# THE EXPERIMENTAL DETERMINATION OF CRUDE OIL PHASE BEHAVIORS

By

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Bachelor of Science
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1986

Submitted to the faculty of
the Graduate College of
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
December, 1996

# THE EXPERIMENTAL DETERMINATION OF CRUDE OIL PHASE BEHAVIORS

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# PREFACE

An apparatus used to determine bubble points and percent liquid volumes at constant temperature of remixed gas condensate mixtures was designed, tested and operated in this work. Measurements were made over the temperature ranges from 80° to 300° F, and at pressures ranging from 20 to 5000 psig. The experimental data has been evaluated to provide bubble point and percent liquid volume curves for two North Sea crude oils. The oil samples were provided by a major oil company on a confidential basis. The composition of these oils can be found in the Oklahoma State University School of Chemical Engineering but they are not open to the general public.

I wish to express my sincere appreciation to my advisor, Dr. Ruth C. Erbar, for her guidance and patience during the course of this study.

I must also thank Dr. R. L. Robinson Jr. and my fellow students Peter Dulcamara and Aaron Raff for their input on the design and construction of the system. Thanks also goes to Dr. Khaled A. Gasem for his assistance with the regression of my data.

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# CHAPTER I

# INTRODUCTION

The proper design and operation of crude oil production and refining facilities is highly dependent upon the phase behavior of the fluids encountered. A thorough knowledge of the behavior of these complex hydrocarbon mixtures is essential before the design of such facilities may begin.

The goal of this work was to design and construct an experimental apparatus capable of determining the phase behavior of crude oil systems at temperatures ranging from 80° to 350° F and pressures from 20 to 5000 psig.

To delineate the state of these systems, bubble point and percent liquid volume measurements were made at a series of isotherms for each crude oil system studied. The data were analyzed to provide a clearer presentation of the system phase behavior within the temperature and pressure limits of the apparatus.

# CHAPTER II

# LITERATURE REVIEW

A literature review was performed during this study to locate information on experimental methods used to determine vapor-liquid equilibrium (VLE) data, and the phase behavior of the $CO_2$ + n-decane system used as a test system in this work.

## Experimental Methods

Limited data are available on crude oil phase behaviors from the oil fields studied due to its proprietary nature. However, there is a good deal of information on the experimental methods used to measure this data. Publications on the study of binary mixtures provide the most complete descriptions of the experimental methods used to determined the phase behavior of petroleum mixtures. A variety of temperature control and sample agitation configurations are used; however, in this study a rocking cell within an air bath arrangement was selected prior to the design of the apparatus, so the literature review centered on the methods and procedures used to determine the phase behavior rather than on the cell and its supporting equipment.

Sage and Lacey (1) provided good background information on experimental methods even though the publication is over 50 years old. Publications covering the use of newer equipment and methods are plentiful. Some of the most recent publications are by Steele at al. (2), and by Jayendra et al. (3).

The works found to be most relevant to crude oils are by Varotsis at al (4), Orr et al. (5), and by Pollack (6). These publications provide information on methods and data collected when studying the effects of gas injection into crudes.

## Experimental Data

Data relating to the carbon dioxide + n-decane system, used as a test system in this study, were easily found. Reamer and Sage (7), Nagarajan and Robinson (8), and Bufkin (9) have measured isothermal phase compositions at various pressures.

No useful data on the two North Sea crude oils was found in open literature.

# CHAPTER III

# EXPERIMENTAL APPARATUS

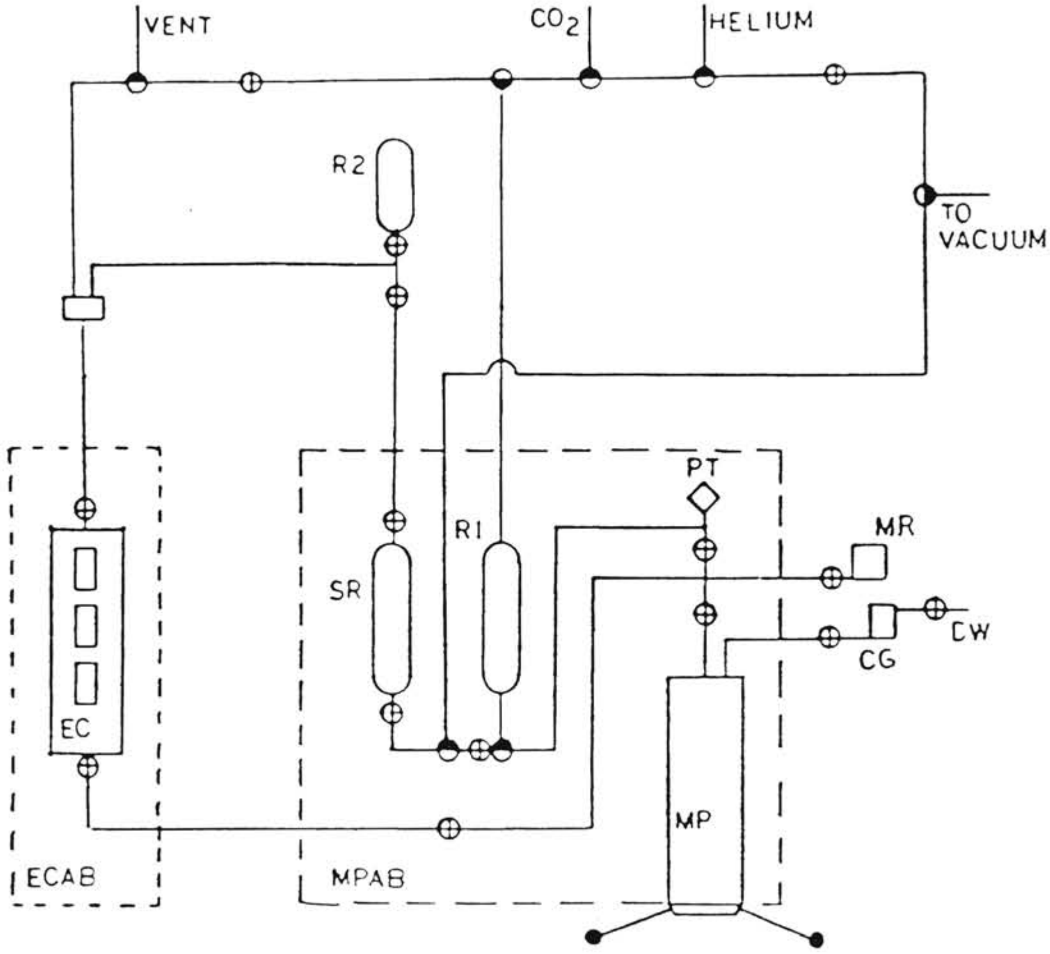
The apparatus in its present form is designed to measure bubble points, dew points and percent liquid volumes of petroleum mixtures. The system can operate at isotherms ranging from 100° to 350° F and pressures as high as 8000 psig. A schematic diagram of the system is shown in Figure 1.

To determine a petroleum mixture phase behavior, the sample is injected into a variable volume windowed equilibrium cell, where its temperature is held constant while the sample is stirred and compressed to provide liquid volumes, bubble point pressures, and dew point pressures.

The bubble point pressure is defined as the pressure at which the vapor phase disappears. Likewise, the dew point pressure is the pressure at which the liquid phase disappears. The percent liquid volume is the percentage of the total sample volume occupied by the liquid phase at a specified temperature and pressure. A general description and arrangement of the apparatus follows.

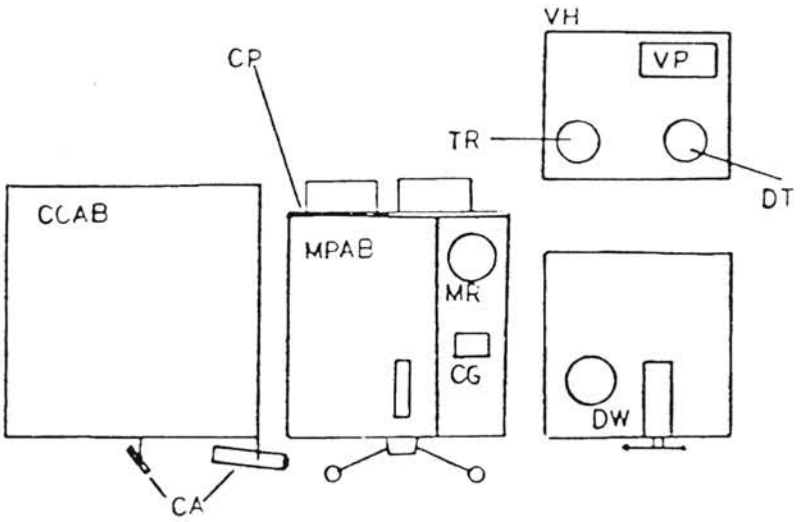
## General Description

The apparatus is housed in two major compartments, the equilibrium cell air bath (ECAB) and the mercury pump air bath (MPAB) (see Figures 1 and 2). The cell air bath is placed adjacent to the pump air bath so that all controls are within reach and are easily



| | |
|---|---|
| ECAB | Equilibrium cell air bath |
| MPAB | Mercury pump air bath |
| EC | Equilibrium cell |
| SR | Sample reservoir |
| R1 | Cleaning fluid reservoir |
| R2 | Mercury - gas interface |
| MP | Mercury Pump |
| DW | Dead weight gauge |
| CG | Oil-mercury contact gauge |
| PT | Pressure transducer |
| MR | Mercury reservoir |

Figure 1. Schematic Diagram of the Isothermal Bubble point - Dew point apparatus



| | | | |
|---|---|---|---|
| CP | Control panel | CA | Cathetometer assembly |
| TR | Trash container | MR | Mercury reservoir |
| VH | Vent hood | VP | Vacuum pump |
| DT | Degassing trap | CCAB | Condensate cell air bath |
| DW | Dead weight gauge | MPAB | Mercury pump air bath |
| CG | Oil-mercury contact gauge | | |

Figure 2. Overhead View of the Experimental Apparatus

visible from the front of the apparatus. The cell air bath also contains the cell rocker mechanism as well as the cathetometer assembly (CA).

The pump air bath is mounted on a large table to the right of the cell bath. This table supports the pump air bath (MPAB), a mercury reservoir (MR), an oil-mercury contact gauge (CG), a mercury pump (MP) and a control panel (CP).

The control panel supports the temperature controllers, the pressure readouts, the digital temperature readouts, and the majority of valves and tubing. The vacuum pump (VP), degassing trap (DT) and the mercury collection container (MC) are all located under the vent hood (VH) to the right of the control panel. The dead weight calibration unit (DW) is also located to the right of the pump air bath.

## The Equilibrium Cell

The main component of the system is a variable volume windowed condensate cell (Ruska model 2306). The cell has a total volume of 400 cc and is constructed of 450 stainless steel. The effective volume of the cell can be varied by introducing and withdrawing mercury from the bottom of the cell (Figure 3). The cell is mounted on a motor driven rocker mechanism that is used to mix the cell contents. Mixing is done with the cell in a horizontal position. The motion of the cell combined with the movement of mercury inside the cell provides thorough mixing of the contents throughout the run. The cell must be rotated to the vertical position to use the cathetometer.

Three glass windows are arranged in the face of the cell so that liquid levels may be determined visually with the aid of the cathetometer. The windows are arranged to provide a clear view of the liquid interface at all times. If the fluid level is hidden between the windows then the levels may be read by inverting the cell. In the upright position, volume readings from approximately 5 to 100, 160 to 210 and 240 to 330 cc can

