
<td>89</td>
</tr>
<tr>
<td>Layers 5-8</td>
<td>65</td>
</tr>
<tr>
<td>Layers 9-12</td>
<td>46</td>
</tr>
<tr>
<td>Layers 13-16</td>
<td>30</td>
</tr>
<tr>
<td>Layers 17-20</td>
<td>15</td>
</tr>
<tr>
<td>Layers 21-24</td>
<td>120</td>
</tr>
<tr>
<td>Layers 25-28</td>
<td>165</td>
</tr>
<tr>
<td>Layers 29-32</td>
<td>235</td>
</tr>
<tr>
<td>Layers 33-36</td>
<td>840</td>
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<tr>
<td>Layers 37-40</td>
<td>370</td>
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<tr>
<td>Porosity</td>
<td>0.25</td>
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<tr>
<td>Residual Water Saturation</td>
<td>0.25</td>
</tr>
<tr>
<td>Residual Gas Saturation</td>
<td>0.25</td>
</tr>
<tr>
<td>Gas End Point Relative Permeability</td>
<td>1.0</td>
</tr>
<tr>
<td>Water End Point Relative Permeability</td>
<td>0.334</td>
</tr>
<tr>
<td>Grid</td>
<td>40×40×40</td>
</tr>
<tr>
<td>Maximum injection pressure (psia)</td>
<td>3300</td>
</tr>
<tr>
<td>Maximum injection rate (MMSCF/D)</td>
<td>50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Description of Components</th>
<th>CO₂</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>Critical Press. (psi)</td>
<td>1070.0</td>
</tr>
<tr>
<td></td>
<td>Critical Temp. (°K)</td>
<td>304.13</td>
</tr>
<tr>
<td></td>
<td>Critical Vol. (cu ft/lb-mole)</td>
<td>1.5076</td>
</tr>
<tr>
<td></td>
<td>Molecular Wt. (lb/lb-mole)</td>
<td>44.01</td>
</tr>
<tr>
<td></td>
<td>Acentric Factor, dimensionless</td>
<td>0.22394</td>
</tr>
<tr>
<td></td>
<td>Parachor, dimensionless</td>
<td>78.0</td>
</tr>
</tbody>
</table>

*Layer 1 is the top layer.
Figure 4 Schematic of aquifer and well locations.

Figure 5 Water-gas relative permeability curves.
Figure 6  Gas saturation at 10 years (vertical slice through the injection well in X-Z direction).

Figure 7  Gas saturation at 1000 years (vertical slice through the injection well in X-Z direction).

Figure 8 shows the aqueous phase density after 1000 years for this same vertical cross-section of the aquifer.
Having established the base case, we conducted a large number of simulations to study the effect of the most important parameters influencing the distribution of CO$_2$ in the aquifer. These parameters include permeability, the ratio of vertical to horizontal permeability, residual gas saturation, salinity, temperature and dip. Table 3 summarizes the sensitivity runs. The trends of total CO$_2$ stored and of the distribution of that CO$_2$ among phases are shown in Figs. 9 through 14. Figure 9 shows that less CO$_2$ is stored in the ten-year injection period when the formation permeability is small. This is because the simulation includes a maximum bottom hole pressure for the injection well, which limits its injection rate. Fig. 11 shows the same effect at large values of residual gas saturation. In this case, the injection well became pressure limited for low values of residual gas saturation, as the end point water relative permeability value decreases significantly with increase in residual gas saturation.
### Table 3 Summary of Simulations Made for Sensitivity Analysis

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Parameter Varied</th>
<th>Results/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Layered Permeability (Injection for 10 years)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K110_3</td>
<td>Base Case</td>
<td></td>
</tr>
<tr>
<td>K105</td>
<td>Temperature = 110 F</td>
<td></td>
</tr>
<tr>
<td>K106</td>
<td>Temperature = 170 F</td>
<td></td>
</tr>
<tr>
<td>K107</td>
<td>Temperature = 200 F</td>
<td>Increase in temperature leads to increased dissolution of gas into brine</td>
</tr>
<tr>
<td>K108</td>
<td>Temperature = 230 F</td>
<td></td>
</tr>
<tr>
<td>K110</td>
<td>Mean Permeability = 10 md</td>
<td>Increase in mean permeability leads to greater injectivity as well as greater migration of CO₂</td>
</tr>
<tr>
<td>K111</td>
<td>Mean Permeability = 1000 md</td>
<td></td>
</tr>
<tr>
<td>K112</td>
<td>Salinity = 0 ppm</td>
<td></td>
</tr>
<tr>
<td>K113</td>
<td>Salinity = 5000 ppm</td>
<td></td>
</tr>
<tr>
<td>K114</td>
<td>Salinity = 200,000 ppm</td>
<td>Increase in salinity leads to decreased dissolution of gas into brine</td>
</tr>
<tr>
<td>K115</td>
<td>Salinity = 300,000 ppm</td>
<td></td>
</tr>
<tr>
<td>K116</td>
<td>Kv / Kh = 0</td>
<td></td>
</tr>
<tr>
<td>K117</td>
<td>Kv / Kh = 0.01</td>
<td>Increase in Kv/Kh value leads to upward migration of gas and finally its migration along seal</td>
</tr>
<tr>
<td>K118</td>
<td>Kv / Kh = 0.1</td>
<td></td>
</tr>
<tr>
<td>K119</td>
<td>Kv / Kh = 1</td>
<td></td>
</tr>
<tr>
<td>k120_3</td>
<td>Sₚ = 0.05</td>
<td></td>
</tr>
<tr>
<td>K121_3</td>
<td>Sₚ = 0.15</td>
<td></td>
</tr>
<tr>
<td>K122_3</td>
<td>Sₚ = 0.35</td>
<td>Low value for Sₚ leads to increased gas migration and dissolution in brine, while high value leads to increased trapping as residual gas</td>
</tr>
<tr>
<td>K123_3</td>
<td>Sₚ = 0.5</td>
<td></td>
</tr>
<tr>
<td>K131</td>
<td>Dip = 0 degree</td>
<td></td>
</tr>
<tr>
<td>K133_1</td>
<td>Dip = 2.5 degree</td>
<td>Increase in dip leads to increased gas migration and dissolution into brine</td>
</tr>
<tr>
<td>K132</td>
<td>Dip = 5 degree</td>
<td></td>
</tr>
<tr>
<td><strong>Layered Permeability (Injection for 30 years)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1002</td>
<td>High Permeability along the injection interval</td>
<td>No significant lateral and vertical migration of CO₂</td>
</tr>
<tr>
<td>1003</td>
<td>High Permeability at the top of the injection interval</td>
<td>CO₂ migrates laterally to the boundary of the aquifer.</td>
</tr>
<tr>
<td>1004</td>
<td>High Permeability with intermediate low permeability layers along the aquifer thickness</td>
<td>No significant lateral and vertical migration of CO₂</td>
</tr>
<tr>
<td>1006</td>
<td>High Permeability layers along the top half of the aquifer.</td>
<td>No significant lateral and vertical migration of CO₂</td>
</tr>
<tr>
<td><strong>Stochastic Permeability (Injection for 50 years)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K249</td>
<td>Stochastic Permeability Base Case</td>
<td></td>
</tr>
<tr>
<td>K250</td>
<td>Mean Permeability = 10 md (other properties correlated)</td>
<td>Increase in mean permeability leads to increased injectivity and dissolution into brine</td>
</tr>
<tr>
<td>K251</td>
<td>Mean Permeability = 1000 md (other properties correlated)</td>
<td></td>
</tr>
<tr>
<td>K245</td>
<td>Vₓp = 0.5</td>
<td>Increase in Vₓp causes decreased gas migration and dissolution into brine</td>
</tr>
<tr>
<td>K246</td>
<td>Vₓp = 0.6</td>
<td></td>
</tr>
<tr>
<td>K247</td>
<td>Vₓp = 0.8</td>
<td></td>
</tr>
<tr>
<td>Run</td>
<td>$k_r/k_i$</td>
<td>Salinity</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>10024</td>
<td>0.001</td>
<td>100,000 ppm</td>
</tr>
<tr>
<td>10026</td>
<td>0.001</td>
<td>100,000 ppm</td>
</tr>
<tr>
<td>10027</td>
<td>0.001</td>
<td>100,000 ppm</td>
</tr>
<tr>
<td>10060</td>
<td>0.1</td>
<td>100,000 ppm</td>
</tr>
<tr>
<td>10054</td>
<td>0.1</td>
<td>100,000 ppm</td>
</tr>
<tr>
<td>10055</td>
<td>0.1</td>
<td>100,000 ppm</td>
</tr>
<tr>
<td>10024a</td>
<td>0.001</td>
<td>100 ppm</td>
</tr>
<tr>
<td>10031</td>
<td>0.001</td>
<td>100 ppm</td>
</tr>
<tr>
<td>10033a</td>
<td>0.001</td>
<td>100 ppm</td>
</tr>
<tr>
<td>10061</td>
<td>0.1</td>
<td>100 ppm</td>
</tr>
<tr>
<td>10056</td>
<td>0.1</td>
<td>100 ppm</td>
</tr>
<tr>
<td>10033a</td>
<td>0.1</td>
<td>100 ppm</td>
</tr>
<tr>
<td>10028</td>
<td>0.001</td>
<td>200,000 ppm</td>
</tr>
<tr>
<td>10029</td>
<td>0.001</td>
<td>200,000 ppm</td>
</tr>
<tr>
<td>10030</td>
<td>0.001</td>
<td>200,000 ppm</td>
</tr>
<tr>
<td>10062</td>
<td>0.1</td>
<td>200,000 ppm</td>
</tr>
<tr>
<td>10058</td>
<td>0.1</td>
<td>200,000 ppm</td>
</tr>
<tr>
<td>10059</td>
<td>0.1</td>
<td>200,000 ppm</td>
</tr>
<tr>
<td>10021</td>
<td>Different Realisation of permeability field</td>
<td></td>
</tr>
<tr>
<td>10022</td>
<td>Different Realisation of permeability field</td>
<td></td>
</tr>
<tr>
<td>10023</td>
<td>Same Realisation as Run - 10022, $k_r/k_i = 0.01$</td>
<td></td>
</tr>
<tr>
<td>Run</td>
<td>Description</td>
<td>Result</td>
</tr>
<tr>
<td>-----</td>
<td>------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>10024</td>
<td>Same Realisation as Run - 10021, $k_v/k_h = 0.01$</td>
<td>$\text{CO}_2$ migrates vertically up to the top of the aquifer.</td>
</tr>
<tr>
<td>10014</td>
<td>Different Realisation, injection for 30 years, $k_v/k_h = 0.01$</td>
<td>$\text{CO}_2$ migrates vertically up to the top of the aquifer.</td>
</tr>
<tr>
<td>10017</td>
<td>Different Realisation, injection for 30 years, $k_v/k_h = 0.01$</td>
<td>$\text{CO}_2$ migrates vertically up to the top of the aquifer.</td>
</tr>
<tr>
<td>10019</td>
<td>Same Realisation as Run - 10017, injection for 10 years, $k_v/k_h = 0.01$</td>
<td>$\text{CO}_2$ migrates vertically up and reaches near the top of the aquifer.</td>
</tr>
<tr>
<td>10018</td>
<td>Same Realisation as Run - 10017, injection for 30 years at 300 ft from the bottom of the aquifer., $k_v/k_h = 0.01$</td>
<td>$\text{CO}_2$ does not reach the top of the aquifer and is far from the top.</td>
</tr>
</tbody>
</table>

### 3 aqueous / 2 mineral reactions

<table>
<thead>
<tr>
<th>Run</th>
<th>Description</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a2m_11</td>
<td>$\text{CO}_2$ injection for 3000 years</td>
<td>Shock velocities from simulation results show good agreement with the analytical solutions for drainage</td>
</tr>
<tr>
<td>3a2m_10</td>
<td>Simultaneous $\text{CO}_2$ and water injection for 3000 years</td>
<td>Mineral dissolution wave from simulation results matches with analytical solutions</td>
</tr>
<tr>
<td>3a2m_12</td>
<td>Inject $\text{CO}_2$ for 3000 years then inject water for 40 years</td>
<td>Shock velocities from simulation results and the analytical solutions match for imbibition.</td>
</tr>
</tbody>
</table>

### 3 aqueous / 5 mineral reactions

<table>
<thead>
<tr>
<th>Run</th>
<th>Description</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a5m_03</td>
<td>$\text{CO}<em>2$ injection (2m$^3$/day) for 10 years ($S</em>{gr}=0.05$)</td>
<td>Large amount of mobile $\text{CO}_2$ (&gt;90%) remains in gas phase for 10000 years</td>
</tr>
<tr>
<td>3a5m_05</td>
<td>$\text{CO}<em>2$ injection (2m$^3$/day) for 10 years and no water injection ($S</em>{gr}=0.25$)</td>
<td>Mobile gas reduced to 70%</td>
</tr>
<tr>
<td>3a5m_06</td>
<td>Simultaneous water injection (2m$^3$/day)</td>
<td>Increase solubility trapping</td>
</tr>
<tr>
<td>3a5m_07</td>
<td>Sequential water injection (2m$^3$/day)</td>
<td>Increase trapping as residual gas saturation and solubility trapping</td>
</tr>
<tr>
<td>3a5m_07c</td>
<td>Sequential water injection (4m$^3$/day)</td>
<td>More solubility trapping than 3a5m_07</td>
</tr>
<tr>
<td>3a5m_09</td>
<td>Increase initial anorthite and simultaneous water injection (2m$^3$/day)</td>
<td>Increase mineral trapping to 45% of injected $\text{CO}_2$</td>
</tr>
</tbody>
</table>

* VSP is Volume Shift Parameter. It specifies the volume shifts to be applied to the equation of state molar volumes. It is used to improve density predictions by modifying the computed phase compressibility ($z$ factor) and molar volume.
Figure 10  Effect of vertical to horizontal permeability ratio on the distribution of CO₂ between phases at 1000 years.