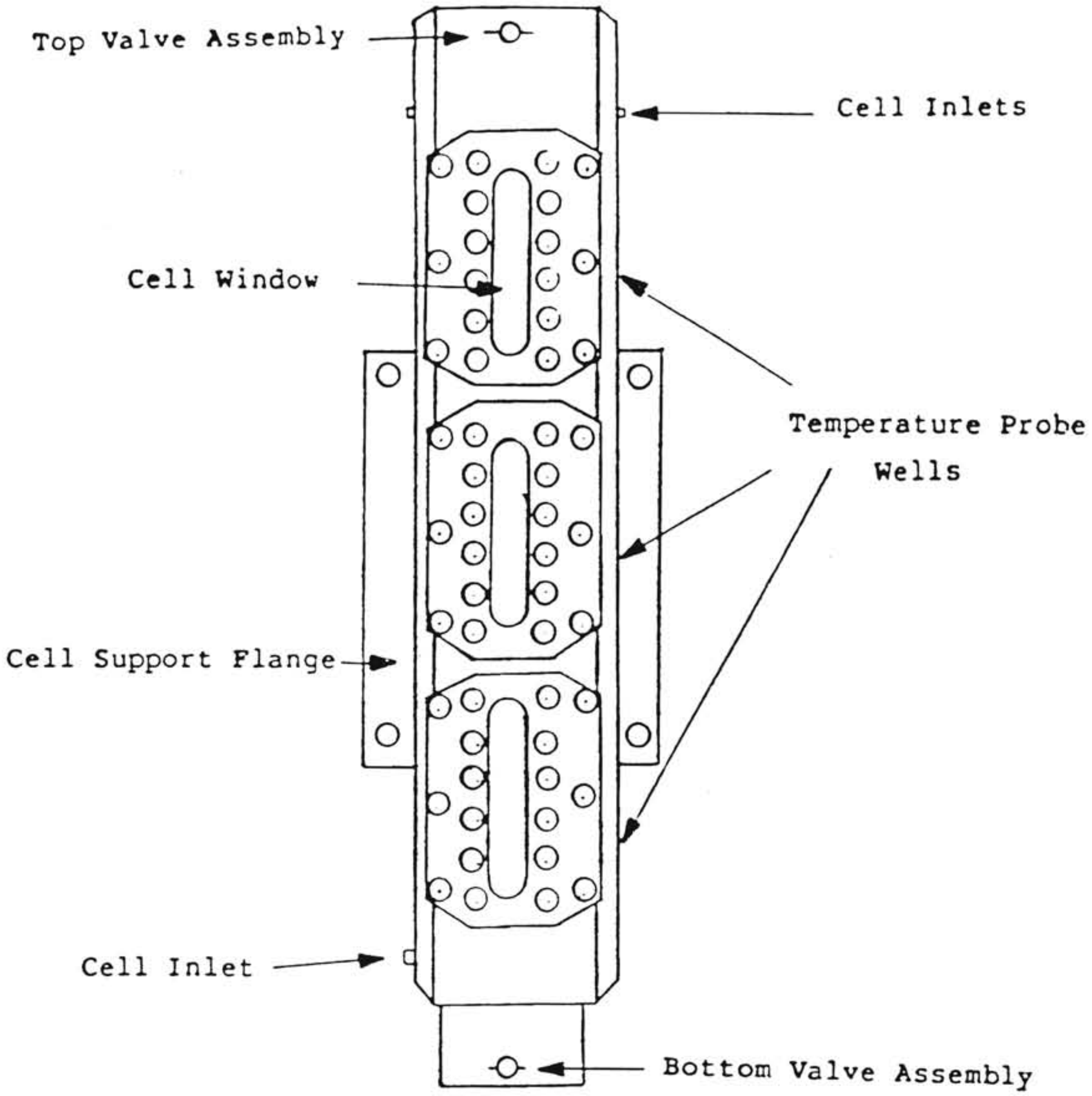


Figure 3. Windowed Equilibrium Cell

be made; while readings from 80 to 170, 200 to 250 and 310 to 400 cc are made with the cell in the inverted position. The readings obtained by the cathetometer are then used in conjunction with fluid level calibration to determine the actual cell volumes.

The tubing leading to the cell is coiled about the cell axis of rotation to allow the cell to rotate freely in the oven with the lines attached. Each line is coiled around the rocker arm three times to minimize the movement of the lines during operation. This arrangement provides for long life but produces a line volume between the cell and the apparatus outside the cell air bath of 12.09 cc.

One benefit of the horizontal cell is its lack of pressure sensitivity to changes in the mercury volumes. Large volumes of mercury can be injected into the cell without dramatically changing the mercury head on the pressure transducers. A similar cell used only in the vertical position could have a maximum variation in mercury levels of 24 inches. This introduces a new pressure head correction required for every change in the mercury volume inside the cell. With the cell in its horizontal position, the mercury head cannot vary by more than 0.5 inches. This allows the use of a single mercury head correction to all pressure measurements. Cell temperatures are measured by three platinum RTD probes located in evenly spaced holes drilled into the cell wall.

## Mercury Injection Pump

A 250 cc positive displacement pump (Ruska model 2250) is used to control condensate cell volumes and system pressures. The pump operates with mercury as the pressure transmitting medium and can maintain pressures as high as 8000 psig. The pump has a resolution of 0.01 cc and the volume can be estimated to 0.005 cc. To prevent pressure fluctuations caused by ambient temperature variations the pump is contained inside a constant temperature air bath.

## Air Baths

Two air baths are used to maintain constant temperatures for the equilibrium cell and the mercury injection pump. Condensate cell temperatures can be adjusted to hold any isotherm between 80° and 325° F. The bath temperature is held within 0.1° F of the set point with a Halikainen proportional-integral temperature controller Model 1053A.

The mercury pump and the pressure transducer are both contained inside the mercury pump air bath (MPAB). This bath is maintained at a constant 122° F (50° C) to negate any pressure effects caused by ambient temperature changes. The injection pump air bath is constructed of plywood and is heated by a 1200 watt electrical resistance heating coil mounted before a fan. A Halikainen model 1053A proportional-integral temperature controller maintains bath temperatures within 0.1° F of the set point.

## Storage Vessels

Several gas cylinders and graduated separatory funnels are employed for storing, charging, and injecting components into the cell as well as providing the gas source for the mercury-gas interface during some stages of the injection procedures. When mixing binary mixtures, the supplied gas sample cylinder (SR) is replaced by a 300 cc monel sample bomb (Hoke 4HDM300) used for injection of light hydrocarbons and cleaning fluids into the condensate cell. This reservoir is rated to withstand pressures up to 5000 psi.

Reservoir one (R1) is used as a gas-mercury interface. This interface is required when a constant pressure must be applied to the sample reservoir (SR) while injecting high pressure single phase mixtures into the equilibrium cell. This stainless steel cylinder R1 (Hoke 4HDY150) has a total volume of 150 cc and is rated for pressures up to 1800 psig. This cylinder can also be used in place of sample cylinders with lower pressure ratings or smaller volumes if required. Both reservoirs are located in the pump air bath to eliminate any ambient temperature effects.

Reservoir two (R2) is a 500 cc graduated separatory funnel used to store and charge cleaning fluids and some liquid samples into the equilibrium cell, the sample reservoir, and reservoir one. A 500 cc mercury reservoir (Ruska model 2419) was used to maintain an adequate amount of mercury for the system.

## Pressure Measurement

Equilibrium cell pressures are measured by a pressure transducer (Sensotec Inc. model TJE 430) with a range of 0 to 10,000 psig. The transducer is kept at a constant temperature at all times inside the pump air bath. Pressures are displayed on a Sensotec 450 D pressure indicator. All pressures are transmitted directly to the transducer via mercury filled lines.

## Temperature Measurement

Temperatures in both air baths are indicated on a digital thermometer manufactured by Fluke Inc. (Model 2180A). Temperatures can be measured with a precision of 0.01°F using platinum resistance thermometers suspended in each air bath. Small platinum resistance thermometers manufactured by Omega (Model PR-11-4-100-1/8-3-E) are used to measure the actual cell temperatures. These thermometers are located in three thermowells in the side of the cell originally designed to hold thermocouples. The platinum resistance thermometers are connected to the same digital thermometers as the air bath probes and have the same resolution of 0.01° F.

## Fittings, Tubing, and Valves

All fittings, tubing and valves used in this apparatus are made of 316 stainless steel. All tubing is 1/8 inch O.D. and is rated to 15,000 psig. Tubing and fittings were manufactured by Autoclave Engineers Inc.

# CHAPTER IV

# EXPERIMENTAL PROCEDURE

This chapter outlines a step by step procedure for operating the apparatus used to determine the bubble points, dew points and percent liquid volumes of hydrocarbon binaries or crude oil systems. Four injection procedures are described; two for mixing and injecting known volumes of solutes and two for injecting multicomponent samples.

The first two injection procedures were used for injecting the carbon dioxide-decane binary mixtures used for testing and evaluating the equipment. The first procedure (Method 1), outlined later in the binary injection portion of this chapter, was used solely to test the ability to reproduce data on the decane-carbon dioxide system. This method allows the mole fraction of the injected sample to be determined only after the injection has been made.

In this method a degassed solvent is first injected into the evacuated equilibrium cell. Cylinder (R1) is then filled with the gas to be injected at a pressure greater than the pressure in the equilibrium cell (EC) containing the solvent (Figure 4). The pressure is then recorded and a valve between the cell and the solute gas is opened, allowing the high pressure gas to flow into the cell. The valve is then closed when the desired cell pressure is reached.

The volume of the injected gas is then determined by forcing mercury into the gas cylinder until the original recorded pressure is reached. The volume of mercury required to achieve this cylinder pressure is equal to the volume of gas injected into the cell. With the temperature and pressure of the injected gas known, the gas density can be found using experimental data or an appropriate equation of state. In this study, injected carbon dioxide solute density was determined using the IUPAC equation of state (9) for carbon dioxide. Using this gas density and the known volume of gas injected, the total moles of gas injected may be determined and the mole fraction of $CO_2$ in the sample may be found.

The second gas injection procedure (Method 2) for injecting the vapor phase was done to test the use of the apparatus to mix specific mole fractions of gases. In this procedure, the volume of cylinder R1 is measured carefully, and the initial gas pressure is recorded. A mass balance is done around R1 to find the amount of gas that is to remain in the cylinder (R1) after the injection. An equation of state is used to determine the final gas pressure needed in R1 to provide the calculated gas density of the remaining gas. The valve between R1 and the equilibrium cell is then carefully opened and the high pressure gas in cylinder R1 is slowly bled into the equilibrium cell until the predicted gas pressure in R1 is reached.

This provided a method for mixing gases to specific mole fractions within the cell for testing the reproducibility and precision of the data at specific mole fractions.

The two procedures outlined for injecting multicomponent mixtures were used for the purpose of injecting part of the sample into the equilibrium cell or for injecting the complete sample in the event that the sample cannot be maintained at a sufficient pressure to allow the injection of a single phase sample.

Special care must be taken to follow the injection directions carefully during operations. Valves should always be operated in the exact sequence given to insure that no sample is lost or contaminated. Patience must be exercised whenever bubble and dew points are being measured. Some points may require as long as one hour to come to equilibrium. All valve numbers refer to the valves shown in Figure 4.

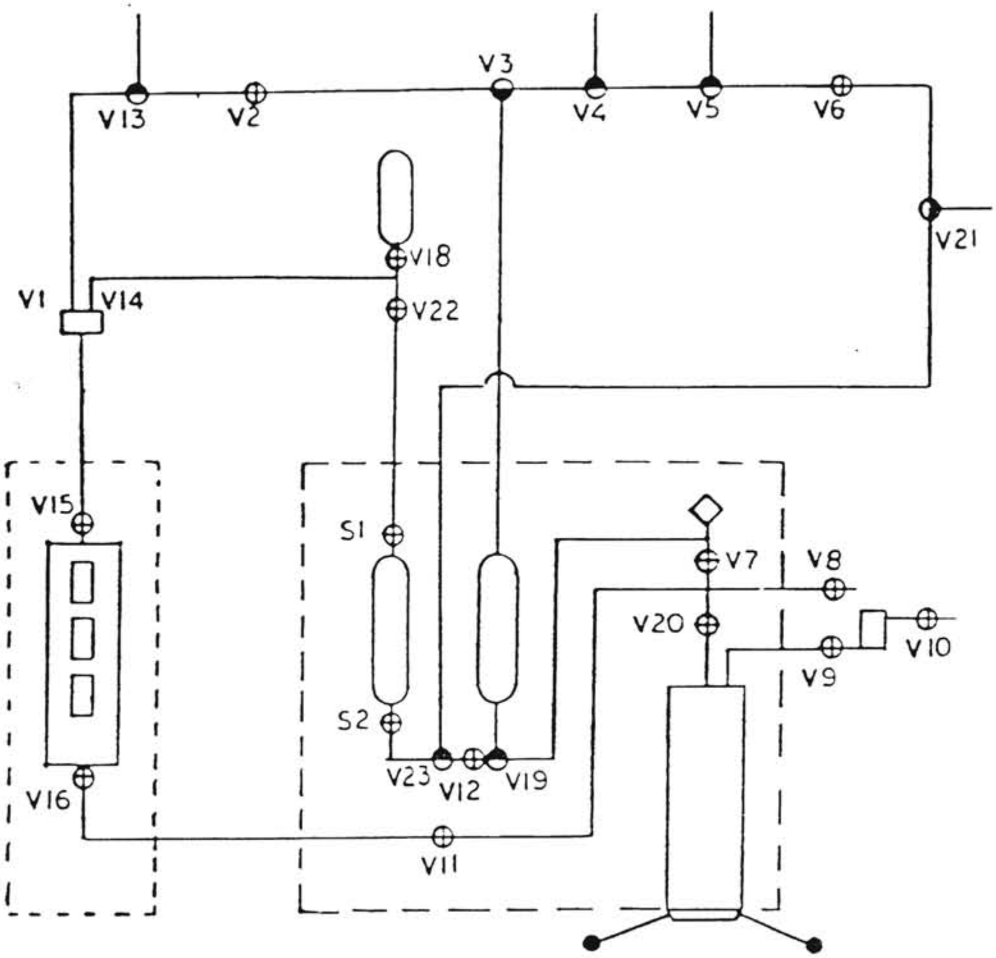


Figure 4. Schematic Diagram of Apparatus with Valve Identification

## Cleaning the Equilibrium Cell

1\. 1. Before a sample may be injected into the equilibrium cell, the cell must be free of all its previous contents to insure that there is no contamination of the sample. A solvent capable of dissolving all the contaminants that may be present is necessary to remove any remnants of prior runs. The solute used for cleaning must have a high vapor pressure so that any solute trapped in the system may be vacuumed out of the cell and lines completely. Benzene or n-pentane are generally used as cleaning solutes.

1\. 2. Starting with all the valves closed and the sample container yet in place, open valves 1, 7, 11, 13, 15, 16, and 20. Using the mercury pump (MP), force mercury into the cell until the mercury can be seen in the sight tube above valve 13. Adjust the $CO_2$ pressure regulator to provide approximately 100 psi and open valves 4 and 2. The $CO_2$ will purge the sight tube and the line volume between valves 2 and 13 of any contaminants. Close valve 13 when all the mercury and residue has been cleared out of the vent line and into the mercury collection container under the vent hood.

1\. 3. With the $CO_2$ line still open, draw mercury from the cell until it is approximately half full of mercury. The mercury level can be checked visually by looking at the cell. Vent the pressured $CO_2$ in the cell by closing valve 2 and opening valve 13. Close valve 13 when the cell pressure steadies at atmospheric. To be sure that no mercury is left in the bottom of the coiled lines leading to the cell, the lines must be cleared with a $CO_2$ purge. Raise the $CO_2$ pressure to 500 psig and open valve 2. The high pressure $CO_2$ will blow any remaining mercury back into the cell. Close valve 2 and open valve 13 to vent the cell. Repeat this procedure three times, then close valve 2 and open valve 13.

1\. 4. Check the liquid nitrogen level in the condensate trap. Turn on the vacuum pump and open valves 6 and 21 to remove the $CO_2$ from the cell. Hold the cell under vacuum for about five minutes. Close valves 2 and 6.

Fill reservoir R2 with 50 cc of cleaning solute. Let the solute be drawn into the evacuated cell by opening valves 18 and 14. Close valves 18, 14, 15, and 16 to isolate the cell. Rock the cell horizontally to insure that the solvent reaches all parts of the cell. Next, return the equilibrium cell to its upright position and open valves 15, 16, 14 and 22. Pump 10 cc of solvent out to the cell through the line between valve 22 and the sample reservoir (SR). Collect the solute and dispose of it. This will remove any oils remaining in the line from the previous run. Close valve 14 and open valve 13.

1. 5. Force the solute from the cell and lines by pumping mercury into the cell until it is visible in the sight tube. Adjust the $CO_2$ pressure to provide about 50 psig of pressure and open valve 2 slowly. The pressurized $CO_2$ will force the used solute out of the line and into the disposal container. When the sight glass is free of solute and mercury, close valves 2 and 13. Clear the lines leading to the cell again by increasing the $CO_2$ pressure to 500 psig and opening valve 2. Vent $CO_2$ to the hood by opening valve 13. Repeat these steps until the lines are clear of mercury.

1. 6. Complete clearing the lines by closing valves 13 and 5 while opening valves 21 and 6. Leave the system under vacuum until there are no visible traces of solute left in the cell. Close valves 6, 1, and 2. The cell may be heated to 150 °F if desired to speed the evacuation of solute from the cell.

## Mixing and Injecting a Binary Sample

2. 1. With a vacuum on the cell from the cleaning operation, close valves 6 and 15. Pump the cell full of mercury and record the pump position (X1) on the injection sheet to be used later for volume measurements (Figure 5). Carefully observe the pressures during this step of the operation. The pressure in the cell should change dramatically when the cell becomes full and then remain steady with time. If the pressure

DECANE - CARBON DIOXIDE INJECTION RECORD

METHOD 1

Run:____________ DATE ________________

T ambient:__________

T cell: __________

T pump bath: _______

X1 _______

VC10=X1-X2________ cc

X2 _______

C10 density __________ gm/cc

Moles C10=________

CO2 temperature________ C CO2 mass ____________ gm

CO2 pressure ________ psia CO2 adjusted P ___________psia

CO2 density __________ gm/cc

X3 = _____________

X4 = _____________

Moles CO2 injected = _________

Total moles CO2 = ____________

Total moles = __________

Mole fraction CO2 =_________

MW C10= 142.29 MW CO2=44.0

COMMENTS:

Figure 5. Method 1, CO2 + n-Decane Injection Record

drops or takes time to line out then there is a gas pocket in the pump, cell or lines. The conditions in the cell may be checked by viewing the top of the cell through the cathetometer. Any vapor bubble in the cell should be visible. The most effective way of eliminating this problem is to pressure up the cell with $CO_2$ and open valves 5 and 15. Using the pump, drain about 20cc of mercury from the cell, leaving a pocket of gas at the top of the cell. Next, evacuate the cell again and restart the binary injection procedure. If the problem remains, repeat the cleaning operation procedure. As a last resort, the system must be completely drained and evacuated to remove any gas from the pump and lines and then refilled with mercury.

2. 2. To prepare the cell for the injection of the solvent or crude sample, raise the $CO_2$ pressure to 200 psig and open valve 4. Lower the pressure in the equilibrium cell using the pump to a pressure below 200 psia. Open valve 15 and drain 100 cc of mercury from the equilibrium cell. Close valve 4 and open valve 13, venting $CO_2$ from the cell. Close valve 13. Open valve 6 and evacuate the remaining $CO_2$ for approximately 10 minutes. The system is capable of providing vacuums below 1 torr absolute; however, this pressure was not recorded for every run. Close valve 6. This will leave an empty volume of 100 cc in the cell.

## Injecting the Solvent into the Equilibrium Cell

3. 1. Fill. reservoir 2 (R2) with the necessary amount of solvent to be injected into the cell. Close valve 1 and let the solvent drain into the cell by opening valve 18 and 14. When the solvent has drained from R2, close valves 18 and 14. Increase the cell volume available for the solvent by drawing about 50cc of mercury out of the cell. Force any solvent remaining in the injection lines into the cell by opening valves 4 and 1. Close valve 4 and vent the $CO_2$ by opening valve 13.

3. 2. Degas the solvent by closing valve 13 and opening valve 6. Leave the solvent under a vacuum for a sufficient time period. The decane used in the carbon dioxide-n-decane system was degassed for 4 hours at 160° F to insure complete degassing. Comparisons with literature data indicate that this time was sufficient for n-decane systems. Shorter degassing times or greater initial solvent volumes will be required when operating with higher vapor pressure solvents, as some of the solvent will be lost in the degassing operation.

Keep the cell contents well mixed by occasionally closing valve 15 and rocking the cell. Remember to allow some time for the solvent to settle after the cell has been returned to its vertical position or some of the solvent may be lost when valve 15 is reopened.

3. 3. With the sample fully degassed, close valve 6 and 15. Pump mercury into the cell to eliminate the dead space above the solvent. Record this pump position (X2) checking to be sure it is at the same pressure as the first pump position reading (X1). The difference between this position and the position recorded in step 1 (X1) is the volume of the injected solvent in cubic centimeters. The number of moles of solvent can now be found using solvent density data (10) at the cell temperature and pressure.

### Injecting a Vapor Phase Solute

4. 1. Two methods of solute injection were used in this study. The first method allows the mole fraction of the solute to be determined only after the solute has been injected. This method is used to determine binary properties where mixing a specific mole fraction is not necessary (Method 1).

The second procedure allows a specific mole fraction of solvent to be mixed. This procedure was used to determine the ability of the system to remix crude samples if necessary and to reproduce data collected at a given mole fraction. Both procedures follow.

### Method 1

5. 1. These valves should be open at the start of this procedure: 1,2,7,11,16,20, and 21. The solvent should already be in the equilibrium cell. Carbon dioxide is used as the solute in this example procedure.

Fill reservoir R1 with $CO_2$ by opening valves 4 and 3. Check the $CO_2$ pressure by closing valve 11 and opening valve 19. This will allow R1 to act as a mercury-gas interface and allow the pressure to be monitored on the digital pressure readout. Adjust the $CO_2$ regulator to provide approximately 500 psig of pressure and close valve 4. Allow the $CO_2$ to come to equilibrium as it is heated to the pump bath temperature (122° F). Record the stabilized pressure (P1) on the injection record sheet. A copy of the injection record sheet is shown in Figure 5.

5. 2. Estimate the volume of solute needed to achieve the desired mole fraction of solute. Close valve 7 and remove a volume of mercury from the cell equal to the desired volume of solute. Inject the solute by opening valve 15 and letting the solute gas flow into the cell. When the cell pressure becomes stable close valve 15.

5. 3. The volume of the injected solute can now be determined. Close valve 11 and open valve 6. Record the pump position (X3) on the injection record sheet. Pump mercury into R1 until the pressure reaches the initial injection pressure P1. Record this pump position as X4. The difference between X3 and X4 is the volume of the solute gas injected at the pressure P1 and the pump bath temperature. The density of the solute can now be determined using an appropriate equation of state (IUPAC was used for the $CO_2$ densities of this study (10)) or experimental data. The number of moles of injected solute

is now calculated. The required adjustments must be made to the pressure value P1 as determined by the pressure transducer calibration before calculating solute densities. More solute injections can be made into the cell to increase solute mole fractions or add different gases. However this will lead to additional error from each injection.

## Method 2 for Solute Injection

This method allows a specific mole fraction of a sample to be mixed as described at the beginning of this chapter.

6. 1. Open valves 3,2 and 13. Allow any gas in R1 to be vented to the hood. Close 13. Open valve 6 and leave R1 under vacuum for 30 minutes. Close valves 6 and 3. Open valve 19 and fill R1 with mercury. Reduce the pressure in R1 to less than 500 psig. Raise the $CO_2$ pressure to 500 psig and open valves 3 and 4. Remove mercury from the equilibrium cell until the desired solute volume is reached (150 cc in this study). Allow the solute pressure to stabilize at the bath temperature and record the solute pressure in R1. The injection sheet used for this procedure is shown in Figure 6.

6. 2. Find the number of moles of solute needed for the injection and calculate required change in molar density of the solute in R1 to deliver the correct amount off solute into the cell. Be sure to account for the additional line volume of 12.09 cc when solute density and volume calculation are done.

6. 3. Using an equation to state or experimental data, find the solute pressure that corresponds to the final solute density needed for the injection. Convert the actual pressure to the pressure reading given on the pressure readout using the transducer calibration corrections. Close valve 7, open valve 11 and drain mercury from the cell with the pump until pressure P2 is reached. Close the valve immediately. Close 19 and 7 to read the cell pressure. The cell pressure should fall slightly as the solute dissolves into the solvent.

DECANE - CARBON DIOXIDE INJECTION RECORD

METHOD 2

Run:____________ DATE ________________

T ambient:__________

T cell: __________

T pump bath: _______

X1 _______

VC10=X1-X2________ cc

X2 _______

C10 density __________ gm/cc

Moles C10=________

mols CO2 required at XCO2=_______. = _____________ mols CO2

CO2 temperature________ C CO2 mass ____________ gm

CO2 pressure ________ psia CO2 adjusted P __________psia

CO2 density __________ gm/cc

CO2 reservoir volume= ________cc

Final CO2 density required = CO2 density-(CO2 mass/VolCO2res)

= _____________gm/cc

Final pressure =________psia

Transducer reading = _________psia

MW C10= 142.29 MW CO2=44.0

COMMENTS:

Figure 6. Method 2, CO2 + n-Decane Injection Record

## Injecting a Multicomponent Sample

This section outlines the procedure for the injection of a multicomponent mixture into the equilibrium cell. Starting after the cleaning step, these valves should be open: 1, 2, 7, 11, 16, 20. The sample cylinder (SR) should not yet be in place.

7. 1. Adjust the $CO_2$ regulator to provide a low pressure of about 20 psig. Place the end of the line leading from valve 23 to S2 in a mercury collection bottle. Open valves 4,6, and 23. This will clear the line of any remaining mercury. Close valve 4 and open valve 13, venting the $CO_2$ to the hood. Close valve 13. Secure the sample cylinder in the brackets and connect the lines leading to the cylinder.

7. 2. Evacuate the lines used for the mercury injection by closing valve 5 and opening valves 21 and 23. Keep the line under vacuum for 10 minutes and then close valve 23. Fill the line with mercury by closing valve 11 and opening valve 12. Pump mercury into the line until it is full. Record the pressure and monitor it as long as necessary for any drop in pressure to insure all fittings are sealed and no leaks exist.

7. 3. Pressure test the connection at S1 by pressuring up the helium to its maximum pressure (not greater than 8000 psig) and closing valve 12 and opening valves 5, 2, 1, 14, 22, 3 and 19. Close valve 5 and record pressures and temperature observations at constant time intervals to insure that the fitting is properly seated and sealed. If a leak is found, tighten the suspect fitting or replace it and repeat the test. A helium detector can be used to locate small leaks.

7. 4. With the sample cylinder (SR) in place and leak tested, evacuate all the lines to be used during the injection procedure. Open valve 13 and vent helium to the hood. Close valves 3 and 19, then open valves 12 and 6. Let the lines evacuate for 1 hour to be sure the lines are clear. Close valves 6 and 1 and turn off the vacuum pump. Open valve S2 and check the sample pressure. If the sample bubble point pressure at the container conditions is below the sample cylinder pressure rating (1800 psi in this study) the sample

may be injected in any desire volume as a single phase liquid. If the bubble point of the sample is above the cylinder pressure limit then the complete sample must be injected into the cell to insure that the sample is of the correct composition. Trying to inject part of the sample in this situation will result in collecting only the light end components of the sample into the equilibrium cell as the sample flashes in SR. If the sample bubble point is not known or cannot be estimated with reasonable accuracy then a scanning procedure similar to the one outlined in the section on determining bubble points (9.1) can be used to determine which injection procedure to follow.