Figure 11  Effect of residual gas saturation on the distribution of CO₂ between phases at 1000 years.
Residual gas saturation has the greatest effect on the distribution of CO₂. Temperature, salinity and aquifer dip also have a significant effect. For small values of residual gas saturation, there is greater movement of CO₂ in general. This increases the extent of contact between CO₂ and brine, which in turn leads to increased dissolution of CO₂ in brine. On the other hand, this also causes considerable migration of CO₂ along the top of the aquifer in the up-dip direction. At higher values of residual gas saturation,
most of the CO$_2$ is trapped as residual gas in the areas near the injection well. There is correspondingly less CO$_2$ dissolved in brine.

Although the horizontal to vertical permeability ratio ($K_h/K_v$) does not affect the distribution of CO$_2$ among phases significantly, it does affect spatial distribution. At small values of $K_h/K_v$, there is more horizontal movement of the CO$_2$ in the layers into which injection occurred. At larger values, there is more vertical migration followed by movement along the top seal.

The effects of temperature and salinity reflect the changes in CO$_2$ solubility and in density of CO$_2$-saturated brine. Solubility of CO$_2$ in brine increases with increase in temperature, hence at higher temperatures there is greater dissolution of CO$_2$. Similarly lower salinity corresponds to more dissolution because of increased solubility. Larger values for dip lead to greater lateral movement of CO$_2$, which in turn leads to increased dissolution.

![Figure 14 Effect of aquifer dip on the distribution of CO$_2$ between phases at 1000 years.](image)

Figures 9–14 show the percentage of the total CO$_2$ stored as dissolved CO$_2$ in the brine, stored as free gas and stored as residual (trapped) gas after 1000 years. The most interesting observation from these plots is that generally only a few percent of the total CO$_2$ is stored in mobile gas, that is, in a gas phase that is free to move. The majority of the injected CO$_2$ is in residual gas, which means it is immobile. The residual gas saturation for the base case is 0.25. This is a typical value of residual gas saturation for moderate porosity and permeability sandstones under conditions where high gas saturation has been displaced by water. It is close to the trend line shown in Fig. 7 of the recent paper by Holtz (2002). Residual gas saturation is a petrophysical property that depends upon rock type. The fraction of CO$_2$ stored as residual gas in Fig. 11 clearly illustrates the importance of the value of residual gas saturation. Earlier simulations conducted in this study underlined this point. For example, if the value of residual gas saturation is 0.05, the ultimate mode of storage depends strongly upon the fate of mobile CO$_2$-rich gas phase after injection ceases.

The strong influence of residual gas saturation on CO$_2$ storage in aquifers is one of the most important findings of this study. The simulations discussed above assume a single value of residual gas saturation for the entire aquifer. In general, this parameter will vary with rock type. For example, the data reviewed
by Holtz (2002) suggest a correlation between residual gas saturation and porosity. To examine the implications of this variability, we conducted simulations with stochastic porosity/permeability realizations. The porosity values for each block were then calculated using the following correlation (Holtz, 2002).

\[ K = 7 \times 10^7 (\phi)^{9.606} \]

Based on the values of porosity for each grid, maximum residual gas saturation and residual water saturation values were found using following correlations (Holtz 2002).

\[ S_{gr}^{\text{max}} = 0.5473 - (0.9696 \phi) \]
\[ S_{wirr} = 5.6709 \times (\log (K) / \phi)^{-1.6349} \]

We also accounted for the fact that the relative permeability of the gas phase depends on whether it is displacing or being displaced by water. GEM models hysteresis with the following equations:

\[ k_{rg}(S_g) = k_{rg}(\text{Drainage};S_g) \text{ during drainage}; \]
\[ k_{rg}(S_g) = k_{rg}(\text{Drainage};S_g(\text{shifted})) \text{ during imbibition}; \]

where

\[ S_g \text{ (shifted)} = S_{gr} + \frac{(S_g - S_{grh})(S_{gh} - S_{gr})}{(S_{gh} - S_{grh})} \]

and

\[ \frac{1}{S_{gr}^{\text{max}} - S_{gr}} = \frac{1}{S_{gr}^{\text{max}} - S_{gr}} = \frac{1}{S_{grh} - S_{gr}} = \frac{1}{S_{gh} - S_{gr}} \]

\[ S_{gh} \text{ is the value of } S_g \text{ when the shift to imbibition occurs} \]
\[ S_{grh} \text{ is the value of } S_{gr} \text{ corresponding to } S_{gh} \text{ via Land’s equation} \]
\[ S_{gr}^{\text{max}} = 1 - S_{wr} \]
\[ S_{gr}^{\text{max}} \text{ has the value of the user-entered parameter } S_{gr}^{\text{max}} \]

The standard version of Land's equation is a special case of the GEM equation, and this is what we used in these simulations:

\[ \frac{1}{S_{gr}^{\text{max}}} = \frac{1}{S_{grh}} - \frac{1}{S_{gh}} \]

A set of ten to fifteen intervals of porosity values was defined. Each interval was assumed to represent a single rock type and hence was assigned a different relative permeability curve and a different value of Sgrmax. The latter was calculated using the average porosity value for the interval. An example relative permeability curve is shown in Fig. 15.
To study the effect of the injection well completion, CO$_2$ was injected only in the lower half of the aquifer. Also, CO$_2$ was injected for 50 years, rather than 10 years, to investigate how the much larger volume of CO$_2$ would affect storage.

The simulations conducted with partial well completion in stochastic porosity/permeability realizations with hysteretic relative permeability and rock-type-dependent residual gas saturation indicate that with time all the gas will be trapped in various forms and will never reach the top seal of the aquifer. Figure 16 shows the gas injection profile at 50 years for a vertical X-Z cross-section through the injection well, while Figs. 17 and 18 show the same profile after 1000 and 100,000 years respectively.
Figure 16  Gas saturation at 50 years (vertical slice through the injection well in X-Z direction).

Figure 17  Gas saturation at 1000 years (vertical slice through the injection well in X-Z direction).
To study the effect of the density of CO$_2$-saturated brine, the volume shift parameter (V.S.P.) in the Peng-Robinson equation-of-state was varied for brines of different salinities to evaluate the uncertainty of the density values. The V.S.P. corresponding to the brine without CO$_2$ was decreased up to three times to obtain the lower density values and increased up to three times to obtain the higher density values. Figures 19 and 20 show the gas saturation profiles for the extreme values of brine salinity of 100 ppm and 200,000 ppm and for the extreme values of the V.S.P.
Figure 20 Gas Saturation at 1000 Years for a brine salinity of 200,000 ppm and $k_v/k_h = 0.001$. Brine density is 70.57 lb/ft³ (with CO₂) and 68.98 lb/ft³ (without CO₂).

Increasing the CO₂-saturated brine density decreases the extent of the lateral and vertical migration of CO₂ in the aquifer, but increases the amount of CO₂ present in a mobile gas phase.

Figure 21 Gas Saturation at 1000 years for a brine salinity of 100 ppm and $k_v/k_h = 0.1$. Brine density is 60.18 lb/ft³ (with CO₂) and 61.81 lb/ft³ (without CO₂).
Figure 22 Gas Saturation at 1000 years for a brine salinity of 200,000 ppm and kv/kh = 0.1. Brine density is 70.57 lb/ft³ (with CO₂) and 68.98 lb/ft³ (without CO₂).

The ratio of vertical to horizontal permeability was increased from 0.001 to 0.1 and these simulations repeated. The results in Figs. 21 and 22 show the migration of the CO₂ is very sensitive to this ratio and more important than the density differences.

Figures 23 - 25 show how gravity-driven fluid movement, aquifer properties, and permeability heterogeneity (as measured by the Dykstra-Parsons coefficient) affect the distribution of stored CO₂ between different phases.
We also studied heterogeneity in the layered permeability distribution of the base case aquifer. In these simulations, CO\(_2\) was injected for 30 years and into the bottom half of the aquifer. The aquifer was divided into 40 layers with different permeability values for each layer. The mean permeability was 100 md. Different simulations were made considering various arrangements of the permeability values of the layers. In all the arrangements, the Dykstra-Parsons coefficient was kept constant at 0.70. In all runs with a value of horizontal to vertical permeability ratio (kv/kh) equal to 0.001, the CO\(_2\) does not migrate to the top seal of the aquifer. As seen from Fig. 26 below, a high permeability layer at the top of the
injection interval allows CO\textsubscript{2} to migrate long distances over time, reaching the boundary of the simulation domain (26,500 ft from the injection well) within 1000 years. If the high permeability layers are located at the bottom or middle portion of the injection interval, CO\textsubscript{2} does not reach the boundary. Also, when there are high permeability layers distributed along the aquifer thickness, CO\textsubscript{2} does not migrate a long distance from the injection well, indicating that injection of CO\textsubscript{2} in the lower half of the aquifer is favorable.

CO\textsubscript{2} storage via mineralization

During the CO\textsubscript{2} injection into geologic formations, geochemical processes are strongly affected by multiphase fluid flow and solute transport. The dissolution of primary minerals and the precipitation of secondary minerals could change formation porosity and permeability, and could affect fluid flow patterns. The coupling of fluid flow and chemical reactions shows the feasibility of CO\textsubscript{2} injection and storage in a deep formation.

In this study, we use a commercial reservoir simulator, GEM, from Computer Modeling Group Ltd. (CMG). GEM is an implicit compositional multiphase flow simulator with chemical equilibrium based on the rate-dependent mineral precipitation/dissolution using the simultaneous solution approach (Nghiem, 2002). The governing equations are mass balances and Darcy’s law. The dispersion and diffusion of components in the aqueous phase contribute to the movement of solutes in the aqueous phase. The solubility of CO\textsubscript{2} in an aqueous phase depends on the partial pressure of the CO\textsubscript{2} in contact with the formation water, the properties of the CO\textsubscript{2}, and temperature. Furthermore, CO\textsubscript{2} solubility is controlled by the chemical equilibrium between CO\textsubscript{2} and the saturated solution. The dissolution of gas into water follows Henry’s law written in terms of fugacity.

Supercritical CO\textsubscript{2} dissolves in the aqueous phase and the reaction between CO\textsubscript{2} in an aqueous phase and CO\textsubscript{2} in a gas phase is reversible, CO\textsubscript{2} (gas) $\leftrightarrow$ CO\textsubscript{2} (aq). As the dissolution rate is very fast (Nghiem, 2002), the gas and the aqueous phase are assumed to be in thermodynamic equilibrium. Therefore, the fugacities of CO\textsubscript{2} in the gas and aqueous phases are equal. The fugacity of CO\textsubscript{2} in the gas phase, $f_{\text{ig}}$, is calculated from an equation of state and the fugacity of CO\textsubscript{2} in the aqueous phase, $f_{\text{iw}}$, is calculated using Henry’s law (Li and Nghiem, 1986):
\[ f_{iw} = y_{iw} k_i \]

where the subscript, \(i\) is a component, e.g., \(CO_2\) and \(k_i\) is a Henry’s law constant of component \(i\). \(y_{iw}\) is the mole fraction of \(i\) in the aqueous phase.

The reaction rates of minerals are controlled by reactions at the surface of the minerals. The rate is expressed as

\[ r_\beta = \hat{A}_\beta k_\beta \left[ 1 - \frac{Q_\beta}{K_{sp,\beta}} \right] \]

where subscript \(\beta\) is a particular mineral reaction. \(\hat{A}_\beta\) is the reactive surface area of mineral reaction \(\beta\) per unit bulk volume of porous medium [m²/m³] and \(k_\beta\) is a rate constant of mineral reaction \(\beta\), [mol/(m²-s)]. \(Q_\beta\) is an activity product of mineral reaction \(\beta\) and \(K_{sp,\beta}\) is the solubility product of mineral reaction \(\beta\). \(r_\beta\) is the precipitation/dissolution rate per unit bulk volume of porous medium, [mol/(m³-s)]. If the activity product is greater than the solubility product, the aqueous phase is supersaturated and the mineral precipitation occurs. Otherwise, the mineral dissolves into the aqueous phase. The reaction rate constant is a function of temperature, \(T\) as follows:

\[ k_\beta = k_{0\beta} \exp \left[ -\frac{E_{a\beta}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \]

where \(E_{a\beta}\) is the activation energy for a reaction \(\beta\), [J/mol] and \(k_{0\beta}\) is the reaction rate constant for a reaction \(\beta\) at \(T_0\) and \(R\) is the universal gas constant, [8.314 J/mol-K].

The simulations described above do not account for mineral dissolution and precipitation. To study the possible contribution of mineralization to \(CO_2\) storage, we considered a one-dimensional tilted aquifer (1° dip) derived from the base case described above and shown schematically in Fig. 27. The horizontal permeability is 197.5 md and the porosity is 0.25. The reservoir temperature is 60 °C and the dispersion coefficient is 2x10⁵ cm²/s. Salinity is 100,000 ppm. For simplicity, \(CO_2\) solubility was modeled with Henry’s law, using a constant of 3.85x10⁵ kPa. Relative permeability curves are shown in Fig. 28 and capillary pressure is ignored.

Figure 27  Schematic of 1D flow field used for simulations that account for mineralization.
The three aqueous reactions and five mineral reactions described in Table 4 and Table 5 were used in all simulations.

**Table 4 Aqueous Reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constant [logK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$</td>
<td>-13.2631</td>
</tr>
<tr>
<td>$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$</td>
<td>-6.3221</td>
</tr>
<tr>
<td>$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow 2\text{H}^+ + \text{CO}_3^{2-}$</td>
<td>-16.5563</td>
</tr>
</tbody>
</table>

Calcite + $\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$
Anorthite + 8$\text{H}^+$ $\leftrightarrow 4\text{H}_2\text{O} + \text{Ca}^{2+} + 2\text{Al}^{3+} + 2\text{SiO}_2(\text{aq})$
Kaolinite + 6$\text{H}^+$ $\leftrightarrow 5\text{H}_2\text{O} + 2\text{SiO}_2(\text{aq}) + 2\text{Al}^{3+}$
Siderite $\leftrightarrow \text{Fe}^{3+} + \text{CO}_3^{2-}$
Glauconite + 14$\text{H}^+$ $\leftrightarrow 1.5\text{K}^+ + 2.5\text{Fe}^{3+} + 0.5\text{Fe}^{2+} + \text{Mg}^{2+} + \text{Al}^{3+} + 7.5\text{SiO}_2(\text{aq}) + 9\text{H}_2\text{O}$

**Table 5 Properties of Mineral Reactions**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>log$K_{sp}$</th>
<th>log$k_\theta$ [mol/m²·s]</th>
<th>$A_\beta$ [m²/m³]</th>
<th>$E_{a\beta}$ [J/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>1.36</td>
<td>-8.8</td>
<td>88</td>
<td>41870</td>
</tr>
<tr>
<td>Anorthite</td>
<td>-8</td>
<td>-12</td>
<td>88</td>
<td>67830</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>5.47</td>
<td>-13</td>
<td>17600</td>
<td>62760</td>
</tr>
<tr>
<td>Siderite</td>
<td>10.7</td>
<td>-9.35</td>
<td>88</td>
<td>41870</td>
</tr>
<tr>
<td>Glauconite</td>
<td>-8.6</td>
<td>-14</td>
<td>4400</td>
<td>58620</td>
</tr>
</tbody>
</table>
Table 6 shows the initial concentrations for aqueous components and the mineral properties and initial volume fractions are shown in Table 7. These mineral compositions are based on a glauconitic sandstone aquifer in the Alberta Sedimentary Basin, Canada (Hitchon, 1996; Xu et al., 2001).

### Table 6 Initial Concentrations for Aqueous Components

<table>
<thead>
<tr>
<th>Aqueous species</th>
<th>Conc. [mol/kg H(_2)O]</th>
<th>Aqueous species</th>
<th>Conc. [mol/kg H(_2)O]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>1.0E-07</td>
<td>Ca(^{2+})</td>
<td>9.12E-05</td>
</tr>
<tr>
<td>SiO(_2)(aq)</td>
<td>2.35E-08</td>
<td>Al(^{3+})</td>
<td>2.32E-11</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>3.22E-06</td>
<td>Fe(^{3+})</td>
<td>4.99E-05</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>5.E-07</td>
<td>K(^+)</td>
<td>5.E-07</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>5.46E-07</td>
<td>CO(_3^{2-})</td>
<td>2.49E-02</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>1.17E-05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7 Mineral Properties

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Molecular Weight</th>
<th>Density [kg/m(^3)]</th>
<th>Initial Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO(_3)</td>
<td>100.1</td>
<td>2710</td>
<td>0.0088</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl(_2)Si(_2)O(_8)</td>
<td>278.2</td>
<td>2740</td>
<td>0.0088</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al(_2)Si(_2)O(_5)(OH)(_4)</td>
<td>258.16</td>
<td>2410</td>
<td>0.0176</td>
</tr>
<tr>
<td>Siderite</td>
<td>Fe(_{II})CO(_3)</td>
<td>115.86</td>
<td>3960</td>
<td>0.0088</td>
</tr>
<tr>
<td>Glaucnite</td>
<td>K(<em>{1.5})(Mg(</em>{0.5})Fe(<em>{II}^{3+}) 2.5Fe(</em>{II}^{II}) 0.5Al(_{0.5}))  (<a href="OH">Al(<em>{0.25}Si(</em>{7.5})O(_{20})</a>(_4))</td>
<td>426.93</td>
<td>2670</td>
<td>0.044</td>
</tr>
</tbody>
</table>

In this example, we set the residual gas saturation to 0.25 and the initial gas saturation to be zero. Supercritical CO\(_2\) is injected for 10 years with the rate of 100 m\(^3\)/day. A production well is placed at each boundary to maintain constant far-field pressure. The total amount of CO\(_2\) injection is 9.2×10\(^9\) moles. Then we stop the CO\(_2\) injection and continue the simulation for 10,000 years.

The gas and aqueous phase concentrations (all expressed per unit mass of water in the pore space) are shown in Fig. 29. Injected CO\(_2\) starts to dissolve into the water and the rest remains in the gas phase. Only a small amount of CO\(_2\) turns to the bicarbonate ion, HCO\(_3^-\).
Figure 29 Gas and aqueous concentrations.

The total masses of calcite and siderite in the aquifer are shown in Fig. 30. During the CO$_2$ injection period, the calcite initially present in the aquifer starts to dissolve. This is because the dissolved CO$_2$ perturbs the initial aqueous phase composition so that it becomes undersaturated with respect to calcite. Figure 30 shows that the mineralization (precipitation of calcite) starts when the CO$_2$ injection ends. Negative changes represent the mineral dissolution. The slope of the calcite curve becomes positive after 10 years, which indicates that the rate of the calcite precipitation exceeded the rate of the dissolution for the entire aquifer. The siderite curve does not show significant responses. The average water saturation decreases for 10 years because of the CO$_2$ injection, and stays constant after injection ends.

Figure 30 Mineralization of injected CO$_2$. 

---

29
Replotting this result on a concentration basis and with a linear time axis, Fig. 31, we see that the calcite concentration increases nonlinearly and stabilizes at 1.62x10³ gmoles/kg water. Calcite precipitation requires a source of calcium cations, provided in this example by the dissolution of anorthite. Thus the calcite precipitation is symmetric with the anorthite dissolution. Figure 32 shows profiles of the change in anorthite and calcite concentrations in the aquifer after 10000 years. Negative values represent mineral dissolution. Because very little fluid migration occurs in this example after injection ends, the perturbation of the aqueous phase composition is limited to the region contacted by CO₂ during injection. This defines the mineralization region in Fig. 32. The initial concentration of anorthite is 87 mol/m³ of bulk volume. Thus Fig. 32 shows that most of the anorthite in the mineralized region has dissolved after 10000 years. Correspondingly, the rate of change of total mass of anorthite in Fig. 32 approaches zero.

Figure 31 Concentration history of anorthite and calcite.
In this example, 90.8% of injected CO₂ remains as a gas phase and 6.4% dissolves into water. About 2.7% of the CO₂ is mineralized into calcite. A relatively small amount of CO₂ stays as the bicarbonate ion (HCO₃⁻) and the amounts of the siderite precipitation and the carbonate ion are negligible. Figure 33 shows the gas saturation profiles. The gas saturation profiles slightly lean to the right because 1º dip is applied. Even though the residual gas saturation is 0.25, about 44% of total CO₂ is still mobile.

In the case described above (Case 1), we consider only CO₂ injection, and the majority of CO₂ remains in the gas phase. To evaluate the potential for reducing the amount of mobile gas in the aquifer, we simulated the injection of water simultaneously with the CO₂ injection (Case 2). We also simulated the injection of the same amount of the water immediately after the CO₂ injection (Case 3). Figure 34 shows the gas saturation profiles for these three cases after 10000 years. The injection of water causes the gas saturation to decrease in the region around the injection well because the CO₂ is displaced, and because the CO₂ remaining dissolves into water. Saturation fronts for Cases 1 and 2 are the same because the same amount of CO₂ is injected for 10 years for both cases. When CO₂ and water are injected sequentially, water pushes the gas saturation front and there is less mobile gas than the simultaneous injection case because CO₂ has more contact with the formation water. Only 10% of injected CO₂ remains mobile after 10,000 years in Case 3.
Figure 33 Gas saturation profiles with time.

Figure 34 Comparison of gas saturation profiles at 10000 years. (1) CO$_2$ injection only for 10 years and shut in, (2) same amount of CO$_2$ injection accompanied with water, (3) same CO$_2$ injection for 10 years, then water injection for 10 years.

Table 8 presents the CO$_2$ storage in various forms for each case at 10000 years. Even though the same amount of water is injected for Cases 2 and 3, more CO$_2$ dissolves into water when we apply the water injection in a sequential manner. The software does not allow the change of porosity and permeability caused by the mineral precipitation. For example, 4.5% of injected CO$_2$ is precipitated as $3.96\times10^8$ mol of calcite in Case 3, which decreases average porosity by 1.19%. Figure 35 shows the porosity profile of Case 3 at 10000 years. It includes the calcite / kaolinite precipitation and the anorthite dissolution. The
porosity changes by the glauconite dissolution and the siderite precipitation are ignored. The porosity around the well is relatively less affected by CO₂ because of the sequential water injection.

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As was mentioned previously, mineral precipitation depends highly on the amount and type of the source minerals, e.g., the anorthite dissolution as a precursor for calcite precipitation. If we inject CO₂ in an anorthite-rich aquifer (Case 4), more calcite precipitation will occur. In Case 4, we increase the initial volume fraction of anorthite to 0.088, which is 10 times larger than Case 3, and the sequential water injection is also applied. Figure 6.36 presents the comparison of the calcite precipitation between Case 3 and 4. In Case 4, 45.9 % and 10.3 % of injected CO₂ remain in the gas phase and the aqueous phase, respectively and the calcite precipitation occupies 43.6 % of CO₂ for 70000 years and keeps increasing. Compared with Case 3, about 22 % of CO₂ in the gas phase is precipitated as calcite and CO₂ dissolution in the aqueous phase is slightly decreased. If all the anorthite in the aquifer were converted to calcite, the theoretical potential of mineral trapping would be 46.2% of the injected CO₂.
The history of the gas saturation profiles is shown in Fig. 37. The injection of water in the interval between $t = 10$ and $t = 20$ years pushes the gas bank further into the aquifer. This increases the dissolution of CO$_2$ into brine, so that the gas saturation decreases. The large gas saturation on the right end is the result of mobile gas continuing to migrate up-dip (to the right in this diagram).