### Injecting the Complete Sample

7. 5. Open valves S1, 22, 14 and 15. Close valve 12 and open valve 11 to read cell pressures on the digital readout. Use the mercury pump to draw the desired volume of mercury from the cell. Open valve 12 and allow the sample to flow into the equilibrium cell. Close 11, open 12 and pump mercury into SR and displace the remaining sample, forcing it into the cell. Pump mercury into SR until mercury is seen entering the equilibrium cell through the line at the top, indicating that SR is free of sample. Close valves 12 and 15 and proceed to the instructions on determining phase envelopes.

### Injecting Part of a Sample from Cylinder SR

Open valves are: 14, 22, 21, 2, 11, 7, 20 and 16.

8. 1. In this step, reservoir one (R1) will act as a $CO_2$-mercury interface to maintain a constant sample pressure provided by a pressure head of $CO_2$. This is done to

keep the sample at a sufficient pressure to maintain a single phase throughout the sample injection. No more than 120cc of the sample should be injected at one time due to the limited volume of R1 (150 cc in this study).

8. 2. Open valve 15 and force mercury into the lines leading from the cell to the sample cylinder. This will prevent the sample from flashing into the empty lines.

8. 3. To be sure an adequate amount of mercury is contained in R1, open valves 3 and 13 to vent off any gas remaining in R1. Evacuate this reservoir for 10 minutes and then close valves 6, 3 and 11. Open valve 19 and fill the cylinder with mercury. Adjust the $CO_2$ regulator to provide a delivery pressure above the sample bubble point.

8. 4. Check the pressure of the mercury in R1 to be certain it is below the $CO_2$ pressure. Open valves 3 and 4 and check pressure in R1. Close valve 19 and open valve 12, isolating R1 and reading the pressure in the sample cylinder. Pump mercury into cylinder SR until the pressure matches that of R1. This step is very important. If the sample is at a pressure well below its bubble point, the mercury in R1 and some of the $CO_2$ may enter the sample container when the pressures in SR and R1 are equalized.

8. 5. With the sample in a single phase, close valve 7 and open valve 19. This couples the sample with the $CO_2$-mercury interface in R1. Observe the pressure readout to be certain that the pressure changes very little and that the sample is maintained at the desired pressure.

8. 6. Open valves 11, S1, 22 and 15. Drain mercury from the cell using the mercury pump until the correct volume of sample is contained in the cell. Close valves 15, S1, 14, 22, S2 and 19, securing the sample cylinder and the system. Read the cell pressures by opening valve 7.

## Determining Phase Envelopes

### Bubble Points.

9. 1. Start the rocking mechanism of the cell and heat the cell to the desired isotherm. Be certain the cell is in the horizontal position or the air flow in the oven will be disrupted enough to produce a temperature gradient along the length of the cell of 2 °F or more. Check all probe temperatures to be certain the cell temperatures are within 0.1° F and that they remain steady.

9. 2. To scan for the bubble point, start at a pressure low enough to insure that the sample is below its bubble point pressure. Pump mercury into the cell in increments of 0.5cc and record the volume and pressure of the sample when it has reached equilibrium. The bubble point pressure has been reached when there is a distinct increase in the magnitude of the pressure change with each 0.5 cc injection of mercury. This occurs when the sample reaches single phase and becomes relatively incompressible compared the two phase region.

9. 3. At this time remove 0.5 cc of mercury from the cell and let the pressure stabilize. Record the cell pressure, volume, and temperature on the data sheet. Figure 7 shows the data sheet used in this study. The system is now ready to begin the bubble point traverse.

9. 4. Pump 0.1 cc of mercury into the cell and let the pressure stabilize. Record the volume change and pressure on the data sheet when the system reaches equilibrium. The cell rocking mechanism should be stopped when pressure readings are taken to eliminate any pressure effects of the moving liquids in the cell. Equilibrium was reached

PRESSURE-VOLUME DATA SHEET

System: ____________________

Run: ______________ DATE ___________

Volume increments: ________ cc

| Pressure | Cell Bath Temperature | Slope dp/dv | Time |
|---|---|---|---|
| | | | |
| | | | |
| | | | |
| | | | |
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COMMENTS:

Figure 7. Pressure - Volume Record Sheet for Bubble points

when the pressure of the system did not change more than 1 psi for a period of one hour in this study.

9. 5. Repeat step 9.4 until 3 points above the bubble point have been found. Plot the data recorded on the data sheet as $P_i$ vs. $(V_i-V_o)$, where $V_i$ is the system volume at point i and Vo represents the original volume reading on the data sheet. Figure 8 shows the results of a typical P-V traverse plot. Fit the best straight lines through the steep single phase slope and the shallower two phase slope. Extrapolate these lines until they intersect. The intersection of these lines occurs at the bubble point pressure.

9. 6. Using the transducer calibration record as shown in Appendix B, linearly interpolate between the two boundary pressure values surrounding the bubble point pressure found on the P-V traverse plot to find the proper transducer correction. Adjust the gauge reading by this correction and record the actual bubble point pressure.

Dew Points.

10. 1. To determine the system dew points, drain mercury from the cell until all the liquid has been vaporized. Slowly increase the cell pressure by forcing mercury into the cell. When liquid can be seen through the cathetometer, stop pumping and record the pressure. Slowly draw out mercury until the liquid is vaporized again and record the pressure.

10. 2. Repeat this process 3 times for each isotherm and use the average of these 3 pressures as the dew point pressure. Remember to correct the pressure shown on the readout with the transducer calibration data.

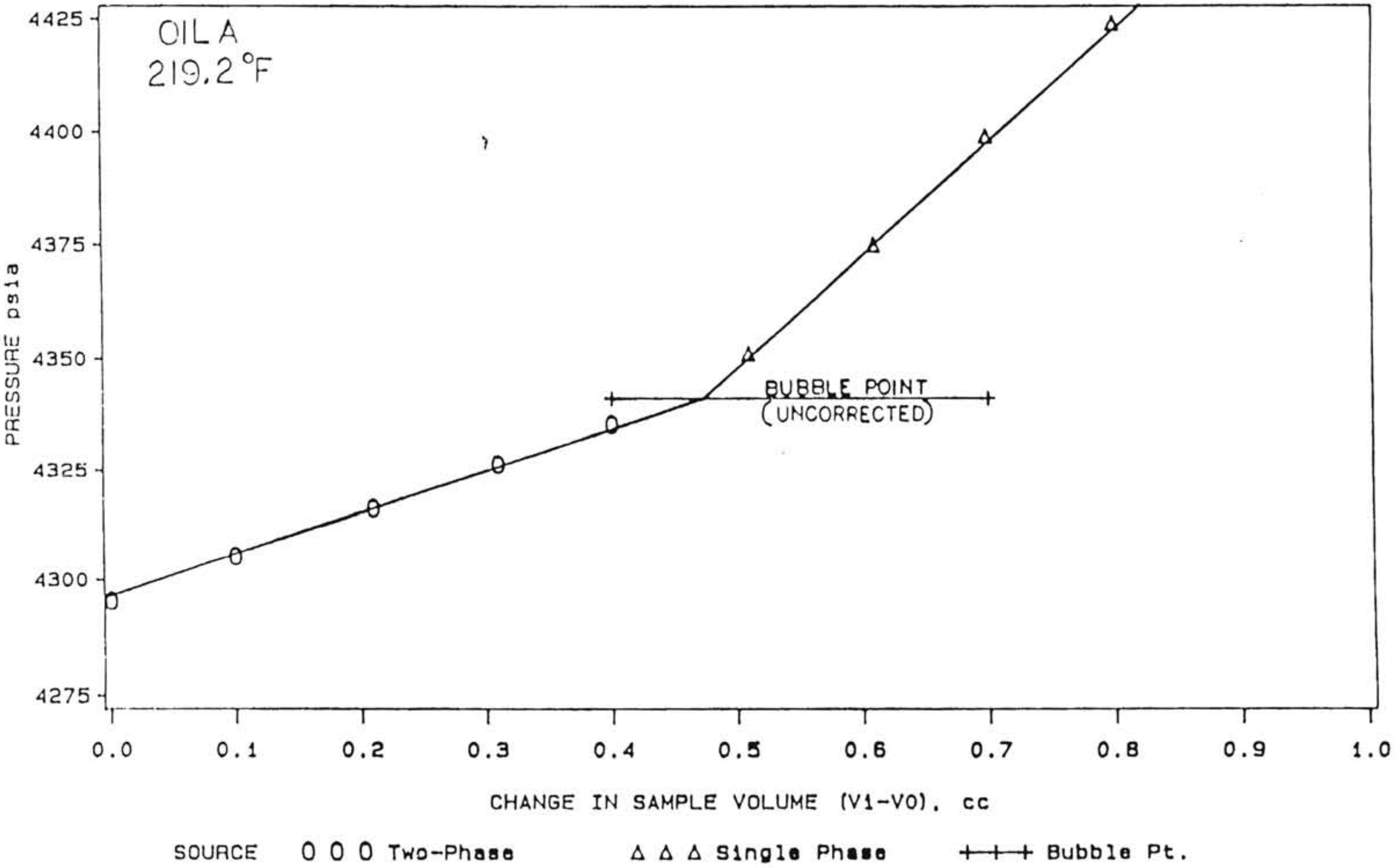

Figure 8. Pressure volume traverse

## Finding Percent Liquid Volumes

11. 1. At various pressures in the two phase region at each isotherm, let the sample come to equilibrium and record the cathetometer positions of the liquid-vapor interface and the mercury levels on the liquid volume record sheet shown in Figure 9. Using the cathetometer calibration, find the liquid phase and total sample volumes and calculate percent liquid volumes at each point.

$$\text{Percent liquid volume} = \text{Liquid volume} * 100 \ / \ \text{Total Volume} \qquad (4.1)$$

Always remember to correct transducer pressure readings with the proper pressure gauge correction.

## Calibration of Pressure Transducers

12. 0. The pressure transducer needs to calibrated regularly to be sure that the indicated pressures are precise. The calibration procedure is simple and easy to perform. The equations to calculate true pressures can be solved quickly with the computer program presented in Appendix B.

12. 1. Before engaging the dead weight gauge, the mercury head correction must be found. First, the heights of the mercury in the equilibrium cell, the mercury in the Jerguson mercury-oil contact gauge and the dead weight reference point must be determined. The mercury head correction takes into account the additional pressure on the transducer produced by the mercury contained in the cell and lines above the level of the pressure transducer. The head correction is calculated using the following equation (11).

$$HC = g(\rho_{Hg}(h_{HgCell} - h_{if}) - \rho_{oil}(h_{ref} - h_{if})) \qquad (4.2)$$

% LIQUID VOLUME

System: ____________________

Run: ________

DATE _______________

| Pressure | Cathetometer | %LV | Temperature |
|---|---|---|---|
|  | ________ |  |  |
| ________ | ________ | ________ | ________ |
|  | ________ |  |  |
|  | ________ |  |  |
| ________ | ________ | ________ | ________ |
|  | ________ |  |  |
|  | ________ |  |  |
| ________ | ________ | ________ | ________ |
|  | ________ |  |  |
|  | ________ |  |  |
| ________ | ________ | ________ | ________ |
|  | ________ |  |  |
|  | ________ |  |  |
| ________ | ________ | ________ | ________ |
|  | ________ |  |  |

COMMENTS:

Figure 9. Liquid Volume Record Sheet.

When measuring the mercury level in the cell be sure that the cell position is the same as when heights are recorded. The mercury head determined for this apparatus was 5.0 psi. The head must only be recalculated if mercury levels change.

12. 2. Open valves 9,10 and the dead weight gauge valve. Check the mercury in the contact gauge to confirm that the level is visible in the gauge. If the mercury level has changed, it may be reset by withdrawing or introducing oil into the contact gauge using the dead weight gauge pump. The gauge should be watched carefully to prevent the injection of oil into the mercury pump.

12. 3. With the dead weight gauge connected to the pressure transducer, turn on the gauge turntable and place the appropriate weight combination on the floating piston. Using the dead weight gauge pump, adjust the system pressure until the reference line on the weight lines up with the reference line on the gauge. Record this transducer reading on the record sheet (see Figure 10) and continue with the next weight combination.

12. 4. Use the computer program in Appendix B to determine pressure transducer corrections.

## PRESSURE TRANSDUCER CALIBRATION RECORD

200 - 4800 psia DATE ____________

| WEIGHTS | TRANSDUCER READING |
|---|---|
| M | |
| MN | |
| LO | |
| LOM | |
| A | |
| AM | |
| AMN | |
| ALO | |
| ALOM | |
| AB | |
| ABM | |
| ABMN | |
| ABLO | |
| ABLOM | |
| ABC | |
| ABCM | |
| ABCMN | |
| ABCLO | |
| ABCLOM | |
| ABCD | |
| ABCDM | |
| ABCDMN | |
| ABCDLO | |
| ABCDLOM | |

ROOM TEMPERATURE..________ ATM. PRESSURE..________

Figure 10. Transducer Calibration Record

# CHAPTER V

# EXPERIMENTAL ERROR ANALYSIS

Precise and accurate experimental data must be collected to properly describe the phase behavior of a multicomponent system. Proper interpretation of this data requires a thorough knowledge of the errors involved and their effects upon the system. The maximum expected errors in the $CO_2$+ n -decane system and the two crude systems tested are calculated in this chapter to estimate the accuracy of the data produced in this study.