Figure 38 shows that mineralization is negligible over the time scales considered in Figs. 10 – 26, i.e. over the span of 1000 years. The fraction of injected CO$_2$ stored as calcite begins to increase after a few thousand years. The transfer of CO$_2$ from the gas phase to the mineral phase (mediated by the aqueous phase dissolution of anorthite) is limited by the rate of anorthite dissolution. Given enough time and a sufficient supply of anorthite, however, this mechanism substantially decreases the amount of CO$_2$ stored as a mobile gas phase. In this simulation, the fraction of injected CO$_2$ stored as free gas drops to 2.7% after 80,000 years.
Figure 37  History of gas saturation profiles for Case 4.

Figure 38  Distribution of injected CO$_2$ into gas, water and calcite for Case 4.
Conclusions

The most significant conclusion from this scoping study is that the effect of residual gas on CO₂ storage can be very large and shows that potentially all of the CO₂ can be stored in an immobile form when advantage is taken of this well-known phenomenon of capillary trapping. Therefore, the magnitude and variation of the residual gas saturation merit further study. This form of immobile storage may actually turn out to be more significant than storage in brine and minerals. The concerns about CO₂ escape pathways would certainly be reduced if all or almost all of the CO₂ were to be stored in the immobile forms of residual gas, dense brine and minerals. Both aquifer dip and horizontal to vertical permeability ratio have a significant effect on gas migration, which in turn effects CO₂ dissolution in brine and mineralization. Well completions play an important role in deciding the fate of CO₂ after injection. When the supercritical CO₂ is injected near the top seal of the aquifer, it is likely to continue to migrate up dip for very long distances and thus may eventually find an escape path. On the contrary, when the CO₂ is injected in the lower half of the aquifer, gravity-driven flow steadily reduces the amount of mobile gas and thus its migration to the top of the aquifer. The time scale for reduction of mobile gas to insignificant values strongly depends on the petrophysical parameters of the aquifer. Over the range of parameters investigated in this scoping study, very little mobile gas remained in the aquifer after a few hundred years. At these time scales, CO₂ storage by mineral trapping is relatively small, around 2 to 3% of the injected CO₂. Injecting water during or after CO₂ injection (a WAG operation) can significantly increase CO₂ dissolution into the aqueous phase, which also promotes calcite mineralization. The mineral trapping in calcite was 4.5% of the injected CO₂ in one simulation example. The ultimate extent of mineralization is limited by the amount of divalent cations initially present in the aquifer minerals. If gravity-driven flow were sufficiently slow (tens to hundreds of thousands of years), mineralization would eventually contribute significantly to the reduction of mobile gas. However, additional modeling of mineralization is needed to address this complex problem in a more complete way. Preliminary simulations with CMG's GEM simulator indicate that such simulations are now feasible.
References


XXXIII. “Sequestration of Carbon Dioxide (CO$_2$) in Coal Seams”

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with
Karl Schroeder (M), NETL
SEQUESTRATION OF CARBON DIOXIDE (CO$_2$) IN COAL SEAMS

Report # 3
December, 2003

Submitted to:

University Partnership Program
Department of Energy (DOE)-National Energy Technology Laboratory (NETL)
P.O.Box 10940, Pittsburgh, PA 15236

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CONTENTS

1. Introduction........................................................................................................................................... 2

2. Transport Phenomena in Coal Seam.................................................................................................... 3
   2.1. Reservoir Characteristics of Coal Seams....................................................................................... 5
   2.2. Gas Storage in Coal Seams .............................................................................................................. 10
   2.3. Gas Transport in Coal Seams ......................................................................................................... 11

3. Modeling of CO$_2$ Sequestration in Coal Seams .............................................................................. 17
   3.1. Modeling Fluid Flow in Coal Seams ................................................................................................. 17
   3.2. Solution of the Governing Equations............................................................................................... 18
   3.3. Modeling of Dewatering and Degasification of a Coal Seam......................................................... 19
   3.3.1. Results for Dewatering and Degasification of a Coal Seam ..................................................... 21
   3.4. Modeling CO$_2$ Sequestration in a Coal Seam .............................................................................. 26
   3.4.1. Results for Model Runs for CO$_2$ Sequestration........................................................................ 28

4. Parametric Studies of the Effect of the Coal Seam Properties on CO$_2$ Sequestration .................. 34
   4.1. Effect of Coal Thickness on CO$_2$ Sequestration ........................................................................ 34
   4.2. Effect of Permeability on CO$_2$ Sequestration ............................................................................ 35
   4.3. Effect of Compressibility of Coal on CO$_2$ Sequestration ............................................................. 36
   4.4. Effect of Cleat Porosity on CO$_2$ Sequestration ........................................................................ 37
   4.5. Effect of Cleat Spacing or Sorption Time Constant on CO$_2$ Sequestration ............................ 38
   4.6. Effect of Adsorption Capacity on CO$_2$ Sequestration ............................................................... 40

5. Concluding Remarks ......................................................................................................................... 41

APPENDIX A ........................................................................................................................................... 42

BIBLIOGRAPHY ........................................................................................................................................ 53
LIST OF FIGURES

Figure 1. Areas of study of CO₂ sequestration in coal seams .................................................. 3
Figure 2. Dual porosity in a coal seam (8) ................................................................. 6
Figure 3. A schematic illustration of coal cleat geometries. (19) (a) Cleat-trace patterns in plan view. (b) Cleat hierarchies in cross-section view. ....................................................... 7
Figure 4. Cross-plot of vitrinite reflectance (%Rₒ) versus mean cleat spacing for coals ranging from lignite to anthracite (25) ................................................................. 9
Figure 5. Cleat spacing and aperture data from Northeast Blanco Unit No. 403, San Juan Basin. (19) ................................................................. 10
Figure 6. Coal bed methane production by pressure depletion method (34) ......................... 12
Figure 7. Coalbed methane production from Allison Unit Field of San Juan Basin (42) .... 16
Figure 8. Model coal seam dewatering/degasification set-up .............................................. 19
Figure 9. Ideally discretized coal seam used in the numerical model .................................. 20
Figure 10. Gas and water production rates during the dewatering and degasification of a coal seam ................................................................................................. 23
Figure 11. Pressure distribution during the dewatering and degasification of a coal seam .... 25
Figure 12. Gas saturation within the coal seam during the degasification process .......... 25
Figure 13. Layout for the CO₂ injection in a coal seam .................................................. 26
Figure 14. CO₂ injection rate and cumulative injected CO₂ predicted by the model .......... 29
Figure 15. Pressure distribution during the CO₂ injection process .................................. 31
Figure 16. Model prediction of the CO₂ adsorption rate over the coal seam during the injection process ...................................................................................... 33
Figure 17. Effect of coal seam thickness on the CO₂ sequestration ................................. 35
Figure 18. Effect of permeability on the CO₂ sequestration .......................................... 36
Figure 19. Effect of coal compressibility on the CO₂ sequestration ............................... 37
Figure 20. Effect of cleat porosity on the CO₂ sequestration ......................................... 38
Figure 21. Effect of cleat spacing or sorption time constant on CO₂ sequestration .......... 40
Figure 22. Effect of adsorption capacity of coal on the CO₂ sequestration ..................... 41
Figure 23. Representation of material balance for a fluid on a differential volume .............. 44
### NOMENCLATURE

**Symbols**

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1. Introduction

Sequestration of CO\textsubscript{2} in coal seams is one of the geological strategies. We have initiated a research to obtain data in order to understand and quantify the extremely complex coal-CO\textsubscript{2} interactions. We divided the problem into two sections as shown schematically in Figure 1. The first section is to understand the storage of injected CO\textsubscript{2} within the coal matrix. The second section is to investigate the transport of gases in the coal seam. The storage of CO\textsubscript{2} in the coal includes the adsorption and desorption of CO\textsubscript{2} on and from the coal matrix as well as the stability of the adsorbed CO\textsubscript{2}. For this purpose, we designed and constructed a volumetric adsorption apparatus to measure the adsorption isotherms of CO\textsubscript{2} on coals at different conditions. We investigated the effects of several parameters on the adsorption and desorption isotherms as well as the adsorption capacity of CO\textsubscript{2} on coals such as rank, moisture content, temperature, pressure, and change in pH. In order to extract valuable information, we developed an equation which can differentiate the adsorbed amount from the artifact due to the volumetric changes during the adsorption isotherm measurements such as coal swelling, solid dissolution, and over- or under-estimation of coal volume due to the adsorption or sieving effect between helium used and the adsorbing gas. We published our findings in peer reviewed journals and presented in national and international conferences. Information gathered from these studies could be employed in present and future coalbed methane/CO\textsubscript{2} sequestration simulators. In the present study, we report our findings on the transport phenomena in CBM production/CO\textsubscript{2} sequestration processes.
2. Transport Phenomena in Coal Seam

Sequestration of carbon dioxide (CO₂) in coal seams has been proposed as one of the geologic strategies to mitigate increasing concentrations of CO₂ in the atmosphere. Coal seam sequestration of CO₂ is particularly attractive in those cases where the coal contains large amounts of methane. In these cases, not only is the CO₂ stored in the coal seam in an adsorbed state but the coalbed methane can also be produced to generate revenue that offsets the expense of sequestration. The following questions need to be addressed to ensure a safe, cost-effective sequestration of large volumes of CO₂ in coal seams:

Figure 1. Areas of study of CO₂ sequestration in coal seams
1) How much CO₂ can be injected into a candidate coal seam?

2) How would the coal swelling influence the injection process?

3) How would the injected CO₂ distribute along the coal seam?

4) What would the injection rate be?, and

5) How stable is the adsorbed CO₂ during the post injection periods?

Effective modeling of the sequestration process is essential both for an understanding of the complex interactions which occur during CO₂ storage and methane production, and for predicting of the economic viability of sequestration under the particular conditions of a given site. Many commercial and research numerical models have been developed to simulate the coalbed methane (CBM) recovery processes.¹,²,³,⁴,⁵,⁶ In a three part survey, King and Ertekin¹,²,³,⁴ reviewed the coalbed methane models which had been developed and published in the literature. They classified the models as: empirical, equilibrium, and non-equilibrium sorption models. The equilibrium models assume that the adsorption and desorption processes are so rapid that the kinetics of the process is negligible. In non-equilibrium models, the adsorption and desorption processes are time dependent and movement of the distributing component into and out of the coal matrix is retarded. These models took into account many of the factors important to coal seam sequestration including the dual porosity nature of coalbeds; multiphase Darcy flow of gas and water in the natural fracture system; single component gas diffusion in the natural fracture system; adsorption and desorption processes of a single and multi gas components on the coal surface; and coal matrix shrinkage due to gas desorption.
Sequestration of CO$_2$ in coal seams with concomitant recovery of coalbed methane is a new technology that has been practiced in a few places but it is not well developed. Off-the-shelf technology is available to perform CO$_2$-enhanced coalbed methane recovery/sequestration (CO$_2$-ECBM/sequestration). For instance, Burlington Resources performed CO$_2$-ECBM production in deep unmineable coal seams in the San Juan Basin in New Mexico since 1996.\(^{(7)}\) Very little information has entered the public domain from this or similar projects. There is a very incomplete understanding of what happens when CO$_2$ is injected into a coal seam. Here, a brief review on general reservoir characteristics, forms of gas storage, transport mechanisms in a coal seam, and modeling methodology is introduced.