Experimental errors can be classified into two categories; systematic and random. Systematic errors are recurring errors generally caused by improper calibration or measurement procedures. They can be eliminated by correcting these faults. Random errors are non-recurring disturbances which cannot be eliminated, predicted or corrected. These errors can only be accounted for statistically (12).

Two checks were made on this apparatus to confirm that all systematic errors were eliminated. First, the vapor pressure of pure $CO_2$ was measured and compared with published data (10) to check the calibration of the system temperature indicators and pressure transducers. Second, a binary mixture of $CO_2$ and decane was studied and results compared to the works of other experimenters to test the procedures and to determine the ability of the apparatus to reproduce published data. No discrepancies were found with published data, so all systematic errors were assumed to be eliminated.

The total random error can be defined as the sum of all prime errors. Prime errors are the errors associated with the measurement of dependent variables such as temperature, pressure and volume. These errors result from the imprecision of the measuring device and its calibration. The prime errors in this study were estimated to be:

ET = 0.10 °K
EP = 0.5 psi
EV = 0.005 cc

where ET, EP, and EV are the uncertainties in the measurement of temperature, pressure and volume respectively.

The uncertainty in the temperature is based on the ability of the apparatus to maintain a constant set point. The pressure uncertainty was estimated to be 0.5 psi because the pressure may vary this amount without indicating a change on the pressure readout. The volume uncertainty was based on the ability to read the scale on the mercury injection pump. The pump was graduated to units of 0.01 cc but could be easily read to 0.005 cc.

To properly analyze both the binary and the crude systems studied, the maximum error must be individually determined for each. The estimated error in the liquid mole fraction of a binary system is (13):

$$\begin{aligned} E_{x1} = x_1 x_2[((E\rho_1)/(\rho_1))^2 + ((E_{v1})/(v_1))^2 + \\ ((E\rho_1)/(\rho_1))^2 + ((E_{v2})/(v_2))^2]^{1/2} \end{aligned} \tag{5.1}$$

The uncertainty in the $CO_2$ density (10) was estimated to be 0.15% based on a sensitivity analysis done by Barrick (13) on the effects of temperature and pressure variation on the IUPAC equation of state used for determining $CO_2$ gas densities.

Density measurements were performed on liquid decane to determine the uncertainty in the decane density (13). A maximum difference of 0.007 g/cc was found between these measurements and was assumed to be the maximum error in the liquid decane measurement.

Typical runs on the $CO_2$+n-decane system consisted of a liquid decane injection of 20 cc with a 50 cc injection of $CO_2$ at 50° C and 500 psia. Substituting these values into equation 5.1 and assuming the mole fraction of each component is 0.5 yields the maximum error as shown below:

$$E_{x1} = 0.003 \qquad (5..2)$$

Therefore, the maximum error in the liquid mole fraction of $CO_2$ and n-decane is 0.003. We may now relate this error to the error in bubble point pressure.

Random error in the bubble point pressure due to prime and propagated errors may be estimated by using the equation (13):

$$E_{bp}^2 = E_P^2 + (\partial P/\partial x_1)^2 * E_{x1}^2 + (\partial P/\partial T)^2 * E_T^2 \qquad (5.3)$$

Assuming the temperature term is negligible and substituting in the maximum error in the liquid mole fraction, the equation becomes:

$$E_{bp}^2 = (0.5)^2 + (\partial P/\partial x_1)^2 * (0.001)^2 \qquad (5.4)$$

Because $\partial P/\partial x_1$ increases with pressure, the maximum value was estimated using the two points taken at the highest pressures. The difference between the two pressures divided by the difference between their corresponding mole fractions resulted in a maximum $\partial P/\partial x_1$ of 1500.

Substituting this value of $\partial P/\partial x_1$ into Equation 5.4 results in a maximum expected error in the bubble point pressure for the $CO_2$ + n-decane binary system of 2.5 psi.

## Crude Oil Systems

The only prime errors associated with the crude oil systems are pressure and temperature. From the uncertainties presented above we know the individual uncertainties attributed to each prime error. Using equation 5.5 the uncertainty in the bubble point pressure of the crude oils due to prime errors may be found.

$$E_{bp}^2 = (0.5)^2 + (\partial P/\partial T)^2 * E_T^2 \qquad (5.5)$$

As before, the temperature term is negligible and may be ignored to give:

$$E_{bp} = E_P = 0.5 \text{ psi} \qquad (5.6)$$

This is the uncertainty due to prime errors for the crude oil mixtures.

This uncertainty is further affected by other error sources not so easily analyzed. One significant source of error is the graphical determination of the bubble point or pressure-volume traverse. Unlike the $CO_2$ + n-decane binary where the change in pressure with respect to a volume change is very small for the two phase region, both the single and two phase regions of the multicomponent crude oils have steep pressure vs. volume slopes (Figure 8). These steep slopes produce significant variations in the bubble point pressures when they are determined by graphical methods.

The estimated uncertainty in the bubble point due to errors in the pressure-volume traverse is 2 psi. Resulting in a total uncertainty in crude oil bubble point pressures of 2.5 psi.

## Percent Liquid Volume

Liquid volume measurements are made with the aid of a cathetometer graduated in millimeters. Each millimeter of height corresponds to a volume change of 1 cc within the equilibrium cell. Readings can be accurately made to 0.5 mm or 0.5 cc.

Each percent liquid volume measurement requires 2 cathetometer readings. One for the liquid volume and the other for the total sample volume. Together, they contribute 1 cc uncertainty in the liquid volume.

The percent liquid volume is defined as the liquid volume divided by the total sample volume. Therefore, the maximum uncertainties are increased as total volumes are reduced. This typically happens as pressures are increased without the addition of more sample. The smallest total volume reached during this study was 28.6 cc. The uncertainty due to the cathetometer volume measurement is 1.0 cc / 28.6 cc or 0.035 .

The uncertainty in temperature is not the same for the liquid volume measurement as it is for the bubble point measurements. Unlike the bubble point measurements, liquid volume data must be collected with the cell in its vertical position so that the cathetometer may be used. As the equilibrium cell changes attitudes within the air bath, the air flow profile within the bath is altered. This change produces temperature gradients along the cell that approach 0.6° C (1.0° F) during the time required to read the cathetometer.

The effect of this temperature change was estimated by finding the maximum change in liquid volume fraction with respect to temperature ($\partial LF/\partial T$).

This temperature-liquid fraction relationship was found from the experimental data to be 0.001 liquid fraction/degree C. Calculating the error in liquid measurement possible in the liquid fraction:

$$E_{LF}^2 = E_c^2 + E_T^2 * (\partial LF/\partial T)^2 \qquad (5.7)$$

Therefore, the maximum uncertainty associated with the prime errors of temperature, pressure, and volume measurement account for an error of 0.035 or +/- 3.5% of the recorded value of volume percent liquid.

A test run was done to find the vapor pressure of pure carbon dioxide to confirm the accuracy of the temperature and pressure indications after calibration. Experimental determination resulted in $CO_2$ vapor pressures of 977 psia at 80.6° F and 1003 psia at 82.7° F. Literature values for carbon dioxide were reported as 976.5 psia and 1002.75 respectively (10). This small discrepancy is acceptable since the pressure readout can only be read to the nearest psi, and the pressure difference is within the minimum claimed error of 2.5 psi for binary systems and 2.5 psi for crude oil mixtures.

The results of this test indicated that all systematic errors had been eliminated and that the calibration equipment and procedures were reliable.

### $CO_2$ + n-decane

A binary mixture was selected for use as a test system to demonstrate the ability of the apparatus to reproduce published data and to test the reliability of the apparatus and procedures used.

The $CO_2$ + n-decane system was selected as the test mixture. This decision was based on the relatively wide pressure range provided by this combination as well as the amount of accurate data available in the literature for comparison.

The bubble point data for the $CO_2$ + n-decane system found in this study is presented in Table I. Figure 11 compares the data obtained in this study with that of other investigators. The data in this figure are plotted with the ordinate being the bubble point pressure divided by the mole fraction of carbon dioxide. The figure is presented in this manner to exaggerate the differences in the bubble point pressure by the reciprocal of the

$CO_2$ mole fraction. This arrangement makes the deviations in the data easier to see and helps to identify any trends.

Comparison of the data produced in this study with the work of previous investigators shows this work is very consistent with those of other experimenters cited.

The magnitude of the scatter in the data may be more easily seen by comparing it to the results of an appropriate equation of state. The data of all investigators was fitted to the Soave-Redlich-Kwong (SRK) equation of state to determine the optimum binary interaction parameters providing the best fit to all the available data (16). The difference between each reported bubble point and SRK predicted bubblepoints was calculated and plotted in Figure 12.

The data of this work appears to deviate slightly negatively from the equation of state, but are well within the experimental error of this apparatus.

The data obtained in this study compared very favorably with that reported by other experimenters. All bubble points were within 1.4 psi of predicted SRK values. The data provided by the experimental apparatus was precise and accurate enough to continue with the crude samples.

## TABLE I

## BUBBLE POINT PRESSURES OF $CO_2$ + N-DECANE AT 344.3 °K (160 °F)

| Mole Fraction $CO_2$ | Bubble Point Pressure psia |
|---|---|
| 0.331 | 653 |
| 0.421 | 844 |
| 0.446 | 916 |
| 0.457 | 929 |
| 0.457 | 930 |
| 0.524 | 1080 |
| 0.597 | 1258 |
| 0.600 | 1247 |
| 0.616 | 1291 |
| 0.698 | 1477 |

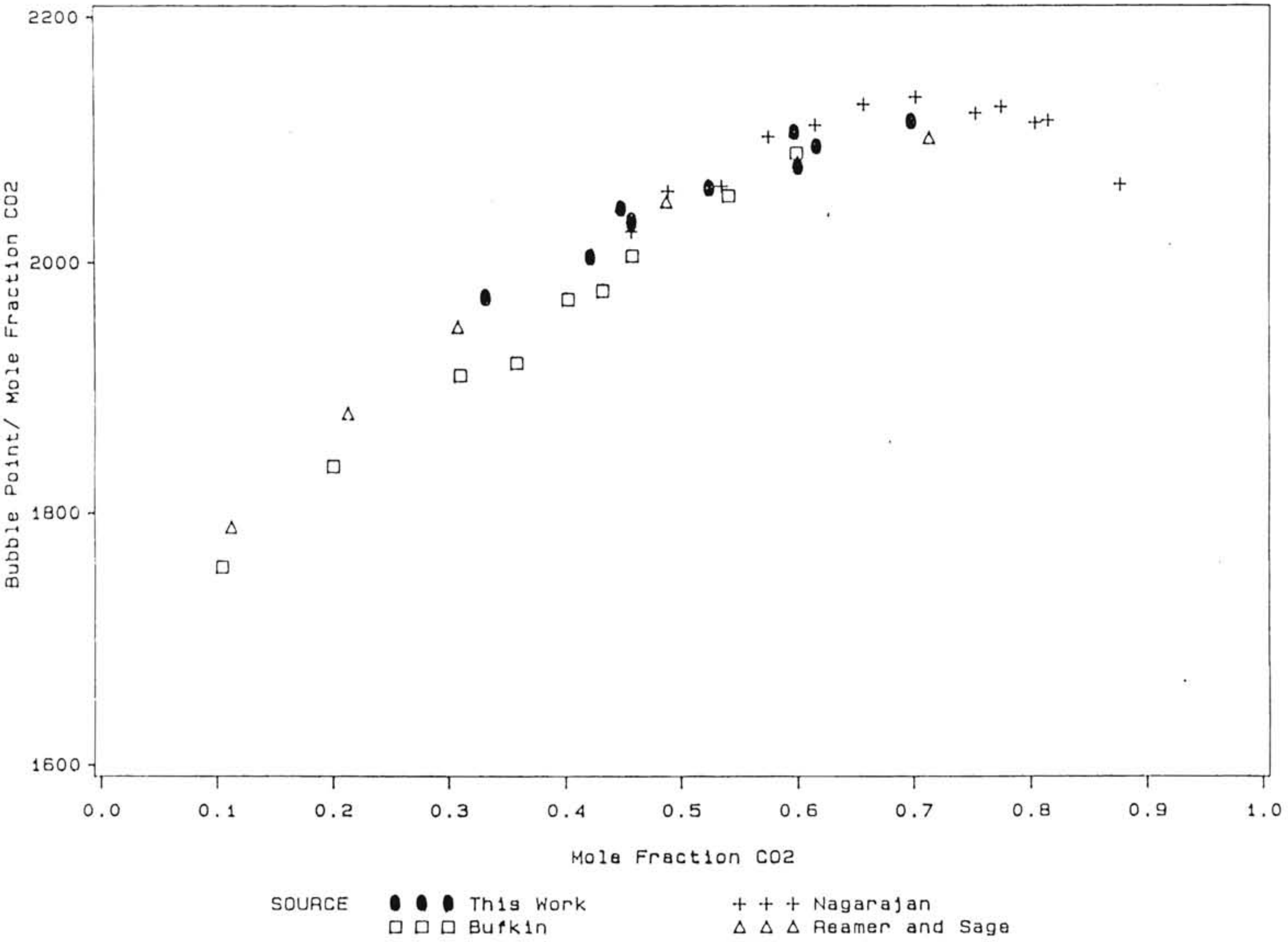

Figure 11. Comparison of CO2 + n-Decane data at 160F with other Investigators

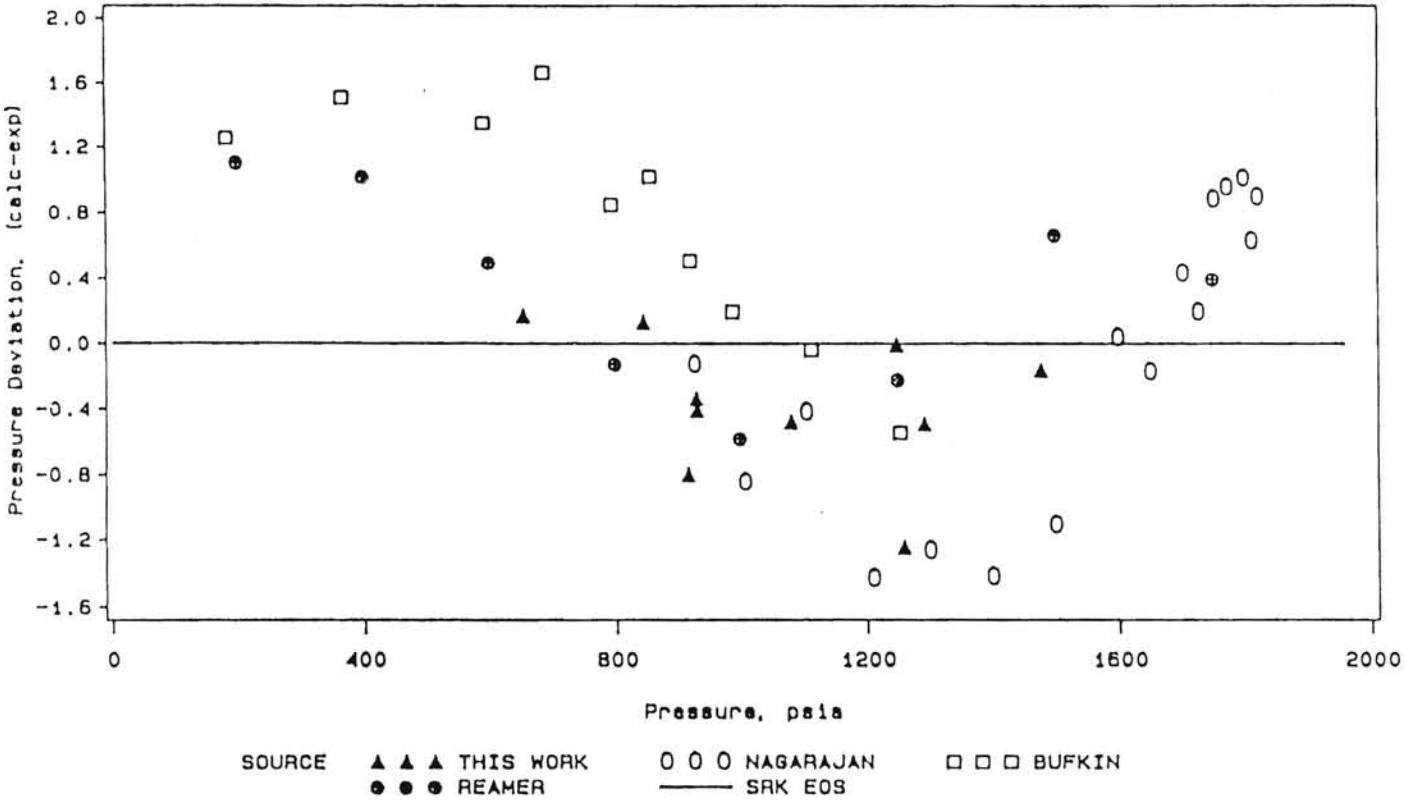

Figure 12. Deviation of Experimental data from predicted SRK values

## Crude Oils

Two North Sea crude oils were tested to determine their phase behaviors. Oil A was a heavy oil composed of approximately 30% C6+ mole fraction. Oil B was a heavier crude with a C6+ mole fraction of 53%.

### Crude Oil A

Due to the volatile mixture of oil A, the resulting high pressure single phase region required that the sample be injected completely into the cell because its container could not withstand the pressure required to inject it as a single phase liquid. After the injection, a series of bubble points and liquid volume measurements were taken between 90° and 250° F. These points are identified in Table II and Table III as Run 1.

To provide a larger range in liquid volume data and lower bubble points, a transfer of a portion of oil A into reservoir R2 was attempted. During the transfer a portion of oil A was trapped in an empty line, resulting in the loss of some light components of oil A.
A number of bubble point pressures and liquid volume fractions were taken on the remaining oil A sample and are presented in Tables IV and V, respectively. The amount of sample lost was calculated to be approximately 1 mole percent of the light components. Further confirmation was found by simulating the loss of the lights on MAXISIM (17) and comparing the predicted curve to the experimental data of Run 2. The bubble point curves of both experimental runs are shown in Figure 13.

Though the loss of the sample has limited the value of the actual data, both runs may be useful for modeling Oil A beyond the temperature and pressure ranges of the first run.

## TABLE II

## BUBBLE POINTS OF OIL A

| Run | Temperature °F | Pressure psia |
|---|---|---|
| 1 | 97.8 | 4025 |
| 1 | 114.5 | 4098 |
| 1 | 120.2 | 4122 |
| 1 | 157.3 | 4253 |
| 1 | 163.2 | 4265 |
| 1 | 198.2 | 4368 |
| 1 | 240.1 | 4448 |
| 1 | 250.5 | 4461 |
| 2 | 124.5 | 4077 |
| 2 | 180.4 | 4265 |
| 2 | 219.2 | 4365 |
| 2 | 252.8 | 4426 |
| 2 | 276.6 | 4446 |
| 2 | 283.4 | 4453 |
| 2 | 323.5 | 4468 |
| 2 | 332.7 | 4466 |
| 2 | 346.5 | 4458 |
| 2 | 353.6 | 4454 |

## TABLE III

## PERCENT LIQUID VOLUME DATA
## CRUDE OIL A

| Run | Temperature °F | Pressure psia | Volume Fraction Liquid |
|---|---|---|---|
| 1 | 80.2 | 999 | 0.368 |
| 1 | 81.0 | 1530 | 0.593 |
| 1 | 81.2 | 2052 | 0.697 |
| 1 | 113.3 | 3853 | 0.980 |
| 1 | 120.3 | 993 | 0.467 |
| 1 | 120.3 | 1930 | 0.626 |
| 1 | 120.2 | 3130 | 0.877 |
| 1 | 120.2 | 4013 | 0.988 |
| 1 | 163.4 | 1111 | 0.309 |
| 1 | 154.7 | 1187 | 0.368 |
| 1 | 156.2 | 1316 | 0.441 |
| 1 | 157.3 | 2891 | 0.798 |
| 1 | 163.4 | 1351 | 0.403 |
| 1 | 163.6 | 2109 | 0.645 |
| 1 | 163.3 | 2809 | 0.771 |
| 1 | 163.2 | 3809 | 0.946 |
| 1 | 157.2 | 4014 | 0.984 |
| 1 | 197.8 | 3761 | 0.913 |
| 1 | 197.8 | 4009 | 0.964 |
| 1 | 250.7 | 2891 | 0.706 |
| 1 | 250.8 | 3576 | 0.833 |
| 2 | 282.6 | 2087 | 0.527 |
| 2 | 282.9 | 2558 | 0.621 |
| 2 | 283.3 | 3041 | 0.712 |
| 2 | 283.0 | 3730 | 0.873 |
| 2 | 322.2 | 3570 | 0.796 |

TABLE III (Continued)

| Run | Temperature °F | Pressure psia | Volume Fraction Liquid |
|---|---|---|---|
| 2 | 322.4 | 4404 | 0.990 |
| 2 | 322.8 | 2967 | 0.710 |
| 2 | 323.0 | 2476 | 0.581 |
| 2 | 322.7 | 2034 | 0.530 |
| 2 | 322.0 | 1561 | 0.349 |
| 2 | 341.1 | 2013 | 0.434 |
| 2 | 341.3 | 2552 | 0.578 |
| 2 | 341.8 | 3056 | 0.681 |
| 2 | 341.0 | 3548 | 0.745 |
| 2 | 344.9 | 1636 | 0.344 |

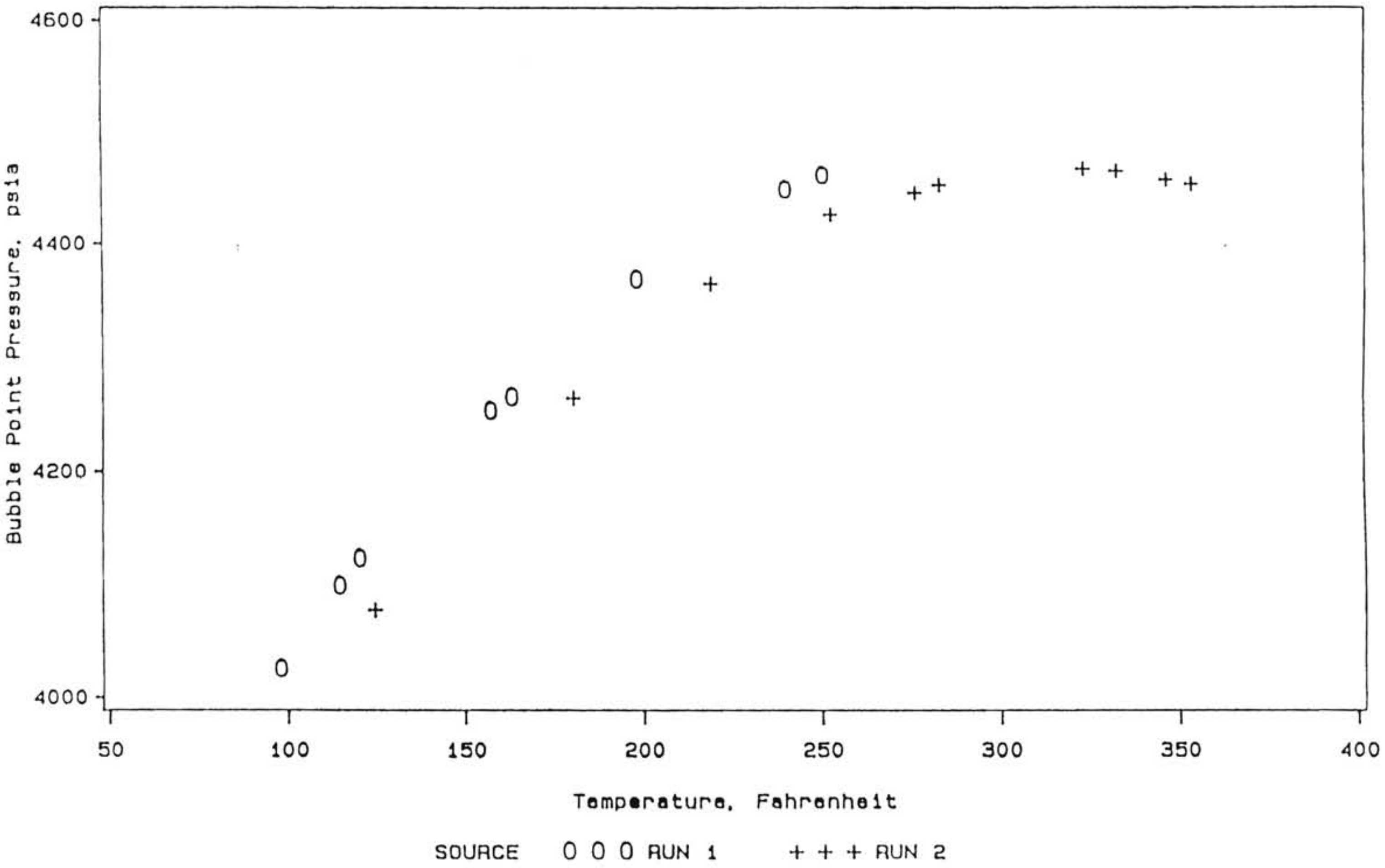

Figure 13. Bubble Point Curve - Crude Oil A

## Crude Oil B

Oil B was analyzed using the same procedure employed in the study of oil A. The lower bubble point pressures of oil B allowed the injection of a small single phase sample.

Bubble point and liquid volume data were taken on oil B at temperatures between 80° F and 350° F. The bubble point data is presented in Table IV. Figure 14 shows the bubble point pressures plotted as a function of temperature.

An unexpected problem occurred while running the oil B sample. The lower surface tension of the heavy crude caused the oil to adhere to the cell surfaces. This low surface tension also caused the high surface tension mercury in the cell to form small spheres, trapping the heavy liquids between them.

During the run, mercury levels within the cell were reduced to allow data to be collected at lower cell pressures. As the mercury was removed, small amounts of the heavy liquid that surrounded the mercury were removed from the cell. The loss of these components may have resulted in a slightly lighter sample as the run continued, producing higher bubble points and greater scatter in the experimental data than that encountered in the oil A sample.

Liquid volume data is presented in Table V and a plot of selected liquid volume fractions is shown in Figure 15.