2.1. Reservoir Characteristics of Coal Seams

Coalbeds are naturally fractured porous solid, which are generally characterized by dual porosity, containing both micropore and macropore systems as shown in Figure 2.\(^{(8)}\). The microporosity of coal is contained within the macromolecular network of the coal matrix. High-resolution transmission electron microscopy (HRTEM)\(^{(9,10)}\) and wide-angle X-ray scattering (WAXRS)\(^{(11)}\) measurements demonstrated that some coal matrices have a layered structure of covalently linked polycyclic aromatic units.\(^{(12)}\) The distance between the layers of the macromolecular units is about 3.5-4.1 Å. This spacing is thought to be responsible for most of the porosity in coal and for the restricted flow associated with the coal pores. However, other measurement techniques which use different molecular probes report different pore sizes, possibly, because of the pseudo polymeric nature of the coal. For instance, $^{129}$Xe-NMR\(^{(13,14)}\) accounts an appreciable fraction of the pores in coals to sizes of 5.2-6.7 Å. The pore sizes
estimated by CO₂ adsorption and ¹H-NMR of pore water provide even larger pore sizes, 13-14 Å\(^{(15)}\) and 22-28 Å\(^{(16)}\), respectively. It appears that micropore sizes are not a unique property of a coal but vary with probe used. Because of the dimensions of the micropores, the micropore system was assumed to be inaccessible to water\(^{(17)}\).

![Figure 2. Dual porosity in a coal seam\(^{(8)}\)](image)

The macroporosity of a coal seam consists of naturally occurring cracks, called cleats.\(^{(18)}\) The characteristics and origins of the cleat structure of coal have been reviewed by Laubach et al.\(^{(19)}\) There are mainly two types of cleats in coal beds: face cleat and butt cleat. These are primary and secondary avenues, respectively for gas and water flow in coal seam. The two are commonly mutually orthogonal, and essentially perpendicular to the bedding surfaces.\(^{(20)}\) The face cleat is laterally extensive, vertical, and continuous throughout the seam. The butt cleat is also vertical, and in most cases discontinuous, ending with an intersection at the face cleat, generally with a right angle. As evidenced by SEM studies, coals also contain a range of
microstructures between the micropores and the cleat system consisting of a variety of shapes and sizes.\textsuperscript{(21)} While the storage of gas is dominated by adsorption within micropores, the cleat system provides the conduit for mass transfer through the formation.\textsuperscript{(22)}

Coal cleats are characterized by their height, length, aperture, and connectivity, where permeability is dependent on. It should be mentioned that data on cleat characteristics are very limited and also vary from seam to seam. Figure 3 shows a schematic illustration of some coal cleat geometries.\textsuperscript{(19)} Here, \textit{length} is defined as the dimension parallel to the cleat surface and parallel to bedding; \textit{height} is the dimension parallel to the cleat surface and perpendicular to bedding; \textit{aperture} is the dimension perpendicular to fracture surface; and \textit{spacing} between the same set of two cleats is the distance between them at right angles to cleat surface.

\textbf{Figure 3.} A schematic illustration of coal cleat geometries.\textsuperscript{(19)} (a) Cleat-trace patterns in plan view. (b) Cleat hierarchies in cross-section view.
Estimates show that the length of cleat pathways varies from several centimeters to up to several meters.\textsuperscript{(19)} Butt cleat length generally intersects at the face cleat and thus is limited with face cleat spacing.\textsuperscript{(19)} Face and butt cleats are likely to cut the coal into rhombus- or cube-shaped coal matrix blocks.\textsuperscript{(23)} Su et al.\textsuperscript{(23)} reported that the cleat length in North China is commonly less than 10 m; the height is less than 30 cm; and the cleat apertures range from 0.001 to 8 mm. The microscopic examination of coal samples showed that the cleat aperture varies from 0.001 to 20 mm.\textsuperscript{(21)} However, because cleat apertures may change as effective stress is altered in coalbeds, few reliable data on cleat apertures are available in the subsurface. The parallel-plate fracture permeability model showed that the cleat apertures range from 3 to 40 µm.\textsuperscript{(19)} Karacan and Okandan\textsuperscript{(24)} studied the fracture system in two medium volatile and one high volatile bituminous coals from Zonguldak Basin of Northwestern Turkey employing X-ray computerized tomography (CT), light microscopy image analysis, and scanning electron microscopy (SEM) analysis. They reported aperture sizes from 10 to 60 µm for cleats and from 2 to 10 µm for microfractures.

Cleat spacing is on the order of centimeters and is known to be affected by coal rank, ash content, and bed thickness. Cleat spacing generally decreases with increasing coal rank from bituminous to anthracite coal; coals with higher ash content show larger cleat spacing; and cleat spacing generally decreases with decreasing layer thickness. The rank dependent cleat spacing of North American coals was reported by Law (1993)\textsuperscript{(25)} as shown in Figure 4. Ash content was not reported although ash content varies among coals and affects cleat spacing. As shown in the figure, the spacing of face cleats ranges from 22 cm in lignites and 0.2 cm in anthracites. The
spacing for butt cleats also shows similar trend ranges from 20 cm in lignite to about 0.2 cm in anthracite. The average face and butt cleat spacings of a high volatile bituminous coal (Average vitrinite reflectance $%R_o = 0.7$) were also reported by Massarotto et al.\(^{(26)}\) as 1.37 cm and 1.36 cm and the mean unstressed apertures were 0.246 mm and 0.212 mm, respectively.

Figure 4. Cross-plot of vitrinite reflectance ($%R_o$) versus mean cleat spacing for coals ranging from lignite to anthracite\(^{(25)}\)

Figure 5 shows the relationship between cleat spacing and aperture size from Northeast Blanco Unit No.403, San Juan Basin.\(^{(19)}\) The plotted spacings represent averages of all measured spacings having a specific aperture measurement. A shown in the figure the average spacing of the cleats is proportional to aperture size, and the ratio of aperture opening to the spacing is less than 3%. This finding is consistent with the literature as cleat-fracture porosity in coal was estimated to be between 0.5 and 2.5%.\(^{(27,28,29)}\)
Figure 5. Cleat spacing and aperture data from Northeast Blanco Unit No. 403, San Juan Basin.\cite{19}

2.2. Gas Storage in Coal Seams

Coals have been recognized as an important resource for a substantial amount of methane\cite{30} and a reservoir for anthropogenic CO$_2$ sequestration;\cite{31} both are important greenhouse gases.\cite{32} Gases in coal are primarily composed of CH$_4$ (98%), CO$_2$, trace amount of hydrocarbons and other gases. Gases present in coalbeds exist mostly in adsorbed state within the micropores. Gases may also be present in coal seam in other forms such as in free gaseous
phase within pores and fractures, and in dissolved form, to a lesser extent, in resident brines.\textsuperscript{(33)}

The storage capacity of the gas in a coal seam can be given as

\[ \text{Storage Capacity} = \text{Adsorbed Gas} + \text{Free Gas} \]  \hspace{1cm} (1)

or

\[ \text{Storage Capacity} = V_c \rho_e (1 - \phi)n_o (1 - a - m) + V_c \phi S_g / B_g \]  \hspace{1cm} (2)

where \( V_c \) is the volume of the coal, \( \rho_e \) is the density of the coal, \( \phi \) is the porosity, \( n_o \) is the adsorption capacity estimated from adsorption isotherms, \( a \) is the ash content, \( m \) is the moisture content, \( S_g \) is the gas saturation, and \( B_g \) is the formation volume factor for the gas phase. Because the bulk porosity of the coal cleat system is small, and the initial gas saturation in the cleat system is typically low, about 90\% of the coalbed methane is stored in adsorbed state in the coal.

2.3. Gas Transport in Coal Seams

The transport of gas from the surface of the micropores to the well bore or vice versa can be described by the three different processes: Sorption/desorption process, diffusion process, and convection process. Figure 6 shows the schematics of the three transport processes.\textsuperscript{(34)}
Figure 6. Coal bed methane production by pressure depletion method\textsuperscript{(34)}

It is generally assumed that the adsorbed gas phase is in contact with the surrounding free gas phase and that these two phases are in equilibrium. Because the cleat porosity is assumed to be 100% saturated with brine initially, the pressure decline during the water production forces the adsorbed methane to be desorbed and diffuse through the microporous matrix to the macropore system. The gas, along with the brine, is then transported through the cleat to the drainage well. In the micropore system, the permeability is negligible and diffusion is the dominant mode of transport.\textsuperscript{(35)} The micropore transport of gas is expressed by the Fick’s law of diffusion under the concentration gradient

\[
\frac{q_g}{A} = -MD_i \nabla C_i
\]

(3)

The diffusion coefficients for most coals have been experimentally determined to be between $10^{-7}$ and $10^{11}$ $m^2/d$.\textsuperscript{(17,36)}
In the fractured system, the gas flow through the cleats to the well bore is a laminar process and obeys Darcy’s law.\textsuperscript{(29)} The Darcy’s law states that the apparent velocity of a flowing fluid in a porous media is directly proportional to the applied pressure gradient. The proportionality constant is related to the permeability of the medium divided by the viscosity of the fluid.

\[
\frac{m_g}{A} = -\frac{k_g}{\mu_g} \nabla P_g
\]  

(4)

The permeability is a macroscopic property of the porous medium regardless of the flowing fluid. The relationship between the permeability and porosity is

\[
\frac{k}{k_o} = \left(\frac{\phi}{\phi_o}\right)^{N_c}
\]  

(5)

where the value of the exponent ($N_c$) is usually 3 or greater. Due to the natural fracture network in coal seams, both the macropore porosity and permeability are depend on the effective stress ($\sigma_e$)\textsuperscript{(27)}

\[
k = k_o \left(e^{-C_p \sigma_e}\right)^3
\]  

(6)

where $C_p$ is the pore compressibility and the effective stress is defined as the difference between the overburden pressure ($\sigma_{OB}$) and gas pressure

\[
\sigma_e = \sigma_{OB} - P_g
\]  

(7)

Therefore, an increase in the confining stress or, equivalently, a reduction in the pore pressure causes cleat closure, and thus, a reduction in the permeability. The absolute permeabilities have been attributed to American coals to be in the range from 0.1 to 250 millidarcies (md), for Australian coals from 1 to 10 md, and for European coals ranging from 1 to 50 md.\textsuperscript{(38)} It should
be emphasized that the permeability values are expected to be lower depending on the burial depths.

2.4. Enhanced Coalbed Methane Production

The natural depletion method has been reported to be inefficient because a maximum recovery of only 30% to 50% of the original gas-in-place can be achieved.\(^{(39,40)}\) Reznik et al.\(^{(39)}\) Conducted a set of experiments injecting CO\(_2\) into large cores of methane- and water-saturated bituminous coals at pressures up to 800 psia in order to simulate enhanced recovery of \textit{in-situ} methane. They showed that CO\(_2\) injection increased the methane recovery by a factor of two to three over that achieved using simple desorption. At high pressures, CO\(_2\) was shown to produce 100% of the methane from the coal core. Puri and Yee\(^{(40)}\) performed similar experimental studies using N\(_2\) as the injection fluid. They showed that almost all of the CH\(_4\) adsorbed on the coal could be recovered using N\(_2\) injection.

It has been suggested that the mechanism of CH\(_4\) recovery differs for the two gases. The injection of CO\(_2\) results in CH\(_4\) being displaced by the strongly adsorbing CO\(_2\) whereas N\(_2\), a gas that is less strongly adsorbed than CO\(_2\), causes desorption by simply lowering the partial pressure of CH\(_4\). The adsorption of a mixture of gases is controlled by both the adsorption capacity of the coal and the partial pressure of the gases.\(^{(41)}\) When nitrogen is injected into a methane saturated coal seam, it is expected that the nitrogen will reduce the partial pressure of methane by sweeping it from the vicinity of the desorbing surface leading to desorption of more methane. In this manner, thermodynamic equilibrium cannot be reached and methane continues to desorb.
For the injection of CO₂, CO₂ is expected both to displace the adsorbed methane and to reduce the partial pressure of the methane in the free gas phase, leading to increased production of methane.

Since 1996, Burlington Resources have conducted a commercial pilot application of CO₂ injection in the Allison production unit of the northern San Juan basin in north-central New Mexico.⁷ Figure 7 shows production of coalbed methane by CO₂ injection in the Allison Unit field. The significance of the preliminary test results from the Allison unit was summarized as follows:⁴²

1. Injection of CO₂ began in 1995 at a rate of 5 MMcfd; since then a loss of injectivity has reduced injection rates to about 3 MMcfd;
2. A sharp increase in water production was observed immediately and during the initial 6-month period of CO₂ injection; and
3. Minimal breakthrough of CO₂ during the 5-years of CO₂ injection.

It appears that the reduction in the injection rate could be due to closing of the cleat structure as a result of the coal swelling or to the reduction in relative permeability in the presence of increasing water content in the cleat porosity. Simulators for CO₂ injection should have the ability to handle complicated mechanisms. A better understanding of these process mechanisms both in the field and in the laboratory will lead to improvements in the numerical simulators and in the understanding of the complex processes occurring during the sequestration of CO₂ in coal seams.
The ideal scenario in \( \text{CO}_2 \) sequestration in coal seams is that when \( \text{CO}_2 \) is injected into a coal seam it will flow through the coal cleat system and be stored within the coal matrix.\(^{35}\) The experience gained from CBM production over the last two decades can be employed for an efficient, cost-effective, and continuous \( \text{CO}_2 \) sequestration in coal seams.\(^{43}\) It should be emphasized that although \( \text{CH}_4 \) production from coalbeds has been studied extensively, \( \text{CO}_2 \) sequestration in actual unmineable coal mines remains to be investigated.

**Figure 7.** Coalbed methane production from Allison Unit Field of San Juan Basin\(^{42}\)
3. Modeling of CO$_2$ Sequestration in Coal Seams

In order to obtain insights into the behavior of CO$_2$ injection process, the transport of fluids into a coal seam was modeled considering different rank of coals. Coals are naturally fractured porous solids containing both micropores which are buried within the coal matrix and natural fractures or cleats which are contained throughout the coal seams. Most coal beds are found to be saturated with water and they contain coalbed methane (CBM). The pressure is near the hydrostatic pressure which varies with the depth of the coal seam. It has been suggested that the methane is adsorbed within the coal matrix and water resides in the cleat system. In order to be able to inject the CO$_2$, the water and adsorbed methane need to be removed first from the coal seam for the effectiveness of the process. Otherwise, the already occupied pores and cleat system may not be replaced by the injected CO$_2$. In this respect, the CO$_2$ sequestration process may be termed as a replacement process.

3.1. Modeling Fluid Flow in Coal Seams

The first stage of the sequestration process is to withdraw the water and CBM from the coal seam. The material balance can be conducted on a differential element in a continuum in a coal seam. The details of the derivation of transport equations the definitions of the symbols were shown in the appendix for gas and water phases in a coal seam. The final forms of the material balance equations for each phase are
for gas phase

\[
\nabla \cdot \left[ 5.615 \frac{kk_{gr} P_g}{\mu_g} \frac{P_g}{z} \nabla P_g + D_a \nabla \left( \frac{P_g}{z} S_g \right) \right] + \frac{RT}{M} q_{ul} = \frac{\partial}{\partial t} \left( \phi S_g \frac{P_g}{z} \right)
\]

(8)

for water phase

\[
\nabla \cdot \left[ \frac{kk_{wr}}{B_w \mu_w} \nabla (P_g - P_{egw}) \right] = \frac{1}{5.615} \frac{\partial}{\partial t} \left[ \phi \left( 1 - S_g \right) \frac{B_w}{B_w} \right]
\]

(9)

3.2. Solution of the Governing Equations

The governing equations, Eq.(8), and (9), can be solved analytically for only certain simplified conditions. On the other hand, these equations are quite complex, non-linear, and a numerical solution should be implemented. There are number of CBM production simulators reported in the literature. One of these simulators is the Penn State University’s CBM production model developed initially by Sung (1997) for the dewatering and degasification of a coal seam. The Sung’s model which was generously donated by the Penn State University was modified to solve the model equations numerically for both the CBM and water production and CO₂ sequestration processes.

The model uses the finite-difference approximations to transform the governing partial differential equations describing the flow of gas and water in a coal seam into algebraic finite-difference equations. The numerical solution was implemented by superimposing a finite-difference grid over the idealized coal seam. The finite-difference solution produces the values of
pressure and saturation at discrete points in the coal seam. More detailed information about the discretization and solution procedure can be found in Sung (1997). 

3.3. Modeling of Dewatering and Degasification of a Coal Seam

In order to solve the governing non-linear differential equations for the water and methane production from a coal seam, the initial and boundary conditions must be specified. Because the water and adsorbed methane need to be withdrawn from the coal seam before the CO$_2$ is injected, it was considered that using multiple wells will assist the dewatering/degasification of the coal seam in shorter times as shown in Figure 8. The distance between each well is more or less the same so that one well and its boundaries can be specified in the model as shown in Figure 9.

![Figure 8. Model coal seam dewatering/degasification set-up](image-url)
The initial condition for pressure can be approximated by the local pressure gradient and depth of the coal seam whereas the initial condition for the gas saturation is set to zero as a default value.

\[ P_g^o = P_{g,sc} + g \cdot d \]  
\[ S_g^o = 0.0 \]  

The initial micropore gas concentration is therefore

\[ q_e^o = \frac{n_o P_g^o}{K + P_g^o} \]
The internal boundary condition at the well can be given as either a pressure constrained well or a rate constrained well. For pressure constrained well, the bottom hole pressure is specified. For rate constrained well, either gas production rate, water production rate, or total production rate can be specified. Similarly, the external boundary condition can be defined as either a constant pressure (constant flow rate) boundary condition or a no-flow outer boundary condition. In the system defined here, the inner boundary condition at the well is

$$P_g = P_{well}$$  \hspace{1cm} (13)

The outer boundary condition can be assumed to be a no-flow outer boundary due to the symmetrically located wells

$$\nabla P_g = 0.0$$  \hspace{1cm} (14)

3.3.1. \textbf{Results for Dewatering and Degasification of a Coal Seam}

A series of computer runs were performed to illustrate the methane and water production from a coal seam. The reservoir parameters used in these simulations are listed in Table 1. Here, the well spacing was taken to be 2400 ft, the reservoir depth to be 3200 ft, cleat porosity to be 2%, permeability to be 2 md, adsorption capacity for methane to be 4.1 lbm/ton-coal, sorption time constant which is related to the cleat spacing and the diffusion coefficient in the coal matrix to be 231.5 days, and the well bore radius to be 0.29 ft. The initial reservoir pressure and gas saturation were selected to be 2200 psia and 0.0, respectively. The pressure at the production well was taken to be 25 psia as the inner boundary and a no-flow condition was taken as the outer boundary condition.
Table 1. Default parameters for computer runs for methane and water production from a coal seam

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir size</td>
<td>2400 ft x 2400 ft</td>
</tr>
<tr>
<td>Reservoir depth</td>
<td>3200 ft</td>
</tr>
<tr>
<td>Reservoir thickness</td>
<td>10 ft</td>
</tr>
<tr>
<td>Cleat porosity</td>
<td>2 %</td>
</tr>
<tr>
<td>Formation compressibility</td>
<td>$1.10^{-6}$ psia$^{-1}$</td>
</tr>
<tr>
<td>Reservoir temperature</td>
<td>153 °F</td>
</tr>
<tr>
<td>Initial reservoir pressure</td>
<td>2200 psia</td>
</tr>
<tr>
<td>Initial water saturation</td>
<td>100 %</td>
</tr>
<tr>
<td>Critical gas saturation (CGS)</td>
<td>0.0</td>
</tr>
<tr>
<td>Critical water saturation (CWS)</td>
<td>0.25</td>
</tr>
<tr>
<td>Permeability (lateral, vertical)</td>
<td>2 md, 2 md</td>
</tr>
<tr>
<td>Relative permeability to gas at CWS</td>
<td>0.174</td>
</tr>
<tr>
<td>Relative permeability to water at CGS</td>
<td>1.0</td>
</tr>
<tr>
<td>Adsorption Capacity</td>
<td>4.1 lbm/ton</td>
</tr>
<tr>
<td>Langmuir Constant</td>
<td>167.6 psia</td>
</tr>
<tr>
<td>Sorption time constant</td>
<td>231.5 days</td>
</tr>
<tr>
<td>(Cleat spacing)</td>
<td>(0.55 in.)</td>
</tr>
<tr>
<td>Number of grid blocks in x, y, and z directions</td>
<td>9, 9, 1</td>
</tr>
<tr>
<td>Well location</td>
<td>5, 5, 1</td>
</tr>
<tr>
<td>Well bore radius</td>
<td>0.2917 ft</td>
</tr>
<tr>
<td>Pressure at well bore</td>
<td>25 psia</td>
</tr>
</tbody>
</table>

Figure 10 shows the gas and water production rates during the degasification and dewatering of a coal seam. Typically, there are three stages in coal dewatering/degasification process. At stage I, a huge amount of water is produced at the initial drainage because water
initially occupies the cleat porosity in the reservoir, which controls the flow to the production well. At this stage, the relative permeability for water is high. As the water production continues, the hydrostatic pressure decreases, which result in the adsorbed methane to desorb and enter into the cleat porosity. At this stage, gas production rate is low and it increases as the water continues to be removed from the cleat system. At this stage, the relative permeability to water decreases while the relative permeability to the gas increases. At the end of about 5 years, most of the water is pumped-off and the gas production rate reached at its maximum. At stage II, the gas production reaches at its maximum while the water production rate is considerably reduced. At this stage, the reservoir flow condition is stabilized until the beginning of the third stage. At stage III, the gas production rate starts to decline. At this stage, the water production is low or negligible. Also, at this stage, both of the relative permeabilities to gas and water change very little.

![Graph showing gas and water production rates](image)

**Figure 10.** Gas and water production rates during the dewatering and degasification of a coal seam
The length of the dewatering and degasification process is controlled by the physical properties of the coal seam and project development parameters. For instance, fracturing the coal seam and a closely spaced well configuration will significantly reduce the time for the dewatering and degasification processes of the coal seams.

Figure 11 shows the pressure distribution along the coal seam and in the vicinity of the production well during the production. As can be seen, the pressure decline is more noticeable at the vicinity of the production well. Because the cleat porosity was occupied by the water and the production of water reduces the hydrostatic pressure, the pressure reduces along the coal seam. As a result of the pressure decline, the adsorbed methane starts to desorb and fill the cleat porosity. This is, as expected, increases the gas saturation in the cleat system as shown in Figure 12. However, the gas saturation could only be increased up to 50% over a 50 year period. This is because, according to the adsorption isotherm, most of the stored gas is still left behind as the seam pressure could only be reduced to about 300 psia (Figure 11). At these conditions, the gas saturation in the cleat porosity along with the irreducible water can reach only up to 50% levels.
Figure 11. Pressure distribution during the dewatering and degasification of a coal seam

Figure 12. Gas saturation within the coal seam during the degasification process

At this configuration and reservoir conditions defined in Table 1, it seems that the pressure could only be reduced to about 300 psia and the gas saturation increased up to 50% at
the end of 50 years of degasification process. This is due to the continuous desorption of adsorbed methane as the pressure further decline in the coal seam. Of course, this is not acceptable for the efficient CO$_2$ sequestration. That is, delaying the injection process for 50 years is not practical. However, the length of the degasification process can significantly be reduced, for instance, by reducing the well spacing and fracturing the coal seam, which could be the subject for another study.

3.4 Modeling CO$_2$ Sequestration in a Coal Seam

The previously defined dewatering and degasification layout (Figure 8) was now converted into the CO$_2$ injection process as shown in Figure 13. In this configuration, the production well at the center is used for the CO$_2$ injection and its surrounding wells are used to continue the degasification and dewatering process.

![Figure 13. Layout for the CO$_2$ injection in a coal seam](image)
A series of computer runs was performed to illustrate the CO$_2$ injection in coal seams. The default reservoir parameters used in these simulations are listed in Table 2. Here, the reservoir size was taken to be 4800 ft by 4800 ft, which is the double size of the field originally selected for the degasification process, the permeability to be 1 md, the sorption capacity to be 5.44 lbm/ton-coal, sorption time constant to be 231.5 days, and bore radius to be 0.29 ft.