## TABLE IV

## BUBBLE POINTS OF OIL B

| Temperature °F | Pressure psia |
|---|---|
| 75.0 | 864 |
| 97.8 | 926 |
| 136.0 | 1016 |
| 179.3 | 1101 |
| 226.0 | 1184 |
| 277.6 | 1279 |
| 333.8 | 1370 |
| 243.6 | 1240 |
| 275.3 | 1266 |
| 319.2 | 1345 |

# TABLE V

## PERCENT LIQUID VOLUME DATA
## CRUDE OIL B

| Temperature °F | Pressure psia | Volume Fraction Liquid |
|---|---|---|
| 73.3 | 306 | 0.550 |
| 73.6 | 470 | 0.876 |
| 74.0 | 580 | 0.937 |
| 74.4 | 711 | 0.954 |
| 134.8 | 221 | 0.293 |
| 135.3 | 262 | 0.353 |
| 135.5 | 334 | 0.440 |
| 135.5 | 404 | 0.576 |
| 135.5 | 473 | 0.656 |
| 135.5 | 542 | 0.783 |
| 135.6 | 643 | 0.917 |
| 178.8 | 1012 | 0.959 |
| 206.3 | 1080 | 0.968 |
| 206.9 | 958 | 0.930 |
| 207.1 | 786 | 0.910 |
| 207.6 | 628 | 0.739 |
| 208.0 | 373 | 0.405 |
| 224.0 | 398 | 0.409 |
| 224.0 | 445 | 0.497 |
| 225.9 | 308 | 0.297 |
| 225.0 | 1129 | 0.966 |
| 225.0 | 501 | 0.547 |
| 225.1 | 615 | 0.714 |
| 225.1 | 840 | 0.895 |
| 225.2 | 348 | 0.351 |
| 225.2 | 556 | 0.653 |
| 225.3 | 740 | 0.874 |

TABLE V (continued)

| Temperature °F | Pressure psia | Volume Fraction Liquid |
|---|---|---|
| 226.2 | 282 | 0.281 |
| 240.3 | 352 | 0.350 |
| 240.0 | 653 | 0.700 |
| 240.4 | 985 | 0.925 |
| 273.1 | 440 | 0.380 |
| 273.1 | 1140 | 0.940 |
| 273.3 | 534 | 0.535 |
| 273.5 | 781 | 0.788 |
| 273.4 | 243 | 0.181 |
| 274.0 | 901 | 0.912 |
| 274.4 | 1204 | 0.970 |
| 274.9 | 271 | 0.214 |
| 275.9 | 297 | 0.227 |
| 276.2 | 352 | 0.271 |
| 276.2 | 558 | 0.517 |
| 319.0 | 1258 | 0.956 |
| 320.1 | 1071 | 0.926 |
| 320.4 | 987 | 0.880 |
| 322.0 | 688 | 0.634 |
| 324.6 | 371 | 0.280 |
| 324.6 | 431 | 0.359 |
| 334.7 | 1130 | 0.930 |
| 335.0 | 902 | 0.881 |
| 336.0 | 719 | 0.580 |
| 336.1 | 802 | 0.733 |

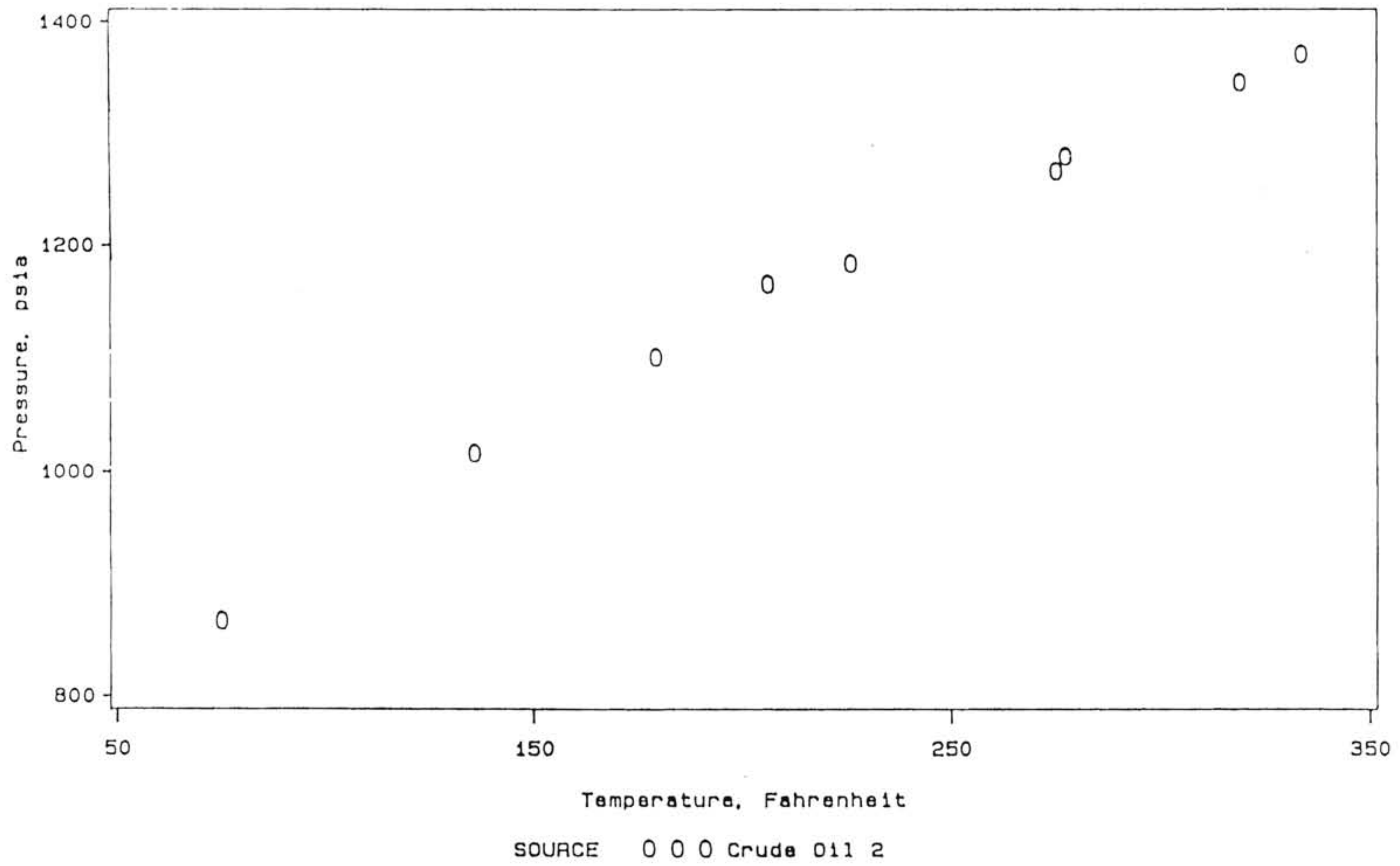

Figure 14. Bubble Point Curve - Crude Oil B

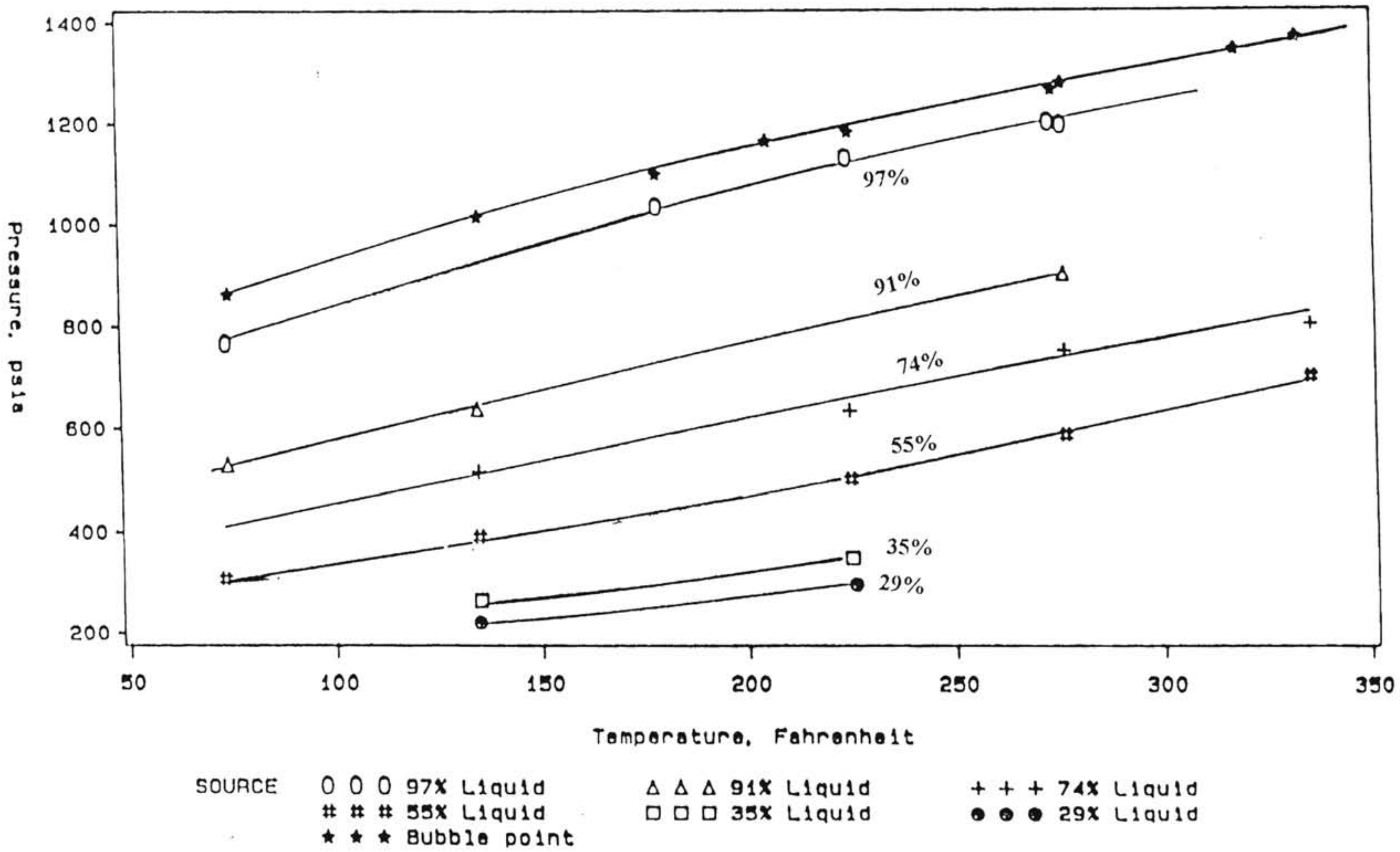

Figure 15. Liquid Volume Curve for Oil B

# CHAPTER VII

# CONCLUSIONS AND RECOMMENDATIONS

## Conclusions

This work involved the design, construction and operation of an experimental apparatus capable of determining the bubble points, dew points and percent liquid volumes of crude oils. Based on this study, the following conclusions are made:

1. An apparatus for measuring bubble points and percent liquid volumes at temperatures between 80 and 350° F and at pressures between 20 and 8000 psia has been designed and tested.

2. Carbon dioxide vapor pressure measurements were made at 80.6° F and 82.7° F to test pressure and temperature accuracies and agreed within 1 psi of literature values.

3. Bubble points were found for the carbon dioxide + n-decane binary system for a range of mole fractions at 160° F to test the accuracy and precision of the apparatus. This data is consistent with the work of other investigators who studied this binary.
4. Bubble point and percent liquid volume measurements have been taken on two North Sea crude oils at temperatures from 80° and 350° F and at pressures between 850 and 4600 psia.