The initial condition for the pressure and gas saturation were selected to be 22 psia and 80%, respectively, considering initially degasified and dewatered coal seam. The internal boundary condition was taken to be 2200 psia as the injection pressure at the well. The external boundary condition was selected as the constant flow condition since the production wells at the outer boundary provides a constant flow rate at atmospheric pressure of about 22 psia.
Table 2. Default (base case) parameters for CO$_2$ injection in a coal seam

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir size</td>
<td>4800 ft x 4800 ft</td>
</tr>
<tr>
<td>Reservoir depth</td>
<td>3200 ft</td>
</tr>
<tr>
<td>Reservoir thickness</td>
<td>10 ft</td>
</tr>
<tr>
<td>Cleat porosity</td>
<td>2 %</td>
</tr>
<tr>
<td>Formation compressibility</td>
<td>$1.10^{-6} \text{ psia}^{-1}$</td>
</tr>
<tr>
<td>Reservoir temperature</td>
<td>153 °F</td>
</tr>
<tr>
<td>Initial reservoir pressure</td>
<td>22 psia</td>
</tr>
<tr>
<td>Water saturation</td>
<td>20 %</td>
</tr>
<tr>
<td>Permeability (lateral, vertical)</td>
<td>1 md, 1 md</td>
</tr>
<tr>
<td>Adsorption Capacity</td>
<td>5.44 lbm/ton</td>
</tr>
<tr>
<td>Langmuir Constant</td>
<td>35.3 psia</td>
</tr>
<tr>
<td>Sorption time constant</td>
<td>231.5 days</td>
</tr>
<tr>
<td>(Cleat spacing)</td>
<td>(0.55 in.)</td>
</tr>
<tr>
<td>Number of grid blocks in x, y, and z directions</td>
<td>9, 9, 1</td>
</tr>
<tr>
<td>Well location</td>
<td>5, 5, 1</td>
</tr>
<tr>
<td>Well bore radius</td>
<td>0.2917 ft</td>
</tr>
<tr>
<td>Skin factor</td>
<td>0</td>
</tr>
<tr>
<td>Pressure at well bore</td>
<td>2200 psia</td>
</tr>
</tbody>
</table>

3.4.1. Results for Model Runs for CO$_2$ Sequestration

The CO$_2$ injection process was modeled to make predictions using the default system. Figure 14 shows the CO$_2$ injection rate and the cumulative of the injected CO$_2$. As shown in the figure, the CO$_2$ injection rate increases sharply soon after the start of the injection process. In a
short time, the injection rate reaches a maximum where it seems to be constant until a breakthrough observed. This is consistent with the actual field data from San Juan basin (Figure 7), where the CO$_2$ injection rate was constant over 3 to 5 years. However, the injection process was not complete to compare with the predicted data. As the injection process continues, the injection rate starts declining, where the coal seam reaches saturation. For the default parameters specified, a total of 4.5*10$^6$ SCF CO$_2$ can be injected over 30 years.

![Graph showing CO$_2$ injection rate and cumulative injected CO$_2$ predicted by the model](image)

**Figure 14.** CO$_2$ injection rate and cumulative injected CO$_2$ predicted by the model

Figure 15 shows the pressure distribution along the coal seam during the CO$_2$ injection process. Here, the origin on the Cartesian coordinates represents the place for the injection well. Normally, the pressure at the injection well is 2200 psia. As shown in the figure, CO$_2$ is adsorbed on the coal upon the injection resulting in the reduction in the pressure. As the coal is saturated in the vicinity of the injection well, the CO$_2$ moves along the coal seam. As it reaches the
advancing front, it is adsorbed on the coal matrix and pressure decreases. As the CO₂ moves through the coal seam, its concentration and pressure are built up over time. The injected CO₂ reaches the production well in about 10 to 15 years showing the first breakthrough. This is consistent with the actual field data from San Juan basin (Figure 7), where no breakthrough was observed even after 5 years of CO₂ injection. The coal seam can reach the injection pressure in about 25 to 30 years, which is supposed to be the pressure before the dewatering and degasification process was conducted. However, in reality, this time period could be shortened since the production wells would be shut in after the first breakthrough was observed.
Figure 15. Pressure distribution during the CO₂ injection process
Figure 16 shows the adsorption rate through the coal seam during the injection process. As shown in the figure, the adsorption rate in the vicinity of the injection well is the highest during the initial injection period. As the injection process continues the injected CO$_2$ moves through the coal seam toward the advancing front where the adsorption rate is higher depending on the pressure. As the pressure exceeds 600 psia, the adsorption rate becomes negligible since the coal is saturated with CO$_2$ at this pressure. Comparing the pressure distribution in Figure 15 with the adsorption rate in Figure 16, the injected CO$_2$ reaches the production well in about 15 years, where adsorption was seen at pressures up to 400 psia. At pressures above this value, there is negligible adsorption since it seems that the coal be saturated by the injected CO$_2$. Furthermore, the additional CO$_2$ injection seems to fill up the cleat porosity by building up the pressure in the cleat system.
Figure 16. Model prediction of the CO$_2$ adsorption rate over the coal seam during the injection process
4. Parametric Studies of the Effect of the Coal Seam Properties on CO₂ Sequestration

A parametric study was conducted to investigate the effects of the intrinsic coal-seam properties as well as the thermodynamic and physical relationships that exist between these properties on CO₂ sequestration in coal seams. The default parameters (base case) shown in Table 2 were used in the model by altering only one parameter at a time for the subsequent runs for comparison. In fact, an actual coal seam sequestration process could have been modeled as a case study where the actual coal seam parameters are used and the results be compared with the field data. However, this is not the case here; instead, it was aimed to analyze the effect of the important parameters on the CO₂ sequestration process in coal seams.

4.1. Effect of Coal Thickness on CO₂ Sequestration

The effect of coal thickness on the CO₂ sequestration was investigated. The model was run for the default parameters listed in Table 2 while replacing the coal thickness values for the subsequent runs. Figure 17 shows the effect of coal seam thickness on the CO₂ sequestration. As can be seen, the CO₂ injection rate increases as the coal thickness increases. In addition, the cumulative stored CO₂ is also increased with the coal thickness. The CO₂ breakthrough does not change. The coal seam thickness is therefore important for the amount of CO₂ that can be sequestered in coal seams at higher injection rates.
Figure 17. Effect of coal seam thickness on the CO$_2$ sequestration

4.2. Effect of Permeability on CO$_2$ Sequestration

Permeability is a property of a porous medium about how fast it can conduct the fluids. Therefore, permeability is one of the most important parameters in coal seam sequestration. Because the site planned for the CO$_2$ sequestration would most probably be the deep, unmineable coal seams, the permeability values for such coal seams is expected to be lower. Therefore, the parametric study for the effect of the permeability on CO$_2$ sequestration in coal seams was conducted by selecting the permeability values to be 0.5, 1.0, and 2.0 md, respectively. As can be seen in Figure 18, there is a huge effect of permeability on the CO$_2$ injection rate where the cumulative injection capacity does not change. The injection rate is higher in those coal seams possessing higher permeability values whereas the injection rate is smaller for those possessing lower permeability values. In addition, as shown in the figure, the breakthrough for those coal
seams possessing higher permeability values results in shorter length of time for the CO₂ breakthrough whereas longer length of time is required for the breakthrough for the low permeability values.

![Diagram showing injection rate and cumulative injection plots for different permeability values.]

**Figure 18.** Effect of permeability on the CO₂ sequestration

### 4.3. Effect of Compressibility of Coal on CO₂ Sequestration

Compressibility of a coal seam is related to the volumetric changes of the coal matrix under the influence of the effective stress. The compressibility of coal can also be related to the permeability because any change in expansion or constriction in coal will affect the cleat opening, and therefore, the cleat porosity within the coal seam. As shown in Figure 19, a low compressibility of $10^{-6}$ to $10^{-5}$ seems to affect the injection process little, however, higher coal
compressibility values, say $10^{-4}$ or lower, decreases the injection rate and increases the length of time for the breakthrough. On the other hand, the total injected CO$_2$ does not change.

![Graph showing the effect of compressibility on CO$_2$ sequestration](image)

**Figure 19.** Effect of coal compressibility on the CO$_2$ sequestration

### 4.4. Effect of Cleat Porosity on CO$_2$ Sequestration

Cleat porosity is the space between the coal matrixes serving as both the conduit for the fluid flow and the space for gas storage. As shown in Figure 20, the cleat porosity does not affect the injection rate when all other parameters, especially the permeability, are set to be constant. It is well recognized that the permeability is a close function of the cleat porosity and the aperture size. However, in this investigation, the permeability value was kept constant for each cleat porosity values. In this case, the effect of cleat porosity was predicted to be negligible on the CO$_2$ injection rate owing that the permeability for each case is the same. However, the
length of time for a breakthrough is longer for the coal seam possessing higher cleat porosity. The cleat porosity provides extra volume for gas storage. As shown in the figure, the coal seam with larger cleat porosity increases the storage capacity for the injected CO₂.

![Diagram showing effect of cleat porosity on CO₂ sequestration](image)

**Figure 20.** Effect of cleat porosity on the CO₂ sequestration

4.5. Effect of Cleat Spacing or Sorption Time Constant on CO₂ Sequestration

Cleat spacing is a characteristic dimension of the coal matrix in a coal seam. The cleat spacing, $s$ (ft), and the matrix diffusion coefficient, $D_t$ ($ft^2/day$), are related to sorption time constant, $\tau$, which determines the rate at which gas is released from the micropores to the cleat system or vice versa by the following equations:

\[^{17}\]
\[ \tau = \frac{s^2}{5.783 \ D_i} \]  \hspace{1cm} (15)

For smaller values of \( \tau \), the diffusion/sorption process is faster. The sorption time constant was calculated to be 1.2, 116.9, and 231.5 days for the cleat spacing of 0.1, 1.0, and 1.4 cm, respectively. As shown in Figure 21, for the larger cleat spacing, the injection rate is faster and the length for the breakthrough is shorter. As expected, when the cleat spacing is larger, that is, the coal matrix becomes thicker; the sorption rate is smaller due to diffusion limitation. Therefore, the injected CO\(_2\) could lead to the production well through the cleat porosity faster. On the other hand, when the cleat spacing is smaller and the cleat matrix is thinner, the diffusion/sorption process is faster. However, because the aperture size for the fluid flow is smaller due to the fixed cleat porosity taken for the model runs, the injection rate is delayed at the initial phase of the injection process. The maximum injection rate is the same for each cleat spacing and the sorption time constant studied. The cumulative injected CO\(_2\) does not change with the cleat spacing or the sorption time constant.
4.6. Effect of Adsorption Capacity on CO₂ Sequestration

Adsorption capacity may vary from seam to seam depending on the chemical and physical nature of the coal seams. For instance, the microporosity within the coal matrix is essential for the storage of gases by adsorption. Coalbed methane is one of the adsorbed components in microporosity in the coal matrix. Another most important component is the moisture. The fact that the adsorbing gases compete with moisture for the adsorption sites and/or the pore volumes in the coal matrix at the laboratory conditions is well known. At the in-seam condition, the injected CO₂ has to compete with the moisture which already occupied the available pore space. Therefore, the adsorption capacity of a coal seam may vary depending on the availability of the microporosity in the bulk coal. Here, the model runs were conducted using three different adsorption capacities as shown in Figure 22. For each adsorption capacity case,
the same maximum injection rate is obtained. As shown in the figure, for the low adsorption capacity condition, the time for the breakthrough is shorter. As the adsorption capacity is increased, the time for the breakthrough becomes longer. As expected, the cumulative amount of stored CO₂ increases when the adsorption capacity is increased.

![Graph showing the effect of adsorption capacity on CO₂ sequestration](image)

**Figure 22.** Effect of adsorption capacity of coal on the CO₂ sequestration

5. **Concluding Remarks**

The injection process is highly affected by the coal seam properties especially permeability, adsorption capacity, cleat spacing, and the presence of both water and CBM in the coal seams. The CO₂ storage in coal seams may take years. The production of methane may offset the sequestration costs.
APPENDIX A

Modeling Fluid Flow in Coal Seams
1. Modeling Fluid Flow in Coal Seams

Most coal beds are saturated with water and CH$_4$ and they are under near-hydrostatic pressure. CH$_4$ is held mostly within the porous coal matrix by an adsorption mechanism which is controlled by the reservoir pressure and temperature. Water also adsorbs within the coal matrix but this water is assumed to be immobile.

There are basically three stages in dewatering and CBM production processes. The first stage is the single phase water production. In this stage, only one phase, water, is present in the macropore spaces. As the water started to be removed, the reservoir pressure starts to reduce. In the second stage, the pressure decline causes the CH$_4$ gas to diffuse into the macropore/cleat system. The gas phase reduces the water saturation and its relative permeability in the cleat system. In the third stage, as the reservoir pressure further decreased, additional gas is desorbed into the cleats where the gas saturation builds until the gas phase forms a continuous pathway to the well bore. Thus, the flow in a coal seam is a two-phase flow including a water phase and a gas phase.

2. Material Balance

The fluid flow in porous coal is generally described by the continuity (or mass conservation) equation assuming the porous medium is a continuum and its physical properties on the entire system can be represented by a control volume element. The transport of fluids thorough a coal seam is considered to be a two-stage process. One is the transport in the natural
fractures or cleats and the other is the transport within the coal matrix. Because the transport in cleat system is much faster than the transport in coal matrix, i.e. convection vs. diffusion, the mass balance is generally conducted on the differential element within macrospores. Figure 1 illustrates the basis for the material balance. The material balance for a fluid flowing through a control volume over a time period is

\[ \text{[mass in]} - \text{[mass out]} \pm \text{[generation/consumption]} = \text{[accumulation]} \quad (16) \]

Figure 23. Representation of material balance for a fluid on a differential volume

The mass of each phase entering and leaving the elemental volume in macrospores can be given in Table 3. Here, the Cartesian coordinates \((x, y, z)\) is considered for the flow geometry.
Table 3. The mass of each phase entering and leaving the elemental volume

<table>
<thead>
<tr>
<th>Coordinates</th>
<th>mass in</th>
<th>mass out</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>$\rho_j \nu_j \ dy \ dz$ (17a)</td>
<td>$\rho_j \nu_j \ dy \ dz + \frac{\partial}{\partial x} \left( \rho_j \nu_j \ dy \ dz \right) dx$ (17b)</td>
</tr>
<tr>
<td>y</td>
<td>$\rho_j \nu_j \ dx \ dz$ (18a)</td>
<td>$\rho_j \nu_j \ dx \ dz + \frac{\partial}{\partial y} \left( \rho_j \nu_j \ dx \ dz \right) dy$ (18b)</td>
</tr>
<tr>
<td>z</td>
<td>$\rho_j \nu_j \ dx \ dy$ (19a)</td>
<td>$\rho_j \nu_j \ dx \ dy + \frac{\partial}{\partial z} \left( \rho_j \nu_j \ dx \ dy \right) dz$ (19b)</td>
</tr>
</tbody>
</table>

The definitions of the symbols used can be found in the nomenclatures. The material balance for each fluid phase including the source/sink and accumulation terms is therefore

$$- \frac{\partial}{\partial x} \left( \rho_j \nu_j \ dy \ dz \right) dx - \frac{\partial}{\partial y} \left( \rho_j \nu_j \ dx \ dz \right) dy - \frac{\partial}{\partial z} \left( \rho_j \nu_j \ dx \ dy \right) dz = \sum Q_j = \frac{\partial}{\partial t} \left[ \phi (V_o) \rho_j S_j \right]$$

(20)

Dividing both sides by the differential volume, $V_o = dx dy dz$, we obtain

$$- \frac{\partial}{\partial x} \left( \rho_j \nu_j \right) - \frac{\partial}{\partial y} \left( \rho_j \nu_j \right) - \frac{\partial}{\partial z} \left( \rho_j \nu_j \right) \cdot q_{wi} = \frac{\partial}{\partial t} \left( \phi \rho_j S_j \right)$$

(21)

Therefore, the general form of the continuity equation for a multi-phase fluid flow in macropores is

$$- \nabla \cdot \left( \rho_j \nu_j \right) \cdot q_{wi} = \frac{\partial}{\partial t} \left( \phi \rho_j S_j \right)$$

(22)
The general forms of the continuity equations which describe the simultaneous flow of gas and water in a coal seam can be written as

For gas phase

$$\nabla \cdot \left( \rho_g \mathbf{v}_g \right) + q_d \frac{\partial}{\partial t} \left( \phi \rho_g \mathbf{v}_g \right) = 0$$

(23)

For water phase

$$\nabla \cdot \left( \rho_w \mathbf{v}_w \right) = \frac{\partial}{\partial t} \left( \phi \rho_w \mathbf{v}_w \right)$$

(24)

It was assumed that the amount of gas dissolved in water phase is negligible comparing to the amount of free gas exists in the pore space. The density of gas phase can be obtained from the equation of state

$$\rho_g = \frac{MP_g}{zRT}$$

(25)

The appropriate equation for a slightly compressible fluid of water can be derived by the definition of compressibility under isothermal conditions as

$$\rho_w = \frac{\rho_{asc.}}{B_w}$$

(26)

where formation volume factor ($B_w$) for water is

$$B_w = e^{-\epsilon'(p_e - p_c)}$$

(27)

Substituting Eq.(25) and Eq.(26) into Eq.(23) and Eq.(24), and dividing by constants $M/RT$ and $\rho_{asc.}$ respectively, yields

for gas phase
\[-\nabla \left( \frac{P}{z} \right) + \frac{RT}{M} q = \frac{\partial}{\partial t} \left( \phi \frac{S}{z} \right) \]  \hspace{1cm} (28)

for water phase

\[-\nabla \left( \frac{v}{B_w} \right) = \frac{\partial}{\partial t} \left( \frac{\phi S}{B_w} \right) \]  \hspace{1cm} (29)

The transport of water is assumed to obey the Darcy’s Law, then, the superficial water velocity in Eq.(29) is

\[v_w = -5.615 \frac{k k_w r}{\mu_w} \nabla P_w \]  \hspace{1cm} (30)

The transport of compressible gas is assumed to be under the influence of two fields, the potential field and the concentration field. Velocity through the potential field is laminar flow process and can be described by Darcy’s Law:

\[v_D = -5.615 \frac{k k_g r}{\mu_g} \nabla P_g \]  \hspace{1cm} (31)

The velocity through the concentration gradient field is a Knudsen flow process and can be described by Fick’s Law of diffusion:

\[v_c = -\frac{M D}{P_g} \nabla C_a \]  \hspace{1cm} (32)

where

\[C_a = \frac{P_g}{M} S \]  \hspace{1cm} (33)

From definition of gas density and concentration, Eq.(32) becomes

\[v_c = -D_a \frac{z}{P_g} \nabla \left( \frac{P_g}{z} S \right) \]  \hspace{1cm} (34)

These two velocities created by the two fields are additive
\[ v_g = v_g^D + v_g^F \]  

Hence, the velocity of the compressible gas phase is

\[ v_g = -5.615 \frac{kk}{\mu_g} \nabla \Phi_g - D_a \frac{z}{P_g} \nabla \left( \frac{P_g}{z} S_g \right) \]  

Substituting Eq.(36) into Eq.(28) for gas phase and Eq.(30) into Eq.(29) for the water phase, the material balance equations for each phase become:

for gas phase

\[ \nabla \left[ 5.615 \frac{kk}{\mu_g} \frac{P_g}{z} \nabla P_g + D_a \nabla \left( \frac{P_g}{z} S_g \right) \right] + \frac{RT}{M} q_{ai} = \frac{\partial}{\partial t} \left( \phi \frac{P_g}{z} \right) \]  

for water phase

\[ \nabla \left( \frac{kk_{we}}{B_w \mu_w} \nabla P_w \right) = \frac{1}{5.615} \frac{\partial}{\partial t} \left( \phi S_w \frac{P_g}{z} \right) \]  

Furthermore, the capillary pressure and saturation relationships for the two-phase flow through the porous media can be given as

\[ P_w = P_g - P_{sw} \]  

and

\[ S_w = 1 - S_g \]  

By substituting Eqs.(39) and (40) into Eq.(38), the final forms of the material balance equations for each phase become:
\[
\n\n\n\n\n\n\n
(41)
\]

for water phase
\[
\n\n\n\n\n\n\n
(42)
\]

The transport flow equations, Eq.(41) and (42), will have three unknown variables \((P_g, S_g, q_{ai})\) with two coupled equations. In order to solve for these three unknowns, a third equation is needed, which is the source term, \(q_{ai}\), as described by a micropore transport equation.

3. Modeling Gas Transport in Micropores of Coal Matrix

The bulk of the gas stored in coal exists in the adsorbed state. As water is withdrawn from the coal seam, the pressure declines in the reservoir and the gas begins to desorb from the coal. King et al. proposed a non-equilibrium sorption rate equation based on a first order kinetic model:

\[
\frac{\partial q}{\partial t} = -D_t \alpha (q - q_e)
\]

(43)

where \(D_t\) is the diffusion rate of gas through the coal matrix, \(\alpha\) is the shape factor based on shape of the coal matrix, \(q\) is the adsorbed gas at the current time and pressure, and \(q_e\) is the equilibrium sorption capacity at the current pressure. The \(D_t\alpha\) can be characterized as \(1/\tau\), where \(\tau\) is the pseudo steady state time constant.

\[
\frac{\partial q}{\partial t} = -\frac{1}{\tau} (q - q_e)
\]

(44)
The amount of the adsorbed gas in equilibrium with the free gas at pressure of $P_g$ is calculated using the simple Langmuir equation

$$q_e = \frac{q_0 P_g}{K + P_g} \quad (45)$$

The source term, $q_{at}$, is obtained from solution of Eq.(44).

4. Dependence of Coefficients in the Governing Equations on Pressure and Solubility

The coefficients such as relative permeability, viscosity, compressibility factor, formation volume factor, capillary pressure, and porosity are also pressure and saturation dependent given as follows:

Stress dependent macropore porosity ($\phi$) and absolute permeability ($k$):

Macropore porosity ($\phi$)

$$\phi = \phi_0 e^{e^{(P_a - \sigma_{at} - \varphi)}} \quad (46)$$

Absolute permeability ($k$)

$$k = k_0 \left( \frac{\phi}{\phi_0} \right)^n \quad (47)$$

where $n$ is generally taken as 3.

Relative permeability to gas and water from Corey’s relationship:
Relative permeability to gas ($k_{rg}$)

$$k_{rg} = k_{rg}^o (1 - S_{sc}) \left[ 1 - \left( \frac{S^*_g}{1 - S^*_g} \right)^{1 - S^*_g} \right]$$  (48)

where

$$S^*_g = \frac{1 - S_g - S_{sc}}{1 - S_{sc} - S_{sc}}$$  (49)

Relative permeability to water ($k_{rw}$)

$$k_{rw} = k_{rw}^o \left( \frac{S_g}{S_w^o} \right)^{1 - S_w^o}$$  (50)

Density of water

$$\rho_w = \frac{\rho_{sc}}{B_w}$$  (51)

Capillary pressure ($P_{cgw}$) between gas and water phases by Corey's relationship:

$$P_{cgw} = \left[ 3.448 (1 - S_g - S_{sc}) \right]^{1.5}$$  (52)

Viscosity of water and gas phases:

Water viscosity ($\mu_w$)

$$\mu_w = 0.02414 \left( \frac{247.6}{T_\infty - 140} \right)^{2.2476} \left[ 1 + \left( \frac{P_g}{14.7} \right)^{12.701 - 4736.09 / T_\infty} \right] \left[ 1.0467 (T_\infty - 305) \right] 10^{-6}$$  (53)

where $T_\infty$ is in °K.
Gas viscosity ($\mu_w$)

$$\mu_w = \left(\frac{\nu_1}{T_f}\right)e^{(\nu_2 + \nu_3 + \nu_4)}$$  \hspace{1cm} (54)

where

$$\nu_1 = T_f \left( 1.709 \times 10^{-3} - \frac{2.0621 \times 10^{-6} M}{28.97} \right) + 8.188 \times 10^{-3} - 6.15 \times 10^{-3} \log\left(\frac{M}{28.97}\right)$$  \hspace{1cm} (55)

where $T_f$ is in °F, and,

$$\nu_1 = -2.4621182 + 2.97054714 P_f - 0.286264054 P_f^2 + 8.05420522 \times 10^{-3} P_f^3$$  \hspace{1cm} (56)

$$\nu_2 = \left( 2.80860949 - 3.49803305 P_f + 0.36037302 P_f^2 - 0.0104432413 P_f^3 \right) P_f$$  \hspace{1cm} (57)

$$\nu_3 = \left( -0.793385684 + 1.39643306 P_f - 0.149144925 P_f^2 + 0.00441051512 P_f^3 \right) P_f^2$$  \hspace{1cm} (58)

$$\nu_4 = \left( 0.0839387178 - 0.186408848 P_f + 0.0203367881 P_f^2 - 0.009579263.10^{-4} P_f^3 \right) P_f^3$$  \hspace{1cm} (59)
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