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# APPENDIXES

# APPENDIX A

## CALCULATION OF CARBON DIOXIDE DENSITIES

This computer program uses the IUPAC (10) equation of state to calculate carbon dioxide densities at given temperatures and pressures.

```
CCC CALCULATE PRESSURE USING ANALYTICAL
EQUATION OF STATE CCC


          IMPLICIT REAL *8 (A-G,O-Z)
          DIMENSION BIJ (10,7), A(4), C(2), D(2)
          DATA
BIJ/-7.25854473D-01,4.47869183D-01,-1.72011999D-01,
          C4.46304911D-03,2.55491571D-01,5.94667298D-02,
          C-1.47960010D-01,1.36710441D-02,3.92284575D-02,
          C-1.19872097D-02,-1.68332974D00,1.26050691D00,
          C-1.83458178D00,-1.76300541D00,2.37414246D00,
          C1.16974683D00,-1.69233071D00,-1.00492330D-01,
          C4.41503812D-01,-8.46051949D-02,2.59587221D-01,
          C5.96957049D00,-4.61487677D00,-1.11436705D01,
          C7.50925141D00,7.43706410D00,-4.86219937D00,
          C-1.63653806D00,8.86741970D-01,4.64564370D-02,
          C3.76945574D-01,1.54645885D01,-3.82121926D00,
          C-2.78215446D01,6.61133318D00,1.50646731D01,
          C-3.13517448D00,-1.87082988D00,0.0D00,0.0D00,
          C-6.70755370D-01,1.94449475D01,3.60171349D00,
          C2.71685720D01,-2.42663210D00,9.57496845D00,
          C0.0D00,0.0D00,0.0D00,0.0D00,-8.71456125D-01,
          C8.64880497D00,4.92265552D00,-6.42177872D00,
          C-2.57944032D00,0.0D00,0.0D00,0.0D00,0.0D00,0.0D00,
          C-1.49156928D-01,0.0D00,0.0D00,0.0D00,0.0D00,0.0D00,
```

```
      C0.0D00,0.0D00,0.0D00,0.0D00/
       DATA A/-6.8849249D00,-9.5924263D00,1.3679755D01,
      C-8.6056439D00/
       DATA C/3.822502D-01,4.2897885D-01/
       WRITE (6,73)
 73    FORMAT (//15X,'****** DETERMINATION OF CARBON
DIOXIDE DENSITY ******
      C*)
       WRITE (6,74)
  74   FORMAT (//20X,'ENTER TEMPERATURE UNITS')
       WRITE (6,175)
 175   FORMAT (20X,' 1-FARENHEIT, 2-RANKINE, 3-KELVIN, 4-CELSIUS?')
       READ (9,176) L1
 176   FORMAT (I1)
       WRITE (6,177)
 177   FORMAT (/20X,'ENTER PRESSURE UNITS')
       WRITE (6,178)
 178   FORMAT (20X,' 1-PSIA, 2-ATM, 3-BAR?')
       READ (9,79) L2
  79   FORMAT (I1)
       WRITE (6,81)
  81   FORMAT (/20X,' ENTER DESIRED DENSITY UNITS')
       WRITE (6,82)
  82   FORMAT(20X,' 1-G/CM3, 2-LB/FT3 ?')
       READ (9,83)
  83   FORMAT (I1)
       WRITE (6,199)
```

```
 199  FORMAT(//15X,'FIX DECIMAL POINT WHEN ENTERING ALL
REQUESTED DATA
      C'//)
       WRITE (6,84)
  84   FORMAT (/5X,'ENTER INITIAL TEMPERATURE')
       READ (9,86) T
  86   FORMAT (D10.4)
       WRITE (6,87)
  87   FORMAT (/5X,'ENTER FINAL TEMERATURE')
       READ (9,88) TFIN
  88   FORMAT (D10.4)
       WRITE (6,89)
  89   FORMAT (/5X,'ENTER TEMPERATURE INCREMENT')
       READ (9,91) TINC
  91   FORMAT (D10.4)
       WRITE (6,92)
  92   FORMAT (/5X,'ENTER INITIAL PRESSURE)
       READ (9,93) P
  93   FORMAT ((D10.4)
       WRITE (6,94)
  94   FORMAT (/5X,'ENTER FINAL PRESSURE)
       READ (9,95) PFIN
  95   FORMAT (D10.4)
       WRITE (6,96)
  96   FORMAT (/5X,'ENTER PRESSURE INCREMENT')
       READ (9,97) PINC
  97   FORMAT (D10.4)
```

```
      WRITE (6,135)
135   FORMAT (/5X,'OUTPUT UNITS ARE:')
      IF (L1.EQ.1) GO TO 251
      IF (L1.EQ.2) GO TO 252
      IF (L1.EQ.4) GO TO 253
      IF (L1.EQ.3) GO TO 302
251   T=(T+459.669)/1.8
      TFIN=(TFIN+459.669)/1.8
      TINC=TINC/1.8
      WRITE (6,135)
136   FORMAT (5X,'TEMPERATURE -  DEGREES FARENHEIT')
      GO TO 254
252   T=T/1.8
      TFIN=TFIN/1.8
      TINC=TINC/1.8
      WRITE (6,137)
137   FORMAT(5X,'TEMPERATURE - DEGREES RANKINE')
      GO TO 254
253   T=T+273.15
      TFIN=TFIN+273.15
      WRITE (6,138)
138   FORMAT (5X,'TEMPERATURE - DEGREES CELSIUS')
      GO TO 254
302   WRITE (6,303)
303   FORMAT (5X,'TEMPERATURE - DEGREES KELVIN')
254   IF (L2.EQ.1) GO TO 155
      IF (L2.EQ.2) GO TO 156
```

```
      IF (L2.EQ.3) GO TO 305
155   P=0.068947*P
      PINC=0.068947*PINC
      PFIN=0.068947*PFIN
141   FORMAT (5X,'PRESSURE - PSIA')
      GO TO 257
156   P=1.01325*P
      PINC=1.01325*PINC
      PFIN=1.01325*PFIN
      WRITE (6,142)
142   FORMAT (5X,'PRESSURE - ATMOSPHERES')
      GO TO 257
305   WRITE (6,306)
306   FORMAT (5X,'PRESSURE - BAR')
257   IF (L3.EQ.1) GO TO 310
      WRITE (6,311)
311   FORMAT (5X,'DENSITY - GRAMS PER CUBIC FT.')
      GO TO 340
310   WRITE (6,312)
312   FORMAT (5X,'DENSITY - GRAMS PER CM3')
340   WRITE (6,98)
 98   FORMAT (/10X,'PRESSURE'8X,'TEMPERATURE',8X,'CO2
DENSITY',13X,'Z')
      WRITE (6,99)
 99   FORMAT (9X,'----------',6X'-------------',6X,'C',-------------',7X,'--------'/)
401   PIN=P
402   P=PIN
```

5. The experimental data have been used to develop liquid volume equilibrium curves for one of the crude oil samples studied (Crude oil B).

## Recommendations

1. A system for mixing large sample containers should be designed and installed. Samples greater than 0.5 liters are difficult to mix and inject into the small reservoirs of the apparatus. A representative sample is crucial for the accuracy of the results.
2. A cathetomer of greater precision should be installed to improve the accuracy of the liquid fraction measurements. The largest known errors are attributed to the cathetometer.

```
78   TC=304.21
     PC=73.825
     RHOC=0.010589
     R=83.143
     IF (T.GT.TC) GO TO 22
     PSUM=0.0
     DO 23 I=1,4
          PCONST=A(I)*(TC/T-1)**I
          PSUM=PSUM+PCONST
23   CONTINUE
     PSAT=PC*DEXP(11.3774*(1-T/TC)**1.935+PSUM)
     HT=T
     HPSAT=PSAT*14.5038
     WRITE (6,122) HT, HPSAT
122  FORMAT (/5X,'SATURATION PRESSURE AT',F6.2,'K=',F10.3,'PSIA')
     IF (P.LT.PSAT) GO TO 22
     SUM = 0.0
     SO 26 I=1,2
          CON=C(I)*(1-T/TC)**((I+1)/3.0)
          SUM=SUM+CON
26   CONTINUE
     RHO=RHOC*(1+1.9073793*(1-T/TC)**0.347+SUM)
28   GO TO 41
22   RHO=P/(R*T)
41   M=0
31   SUM=0.0
     TAU=304.2/T
```

```
      OMEGA=RHO/0.01063
      DO 100 J=1,7
           DO 90 I=1,10
                CONST=BIJ(I,J)*(TAU-1)**9J-1)*(OMEGA-1)**(I-1)
                SUM=SUM+CONST
 90        CONTINUE
100   CONTINUE
      Z=1.0+OMEGA*SUM
      R=83.143
          PA=RHO*Z*R*T      CCCC          CALCULATE       CRITICAL
EQUATIONPARAMETERS CC
      DELA=DABS((T-TC)/TC)
      DELRHO=DABS((RHO-RHOC)/RHOC)
      R=DELT+(0.6471102*DELRHO**2)**1.4409
 25   X=R-0.6471102*R**0.306*DELRHO**2-DELT
      ABSX=DABS(X)
      IF (ABSX.LT.1E-5) GO TO 20
      DX=1-0.198016*DELRHO**2/R**0.694
      R=R-X/DX
      GO TO 25
 20   THETA=0.670302*DELRHO/R**0.347
      QT1=37.26895-82.70074*THETA**2+57.089747*THETA**4
      IF (T.GE.TC) GO TO 30
      CCAL=-53.81157
      GO TO 40
      GO TO 353
350   HT4=1.8*T-459.669
```

```
      GO TO 453
351   HT4=1.8*T
      GO TO 453
352   HT4=T-273.15
      GO TO 453
353   HT4=T
453   IF (L2.EQ.1) GO TO 354
      IF (L2.EQ.2) GO TO 255
      GO TO 356
354   HP4=14.504*P
      GO TO 256
255   HP4=P/1.01325
      GO TO 256
356   HP4=P
256   IF (L3.EQ.1) GO TO 378
      HRHO4=RHO*62.371
      GO TO 379
378   HRHO4=RHO
379   R=83.143
      Z=(PCALC*44.009)/(RHO*R*T)
      HZ=Z
      WRITE (6,170) HP4,HT4,HRHO4,HZ
170   FORMAT (7X,F10.2,8X,F10.2,10X,F10.6,8X,F10.5/)
      P=P+PINC
      IF (PINC.EQ.0.0) GO TO 75
      IF (P.GT.PFIN) GO TO 75
      GO TO 78
```

```
75  T=T+TINC
    IF (TINC.EQ.0.0) GO TO 77
    IF (T.GT.TFIN) GO TO 77
    GO TO 402
77  STOP
    END $ENTRY $IBSYS
```

# APPENDIX B

# EXPLANATION OF THE PRESSURE TRANSDUCER CALIBRATION PROGRAM

This computer program calculates the gauge correction to the pressure transducer readout necessary to adjust the shown pressure to the true pressure. The program first calculates the gauge correction by taking the difference between the gauge pressure and the reference pressure provided by the Ruska dead weight gauge (model 2400). Next the mercury head is subtracted from the gauge correction to give the transducer correction. This transducer correction is then added to the transducer readings to provide the true pressure.

The reference pressure is calculated using an equation provided in the dead weight gauge operating manual (14). This equation is a function of ten parameters: piston mass, tare mass, acceleration of gravity, temperature, atmospheric pressure, and five constants unique to each dead weight gauge.

Required input data consists of the transducer readings and the corresponding mass of each dead weight combination entered at the end of the program. Dead weight masses are listed in the Ruska test report (11). Figure 10 shows the record sheet used for the transducer calibration with the weight combinations and blanks for transducer readings. The letters on the left side represent different tare weight combinations.

A mercury head correction must be added to the gauge correction to account for pressure increases due to the placement of the cell at a level above the pressure transducer. The mercury head correction of this apparatus was calculated to be 5.0 psi.

The transducer reading and the mercury head correction are subtracted from the reference pressure to produce the transducer correction after the reference pressure is calculated. The program generates a table providing transducer corrections as a function of transducer readings. Transducer corrections for pressures between the listed values are estimated using linear interpolation.

```
C      This computer program transducer corrections for the pressure transducer from
C      dead weight test data.

       DIMENSION SUMMAS(25),GAUGEP(2,25),DWP(2,25),
              GC(2,25),TRANSP(2,25),HEAD(2),GAUGE(2)
       DOUBLE PRECISION C1,C2
       DATA C1,C2,C3,C4/0.99895179,0.0260335,1.0,0.000017/
       DATA C5,C6/25.0,0.2356E-08/
       DATA TEMP/26.1/
       DATA HEAD/5.0,0.0/
       DATA NUMP, TARMAS/25,0.781067/
       DATA MONTH,NDATE,NYEAR/06,07,88/
       WRITE (6,1)
  1    FORMAT (/5X,'ENTER ATMOSPHERIC PRESSURE,PSIA')
       READ(9,2) PATM
  2    FORMAT (F10.4)
       DO 20 N=1,2
              DO 10 M=1,NUMP
                     READ (5,5)=TRANSP(N,M)
  5                  FORMAT (F9.3)
  10          CONTINUE
  20   CONTINUE
       DO 40 N=1,2
              DO 30 M=1,NUMP
                     GAUGE (N,M)=TRANSP(N,M)
  30          CONTINUE
  40   CONTINUE
```

```
      READ (5,50) (SUMMAS(I),I=1,NUMP)
50    FORMAT (F10.6)
      DO 70 N=1,2
            DO 60 M=1,NUMP
                  DWPN=(SUMMAS(M)+TARMAS)*C1
                  DWPD=C2*(C3+C4*(TEMP-C5))*(C3-C6*GAUGEP(N,M)
                  DWP(N,M)=DWPN/DWPD)
                  TRUEP=SWP(N,M)+PATM
                  GC(N,M)=TRUEP-GAUGE(N,M)-HEAD(1)
60          CONTINUE
70    CONTINUE
      WRITE (6,120) MONTH,NDATE,NYEAR
120   FORMAT (////40X,'DATE:',1X,I2,' /',I2,' /'.I2//)
      WRITE (6,130)
130   FORMAT (10X,'INPUT UNITS ARE DEG C AND PSIA'////)
      WRITE (6,80)
80    FORMAT (////20X,'TRANSDUCER CORRECTIONSA'//)
      WRITE (6,90)
90    FORMAT (15X,'TRANS PRESS',5X,'D.W. PRESS',5X,'TRANSD CORR'//)
      WRITE (6,100) (TRANSP(1,M),DWP(1,M),GC(1,M),M=1,NUMP)
100   FORMAT (18X,F7.2,8X,F7.2,9X,F5.2)
      WRITE (6,110)
110   FORMAT(/1X,------------------------------------------------------',/////)
      STOP
      END
```

# VITA

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